Doc Code: TRACK1.REQ
Document Description: TrackOne Request

PTO/AIA/424 (04-14)

CERTIFICATION AND REQUEST FOR PRIORITIZED EXAMINATION UNDER 37 CFR 1.102(e) (Page 1 of 1)

First Named Inventor:	Guido William ARU	Nonprovisional Application Number (if known):	
Title of Invention:	A CO TO CO2 COMBUSTION PROMOTER		

APPLICANT HEREBY CERTIFIES THE FOLLOWING AND REQUESTS PRIORITIZED EXAMINATION FOR THE ABOVE-IDENTIFIED APPLICATION.

1. The processing fee set forth in 37 CFR 1.17(i)(1) and the prioritized examination fee set forth in 37 CFR 1.17(c) have been filed with the request. The publication fee requirement is met because that fee, set forth in 37 CFR 1.18(d), is currently $0. The basic filing fee, search fee, and examination fee are filed with the request or have been already been paid. I understand that any required excess claims fees or application size fee must be paid for the application.

2. I understand that the application may not contain, or be amended to contain, more than four independent claims, more than thirty total claims, or any multiple dependent claims, and that any request for an extension of time will cause an outstanding Track I request to be dismissed.

3. The applicable box is checked below:

I. ☑ Original Application (Track One) - Prioritized Examination under § 1.102(e)(1)

i. (a) The application is an original nonprovisional utility application filed under 35 U.S.C. 111(a). This certification and request is being filed with the utility application via EFS-Web.

---OR---

(b) The application is an original nonprovisional plant application filed under 35 U.S.C. 111(a). This certification and request is being filed with the plant application in paper.

ii. An executed inventor's oath or declaration under 37 CFR 1.63 or 37 CFR 1.64 for each inventor, **or** the application data sheet meeting the conditions specified in 37 CFR 1.53(f)(3)(i) is filed with the application.

II. ☐ Request for Continued Examination - Prioritized Examination under § 1.102(e)(2)

i. A request for continued examination has been filed with, or prior to, this form.
ii. If the application is a utility application, this certification and request is being filed via EFS-Web.
iii. The application is an original nonprovisional utility application filed under 35 U.S.C. 111(a), or is a national stage entry under 35 U.S.C. 371.
iv. This certification and request is being filed prior to the mailing of a first Office action responsive to the request for continued examination.
v. No prior request for continued examination has been granted prioritized examination status under 37 CFR 1.102(e)(2).

Signature /Nicole D. Kling/	Date 2021-02-16
Name (Print/Typed) Nicole D. Kling	Practitioner Registration Number 71959

Note: *This form must be signed in accordance with 37 CFR 1.33. See 37 CFR 1.4(d) for signature requirements and certifications. Submit multiple forms if more than one signature is required.**

☑ *Total of 1 forms are submitted.

Privacy Act Statement

The **Privacy Act of 1974 (P.L. 93-579)** requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether disclosure of these records is required by the Freedom of Information Act.
2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.
3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.
4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).
5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.
6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).
7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (*i.e.*, GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.
8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspection or an issued patent.
9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

ABSTRACT

The invention is directed to a CO to CO_2 combustion promoter comprising microsphere sized porous silica and/or alumina comprising particles further comprising on or more Group VIII noble metals wherein the noble metal is distributed in the particle as an eggshell such that a higher content of noble metal is present in the outer region of the particle as compared to the content of noble metal in the center of the particle.

Electronic Acknowledgement Receipt	
EFS ID:	41913713
Application Number:	17176222
International Application Number:	
Confirmation Number:	3640
Title of Invention:	A CO TO CO2 COMBUSTION PROMOTER
First Named Inventor/Applicant Name:	Guido William ARU
Customer Number:	53143
Filer:	Nicole Dian Kling/Lauren Donaghy
Filer Authorized By:	Nicole Dian Kling
Attorney Docket Number:	071816-091960USC1
Receipt Date:	16-FEB-2021
Filing Date:	
Time Stamp:	09:32:06
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	yes
Payment Type	DA
Payment was successfully received in RAM	$3100
RAM confirmation Number	E20212F032431277
Deposit Account	500850
Authorized User	Lauren Donaghy
The Director of the USPTO is hereby authorized to charge indicated fees and credit any overpayment as follows: 37 CFR 1.16 (National application filing, search, and examination fees) 37 CFR 1.17 (Patent application and reexamination processing fees)	

37 CFR 1.19 (Document supply fees)

37 CFR 1.21 (Miscellaneous fees and charges)

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1		2021-02-16-Continuation-Specification-071816-091960USC1.pdf	199179 ea1f9572bd81c362da31c9aae1ec9173d97398ee	yes	24
	Multipart Description/PDF files in .zip description				
	Document Description		**Start**	**End**	
	Abstract		24	24	
	Claims		21	23	
	Specification		1	20	
Warnings:					
Information:					
2	Drawings-other than black and white line drawings	2021-02-16-CON-Drawings-071816-091960USC1.pdf	169330 51677e4655931e86d54c4fc892f8868c700e6a7e	no	3
Warnings:					
Information:					
3	TrackOne Request	2021-02-16-Track-One-Request-071816-091960USC1.pdf	117172 3f2a69648083d50d75b1bea5fdab2584793a156a	no	2
Warnings:					
Information:					
4	Transmittal of New Application	2021-02-16-Application-Transmittal-071816-091960USC1.pdf	289749 128653d74b02f45d6a7b8b4a1cd362b0e55554c1	no	2
Warnings:					
Information:					
5	Transmittal Letter	2021-02-16-EFS-Transmittal-071816-091960USC1.pdf	120248 4936710bb173672f3cbf4798688e0cbdfef5043d	no	1

Warnings:					
Information:					
6	Application Data Sheet	2021-02-16-ADS-071816-091960USC1.pdf	1342235 69e428753a6a37229560e2be732c8f4d6de3bb98	no	8
Warnings:					
Information:					
7	Information Disclosure Statement (IDS) Form (SB08)	2021-02-16-SB08-071816-091960USC1.pdf	1034375 1a584e353504a10c88bb03dc66371c5c17a876fa	no	4
Warnings:					
Information:					
8	Oath or Declaration filed	2021-02-16-Declaration-Executed-071816-091960USC1.pdf	640961 181e7b0ea55c7ac20dd075491a753e528598c966	no	1
Warnings:					
Information:					
9	Power of Attorney	2021-02-16-POA-Executed-071816-091960USC1.pdf	256951 2bf422e567a27d1f30211166d984d9708bd78e10	no	2
Warnings:					
Information:					
10	Fee Worksheet (SB06)	fee-info.pdf	41806 562abb516b2d75b35406d1ffe4385681fb680cfc	no	2
Warnings:					
Information:					
		Total Files Size (in bytes):	4212006		

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

Doc Code: PA..
Document Description: Power of Attorney

PTO/AIA/82A (07-13)
Approved for use through 01/31/2018. OMB 0651-0035
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

TRANSMITTAL FOR POWER OF ATTORNEY TO ONE OR MORE REGISTERED PRACTITIONERS

NOTE: This form is to be submitted with the Power of Attorney by Applicant form (PTO/AIA/82B) to identify the application to which the Power of Attorney is directed, in accordance with 37 CFR 1.5, unless the application number and filing date are identified in the Power of Attorney by Applicant form. If neither form PTO/AIA/82A nor form PTO/AIA82B identifies the application to which the Power of Attorney is directed, the Power of Attorney will not be recognized in the application.

Application Number	Herewith
Filing Date	2021-02-16
First Named Inventor	Guido William ARU
Title	A CO TO CO2 COMBUSTION PROMOTER
Art Unit	Not Yet Assigned
Examiner Name	Not Yet Assigned
Attorney Docket Number	071816-091960USC1

SIGNATURE of Applicant or Patent Practitioner

Signature	/Nicole D. Kling/	Date (Optional)	2021-02-16
Name	Nicole D. Kling	Registration Number	71959
Title (if Applicant is a juristic entity)	Agent		
Applicant Name (if Applicant is a juristic entity)	COCHISE TECHNOLOGY, LLC		

NOTE: This form must be signed in accordance with 37 CFR 1.33. See 37 CFR 1.4(d) for signature requirements and certifications. If more than one applicant, use multiple forms.

☑ *Total of 1 forms are submitted.

This collection of information is required by 37 CFR 1.131, 1.32, and 1.33. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 3 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

Doc Code: PA..
Document Description: Power of Attorney

PTO/AIA/82B (07-13)
Approved for use through 01/31/2018. OMB 0651-0035
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number

POWER OF ATTORNEY BY APPLICANT

I hereby revoke all previous powers of attorney given in the application identified in either the attached transmittal letter or the boxes below.

Application Number	Filing Date

(Note: The boxes above may be left blank if information is provided on form PTO/AIA/82A.)

☑ I hereby appoint the Patent Practitioner(s) associated with the following Customer Number as my/our attorney(s) or agent(s), and to transact all business in the United States Patent and Trademark Office connected therewith for the application referenced in the attached transmittal letter (form PTO/AIA/82A) or identified above: 53143

OR

☐ I hereby appoint Practitioner(s) named in the attached list (form PTO/AIA/82C) as my/our attorney(s) or agent(s), and to transact all business in the United States Patent and Trademark Office connected therewith for the patent application referenced in the attached transmittal letter (form PTO/AIA/82A) or identified above. (Note: Complete form PTO/AIA/82C.)

Please recognize or change the correspondence address for the application identified in the attached transmittal letter or the boxes above to:

☑ The address associated with the above-mentioned Customer Number

OR

☐ The address associated with Customer Number:

OR

☐ Firm or Individual Name					
Address					
City		State		Zip	
Country					
Telephone		Email			

I am the Applicant (if the Applicant is a juristic entity, list the Applicant name in the box):

COCHISE TECHNOLOGY, LLC

☐ Inventor or Joint Inventor (title not required below)
☐ Legal Representative of a Deceased or Legally Incapacitated Inventor (title not required below)
☑ Assignee or Person to Whom the Inventor is Under an Obligation to Assign (provide signer's title if applicant is a juristic entity)
☐ Person Who Otherwise Shows Sufficient Proprietary Interest (e.g., a petition under 37 CFR 1.46(b)(2) was granted in the application or is concurrently being filed with this document) (provide signer's title if applicant is a juristic entity)

SIGNATURE of Applicant for Patent

The undersigned (whose title is supplied below) is authorized to act on behalf of the applicant (e.g., where the applicant is a juristic entity).

Signature		Date (Optional)	October 5 2020
Name	GUIDO WILLIAM ARU		
Title	OWNER		

NOTE: Signature - This form must be signed by the applicant in accordance with 37 CFR 1.33. See 37 CFR 1.4 for signature requirements and certifications. If more than one applicant, use multiple forms.

☑ Total of 1 forms are submitted.

This collection of information is required by 37 CFR 1.131, 1.32, and 1.33. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 3 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

A CO TO CO_2 COMBUSTION PROMOTER

Cross-Reference To Related Applications

This application is a continuation under 35 U.S.C. § 120 of co-pending U.S. Application No. 17/043,031 filed September 29, 2020, which is a 35 U.S.C. § 371 National Phase Entry Application of International Application No. PCT/US2019/024742 filed March 29, 2019, which designates the U.S. and claims benefit under 35 U.S.C. § 119(a) of N.L. Provisional Application No. 2020819 filed April 24, 2018 and under 35 U.S.C. § 119(e) of U.S. Provisional Application No. 62/651,295 filed April 2, 2018, the contents of which are incorporated herein by reference in their entireties.

Field of the invention

The invention is directed to a CO to CO_2 combustion promoter comprising microsphere sized porous alumina particles comprising one or more Group VIII noble metals.

Background of the invention

Such CO to CO_2 combustion promoters are well known and are used in a fluid catalytic cracking (FCC) unit. In such a FCC process fluidizable catalyst particles are contacted in a conversion zone at high temperatures with hydrocarbons such to crack higher boiling hydrocarbons to lower boiling hydrocarbons, typically boiling in the gasoline range. The catalyst may be a crystalline zeolitic aluminosilicate component, usually an ion-exchanged form of a synthetic crystalline Faujasite, and a porous inorganic oxide matrix. This type of catalyst must be regenerated to low carbon levels, typically 0.5% or less, to assure that the catalyst particles possess desired activity and selectivity before the particles are recycled to the conversion zone, also referred to as cracking zone. In most regenerators the combustible solids deposited on the spent solid catalyst particles from the cracking zone are burned in a confined regeneration zone in the form of a fluidized bed which has a relatively high

concentration of catalyst particles (dense phase). A region of lower solids concentration (dilute phase) is maintained above the dense phase.

High residual concentration of carbon monoxide in flue gases from regenerators has been a problem. The oxidation of carbon monoxide is highly exothermic and can result in so-called "carbon monoxide afterburning" which can take place in the dilute catalyst phase, in the cyclones or in the flue gas lines. Afterburning has caused significant damage to plant equipment. CO to CO_2 combustion promoters are added to the FCC catalyst inventory of the regenerator with the objective to achieve a complete combustion of carbon monoxide in the regenerator dense phase and thereby avoiding this afterburning. The combustion promoters are separate particles from the cracking catalyst particles. The combustion promoters will be circulated with the rest of the FCC catalyst inventory from the regenerator to the riser, to the stripper and back to the regenerator.

Such CO to CO_2 combustion promoters are commonly made from impregnation of Group VIII noble metal or metals, commonly platinum and/or palladium, onto a porous alumina and/or other substrate microspheres of average particle size 60 to 90 microns, with physical properties very similar to the base FCCU catalysts. Such impregnation results in a uniform distribution of the Group VIII noble metal throughout the internal and external surfaces of the porous microsphere.

EP1879982 describes a CO to CO_2 combustion promoter for use in FCC containing platinum or palladium predominately present in the core of the particle and a metal active for catalysing NOx decomposition in a shell around the platinum or palladium.

US2005/0042158 describes a CO to CO_2 combustion promoter for use in FCC containing cerium oxide and a noble metal, like platinum and/or rhodium.

Other background publications are US6165933, US2005042158, US4812431, US4300997.

A disadvantage of all noble metal based CO to CO_2 combustion promoters is that relatively large amounts of noble metal are required to achieve the desired CO combustion in the FCC process. It is an objective of the present invention to provide a CO to CO_2 combustion promoter which requires less noble metal to achieve the same level of CO combustion in the FCC process.

Summary of the invention

This is achieved with the following CO to CO_2 combustion promoter. A CO to CO_2 combustion promoter comprising microsphere sized porous silica and/or alumina comprising particles further comprising one or more Group VIII noble metals wherein the noble metal is distributed in the particle as an eggshell such that a higher content of noble metal is present in the outer region of the particle as compared to the content of noble metal in the center of the particle. In one aspect of any of the embodiments, described herein is a CO to CO_2 combustion promoter comprising a particle, e.g., spherical particle, comprising i) silica and/or alumina and ii) one or more Group VIII noble metals, wherein the one or more noble metals is distributed in the particle in a gradient, with the concentration of each noble metal increasing toward the outer surface of the particle relative to the center of the particle. In some embodiments, the particles are less than 1 mm across the largest dimension, e.g., they are microspheres. The concentration of the noble metal can be zero, or any detectable concentration at the lowest point of the gradient. The concentration of the one or more noble metals can increase along the gradient at a constant or inconstant rate. In some embodiments, the particle can comprise two regions – a first inner region not comprising the one or more noble metals or a very low concentration of such metals and a second outer region, referred to herein as an "eggshell" comprising the one or more noble metals.

In one aspect of any of the embodiments, described herein is a CO to CO_2 combustion promoter comprising a particle, e.g., spherical particle, comprising i) a first region comprising porous silica and/or alumina and ii) a second region comprising the surface of the particle and (eggshell) comprising one or more Group VIII noble metals, wherein the concentration of one or more noble metals is greater in the second region than in the inner region and/or than in the pores of the inner region. In some embodiments, the particles are less than 1 mm across the largest dimension, e.g., they are microspheres. The concentration of the noble metal can be zero, or any detectable concentration in the first region or in the pores of the first region.

Applicants found that the CO to CO_2 combustion promoter was active as combustion promoter while the combustion promoter itself contained almost only the Group VIII noble metal in an eggshell of the particle. Thus the same activity could be

achieved using essentially significantly less noble metal per particle. Without wanting to be limited by the following theory applicants believe that the presence of the noble metal in the outer eggshell of a microsphere particle is sufficient to achieve an active combustion promoter. This is because the CO to CO_2 oxidation as catalyzed by a Group VIII noble metal is a very rapid, essentially instantaneous, reaction at the FCC regenerator temperatures of approximately 704 °C (1,300 °F) which is known as a diffusion limited or a mass-transfer limited reaction. Thus, the noble metal in the center of the particle is not active for CO to CO_2 oxidation as the reactant gases (CO and O_2) react before reaching this noble metal.

A further advantage with the eggshell of noble metal is that less NOx formation is achieved. This may be explained as follows. NOx forming reactions are slower and thus less diffusion limited than the CO to CO_2 reactions. Thus, the prior art combustion promoters having a uniform distribution and higher loading of the noble metal will generate more NOx as this additional noble metal will catalyse NOx forming reactions.

Further, it is known the noble metal will sinter in time making the combustion promoter less active for CO to CO_2 oxidation. The sintered particle will, however, still remain in the catalyst inventory of a FCC unit and continue to catalyse the NOx forming reactions. It has been reported that the sintered noble metal even promotes the NOx forming reactions better than the fresh-non-sintered noble metal. The sintered metal within the entire particle will promote the NOx forming reactions because these reactions are less diffusion limited. The noble metal of the combustion promoters according to the invention will also sinter. But because such a particle will contain considerably less noble metal the catalytic activity for the NOx forming reaction of such degraded combustion promoters will be less compared to the degraded combustion promoters of the prior art.

Brief description of the Figures

Fig. 1 shows a cross-section of a state of the art combustion promoter.

Fig. 2 shows a cross-section of a combustion promoter according to the invention.

Fig. 3 shows a graph with time on the x-axis after injecting a promoter in a FCC regenerator and on the y-axis the temperature change of the dilute phase of the FCC regenerator.

Fig. 4 shows the relative promoter concentrations of the combustion promoter according to this invention and state of the art promoter on the left hand y-axis and the flue gas NOx concentration in ppm on the right hand y-axis. The x-axis were the dates during the period the FCC regenerator was monitored.

Detailed description of the invention

In this description the following terms are used having the following definition.

FCC process: process to crack heavy oil fractions to lighter oil fractions by contacting the heavy oil fraction in a riser reactor where the heavy oil cracks to lighter oil in the presence of hot FCC catalyst inventory and deposits coke on the FCC catalyst inventory, by separating light oil fractions from the catalyst inventory by means of cyclones and by stripping and wherein coke is removed from the catalyst inventory by combustion in a regenerator to obtain a flue gas and hot catalyst inventory for reuse in the riser.

FCC Unit: Installation comprising of a riser, a stripper and a regenerator and means to circulate FCC catalyst inventory from the riser to the stripper and to the regenerator and back to the riser.

FCC catalyst inventory or catalyst inventory: the total of solid particles comprising of FCC catalyst and additives which are circulated from the regenerator to the riser, to the stripper and back to the regenerator.

FCC catalyst: a silica-alumina comprising particle comprising a zeolite.

Spent FCC catalyst: deactivated FCC catalyst obtained from a FCC process containing coke depositions.

Equilibrium FCC catalyst: mixture of active and deactivated FCC catalyst representing an average activity of a stable running FCC process.

Eggshell catalysts are known for larger catalyst particles. Applicant now discovered that it is possible to also form such an eggshell distribution on microsphere sized porous particles. The microsphere sized particles suitably have an average (D50) size of between 60 and 90 micron as measured by laser light scattering, also referred to as laser diffraction, using for example a Malvern Mastersizer 3000.

The eggshell or outer shell suitably has a depth from the outer surface towards the interior of the particle of between 1 to 10 microns. In this eggshell, which includes the outer surface of the particle, suitably more than 60 wt%, suitably more than 80 wt% and even more suitably more than 90 wt% of the noble metal is present of the total of noble metal present in the particle.

The silica and/or alumina comprising particle of the CO to CO_2 combustion promoter may be a particle based on a predominately only silica particle. Examples of suitable silica particles are spray dried silica particles. Such a silica particle may be impregnated as described here below with the noble metal or metals to obtain the promoter according to the invention.

The silica and/or alumina comprising particle of the CO to CO_2 combustion promoter may also be a particle comprising both alumina and silica. Suitable examples of such particles are FCC catalyst particles which may comprise between 30 and 70 wt% alumina, between 35 and 70 wt% silica. Such particles will also comprise of a zeolite, suitably Faujasite or Type Y zeolite, and/or ZSM-5, and binders such as silica sol, alumina sol, pseudo-boehmite alumina or a clay-based matrix. Suitably equilibrium FCC catalyst particles or spent FCC catalyst particles are used as obtained from a fluidized catalytic cracking (FCC) process. The equilibrium or spent FCC catalyst is obtained from a FCC process wherein fresh FCC catalyst has deactivated to some degree. Such catalyst particles may thus find a suitable second use as CO to CO_2 combustion promoter. By impregnating the FCC catalyst particles as described here below with the noble metal or metals the promoter according to the invention may be obtained.

The silica and/or alumina comprising particle of the CO to CO_2 combustion promoter is suitably an alumina particle and more preferably a gamma or theta alumina particle. Such an alumina starting particle may consist of predominately only alumina, suitably resulting in a CO to CO_2 combustion promoter wherein the support, thus excluding the noble metals, has an alumina content of above 95 wt% and more preferably above 99 wt%. The starting gamma or theta alumina particles suitably have an average (D50) size of between 60 and 90 micron, have a surface area (BET) of between 50 and 300 m^2/g and preferably between 50-150 m^2/g and a pore volume of between 0.05 and 0.50 mL/g and preferably between 0.10 – 0.40 mL/g. Examples of suitable starting alumina particles are obtainable from Sasol, such as

Puralox and Catalox. Such starting alumina particles may be impregnated as described here below with the noble metal or metals to obtain the promoter according to the invention.

The Group VIII noble metal is suitably platinum, palladium, iridium, ruthenium and/or rhodium. Platinum can be preferred because of its availability. Palladium and rhodium can be preferred because they promote the NOx forming reactions less than platinum. A problem in prior art devices is their availability. Because the combustion promoter according to the inventions requires less noble metal for achieving the same activity noble metals like palladium and rhodium may be practically applied.

The average content of noble metal per grams of combustion promoter may range from 1 to 5000 ppm and preferably between 100 and 1500 ppm. Locally, in the eggshell, this concentration will of course be larger. The concentration of noble metal in the eggshell may suitably be in the same range as the concentration of noble metal in the prior art combustion promoters which have the noble metal evenly distributed within the particle. The optimal content of noble metal will depend on their catalytic activity for promoting the CO to CO_2 combustion, wherein it is known that platinum is very active and will thus require a lower content than for example palladium which is known to be less active.

The concentration of the noble metal on the support is typically very low. To establish whether the metals are homogeneously distributed or present as an eggshell it is possible to use Low Electron Ion Scattering. This technique (Platinum Metals Rev., 2010, 54, (2), 81 87) can establish surface concentrations already at 0.01 at%, which is in the applicable range. By combining this surface technique together with a bulk chemical analysis technique such as X-ray fluorescence (XRF) or inductively coupled plasma (ICP) it can be established whether the surface is enriched in noble metal, and the metal is predominantly present as an eggshell. For example, if the concentration at the surface is 2 times as high as the bulk concentration using a technique that has a penetration depth of 10 micron, the metal distribution is predominantly at the surface and hence is considered an eggshell type distribution.

The combustion promoter may comprise co-catalytical compounds as for example known for prior art combustion promoters. For the example cerium oxide which may be added to provide oxygen storage or copper oxide to reduce NOx

forming reactions. Such co-catalyst compounds are preferably present in the eggshell comparable to the noble metal distribution in the particle. Preferably cerium oxide is distributed in the particle as an eggshell such that a higher content of cerium oxide is present in the outer region of the particle as compared to the content of cerium oxide in the centre of the particle. Accordingly, in some embodiments, described herein is a CO to CO_2 combustion promoter comprising a particle (e.g., spherical particle) comprising i) silica and/or alumina and ii) one or more Group VIII noble metals and one or more co-catalytical compounds, wherein the metals and compounds of ii) are distributed in the particle in a gradient, with the concentration of each noble metal and co-catalytical compound increasing toward the outer surface of the particle relative to the center of the particle. In some embodiments, the particle can comprise two regions – a first inner region not comprising the one or more noble metals and a second outer region, referred to herein as an "eggshell", comprising the one or more noble metals and one or more co-catalytical compounds.

Typically, the sensitivity to attrition of the CO to CO_2 combustion promoter particles is about the same or even better than the FCC catalyst inventory to which the promoter particles are added. Applicants have now found that it is advantageous to use CO to CO_2 combustion promoter particles which have a higher sensitivity to attrition than the typical FCC catalyst. The advantage is that in this way deactivated CO to CO_2 combustion promoter particles comprising sintered noble metal or metals will reduce in size, by for example wear or fracture, quicker than in the prior art processes. The smaller sized CO to CO_2 combustion promoter particles will subsequently be removed from the FCC process via the flue gas leaving the FCC regenerator. These fines in the flue gas may be suitably removed from the flue gas by means of advance external particulate emissions control devices such as Electro-Static Precipitators (ESP) or wet-gas scrubbers. In this way the content of deactivated CO to CO_2 combustion promoter containing sintered noble metals in the FCC catalyst inventory will be lower than when promoter particles are used having a lower sensitivity to attrition. This results in turn in less NOx forming because the content of particles with sintered noble metal or metals is lower. See also the explanation regarding NOx formation above. The sensitivity may be expressed in the so-called Attrition Index as measured according to ASTM D-5757. The Attrition Index of the CO to CO_2 combustion promoter for a sieve fraction of combustion promoter

particles of between 40 and 105 micron is preferably between 5 and 25 and more preferably between 10 and 20. Preferably this Attrition Index of the CO to CO_2 combustion promoter is higher than the Attrition Index of the FCC catalyst itself. FCC catalyst particles typically have a sensitivity to attrition which results in that the average catalyst residence time of the FCC catalyst in a FCC unit is between 2 weeks and 2 months. The residence time is an average residence time. The residence time of individual particles varies greatly when one realises that typically on a daily basis catalyst is added and withdrawn and partially lost to attrition in a FCC Unit.

The higher sensitivity to attrition of the CO to CO_2 combustion promoter preferably results in that an average residence time of less than 5 days, more preferably less than 3 days and even more preferably less than one day in the FCC catalyst inventory. Even shorter residence times will reduce NOx emissions even further. For the lowest NOx emissions at reasonable expenses, a residence time of half a day, or a quarter of a day would be considered optimal. At these lower residence times significant amounts of partially active combustion promoter will be lost as fines resulting in that more fresh CO to CO_2 combustion promoter will be required to be added to the catalyst inventory. The skilled person will be able to find the optimal Attrition Index for the CO to CO_2 combustion promoter depending for example on the desired residence time and the influence of the FCC unit itself to the attrition of the FCC catalyst inventory. This process of finding the optimal Attrition Index may for example be an empirical iteration, where the attrition resistance of the additive is lowered (attrition increased) until the NOx emissions are lowered, and further reduction in the attrition resistance requires an increase in the addition rate of the combustion promoter. In a FCC process the aged CO to CO_2 combustion promoter will be removed from the process as fines and together with the catalyst purge which removes a part of the catalyst inventory from the FCC process. When the CO to CO_2 combustion promoter particles having the lower residence times than the 2 weeks and 2 months for FCC catalysts are used as described above it is preferred that more than 70 wt% of the CO to CO_2 combustion promoter as added to the process is removed as fines together with the flue gas wherein any remainder may be removed from the catalyst inventory by means of a catalyst withdrawal of the FCC catalyst inventory.

Applicant believe that being able to influence, i.e. lower, the residence time of part of the FCC catalyst inventory by increasing the sensitivity to attrition is novel and may also be applied in an inventive manner for other FCC additives and even for FCC catalyst itself. Catalyst and additives used in the FCC process have always been designed with physical properties such as density and attrition that maximize the retention of the catalyst or additive in the circulating FCC catalyst inventory. Such retention characteristics have been designed for these catalyst and additives irrespective of the life or half-life of the intended catalytic function of the individual additives or catalyst and without consideration for any detrimental effects such aged additives and/or FCC catalysts may have when left in the FCC catalyst inventory. By influencing the sensitivity to attrition of the additives, such as CO combustion promoters, and/or FCC catalyst one has a means to minimise these detrimental effects of the aged additives and/or catalyst.

Next to the earlier described CO to CO_2 combustion promoter, it may be preferable that other FCC additives may also have a higher sensitivity to attrition than the FCC catalyst. Propylene enhancing additives based on medium pore zeolites, such as ZSM-5, is initially more selective to propylene production but becomes more butylene selective as it ages due to dealumination. Such additives are well known and for example described in Magee and Mitchell (editors), Studies in Surface Science and Catalysis vol. 76, Elsevier Amsterdam 1993. Both the fresh ZSM-5 based additive and the deactivated additive are in competition in the FCC catalyst inventory for the same feed molecules to crack. Therefore, the presence of (partially) deactivated ZSM-5 reduces the overall propylene selectivity and enhances the butylene selectivity. For maximum propylene selectivity it is advantageous to limit the residence time of the ZSM-5 based additive in the FCC catalyst inventory to below 7 days, more preferred below 5 days and even more preferred to below 3 days. The residence time may suitably be established using chemical markers. For example, when to catalysts are added each at 5 tons per day to an FCC unit, with an inventory of 100 tons, the average residence time in inventory would be when all physical properties are equal 100/(5+5) = 10 days. When one of the catalysts or additives is provided with a chemical marker, and only half of that marker is present in the catalytic inventory, that means the residence time is half of the average residence time of the total inventory, i.e. 5 days.

Y zeolite used in FCC catalysts and in some FCC additives may lose their hydrogen transfer capability and other desirable properties as they age, going through various phases of reduced and/or undesirable catalytic functionality until they finally become catalytically inert. By choosing a suitable Attrition Index for such Y zeolite based FCC catalyst particles and/or Y zeolite based additives one may avoid such reduced and/or undesirable catalytic functionality of the aged particles. This is because their residence time is reduced.

The invention is also directed to a FCC process wherein one or more FCC catalysts and/or FCC additives in the catalyst inventory have a shorter residence time in the catalyst inventory than the residence time of a more catalytically stable FCC catalysts and/or FCC additives and wherein the one or more FCC catalysts and/or FCC additives in the catalyst inventory having a shorter residence time are more than 70 wt% removed from the process as fines in the flue gas shorter while the remainder is removed from the FCC process via a catalyst withdrawal of part of the FCC catalyst inventory.

The invention is also directed to a FCC process wherein one or more FCC catalysts and/or FCC additives in the catalyst inventory have a shorter residence time in the catalyst inventory than the residence time of a more catalytically stable FCC catalysts and/or FCC additives and wherein the shorter residence time is a result of a higher sensitivity to attrition of said FCC catalysts and/or FCC additives as compared to the sensitivity to attrition of the more catalytically stable FCC catalysts and/or FCC additives.

The invention is also directed to a FCC unit comprising a catalyst inventory comprising:

a. a first FCC catalyst, and

b. a second FCC catalyst and/or additive having a catalytic active component having a catalytic activity,

whereby the catalytic activity of the second FCC catalyst and/or additive is negatively altered by the effects on the catalytically active component, whereby the second FCC catalyst and/or additive is more sensitive to attrition and has a shorter residence time in the catalyst inventory as compared to the first FCC catalyst.

In the above FCC unit the additive may be a CO to CO_2 combustion promoter, more specially a CO to CO_2 combustion promoter wherein at least one of the

catalytically active components of the additive comprises a metal and wherein the catalytic effect of the metal is negatively altered by sintering of the metal. The metal or metals may be as described above for the promoter according to the invention. The metal may be distributed homogenously or according to a gradient. The promoter is preferably a CO to CO_2 combustion promoter is a CO to CO_2 combustion promoter according to this invention. The additive may also be ZSM-5 or a ZSM-5 comprising additive and wherein the catalytic effect of the ZSM-5 is negatively altered by dealumination of the zeolite.

The CO to CO_2 combustion promoter having a gradient in metal content may be obtainable by known processes to prepare eggshell type of catalysts as for example described in WO2016/151454. The CO to CO_2 combustion promoter is suitably obtainable by a process comprising the following steps (a) introducing a medium in the pores of starting porous silica and/or alumina comprising particles to obtain filled porous particles and (b) contacting the filled porous particles with an aqueous salt solution of the Group VIII noble metal or metals wherein the Group VIII noble metal deposits predominantly in in the outer region of the particles thereby obtaining intermediate eggshell particles and optionally (c) dry and/or calcine the intermediate eggshell particles. The invention is also directed to this process as such.

The starting porous silica and/or alumina comprising particles may be the aforementioned starting porous particles described above.

By introducing a medium which does not contain a Group VIII noble metal or noble metal salt in step (a) the pores of the porous alumina particle and especially the pores in the centre of the porous silica and/or alumina comprising particle will be filed with this medium. When the obtained filled porous particle is contacted in step (b) with an aqueous salt solution of the Group VIII noble metal or metals the pre-filled pores in the centre of the particle will be more difficult to reach. This results in that the noble metal is deposited predominately in the eggshell of the particle.

The medium in such a process may be water, an oil, a solvent for the noble metal salt or a liquid in which the noble metal salt barely dissolves. It is understood that the medium preferably does not contain the noble metal or its salt to avoid that noble metal deposits in the centre of the particle. The water may contain other

additives which suitably do not deposit on the alumina surface of the pores. Such additives may be gel-forming additives which make it even more difficult for the aqueous salt solution of the Group VIII noble metal or metals to enter the pores in the centre of the particle. Alternatively, the filled porous particles may be reduced in temperature such that the water in the pores solidifies. When such a particle is contacted in step (b) with the aqueous salt solution of the Group VIII noble metal or metals the deposition of metals will take place in the eggshell where any frozen water will first melt and not in the pores which contain the frozen water which will melt at a later moment in time.

For performing step (a) it is important to know the volume of the pores of the starting porous silica and/or alumina comprising particles, also referred to as the support, which are to be filled with medium. The pore volume may be measured using nitrogen and / or quick porosimetry to measure micro-, meso- and macro-pore volumes. A preferred method is to establish the "water pore volume". In this the particles are fully soaked in excess water. With the aid of a laboratory centrifuge the excess water that is not contained in the pores is removed. The difference in weight of the water equals the pore volume as occupied by the water. When no centrifuge is available, the pore volume can be established by adding water drop wise to a dry powder. The powder is well mixed during the addition of water. The moment when the powder no longer adsorbs the water and mixing of the place where the drop impacted with dry parts of the powder, the powder is considered to be fully saturated. This method is comparable to the incipient wetness technique but is now used to establish the pore volume of the support.

In step (a) the support is pre-contacted with a liquid medium, preferably water. The liquid can be a solvent for the salt, such as water, or a non-solvent, such as paraffinic oil. The quantity of the added medium is suitably between 50 and 100 vol% of the pore volume of the support, as established in the steps mentioned above. More preferred the quantity of the added medium is at least 60% and even more preferred is at least 70% of the pore volume of the support. Higher than 80% filling of the pores will be possible, but this does require skill and careful execution to homogeneously distribute the liquid. Pre-filling the pores to 90%, or even up to 95% will help to achieve the highest activity for the noble metal but will require a careful execution of the pre-contacting step. A 100 vol% filing is preferred when one desires to only deposit noble metals on the outer surface of the particle. The key here is the

slow addition of the liquid medium to the support while mixing and/or agitating the support. An alternative can be condensation of the pre-contacting liquid in the pores, using the appropriate partial pressures to fill a certain fraction of the pores. The pre-contacting liquid can potentially be solidified via the addition of a gelling agent, by lowering the temperature, potentially even freezing the pre-contacting liquid in the pores, or a combination of both. Another method of adding the medium is to saturate the particles in a fluid bed in a stream containing the medium, where the medium can condense in the pores. The medium will be homogeneously distributed in this way over all the particles.

The higher the fraction of pores filled in the initial liquid medium the more the noble metal will be concentrated on an outer eggshell resulting in a more active combustion promoter. The noble metal salt will be added in the remainder of the pore volume in step (b). For example, when 80 vol% of the pores are filled with the liquid medium, at most 20 vol% of pores can be filled with the noble metal solution. When the total of the 20 vol% of the remaining pore volume is used to add the noble metal this method resembles a two-step incipient wetness technique. If less than all the pore volume is used to add the noble metal, the method resembles a two-step pore volume impregnation.

Contacting in step (b) may be performed by state of the art methods known for depositing metals on the surface of silica and/or alumina comprising particles and the surface of the pores of the silica and/or alumina comprising particles. In this method the salt solution of the Group VIII noble metal is added in about the same volume as the remaining pores to be filled with the salt solution. In step (b) of the present process the filled porous particles are contacted with a volume of the aqueous salt solution of the Group VIII noble metal or metals which is less than the total volume of the pores of the porous silica and/or alumina comprising particles. This because the pore volume in the centre of the particles is already filled with the medium. In this manner only the pores in the outer shell of the particle, i.e. the eggshell, are filled with the aqueous salt solution and the noble metal predominately deposit in the eggshell of the particle. The contact time in step (b) is preferably at most 30 minutes, more preferred at most 20 minutes, even more preferred at most 10 minutes. Contact times of at most 5 minutes or even at most 3 minutes may be even more preferred. For example, a one minute contact time could be suitable when the pores are filled for 100 vol%. The impregnated particles and the aqueous salt solution may be

separated by means of filtration, for example using a filter, covered with a filter cloth to contain the small support particles. The filtration may be performed by means of a filter press, a belt filter or any other filtration device suitable to separate the quantity of catalyst prepared from the liquid slurry. The filtrate may contain noble metal salts which are suitably recovered and reused to contact a next batch of filled porous particles.

In step (c) the particle containing the deposited noble metal as obtained in step (b) may be optionally dried and/or calcined. Drying suitably takes place at temperatures between 100 to 250 ºC (212 to 482 °F) and calcination suitably takes place at a temperature of between 250 and 750 ºC (482 to 1382 °F). Drying and/or calcination may be with or without vacuum. Drying is preferred to limit sintering of the noble metal or metals.

Prior to or after performing steps (a)-(b) the starting silica and/or alumina comprising particles or impregnated particles can also be subjected to a process comprising steps (a)-(c) wherein in step (b) the filled porous particles are contacted with an aqueous salt solution of a cerium salt instead of the aqueous salt solution of the Group VIII noble metal or metals Group VIII noble metal to obtain particles in step (c) comprising cerium oxide which is distributed in the particle as an eggshell such that a higher content of cerium oxide is present in the outer region of the particle as compared to the content of cerium oxide in the centre of the particle.

The invention is also directed to the use of the CO to CO_2 combustion promoter as described above in a fluid catalytic cracking (FCC) unit.

Detailed description of the Figures

Fig.1 shows a state of the art combustion promoter where the Group VIII metal is distributed homogeneously throughout an alumina microspheres of average particle size 60 to 90 microns (twice the radius r). The alumina support has mesopores (pores less than 50 nanometers) distributed throughout the particle. The capillary effects, both hydraulic and evaporative, in mesopores are well documented and are characterized by extremely rapid uptake of any liquid, including one with dissolved noble metal salts. This rapid uptake into the pores of the support is what results in the homogenous distribution of the noble metals with the impregnation

methods previously employed and documented to manufacture FCC CO combustion promoters.

Fig. 2 shows a combustion promoter as prepared according to process of the invention. The alumina microsphere has the same dimension and mesopore structure as the alumina microsphere of Fig. 1. The core of the particle contains little to no Group VIII metals and an outer eggshell which may have a thickness (d) of between 1 to 10 microns will contain almost all of the Group VIII metal.

The invention will be illustrated by means of the following non-limiting examples.

EXAMPLE 1

A two-step impregnation was carried out using a high purity gamma alumina support as purchased from Sasol. In the first step, 10 g of alumina powder was impregnated with water to fill 90% of the pore volume. At a pore volume of 0.5 mL/g, 4.5 mL of water was required for 10 g of alumina powder. For the second step, the wet alumina particles from step 1 with 90% of the pore volume filled with water were impregnated with a solution of palladium nitrate and dried to achieve an eggshell of palladium on the particle surface. The second impregnation step was completed before the pre-filled alumina particles were dried. After completing both impregnation steps, the impregnated particles were calcined at 600 °C for 1 hour to form a particle with the composition in accordance with this invention.

EXAMPLE 2

0.1 g of the composition of Example 1 was mixed with 10 g of a commercial FCC catalyst. The mixture was then used to measure the oxidation of CO in a fluid bed reactor fitted with a thermocouple. The catalyst bed was heated to 600 °C prior to the start of CO/O_2 flow. Oxidation response was measured using a mixture of 1.8 v/v% CO and 0.9 v/v% O_2, balanced with He, under a gas flow rate of 1000 cc/min. The oxidation response is a measure of the amount of CO which is combusted (oxidized) to CO_2.

Comparative Experiment A

Example 2 was repeated using a state of the art FCC combustion promoter containing twice the amount of palladium as compared to the promoter of Example 1. In the state of the art FCC combustion promoter palladium was homogenously distributed over the particle. The CO oxidation response for the composition of Example 1 was comparable to the state of the art FCC combustion promoter despite having half the palladium loading.

Comparative Experiment B

Example 2 was repeated using a lab prepared FCC combustion promoter with the same palladium loading as in Example 1 and prepared by standard homogeneous impregnation method. This resulted in a homogeneous distribution of palladium throughout the alumina support. The CO oxidation response for the composition of Example 1 was better than the lab prepared FCC combustion promoter.

EXAMPLE 3

A two-step impregnation was carried out using a high purity gamma alumina support as purchased from Sasol. In the first step, 10 g of alumina powder was impregnated with water to fill 90% of the pore volume. At a pore volume of 0.5 mL/g, 4.5 mL of water was required for 10 g of alumina powder. For the second step, the wet alumina particles from step 1 with 90% of the pore volume filled with water were impregnated with a solution of platinum nitrate and dried to achieve an eggshell of platinum on the particle surface. The second impregnation step was completed before the pre-filled alumina particles were dried. After completing both impregnation steps, the impregnated particles were calcined at 600 °C.

EXAMPLE 4

Example 2 was repeated using 0.1 g of the composition of Example 3.

Comparative Experiment C

Example 4 was repeated using a state of the art FCC combustion promoter containing twice the amount of platinum as compared to the promoter of Example 3. In the state of the art FCC combustion promoter, platinum was homogenously distributed throughout the particle. The CO oxidation response for the composition of

Example 3 was comparable to the commercial FCC combustion promoter despite having half the platinum loading.

Comparative Experiment D

Example 4 was repeated using a lab prepared FCC combustion promoter with the same platinum loading as in Example 3 and prepared by standard homogeneous impregnation method. This resulted in a homogeneous distribution of platinum throughout the particle. The CO oxidation response for the composition of Example 3 was better than the lab prepared FCC combustion promoter.

EXAMPLE 5

Three alumina supports with varying attrition indices were provided by catalyst manufacturers. The attrition index of the three alumina supports ranged from 2 to 25 as measured according to ASTM D-5757. A two-step impregnation was carried out for each of the three as supplied alumina powders. In the first step, 10 g of alumina powder was impregnated with water to fill 90% of the pore volume. At a pore volume of 0.5 mL/g, 4.5 mL of water was required for 10 g of alumina powder. For the second step, wet alumina particles with 90% of the pore volume filled with water were impregnated with a solution of palladium nitrate and dried to achieve an eggshell of palladium on the particle surface. The second impregnation step was completed before the pre-filled alumina particles were dried. After completing both impregnation steps, the impregnated particles were calcined at 600 °C for 1 hour to form a particle with the composition in accordance with this invention.

EXAMPLE 6

0.1 g of each of the compositions of Example 5 was mixed with 10 g of a commercial FCC catalyst to prepare 3 different mixtures. Each mixture was then used to measure the oxidation of CO in a fluid bed reactor fitted with a thermocouple. The catalyst bed was heated to 600 °C prior to the start of CO/ O_2 flow. Oxidation response was measured using a mixture of 1.8 v/v% CO and 0.9 v/v% O_2, balanced with He, under a gas flow rate of 1000 cc/min.

Comparative Experiment E

For comparison Example 6 was repeated but now with a state of the art FCC combustion promoter and lab synthesized FCC combustion promoter prepared by standard homogeneous impregnation method. The CO oxidation response for each of the compositions of Example 5 as measured in Example 6 was comparable to the commercial FCC combustion promoter despite having half the palladium loading. Further, the CO oxidation response for each of the compositions of Example 5 as measured in Example 6 was enhanced compared to lab prepared FCC combustion promoter with the same palladium loading prepared by standard homogeneous impregnation method. Further, the reduction in attrition resistance of the alumina support did not reduce the CO oxidation response.

EXAMPLE 7

136 kg (300 lbs) of palladium-based CO combustion promoter according to the invention (Promoter A) was supplied to Refinery A. During a one week trial, Refinery A evaluated the performance in comparison to a state of the art CO combustion promoter (Promoter B) that has approximately twice the palladium content with the palladium distributed homogenously throughout the particles. Afterburn control was maintained using 20% less Promoter A (line (a)) compared to Promoter B (line (b)) as demonstrated in Figure 3.

EXAMPLE 8

136 kg (300 lbs) of palladium-based CO combustion promoter according to the invention (Promoter C) was supplied to Refinery B. During a two week trial, Refinery B evaluated the performance in comparison to a state of the art CO combustion promoter (Promoter D) that has approximately twice the palladium content with the palladium distributed homogenously throughout the particles.

Refinery B provided comparative data from the trial, which included data from three weeks prior to the start of the Promoter C trial when Promoter D was used for comparison. The first week of Promoter C trial is the transition from Promoter D, and therefore the second week of Promoter C data was used for comparison purposes and summarized in Table 1.

TABLE 1

		Promoter D 3 week average	Promoter C 2nd week average
Flue Gas O_2	mol %	1.2	1.4
Flue Gas CO	ppm	213.0	140.7
Flue Gas NOx	ppm	52.2	36.2
CO Promoter Additions	kg/day	11	9

Average flue gas composition and CO Promoter addition rates are given in Table 1. Promoter C controlled CO to lower levels compared to Promoter D despite having half the palladium content. Promoter C and Promoter D both controlled afterburn to acceptable and safe limits. Promoter C achieved this with half the palladium loading and an 18% lower addition rate. NOx emissions declined as Promoter C replaced the Promoter D in the FCC unit inventory, declining by over 30%. This result is attributed to less total palladium, both fresh and sintered, present in the catalyst inventory.

The NOx emissions are shown in Fig. 4 where the relative promoter concentrations of Promoter C and Promoter D are on the left hand y-axis and the flue gas NOx concentration in ppm (e) on the right hand y-axis. The x-axis were the dates the regenerator was monitored. Fig. 4 shows the NOx reduction over time when the relative content of Promoter D decreases as Promoter C increases. The content is expressed as a percentage of the maximum concentration of Promoter D. On Jan 20-21, Promoter D was accidently injected and an increase in NOx emissions is observed.

Refinery B conducted comparative shot tests of Promoter C and Promoter D by injecting 13.6 kg (30 lb) of each promoter. Each injection of 13.6 kg (30 lb) of promoter reduced the FCC afterburn by 5.6 ºC (10 ºF). NOx emissions from the injections of Promoter C and Promoter D were different. 13.6 kg (30 lb) of Promoter D increased NOx emissions from 45 to 67 ppm, and 180 minutes after injection the NOx emissions remained at 55 ppm. 13.6 kg (30 lb) of Promoter C increased NOx emissions from 45 to 54 ppm, and 180 minutes after injection the NOx emissions remained at 50 ppm. Therefore, Promoter C has a reduced impact on NOx emissions.

Claims

What is claimed herein is:

1. A CO to CO_2 combustion promoter comprising microsphere sized porous particles, each microsphere sized porous particle independently comprising:
silica, alumina, or mixtures thereof; and
one or more Group VIII noble metals distributed in the particle as an eggshell such that a higher content of the one or more Group VIII noble metals is present in the outer region of the microsphere sized porous particle as compared to the content of the one or more Group VIII noble metals in the centre of the microsphere sized porous particle.

2. The combustion promoter according to claim 1, comprising a plurality of microsphere sized porous particles comprising silica.

3. The combustion promoter according to claim 1, comprising a plurality of microsphere sized porous particles comprising alumina.

4. The combustion promoter according to claim 1, comprising a first plurality of microsphere sized porous particles comprising silica and a second plurality of microsphere sized porous particles comprising alumina.

5. The combustion promoter according to claim 1, comprising a plurality of microsphere sized porous particles comprising silica and alumina.

6. The combustion promoter according to claim 1, wherein the microsphere sized porous particles have an average (D50) size of between 60 and 90 microns as measured by laser diffraction.

7. The combustion promoter according to claim 1, wherein the microsphere sized porous particles are gamma or theta alumina particles.

8. The combustion promoter according to claim 1, wherein the microsphere sized porous particles are spray dried silica particles.

9. The combustion promoter according to claim 1, wherein the microsphere sized porous particles are an equilibrium or spent catalyst as obtained from a fluidized catalytic cracking (FCC) process.

10. The combustion promoter according to claim 1, wherein the attrition index as measured according to ASTM D-5757 of the CO to CO_2 combustion promoter for a sieve fraction of combustion promoter particles of between 40 and 105 microns is between 5 and 25.

11. The combustion promoter according to claim 10, wherein the attrition index of the CO to CO_2 combustion promoter for a sieve fraction of combustion promoter particles of between 40 and 105 microns is between 10 and 20.

12. The combustion promoter according to claim 1, wherein the one or more Group VIII noble metals comprises one or more of platinum, palladium, iridium, ruthenium, and rhodium.

13. The combustion promoter according to claim 12, wherein the one or more Group VIII noble metals comprises platinum and palladium.

14. The combustion promoter according to claim 12, wherein the one or more Group VIII noble metals comprises platinum.

15. The combustion promoter according to claim 12, wherein the one or more Group VIII noble metals comprises palladium.

16. The combustion promoter according to claim 1, wherein the microsphere sized porous particles further comprise at least one of cerium oxide and copper oxide.

17. The combustion promoter according to claim 16, wherein the at least one of cerium oxide and copper oxide is distributed in the microsphere sized porous particle as an eggshell such that a higher content of the at least one of cerium oxide and copper oxide is present in the outer region of the microsphere sized porous particle as compared to the content of the at least one of cerium oxide and copper oxide in the centre of the microsphere sized porous particle.

18. The combustion promoter according to claim 1, obtained by a process comprising the following steps:
(a) introducing a medium in the pores of microsphere sized porous particles to obtain filled microsphere sized porous particles; and
(b) contacting the filled microsphere sized porous particles with an aqueous salt solution of the one or more Group VIII noble metals wherein the one or more Group VIII noble metals deposits predominantly in in the outer region of the filled microsphere sized porous particles thereby obtaining eggshell particles.

19. The combustion promoter of claim 18, the process further comprising a step:
(c) at least one of drying and calcining the eggshell particles.

20. The combustion promoter according to claim 18, wherein the starting microsphere sized porous particles are gamma alumina particles having an average (D50) size of between 60 and 90 microns, have a surface area (BET) of between 50 and 300 m^2/g, and a pore volume of between 0.05 and 0.50 mL/g as measured as the water pore volume.

21. The combustion promoter according to claim 18, wherein the medium in step (a) is water.

22. The combustion promoter according to claim 18, wherein in step (b) the filled microsphere sized porous particles are contacted in step (b) with a volume of the aqueous salt solution of the one or more Group VIII noble metals which is less than the total volume of the pores of the starting microsphere sized particles.

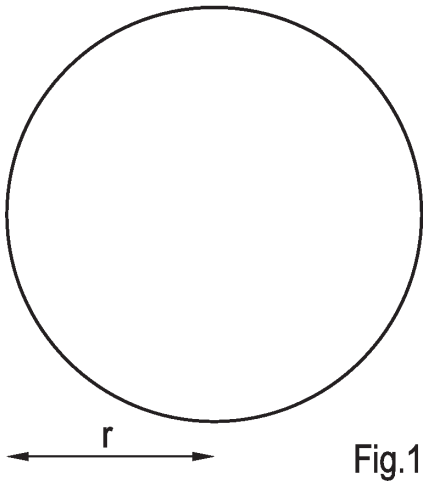


Fig.1

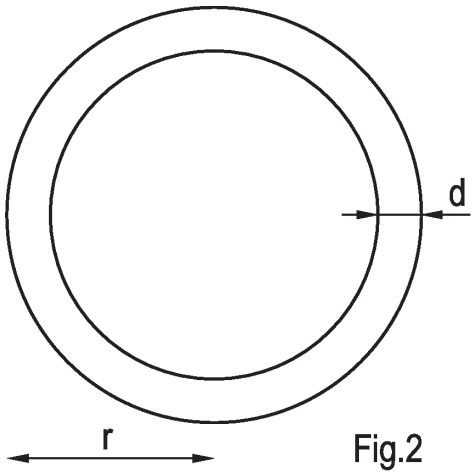


Fig.2

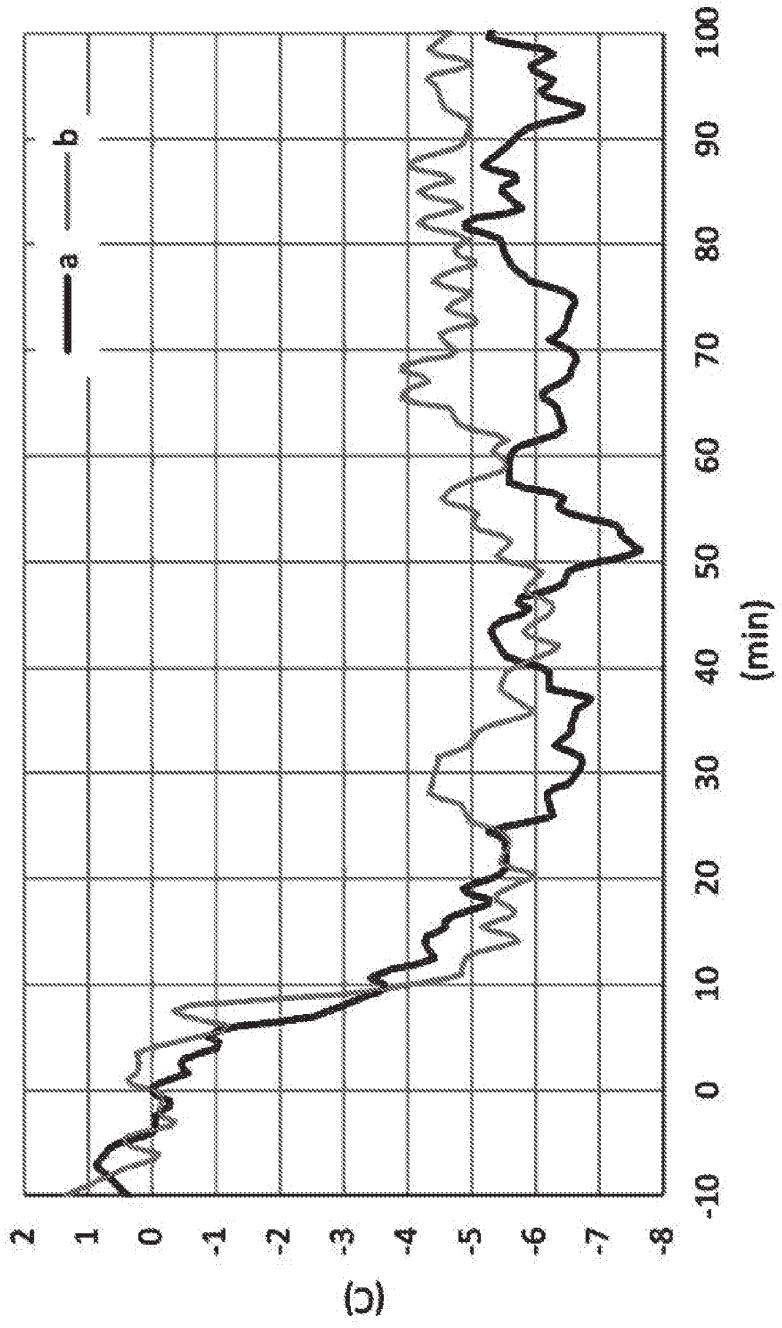


Fig.3

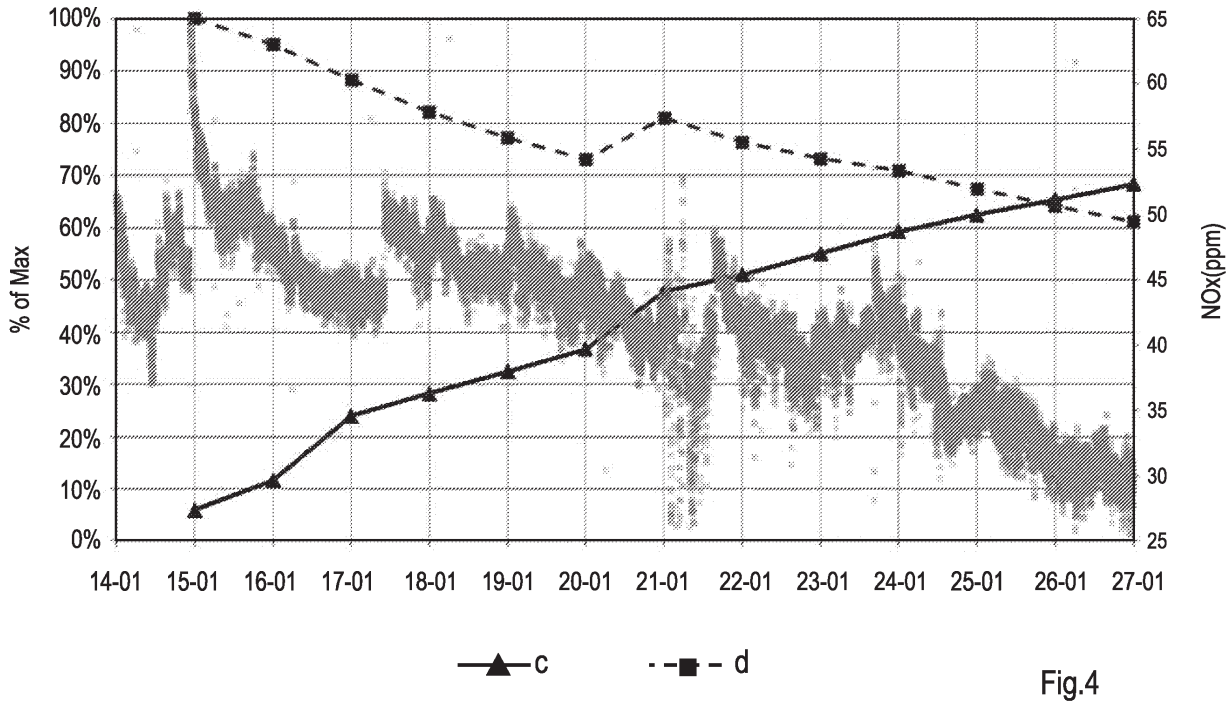

100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
% of Max
65
60
55
50
45
40
35
30
25
NOx(ppm)
14-01
15-01
16-01
17-01
18-01
19-01
20-01
21-01
22-01
23-01
24-01
25-01
26-01
27-01
c
d

Fig.4

Electronic Patent Application Fee Transmittal	
Application Number:	
Filing Date:	
Title of Invention:	A CO TO CO2 COMBUSTION PROMOTER
First Named Inventor/Applicant Name:	Guido William ARU
Filer:	Nicole Dian Kling/Lauren Donaghy
Attorney Docket Number:	071816-091960USC1
Filed as Small Entity	
Filing Fees for Track I Prioritized Examination - Nonprovisional Application under 35 USC 111(a)	

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Basic Filing:				
UTILITY FILING FEE (ELECTRONIC FILING)	4011	1	80	80
UTILITY SEARCH FEE	2111	1	350	350
UTILITY EXAMINATION FEE	2311	1	400	400
REQUEST FOR PRIORITIZED EXAMINATION	2817	1	2100	2100
Pages:				
Claims:				
CLAIMS IN EXCESS OF 20	2202	2	50	100
Miscellaneous-Filing:				

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
PUBL. FEE- EARLY, VOLUNTARY, OR NORMAL	1504	1	0	0
PROCESSING FEE, EXCEPT PROV. APPLS.	2830	1	70	70
Petition:				
Patent-Appeals-and-Interference:				
Post-Allowance-and-Post-Issuance:				
Extension-of-Time:				
Miscellaneous:				
		Total in USD ($)		**3100**

Attorney's Docket No. 071816-091960USC1 *PATENT*

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:	ARU, Guido William	Confirmation No.:	Herewith
Application No.:	Herewith (CON of 17/043,031)	Art Unit:	Not Yet Assigned
Filing Date:	February 16, 2021	Examiner:	Not Yet Assigned
For:	A CO TO CO2 COMBUSTION PROMOTER		

VIA EFS-WEB
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

GENERAL TRANSMITTAL & CERTIFICATE OF EFS SUBMISSION

Pursuant to 37 C.F.R. § 1.8(a)(1)(i)(C) I hereby certify that the following documents are being submitted to the Patent and Trademark Office via the Office Electronic Filing System in accordance with § 1.6(a)(4) on **February 16, 2021**:

1. **General Transmittal & Certificate of EFS Submission (1 pg.);**
2. **U.S. TrackOne Continuation Application (27 pp.): Specification (20 pp.); Claims (3 pp.); Abstract (1 pg.); and Drawings (3 pp.);**
3. **TrackOne Request (1 pg.);**
4. **Utility Patent Application Transmittal (2 pp.);**
5. **Application Data Sheet (8 pp.);**
6. **Form PTO/SB/08a (4 pp.);**
7. **Declaration (1 pg.);**
8. **Power of Attorney (2 pp.); and**
9. **Electronic Fee Transmittal (2 pp.).**

AUTHORIZATION TO CHARGE/CREDIT DEPOSIT ACCOUNT

The Director of the USPTO is hereby authorized to charge any fee deficiencies associated with the instant filing, **except excess claims fees**, and credit any overpayments to NIXON PEABODY LLP Deposit Account No. **50-0850**, from which the undersigned is authorized to withdraw.

Customer No.: 53143

Date: February 16, 2021

Respectfully submitted,

/Nicole D. Kling/

Ronald I. Eisenstein (Reg. No. 30,628)
Nicole D. Kling (Reg. No. 71,959)
NIXON PEABODY LLP
Exchange Place
53 State Street
Boston, MA 02109-2835
Tel. (617) 345- 6054/1013
Fax (617) 345-1300
Email: bostonpatent@nixonpeabody.com

4817-1937-8140.1

PTO/AIA/14 (02-18)
Approved for use through 11/30/2020. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	071816-091960USC1
	Application Number	
Title of Invention	A CO TO CO2 COMBUSTION PROMOTER	

The application data sheet is part of the provisional or nonprovisional application for which it is being submitted. The following form contains the bibliographic data arranged in a format specified by the United States Patent and Trademark Office as outlined in 37 CFR 1.76.
This document may be completed electronically and submitted to the Office in electronic format using the Electronic Filing System (EFS) or the document may be printed and included in a paper filed application.

Secrecy Order 37 CFR 5.2:

☐ Portions or all of the application associated with this Application Data Sheet may fall under a Secrecy Order pursuant to 37 CFR 5.2 (Paper filers only. Applications that fall under Secrecy Order may not be filed electronically.)

Inventor Information:

Inventor 1 — Remove

Legal Name

Prefix	Given Name	Middle Name	Family Name	Suffix
	Guido	William	ARU	

Residence Information (Select One) ● US Residency ○ Non US Residency ○ Active US Military Service

City	State/Province	Country of Residence
Conifer	CO	US

Mailing Address of Inventor:

Address 1	12045 Cochise Circle
Address 2	PO Box 1129

City	State/Province	Postal Code	Country
Conifer	CO	80433	US

All Inventors Must Be Listed - Additional Inventor Information blocks may be generated within this form by selecting the **Add** button. Add

Correspondence Information:

Enter either Customer Number or complete the Correspondence Information section below.
For further information see 37 CFR 1.33(a).

☐ **An Address is being provided for the correspondence Information of this application.**

Customer Number	53143		
Email Address	bostonpatent@nixonpeabody.com	Add Email	Remove Email

Application Information:

Title of the Invention	A CO TO CO2 COMBUSTION PROMOTER		
Attorney Docket Number	071816-091960USC1	**Small Entity Status Claimed**	☒
Application Type	Nonprovisional		
Subject Matter	Utility		
Total Number of Drawing Sheets (if any)	3	**Suggested Figure for Publication (if any)**	2

PTO/AIA/14 (02-18)
Approved for use through 11/30/2020. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	071816-091960USC1
	Application Number	
Title of Invention	A CO TO CO2 COMBUSTION PROMOTER	

Filing By Reference:

Only complete this section when filing an application by reference under 35 U.S.C. 111(c) and 37 CFR 1.57(a). Do not complete this section if application papers including a specification and any drawings are being filed. Any domestic benefit or foreign priority information must be provided in the appropriate section(s) below (i.e., "Domestic Benefit/National Stage Information" and "Foreign Priority Information").

For the purposes of a filing date under 37 CFR 1.53(b), the description and any drawings of the present application are replaced by this reference to the previously filed application, subject to conditions and requirements of 37 CFR 1.57(a).

Application number of the previously filed application	Filing date (YYYY-MM-DD)	Intellectual Property Authority or Country

Publication Information:

☐ Request Early Publication (Fee required at time of Request 37 CFR 1.219)

☐ **Request Not to Publish.** I hereby request that the attached application not be published under 35 U.S.C. 122(b) and certify that the invention disclosed in the attached application **has not and will not** be the subject of an application filed in another country, or under a multilateral international agreement, that requires publication at eighteen months after filing.

Representative Information:

Representative information should be provided for all practitioners having a power of attorney in the application. Providing this information in the Application Data Sheet does not constitute a power of attorney in the application (see 37 CFR 1.32).
Either enter Customer Number or complete the Representative Name section below. If both sections are completed the customer Number will be used for the Representative Information during processing.

Please Select One:	● Customer Number	US Patent Practitioner	◯ Limited Recognition (37 CFR 11.9)
Customer Number	53143		

Domestic Benefit/National Stage Information:

This section allows for the applicant to either claim benefit under 35 U.S.C. 119(e), 120, 121, 365(c), or 386(c) or indicate National Stage entry from a PCT application. Providing benefit claim information in the Application Data Sheet constitutes the specific reference required by 35 U.S.C. 119(e) or 120, and 37 CFR 1.78.
When referring to the current application, please leave the "Application Number" field blank.

Prior Application Status	Pending		Remove
Application Number	Continuity Type	Prior Application Number	Filing or 371(c) Date (YYYY-MM-DD)
	Continuation of	17043031	2020-09-29

PTO/AIA/14 (02-18)
Approved for use through 11/30/2020. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	071816-091960USC1
	Application Number	
Title of Invention	A CO TO CO2 COMBUSTION PROMOTER	

Prior Application Status	Expired		Remove
Application Number	Continuity Type	Prior Application Number	Filing or 371(c) Date (YYYY-MM-DD)
17043031	a 371 of international	PCT/US2019/024742	2019-03-29
Prior Application Status	Expired		Remove
Application Number	Continuity Type	Prior Application Number	Filing or 371(c) Date (YYYY-MM-DD)
PCT/US2019/024742	Claims benefit of provisional	62651295	2018-04-02
Additional Domestic Benefit/National Stage Data may be generated within this form by selecting the **Add** button.			Add

Foreign Priority Information:

This section allows for the applicant to claim priority to a foreign application. Providing this information in the application data sheet constitutes the claim for priority as required by 35 U.S.C. 119(b) and 37 CFR 1.55. When priority is claimed to a foreign application that is eligible for retrieval under the priority document exchange program (PDX)[i] the information will be used by the Office to automatically attempt retrieval pursuant to 37 CFR 1.55(i)(1) and (2). Under the PDX program, applicant bears the ultimate responsibility for ensuring that a copy of the foreign application is received by the Office from the participating foreign intellectual property office, or a certified copy of the foreign priority application is filed, within the time period specified in 37 CFR 1.55(g)(1).

			Remove
Application Number	Country[i]	Filing Date (YYYY-MM-DD)	Access Code[i] (if applicable)
2020819	NL	2018-04-24	
Additional Foreign Priority Data may be generated within this form by selecting the **Add** button.			Add

Statement under 37 CFR 1.55 or 1.78 for AIA (First Inventor to File) Transition Applications

☐ This application (1) claims priority to or the benefit of an application filed before March 16, 2013 and (2) also contains, or contained at any time, a claim to a claimed invention that has an effective filing date on or after March 16, 2013.
NOTE: By providing this statement under 37 CFR 1.55 or 1.78, this application, with a filing date on or after March 16, 2013, will be examined under the first inventor to file provisions of the AIA.

PTO/AIA/14 (02-18)
Approved for use through 11/30/2020. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	071816-091960USC1
	Application Number	
Title of Invention	A CO TO CO2 COMBUSTION PROMOTER	

Authorization or Opt-Out of Authorization to Permit Access:

When this Application Data Sheet is properly signed and filed with the application, applicant has provided written authority to permit a participating foreign intellectual property (IP) office access to the instant application-as-filed (see paragraph A in subsection 1 below) and the European Patent Office (EPO) access to any search results from the instant application (see paragraph B in subsection 1 below).

Should applicant choose not to provide an authorization identified in subsection 1 below, applicant **must opt-out** of the authorization by checking the corresponding box A or B or both in subsection 2 below.

NOTE: This section of the Application Data Sheet is **ONLY** reviewed and processed with the **INITIAL** filing of an application. After the initial filing of an application, an Application Data Sheet cannot be used to provide or rescind authorization for access by a foreign IP office(s). Instead, Form PTO/SB/39 or PTO/SB/69 must be used as appropriate.

1. Authorization to Permit Access by a Foreign Intellectual Property Office(s)

A. Priority Document Exchange (PDX) - Unless box A in subsection 2 (opt-out of authorization) is checked, the undersigned hereby **grants the USPTO authority** to provide the European Patent Office (EPO), the Japan Patent Office (JPO), the Korean Intellectual Property Office (KIPO), the State Intellectual Property Office of the People's Republic of China (SIPO), the World Intellectual Property Organization (WIPO), and any other foreign intellectual property office participating with the USPTO in a bilateral or multilateral priority document exchange agreement in which a foreign application claiming priority to the instant patent application is filed, access to: (1) the instant patent application-as-filed and its related bibliographic data, (2) any foreign or domestic application to which priority or benefit is claimed by the instant application and its related bibliographic data, and (3) the date of filing of this Authorization. See 37 CFR 1.14(h)(1).

B. Search Results from U.S. Application to EPO - Unless box B in subsection 2 (opt-out of authorization) is checked, the undersigned hereby **grants the USPTO authority** to provide the EPO access to the bibliographic data and search results from the instant patent application when a European patent application claiming priority to the instant patent application is filed. See 37 CFR 1.14(h)(2).

The applicant is reminded that the EPO's Rule 141(1) EPC (European Patent Convention) requires applicants to submit a copy of search results from the instant application without delay in a European patent application that claims priority to the instant application.

2. Opt-Out of Authorizations to Permit Access by a Foreign Intellectual Property Office(s)

☐ A. Applicant **DOES NOT** authorize the USPTO to permit a participating foreign IP office access to the instant application-as-filed. If this box is checked, the USPTO will not be providing a participating foreign IP office with any documents and information identified in subsection 1A above.

☐ B. Applicant **DOES NOT** authorize the USPTO to transmit to the EPO any search results from the instant patent application. If this box is checked, the USPTO will not be providing the EPO with search results from the instant application.

NOTE: Once the application has published or is otherwise publicly available, the USPTO may provide access to the application in accordance with 37 CFR 1.14.

PTO/AIA/14 (02-18)
Approved for use through 11/30/2020. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	071816-091960USC1
	Application Number	
Title of Invention	A CO TO CO2 COMBUSTION PROMOTER	

Applicant Information:

Providing assignment information in this section does not substitute for compliance with any requirement of part 3 of Title 37 of CFR to have an assignment recorded by the Office.

Applicant 1 Remove

If the applicant is the inventor (or the remaining joint inventor or inventors under 37 CFR 1.45), this section should not be completed. The information to be provided in this section is the name and address of the legal representative who is the applicant under 37 CFR 1.43; or the name and address of the assignee, person to whom the inventor is under an obligation to assign the invention, or person who otherwise shows sufficient proprietary interest in the matter who is the applicant under 37 CFR 1.46. If the applicant is an applicant under 37 CFR 1.46 (assignee, person to whom the inventor is obligated to assign, or person who otherwise shows sufficient proprietary interest) together with one or more joint inventors, then the joint inventor or inventors who are also the applicant should be identified in this section.

Clear

● Assignee	Legal Representative under 35 U.S.C. 117	Joint Inventor
Person to whom the inventor is obligated to assign.	Person who shows sufficient proprietary interest	

If applicant is the legal representative, indicate the authority to file the patent application, the inventor is:

Name of the Deceased or Legally Incapacitated Inventor:

If the Applicant is an Organization check here. ☒

Organization Name	COCHISE TECHNOLOGY, LLC		
Mailing Address Information For Applicant:			
Address 1	12045 Cochise Circle		
Address 2	PO Box 1129		
City	Conifer	**State/Province**	CO
Country	US	Postal Code	80433
Phone Number		Fax Number	
Email Address			

Additional Applicant Data may be generated within this form by selecting the Add button. Add

Assignee Information including Non-Applicant Assignee Information:

Providing assignment information in this section does not substitute for compliance with any requirement of part 3 of Title 37 of CFR to have an assignment recorded by the Office.

PTO/AIA/14 (02-18)
Approved for use through 11/30/2020. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	071816-091960USC1
	Application Number	
Title of Invention	A CO TO CO2 COMBUSTION PROMOTER	

Assignee 1

Complete this section if assignee information, including non-applicant assignee information, is desired to be included on the patent application publication. An assignee-applicant identified in the "Applicant Information" section will appear on the patent application publication as an applicant. For an assignee-applicant, complete this section only if identification as an assignee is also desired on the patent application publication.

Remove

If the Assignee or Non-Applicant Assignee is an Organization check here. ☒

Organization Name	COCHISE TECHNOLOGY, LLC

Mailing Address Information For Assignee including Non-Applicant Assignee:

Address 1	12045 Cochise Circle		
Address 2	PO Box 1129		
City	Conifer	**State/Province**	CO
Country i	US	Postal Code	80433
Phone Number		Fax Number	
Email Address			

Additional Assignee or Non-Applicant Assignee Data may be generated within this form by selecting the Add button. Add

Signature:

Remove

NOTE: This Application Data Sheet must be signed in accordance with 37 CFR 1.33(b). **However, if this Application Data Sheet is submitted with the INITIAL filing of the application and either box A or B is not checked in subsection 2 of the "Authorization or Opt-Out of Authorization to Permit Access" section, then this form must also be signed in accordance with 37 CFR 1.14(c).**

This Application Data Sheet **must** be signed by a patent practitioner if one or more of the applicants is a **juristic entity** (e.g., corporation or association). If the applicant is two or more joint inventors, this form must be signed by a patent practitioner, **all** joint inventors who are the applicant, or one or more joint inventor-applicants who have been given power of attorney (e.g., see USPTO Form PTO/AIA/81) on behalf of **all** joint inventor-applicants.

See 37 CFR 1.4(d) for the manner of making signatures and certifications.

Signature	/Nicole D. Kling/			Date (YYYY-MM-DD)	2021-02-16
First Name	Nicole D.	Last Name	Kling	Registration Number	71959

Additional Signature may be generated within this form by selecting the Add button. Add

PTO/AIA/14 (02-18)
Approved for use through 11/30/2020. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	071816-091960USC1
	Application Number	
Title of Invention	A CO TO CO2 COMBUSTION PROMOTER	

This collection of information is required by 37 CFR 1.76. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 23 minutes to complete, including gathering, preparing, and submitting the completed application data sheet form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

Privacy Act Statement

The Privacy Act of 1974 (P.L. 93-579) requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1 The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C. 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether the Freedom of Information Act requires disclosure of these records.

2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.

3 A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.

4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).

5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent CooperationTreaty.

6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).

7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.

8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspections or an issued patent.

9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

PTO/AIA/15 (10-17)
Approved for use through 11/30/2020. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995 no persons are required to respond to a collection of information unless it displays a valid OMB control number.

UTILITY PATENT APPLICATION TRANSMITTAL

(Only for new nonprovisional applications under 37 CFR 1.53(b))

Attorney Docket No.	071816-091960USC1
First Named Inventor	Guido William ARU
Title	A CO TO CO2 COMBUSTION PROMOTER
Priority Mail Express® Label No.	

APPLICATION ELEMENTS

See MPEP chapter 600 concerning utility patent application contents.

1. [✔] **Fee Transmittal Form** (PTO/SB/17 or equivalent)
2. [✔] **Applicant asserts small entity status.** See 37 CFR 1.27
3. [ ] **Applicant certifies micro entity status.** See 37 CFR 1.29. Applicant must attach form PTO/SB/15A or B or equivalent.
4. [✔] **Specification** [*Total Pages* 24] Both the claims and abstract must start on a new page. *(See MPEP § 608.01(a) for information on the preferred arrangement)*
5. [✔] **Drawing(s)** (35 U.S.C. 113) [*Total Sheets* 3]
6. **Inventor's Oath or Declaration** [*Total Pages* 1] *(including substitute statements under 37 CFR 1.64 and assignments serving as an oath or declaration under 37 CFR 1.63(e))*
   a. [ ] Newly executed (original or copy)
   b. [✔] A copy from a prior application (37 CFR 1.63(d))
7. [✔] **Application Data Sheet** ** See note below.* See 37 CFR 1.76 (PTO/AIA/14 or equivalent)
8. **CD-ROM or CD-R** in duplicate, large table, or Computer Program (*Appendix*)
   [ ] Landscape Table on CD
9. **Nucleotide and/or Amino Acid Sequence Submission** (*if applicable, items a. – c. are required*)
   a. [ ] Computer Readable Form (CRF)
   b. [ ] Specification Sequence Listing on:
      i. [ ] CD-ROM or CD-R (2 copies); or
      ii. [ ] Paper
   c. [ ] Statements verifying identity of above copies

ADDRESS TO: **Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450**

ACCOMPANYING APPLICATION PAPERS

10. [ ] **Assignment Papers** (cover sheet & document(s)) Name of Assignee _____
11. [ ] **37 CFR 3.73(c) Statement** (*when there is an assignee*) [✔] **Power of Attorney**
12. [ ] **English Translation Document** (*if applicable*)
13. [✔] **Information Disclosure Statement** (PTO/SB/08 or PTO-1449)
    [ ] Copies of citations attached
14. [ ] **Preliminary Amendment**
15. [ ] **Return Receipt Postcard** (*MPEP § 503*) (*Should be specifically itemized*)
16. [ ] **Certified Copy of Priority Document(s)** (*if foreign priority is claimed*)
17. [ ] **Nonpublication Request** Under 35 U.S.C. 122(b)(2)(B)(i). Applicant must attach form PTO/SB/35 or equivalent.
18. [✔] **Other:** TrackOne Request

Note*: (1) Benefit claims under 37 CFR 1.78 and foreign priority claims under 1.55 **must be included in an Application Data Sheet (ADS).
(2) For applications filed under 35 U.S.C. 111, the application must contain an ADS specifying the applicant if the applicant is an assignee, person to whom the inventor is under an obligation to assign, or person who otherwise shows sufficient proprietary interest in the matter. See 37 CFR 1.46(b).

19. CORRESPONDENCE ADDRESS

[✔] The address associated with Customer Number: 53143 **OR** [ ] Correspondence address below

Name					
Address					
City		State		Zip Code	
Country		Telephone		Email	

Signature	/Nicole D. Kling/	Date	2021-02-16
Name (Print/Type)	Nicole D. Kling	Registration No. (Attorney/Agent)	71959

This collection of information is required by 37 CFR 1.53(b). The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

Privacy Act Statement

The **Privacy Act of 1974 (P.L. 93-579)** requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether disclosure of these records is required by the Freedom of Information Act.
2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.
3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.
4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).
5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.
6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).
7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (*i.e.*, GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.
8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspection or an issued patent.
9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

DocCode – SCORE

SCORE Placeholder Sheet for IFW Content

Application Number: 17176222 Document Date: 02/16/2021

The presence of this form in the IFW record indicates that the following document type was received in electronic format on the date identified above. This content is stored in the SCORE database.

Since this was an electronic submission, there is no physical artifact folder, no artifact folder is recorded in PALM, and no paper documents or physical media exist. The TIFF images in the IFW record were created from the original documents that are stored in SCORE.

- Drawing

At the time of document entry (noted above):

- USPTO employees may access SCORE content via DAV or via the SCORE web page.
- External customers may access SCORE content via PAIR using the Supplemental Content tab.

Form Revision Date: March 1, 2019

PTO/SB/08a (02-18)
Approved for use through 11/30/2020. OMB 0651-0031
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

INFORMATION DISCLOSURE STATEMENT BY APPLICANT
(Not for submission under 37 CFR 1.99)

Application Number	
Filing Date	2021-02-16
First Named Inventor	Aru, Guido William
Art Unit	
Examiner Name	
Attorney Docket Number	071816-091960USC1

U.S.PATENTS Remove

Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1	4755282	A	1988-07-05	SAMISH et al.	
	2	6881390	B2	2005-04-19	YALURIS et al.	
	3	7045056	B2	2006-05-16	KELKAR et al.	

If you wish to add additional U.S. Patent citation information please click the Add button. Add

U.S.PATENT APPLICATION PUBLICATIONS Remove

Examiner Initial*	Cite No	Publication Number	Kind Code[1]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1	20050042158	A1	2005-02-24	YALURIS et al.	
	2	20060204420	A1	2006-09-14	VAARKAMP et al.	

If you wish to add additional U.S. Published Application citation information please click the Add button. Add

FOREIGN PATENT DOCUMENTS Remove

Examiner Initial*	Cite No	Foreign Document Number[3]	Country Code[2] i	Kind Code[4]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear	T[5]

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	
	Filing Date	2021-02-16
	First Named Inventor	Aru, Guido William
	Art Unit	
	Examiner Name	
	Attorney Docket Number	071816-091960USC1

	1							

If you wish to add additional Foreign Patent Document citation information please click the Add button Add

NON-PATENT LITERATURE DOCUMENTS Remove

Examiner Initials*	Cite No	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc), date, pages(s), volume-issue number(s), publisher, city and/or country where published.	T[5]
	1		

If you wish to add additional non-patent literature document citation information please click the Add button Add

EXAMINER SIGNATURE

Examiner Signature		Date Considered	

*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through a citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

[1] See Kind Codes of USPTO Patent Documents at www.USPTO.GOV or MPEP 901.04. [2] Enter office that issued the document, by the two-letter code (WIPO Standard ST.3). [3] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. [4] Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [5] Applicant is to place a check mark here if English language translation is attached.

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	
	Filing Date	2021-02-16
	First Named Inventor	Aru, Guido William
	Art Unit	
	Examiner Name	
	Attorney Docket Number	071816-091960USC1

CERTIFICATION STATEMENT

Please see 37 CFR 1.97 and 1.98 to make the appropriate selection(s):

That each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(1).

OR

☐ That no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing the certification after making reasonable inquiry, no item of information contained in the information disclosure statement was known to any individual designated in 37 CFR 1.56(c) more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(2).

See attached certification statement.

The fee set forth in 37 CFR 1.17 (p) has been submitted herewith.

☒ A certification statement is not submitted herewith.

SIGNATURE

A signature of the applicant or representative is required in accordance with CFR 1.33, 10.18. Please see CFR 1.4(d) for the form of the signature.

Signature	/Nicole D. Kling/	Date (YYYY-MM-DD)	2021-02-16
Name/Print	Nicole D. Kling	Registration Number	71,959

This collection of information is required by 37 CFR 1.97 and 1.98. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 1 hour to complete, including gathering, preparing and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

Privacy Act Statement

The Privacy Act of 1974 (P.L. 93-579) requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C. 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether the Freedom of Information Act requires disclosure of these record s.

2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.

3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.

4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).

5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.

6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).

7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.

8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspections or an issued patent.

9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

DECLARATION UNDER 37 CFR §1.63 FOR UTILITY APPLICATION USING AN APPLICATION DATA SHEET

TITLE OF INVENTION:

A CO TO CO_2 COMBUSTION PROMOTER

As the below named inventor, I hereby declare that:

This Declaration is directed to:

- ■ The attached application, or
- ■ United States application or PCT international application number **PCT/US2019/024742** filed on **March 29, 2019.**
- □ I have reviewed the preliminary amendment filed _____.

The above-identified application was made or authorized to be made by me.

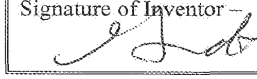
I believe that I am the original inventor or an original joint inventor of a claimed invention in the application.

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, §1.56(a).

I hereby further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further, that these statements were made with the knowledge that any willful false statements and the like so made in this declaration are punishable by fine or imprisonment of not more than 5 years, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

LEGAL NAME OF INVENTOR	LAST NAME	FIRST NAME	MIDDLE NAME
	ARU	**GUIDO**	WILLIAM

Signature of Inventor –	Date:
	OCTOBER 5, 2020

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NUMBER	FILING or 371(c) DATE	GRP ART UNIT	FIL FEE REC'D	ATTY.DOCKET.NO	TOT CLAIMS	IND CLAIMS
17/176,222	02/16/2021	1736	930	071816-091960USC1	22	1

CONFIRMATION NO. 3640

53143
RONALD I. EISENSTEIN
NIXON PEABODY LLP
Exchange Place, 53 State Street
BOSTON, MA 02109

FILING RECEIPT

OC000000123838989

Date Mailed: 02/26/2021

Receipt is acknowledged of this non-provisional utility patent application. The application will be taken up for examination in due course. Applicant will be notified as to the results of the examination. Any correspondence concerning the application must include the following identification information: the U.S. APPLICATION NUMBER, FILING DATE, NAME OF FIRST INVENTOR, and TITLE OF INVENTION. Fees transmitted by check or draft are subject to collection.

Please verify the accuracy of the data presented on this receipt. If an error is noted on this Filing Receipt, please submit a written request for a corrected Filing Receipt, including a properly marked-up ADS showing the changes with strike-through for deletions and underlining for additions. If you received a "Notice to File Missing Parts" or other Notice requiring a response for this application, please submit any request for correction to this Filing Receipt with your reply to the Notice. When the USPTO processes the reply to the Notice, the USPTO will generate another Filing Receipt incorporating the requested corrections provided that the request is grantable.

Inventor(s)

Guido William ARU, Conifer, CO;

Applicant(s)

COCHISE TECHNOLOGY, LLC, Conifer, CO;

Assignment For Published Patent Application

COCHISE TECHNOLOGY, LLC, Conifer, CO

Power of Attorney: The patent practitioners associated with Customer Number 53143

Domestic Priority data as claimed by applicant

This application is a CON of 17/043,031 09/29/2020
which is a 371 of PCT/US2019/024742 03/29/2019
which claims benefit of 62/651,295 04/02/2018

Foreign Applications (You may be eligible to benefit from the **Patent Prosecution Highway** program at the USPTO. Please see http://www.uspto.gov for more information.)
NETHERLANDS 2020819 04/24/2018 No Access Code Provided

Permission to Access Application via Priority Document Exchange: Yes

Permission to Access Search Results: Yes

Applicant may provide or rescind an authorization for access using Form PTO/SB/39 or Form PTO/SB/69 as appropriate.

If Required, Foreign Filing License Granted: 02/24/2021

The country code and number of your priority application, to be used for filing abroad under the Paris Convention, is **US 17/176,222**

Projected Publication Date: 06/03/2021

Non-Publication Request: No

Early Publication Request: No
**** SMALL ENTITY ****
Title

CO TO CO2 COMBUSTION PROMOTER

Preliminary Class

502

Statement under 37 CFR 1.55 or 1.78 for AIA (First Inventor to File) Transition Applications: No

PROTECTING YOUR INVENTION OUTSIDE THE UNITED STATES

Since the rights granted by a U.S. patent extend only throughout the territory of the United States and have no effect in a foreign country, an inventor who wishes patent protection in another country must apply for a patent in a specific country or in regional patent offices. Applicants may wish to consider the filing of an international application under the Patent Cooperation Treaty (PCT). An international (PCT) application generally has the same effect as a regular national patent application in each PCT-member country. The PCT process **simplifies** the filing of patent applications on the same invention in member countries, but **does not result** in a grant of "an international patent" and does not eliminate the need of applicants to file additional documents and fees in countries where patent protection is desired.

Almost every country has its own patent law, and a person desiring a patent in a particular country must make an application for patent in that country in accordance with its particular laws. Since the laws of many countries differ in various respects from the patent law of the United States, applicants are advised to seek guidance from specific foreign countries to ensure that patent rights are not lost prematurely.

Applicants also are advised that in the case of inventions made in the United States, the Director of the USPTO must issue a license before applicants can apply for a patent in a foreign country. The filing of a U.S. patent application serves as a request for a foreign filing license. The application's filing receipt contains further information and guidance as to the status of applicant's license for foreign filing.

Applicants may wish to consult the USPTO booklet, "General Information Concerning Patents" (specifically, the section entitled "Treaties and Foreign Patents") for more information on timeframes and deadlines for filing foreign patent applications. The guide is available either by contacting the USPTO Contact Center at 800-786-9199, or it can be viewed on the USPTO website at http://www.uspto.gov/web/offices/pac/doc/general/index.html.

For information on preventing theft of your intellectual property (patents, trademarks and copyrights), you may wish to consult the U.S. Government website, http://www.stopfakes.gov. Part of a Department of Commerce initiative, this website includes self-help "toolkits" giving innovators guidance on how to protect intellectual property in specific

countries such as China, Korea and Mexico. For questions regarding patent enforcement issues, applicants may call the U.S. Government hotline at 1-866-999-HALT (1-866-999-4258).

LICENSE FOR FOREIGN FILING UNDER

Title 35, United States Code, Section 184

Title 37, Code of Federal Regulations, 5.11 & 5.15

GRANTED

The applicant has been granted a license under 35 U.S.C. 184, if the phrase "IF REQUIRED, FOREIGN FILING LICENSE GRANTED" followed by a date appears on this form. Such licenses are issued in all applications where the conditions for issuance of a license have been met, regardless of whether or not a license may be required as set forth in 37 CFR 5.15. The scope and limitations of this license are set forth in 37 CFR 5.15(a) unless an earlier license has been issued under 37 CFR 5.15(b). The license is subject to revocation upon written notification. The date indicated is the effective date of the license, unless an earlier license of similar scope has been granted under 37 CFR 5.13 or 5.14.

This license is to be retained by the licensee and may be used at any time on or after the effective date thereof unless it is revoked. This license is automatically transferred to any related applications(s) filed under 37 CFR 1.53(d). This license is not retroactive.

The grant of a license does not in any way lessen the responsibility of a licensee for the security of the subject matter as imposed by any Government contract or the provisions of existing laws relating to espionage and the national security or the export of technical data. Licensees should apprise themselves of current regulations especially with respect to certain countries, of other agencies, particularly the Office of Defense Trade Controls, Department of State (with respect to Arms, Munitions and Implements of War (22 CFR 121-128)); the Bureau of Industry and Security, Department of Commerce (15 CFR parts 730-774); the Office of Foreign AssetsControl, Department of Treasury (31 CFR Parts 500+) and the Department of Energy.

NOT GRANTED

No license under 35 U.S.C. 184 has been granted at this time, if the phrase "IF REQUIRED, FOREIGN FILING LICENSE GRANTED" DOES NOT appear on this form. Applicant may still petition for a license under 37 CFR 5.12, if a license is desired before the expiration of 6 months from the filing date of the application. If 6 months has lapsed from the filing date of this application and the licensee has not received any indication of a secrecy order under 35 U.S.C. 181, the licensee may foreign file the application pursuant to 37 CFR 5.15(b).

SelectUSA

The United States represents the largest, most dynamic marketplace in the world and is an unparalleled location for business investment, innovation, and commercialization of new technologies. The U.S. offers tremendous resources and advantages for those who invest and manufacture goods here. Through SelectUSA, our nation works to promote and facilitate business investment. SelectUSA provides information assistance to the international investor community; serves as an ombudsman for existing and potential investors; advocates on behalf of U.S. cities, states, and regions competing for global investment; and counsels U.S. economic development organizations on investment attraction best practices. To learn more about why the United States is the best country in the world to develop

technology, manufacture products, deliver services, and grow your business, visit http://www.SelectUSA.gov or call +1-202-482-6800.

PATENT APPLICATION FEE DETERMINATION RECORD

Substitute for Form PTO-875

Application or Docket Number: 17/176,222

APPLICATION AS FILED - PART I

FOR	(Column 1) NUMBER FILED	(Column 2) NUMBER EXTRA	SMALL ENTITY RATE($)	SMALL ENTITY FEE($)	OR	OTHER THAN SMALL ENTITY RATE($)	OTHER THAN SMALL ENTITY FEE($)
BASIC FEE (37 CFR 1.16(a), (b), or (c))	N/A	N/A	N/A	80		N/A	
SEARCH FEE (37 CFR 1.16(k), (i), or (m))	N/A	N/A	N/A	350		N/A	
EXAMINATION FEE (37 CFR 1.16(o), (p), or (q))	N/A	N/A	N/A	400		N/A	
TOTAL CLAIMS (37 CFR 1.16(i))	22 minus 20 =	* 2	x 50 =	100	OR		
INDEPENDENT CLAIMS (37 CFR 1.16(h))	1 minus 3 =	*	x 240 =	0.00			
APPLICATION SIZE FEE (37 CFR 1.16(s))	If the specification and drawings exceed 100 sheets of paper, the application size fee due is $310 ($155 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s).			0.00			
MULTIPLE DEPENDENT CLAIM PRESENT (37 CFR 1.16(j))				0.00			
* If the difference in column 1 is less than zero, enter "0" in column 2.			TOTAL	930		TOTAL	

APPLICATION AS AMENDED - PART II

		(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA	SMALL ENTITY RATE($)	SMALL ENTITY ADDITIONAL FEE($)	OR	OTHER THAN SMALL ENTITY RATE($)	OTHER THAN SMALL ENTITY ADDITIONAL FEE($)
AMENDMENT A	Total (37 CFR 1.16(i))	*	Minus	**	=	x =		OR	x =	
	Independent (37 CFR 1.16(h))	*	Minus	***	=	x =		OR	x =	
	Application Size Fee (37 CFR 1.16(s))									
	FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))							OR		
						TOTAL ADD'L FEE		OR	TOTAL ADD'L FEE	

		(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA	SMALL ENTITY RATE($)	SMALL ENTITY ADDITIONAL FEE($)	OR	OTHER THAN SMALL ENTITY RATE($)	OTHER THAN SMALL ENTITY ADDITIONAL FEE($)
AMENDMENT B	Total (37 CFR 1.16(i))	*	Minus	**	=	x =		OR	x =	
	Independent (37 CFR 1.16(h))	*	Minus	***	=	x =		OR	x =	
	Application Size Fee (37 CFR 1.16(s))									
	FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))							OR		
						TOTAL ADD'L FEE		OR	TOTAL ADD'L FEE	

* If the entry in column 1 is less than the entry in column 2, write "0" in column 3.
** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20".
*** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, enter "3".
The "Highest Number Previously Paid For" (Total or Independent) is the highest found in the appropriate box in column 1.

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
17/176,222	02/16/2021	Guido William ARU	071816-091960USC1	3640

53143 7590 03/17/2021

RONALD I. EISENSTEIN
NIXON PEABODY LLP
Exchange Place, 53 State Street
BOSTON, MA 02109

EXAMINER	
ART UNIT	PAPER NUMBER
1771	

NOTIFICATION DATE	DELIVERY MODE
03/17/2021	ELECTRONIC

Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

Notice of the Office communication was sent electronically on above-indicated "Notification Date" to the following e-mail address(es):

bostonpatent@nixonpeabody.com
ipairlink@nixonpeabody.com

Decision Granting Request for Prioritized Examination (Track I)	**Application No.** 17/176,222	**Applicant(s)** ARU, Guido William	
	Examiner BRIAN W BROWN	**Art Unit** OPET	**AIA (FITF) Status** Yes

1. THE REQUEST FILED 16 February 2021 IS **GRANTED** .

The above-identified application has met the requirements for prioritized examination

A. ☑ for an original nonprovisional application (Track I).
B. ☐ for an application undergoing continued examination (RCE).

2. **The above-identified application will undergo prioritized examination**. The application will be accorded special status throughout its entire course of prosecution until one of the following occurs:

A. filing a **petition for extension of time** to extend the time period for filing a reply;

B. filing an **amendment to amend the application to contain more than four independent claims, more than thirty total claims** , or a multiple dependent claim;

C. filing a **request for continued examination** ;

D. filing a notice of appeal;

E. filing a request for suspension of action;

F. mailing of a notice of allowance;

G. mailing of a final Office action;

H. completion of examination as defined in 37 CFR 41.102; or

I. abandonment of the application.

Telephone inquiries with regard to this decision should be directed to BRIAN BROWN at (571)272-5338. In his/her absence, calls may be directed to Petition Help Desk at (571) 272-3282.

/BRIAN W BROWN/ Petitions Examiner, OPET	

U.S. Patent and Trademark Office
PTO-2298 (Rev. 02-2012)

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
17/176,222	02/16/2021	Guido William ARU	071816-091960USC1	3640

53143 7590 04/07/2021

RONALD I. EISENSTEIN
NIXON PEABODY LLP
Exchange Place, 53 State Street
BOSTON, MA 02109

EXAMINER	
SOLIMAN, HAYTHAM	

ART UNIT	PAPER NUMBER
1736	

NOTIFICATION DATE	DELIVERY MODE
04/07/2021	ELECTRONIC

Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

Notice of the Office communication was sent electronically on above-indicated "Notification Date" to the following e-mail address(es):

bostonpatent@nixonpeabody.com
ipairlink@nixonpeabody.com

Office Action Summary	Application No. 17/176,222	Applicant(s) ARU, Guido William	
	Examiner HAYTHAM SOLIMAN	Art Unit 1736	AIA (FITF) Status Yes

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --

Period for Reply

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE 3 MONTHS FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133). Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

Status

1)☑ Responsive to communication(s) filed on 2/16/2021.

☐ A declaration(s)/affidavit(s) under **37 CFR 1.130(b)** was/were filed on _____.

2a)☐ This action is **FINAL.** 2b) ☑ This action is non-final.

3)☐ An election was made by the applicant in response to a restriction requirement set forth during the interview on _____; the restriction requirement and election have been incorporated into this action.

4)☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

Disposition of Claims*

5) ☑ Claim(s) 1-22 is/are pending in the application.

5a) Of the above claim(s) _____ is/are withdrawn from consideration.

6) ☐ Claim(s) _____ is/are allowed.

7) ☑ Claim(s) 1-22 is/are rejected.

8) ☐ Claim(s) _____ is/are objected to.

9) ☐ Claim(s) _____ are subject to restriction and/or election requirement

* If any claims have been determined allowable, you may be eligible to benefit from the **Patent Prosecution Highway** program at a participating intellectual property office for the corresponding application. For more information, please see http://www.uspto.gov/patents/init_events/pph/index.jsp or send an inquiry to **PPHfeedback@uspto.gov.**

Application Papers

10)☐ The specification is objected to by the Examiner.

11)☐ The drawing(s) filed on _____ is/are: a)☐ accepted or b)☐ objected to by the Examiner.

Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).

Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).

Priority under 35 U.S.C. § 119

12)☑ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

Certified copies:

a)☑ All b)☐ Some** c)☐ None of the:

1.☐ Certified copies of the priority documents have been received.

2.☑ Certified copies of the priority documents have been received in Application No. 17043031.

3.☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).

** See the attached detailed Office action for a list of the certified copies not received.

Attachment(s)

1) ☑ Notice of References Cited (PTO-892)

2) ☑ Information Disclosure Statement(s) (PTO/SB/08a and/or PTO/SB/08b) Paper No(s)/Mail Date 2/16/2021.

3) ☑ Interview Summary (PTO-413) Paper No(s)/Mail Date 20210403.

4) ☐ Other: _____.

Notice of Pre-AIA or AIA Status

The present application, filed on or after March 16, 2013, is being examined under the first inventor to file provisions of the AIA.

Claim Rejections - 35 USC § 112

The following is a quotation of 35 U.S.C. 112(b):
(b) CONCLUSION.—The specification shall conclude with one or more claims particularly pointing out and distinctly claiming the subject matter which the inventor or a joint inventor regards as the invention.

The following is a quotation of 35 U.S.C. 112 (pre-AIA), second paragraph:
The specification shall conclude with one or more claims particularly pointing out and distinctly claiming the subject matter which the applicant regards as his invention.

Claim 1 is rejected under 35 U.S.C. 112(b) or 35 U.S.C. 112 (pre-AIA), second paragraph, as being indefinite for failing to particularly point out and distinctly claim the subject matter which the inventor or a joint inventor (or for applications subject to pre-AIA 35 U.S.C. 112, the applicant), regards as the invention.

Claim 1 recites the limitation "microsphere sized porous particles" which is renders the claim indefinite because one of ordinary skill in the art would have not been able to determine the metes and bounds of the claimed "microsphere sized" limitation. Which dimension of the sphere is being referred to as "micro ... sized"? The specification states, "In some embodiments, the particles are less than 1 mm across the largest dimension, e.g., they are microspheres," p3, lines 21-30, as filed, which adds to the ambiguity as to which dimension is being referred to since the specification allows for multiple unequal dimensions. Moreover, what constitutes "micros... sized"? Would a 0.1 micron read on the claimed invention? How about 1,500 microns, or 1.5 mm? As cited above, the specification gives an example of "some embodiments" which allows for the microsphere sized particles to have a largest dimension above the 1 mm. At which point,

the term “micro... sized” becomes ambiguous, and thus is indefinite. For purposes of examination, the claimed “microsphere sized porous particles” will be interpreted to mean particles that have a shape of a sphere, are porous, and have a diameter that is less than 1 mm and more than 1000 nm.

Claim 6 recites the limitation “wherein the ... particles have an average (D50) size...” which renders the claimed indefinite as its unclear if the particles collectively, i.e., put together, have the claimed average diameter or each of the particles has the claimed average diameter. For purposes of examination, this limitation will be interpreted to mean each of the particles has the claimed average diameter.

Claim 12 is also rejected as indefinite. A broad range or limitation together with a narrow range or limitation that falls within the broad range or limitation (in the same claim) may be considered indefinite if the resulting claim does not clearly set forth the metes and bounds of the patent protection desired. See MPEP § 2173.05(c). In the present instance, claim 12 recites the broad recitation one or more Group VIII noble metals, and the claim also recites “comprises one or more of platinum, palladium, iridium ....,” which is the narrower statement of the range/limitation. . The claim(s) are considered indefinite because there is a question or doubt as to whether the feature introduced by such narrower language is (a) merely exemplary of the remainder of the claim, and therefore not required, or (b) a required feature of the claims.

Claim 18 recites the term “predominantly,” which is a relative term which renders the claim indefinite. The term "predominantly" is not defined by the claim, the specification does not provide a standard for ascertaining the requisite degree, and one of ordinary skill in the art would not be reasonably apprised of the scope of the invention. The term “predominantly” means “more than” but the claim is silent with

regards to (a) the conditions of this relative term (i.e., is the term referring to the concentration, volume, bulk density, etc., of the claimed noble metal in the outer region?), as well as to (b) what is the relative time comparing the outer region to? See http://citadel.sjfc.edu/faculty/kgreen/vector/block3/jacob/node13.html for examples of the many regions of a sphere. The claimed term is interpreted to mean that the content of the noble metal in the outer region of the microsphere is more than the content of the noble metal in the center of the sphere as recited in claim 1.

Claim 20 recites the limitation "the starting microsphere sized particles are..." There is insufficient antecedent basis for this limitation in the claim. The word "starting" isn't in claim 18 or in claim 1, and as such it's unclear to which microsphere sized particles" is the claim referring? For purposes of examination, this limitation will be interpreted as referring to the microsphere sized particles of step (a) in the product by process claim 18.

All the claims which depend from any of the aforementioned claims are also rejected as indefinite since said claims depend from the claims mentioned above and fail to remedy the stated deficiencies.

Claim Rejections - 35 USC § 102

The following is a quotation of the appropriate paragraphs of 35 U.S.C. 102 that form the basis for the rejections under this section made in this Office action:

> A person shall be entitled to a patent unless –
>
> (a)(1) the claimed invention was patented, described in a printed publication, or in public use, on sale, or otherwise available to the public before the effective filing date of the claimed invention.

Claims 1-6, 8, 9, 12, 14, 15, 16-19, and 21-22 are rejected under 35 U.S.C. 102(a)(1) as being anticipated by Yaluris et al. (US 2005/0042158).

With regards to **claims 1-6, 9, 12, 14, and 16-17**, Yaluris teaches particles that minimize the content of harmful gasses present in regenerator units during the regeneration of spent FCC catalysts. See, e.g., ¶0022-24. The particles are microsphere with a dimension capable of passing through a No. 200 screen (i.e., 74 microns). ¶0083. Yaluris teaches that the particles are porous in that they are mixed and sprayed with a solution that is adjusted to not exceed the water pore volume of the powder. ¶0085.

The particles have alumina and silica support and are shaped as microspheroidal (i.e., eggshell), contains cerium oxide, and is impregnated with platinum. Examples 4 and 5. Because the support has a microspheroidal shape, then the platinum and cerium are in an eggshell shape, too. Moreover, because the volume center is substantially smaller than the outer region of the particle, then the content of platinum and cerium oxide in the outer region must be higher in the outer region than in the center of the particle.

With regards to **claims 8, 18, 19, 21 and 22**, the claims are product by process claims. When the examiner has found a substantially similar product as in the applied prior art, the burden of proof is shifted to the applicant to establish that their product is patentably distinct and not the examiner to show the same process as making. *In re Brown*. 173 USPQ 685, *In re Fessman*, 180 USPQ 324 and *In re Marosi*, 218 USPQ 289.

Even though these are product-by-process claims, it is noted that Yaluris teaches the claimed process steps (see Examples).

With regards to **claim 15**, Yaluris teaches that the particles contain palladium. See claim 1.

Claim Rejections - 35 USC § 103

The following is a quotation of 35 U.S.C. 103 which forms the basis for all obviousness rejections set forth in this Office action:

> A patent for a claimed invention may not be obtained, notwithstanding that the claimed invention is not identically disclosed as set forth in section 102, if the differences between the claimed invention and the prior art are such that the claimed invention as a whole would have been obvious before the effective filing date of the claimed invention to a person having ordinary skill in the art to which the claimed invention pertains. Patentability shall not be negated by the manner in which the invention was made.

Claims 10, 11, 13, and 15 are rejected under 35 U.S.C. 103 as being unpatentable over Yaluris et al. (US 2005/0042158).

With regards to **claims 10 and 11**, the teachings of Yaluris are as set forth above. Yaluris teaches that the particles have an attrition index of from 0 to 15, which overlaps with the claimed range and thus renders it obvious. See MPEP 2144.05 (I).

With regards to **claims 13 and 15**, the teachings of Yaluris are as set forth above. Yaluris teaches that the noble metal utilized in their particles can be a mixture of palladium and platinum. See ¶0051 and claim 1. As such, it would have been obvious to one of ordinary skill in the art to include both pt and pd in carrying out the exemplified embodiments of Yaluris.

Claim 7 is rejected under 35 U.S.C. 103 as being unpatentable over Yaluris et al. (US 2005/0042158) in view of Vaarkamp et al. (US 2006/0204420).

With regards to **claim 7**, the teachings of Yaluris are as set forth above. Yaluris teaches that the metal support (i.e., the alumina containing component) may be crystalline or amorphous, but is silent with regards to containing gamma or theta alumina.

Vaarkamp teaches particles for minimizing the emission of harmful gasses during regeneration of FCC catalysts. See, e.g., abstract and ¶0006. Vaarkamp states that it is known in the art that porous gamma alumina is used as part the promoter, ¶0011, and teaches that the support maybe crystalline or amorphous and can be gamma or theta alumina. ¶0033. As such, one of ordinary skill in the art would have found it obvious to modify Yaluris' invention by using gamma or theta alumina as the support

Claims 20 is rejected under 35 U.S.C. 103 as being unpatentable over Yaluris et al. (US 2005/0042158) in view of Loganathan et al. (US 2015/0352525).

With regards to **claim 20**, the teachings of Yaluris are as set forth above. Yaluris teaches that the microsphere particle has surface area of 135 m2/g (Example 5), with a particle size of 74 microns (¶0083).

Yaluris is silent with regards to the porous particles including gamma alumina and with regards to the claimed pore volume.

Loganathan teaches a CO oxidation promoter additive for use in the regeneration of an FCC catalyst. See abstract and background of the invention sections. The promoter has a gamma alumina with a pore volume of from 0.3 to 0.6 cm3/g, which overlaps with the claimed invention. See MPEP 2144.05.I. Loganathan teaches that such a support allows it's shaping into microspheres having high density and low attrition strength without employing any alumina based dispersants like aluminum chlorohydrate, hydroxy nitrate or phosphate. ¶ 0066-67. As such, it would have been obvious to one of ordinary skill in the art at the time of the invention to modify the teachings of Yaluris to include Loganathan's gamma alumina with a pore volume that overlaps with the

claimed invention to allow for shaping the microspheres without using alumina based dispersants.

Conclusion

Any inquiry concerning this communication or earlier communications from the examiner should be directed to HAYTHAM SOLIMAN whose telephone number is (571)270-7192. The examiner can normally be reached on M-F 8:00-500.

Examiner interviews are available via telephone, in-person, and video conferencing using a USPTO supplied web-based collaboration tool. To schedule an interview, applicant is encouraged to use the USPTO Automated Interview Request (AIR) at http://www.uspto.gov/interviewpractice.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Stanley Silverman can be reached on 5712721358. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see https://ppair-my.uspto.gov/pair/PrivatePair. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free). If you would like assistance from a USPTO Customer Service Representative or access to the automated information system, call 800-786-9199 (IN USA OR CANADA) or 571-272-1000.

/HAYTHAM SOLIMAN/
Primary Examiner, Art Unit 1736

Doc code: IDS
Doc description: Information Disclosure Statement (IDS) Filed

PTO/SB/08a (02-18)
Approved for use through 11/30/2020. OMB 0651-0031
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

INFORMATION DISCLOSURE STATEMENT BY APPLICANT
(Not for submission under 37 CFR 1.99)

Application Number	
Filing Date	2021-02-16
First Named Inventor	Aru, Guido William
Art Unit	
Examiner Name	
Attorney Docket Number	071816-091960USC1

U.S.PATENTS Remove

Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1	4755282	A	1988-07-05	SAMISH et al.	
	2	6881390	B2	2005-04-19	YALURIS et al.	
	3	7045056	B2	2006-05-16	KELKAR et al.	

If you wish to add additional U.S. Patent citation information please click the Add button. Add

U.S.PATENT APPLICATION PUBLICATIONS Remove

Examiner Initial*	Cite No	Publication Number	Kind Code[1]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1	20050042158	A1	2005-02-24	YALURIS et al.	
	2	20060204420	A1	2006-09-14	VAARKAMP et al.	

If you wish to add additional U.S. Published Application citation information please click the Add button. Add

FOREIGN PATENT DOCUMENTS Remove

Examiner Initial*	Cite No	Foreign Document Number[3]	Country Code[2] i	Kind Code[4]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear	T[5]

EFS Web 2.1.18

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /H.S/

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	
	Filing Date	2021-02-16
	First Named Inventor	Aru, Guido William
	Art Unit	
	Examiner Name	
	Attorney Docket Number	071816-091960USC1

	1							

If you wish to add additional Foreign Patent Document citation information please click the Add button Add

NON-PATENT LITERATURE DOCUMENTS Remove

Examiner Initials*	Cite No	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc), date, pages(s), volume-issue number(s), publisher, city and/or country where published.	T[5]
	1		

If you wish to add additional non-patent literature document citation information please click the Add button Add

EXAMINER SIGNATURE

Examiner Signature	/HAYTHAM SOLIMAN/	Date Considered	04/04/2021

*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through a citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

[1] See Kind Codes of USPTO Patent Documents at www.USPTO.GOV or MPEP 901.04. [2] Enter office that issued the document, by the two-letter code (WIPO Standard ST.3). [3] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. [4] Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [5] Applicant is to place a check mark here if English language translation is attached.

EFS Web 2.1.18

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /H.S/

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	
	Filing Date	2021-02-16
	First Named Inventor	Aru, Guido William
	Art Unit	
	Examiner Name	
	Attorney Docket Number	071816-091960USC1

CERTIFICATION STATEMENT

Please see 37 CFR 1.97 and 1.98 to make the appropriate selection(s):

That each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(1).

OR

☐ That no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing the certification after making reasonable inquiry, no item of information contained in the information disclosure statement was known to any individual designated in 37 CFR 1.56(c) more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(2).

See attached certification statement.

The fee set forth in 37 CFR 1.17 (p) has been submitted herewith.

☒ A certification statement is not submitted herewith.

SIGNATURE

A signature of the applicant or representative is required in accordance with CFR 1.33, 10.18. Please see CFR 1.4(d) for the form of the signature.

Signature	/Nicole D. Kling/	Date (YYYY-MM-DD)	2021-02-16
Name/Print	Nicole D. Kling	Registration Number	71,959

This collection of information is required by 37 CFR 1.97 and 1.98. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 1 hour to complete, including gathering, preparing and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

EFS Web 2.1.18

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /H.S/

Privacy Act Statement

The Privacy Act of 1974 (P.L. 93-579) requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C. 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether the Freedom of Information Act requires disclosure of these record s.

2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.

3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.

4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).

5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.

6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).

7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.

8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspections or an issued patent.

9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /H.S/

Bibliographic Data

Application No: 17/176,222

Foreign Priority claimed: (●) Yes ( ) No

35 USC 119 (a-d) conditions met: ☐ Yes ☑ No ☐ Met After Allowance

Verified and Acknowledged: /HAYTHAM SOLIMAN/ Examiner's Signature | Initials

Title: CO TO CO2 COMBUSTION PROMOTER

FILING or 371(c) DATE	CLASS	GROUP ART UNIT	ATTORNEY DOCKET NO.
02/16/2021	208	1736	071816-091960USC1
RULE			

APPLICANTS

COCHISE TECHNOLOGY, LLC, Conifer, CO, UNITED STATES

INVENTORS

Guido William ARU, Conifer, CO, UNITED STATES

CONTINUING DATA

This application is a CON of 17043031 09/29/2020

17043031 is a 371 of PCT/US2019/024742 03/29/2019

PCT/US2019/024742 has PRO of 62651295 04/02/2018

FOREIGN APPLICATIONS

NETHERLANDS NL2020819 04/24/2018

IF REQUIRED, FOREIGN LICENSE GRANTED**

02/24/2021

**** SMALL ENTITY ****

STATE OR COUNTRY

UNITED STATES

ADDRESS

RONALD I. EISENSTEIN
NIXON PEABODY LLP
Exchange Place, 53 State Street
BOSTON, MA 02109
UNITED STATES

FILING FEE RECEIVED

$3,100

Notice of References Cited	Application/Control No. 17/176,222	Applicant(s)/Patent Under Reexamination ARU, Guido William	
	Examiner HAYTHAM SOLIMAN	Art Unit 1736	Page 1 of 1

U.S. PATENT DOCUMENTS

*		Document Number Country Code-Number-Kind Code	Date MM-YYYY	Name	CPC Classification	US Classification
*	A	US-20150352525-A1	12-2015	Loganathan; Kumaresan	B01J23/42	208/113
	B					
	C					
	D					
	E					
	F					
	G					
	H					
	I					
	J					
	K					
	L					
	M					

FOREIGN PATENT DOCUMENTS

*		Document Number Country Code-Number-Kind Code	Date MM-YYYY	Country	Name	CPC Classification
	N					
	O					
	P					
	Q					
	R					
	S					
	T					

NON-PATENT DOCUMENTS

*		Include as applicable: Author, Title Date, Publisher, Edition or Volume, Pertinent Pages)
	U	
	V	
	W	
	X	

*A copy of this reference is not being furnished with this Office action. (See MPEP § 707.05(a).)
Dates in MM-YYYY format are publication dates. Classifications may be US or foreign.

Applicant-Initiated Interview Summary	**Application No.** 17/176,222	**Applicant(s)** ARU, Guido William		
	Examiner HAYTHAM SOLIMAN	**Art Unit** 1736	**AIA (First Inventor to File) Status** Yes	**Page** 1 of 1

All Participants (applicant, applicants representative, PTO personnel)	**Title**	**Type**
HAYTHAM SOLIMAN	Primary Examiner	Telephonic
Nicole Kling	Agent of Record	

Date of Interview: 19 March 2021

Issues Discussed:

Other

Applicant reached out to inform the Examiner about this Track One application. The Examiner informed the Applicant that there might be an obviousness type double patenting rejection based on the co-pending application 17/043,031. The Applicant later contacted the Examiner and informed him that the an Express Abandonment request was filed in the co-pending application, which the Examiner confirmed on 03/22/2021.

/HAYTHAM SOLIMAN/ Primary Examiner, Art Unit 1736	

Applicant is reminded that a complete written statement as to the substance of the interview must be made of record in the application file. It is the applicants responsibility to provide the written statement, unless the interview was initiated by the Examiner and the Examiner has indicated that a written summary will be provided. See MPEP 713.04
Please further see:
MPEP 713.04
Title 37 Code of Federal Regulations (CFR) § 1.133 Interviews, paragraph (b)
37 CFR § 1.2 Business to be transacted in writing

Applicant recordation instructions: The formal written reply to the last Office action must include the substance of the interview. (See MPEP section 713.04). If a reply to the last Office action has already been filed, applicant is given a non-extendable period of the longer of one month or thirty days from this interview date, or the mailing date of this interview summary form, whichever is later, to file a statement of the substance of the interview.

Examiner recordation instructions: Examiners must summarize the substance of any interview of record. A complete and proper recordation of the substance of an interview should include the items listed in MPEP 713.04 for complete and proper recordation including the identification of the general thrust of each argument or issue discussed, a general indication of any other pertinent matters discussed regarding patentability and the general results or outcome of the interview, to include an indication as to whether or not agreement was reached on the issues raised.

Search Notes	Application/Control No.	Applicant(s)/Patent Under Reexamination
	17/176,222	ARU, Guido William
	Examiner	Art Unit
	HAYTHAM SOLIMAN	1736

CPC - Searched*		
Symbol	Date	Examiner
B01J23/8926, B01J37/0236, B01J21/12, B01J8/26, B01J23/42, C01B32/50, B01J35/1019, B01J37/0221, B01J35/1038, B01J23/44, B01J35/08, B01J21/04, B01J35/1014, B01J8/1827, C10G11/04, B01J21/08, B01J37/088, B01J23/63, B01J35/008	04/04/2021	/HS/

CPC Combination Sets - Searched*		
Symbol	Date	Examiner

US Classification - Searched*			
Class	Subclass	Date	Examiner
208	120.35	04/04/2021	/HS/

* See search history printout included with this form or the SEARCH NOTES box below to determine the scope of the search.

Search Notes		
Search Notes	Date	Examiner
Searched EAST	04/04/2021	/HS/
Preformed Inventor Search	04/04/2021	/HS/
Preformed USPC and CPC search	04/04/2021	/HS/
Preformed Assignee search	04/04/2021	/HS/
Considered IDS and ISR of sister app # 17043031	04/04/2021	/HS/

/HAYTHAM SOLIMAN/ Primary Examiner, Art Unit 1736	

Search Notes	Application/Control No.	Applicant(s)/Patent Under Reexamination
	17/176,222	ARU, Guido William
	Examiner	Art Unit
	HAYTHAM SOLIMAN	1736

Interference Search			
US Class/CPC Symbol	US Subclass/CPC Group	Date	Examiner

/HAYTHAM SOLIMAN/ Primary Examiner, Art Unit 1736	

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NUMBER	FILING OR 371(C) DATE	FIRST NAMED APPLICANT	ATTY. DOCKET NO./TITLE
17/176,222	02/16/2021	Guido William ARU	071816-091960USC1

CONFIRMATION NO. 3640

53143
RONALD I. EISENSTEIN
NIXON PEABODY LLP
Exchange Place, 53 State Street
BOSTON, MA 02109

PUBLICATION NOTICE

OC00000126047877

Title:CO TO CO2 COMBUSTION PROMOTER

Publication No.US-2021-0162377-A1
Publication Date:06/03/2021

NOTICE OF PUBLICATION OF APPLICATION

The above-identified application will be electronically published as a patent application publication pursuant to 37 CFR 1.211, et seq. The patent application publication number and publication date are set forth above.

The publication may be accessed through the USPTO's publically available Searchable Databases via the Internet at www.uspto.gov. The direct link to access the publication is currently http://www.uspto.gov/patft/.

The publication process established by the Office does not provide for mailing a copy of the publication to applicant. A copy of the publication may be obtained from the Office upon payment of the appropriate fee set forth in 37 CFR 1.19(a)(1). Orders for copies of patent application publications are handled by the USPTO's Public Records Division. The Public Records Division can be reached by telephone at (571) 272-3150 or (800) 972-6382, by facsimile at (571) 273-3250, by mail addressed to the United States Patent and Trademark Office, Public Records Division, Alexandria, VA 22313-1450 or via the Internet.

In addition, information on the status of the application, including the mailing date of Office actions and the dates of receipt of correspondence filed in the Office, may also be accessed via the Internet through the Patent Electronic Business Center at www.uspto.gov using the public side of the Patent Application Information and Retrieval (PAIR) system. The direct link to access this status information is currently https://portal.uspto.gov/pair/PublicPair. Prior to publication, such status information is confidential and may only be obtained by applicant using the private side of PAIR.

Further assistance in electronically accessing the publication, or about PAIR, is available by calling the Patent Electronic Business Center at 1-866-217-9197.

Office of Data Managment, Application Assistance Unit (571) 272-4000, or (571) 272-4200, or 1-888-786-0101

Electronic Acknowledgement Receipt	
EFS ID:	43183642
Application Number:	17176222
International Application Number:	
Confirmation Number:	3640
Title of Invention:	CO TO CO2 COMBUSTION PROMOTER
First Named Inventor/Applicant Name:	Guido William ARU
Customer Number:	53143
Filer:	Nicole Dian Kling/Ali Yamakaitis
Filer Authorized By:	Nicole Dian Kling
Attorney Docket Number:	071816-091960USC1
Receipt Date:	07-JUL-2021
Filing Date:	16-FEB-2021
Time Stamp:	14:54:27
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	yes
Payment Type	DA
Payment was successfully received in RAM	$180
RAM confirmation Number	E202177E54541841
Deposit Account	
Authorized User	
The Director of the USPTO is hereby authorized to charge indicated fees and credit any overpayment as follows:	

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1		2021-07-07_Response_to_NFOA_071816-091960USC1.pdf	202806 f0c56160b612ef3782f3f418d4d4498774784f86	yes	13
	Multipart Description/PDF files in .zip description				
	Document Description		**Start**	**End**	
	Applicant Arguments/Remarks Made in an Amendment		6	13	
	Claims		2	5	
	Amendment/Req. Reconsideration-After Non-Final Reject		1	1	
Warnings:					
Information:					
2	Affidavit-traversing rejectns or objectns rule 132	2021-07-07-Declaration_of_Expert_071816-091960USC1.pdf	1384582 ea3eb6615db3f727d33ef1b4a66460e3073c2be8	no	3
Warnings:					
Information:					
3	Affidavit-traversing rejectns or objectns rule 132	2021-07-07-Exhibit_A_Resume_NHerring_071816-091960USC1.pdf	170221 38779c5be4734ac15af1123db81b8323e7253e8f	no	3
Warnings:					
Information:					
4	Affidavit-traversing rejectns or objectns rule 132	2021-07-07-Exhibit_1_071816-091960USC1.pdf	5529665 131464247456 2cc419817ca65abe82f5345adb61	no	7
Warnings:					
Information:					
5	Affidavit-traversing rejectns or objectns rule 132	2021-07-07-Exhibit_3_071816-091960USC1.pdf	352074 19f2d15ef5df0b73a240330a6f056733d3f5ff9c	no	13

Warnings:					
Information:					
6	Affidavit-traversing rejectns or objectns rule 132	2021-07-07-Exhibit_4_071816-091960USC1.pdf	657572 40b00f65a70ef56bcbc8f96b82dfdd50bd5a4fd5	no	15
Warnings:					
Information:					
7	Affidavit-traversing rejectns or objectns rule 132	2021-07-07-Exhibit_2_071816-091960USC1.pdf	1945570 d9a25b75a279f81538929464f9a1679f2c02ec6	no	5
Warnings:					
Information:					
8	Affidavit-traversing rejectns or objectns rule 132	2021-07-07-Exhibit_5_071816-091960USC1.pdf	5549087 c6162dca0b70beaab916ddd61f0058c9ca8b760c	no	32
Warnings:					
Information:					
9	Non Patent Literature	NPL_Microspheres_2020_1.pdf	5527341 10f27181e7af84bd11023be200c79142eb1c49d2	no	7
Warnings:					
Information:					
10	Non Patent Literature	NPL_Munnik_2015_6687.pdf	5555227 823f13ea14ad6e396987f4fdebb95f5be2988f2d	no	32
Warnings:					
Information:					
11	Non Patent Literature	NPL_Papageorgiou_1996_439.pdf	351361 9a6ece383a65ab7d49ff194cece5e97292f8c8c7	no	13
Warnings:					
Information:					
12	Non Patent Literature	NPL_Russo_2020_1.pdf	657453 97e8c51768bfe4efbbb167f663db9a82a3d6c2a4	no	15
Warnings:					
Information:					

13	Non Patent Literature	NPL_Venuto_1979_30.pdf	1945569 d14a413023b5b8e4399d0a84c341b01295cd2b5c	no	5
Warnings:					
Information:					
14	Information Disclosure Statement (IDS) Form (SB08)	2021-07-07-SB08-071816-091960USC1.pdf	87884 a45c624e3f3d8ae29c3bac0a34665985291a2879	no	4
Warnings:					
Information:					
This is not an USPTO supplied IDS fillable form					
15	Transmittal Letter	2021-07-07-EFS_Transmittal_071816-091960USC1.pdf	118769 8023a5735a343c8c8fecd361b52a033db97e86f1	no	1
Warnings:					
Information:					
16	Fee Worksheet (SB06)	fee-info.pdf	32274 c7037a56fac8f2ca588ecc51a301e0adf43046ba	no	2
Warnings:					
Information:					
			Total Files Size (in bytes):	30067455	

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

Amendments to the Claims:

This listing of claims will replace all prior versions, and listings, of claims in the application:

1. (CURRENTLY AMENDED) A CO to CO_2 combustion promoter comprising microsphere sized porous particles, each microsphere sized porous particle having a diameter of less than 1 mm, and independently comprising:
   silica, alumina, or mixtures thereof; and
   one or more Group VIII noble metals distributed in the particle as an eggshell such that a higher ~~content~~ concentration of the one or more Group VIII noble metals is present in the outer region of the microsphere sized porous particle as compared to the ~~content~~ concentration of the one or more Group VIII noble metals in the centre of the microsphere sized porous particle.

2. (ORIGINAL) The combustion promoter according to claim 1, comprising a plurality of microsphere sized porous particles comprising silica.

3. (ORIGINAL) The combustion promoter according to claim 1, comprising a plurality of microsphere sized porous particles comprising alumina.

4. (ORIGINAL) The combustion promoter according to claim 1, comprising a first plurality of microsphere sized porous particles comprising silica and a second plurality of microsphere sized porous particles comprising alumina.

5. (ORIGINAL) The combustion promoter according to claim 1, comprising a plurality of microsphere sized porous particles comprising silica and alumina.

6. (CURRENTLY AMENDED) The combustion promoter according to claim 1, wherein the microsphere sized porous particles collectively have an average (D50) size of between 60 and 90 microns as measured by laser diffraction.

7. (ORIGINAL) The combustion promoter according to claim 1, wherein the microsphere sized porous particles are gamma or theta alumina particles.

8. (ORIGINAL) The combustion promoter according to claim 1, wherein the microsphere sized porous particles are spray dried silica particles.

9. (ORIGINAL) The combustion promoter according to claim 1, wherein the microsphere sized porous particles are an equilibrium or spent catalyst as obtained from a fluidized catalytic cracking (FCC) process.

10. (ORIGINAL) The combustion promoter according to claim 1, wherein the attrition index as measured according to ASTM D-5757 of the CO to CO_2 combustion promoter for a sieve fraction of combustion promoter particles of between 40 and 105 microns is between 5 and 25.

11. (ORIGINAL) The combustion promoter according to claim 10, wherein the attrition index of the CO to CO_2 combustion promoter for a sieve fraction of combustion promoter particles of between 40 and 105 microns is between 10 and 20.

12. (ORIGINAL) The combustion promoter according to claim 1, wherein the one or more Group VIII noble metals comprises one or more of platinum, palladium, iridium, ruthenium, and rhodium.

13. (ORIGINAL) The combustion promoter according to claim 12, wherein the one or more Group VIII noble metals comprises platinum and palladium.

14. (ORIGINAL) The combustion promoter according to claim 12, wherein the one or more Group VIII noble metals comprises platinum.

15. (ORIGINAL) The combustion promoter according to claim 12, wherein the one or more Group VIII noble metals comprises palladium.

16. (ORIGINAL) The combustion promoter according to claim 1, wherein the microsphere sized porous particles further comprise at least one of cerium oxide and copper oxide.

17. (CURRENTLY AMENDED) The combustion promoter according to claim 16, wherein the at least one of cerium oxide and copper oxide is distributed in the microsphere sized porous particle as an eggshell such that a higher concentration ~~content~~ of the at least one of cerium oxide and copper oxide is present in the outer region of the microsphere sized porous particle as compared to the concentration ~~content~~ of the at least one of cerium oxide and copper oxide in the centre of the microsphere sized porous particle.

18. (CURRENTLY AMENDED) The combustion promoter according to claim 1, obtained by a process comprising the following steps:
(a) introducing a medium in the pores of microsphere sized porous particles having a diameter of less than 1 mm to obtain ~~filled~~ microsphere sized porous particles with filled pores; and
(b) contacting the ~~filled~~ microsphere sized porous particles with filled pores with an aqueous salt solution of the one or more Group VIII noble metals wherein the one or more Group VIII noble metals deposits ~~predominantly in~~ at a higher content in the outer region of the ~~filled~~ microsphere sized porous particles with filled pores as compared to the content of the one or more Group VIII noble metals in the centre of the microsphere sized porous particles with filled pores, thereby obtaining eggshell particles.

19. (ORIGINAL) The combustion promoter of claim 18, the process further comprising a step:
(c) at least one of drying and calcining the eggshell particles.

20. (CURRENTLY AMENDED) The combustion promoter according to claim 18, wherein the ~~starting~~ microsphere sized porous particles having pores filled in step (a) are gamma alumina particles having an average (D50) size of between 60 and 90 microns, have a surface area (BET) of between 50 and 300 m^2/g, and a pore volume of between 0.05 and 0.50 mL/g as measured ~~as~~ by the water pore volume.

21. (ORIGINAL) The combustion promoter according to claim 18, wherein the medium in step (a) is water.

22. (ORIGINAL) The combustion promoter according to claim 18, wherein in step (b) the filled microsphere sized porous particles are contacted in step (b) with a volume of the aqueous salt solution of the one or more Group VIII noble metals which is less than the total volume of the pores of the starting microsphere sized particles.

23. (NEW) A CO to CO_2 combustion promoter comprising porous particles, each porous particle having a diameter of less than 1 mm, and independently comprising:
silica, alumina, or mixtures thereof; and
one or more Group VIII noble metals distributed in the particle such that a higher concentration of the one or more Group VIII noble metals is present in the outer region of the porous particle as compared to the concentration of the one or more Group VIII noble metals in the centre of the porous particle.

PTO/SB/08a (02-18)
Approved for use through 11/30/2020. OMB 0651-0031
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (**Not for submission under 37 CFR 1.99)**		
	Application Number	17176222
	Filing Date	2021-02-16
	First Named Inventor	Aru, Guido William
	Art Unit	1736
	Examiner Name	Soliman, Haytham
	Attorney Docket Number	071816-091960USC1

U.S.PATENTS						
Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1					
If you wish to add additional U.S. Patent citation information please click the Add button.						

U.S.PATENT APPLICATION PUBLICATIONS						
Examiner Initial*	Cite No	Publication Number	Kind Code[1]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1					
If you wish to add additional U.S. Published Application citation information please click the Add button.						

FOREIGN PATENT DOCUMENTS								
Examiner Initial*	Cite No	Foreign Document Number[3]	Country Code[2] ¡	Kind Code[4]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear	T[5]
	1							☐
If you wish to add additional Foreign Patent Document citation information please click the Add button								

NON-PATENT LITERATURE DOCUMENTS			
Examiner Initials*	Cite No	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc), date, pages(s), volume-issue number(s), publisher, city and/or country where published.	T[5]

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	17176222
	Filing Date	2021-02-16
	First Named Inventor	Aru, Guido William
	Art Unit	1736
	Examiner Name	Soliman, Haytham
	Attorney Docket Number	071816-091960USC1

	1	Microspheres Online. "12 Essential Properties of Microspheres - Detailed Guide to Achieve Results." Retrieved from web 2021-04-20. URL: <https://www.microspheres.us/properties-of-microspheres/>. 7 pages. (2020)	☐
	2	MUNNIK et al. "Recent developments in the synthesis of supported catalysts." Chemical Reviews 115(14): 6687-6718 (2015)	☐
	3	PAPAGEORGIOU et al. "Preparation of Pt/γ-Al2O3Pellets with Internal Step-Distribution of Catalyst: Experiments and Theory." Journal of Catalysis 158(2): 439-451 (1996)	☐
	4	RUSSO et al. "Intraparticle Modeling of Non-Uniform Active Phase Distribution Catalyst." ChemEngineering 4(2): 24 pp. 1-15 (2020)	☐
	5	VENUTO et al. "Fluid catalytic cracking with zeolite catalysts." Marcel Dekker, Inc. New York. Pages 30-31, 42-47 (1979)	☐

If you wish to add additional non-patent literature document citation information please click the Add button

EXAMINER SIGNATURE

Examiner Signature		Date Considered	

*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through a citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

[1] See Kind Codes of USPTO Patent Documents at www.USPTO.GOV or MPEP 901.04. [2] Enter office that issued the document, by the two-letter code (WIPO Standard ST.3). [3] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. [4] Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [5] Applicant is to place a check mark here if English language translation is attached.

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	17176222
	Filing Date	2021-02-16
	First Named Inventor	Aru, Guido William
	Art Unit	1736
	Examiner Name	Soliman, Haytham
	Attorney Docket Number	071816-091960USC1

CERTIFICATION STATEMENT

Please see 37 CFR 1.97 and 1.98 to make the appropriate selection(s):

☐ That each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(1).

OR

☐ That no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing the certification after making reasonable inquiry, no item of information contained in the information disclosure statement was known to any individual designated in 37 CFR 1.56(c) more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(2).

☐ See attached certification statement.

☒ The fee set forth in 37 CFR 1.17 (p) has been submitted herewith.

☒ A certification statement is not submitted herewith.

SIGNATURE

A signature of the applicant or representative is required in accordance with CFR 1.33, 10.18. Please see CFR 1.4(d) for the form of the signature.

Signature	/Nicole D. Kling/	Date (YYYY-MM-DD)	2021-07-07
Name/Print	Nicole D. Kling	Registration Number	71,959

This collection of information is required by 37 CFR 1.97 and 1.98. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 1 hour to complete, including gathering, preparing and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

Privacy Act Statement

The Privacy Act of 1974 (P.L. 93-579) requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C. 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether the Freedom of Information Act requires disclosure of these record s.

2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.

3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.

4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).

5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.

6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).

7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.

8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspections or an issued patent.

9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:	Guido William ARU *et al.*	Confirmation No.:	3640
Application No.:	17/176,222	Art Unit:	1736
Filing Date:	February 16, 2021	Examiner:	Haytham SOLIMAN
For:	A CO TO CO2 COMBUSTION PROMOTER		

VIA EFS-WEB
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

GENERAL TRANSMITTAL & CERTIFICATE OF EFS SUBMISSION

Pursuant to 37 C.F.R. § 1.8(a)(1)(i)(C) I hereby certify that the following documents are being submitted to the Patent and Trademark Office via the Office Electronic Filing System in accordance with § 1.6(a)(4) on **July 7, 2021;**

1. **General Transmittal & Certificate of EFS Submission (1 pg.);**
2. **Response to Non-Final Office Action (13 pgs.)**
3. **Declaration of Expert (3 pgs.)**
4. **Exhibit A – Resume – Natalie Herring (3 pgs.)**
5. **Exhibit 1 (7 pgs.)**
6. **Exhibit 2 (5 pgs.)**
7. **Exhibit 3 (13 pgs.)**
8. **Exhibit 4 (15 pgs.)**
9. **Exhibit 5 (32 pgs.)**
10. **Information Disclosure Statement (4 pgs.)**
11. **5 Non-Patent Literature Documents; and**
12. **Fee Transmittal (1 pg.)**

AUTHORIZATION TO CHARGE/CREDIT DEPOSIT ACCOUNT

The Director of the USPTO is hereby authorized to charge any fee deficiencies associated with the instant filing, **except excess claims fees**, and credit any overpayments to NIXON PEABODY LLP Deposit Account No. **50-0850**, from which the undersigned is authorized to withdraw.

Customer No.: 53143

Date: July 7, 2021

Respectfully submitted,

/NICOLE D. KLING/

NICOLE D. KLING (Reg. No. 71,959)
RONALD I. EISENSTEIN (Reg. No. 30,628)
NIXON PEABODY LLP
Exchange Place – 53 State Street
Boston, MA 02109-2835
Tel. (617) 345-1013/6054
Fax (617) 345-1300
Email: bostonpatent@nixonpeabody.com

4833-4902-4040.1

REMARKS

This response addresses the issues noted in the Non-Final Office Action mailed April 7, 2021.

Claims 1-22 were pending in the present application prior to the amendment directed herein.

Claims 1, 6, 17, 18, and 20 are amended herein. New claim 23 is entered herein. Applicant submits that the amendments add no new matter and find support throughout the specification and claims as originally filed. For example, the amendments to claim 1 find support at least at page 3, line 13 and page 3, lines 7-20 of the specification as filed.

The above amendment is not to be construed as acquiescence with regard to the Examiner's rejections and is made solely to clarify particular aspects of the presently claimed invention and expedite prosecution. Applicant does not hereby abandon or waive any rights to cancelled subject matter or cancelled claims and reserves the right to pursue any cancelled subject matter or cancelled claims in this or a further continuation, divisional, or continuation-in-part application claiming benefit to this application. Favorable reconsideration of the subject application is respectfully requested in view of the above amendments and the following remarks.

Rejection under 35 U.S.C. §112(b)

Claim 1 is rejected under 35 U.S.C. §112(b) as allegedly being indefinite. The Office appears to take the position that "microsphere sized" is indefinite.

Applicant submits that the term "microsphere" is a term of art, the metes and bounds of which are readily understood by one of ordinary skill in the art. For example, Microspheres Online, a collection of technical information written by industry experts, defines microspheres as spherical particles "as small as 1 micron in diameter and as large as 1,000 microns (1 mm)." *See* Exhibit 1 submitted herewith. This term is particularly well-established within the relevant field of FCC catalysts, appearing without the need for definition or elaboration in U.S. Patents even before WWII (*See* U.S. Patents 2,283,172; 2,933,456; and 3,243,262) and technical books from at least 40 years ago (*See* Fig. 13 of Venuto and Habib "Fluid catalytic cracking with zeolite catalysts." Marcel Dekker, Inc. New York (1979); Section VII of which is provided herewith as Exhibit 2). Clearly, to one of ordinary skill in the art, there is no indefiniteness in this phrase.

Without contradicting the foregoing or conceding the correctness of the rejection, and merely in order to expedite prosecution, Applicant has also entered claim 23, which does not recite "microsphere" for the Examiner's consideration.

Claim 6 is rejected under 35 U.S.C. §112(b) as allegedly being indefinite. The Office takes the position that the reference to "average" is indefinite. Applicant maintains that the meaning of "average" is definite at least in context, but merely in order to expedite prosecution, has added "collectively" to the claim as suggested by the Examiner.

Claim 12 is rejected under 35 U.S.C. §112(b) as allegedly being indefinite. The Office takes the position that the claim recites a broader and narrower range or limitation, which is prohibited by MPEP 2173.05(c). Applicant respectfully disagrees. As explained in MPEP 2173.05(c):

> . . .it is not improper under 35 U.S.C. 112(b) or pre-AIA 35 U.S.C.112, second paragraph, to present a dependent claim that sets forth a narrower range for an element than the range set forth in the claim from which it depends. For example, if claim 1 reads "A circuit … wherein the resistance is 70-150 ohms." and claim 2 reads "The circuit of claim 1 wherein the resistance is 70-100 ohms.", then claim 2 should not be rejected as indefinite.

Applicant submits that this is directly analogous to the instant claims. Claim 1 recites the limitation "one or more Group VIII noble metals." Claim 12 depends from claim 1 and further limits claim 1 by specifying that the "one or more Group VIII noble metals comprises one or more of platinum, palladium, iridium, ruthenium, and rhodium." Accordingly, claim 12 itself does not present two ranges, it is clearly and unambiguously providing a narrower range of what is first recited in claim 1, as is proper.

Claim 18 is rejected under 35 U.S.C. §112(b) as allegedly being indefinite. The Office takes the position that the claim is indefinite for reciting "predominantly." Claim 18 is amended herein to obviate the rejection.

Claim 20 is rejected under 35 U.S.C. §112(b) as allegedly being indefinite for a lack of antecedent basis. Claim 20 is amended herein to obviate the rejection.

In view of the above, Applicants submit that the claimed invention is definite. Reconsideration and withdrawal of the rejection under 35 U.S.C. §112(b) is respectfully requested.

Rejections under 35 U.S.C. §102

Claims 1-6, 8, 9, 12, 14-19, and 21-22 are rejected under 35 U.S.C. §102(a)(1) as allegedly being anticipated by Yaluris (US 2005/0042158). Applicant traverses and respectfully submits that the Office's characterization and understanding of Yaluris is incorrect in at least the following respects:

1. *The Office has erred in not according the claim limitation "eggshell" patentable weight*

At page 5 of the Non-Final Office Action, the Office states of Yaluris that "the particles. . . are shaped as microspheroidal (i.e., eggshell) . . ." To the contrary, Applicant submits that "microspheroidal" and "eggshell" are terms of art which are in no way interchangeable. As demonstrated above, "microspheroidal" refers to spherical particles having a diameter of 1 micron to 1,000 microns (1 mm). In contrast, "eggshell", at least within the fields of nanoparticles and in particular catalyst particles, refers to a structure with a thin layer or "shell" surrounding an inner layer that is chemically distinct from the outer layer. In particular, an "eggshell" particle that comprises a catalyst comprises higher levels of catalyst in the outer layer. In this particular instance, the use of "eggshell" of instant claim 1 would be understood by one of ordinary skill in the art to indicate that the particle has an outer layer (e.g., a shell) with a relatively high concentration of the one or more Group VIII noble metals and an inner layer (e.g., a core) with a relatively lower concentration of the one or more Group VIII noble metals. The instant specification provides a relevant schematic cross-section of exemplary particles in Fig. 2, which is provided herein for convenience:

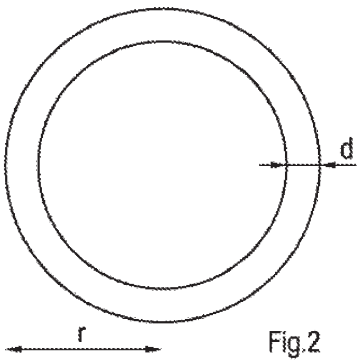


Fig.2

The foregoing is substantiated by the accompanying Exhibits 3-5[1], which demonstrate that "eggshell" is a term of art with the meaning articulated above. In particular, please see Exhibit 3 page 1, left column, third paragraph; Exhibit 3 Fig. 5; Exhibit 4 pages 1-2 including Fig. 1; and Exhibit 5 pages 6688-6699 including Fig. 1 Additionally, the accompanying Declaration of Dr. Herring further substantiates that these two terms are well understood by one of ordinary skill in the art and are not synonymous. *See*, paragraphs 6 and 7 of the Declaration of Dr. Herring.

Applicant requests that the limitations recited in the claims be accorded their ordinary and customary meanings and accorded patentable weight. MPEP 2111.01(III) and 2143.03.

Additionally, in case the remarks on pages 4-5 are meant to imply that "eggshell" particles as recited in the claims read on hollow particles, Applicant traverses such a reading of the claims. As noted above, "eggshell" does not indicate a hollow particle. As illustrated in the specification at, e.g., page 3 lines 15-27, eggshell particles of the instant application have a first inner region and a second outer region, both of which comprise certain materials. While the silica and/or alumina present in an instant particle is porous, it does not comprise a void that would render the particle hollow.

Finally, Applicant notes that on page 5 of the Office Action, the Office's interpretation of the term of "content" may be in conflict with a proper understanding of the term "eggshell." Without conceding the correctness of the Office's interpretation and merely in order to expedite prosecution, Applicant has amended claim 1 to recite that the "concentration" of the Group VII noble metals is greater in the outer region of the particles.

2. *Yaluris does not disclose eggshell particles*

Having established that "eggshell" is claim limitation distinct from "microspheroidal," Applicant submits that Yaluris does not and cannot teach "eggshell" particles according to the instant claims. Indeed, Yaluris does not contain a single reference to "eggshell," "gradient," or "coating" and uses the term "layer" only in reference to layers of material applied to trays, not

[1] Exhibit 3 = Papageriou et al. Journal of Catalysis 1996 158:439-451. Exhibit 4 = Russo et al. Chemengineering 2020 4:1-15. Exhibit 5 = Munnik et al. Chemical Reviews 2015 115:6687-6718.

particles. It is therefore clear that Yaluris does not disclose a particle with an eggshell distribution and therefore cannot anticipate the instant claims.

3. *Yaluris cannot inherently anticipate*

Additionally, Applicant submits that it is impossible for Yaluris to inherently anticipate because Examples 4 and 5 of Yaluris (to which the Office cited), describe a process which cannot possibly provide an eggshell distribution.

Briefly, in Example 4 no Group VIII noble metals are present, and Example 4 alone cannot anticipate.

What Example 4 does describe is the preparation of a slurry comprising both alumina and cerium carbonate crystals, which is then spray dried to form "microspheres" as a "base material." In Example 5, the base material is "impregnated" with a platinum solution. But as the instant specification itself describes:

> . . .CO to CO2 combustion promoters are commonly made from impregnation of Group VIII noble metal or metals, commonly platinum and/or palladium, onto a porous alumina and/or other substrate microspheres of average particle size 60 to 90 microns, with physical properties very similar to the base FCCU catalysts. ***Such impregnation results in a uniform distribution of the Group VIII noble metal throughout the internal and external surfaces of the porous microsphere***.
>
> (page 2, lines 14-19; emphasis added)

The instant specification then cites Yaluris as a specific example of such compositions. *See* page 2, line 24. The instant specification further emphasizes that:

> The capillary effects, both hydraulic and evaporative, in mesopores are well documented and are characterized by extremely rapid uptake of any liquid, including one with dissolved noble metal salts. This rapid uptake into the pores of the support is what results in ***the homogenous distribution of the noble metals with the impregnation methods previously employed and documented to manufacture FCC CO combustion promoters***.
>
> (page 15 line 28- page 16 line 2; emphasis added)

To further substantiate that Yaluris does not describe an eggshell particle, Applicant submits herewith the Declaration of Dr. Herring. As Dr. Herring states "the "base material" formed in Example 4 of Yaluris will "***necessarily*** comprise pores" and "impregnation of the "base

material" as described in Example 5 of Yaluris will "***necessarily*** result in the platinum being found homogenously throughout the base material particles." Dr. Herring is clear that "it is physically impossible for a method as described in Examples 4 and 5 of Yaluris to form an eggshell particle, as there is no mechanism in place to prevent capillary effects from forcing the platinum solution to penetrate throughout the entire depth of the pores of the particle."

It is therefore abundantly clear that Yaluris' method did not and cannot result in eggshell particles according to instant claim 1.

For the foregoing reasons, the record is clear that Yaluris fails to disclose, explicitly or inherently, any eggshell particles according to instant claim 1. Where Yaluris therefore fails to teach each and every limitation of the claims, Applicants submit that the current claims are not anticipated by any of the prior art provided. Reconsideration and withdrawal of the rejection under 35 U.S.C. §102, is respectfully requested.

Comments on obviousness

In order to expedite prosecution, Applicant notes that the invention of claim 1 is both novel and nonobvious over Yaluris. As established above, the instant invention is physically distinct from what is described by Yaluris, e.g., at least by having an eggshell distribution. As the instant specification describes at pages 3-4, this physical distinction results in a number of surprising advantages over compositions such as those described in Yaluris. Such advantages include:

1. The instant combustion promoters provide the same level of combustion promoter activity as the prior art non-eggshell promoters, while using significantly less noble metal per particle.

2. The instant invention provides combustion with less NOx formation

Yaluris provides no suggestion or motivation to seek such improvements, much less a suggestion or motivation that such improvements can be achieved by combustion promoters comprising the eggshell distribution of instant claim 1. The instant invention therefor provides unexpected results relative to the prior art and as a consequence is nonobvious.

Rejections under 35 U.S.C. §103

Claims 10, 11, 13, and 15 are rejected under 35 U.S.C. §103 as allegedly being unpatentable over Yaluris (US 2005/0042158). Applicants submit that because Yaluris fails to disclose or suggest the invention described in the independent claims for at least the reasons discussed above, Yaluris cannot render the indicated claims obvious.

Claim 7 is rejected under 35 U.S.C. §103 as allegedly being unpatentable over Yaluris (US 2005/0042158) in view of Vaarkamp (US 2006/0204420). Vaarkamp is alleged to teach no more than the existence of gamma or theta alumina. Applicants submit that because Yaluris fails to disclose or suggest the invention described in the independent claims for at least the reasons discussed above, no combination of Yaluris and Vaarkamp can render claim 7 obvious.

Claim 20 is rejected under 35 U.S.C. §103 as allegedly being unpatentable over Yaluris (US 2005/0042158) in view of Loganathan (US 2015/0352525). Loganathan is alleged to teach no more than the existence of gamma alumina and certain pore volumes. Applicants submit that because Yaluris fails to disclose or suggest the invention described in the independent claims for at least the reasons discussed above, no combination of Yaluris and Loganathan can render claim 20 obvious.

In view of the foregoing, Applicants submit that the current claims are not obvious in view of any of the prior art provided. Reconsideration and withdrawal of the rejection under 35 U.S.C. §103, is respectfully requested.

In view of the above, Applicant submits that all issues raised in the Office Action are addressed herein. Entry of the proposed amendments and reconsideration of the claims is respectfully requested.

Applicant does not acquiesce in the Examiner's characterizations of the art including the alleged motivation to combine references. For brevity and to advance prosecution, however, applicants may have not addressed all characterizations of the art and reserve the right to do so in further prosecution of this or a subsequent application. The absence of an explicit response by the applicants to any of the Examiner's positions does not constitute a concession of the Examiner's positions. The fact that applicants' comments have focused on particular arguments does not constitute a concession that there are no other arguments for patentability of the claims. All of the dependent claims are patentable for at least the reasons given with respect to the claims on which they depend.

AUTHORIZATION TO CHARGE/CREDIT DEPOSIT ACCOUNT

The Director of the USPTO is hereby authorized to charge any fee deficiencies associated with the instant filing, **except excess claims fees**, and credit any overpayments to NIXON PEABODY LLP Deposit Account No. **50-0850**, from which the undersigned is authorized to withdraw.

Customer No.: 53143

Respectfully submitted,

Date: July 7, 2021

/Nicole D. Kling/

Ronald I. Eisenstein (Reg. No. 30,628)
Nicole D. Kling (Reg. No. 71,959)
NIXON PEABODY LLP
Exchange Place
53 State Street
Boston, MA 02109-2835
Tel. (617) 345- 6054/1013
Fax (617) 345-1300
Email: bostonpatent@nixonpeabody.com

Electronic Patent Application Fee Transmittal					
Application Number:	17176222				
Filing Date:	16-Feb-2021				
Title of Invention:	CO TO CO2 COMBUSTION PROMOTER				
First Named Inventor/Applicant Name:	Guido William ARU				
Filer:	Nicole Dian Kling/Ali Yamakaitis				
Attorney Docket Number:	071816-091960USC1				
Filed as Small Entity					
Filing Fees for **Utility under 35 USC 111(a)**					
Description		**Fee Code**	**Quantity**	**Amount**	**Sub-Total in USD($)**
Basic Filing:					
Pages:					
Claims:					
CLAIMS IN EXCESS OF 20		2202	1	50	50
Miscellaneous-Filing:					
Petition:					
Patent-Appeals-and-Interference:					
Post-Allowance-and-Post-Issuance:					

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Extension-of-Time:				
Miscellaneous:				
SUBMISSION- INFORMATION DISCLOSURE STMT	2806	1	130	130
		Total in USD ($)		**180**

JOURNAL OF CATALYSIS 158, 439–451 (1996)
ARTICLE NO. 0045

Preparation of Pt/γ-Al_2O_3 Pellets with Internal Step-Distribution of Catalyst: Experiments and Theory

Panayiotis Papageorgiou, Douglas M. Price, Asterios Gavriilidis,[1] and Arvind Varma[2]

Department of Chemical Engineering, University of Notre Dame, Notre Dame, Indiana 46556

Received November 30, 1994; revised September 12, 1995

Step-type Pt/γ-Al_2O_3 catalyst pellets were prepared by coimpregnation and sequential impregnation of hexachloroplatinic and citric acids. A diffusion–adsorption model based on Fickian diffusion and Langmuir adsorption was formulated. The parameters of the model were determined from separate experiments. Adsorption constants were obtained in the absence of diffusional resistances, while effective diffusivities were obtained in the absence of adsorption or desorption. In order to extend the Langmuir adsorption equations to the multicomponent system, two new parameters were introduced, which accounted for solution effects and steric hinderances. Catalyst distribution inside the pellet and the effects of various impregnation parameters were predicted satisfactorily by the multicomponent diffusion–adsorption model. The platinum distribution of pellets prepared by the two impregnation techniques was similar, although sequential impregnation gave thinner catalyst step widths. © 1996 Academic Press, Inc.

INTRODUCTION

Catalysts involving group VIII metals are usually prepared by dispersing the metal on a high-surface-area support, so that a large fraction of metal atoms becomes available for reaction. The supports used in industrial reactors are generally spherical or cylindrical pellets, with the catalytic agent deposited on the external surface or uniformly within the pellet.

The location of the catalytic material in the support can have a significant effect on catalyst performance, especially when diffusional resistances during reaction are important. For an isothermal reaction exhibiting positive-order kinetics, it is desirable to place the catalyst on the external surface of the support where the reaction concentration is the highest, while for negative-order kinetics (as in some concentration regimes of bimolecular Langmuir–Hinshelwood reactions), it is beneficial to locate the catalyst in the interior of the support where reactant concentration is lower (1). For exothermic reactions, even if they are of positive order, catalyst effectiveness can be increased by locating the catalytic agent inside the support, thus taking advantage of heat transport resistances (2).

The theory of optimal catalyst distribution has been developed even for the most general case of reacting systems: for any catalyst performance index (i.e., conversion, selectivity or yield) and for an arbitrary number of reactions, following arbitrary kinetics, occurring in a nonisothermal pellet, with finite external mass and heat transfer resistances, the optimal catalyst distribution is a Dirac delta function (3). It has also been shown that a step distribution of catalyst with step width about 5% of the pellet radius provides virtually the same results achieved by the optimal distribution (1). A step-type distribution is the true optimal distribution and not only an approximation, when the local catalyst concentration is considered to be bounded by an upper limit (4). Developments in the area of optimal distribution of catalyst have been reviewed recently (5).

A common method of catalyst preparation is by impregnation. A high-surface-area porous support is contacted with a liquid solution of active component. The active agent enters the porous support via capillary action and diffusion and adsorbs on the available surface sites. Supported platinum catalysts are usually prepared by contacting hexachloroplatinic acid with either a dry or solvent-filled support. When γ-Al_2O_3 pellets are impregnated with hexachloroplatinic acid, the resulting catalyst profile is of the eggshell type; i.e., the platinum is located in a thin shell at the support surface. Maatman (6) found that the platinum distribution could be made more uniform by the addition of various acids to the impregnating solution. Michalko (7) and others (cf. (8)) demonstrated that the presence of citric acid in the impregnation solution results in a subsurface band of platinum in alumina pellets. Shyr and Ernst (9) have shown that a variety of platinum profile shapes can be obtained by using different coimpregnants. In all of the above investigators, the preparation of the

[1] Current address: Department of Chemical and Biochemical Engineering, University College London, United Kingdom.

[2] To whom correspondence should be addressed. E-mail: avarma@darwin.cc.nd.edu

0021-9517/96 $12.00
Copyright © 1996 by Academic Press, Inc.
All rights of reproduction in any form reserved.

TABLE 1

Physical Characteristics of γ-Al_2O_3 Pellets

Pellet length	0.32 cm
Pellet diameter	0.32 cm
Apparent density	1.73 g/cm^3
Surface area[a]	78.4 m^2/g
Average pore radius[a]	51.4 Å
Porosity	0.57

[a] Obtained by multipoint BET method.

supported platinum catalyst was based on the coimpregnation of hexachloroplatinic acid with another acid (usually citric acid). Lee and Aris (10) have provided an extensive review of catalyst preparation and have described models for various phases of single- and multicomponent impregnation.

Kulkarni *et al.* (11) used a simple model of plug flow into a single pore considering only two types of resistances at the liquid–solid interface: mass transfer and adsorption kinetics. Hegedus *et al.* (12) modeled competitive multicomponent adsorption on wet pellets by using adsorption constants determined from separate experiments. The model was used to predict the Rh distribution inside the pellet, when HF was used as the site blocking agent; diffusion constants were treated as adjustable parameters. Scelza *et al.* (13) used a similar model, but they treated not only the diffusion constants but also the adsorption constants as adjustable parameters. More detailed models have also been suggested, which take into account the chemistry of the solution–solid interface (14–16).

The present work addresses the preparation of step-type Pt/γ-Al_2O_3 pellets by impregnation. A diffusion–adsorption model which predicts satisfactorily the catalyst distribution inside the pellet is proposed. The parameters of the model, i.e., adsorption constants and effective diffusivities, were determined from separate experiments. In addition to coimpregnation, sequential impregnation was also used to prepare step-type catalyst pellets and yielded thinner step widths as compared with the former.

EXPERIMENTAL

Preparation of Step-Type Catalysts

Thin step-type Pt/γ-Al_2O_3 catalysts were prepared by coimpregnation and sequential impregnation techniques using citric acid as the competitive adsorbate. Harshaw–Filtrol AL-0104 cylindrical γ-Al_2O_3 pellets were used, and their physical characteristics are given in Table 1. Hexachloroplatinic acid solution was prepared by adding dihydrogen hexachloroplatinate (IV) (Aldrich A.C.S. grade) to deionized water. Citric acid (Fisher Scientific A.C.S. grade) was prepared in the same way. Before impregnation, the pellets were heated in air at 125°C and stored in a desiccator prior to use.

For *coimpregnation*, the pellets (about 4 g) were put in a flask and contacted with a mixture of citric acid and hexachloroplatinic acid (18 ml) for a given length of time. The flask was kept on a shaker (120 rpm) for the total impregnation period. The solution was then removed, and the pellets were washed with deionized water to remove the excess hexachloroplatinic acid from the exterior of the pellets. Two differential initial concentrations of hexachloroplatinic acid (0.00589 and 0.0117 *M*) and three different concentrations of citric acid (0.0556, 0.1111, 0.1667 *M*) were used, and the impregnation time was varied from 15 min to 2.5 h.

Sequential impregnation involved contacting the pellets in a similar manner as before with a solution of hexachloroplatinic acid (18 ml) for 15 min. The solution was removed and the pellets were washed with deionized water. They were then placed in a solution of citric acid (18 ml) for the desired impregnation duration. At the end of this period, the solution was removed and the pellets were washed with deionized water. Two different concentrations of hexachloroplatinic acid (0.00589 and 0.0117 *M*) and four different concentrations of citric acid (0.0556, 0.1111, 0.2222, 0.3333 *M*) were used, and the impregnation time (for the second step) was varied from 15 to 60 min.

At the end of the coimpregnation or the sequential impregnation period, the pellets were dried at 125°C for 18 h to immobilize both the citrate and the chloroplatinate ions. For visual observation the pellets were sectioned radially and dipped in boiling $SnCl_2$ solution. The location and width of the resulting platinum profile were determined by photographing the pellet and measuring the distances from the photographs. The pellets were calcined under a stream of oxygen from 25 to 500°C over a period of half an hour, followed by treatment in hydrogen for 1 h at 500°C. After this, the pellets were cooled in a nitrogen atmosphere.

Measurement of the platinum loading was performed by first crushing the pellets and extracting the platinum by a mixture of double-distilled HCl, HNO_3, and HF, in a ratio 3 : 3 : 1. The concentration of platinum in solution was then determined by ICP mass spectroscopy.

The catalyst dispersion was determined by measuring the platinum surface area by using hydrogen chemisorption according to the procedure described by Lemaitre *et al.* (17). Details of the pulse chemisorption setup used for the experiments are given elsewhere (18). The catalyst in powder form was first treated in hydrogen at 450°C for 1 h and after cooling to 25°C, was subjected to an oxidation–reduction–oxidation cycle, to obtain reproducible results.

Determination of Equilibrium Adsorption Constants and Adsorption Rate Constants

The single-component equilibrium adsorption parameters were determined by contacting a known amount of γ-Al_2O_3 that was ball-milled to 20 μm and dried at 125°C for 8 h, with a known concentration of citric acid or hexachloroplatinic acid. The slurries were kept in a shaker during the impregnation period. They were then filtered and the filtrate concentration was determined by either atomic absorption spectroscopy for hexachloroplatinic acid or sodium hydroxide titration (using a Fisher Accumet Model 805MP pH meter) for citric acid. The amount of solute adsorbed on γ-Al_2O_3 was determined from the difference in solution concentration before and after impregnation.

Adsorption rate constants were measured by transient adsorption experiments. In each experiment, approximately 30 g powdered γ-Al_2O_3 was added to 200 ml impregnating solution of known concentration. The slurry was kept in a shaker at all times. At selected time intervals, 0.1 ml of the slurry was removed and immediately filtered. The filtrate concentration was then measured by the techniques described previously. The adsorption rate constants were determined by fitting the transient data.

Some transient multicomponent adsorption experiments which mimic the sequential impregnation of γ-Al_2O_3 pellets were also carried out. For these, γ-Al_2O_3 powder was first impregnated with a solution of hexachloroplatinic acid for 1 h and the slurry was then centrifuged to separate the solid from the liquid. Afterward, the liquid phase was decanted off, and citric acid was added to the solid for further impregnation, which was allowed to progress for 1 h.

Effective Diffusivity Measurement

Effective diffusivities of citric and hexachloroplatinic acid were measured under well-mixed conditions in a spinning basket and a packed-bed apparatus. The first consisted of four stainless-steel baskets mounted on a common axis that was rotated by a stirring motor. The baskets were placed in a closed vessel which contained the fluid. The fluid was stirred by a magnetic spin bar rotating counter to the baskets. This kept the liquid flowing over the pellet surface maintaining high interphase mass transfer. The packed-bed apparatus consisted of a quartz tube containing the pellets. A peristaltic pump recycled the bulk fluid over the pellets to achieve good mass transfer. More details about the effective diffusivity measurements have been reported elsewhere (19). Interphase mass transfer between the liquid and the solid phase for both setups was much faster than intraphase mass transfer (19) and therefore the concentration of solute in the pore fluid at the pellet surface was equal to the bulk fluid concentration.

To decouple diffusion from adsorption/desorption phenomena, the pellets were first placed in a high-concentration solution of citric acid or hexachloroplatinic acid for several days to achieve equilibrium between the adsorbed phase and the bulk phase. The pellets were then loaded in either apparatus, bulk fluid of a different (but still high) concentration was added, and the units were turned on. At various time intervals, the bulk fluid was sampled and the concentration was measured. All experiments were performed at room temperature.

SINGLE-COMPONENT EQUILIBRIUM AND TRANSIENT ADSORPTION RESULTS

If adsorption of citric acid or hexachloroplatinic acid is described by the Langmuir model, the rate of adsorption in the absence of mass transfer resistance is given by

$$\frac{dn}{dt} = k^+ c(n_s - n) - k^- n. \qquad [1]$$

At equilibrium, the amount adsorbed can be calculated by setting the transient term equal to zero, thus giving the Langmuir adsorption isotherm

$$n_e = \frac{Kc_e n_s}{1 + Kc_e}, \qquad [2]$$

where $K = k^+/k^-$ is the equilibrium adsorption constant. Note that c_e is the solution concentration and n_e the corresponding surface concentration at equilibrium. The quantity n_e is calculated from the difference between the initial and equilibrium solution concentrations. It was found that the above isotherm fitted both citric acid and hexachloroplatinic acid adsorption data well. By using a nonlinear least-squares algorithm (Levenberg–Marquardt), the equilibrium adsorption constant, K, and the surface saturation coverage, n_s, were obtained for each component. During the adsorption experiments for both citric acid and hexachloroplatinic acid, it was observed that the fluid concentration changed relatively little with time after approximately 60 min.

From the equilibrium data, hexachloroplatinic acid was found to have a surface saturation coverage of 121 μmol/g (1.55 μmol/m^2) and an equilibrium adsorption constant of 606 liter/mol. For citric acid, the surface saturation coverage was found to be 209 μmol/g (2.68 μmol/m^2) and the equilibrium constant was 19530 liter/mol. Figure 1 shows the experimental results of the equilibrium experiments along with the predicted isotherms using the calculated parameters for hexachloroplatinic acid and citric acid, respectively. It is worth noting that Freundlich isotherms could not describe the adsorption of either the hexachloroplatinic acid or citric acid on the support.

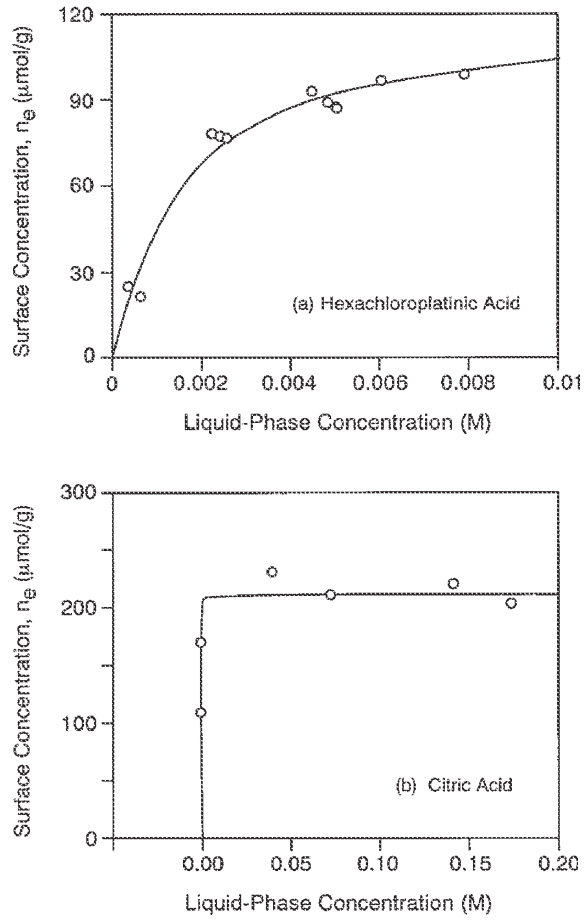


FIG. 1. Equilibrium adsorption isotherm of (a) hexachloroplatinic acid (c_{bo} = 0.01287 *M*) and (b) citric acid (c_{bo} = 0.00544 *M*) on γ-Al_2O_3 powder and the fitted Langmuir adsorption models.

For hexachloroplatinic acid, the surface saturation coverage reported in the literature ranges from 110 to 290 μmol/g, while the value of adsorption equilibrium constant varies from 110 to 31000 l/mol (see Table 2). The values obtained in this work are within the above ranges. The large range of the adsorption equilibrium constant, though, makes the comparison more difficult. Note that if the surface saturation coverage is based on the surface area of the support, the above range of values becomes 0.73 to 1.5 μmol/m^2, while the saturation coverage obtained in this study is 1.55 μmol/m^2.

Data for citric acid adsorption are relatively scarce (see Table 3). Shyr and Ernst (9) reported that even though the adsorption isotherm showed a saturation behavior, a Langmuir adsorption model did not fit their data obtained for citric acid on γ-Al_2O_3. However, Engels *et al.* (20) fitted their data with a Langmuir model and found the equilibrium adsorption constant to be 2070 liter/mol. This value is smaller than that obtained in the present study, and this may be because it was calculated by linearizing the adsorption equation. In this case, *K* is obtained from the line intercept. For large *K* values, the intercept being close to zero renders this method unreliable.

The surface saturation coverage reported by Shyr and Ernst (9) was 215 μmol/g (1.43 μmol/m^2). Jianguo *et al.* (21) fitted adsorption data of citric acid on η-Al_2O_3 and found that the saturation coverage was 820 μmol/g (3.35 μmol/m^2). Engles *et al.* (20) obtained a value of 444 μmol/g (2.02 μmol/m^2). In the present study, the equilibrium data gave a value of 209 μmol/g (2.68 μmol/m^2). The differences among the various studies may lie partly in the duration of impregnation.

When comparing the adsorption data from various γ-Al_2O_3 supports, caution should be exercised due to the variances that may be present in the supports. Jiratova (22) demonstrated that the isoelectric point (the pH where no adsorption occurs) of alumina varies strongly with trace impurities in the solid and the value of isoelectric point influences the amount of adsorption that occurs for a given solution pH. Furthermore, the solution pH also greatly affects the adsorption properties of a given γ-Al_2O_3 sample (23) and in turn depends on the hexachloroplatinic acid concentration. In addition, even for a specific concentration of hexachloroplatinic acid, solely the amount of γ-Al_2O_3 added can alter the solution pH; i.e., the pH depends on the ratio of solution volume to mass of alumina (*V*/*G*) (24). These investigators have shown that when alumina is added gradually to a solution, its pH changes and approaches the isoelectric point of the oxide. Considering the fact that the data shown in Table 2 were obtained over a large range of *V*/*G* values (5–80 ml/g) and with different alumina samples, the large range of adsorption parameters obtained may be justifiable.

Once the equilibrium adsorption constant and surface saturation coverage are known, the only parameter in the Langmuir adsorption model remaining to be calculated is the adsorption rate coefficient k^+. For this purpose, a transient adsorption equation based on measurable quantities is developed as follows.

The amount of solute adsorbed, *n*, can be calculated by knowing the solution concentration at a particular time *t*:

$$n(t) = \frac{V}{G}[c_0 - c(t)]. \qquad [3]$$

Substituting Eq. [3] into [1], the concentration of bulk solution as a function of time is obtained:

$$-\frac{dc}{dt} = k^+c^2 + \left(k^- + \frac{G}{V}k^+n_s - k^+c_0\right)c - k^-c_0. \qquad [4]$$

TABLE 2

Values of Adsorption Parameters of Hexachloroplatinic Acid on γ-Al_2O_3 in Water Solution

Area (m^2/g)	K (liter/mol)	k^+ (liter/mol·s)	n_s (μmol/g)	n_s (μmol/m^2)	t_e (h)	Reference
177	459	1.21	265	1.50	3–8	(35)
150	1330		110	0.73	2	(9)
170	31000		140	0.82	6	(34)
245			275	1.12	6	(21)[a]
	7200	1.70				(13)
190	1550		151	0.79	0.3	(36)
195	110	0.18	290	1.48	2	(37)
227			205	0.90	1	(23)
78	606	2.46	121	1.55	1.5	This study

[a] Solid was η-Al_2O_3.

Equation [4] is then fitted to transient adsorption data to determine k^+. For hexachloroplatinic acid, its value was calculated to be 2.46 liter/mol·s, while for citric acid, it was 7.97 liter/mol·s. Values of adsorption rate constant for hexachloroplatinic acid reported in the literature (see Table 2) vary to some extent. No constants have been reported for the transient adsorption of citric acid.

Figure 2 shows experimental results from transient experiments along with the model predictions for both hexachloroplatinic acid and citric acid. It should be noted that the adsorption rate for citric acid was extremely fast.

MULTICOMPONENT EQUILIBRIUM AND TRANSIENT ADSORPTION RESULTS

When more than one adsorbate are present in solution, competition between them for adsorption sites must be taken into account. For this, initially a purely competitive model (i.e., no interactions between the adsorbates either on the support surface or in the fluid phase) was formulated. The adsorption equation of the ith component in a two-component system is given by

$$\frac{dn_i}{dt} = k_{mi}^+ c_i (n_{ms} - \lambda_i n_i - \lambda_j n_j) - k_{mi}^- n_i. \qquad [5]$$

The multicomponent expression should collapse into the single component expression (Eq. [1]) when only one adsorbate is present; therefore the ratio n_{ms}/λ_i should equal the single-component surface saturation coverage, n_{si}, and $\lambda_i k_{mi}^+$ the single-component adsorption rate constant, k_i^+. Also, the ratio λ_j/λ_i should equal the ratio of the single-component saturation coverages n_{si}/n_{sj}, and k_{mi}^- the single component desorption rate constant, k_i^-. Thus, Eq. [5] can be rearranged as

$$\frac{dn_i}{dt} = k_i^+ c_i \left(n_{si} - n_i - \frac{n_{si}}{n_{sj}} n_j \right) - k_i^- n_i. \qquad [6]$$

This model, however, was unable to describe the multicom-

TABLE 3

Values of Adsorption Parameters of Citric Acid on γ-Al_2O_3 in Water Solution

Area (m^2/g)	K (liter/mol)	k^+ (liter/mol·s)	n_s (μmol/g)	n_s (μmol/m^2)	t_e (h)	Reference
150			215	1.43	2	(9)
245			820	3.35	6	(21)[a]
220	2070		444	2.02	2	(20)
78	19530	7.97	209	2.68	1.5	This study

[a] Solid was η-Al_2O_3.

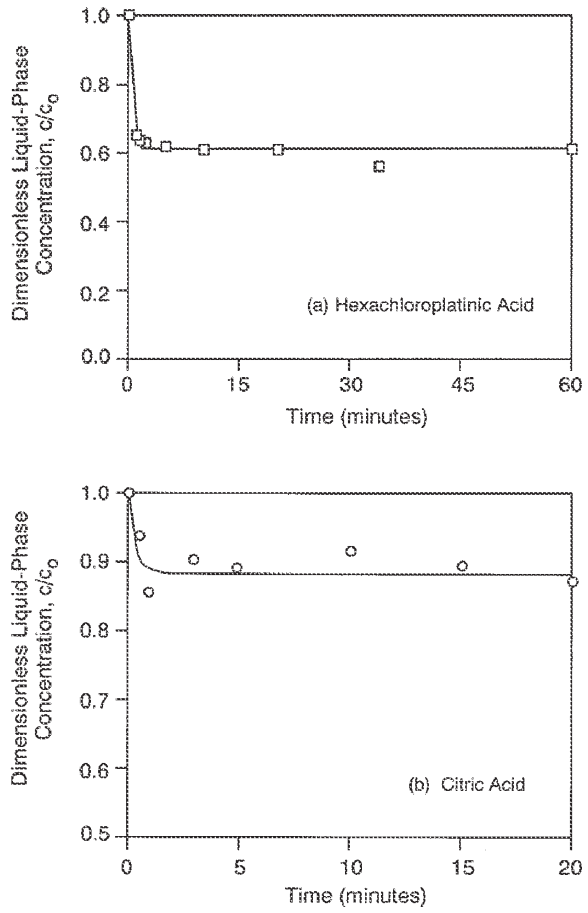


FIG. 2. Transient adsorption during impregnation of γ-Al_2O_3 powder with (a) hexachloroplatinic acid (G/V = 50.2 g/liter) and (b) citric acid (G/V = 3.12 g/liter) and fitted Langmuir adsorption models.

ponent experimental data satisfactorily. For this reason, a model which accounted for *solution effects* for hexachloroplatinic acid and *steric hinderances effects* for citric acid was formulated.

In the multicomponent adsorption experiments, the γ-Al_2O_3 initially contained adsorbed hexachloroplatinic acid. The amount of hexachloroplatinic acid desorbed when γ-Al_2O_3 was subsequently placed in the citric acid solution was in excess of that predicted by the single-component model but less than that predicted from the purely competitive model. Also, the initial desorption rate of hexachloroplatinic acid was larger than that computed from both models, suggesting that its desorption is enhanced by the presence of citric acid in solution. This was accounted for by introducing an additional desorption term in the single-component adsorption expression as follows:

$$\frac{dn_1}{dt} = k_1^+ c_1(n_{s1} - n_1) - k_1^- n_1 - k_1^{sol} c_2 n_1. \qquad [7]$$

The amount of citric acid adsorbed during the multicomponent experiments was less than the amount which would be expected based on a purely competitive model described by Eq. [6] for citric acid and Eq. [7] for hexachloroplatinic acid. Such behavior could be due to steric hinderances provided by the platinum adsorbed on the surface of γ-Al_2O_3. This was accounted for by introducing a new equilibrium adsorption constant K_2^{st}, due to steric hinderances,

$$\frac{dn_2}{dt} = k_2^+ c_2(n_{s2} - n_2 - K_2^{st} n_1) - k_2^- n_2. \qquad [8]$$

By comparing Eq. [8] with [6], it can easily be seen that K_2^{st} for a purely competitive model corresponds to n_{s2}/n_{s1}; thus it is the ratio of the stoichiometric factors (λ_1/λ_2) for hexachloroplatinic acid and citric acid adsorption equilibria. The equilibrium expressions including the new terms are

$$n_{1e} = \frac{K_1 c_{1e} n_{sl}}{1 + K_1 c_{1e} + K_1^{sol} c_{2e}} \qquad [9]$$

$$n_{2e} = \frac{K_2 c_{2e}}{1 + K_2 c_{2e}} (n_{s2} - K_2^{st} n_{1e}). \qquad [10]$$

The two new parameters in the multicomponent equilibrium model expressed by Eqs. [9] and [10], namely K_1^{sol} and K_2^{st}, were determined by fitting the equilibrium data to be 735 and 3.18 liter/mol, respectively.

In the kinetic expressions (Eqs. [7] and [8]), once the equilibrium constants (i.e., K_1 and K_2) have been obtained, only one parameter for each component needs to be determined (i.e., k_1^+ and k_2^+). The values of the desorption rate constants can then be calculated from the equilibrium constants.

Figure 3 shows the transient multicomponent adsorption experimental data for hexachloroplatinic and citric acids along with the model curves. It was found that use of the single-component adsorption rate constant for hexachloroplatinic acid (2.46 liter/mol·s) was satisfactory also in the transient multicomponent adsorption; however, the adsorption rate constant of citric acid had to be lowered to 0.2 liter/mol·s in order to achieve the best fit. Note that in Fig. 3a, the model curve is based on the adsorption rate constant which was determined by fitting the data of a *different* experiment. Thus the model predictions of the liquid-phase concentrations are satisfactory. In the same figure, the hexachloroplatinic acid concentration calculated from the model shows an initial maximum and then it declines to the steady-state value. The reason for this is that the concentration of citric acid decreases with time as

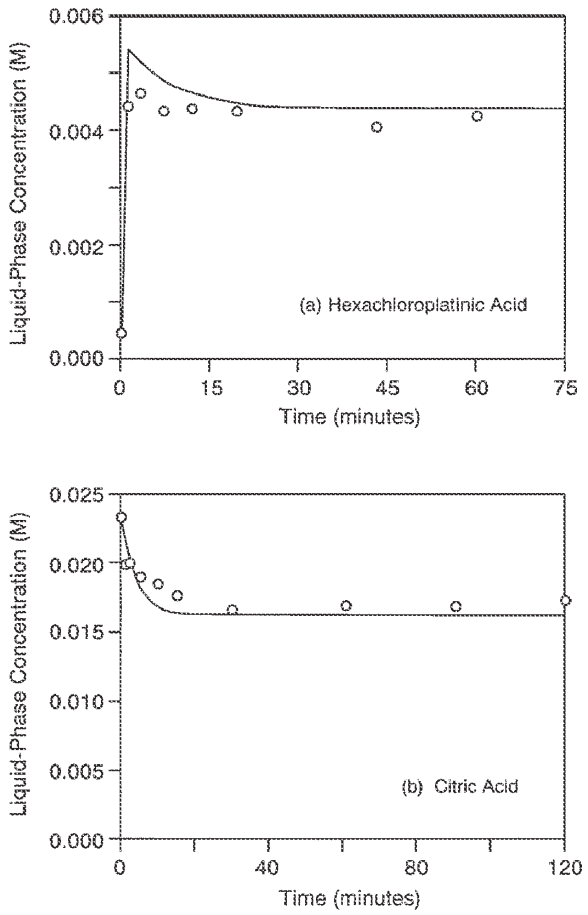


FIG. 3. Transient multicomponent adsorption on γ-Al_2O_3 powder with model predictions of liquid-phase concentration as a function of time for (a) hexachloroplatinic acid and (b) citric acid.

it adsorbs on γ-Al_2O_3. At the onset of citric acid impregnation, the fluid-phase concentration of citric acid is relatively high, thus causing some desorption of the platinum from the γ-Al_2O_3 support. As the solution concentration of citric acid declines due to adsorption, there is a readsorption of platinum, which decreases the liquid-phase concentration of hexachloroplatinic acid, as also observed in the experimental data.

As noted earlier, more detailed models which take into account electrokinetic and ionic dissociation effects have been suggested in the literature (cf. (14–16)). They include a more realistic description of the surface chemistry at the expense of model complexity. In the present study, it was intended to keep the model simple such that kinetics and equilibria for multicomponent systems collapse into the appropriate single-component expressions in the limit as concentration of one component goes to zero.

EFFECTIVE DIFFUSIVITIES

The equation governing the transient transport and adsorption of a solute in a porous solid of cylindrical geometry, initially filled with solvent, is

$$\varepsilon \frac{\partial c_p}{\partial t} + \rho_s \frac{\partial n}{\partial t} = D_e \left\{ \frac{\partial^2 c_p}{\partial x^2} + \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial c_p}{\partial r} \right) \right\}. \qquad [11]$$

Since the interphase mass transport resistances during the effective diffusivity measurement experiments are negligible, the boundary conditions are

$$c_p(x, R) = c_p(\pm L/2, r) = c_b(t) \qquad [12a]$$

$$\left. \frac{\partial c_p}{\partial x} \right|_{x=0} = \left. \frac{\partial c_p}{\partial r} \right|_{r=0} = 0. \qquad [12b]$$

Absorbate concentration in the bulk solution (assumed to be well mixed) changes as the solute diffuses into and adsorbs on the support, because the bulk reservoir is finite. The change of bulk solute concentration is given by

$$V \frac{dc_b}{dt} = -N_p D_e 4\pi \left\{ R \int_0^{L/2} \left. \frac{\partial c_p}{\partial r} \right|_{r=R} dx + \int_0^R r \left. \frac{\partial c_p}{\partial x} \right|_{x=L/2} dr \right\}. \qquad [13]$$

In Langmuir adsorption, surface concentration of adsorbate does not change appreciably once the fluid concentration reaches a sufficiently high value. By keeping both the pore and the bulk fluid in this concentration range, adsorption/desorption do not occur and hence are decoupled from diffusion, thus simplifying the diffusion–adsorption Eq. [11] (i.e., $\partial n/\partial t = 0$). To ensure that no further adsorption could occur, equilibrium was established for the pellets prior to their use in diffusivity experiments.

Since there was some occluded liquid between the pellets when they were first loaded into the apparatus, the bulk fluid concentration was altered from its initial concentration, which had to be accounted for. To calculate the correct initial value, a material balance was performed after the pellets were equilibrated with the bulk fluid. The corrected initial concentration is given by

$$c_{bo} = \frac{c_{b\infty}(V + N_p \varepsilon \pi R^2 L) - N_p \varepsilon \pi R^2 L c_{po}}{V}. \qquad [14]$$

Effective diffusivities were determined by solving Eqs. [11] and [13], using the value of D_e as the fitting parameter. One octant of the pellet was divided into a grid containing

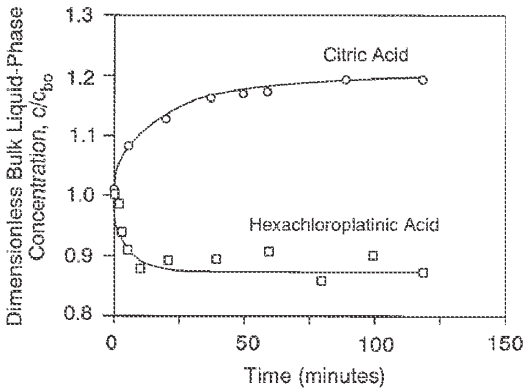


FIG. 4. Effective diffusivity measurements of hexachloroplatinic acid and citric acid with fitted model predictions. Experimental conditions for (a) citric acid: $c_{po} = 2.78$ *M*, $c_{bo} = 0.229$ *M* and (b) hexachloroplatinic acid: $c_{po} = 0.0283$ *M*, $c_{bo} = 0.1071$ *M*.

10 points in the axial and radial directions. Orthogonal collocation (25) was used for the spatial variables, while Gear's method (IMSL subroutine DGEAR) was used to solve for the time dependence of the concentration at each collocation point and the concentration in the bulk fluid.

Figure 4 shows the results for one citric acid (spinning basket) and one hexachloroplatinic acid (packed bed) effective diffusivity runs. D_e was determined to be 0.96×10^{-6} cm^2/s for citric acid and 3.12×10^{-6} cm^2/s for hexachloroplatinic acid. The molecular diffusivity, D_m, of citric acid in water at 25°C and 0.1 *M* concentration is 6.61×10^{-6} cm^2/s (26). With this value and the effective diffusivity value determined experimentally, the tortuosity factor $\tau = \varepsilon D_m/D_e$ is 3.9, which is within the range 2–7 of typical tortuosity factors (27). The molecular diffusivity of hexachloroplatinic acid was not available in the literature. Scelza *et al.* (13) report an effective diffusivity of 2.25×10^{-5} cm^2/s for hexachloroplatinic acid in γ-Al_2O_3 particles. This value is higher than that reported in the present work. This may be due to the fact that they calculated *both* effective diffusivities *and* adsorption rate constants by fitting a diffusion–adsorption model with experimental data obtained under conditions where both diffusion and adsorption were present. Santacesaria et al. (28), by fitting the diffusion-controlled hexachloroplatinic acid impregnation of γ-Al_2O_3 pellets with an unreacted-core shrinking model, calculated an effective diffusivity of 3.55×10^{-6} cm^2/s, which agrees well with this work.

DIFFUSION-ADSORPTION MODEL

Model Formulation

For multicomponent impregnation of cylindrical pellets in a finite reservoir of solution, the material balance inside the pellet for species i is given by the multicomponent version of Eq. [11]:

$$\varepsilon \frac{\partial c_{p,i}}{\partial t} + \rho_s \frac{\partial n_i}{\partial t} = D_{e,i}\left\{\frac{\partial^2 c_{p,i}}{\partial x^2} + \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial c_{p,i}}{\partial r}\right)\right\}. \quad [15]$$

The multicomponent adsorption kinetics (Eqs. [7] and [8]) were used to describe the adsorption rates, $\partial n_i/\partial t$. Even though these kinetics were obtained under conditions of sequential impregnation, the results were utilized also for describing the coimpregnation of γ-Al_2O_3 pellets. The depletion of species i in the bulk solution is given by

$$V\frac{dc_{b,i}}{dt} = -N_p D_{e,i} 4\pi\left\{R\int_0^{L/2}\left.\frac{\partial c_{p,i}}{\partial r}\right|_{r=R} dx + \int_0^R r\left.\frac{\partial c_{p,i}}{\partial x}\right|_{x=L/2} dr\right\}. \quad [16]$$

The boundary conditions are

$$c_{p,i}(x, R) = c_{p,i}(\pm L/2, r) = c_{b,i}(t) \quad [17a]$$

$$\left.\frac{\partial c_{p,i}}{\partial x}\right|_{x=0} = \left.\frac{\partial c_{p,i}}{\partial r}\right|_{r=0} = 0. \quad [17b]$$

For citric acid, the initial conditions for both types of impregnation are

$$c_{b,2} = c_{bo,2} \quad \text{at } t = 0 \quad [18a]$$

$$c_{p,2} = n_2 = 0 \quad (0 \le r \le R, 0 \le x \le L/2) \quad \text{at } t = 0. \quad [18b]$$

In coimpregnation and in the first impregnation (where only hexachloroplatinic acid is present) of the pellets during sequential impregnation, initial conditions for hexachloroplatinic acid are similar to those described by Eqs. [18]. In sequential impregnation, after the pellets are removed from the hexachloroplatinic acid and placed in the citric acid solution, the new initial conditions for hexachloroplatinic acid are

$$c_{b,1} = 0 \quad \text{at } t = 0 \quad [19a]$$

$$c_{p,1}(r, x) = c^*_{p,1}(r, x); \quad n_1(r, x) = n^*_1(r, x) \quad \text{at } t = 0, \quad [19b]$$

where $c^*_{p,1}(r, x)$ and $n^*_1(r, x)$ are the pore-fluid and surface concentrations at the end of the first impregnation.

Note that even though during the experiments the pellets were initially dry, thus some of the solution entered by imbibition, Eq. [15] assumes that the pores of the pellet are initially filled with solvent. Lee and Aris (10) showed by numerical calculations that for the impregnation of γ-

Al_2O_3 pellets with hexachloroplatinic acid in which the pore-filling time was approximately 20 s, there was no noticeable difference between the platinum distributions in solvent-filled and dry supports when the impregnation period lasted 5 min or more. The reason for this is the short pore-filling time of the pellets. During the pore-filling stage, hexachloroplatinic acid adsorbs near the external surface of the pellet; thus the pores become filled with pure solvent. In our experiments the average pore-filling time was 12 s, while the impregnation periods varied from 15 min to 2.5 h; thus using a solvent-filled pellet to describe the impregnation of dry pellets does not induce any significant error.

Citric acid and hexachloroplatinic acid adsorb strongly on γ-Al_2O_3. Due to the strong precursor–support interaction, redistribution during the washing and drying steps is unlikely, and the final distribution of active phase is determined mainly in the impregnation step (cf. (29)).

Numerical Solution

The partial differential equations [15]–[19] describing the multicomponent diffusion and adsorption in a finite cylinder were solved by dividing one octant of the pellet into a region of $N \times N$ grid points (recall from Table 1 that pellet $L/2R = 1$) extending from the pellet center to the radial and axial surfaces. The spatial derivatives were solved using the finite difference technique with central differencing (25). This reduced Eqs. [15] and [16] to a system of coupled nonlinear ordinary differential equations (ODEs), with time as the independent variable.

A sixth-order Runge–Kutta algorithm (IMSL subroutine DVERK) was used to integrate the equations. It was found that to achieve a reasonable spatial resolution a large number of grid points was required ($N = 50$), resulting in large computational times. To alleviate this problem one-dimensional geometry (i.e., sphere) was used. The external geometric surface area of a cylinder with length equal to its diameter is 1.5 times larger than that of a sphere with the same diameter. So, to have the equivalent geometric surface area, the number of spherical pellets, M_p, should be 1.5 times the number of cylindrical ones, N_p. By using this factor, there is no difference between the mass of the supports if the same pellet density is used. The dimensionless multicomponent equations describing the impregnation of a sphere are

$$\varepsilon \frac{\partial c_{p,i}}{\partial t} + \rho_s \frac{\partial n_i}{\partial t} = D_{e,i}\left\{\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial c_{p,i}}{\partial r}\right)\right\} \qquad [20]$$

$$V \frac{dc_{b,i}}{dt} = -M_p D_{e,i} A \pi R^2 \left\{\left.\frac{\partial c_{p,i}}{\partial r}\right|_{r=R}\right\}. \qquad [21]$$

Using the above equations for the model the reduction in computational time was substantial. The average error in the pore-fluid concentration predictions, using the spherical geometry equations (Eqs. [20], [21]) as compared to the cylindrical geometry (Eqs. [15], [16]), was typically less than 10%.

EXPERIMENTAL OBSERVATIONS AND COMPARISON WITH MODEL PREDICTIONS

The diffusion–adsorption model described previously predicted successfully the effects of the various impregnation parameters on the platinum distribution within the pellet. The cross sections of pellets prepared by sequential and coimpregnation techniques are shown in Fig. 5. The dark rings in Figs. 5a–5i are the platinum catalyst, while the lighter portion is the γ-Al_2O_3 support. For comparison, eggshell, egg-yolk, and uniform pellets are also shown in Figs. 5j–5l.

For both types of impregnations, the platinum band was located deeper inside the pellet for higher initial critic acid concentration (compare Figs. 5b–5c, 5e–5f, 5h–5i). In addition, higher impregnation time forced the platinum to move closer to the pellet center, since the citric acid could diffuse further inside the pellet and displace the adsorbed platinum (compare Figs. 5a–5b, 5d–5e, 5g–5h). Similar effects during coimpregnation of alumina pellets with hexachloroplatinic and citric acid were also observed by Becker and Nuttall (8).

The initial hexachloroplatinic acid concentration did not have any noticeable effect on the catalyst location; however, it resulted in catalysts with higher loading and somewhat larger bandwidths (compare Figs. 5a–5d, 5b–5e, 5c–5f). The bandwidth was also influenced by impregnation time, owing primarily to geometric effects. Since the diameter of the ring, where the platinum was located, decreased with time, its width increased to accommodate the deposited metal (compare Figs. 5a–5b, 5d–5e, 5g–5h). In general, for the same impregnation time and adsorbate concentrations, a similar penetration depth was achieved by both types of impregnations (compare Figs. 5a–5g, 5b–5h), but the bandwidth was smaller (as small as 50 μm) when using sequential impregnation.

In coimpregnation experiments the platinum loading of the samples was affected not only by the initial hexachloroplatinic acid concentration but also to a smaller extent, by the citric acid concentration. The loading decreased with higher initial concentration of citric acid. However, during sequential impregnation, the platinum loading of the pellets depended primarily on the conditions of the first impregnation step. It could be kept approximately constant by using the same hexachloroplatinic acid concentration for the first step. The fact that citric acid concentration did not affect the platinum loading of pellets prepared by sequential impregnation indicates a different mode of action: in coimpregna-

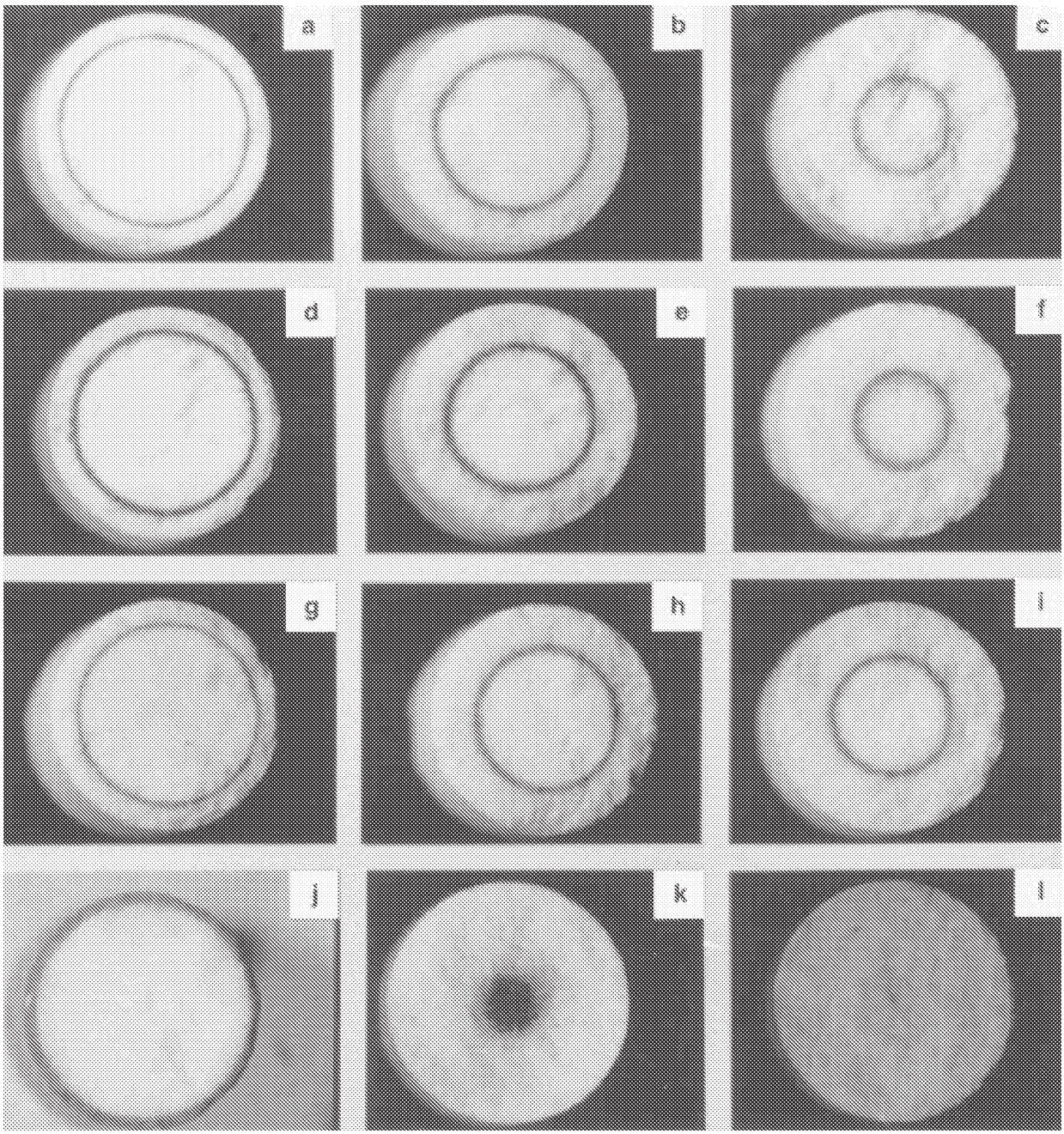


FIG. 5. Step-type platinum catalysts prepared by sequential impregnation (a) 0.00589 *M* hexachloroplatinic acid (15 min), 0.1111 *M* citric acid (15 min); (b) 0.00589 *M* hexachloroplatinic acid (15 min), 0.1111 *M* citric acid (60 min); (c) 0.00589 *M* hexachloroplatinic acid (15 min), 0.3333 *M* citric acid (60 min); (d) 0.0117 *M* hexachloroplatinic acid (15 min), 0.1111 *M* citric acid (15 min); (e) 0.0117 *M* hexachloroplatinic acid (15 min), 0.1111 *M* citric acid (60 min); (f) 0.0117 *M* hexachloroplatinic acid (15 min), 0.3333 *M* citric acid (60 min) and coimpregnation (g) 0.00589 *M* hexachloroplatinic acid and 0.1111 *M* citric acid (15 min); (h) 0.00589 *M* hexachloroplatinic acid and 0.1111 *M* citric acid (60 min); (i) 0.00589 *M* hexachloroplatinic acid and 0.1667 *M* citric acid (60 min); (j) 0.0117 *M* hexachloroplatinic acid (15 min); (k) 0.0117 *M* hexachloroplatinic acid and 0.1667 *M* citric acid (3 h); (l) 0.0117 *M* hexachloroplatinic acid and 0.1667 *M* citric acid (10 h).

tion it competes with hexachloroplatinic acid for adsorption on the support, while in sequential impregnation it enhances the desorption of adsorbed platinum. The platinum loading of the pellets as measured by ICP mass spectroscopy was in the range 0.1–0.4 wt%, depending on the initial hexachloroplatinic acid concentration.

The eggshell distribution (Fig. 5j) was prepared by impregnating the pellet in a solution of hexachloroplatinic acid alone. The egg-yolk distribution (Fig. 5k) could be achieved by both sequential and coimpregnation, provided that the impregnation periods were sufficiently long, while the uniform distribution (Fig. 5l) was obtained using the coimpregnation method. Note that the difference in the preparation procedure of pellets depicted in Fig. 5k and Fig. 5l is only the impregnation duration. Thus, for short coimpregnation time an egg-white deposition is obtained, while for longer impregnation periods egg-yolk and ultimately uniform distributions are attained. Catalyst dispersion of the pellets, including both step and uniform distributions, as measured by hydrogen chemisorption, ranged between 60 and 70%. Hence, for pellets with relatively low platinum loadings as considered in this study, the dispersion is virtually unaltered when concentrating the metal in a thin step-type distribution. These dispersion values are within the range reported for typical Pt/γ-Al_2O_3 catalysts (cf. (30, 31)).

Figures 6 and 7 show the predicted dimensionless platinum surface concentration profiles, along with the experimentally measured platinum band positions denoted by the shadowed regions for the sequential and coimpregnation studies, respectively. The numbers on the bands give the impregnation time (for sequential impregnation it is the time in the citric acid solution). The penetration depth of platinum predicted by the model for both impregnation techniques is greater with increasing impregnation time, as also observed experimentally. In addition, the model is able to predict that the bandwidths are broader for the coimpregnation than for the sequential impregnation technique (compare Figs. 6b and 7b), as well as the fact that bandwidth increases with impregnation time. Note that the model predicts that some adsorbed platinum extends from the peak to the pellet surface, with coimpregnation exhibiting more platinum in that region than sequential impregnation. Our pellets showed evidence (i.e., light-gray color) of small amounts of platinum deposited between the step distribution and the pellet external surface. This was also observed previously by Kunimori *et al.* (32) in the preparation of similar catalysts using hexachloroplatinic acid and citric acid.

Figure 8 compares model predictions for the platinum peak location with experimental data, for various citric acid concentrations and impregnation time. The model agrees well with the experimental data and demonstrates that by increasing citric acid concentration for both impregnation techniques, the platinum band moves deeper within the pellet. The maximum difference between the experimental and the theoretical peak locations is less than 8% of the pellet radius. An interesting feature is that the model predictions are closer to the experimental data for deeper band penetrations (cf. Fig. 8b). This was also observed by Hegedus *et al.* (12) in the coimpregnation of γ-Al_2O_3 pellets with a rhodium complex and hydrofluoric acid.

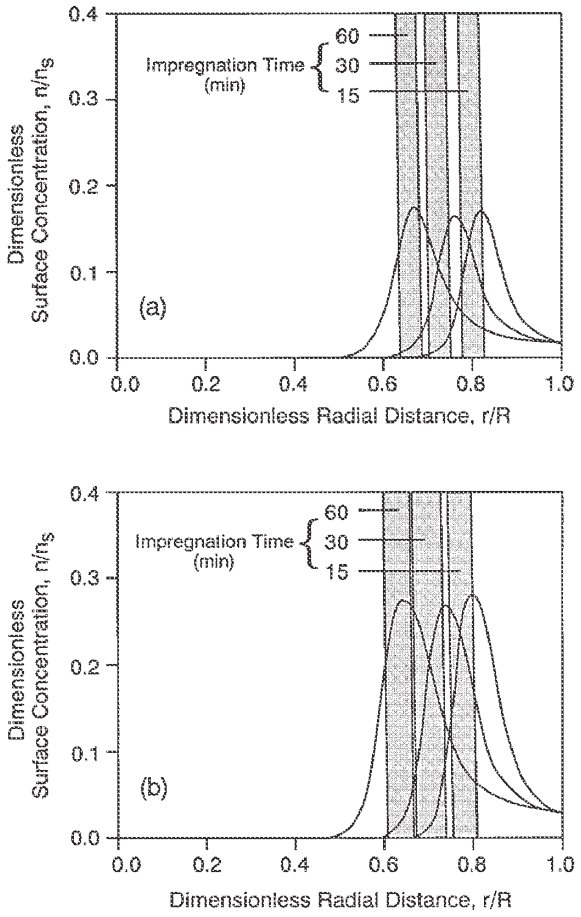
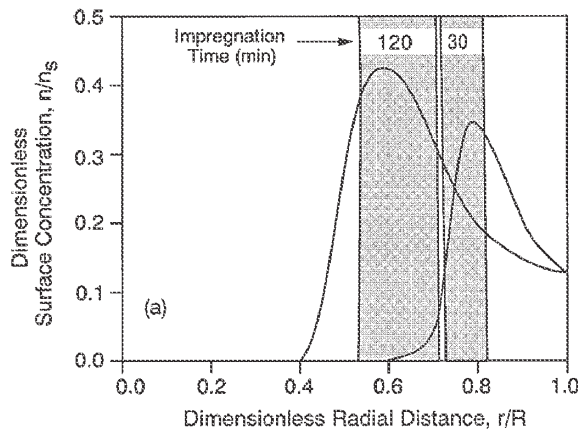


FIG. 6. Comparison of model predictions and experimental measurements of the surface concentration profiles of platinum for sequential impregnation with 0.1111 *M* citric acid, (a) 0.00589 *M* hexachloroplatinic acid, (b) 0.0117 *M* hexachloroplatinic acid. The shaded bands indicate the experimentally measured platinum step positions, and the numbers on the bands give the impregnation time in the citric acid solution.

CONCLUDING REMARKS

Since the adsorption and diffusion parameters were not adjusted to fit the diffusion–adsorption model, accord of the model with experimental data as shown in Figs. 6–8 appears to be satisfactory. These parameters were determined from separate experiments in which diffusion and



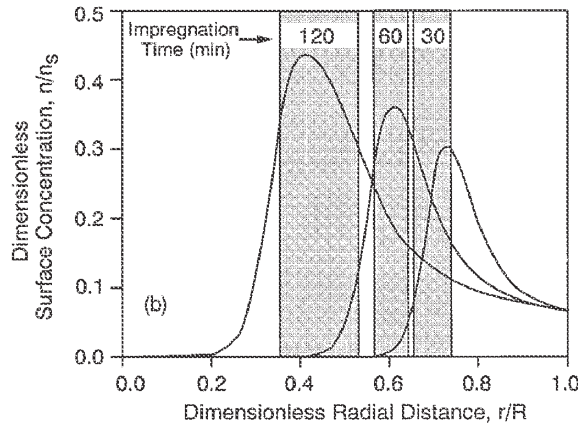
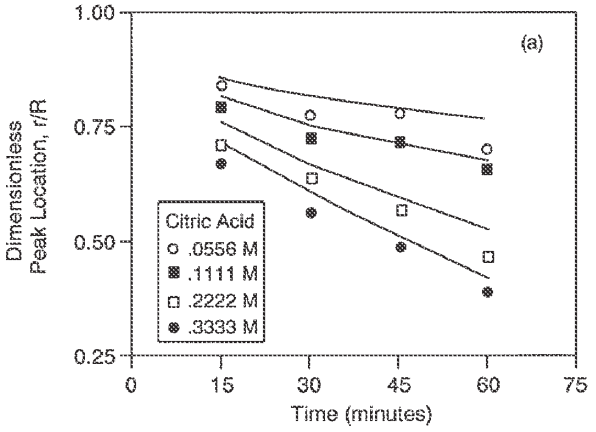


FIG. 7. Comparison of model predictions and experimental measurements of the surface concentration profiles of platinum for coimpregnation with 0.0117 *M* hexachloroplatinic acid, (a) 0.0556 *M* citric acid, (b) 0.1111 *M* citric acid. The shaded bands indicate the experimentally measured platinum step positions, and the numbers on the bands give the impregnation time.



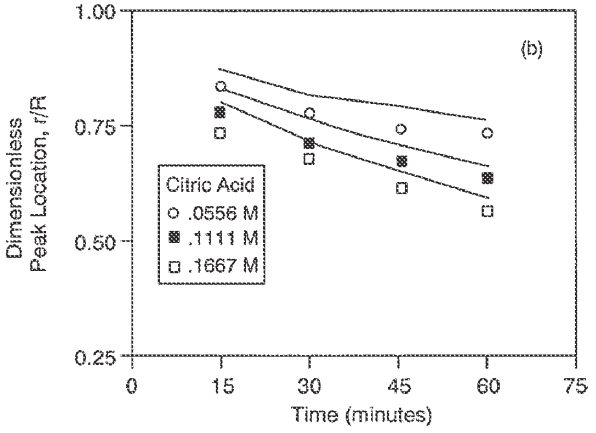


FIG. 8. Experimental platinum step locations and model predictions using 0.00589 *M* hexachloroplatinic acid and various citric acid concentrations: (a) sequential impregnation, (b) coimpregnation.

adsorption were decoupled. Specifically, diffusion coefficients were measured in the absence of adsorption, while adsorption constants were determined in the absence of diffusion resistances. In similar nonuniform catalyst preparation studies reported in the literature, adjustment of parameters was frequently employed in the diffusion–adsorption model. For example, Melo *et al.* (33) and Castro *et al.* (34) altered the single-component saturation coverages to fit the diffusion–adsorption model to the experimental data. Also, Chu *et al.* (15) required the use of larger effective diffusivity of hydrogen ions than typical values to fit distribution profiles of nickel in γ-Al_2O_3. However, their diffusion–adsorption model which took into account the surface chemistry by employing a triple-layer electrostatic model, showed excellent agreement on a qualitative level and in many cases also on a quantitative level with experimental distributions.

From the comparison of model predictions with experimental platinum profiles (Figs. 6–7), it may be seen that those determined by the model are wider. This may be due to the measurement procedure which uses optical microscopy. Schwarz and Heise (16) measured platinum profiles in γ-Al_2O_3 pellets using a scanning microdensitometer and found Pt distributions which resembled more the theoretical curves; i.e., the platinum was deposited not as a sharp band but more as a normal distribution with a tail toward the external surface of the pellet.

APPENDIX: NOTATION

c	liquid-phase concentration
D_e	effective diffusivity
D_m	molecular diffusivity
G	mass of support
K	k^+/k^-, equilibrium adsorption constant

K_i^{sol}	k_i^{sol}/k^-, equilibrium adsorption constant due to solution effects
K_2^{st}	equilibrium adsorption constant due to steric hinderances
k^+	adsorption rate constant
k^-	desorption rate constant
k_i^{sol}	desorption rate constant due to solution effects
L	pellet length
M_p	number of spherical pellets
n	surface concentration
n_s	surface saturation coverage
n_{ms}	multicomponent surface saturation coverage
N_p	number of cylindrical pellets
r	radial distance
R	pellet radius
t	time
t_e	impregnation time for equilibrium adsorption experiments
V	volume of bulk solution
x	axial distance

Subscripts

b	bulk fluid
e	equilibrium
i	component i
j	component j ($j \neq i$)
m	multicomponent
0	for $t = 0$ s
p	pore
1	hexachloroplatinic acid
2	citric acid
∞	for $t = \infty$ s

Superscripts

*	at the end of the first impregnation in the sequential impregnation technique

Greek Letters

ε	pellet porosity
λ	stoichiometric factor
ρ_s	density of the pellet
τ	tortuosity factor

ACKNOWLEDGMENT

This work was supported by the National Science Foundation.

REFERENCES

1. Morbidelli, M., Servida, A., and Varma, A., *Ind. Eng. Chem. Fundam.* **21,** 278 (1982).
2. Morbidelli, M., Servida, A., Carra, S., and Varma, A., *Ind. Eng. Chem. Fundam.* **24,** 116 (1985).
3. Wu, H., Brunovska, A., Morbidelli, M., and Varma, A., *Chem. Eng. Sci.* **45,** 1855 (1990); see also **46,** 3328 (1991).
4. Baratti, R., Wu, H., Morbidelli, M., and Varma, A., *Chem. Eng. Sci.* **48,** 1869 (1993).
5. Gavriilidis, A., Varma, A., and Morbidelli, M., *Catal. Rev. -Sci. Eng.* **35,** 399 (1993).
6. Maatman, R. W., *Ind. Eng. Chem.* **51,** 913 (1959).
7. Michalko, E., U.S. Patent 3,259,589 (1966).
8. Becker, E. R., and Nuttall, T. A., *in* "Preparation of Catalysts II" (B. Delmon, P. Grange, P. A. Jacobs, and G. Poncelet, Eds.), p. 159. Elsevier, Amsterdam, 1979.
9. Shyr, Y.-S., and Ernst, W. R., *J. Catal.* **63,** 425 (1980).
10. Lee, S.-Y., and Aris, R., *Catal. Rev. -Sci. Eng.* **27,** 207 (1985).
11. Kulkarni, S. S., Mauze, G. R., and Schwarz, J. A., *J. Catal.* **69,** 445 (1981).
12. Hegedus, L. L., Chou, T. S., Summers, J. C., and Potter, N. M., *in* "Preparation of Catalysts II" (B. Delmon, P. Grange, P. A. Jacobs, and G. Poncelet, Eds.), p. 171. Elsevier, Amsterdam, 1979.
13. Scelza, O. A., Castro, A. A., Ardiles, D. R., and Parera, J. M., *Ind. Eng. Chem. Fundam.* **25,** 84 (1986).
14. Ruckenstein, E., and Karpe, P., *Langmuir* **5,** 1393 (1989).
15. Chu, P., Petersen, E. E., and Radke, C. J., *J. Catal.* **117,** 52 (1989).
16. Schwarz, J. A., and Heise, M. S., *J. Colloid Interface Sci.* **135,** 461 (1990).
17. Lemaitre, L. J., Menon, P. G., and Delannay, F., *in* "Characterization of Heterogeneous Catalysts" (F. Delannay, Ed.), p. 299. Dekker, New York, 1984.
18. Gavriilidis, A., Sinno, B., and Varma, A., *J. Catal.* **139,** 41 (1993).
19. Price, D. M., and Varma, A., *AIChE Symp. Ser.* **266,** 88 (1988).
20. Engels, S., Lausch, H., and Schwokowski, R., *Chem. Technik (Leipzig)* **39,** 387 (1987).
21. Jianguo, W., Jiayu, Z., and Li, P., *in* "Preparation of Catalysts III" (G. Poncelet, P. Grange, and P. A. Jacobs, Eds.), p. 57. Elsevier, Amsterdam, 1983.
22. Jiratova, K., *Appl. Catal.* **1,** 165 (1981).
23. Mang, Th., Breitscheidel, B., Polanek, P., and Knoezinger, H., *Appl. Catal. A* **106,** 239 (1993).
24. Subramanian, S., Noh, J. S., and Schwarz, J. A., *J. Catal.* **114,** 433 (1988).
25. Finlayson, B. A., "Nonlinear Analysis in Chemical Engineering," McGraw–Hill, New York, 1980.
26. "CRC Handbook of Chemistry and Physics," 67th ed. CRC Press, Boca Raton, FL, 1987.
27. Satterfield, C. N., "Heterogeneous Catalysis in Industrial Practice," 2nd ed., McGraw–Hill, New York, 1991.
28. Santacesaria, E., Galli, C., and Carra, S., *React. Kinet. Catal. Lett.* **6,** 301 (1977).
29. Foger, K., *in* "Catalysis Science and Technology, Vol. 6" (J. R. Anderson and M. Boudart, Eds.), p. 227. Springer-Verlag, Berlin, 1984.
30. Wilson, G. R., and Hall, W. K., *J. Catal.* **17,** 190 (1970).
31. Wanke, S. E., and Flynn, P. C., *Catal. Rev. -Sci. Eng.*, **12,** 93 (1975).
32. Kunimori, K., Nakajima, I., and Uchijima, T., *Chem. Lett.*, 1165 (1982).
33. Melo, F., Cervello, J., and Hermana, E., *Chem. Eng. Sci.* **35,** 2175 (1980).
34. Castro, A. A., Scelza, O. A., Benvenuto, E. R., Baronetti, G. T., De Miguel, S. R., and Parera, J. M., *in* "Preparation of Catalysts III" (G. Poncelet, P. Grange, and P. A. Jacobs, Eds.), p. 47. Elsevier, Amsterdam, 1983.
35. Santacesaria, E., Carra, S., and Adami, I., *Ind. Eng. Chem. Prod. Res. Dev.* **16,** 41 (1977).
36. Heise, M. S., and Schwarz, J. A., *J. Colloid Interface Sci.* **123,** 51 (1988).
37. Subramanian, S., and Schwarz, J. A., *Langmuir* **7,** 1436 (1991).

Natalie Herring, Ph.D.
+1 434-480-1629 • Natalie.Herring@gwaru.com

EXPERIENCE

Director of Technology • G. W. Aru, LLC • June 2018 – Present

- Commercialized new refinery catalysts; from concept through scale up and on-site trial at refinery
- Engaged with refiners to introduce new refinery catalysts and supported refinery trials
- Researched refinery catalysts to increase understanding towards the development of new, state-of-art catalyst formulations

Regional Sales Manager • Johnson Matthey • April 2017 – June 2018

- Utilized commercial strategies and sales plans to deliver revenue
- Worked in functional teams to deliver new products to the market
- Established meaningful relationships with customers across multiple levels

Catalyst Development Scientist • Johnson Matthey • June 2013 – March 2017

- Led joint development project focused on development, scale-up and commercialization of a new catalyst at the customer for a biomass conversion application
- Formulated catalysts for reducing SOx emissions from FCC units
- Directed research projects by designing experiments and managing a team of chemists and technicians
- Collected and interpreted catalyst performance data to understand and implement catalyst modifications
- Implemented successful pilot plant projects into manufacturing plant using scale-up methodologies
- Evaluated and implemented process changes in both the pilot plant and manufacturing plant
- Organized and oversaw plant trials in manufacturing to evaluate new products and processes
- Investigated catalyst syntheses processes using *in-situ* synchrotron studies
- Established methods for evaluating raw materials utilizing zeta potential and dynamic light scattering

Graduate Research • Virginia Commonwealth University, Department of Chemistry • Aug. 2009 – May 2013
Formation Mechanisms and Catalytic Properties of Nanomaterials by Microwave Assisted Synthesis

- Synthesized and characterized metallic, bimetallic and semiconductor nanomaterials to understand growth kinetics and formation mechanisms.
- Developed novel synthesis procedures using microwave irradiation, thermal heating and laser ablation techniques.
- Evaluated catalytic activity of nanomaterials for photocatalysis and CO oxidation.
- Supervised undergraduate and graduate students, including training on procedures, instrumentation, and data analysis.

Graduate Research • UNC Charlotte, Department of Chemistry • Aug. 2007 – Aug. 2009
Aggregation of Colloidal Gold Nanoparticles Induced Using Ruthenium Coordination Complexes.

- Studied aggregation kinetics and morphology of gold colloids using UV-Visible absorbance spectroscopy and scanning electron microscopy toward the development of nano-building blocks.

Research Assistant • Virginia Tech Southern Piedmont Agriculture & Research Extension Center • May '05 – Aug. '07

- Maintained and evaluated small fruits as part of a strawberry-breeding program.
- DNA extraction and evaluation using polymerase chain reaction and gel electrophoresis

Undergraduate Research • College of William and Mary, Department of Chemistry • Aug. 2006 – May 2007

- Modeled ecosystems using the language of MATLAB toward understanding ecosystem stability.

EDUCATION

Virginia Commonwealth University, Richmond, VA

- Ph.D. in Chemistry 2013

University of North Carolina at Charlotte, Charlotte, NC

- M.S. in Chemistry 2009

The College of William and Mary, Williamsburg, VA

- B.S. in Chemistry 2007

SKILLS and TECHNIQUES

- Experienced with various chromatographic techniques: gas chromatography (GC), gas chromatography coupled with mass spectrometry (GC/MS), and high-performance liquid chromatography (HPLC).
- Proficient in a variety of spectroscopy techniques: absorbance (UV-Visible), fluorescence (PL), Raman, nuclear magnetic resonance (NMR), and energy electron loss spectroscopy (EELS).
- Surface evaluation of materials by X-Ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR).
- Size and morphology characterization by scanning electron microscopy (SEM), atomic force microscopy (AFM), and transmission electron microscopy (TEM).
- Evaluate crystalline material by X-Ray diffraction using both powder XRD and electron diffraction as coupled with TEM.
- Chemical composition analysis by X-Ray Fluorescence.
- Mathematical modeling techniques using a variety of software: Matlab, Maple, Mathcad, and Mathematica.
- Molecular modeling techniques using Gaussian.
- Analysis of colloidal systems by dynamic light scattering and zeta potential.
- Electrochemical characterization by cyclic voltammetry and impedance measurements.
- Experienced with pilot and manufacturing scale batch reactors, spray dryers, rotary kilns, ribbon blenders

PUBLICATIONS

N. P. Herring; L. S. Panchakarla, M. S. El-Shall. P-Type Nitrogen-Doped Nanostructures with Controlled Shape and Doping Level by Facile Microwave Synthesis, *Langmuir*, 2014, 30: 2230.

A. A. Ameen; A. N. Giordano; J. R. Alston; M. W. Forney; **N. P. Herring,** S. Kobayashi; S. G. Ridlen; S. S. Subaran; T. J. Younts; J. C. Poler. Aggregation Kinetics of Single-Walled Carbon Nanotubes Investigated using Mechanically Wrapped Multinuclear Complexes: Probing the Tube-Tube Repulsive Barrier, *Physical Chemistry Chemical Physics*, 2014, 16: 5855.

N. P. Herring; S. Almahoudi; C. R. Olson; M. S. El-Shall. Enhanced Photocatalytic Activity of ZnO-Graphene Nanocomposites Prepared by Microwave Synthesis, *Journal of Nanoparticle Research*, 2012, 14: 1277.

N. P. Herring; A. B. Panda; K. AbouZeid; C. R. Olson; A. Patel; M. S. El-Shall; Microwave Synthesis of Metal Oxide Nanoparticles. In *Metal Oxide Nanomaterials for Chemical Sensors*; Springer: 2012.

N. P. Herring; K. AbouZeid; M. B. Mohammed; J. Pinsk; M. S. El-Shall. Formation Mechanisms of Gold-Zinc Oxide Nanopyramids by Heterogeneous Nucleation using Microwave Synthesis, *Langmuir*, 2011, 27 (24), pp 15146-15154. (Cover Feature)

J. Alston; H. Chaturvedi; M. Forney; **N. P. Herring**; J. C. Poler. Dispersions and Aggregation of Carbon Nanotubes. In *The Handbook of Nanophysics;* Sattler, K., Eds.; Taylor & Francis Publisher (CRC Press): 2010.

T. Ventham; C. Farley; **N. Herring**. FCC SOx Additives and Security of Supply, *Petroleum Technology Quarterly, 2021*, Q2, pp

SYNERGISTIC ACTIVITIES

- Organized 10 International Workshops on Advanced Materials in Ras Al-Khaimah, U.A.E.
- Organized NSF sponsored US-Egypt Advanced Studies Institute, March 2010
- Designed and implemented 3 original experiments for undergraduate course Physical Chemistry Laboratory II at Virginia Commonwealth University
- Established a chemistry graduate student organization at VCU that remains active
- Built and maintained website for SERMACS 2011 (Regional ACS Meeting)
- Supervised research of 6 undergraduate students and 2 master's students

WORKSHOPS and COURSES

- 10 International Workshops on Advanced Materials in Ras Al-Khaimah, U.A.E.
- JM Global Management Development Program, April 2016
- International Fine Particles Research Institute, June 2014
- JM Manufacturing Excellence Program: Lean Training, Feb. 2014
- JM Manufacturing Excellence Program: Mixing Operations Course, Oct. 2013
- Swagelok Certified Installation Training Seminar, Oct. 2013
- JM sponsored spray drying course including "Dryer Technology" and "Atomization and Spray Technology" Focus on Spray Drying", July 2013
- US-Egypt Advanced Studies Institute on "Nanomaterials and Nanocatalysis for Energy, Petrochemicals and Environmental Applications", March 27 – April 5, 2010, Cairo, Egypt
- International Symposium on Clusters and Nano-Structures, Nov. 7-10, 2011, Richmond, VA.

AWARDS

- VCU Chemistry Department Altria Fellow, 2012-2013
- Gerald and Susan Bass Scholarship, VCU Department of Chemistry, 2012
- Lidia M. Vallarino Scholarship recipient, VCU Department of Chemistry, 2011
- Conference of Southern Graduate Schools Mathematics, Physical Sciences and Engineering Master's Thesis Award, 2011.
- UNCC 2011 Graduate Dean's Outstanding Master's Thesis Award
- Altria Summer Fellowship, Summer 2010
- Thomas Walsh Tuition Fellowship, August 2007-May 2009.
- Carolina Chemical Club McKernan Scholarship for Excellence in Research, February 2009.
- 1st Place Poster Category, 8th Annual Graduate Research Fair, University of North Carolina Charlotte, March, 2008.

Atty. Docket No.: 071816-091960USC1 PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Application of:	Guido William ARU	Examiner:	Haytham SOLIMAN
Serial No.:	17/176,222		
Filed:	February 16, 2021	Group Art Unit:	1736
Entitled:	A CO TO CO_2 COMBUSTION PROMOTER		
		Conf. No.:	3640

MAIL STOP AMENDMENT
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

RESPONSE

Dear Sir:

This Amendment is being filed in response to the Non-Final Office Action dated April 7, 2021. The response is timely and no fees are believed to be due. Please consider the following amendments and remarks in connection with the above-identified application:

Amendments to the Claims are reflected in the listing of claims, which begins on **page 2** of this response.

Remarks begin on **page 6** of this paper.

chemengineering

MDPI

Article

Intraparticle Modeling of Non-Uniform Active Phase Distribution Catalyst

Vincenzo Russo [1,2,*], Luca Mastroianni [1], Riccardo Tesser [1], Tapio Salmi [2] and Martino Di Serio [1]

[1] Chemical Sciences Department, University of Naples Federico II, IT-80126 Napoli, Italy; luca.mastro7774@gmail.com (L.M.); riccardo.tesser@unina.it (R.T.); diserio@unina.it (M.D.S.)

[2] Laboratory of Industrial Chemistry and Reaction Engineering, Åbo Akademi, FI-20500 Turku/Åbo, Finland; tapio.salmi@abo.fi

* Correspondence: v.russo@unina.it; Tel.: +39-081-674-036

Received: 16 January 2020; Accepted: 8 April 2020; Published: 9 April 2020



Abstract: To maximize the performances of heterogeneous catalytic reactors, it is necessary to consider many parameters. Catalytic particle morphology (dimension, shape, active phase distribution) is generally previously established and seldom considered in the optimization of the catalyst to be specific for a given process. In this work, the influence of active phase distribution within spherical catalytic particles (egg-shell, egg-yolk and egg-white), on the yield and selectivity of a product is shown for a consecutive reaction network; here, the intermediate component is the main product of interest. Intraparticle mass and energy balances under non-steady conditions were implemented. Sensitivity studies lead to the identification of the optimal conditions, thus maximizing the yield of the intermediate for each active phase distribution. It was demonstrated that the egg-shell catalyst can maximize the intermediate yield, with a lower active-phase usage.

Keywords: heterogeneous catalysis; non-uniform catalyst; intraparticle diffusion model; catalyst performance enhancement; in-series reaction modelling

1. Introduction

The chemical industry has developed a growing interest in the enhancement of heterogeneously catalyzed processes. A heterogeneous catalysis offers several advantages compared to technologies in which the reagents and catalytic species co-exist in the same phase; easy catalyst separation and regeneration flexibility are two typical examples.

It is necessary to consider many variables to maximize the performance of a heterogeneous catalytic reactor in terms of yield and selectivity. As is generally known, the catalyst modifies the reaction pathway, leading to a desired increase in the overall reaction rates, improving the selectivity toward the desired product in complex reaction network systems.

The catalytically active component is often dispersed on a thermostable support stabilizing itself and increasing the specific contact area. Conventional heterogeneous catalyst particles have a uniform distribution of the active species, e.g., metals. Nevertheless, a uniform active phase distribution could be undesirable if the catalyst cost is high [1] or the system is limited by internal mass transfer [2]. Thus, designing the active phase distribution correctly is an attractive opportunity and a great challenge.

Four main active phase profiles are reported in the literature. Figure 1 depicts the specific cases for a spherical particle:

(1) **Uniform**: the active phase is homogeneously distributed in the support;
(2) **Egg-shell**: the active phase is located in the outer surface of the support;

(3) **Egg-white**: the active phase is included in a region between the outer-shell and the inner-core;
(4) **Egg-yolk**: the active phase is present in the inner-core of the support.

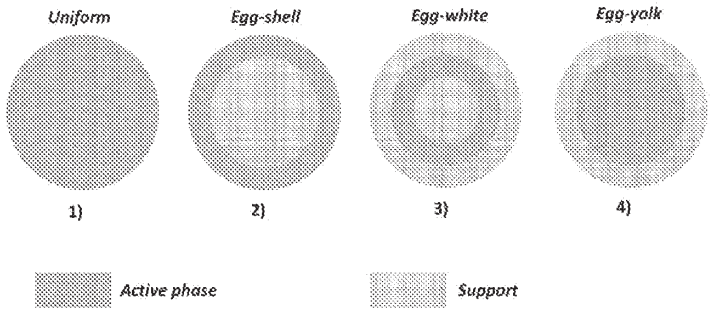


Figure 1. Active phase distributions for a spherical catalyst particle.

Different catalyst preparation methods are well-known, and the specific choice influences the properties of the final catalyst [3]. The most common techniques are listed here: (i) support and active phases are simultaneously precipitated from a supersaturated solution in coprecipitation; (ii) gaseous components are fixed on the support in adsorption; (iii) the catalytically active metal is precipitated from the solution to the support powder, suspended in it, with the addition of a strong base (e.g., NaOH) in the deposition–precipitation technique. Non-traditional preparation methods are based on microemulsions, atomic-layer epitaxy, plasma and electro-spinning [4]. The solid support is in contact with a precursor solution in impregnation techniques: it is either dipped in the metal salt solution for a certain time (wet impregnation) or sprinkled by sprayers (dry impregnation or incipient wetness impregnation IWI).

As is pointed out above, during catalyst preparation, the active phase distribution is strongly influenced by intraparticle mass transfer limitations. Egg-shell catalysts are well obtained by modulating the immersion time of the support in the precursor solution [5], as lower impregnation times prevent the migration of the active phase toward the inner core of the support. Nevertheless, some research groups preserve the advantages of the IWI approach [5,6], leading to easy control of the active phase loading. Viscosity, active phase solubility in the precursor solution, concentration, impregnation time and temperature are the operating parameters that optimize the final active phase distribution.

The prediction of the right active phase profile within the support material is still a great challenge to be faced by both industrial and academic researchers [7], as it is known that this aspect strongly influences the catalytic performance and, ultimately, the chemical reactor design. Uniform distribution is surely the best choice when studying a simple irreversible reaction under isothermal conditions. The choice of the best possible distribution becomes crucial either when multiple reactions, for example series and parallel reactions, comprise the overall network or if mass and heat transfer limitations are remarkable, which is a very common feature in the field of heterogeneously catalyzed reactions. For the latter cases, it is necessary to distribute the active phase only where the reaction really occurs, meaning the outer shell of the solid material. Thus, egg-shell catalysts are often the best choice; the exceptions are well represented by processes in which the catalyst could be shell-poisoned.

Several case studies are reported in the literature which reflect the importance of non-uniform active phase profiles. Some industrially interesting cases are listed below.

Ethylene oxide (EO) is synthesized using an Ag-based catalyst, for which the cost is rather high, thus it is dispersed on a support to maximize the specific contact area. EO worldwide production capacity exceeds 34 million of tons/year [8], hence optimizing the process has a huge economic impact [9]. Gravidilis and Varma [10] compared a catalyst with different active-layer positions,

concluding that both yield and selectivity toward EO can be optimized by locating Ag on the support surface. Non-uniform distribution avoids thermal runaways in the reactor [11]. Catalytic configuration studies have been used in the optimization of temperature reactor profiles [9] and in modern microreactor technologies [12].

Intraparticle diffusion is relevant in Fisher–Tropsch synthesis, which converts syngas into liquid hydrocarbon. The optimal position of the active phase layer in the particle is related to the desired product yield maximization [13]. Several approaches can be used to minimize transport limitations: egg-shell catalyst with a specific thickness of the active layer [14,15], wash-coated monoliths [16], solid foams, and micro- and millireactors. Mazdidi et al. have demonstrated that, by using a tubular fixed bed reactor, it is convenient to use different catalyst distributions along the bed length, as the diffusion limitations strongly depend on the reactant conversion [17].

In the catalytic aromatization of methyl cyclopentane an increase in the conversion was observed when the metallic sites are distributed on the external surface of the particle [18]; egg-shell catalysts are also widely used in the hydrogenation of pyrolysis gasoline [19], ammonia decomposition [8], and the purification of automobile exhaust gases [20,21]. Recently, core-shell and core-double-shell catalysts have been compared in terms of amide production in reactors heated under radiofrequencies (RF), demonstrating that the reaction rates are increased by using an intermediate non-magnetic support layer [22].

It is evident that the active phase distribution optimization for a given reaction is a key aspect to be faced both experimentally and theoretically. The development of a reliable mathematical model would allow the a priori design of the best catalyst to optimize the reactor performances. Many studies have reported on the implementation of specific mathematical models [23]. Despite the academic and industrial interest, the models reported on in the literature are based on a simplified approach. Boukezoula and Bencheikh [17] developed a steady-state modelling approach for the aromatization of methyl cyclopentane. Thus, all the dynamic aspects are neglected; that is an essential issue to be considered within the start-up operation of a chemical plant. Hwang et al. [9] published an interesting modelling approach dealing with ethylene oxide synthesis, writing mass, and energy balance equations for both the bulk and particle phase. Therefore, even in the most advanced till to date, the authors included fluid–solid mass and heat transfer resistance only in the bulk phase equations, and not in the particle boundary condition, leading to a certain approximation of the results.

Thus, there is a real need to develop more robust mathematical models which could be used to optimize the catalyst performance. Besides, an intraparticle sensitivity study, allowing the catalytic performance optimization, is needed. In this work, the influence of active phase distribution on both yield and selectivity is shown for a consecutive reaction network (A→B→C), selected as a reference study, where B is the main product of interest. Mass and energy balances have been developed in dynamic conditions for a single spherical particle and sensitivity studies identify the optimal conditions to maximize the yield of B. The reference particle is egg-shell type; comparisons with other active phase distributions have been carried out.

2. Mathematical Model

The main assumption of the present model is to consider a single catalyst particle in contact with a gaseous bulk phase characterized by a volume high enough to neglect any variations in its composition and temperature. Therefore, fluid–solid mass and heat transfer resistance were included in the model, specifically in the boundary conditions, to establish the opportune mass and energy fluxes between the single catalyst particle and the bulk phase.

2.1. Intraparticle Mass and Energy Balances

Under dynamic conditions, the mass balance of an arbitrary component in a single spherical particle can be written as Equation (1) [24],

$$\varepsilon \frac{\partial C_i}{\partial t} = r_p^{-2} \frac{\partial}{\partial r_p}\left(D_{eff,i} r_p^2 \frac{\partial C_i}{\partial r_p}\right) + \sum_{j=1}^{N_R} \nu_{ij} r_j \rho_p \quad (1)$$

To simulate non-uniform active-phase profiles, distribution functions need to be defined. In this work, analytical functions (Ω_k) have been chosen, whose co-domains vary from 0 to 1. Defining a smoothing factor (b) (needed to modify the function steepness), a_s and a_{st} are the coordinates of the distribution domains, Equations (2)–(4),

Egg-shell

$$0.5 + 0.5\tanh\left(\frac{x - a_1}{b}\right) \quad (2)$$

Egg-yolk

$$0.5 - 0.5\tanh\left(\frac{x - a_2}{b}\right) \quad (3)$$

Egg-white

$$0.5\tanh\left(\frac{x - a_{32}}{b}\right) - 0.5\tanh\left(\frac{x - a_{31}}{b}\right) \quad (4)$$

Two coordinates for the egg-white catalyst are needed; hence, the active phase thickness can be defined as in Equation (5).

$$\delta = a_{31} - a_{32} \quad (5)$$

It should be noted that egg-white distribution could be centered differently within the support particle. Thus, a_{31} and a_{32} can be correctly calculated as in Equations (6) and (7).

$$a_{31} = \chi + \frac{\delta}{2} \quad (6)$$

$$a_{32} = \chi - \frac{\delta}{2} \quad (7)$$

where χ is the midpoint coordinate.

Regarding the egg-shell distribution, the active-phase thickness layer (δ) is defined as $1 - a_1$, while it is equal to a_2 for the egg-yolk catalyst.

The distribution functions are illustrated in Figure 2, setting an active phase layer thickness of 0.4 for all the mentioned cases, with $a_1 = 0.6$, $a_2 = 0.4$, $a_{31} = 0.7$, $a_{32} = 0.3$, centering the catalytic layer for the egg-white case in the middle of the particle.

The distribution functions were introduced in Equation (1), in the reaction rate term, that becomes Equation (8) after introducing a dimensionless particle radius $x = r_p/R_p$.

$$\varepsilon \frac{\partial C_i}{\partial t} = x^{-2} \frac{\partial}{\partial x}\left(\frac{D_{eff,i}}{R_p^2} x^2 \frac{\partial C_i}{\partial x}\right) + \sum_{j=1}^{N_R} \Omega_k \nu_{ij} r_j \rho_p \quad (8)$$

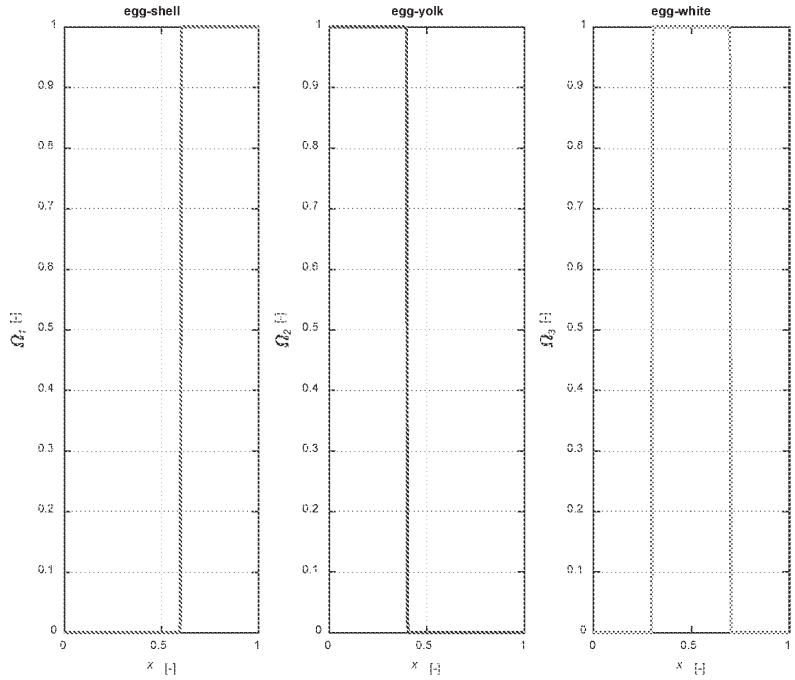


Figure 2. The distribution functions (2)–(4).

The generation term is multiplied by Ω_k x; thus, it is possible to discriminate the inert zone (Ω_k $x = 0$, (no reaction) and a catalytically active zone (Ω_k $x \neq 0$, where both reaction and diffusion take place. The boundary conditions (BCs) needed to solve the partial differential equation are listed in Equation (9),

$$\begin{cases} \left.\frac{\partial C_i}{\partial x}\right|_{x=0} = 0 \\ \left.\frac{D_{eff,i}}{R_p}\frac{\partial C_i}{\partial x}\right|_{x=1} = k_m(C_{i0} - C_i|_{x=1}) \end{cases} \quad (9)$$

In detail, symmetry was considered in the centre of the particle ($x = 0$); the boundary condition at the particle surface includes the possibility of external mass transfer limitation, as the flux in the film must be equal to the intraparticle diffusion rate at $x = 1$ (no accumulation is considered). This aspect is seldom considered in the published models in this field.

For highly exothermic or endothermic reactions, temperature gradients can become important. Hence, it is necessary to implement both mass and energy balances to investigate the intraparticle temperature profiles and their influence on the concentration profiles inside the catalyst particle.

Energy balance is written as follows [24],

$$\left(c_{p,p}\rho_p(1-\varepsilon) + \sum_{i=1}^{N_c} c_{p,i}C_i\varepsilon\right)\frac{\partial T}{\partial t} = x^{-2}\frac{\partial}{\partial x}\left(\frac{k_{T,p}}{R_p^2}\frac{\partial T}{\partial x}x^2\right) - \sum_{j=1}^{N_R}\Omega_k\Delta_r H_j\rho_p r_j \quad (10)$$

It should be noted that the temperature dependences of density, specific heat and diffusivity are assumed to be negligible to simplify the calculations, particularly because in the present study no specific chemical system was considered, as the model is based on generic terms.

The boundary conditions needed to solve the energy balance are reported in Equation (11).

$$\begin{cases} \frac{\partial T}{\partial x}\Big|_{x=0} = 0 \\ \frac{k_{T,p}}{R_p}\frac{\partial T}{\partial x}\Big|_{x=1} = h(T_o - T|_{x=1}) \end{cases} \quad (11)$$

The external thermic resistance is not neglected at this stage. The Chilton–Colburn analogy was implemented as it provides an easy relationship between the heat and mass transport coefficients in the fluid bulk, Equation (12).

$$h = \frac{k_m}{D_e}\left(\frac{\rho D_{eff} c_{p,f}}{k_{T,f}}\right)^{1/3} k_{T,f} \quad (12)$$

2.2. Reaction Network

The reference reaction network being studied is

$$A \xrightarrow{r_1} B \xrightarrow{r_2} C$$

Both reactions are assumed to be described by first order kinetics, and the temperature dependences of the kinetic constants are described with the modified Arrhenius law,

$$r_1 = k_1 C_A = k_{ref1} e^{-\frac{E_{a1}}{R}\left(\frac{1}{T}-\frac{1}{T_{ref}}\right)} C_A \quad (13)$$

$$r_2 = k_2 C_B = k_{ref2} e^{-\frac{E_{a2}}{R}\left(\frac{1}{T}-\frac{1}{T_{ref}}\right)} C_B \quad (14)$$

The stoichiometric matrix for the system is given by Equation (15),

$$\nu_{ij} = \begin{bmatrix} -1 & 0 \\ 1 & -1 \\ 0 & 1 \end{bmatrix} \quad (15)$$

The Thiele modulus for a first-order reaction rate can be roughly estimated by Equation (16),

$$\varphi_j = R_p \sqrt{\frac{\rho_p k_j}{D_{eff}}} \quad (16)$$

It is possible to calculate two Thiele moduli for the proposed reaction network; nevertheless, only φ_1 was considered, as A→B is the desired reaction. This calculation does not account for the specific distribution.

The catalytic efficiency is determined by Equation (17),

$$\eta = \frac{3}{\varphi^2}(\varphi \coth(\varphi) - 1) \quad (17)$$

The model was implemented in Matlab R2018b, solving the partial differential equations system using the built-in *pdepe* function, fixing 50 grid points for the dimensionless particle radius coordinate.

3. Results and Discussion

3.1. Model Validation

The mass and energy balances were implemented, fixing a set of parameters that are valid for a generic gas–solid system. The reference parameters for all the simulations conducted in the present work are listed in Tables 1–3, inspired by the properties of the main components involved in ethylene

oxide synthesis reaction promoted by silver catalyst [9,12]. The listed parameters can be considered valid for all the active phase distributions. Within the parametric investigations, a chosen parameter is varied in a range that is cited in the related text.

Table 1. Main parameters for the fluid and solid phases.

PARAMETER	VALUE
R_p [m]	1×10^{-2}
a_1 [-]	6×10^{-1}
a_2 [-]	4×10^{-1}
a_{31} [-]	7×10^{-1}
a_{32} [-]	3×10^{-1}
b [-]	1×10^{-5}
T_0 [K]	2.98×10^{2}
ρ_p [kg m^{-3}]	4×10^{3}
k_m [m s^{-1}]	1×10^{2}
ε [-]	5×10^{-1}
$k_{T,p}$ [W m^{-1} K^{-1}]	1×10^{-1}
$k_{T,f}$ [W m^{-1} K^{-1}]	0.25
h [W m^{-2} K^{-1}]	8×10^{2}
$c_{p,p}$ [J kg^{-1} K^{-1}]	6×10^{2}

Table 2. Fluid component parameters.

	A	B	C
MW_i [kg kmol^{-1}]	30	30	30
$D_{eff,i}$ [m^2 s^{-1}]	1×10^{-7}	1×10^{-7}	1×10^{-7}
C_{i0} [mol m^{-3}]	1	0	0
$c_{p,i}$ [J mol^{-1} K^{-1}]	30	30	30

Table 3. Kinetic and thermodynamic data. T_{ref} = 298 K.

Reaction	1	2
$\Delta_r H_j$ [J mol^{-1}]	-5×10^{4}	-5×10^{4}
$E_{a,j}$ [J mol^{-1}]	8×10^{4}	8×10^{4}
$k_{ref,j}$ [m^3 kg^{-1} s^{-1}]	1×10^{-5}	5×10^{-7}

The reaction occurs within an egg-shell catalyst (distribution function, as in Equation (2)); the active phase is located on the outer shell of the solid particle, accounting for the 40% of the total radius (1 cm). The external mass transfer coefficient is sufficiently high to neglect the film diffusion resistance. In order to investigate the possibility of temperature gradients in the particle, h is not calculated with Equation (12): if external mass transfer is too high, an isothermal condition could be obtained.

The calculated intraparticle concentration and temperature profiles are displayed in Figure 3.

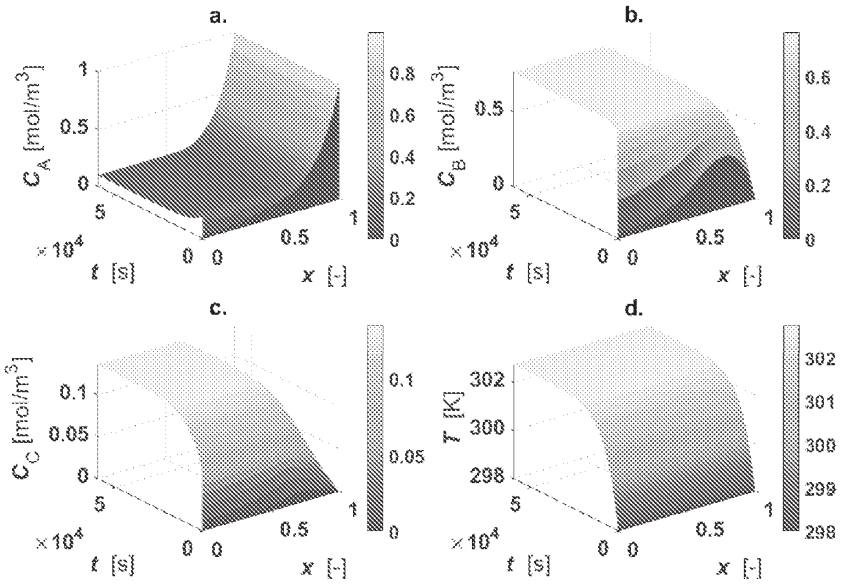


Figure 3. Intraparticle profiles for egg-shell catalyst. Calculated profiles for: (**a**) C_A; (**b**) C_B; (**c**) C_C; (**d**) T. Color-bar of each plot is located on the right-hand-side.

As revealed by the figure, the reactant A is consumed only in the active region, where $a_1 \leq x \leq 1$ (Figure 3a); C_B shows a maximum inside the particle, since the intermediate B is formed in reaction 1 and consumed in reaction 2 (Figure 3b). For $0 \leq x < a_1$, each profile is described by the diffusive mechanism only, as no active phase is present in the inner part of the particle. The final product C is formed in the outer shell of the catalyst particle by the progress of the second reaction, then it diffuses in the inner core of the particle (Figure 3c). A temperature rise (4 K) under steady-state conditions was calculated (Figure 3d).

Thiele modulus and the catalytic efficiency were calculated under steady-state conditions by means of Equations (16) and (17), obtaining $\varphi = 8.15$ and $\eta = 0.32$. Under the selected conditions, the system is highly limited by intraparticle mass transfer.

3.2. Egg-Shell: Sensitivity Study

The influence of the active phase thickness layer was investigated. The physical and chemical parameters adopted in the sensitivity study are listed in Tables 1–3. The egg-shell distribution domain coordinate, a_1, is varied from 0 to 1, simulating the cases ranging from a uniform distribution to an inert particle. Figure 4 shows the steady state intraparticle profiles of component A conversion, yield and selectivity to B for $a_1 = [0, 0.2, 0.4, 0.6, 0.8, 1]$.

The conversion degree is in inverse relationship with a_1: an increase in the amount of the active phase leads to a corresponding increase in the conversion of component A (Figure 4a). The selectivity to B is equal to 1 for an inert particle, since, considering an infinitesimal active-phase thickness, A reacts to give the only the intermediate, thus a fictitious unitary selectivity is computed. It is interesting to observe that the yield to B is zero for an inert particle and a finite value, not the maximum one, for a uniform distribution (Figure 4b). Temperature profiles at steady state show a maximum temperature gradient of roughly 5 K for the uniformly distributed active phase catalyst (Figure 4c). This value decreases when a lower amount of the active phase is present in the catalyst particle. Maximizing the yield to B is surely possible with the developed model, as the simulation results suggest the possibility

of optimizing the steady state yield of the desired product by varying the active-phase thickness. The plot y_B vs. a_1 is depicted in Figure 5.

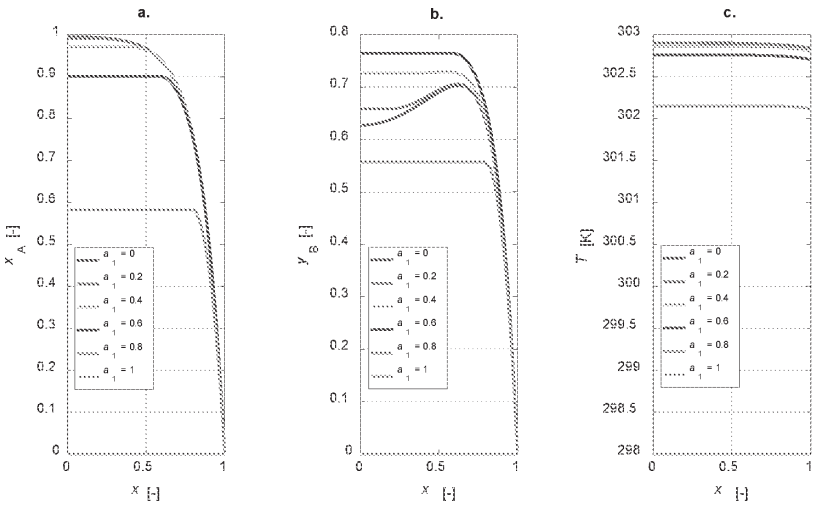


Figure 4. Intraparticle profiles calculated for the egg-shell catalyst varying the active phase content: (**a**) A conversion; (**b**) yield to B; (**c**) temperature.

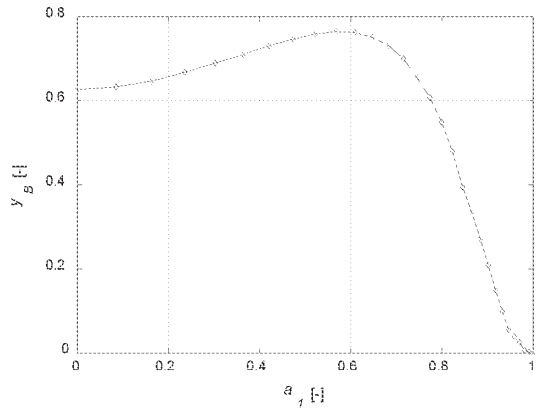


Figure 5. Yield to B (y_B) vs. active phase inert fraction coordinate (a_1) for the egg-shell catalyst.

It emerges that the yield of the intermediate component can be optimized designing correctly the catalyst active phase distribution. It should be noted that, in the case of maximum yield to B, the reactant conversion is not the maximum possible, as a uniform distribution would surely lead to a higher conversion.

A sensitivity study on the influence of the kinetic constants on the steady state intraparticle profiles was conducted. The ratio $\sigma = k_{ref2}/k_{ref1}$ is defined for each simulation; intraparticle profiles under steady-state conditions for $\sigma = [0.01, 0.05, 0.1]$ are displayed in Figure 6.

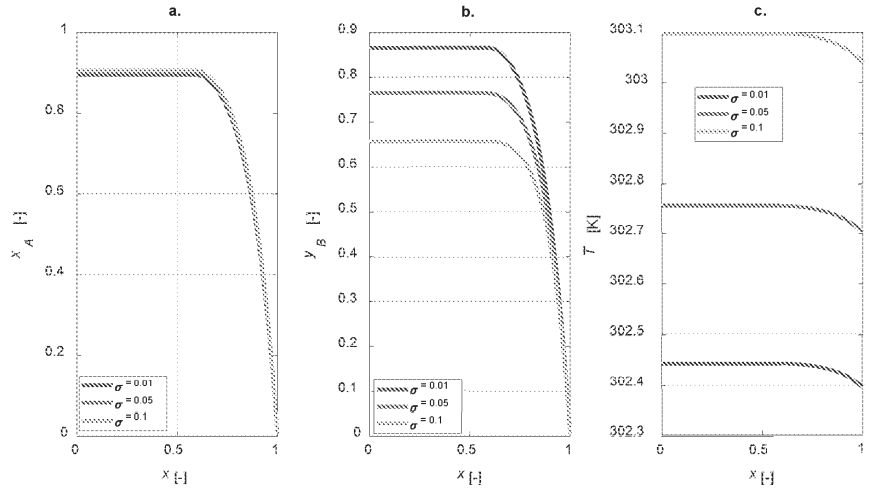


Figure 6. Intraparticle profiles computed varying the ratio between the kinetic constants at the reference temperature of reactions 2 and 1 for the egg-shell catalyst: (**a**) A conversion; (**b**) yield to B; (**c**) temperature.

As expected, the yield of component B is improved for lower σ, i.e., lower k_{ref2} (Figure 6b); besides, σ does not affect the conversion degree, as k_{ref1} is constant (Figure 6a). Moreover, by increasing σ, a corresponding increase in the temperature inside the particle is predicted (Figure 6c).

The overall thermal conductivity of the particle is included in the energy balance (Equation (10)). This parameter affects the intraparticle steady state temperature profiles and, therefore, the concentrations of the gaseous components inside the particle. In Figure 7, a sensitivity study on $k_{T,p}$ is shown, with $k_{T,p} = [0.01, 0.05, 0.1]$ W m^{-1} K^{-1}.

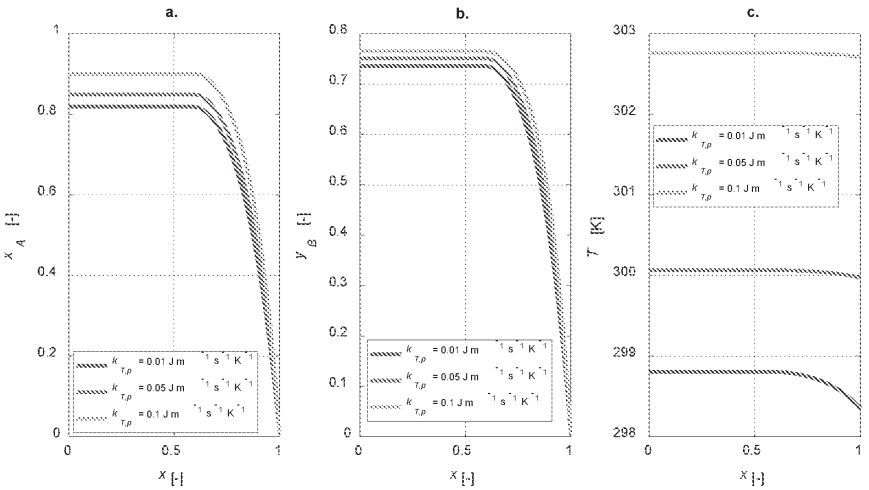


Figure 7. Intraparticle profiles: $k_{T,p}$ sensitivity study. (**a**) A conversion; (**b**) yield to B; (**c**) temperature.

For high values of the thermal conductivity, flat temperature profiles are observed (Figure 7c); both the conversion and yield increase were simulated (Figure 7a,b). Therefore, it must be pointed

out that the overall selectivity becomes lower. Besides, higher heat conductivity leads to higher temperatures within the particle: this is the main reason for the improved conversion degrees.

The influence of external mass transfer coefficient on the concentration profiles is shown in Figure 8, adopting the thermal conductivity of air for the fluid phase (Table 1). The simulation was executed by diminishing the fluid–solid mass transfer coefficient, k_m, by a factor of 100 (k_m = 1 m s^{-1}), and the heat transfer coefficient h was calculated from Equation (12).

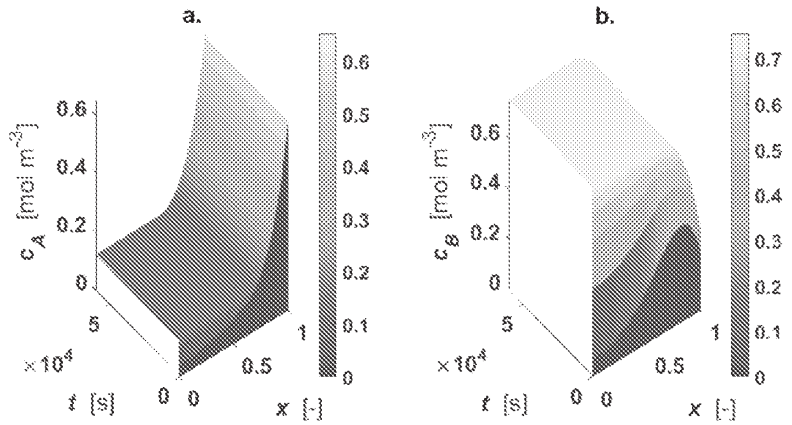


Figure 8. Intraparticle concentration and temperature profiles; k_m = 1 m s^{-1}; h = 4218 W m^{-1} K^{-1}. (**a**) concentration of A; (**b**) concentration of B. Color-bar of each plot is located on the right-hand-side.

The surface plots show the appearance of external mass transfer limitation because at x = 1, $C_i \neq C_{i0}$. This fact strongly influences the concentration gradients, as demonstrated.

The influence of effective diffusivity values was studied through a dedicated parametric investigation, varying $D_{eff,i}$ = [1 × 10^{-7}, 1 × 10^{-8}, 1 × 10^{-9}] m^2 s^{-1}. The steady state results are reported in Figure 9.

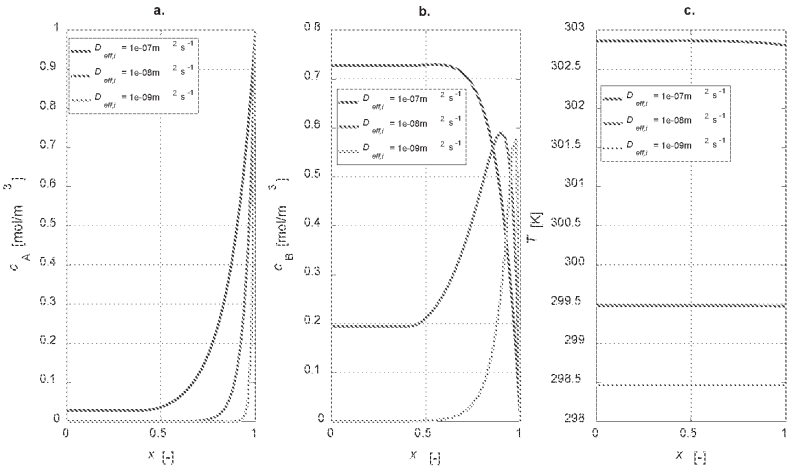


Figure 9. Intraparticle profiles: $D_{eff,i}$ sensitivity study. (**a**) A concentration; (**b**) B concentration; (**c**) temperature.

It is evident that, by increasing the effective diffusivity value, reactant A is transported from the catalyst interface to the inner part with a higher velocity (Figure 9a). In these conditions, conversion is not complete. Moreover, a higher diffusivity value leads to an increase in the concentration of the intermediate B, leading to a higher yield. This result is reasonable as, by lowering the diffusivity, a lower amount of B is produced, which is converted to C (Figure 9b). Temperature profiles are rather flat in any case, but the higher the diffusivity, the higher the temperature level, which is connected to the major activity of the system in the case of high diffusion coefficients.

3.3. Egg-Yolk, Egg-White and Comparisons

The model can be simply extended to other active-phase distributions by using a suitable distribution function (respectively, egg-yolk and egg-white are simulated with Equations (3) and (4)).

To implement egg-white balances, $\chi = 0.5$ was adopted. In analogy with egg-shell distribution, the sensitivity studies on egg-yolk and egg-white catalyst were carried out by varying the amount of active phase and calculating the steady state yield to B. The results are shown in Figure 10.

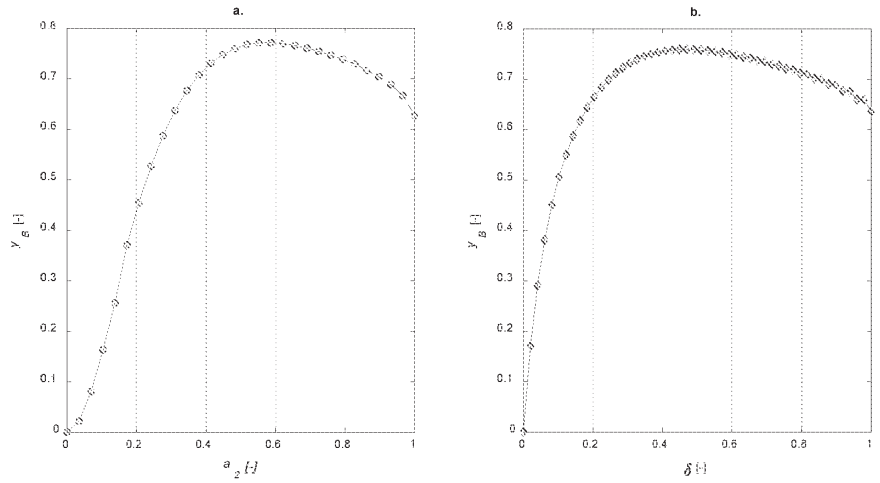


Figure 10. Yield to B vs. active phase thickness for (**a**) egg-yolk catalyst (**b**) egg-white catalyst.

As expected, both egg-yolk and egg-white catalysts enhance the yield of the intermediate product compared to the uniform distribution of the active phase. It is interesting to compare different active-phase distributions in order to establish which one is the best for the current case study. With regard to the egg-shell structure, the active-phase thickness layer is defined as $1-a_1$; it is equal to a_2 for the egg-yolk catalyst. No comparisons with the egg-white distribution are possible because δ, in this case, requires two coordinates to be determined.

The curves of steady state y_B vs. δ for different distributions are depicted in Figure 11. It must be noted that, when $\delta = 1$, the active phase is uniformly distributed within the catalyst. Thus, Figures 10 and 11 show identical values of y_B when $\delta = 1$.

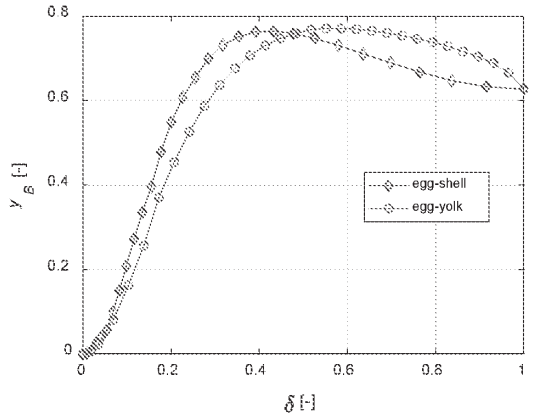


Figure 11. Egg-shell vs. egg-yolk: comparisons.

It is finally demonstrated that, for the current case study, egg-shell catalysts maximize the yield of B with a lower active phase usage. The present model can be applied to real reaction networks to investigate the optimal catalyst design; if the active phase cost is high, this a priori analysis can also have a high economic impact on the process.

4. Conclusions

In this work, the influence of the active phase distribution toward the yield of a desired product was investigated. The consecutive reaction scheme A→B→C was adopted as a reference study, where B is the desired product. Assuming a spherical support particle, mass and energy balances were widely implemented for the egg-shell catalyst investigating by simulations the best conditions to maximize the yield to the component B. The egg-yolk and egg-white distributions were simulated using the respective distribution functions: the maximum yield to B was found for each profile. General comparisons concluded that, for the reference case-study, egg-shell catalysts maximize the yield of B with a lower active-phase usage.

The implemented model can be easily adapted for a preliminary study in real systems to correctly design the active phase distribution within the supported catalyst.

Future works will include the development of bulk phase mass and energy balance to extend the treatise from a single particle to a real reactor, possibly working under flow condition, extending the treatise by including other possible reaction mechanisms.

Author Contributions: Conceptualization, V.R., R.T., T.S. and M.D.S.; Project administration, V.R.; Software, V.R. and L.M.; Supervision, V.R.; Writing—original draft, V.R. and L.M.; Writing—review and editing, R.T., T.S. and M.D.S. All authors have read and agreed to the published version of the manuscript.

Acknowledgments: MDPI chemengineering is acknowledged for the 2019 Travel Award given to Vincenzo Russo.

Conflicts of Interest: The authors declare no conflict of interest.

Notation

A	reactant
a_1	inflection point for egg-shell profile, [-]
a_2	inflection point for egg-yolk profile, [-]
a_{31}	inflection point 1 for egg-white profile, [-]
a_{32}	inflection point 2 for egg-white profile, [-]
B	intermediate
b	smoothing factor, [-]
C	product
C_{i0}	concentration of species i in bulk phase at time = 0, [mol m^{-3}]
C_i	concentration of species i, [mol m^{-3}]
$c_{p,i}$	specific heat of the fluid component, [J mol^{-1} K^{-1}]
$c_{p,p}$	specific heat of the particle, [J mol^{-1} K^{-1}]
$D_{eff,i}$	effective diffusivity, [m^2 s^{-1}]
$E_{a,j}$	activation energy, [J mol^{-1}]
h	heat exchange coefficient, [W m^{-2} K^{-1}]
k_j	kinetic constant, [m^3 kg^{-1} s^{-1}]
k_m	mass transfer coefficient, [m s^{-1}]
$k_{ref,j}$	reference kinetic constant, [m^3 kg^{-1} s^{-1}]
$k_{T,f}$	fluid thermal conductivity, [W m^{-1} K^{-1}]
$k_{T,p}$	particle thermal conductivity, [W m^{-1} K^{-1}]
MW_i	molecular weight, [-]
N_c	number of components, [-]
r_j	reaction rate j, [mol kg^{-1} s^{-1}]
R_p	particle radius, [m]
r_p	radial coordinate, [m]
T	temperature, [K]
t	time, [s]
T_0	surface temperature at time = 0, [K]
x	dimensionless radial coordinate, [-]
x_A	conversion degree, [-]
y_B	yield in B, [-]
Subscripts	
f	fluid
i	component
j	reaction
k	distribution type
p	particle
s	coordinate domain
t	coordinate domain
Greek letters	
$\Delta_r H_j$	reaction enthalpy j, [J mol^{-1}]
δ	active-phase thickness, [-]
ε	void degree, [-]
ϕ_B	selectivity to B, [-]
φ	Thiele modulus, [-]
η	efficiency factor, [-]
ν_{ij}	stoichiometric matrix, [-]
ρ_p	particle density, [kg m^{-3}]
σ	kinetic constant ratio, [-]
Ω_k	distribution function, [-]

References

1. Chaudhuri, R.G.; Paria, S. Core/Shell Nanoparticles: Classes, Properties, Synthesis Mechanisms, Characterization, and Applications. *Chem. Rev.* **2012**, *112*, 2373–2433. [CrossRef]
2. Morbidelli, M.; Varma, A. On shape normalization for non-uniformly active catalyst pellets. *Chem. Eng. Sci.* **1983**, *38*, 297–305. [CrossRef]
3. Perego, C.; Villa, P. Catalyst preparation methods. *Catal. Today* **1997**, *34*, 281–305. [CrossRef]
4. Deraz, N.M. The importance of catalyst preparation. *J. Ind. Environ. Chem.* **2018**, *2*, 16–18.
5. Silva, H.; Nielsen, M.G.; Fiordaliso, E.M.; Damsgaard, C.D.; Gundlach, C.; Kasama, T.; Chorkendorff, I.B.; Chakraborty, D. Synthesis and characterization of Fe-Ni/γ-Al_2O_3 egg-shell catalyst for H_2 generation by ammonia decomposition. *Appl. Catal. A-Gen.* **2016**, *505*, 548–556. [CrossRef]
6. Bueno, A.C.; Mayer, M.; Weber, M.; Bachelany, M.; Klotz, M.; Farruseng, D. Impregnations protocols on Alumina Beads for Controlling the Preparation od Supported Metal Catalysts. *Catalysts* **2019**, *9*, 577. [CrossRef]
7. Komiyama, M. Design and Preparation of Impregnated Catalysts. *Catal. Rev.* **1985**, *27*, 341–372. [CrossRef]
8. ReportsnReports. Available online: https://www.reportsnreports.com (accessed on 1 October 2019).
9. Hwang, S.; Linke, P.; Smith, R. Heterogeneous catalytic reactor design with optimum temperature profile II: Application of non-uniform catalyst. *Chem. Eng. Sci.* **2004**, *59*, 4245–4260. [CrossRef]
10. Gavriilidis, A.; Varma, A. Optimal catalyst activity profiles in pellets: 9. Study of ethylene epoxidation. *AIChE J.* **1992**, *38*, 291–296. [CrossRef]
11. Johnson, D.L.; Verykios, X. Selectivity enhancement in ethylene oxidation employing partially impregnated catalysts. *J. Catal.* **1983**, *79*, 156–163. [CrossRef]
12. Russo, V.; Kilpiö, T.; Hernandez, J.C.; Di Serio, M.; Salmi, T.O. Modelling of microreactors for ethylene epoxidation and total oxidation. *Chem. Eng. Sci.* **2015**, *134*, 563–571. [CrossRef]
13. Zarrin, H.; Sadeghi, M.T.; Marvast, M.A. Modeling of a catalyst pellet with non-uniform activity distribution in Fisher-Tropsch synthesis. *Int. J. Chem. React. Eng.* **2009**, *7*. [CrossRef]
14. Bukur, D.B.; Mandić, M.; Todić, B.; Nikačević, N. Pore diffusion effects on catalyst effectiveness and selectivity of cobalt based Fisher-Tropsch catalyst. *Catal. Today* **2018**, *343*, 146–155. [CrossRef]
15. Gardezi, A.G.; Babu, J. Performance Characteristics of Eggshell Co/SiO_2 Fischer-Tropsch Catalysts: A Modeling Study. *Ind. Eng. Chem. Res.* **2015**, *54*, 8080–8092. [CrossRef]
16. Mandić, M.; Todić, B.; Živanić, L.; Nikačević, N.; Bukur, D.B. Effects of Catalyst Activity, Particle Size and Shape, and Process Conditions on Catalyst Effectiveness and Methane Selectivity for Fischer–Tropsch Reaction: A Modeling Study. *Ind. Eng. Chem.* **2017**, *56*, 2733–2745. [CrossRef]
17. Mazdidi, S.K.; Sadeghi, M.T.; Marvast, M.A. Optimization of Fischer-Tropsch Process in a Fixed-Bed Reactor Using Non-uniform Catalysts. *Chem. Eng. Technol.* **2012**, *36*, 62–72. [CrossRef]
18. Boukezoula, T.F.; Bencheikh, L. Theoretical investigation of non-uniform bifunctional catalyst for the aromatization of methyl cyclopentane. *React. Kinet. Mech. Catal.* **2017**, *124*, 15–25. [CrossRef]
19. Zhou, Z.; Zeng, T.; Cheng, Z.; Yuan, W. Kinetics of selective dehydrogenation of pyrolysis gasoline over an egg-shell catalyst. *Chem. Eng. Sci.* **2010**, *65*, 1832–1839. [CrossRef]
20. Liu, B.; Chai, Y.; Liu, Y.; Wang, Y.; Liu, Y.; Liu, C. A simple method for preparation of presulfided eggshell CoMoS/γ-Al_2O_3 catalysts for hydrodesulfurization of dibenzothiophene. *Fuel* **2012**, *95*, 457–463. [CrossRef]
21. Vakros, J.; Papadopoulou, C.; Lycourghiotis, A.; Kordulis, C. Hydrodesulfurization catalyst bodies with various Co and Mo profiles. *Appl. Catal. A-Gen.* **2011**, *399*, 211–220. [CrossRef]
22. Liu, Y.; Cherkasov, N.; Gao, P.; Fernández, J.; Lees, M.R.; Evgeny, V.R. The enanchement of direct amide synthesis reaction rate over TiO_2@SiO_2@$NiFe_2O_4$ magnetic catalysts in the continuous flouw under readiofrequency heating. *J. Catal.* **2017**, *355*, 120–130. [CrossRef]
23. Morbidelli, M.; Gavriilides, A.; Varma, A. *Optimal Distribution of Catalyst in Pellets, Reactors and Membranes*; Cambridge University Press: Cambridge, UK, 2001.
24. Fogler, H.S. *Elements of Chemical Reaction Engineering*, 5th ed.; Prentice Hall Press: Boston, MA, USA, 2016.



© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).

Contents [hide]

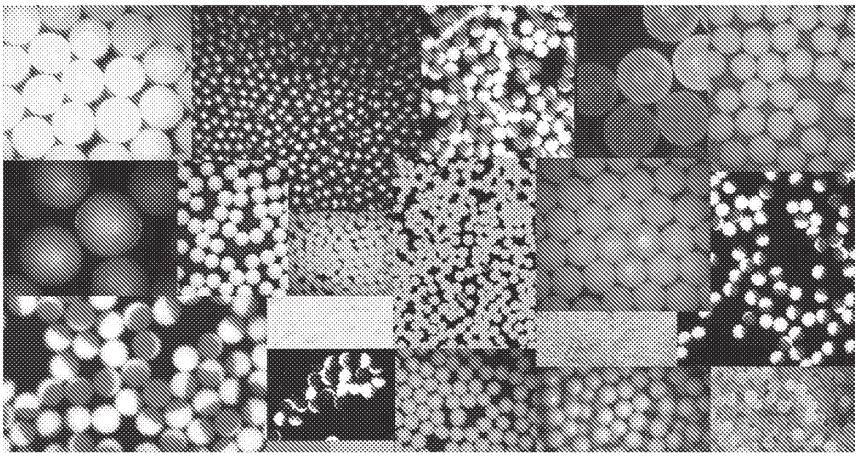
Properties of Microspheres – Composition
Properties of Microspheres – Density/Specific Gravity
Properties of Microspheres – Durability
Crush Strength
Operating Temperature
Chemical Stability/Solvent Resistance
Shelf Life
Safety
Properties of Microspheres – Particle Size and Distribution
Properties of Microspheres – Electrostatic Charge, Conductivity, Magnetism
Properties of Microspheres – Optical Characteristics
Properties of Microspheres – Color
Properties of Microspheres – Fluorescence and Phosphorescence
Properties of Microspheres – Shape and Quality
Properties of Microspheres – Summary
Share this:

Microspheres are engineered materials that are used in a wide variety of industries and applications. Microspheres are not all created equal and functional properties of microspheres need to be carefully considered when choosing the right microsphere for the specific project.

The properties of microspheres that are often considered in product selection are specific gravity (true particle density), particle size (diameter) and particle size distribution, melting point (temperature tolerance), solvent resistance, durability, crush strength (pressure and shear tolerance), color (reflective, fluorescent, or phosphorescent response), optical properties (reflective index or retroreflection), conductivity, bio-compatibility, safety, surface properties (porosity, roughness, hydrophobic vs. hydrophilic surface, ability to coat or functionalize the spheres) among many other properties.

Detailed knowledge of the application, the technical judgment of scientists and engineers working on a project, and sometimes a simple trial-and-error approach, are often used to select the appropriate properties of microspheres for the application.

Properties of Microspheres – Composition



Properties of Microspheres

The most common and widely available microsphere materials are polymer, ceramic, and glass. However, each one of these large categories of materials can be further divided into much narrower categories which vary dramatically in their properties. For example, polymer microspheres may be manufactured out of polyethylene, polystyrene, polypropylene, poly(methyl methacrylate). Each of these polymers varies in their melt temperature, resistance to solvents, and ability for the surface to be

Operated by

Cospheric
Precision Spherical Particles
www.Cospheric.com

Categories

- Applications of Microspheres
- Biomedical Microspheres
- Bond Line Spacers
- Calibration Program
- Charge Measurement Techniques
- Charge Microspheres and Microparticles
- Clinical Studies
- Coatings
- Color Microspheres
- Conductive Microspheres
- Density Markers
- DNA Research
- Drug Delivery
- FDA-approved Microspheres
- Flow Visualization
- Fluorescent Microspheres
- Glass microspheres
- Magnetic Microspheres
- Medical Devices
- Metal Microspheres
- Microparticles
- Microplastics
- Microsphere Basics

Most common ceramic materials used for microspheres are silica and zirconia, which are often used as fillers or grinding media.

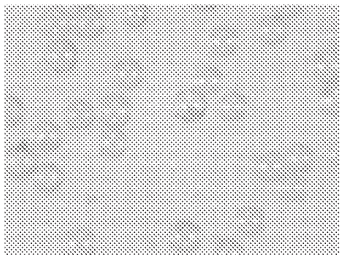
Made of these materials are available in solid and hollow forms, clear or colored, and with a variety of coatings that make them suitable for particular applications. The materials from which microspheres are made vary widely in density, operating temperature, crush strength and solvent resistance. Microspheres possess different physical and optical properties, which may present advantages or limitations for different applications, based on their material composition.

Properties of Microspheres – Density/Specific Gravity

True particle density or specific gravity of the particles is one of the critical properties of microspheres which needs to be precisely controlled in many applications. Specifically this property becomes important in systems where the spheres are a component embedded or dispersed into another media, whether suspended in a fluid or used as a filler.

Particles that are heavier than the media in which they are dispersed will settle and collect at the bottom of a container over time. Particles that are lighter than the media will float up and accumulate on the surface. Matching the specific gravity of microspheres to
that of a matrix solution creates a stable suspension of particles, ensures uniform distribution of microspheres in a product, and prevents settling or surface collection over time.

If microspheres need to be suspended in a particular solution without floating to the top or sinking to the bottom, matching the specific gravity of the particle and the solution is a critical factor. Solid glass and ceramic microspheres have specific gravity greater than 2 g/mL. Polyethylene microspheres are available in specific gravities of 0.96 g/ml to 1.3 g/ml, which is close to that of water. A variety of polyethylene microspheres that have been designed with precision density to be neutrally-buoyant in an aqueous solution are commercially available.



Microballoons and Microbubbles: Hollow Glass Microspheres

The most obvious benefit of hollow microspheres is their potential to reduce part weight, which is a function of density. Compared to traditional mineral-based additives such as calcium carbonate, gypsum, mica, silica and talc, hollow microspheres have much lower densities. For example, at a density of 0.6 g/ml, hollow glass microspheres can displace the same volume as talc at one-quarter of the weight. Densities and crush ratings, however, vary dramatically across product lines.

When microspheres are being used a a bond line spacer to be mixed into epoxy or another adhesive, manufacturer might need the spheres to stay in suspension for a significant period of time. Density of the bondline spacer particles is important to maximize the residence time in the dispensing vessel to increase the amount of time the mix can be used after the particles have been incorporated. To achieve this dispersion the density of microspheres needs to match to the density of the epoxy as closely as possible. Ability to pre-mix offers significant cost savings and efficiency improvements for the manufacturer, as compared to having to disperse particles at the time of use.

Properties of Microspheres – Durability

Durability may be one of the critical properties of microspheres. Depending on the applications microspheres might need to be able to withstand high pressure, temperature, and aggressive solvents, or operate in harsh conditions and aggressive environments.

Crush Strength

Crush strength is important when microspheres need to survive high-shear forces and high pressures involved in manufacturing processes such as plastics compounding and injection molding. Typically, solid glass microspheres have better crush strength compared to
hollow glass microspheres. If microspheres have to undergo an aggressive mechanical process, solid glass microspheres will most likely be required.

Historically, crush strength for hollow glass microspheres has been directly linked to density. That is, a glass sphere with a density of 0.125 g/ml is rated at 250 psi (1.8 MPa) while one with a density of 0.60 g/ml is rated at 18,000 psi (124 MPa). To some degree, there is a correlation between density and crush strength. The density and crush strength of microspheres made from a particular material depends, in part, on two structural variables: wall thickness and particle size.

- Microspheres Market
- Nanoparticles
- Nanospheres
- Particle Image Velocimetry
- Phosphorescent Particles
- PMMA microspheres
- Polyethylene Microspheres
- Polymer Microspheres
- Polystyrene Microspheres
- Porous Ceramics
- Precision Spheres
- Quality Management System
- Research
- Retroreflective additive
- Retroreflective Microspheres
- Silver Microspheres

Topics

beads (23) Biodegradable (2) Biomedical Microspheres (16) bond line spacer (2) calibration (2) Charge Measurement Techniques (2) Coatings (3) Conductive Microspheres (3) controlled drug release (5) cosmetic (7) Cosmetic Microspheres (3) density marker beads (3) drug delivery (10) Electrically conductive (3) Emulsion (3) extruding (2) flow visualization (7) Fluorescent Microspheres (12) glass (9) Glass microspheres (10) high density (3) hollow glass (5) Injectable (6) Luminescent (3) magnetic (4) Medical Microspheres (9) microbeads (14) microparticles (7) Microscopy (3) Microsphere Manufacturing (7) microspheres (10) opaque (7) Paramagnetic (3) personal care (3) PIV (5) polyethylene (10) polyethylene

Potters' Sphericel glass microspheres, for example, range in size from 11 to 18 microns and have crush strengths ranging from 8,000 to 10,000 psi (55 to 69 MPa), depending on the grade. They have been compounded successfully with a 25.4 mm/1-inch-diameter Killion two-stage single-screw extruder and injection molded on a 75-ton Newbury machine without significant sphere breakage.

Operating Temperature

It is critical to know the maximum operating temperature to which microspheres will be exposed during manufacturing processes and in final applications.

Polyethylene Microspheres – The melting point of polyethylene microspheres varies somewhat depending on the grade and molecular weight of the polymer, but is usually between 110C for low molecular weight grades and 130C for higher molecular weight material. The melting point is typically low and sharp, since polyethylene goes through a fast phase transition. This is a very important feature for applications where the spheres are used as a temporary filler but would need to be "melted away" at a later point to create holes or cavities for a sponge effect.

Glass Microspheres – The melting point of glass microspheres is from 500C – 800C, depending on the product. High melting point makes glass microspheres attractive for high temperature applications, where the product needs to withstand severe environmental or processing conditions.

Ceramic Microspheres – With operating temperatures up to 1000 degrees C, superior toughness and high resistance to wear ceramic beads can be used in high energy and high temperature processes and applications where other materials would not survive.

Chemical Stability/Solvent Resistance

Polyethylene Microspheres – Most grades of polyethylene have excellent chemical resistance and do not dissolve at room temperature because of their crystallinity. Polyethylene microspheres usually can be dissolved at elevated temperatures in aromatic hydrocarbons such as toluene or xylene, or in chlorinated solvents such as trichloroethane or trichlorobenzene. This feature is benefitial if microspheres need to be dissolved at a precise point in the process.

Glass Microspheres – Glass has very high chemical resistance and is the right choice for applications where microspheres need to withstand contact with aggressive solvents at elevated temperatures.

Shelf Life

Shelf life may be an important property of microspheres, as it might limit the options of how the materials are stored, handled, and used. Most microspheres that are sold as a dry powder have indefinite shelf-life if stored in a sealed container under controlled conditions (low humidity, no temperature extremes). Microspheres that are provided suspended in solution typically have a limited shelf life and need to be either refrigerated or frozen to extend useability.

Safety

Safety always needs to be considered when working with materials. Three potential hazards are unique to some microspheres and need to be considered: **slip hazard, combustible dust, inhalation hazard.**

Ball-bearing effect is one of unique properties of microspheres that applies to spherical particles regardless of what material they are made out of. When spheres are **extremely slippery when spilled**, so good housekeeping and prompt clean up of any spills is essential.

Like most fine powders (e.g. flour), microspheres made of flammable materials in **certain size ranges may be combustible** when present in air in certain concentrations. Caution should be taken to read the Safety Data Sheets, prevent creation of dust clouds, and eliminate any potential sources of ignition when working with microspheres. Good housekeeping practices need to be in place to ensure no layers of particles are collecting on surfaces. Only approved vacuums can be used and correct clean-up procedures implemented (e.g. wet wiping as opposed to sweeping to prevent dust clouds).

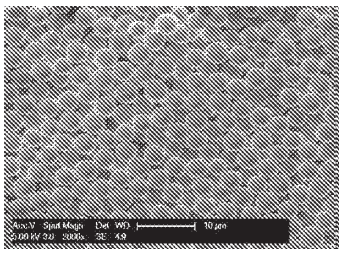
Lastly, microspheres that are less than 10 micron in diameter **may pose an inhalation hazard** in some situations. Correct handling of these microspheres requires combination of engineering controls (e.g. exhaust hood, ventilation), personal protective equipment (e.g. dust mask, respirator), and good laboratory practices to minimize potential inhalation of the particles.

As any hazard, **the risk depends on the amount of material** we are working with and the level of exposure. The risks are low for scientists working with very small quantities of materials in a controlled laboratory environment. The risks are higher when we

Requirements for particle size vary widely. For example, a scientist might be looking for microspheres less than 10 micron to simulate a human cell in a biological application or a 5 micron sphere to simulate bacteria. A microsphere of 50um diameter might be needed to hold a precision epoxy bondline, or a reference particle of 500um might be required to calibrate an optical instrument or a medical device. When used as a filler, smaller microspheres are better able to withstand the processing conditions of higher shear rates and faster screws.and 850 to 1,000 microns (1 mm). When used as a tracer particle in a flow visualization experiments, smaller particles tend to stay in suspension longer, while larger particles are easier to observe.

Microsphere size may be critical to the proper function of an assay, or it may be secondary to other characteristics. Diameter also determines surface area. Small-diameter spheres present more surface area per unit weight while larger spheres present more surface area per bead. Size also affects ease of handling, processing considerations (such as the method used for separations (centrifugation, dialysis, filtration)) and the amount of reagent needed for coating.

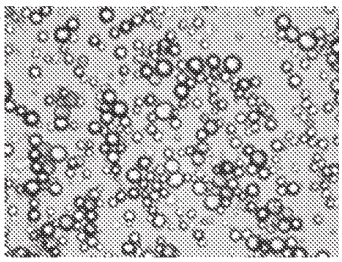
Particle size distribution is typically specified in one of two ways:

1. 

Monodisperse Silica Microspheres

Median diameter (D50) of microspheres with an associated coefficient of variation (CV%). Sometimes D10 and D90 are also specified. This method of reporting particle size assumes a normal (bell-shaped) distribution of particle diameters.

The lower the coefficient of variation, the tighter (narrower) the size distribution of the spheres in the sample. Please note that no measurement is infinitely precise. Even if very tight tolerances (low CV%) are reported, there is always a level of measurement uncertainty associated with the measurement technique and equipment.

2. 

Polydisperse Silica Particles

When particle size distribution does not have a bell shape, the property that is specified is size range, as opposed to a median diameter. For example, 1-5um or 53-63um, where the first number is the minimum diameter and the second number is the maximum diameter. In this method, % of particles in this size range are also specified. For example, greater than 95% of particles are between 1 and 5um in diameter.

For either of the above scenarios there is a science to ensuring a statistically significant and representative sample of the powdered material is measured.

For life sciences applications, monodisperse microspheres are typically the most desirable but also the most expensive. For large-volume, low-cost filler and texturizer applications, a wider size distribution might be preferred due to improved packing efficiency. The requirements of each unique formulation must be investigated to find the most economical solution. The wider the particle-size distribution, the more affordable the spheres.

Properties of Microspheres – Electrostatic Charge, Conductivity, Magnetism

Microspheres can be neutrally, positively or negatively charged, allowing formulators to design products that are attracted to or repelled from the surface as needed. Since like charges repel and opposite charges attract, the charge of a coating can be manipulated to be attracted to the surface or repel dust. Charged microparticles also enable formulators to control how the various materials within a formula interact.

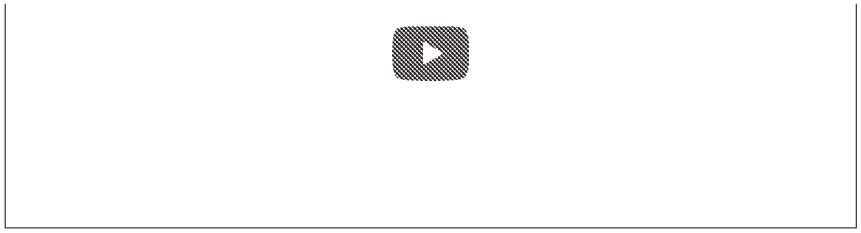
A positive or negative charge is internally embedded into each microsphere, and proprietary additives are acquired during the microsphere manufacturing process. The charge is permanent; it does not dissipate over time and cannot be grounded. The whole microsphere is charged and will respond to the electric field. Further, dark-colored or black microspheres can be made magnetic or static-dissipative. Metal or metal-coated microspheres offer electrical conductivity and provide shielding against EMI.

Janus particles, which are bipolar and bichromal can be manufactured with with dipole precisely aligned with two differently colored hemispheres. Due to the dipole the sphere will rotate in electromagnetic field to align more positive hemisphere to the

MICROSPHERES ONLINE

Supporting Microspheres Research Woldwide

LEARN RESEARCH ABOUT

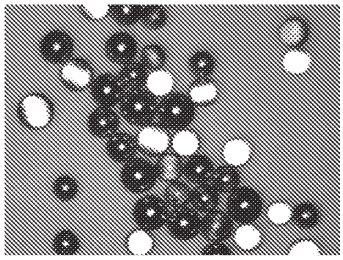


Properties of Microspheres – Optical Characteristics

Microspheres can be transparent or invisible to the eye, partially translucent or opaque, providing maximum hiding power. Generally, when light strikes an interface between two substances, some of the light is reflected, some is absorbed, some is scattered and the remainder is transmitted.

An opaque substance transmits little if any light and thus light is reflected, scattered or absorbed. One cannot see through an opaque particle since the surface behind it is completely hidden. Since opaque microspheres do not allow light to pass through them, this means that a 50-micron monolayer of opaque spheres will not transmit light, thus resulting in maximum hiding power in one layer of microspheres. Opacity of microspheres is often desired in color products such as paint coatings and in color cosmetics such as powder, concealer, blush, lipstick, eye shadow and nail polish, where uniform color and hiding color underneath the area on which the cosmetic product applied is required.

In general, high levels of opacity become more difficult to achieve in microscopic particles because opacity is proportional to the thickness of the material. Due to the chemistry of glass, it is very difficult to create opaque glass spheres. Most colored glass microspheres are made by attaching dyes to the surface of the particle and do not achieve significant opacity. Ceramic microspheres can be opaque but microspheres in a batch usually do not have the same level of opacity, with some more opaque than others.



Retroreflective Beads
Cospheric LLC

Hollow glass spheres can be used to replace some of the titania in a formulation. Hollow glass spheres redirect the angle of light, imparting opacity. Depending on the formulation, equivalent tint strength can be achieved with 2% to 5% replacement of titania.

Retroreflective hemispherically-aluminized high-refractive-index glass beads are used on airport runways, specialized signs and in other applications that require high-intensity retroreflectivity. Reflective pavement marking lines make a significant contribution to highway safety, especially in conditions of poor visibility at night and in wet weather. Applying retroreflective spheres is one of the most cost-effective ways to increase highway safety in these conditions.

Different formulations of glass have different index of refraction. For example, Barium Titanate glass spheres offer a higher Refractive Index (n) than most other glass formulations. Depending on the grade of material, reflecting index of Barium Titanate glass is between 1.9 to 2.2 compared to n~~1.5 of Soda Lime and Borosilicate glasses. Barium Titanate glass microspheres will reflect back more light directly to the viewer, which is beneficial for applications where retroreflectivity is desired, such as motion tracking targets in medical devices, endoscopy, micro-optics, defense and microscopy.

Properties of Microspheres – Color

Colored microspheres add color to a product without the use of other colorants (pigments or dyes) and also offer functional benefits such as lower viscosity and improved flow. Solid polyethylene microspheres can be manufactured in any color, including flesh tone, clear, grey, fluorescent, glow-in-the-dark and multicolor, which provides a multitude of options for color effects in a wide variety of products.

Microspheres can be used to add saturated color, a hint of color or a sparkle to a formula. Colored microspheres enable formulators to achieve saturated colors or desired color effects with much larger particles, which are not respirable and come in a free- flowing dry powder, ensuring a simpler formulation process. In addition, since larger microspheres tend to not agglomerate as easily as submicron pigments, the challenge of pressed-powder agglomeration is greatly reduced.

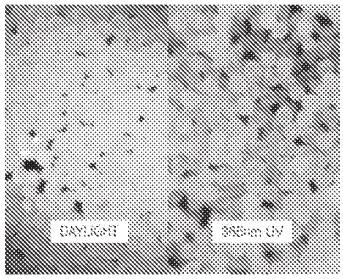


Red Polymer Spheres

important properties of microspheres, especially when used as tracer particles that need to have high contrast and visibility in the system, such as in-vivo studies, process diagnostics and troubleshooting, contamination studies, flow visualization, and instrument calibration, to name a few applications.

Colored polyethylene microspheres have colorant embedded into the polyethylene matrix which will not leach out or degrade in a solution.

Properties of Microspheres – Fluorescence and Phosphorescence



UV Fluorescent Polymers Spheres – Color Changing

Fluorescent microspheres are round spherical particles that emit bright colors when illuminated by UV light. Ability to emit intense color under UV (black light) illumination provides contrast and visibility of microspheres relative to background materials. In addition to the benefits of conventional high quality microspheres, such as sphericity, smoothness and spreadability among others, fluorescent spheres offer extra sensitivity and detectability for analytical methods. For example, fluorescent microbeads are often used as traces to simulate spread of viruses in medical research.

Typical applications of fluorescent spheres include: testing of filtration media and systems, vial and container cleaning studies, flow tracing, flow visualization, and fluid mechanics studies, medical imaging and flow cytometry, fluorescence microscopy and photography, as well as biomedical technology research, qualification and validation of medical devices, biomedical diagnostics, process troubleshooting and process flow among others. Specifically fluorescent microspheres are often used for water- and air-flow testing and bead-based diagnostic applications. New unique applications of fluorescent spheres are being discovered daily.

Phosphorescent particles are used for process study and blind tests especially in medical technology industry, diagnostics, troubleshooting, process flow, medical research and other industries. Particles exhibit a strong long-afterglow phosphorescent response and are stable in solution.

Properties of Microspheres – Shape and Quality

While high-quality microspheres tend to be more expensive, some lower-cost microspheres have limitations such as poor shape and uniformity or lack of consistency between batches, wide particle-size distribution, the presence of dust and debris, poor roundness and sphericity. It is not uncommon for low-cost low-quality microspheres to contain a significant amount of crushed, oblong and non-spherical particles, which could negatively impact the texture, appearance and feel of finished products and/or performance in an application.

It is important for formulators to select a supplier that manufactures particles in a controlled environment and thoroughly screens them to prevent any dust, debris and nonspherical microparticles entering the system. Depending upon the requirements for a formulation and properties of microspheres, specifications for the maximum amount of unacceptable particles must be determined and communicated to the supplier.

For example, with luxury cosmetic applications, most formulators will look for high-quality identical polymer spheres with excellent uniformity. For large-volume low-density concrete-filler applications sold by the truckload, price may be a more critical factor than particle size and color uniformity.

Properties of Microspheres – Summary

To summarize, there are many different microsphere products on the market with properties of microspheres varying dramatically due to the composition of raw materials and additives, particle size and distribution, levels of sphericity and roundness, among other factors. It is essentials to truly understand the technical requirements of the project and the intended functionality of microspheres to select the right product for the application.

Share this:

MICROSPHERES ONLINE

Supporting Microspheres Research Woldwide

LEARN RESEARCH ABOUT

MICROSPHERES ONLINE:

Microspheres Online is a digital database and a compilation of technical resources on microspheres and precision spherical particles. The resources are compiled and maintained by Cospheric LLC - the leading manufacturer and global supplier of precision spherical particles based in Santa Barbara, CA, USA.
The intention for this resource is to provide a service to the scientific community word-wide enabling breakthroughs in science and technology.

WHAT ARE MICROSPHERES?

Microspheres are spherical particles on the micro scale (between 1micron and 1000micron (1mm) in diameter). Spherical particles below 1micron we consider to be nanoscale and therefore call them nanospheres. Spheres over 1mm in diameter are simply called spheres, beads, or balls.
Microspheres are solid, meaning they might be completely solid throughout or they might have a solid wall (shell).

CONTACT INFO:

Do you have feedback? Requests? Are you looking for specific information or product recommendation? Do you have research that you would like to see featured on Microspheres Online?
Let us know! We would love to hear from you.
Email us or Call +1-805-687-3747

PO Box 6762
Santa Barbara, CA 93160

LEARN MORE:

- Learn
- Materials
- Applications
- Properties
- Sourcing
- Research
- About

Copyright © Cospheric 2020. All rights reserved

Atty. Docket No.: 071816-091960USC1 PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Application of:	Guido William ARU	Examiner:	Haytham SOLIMAN
Serial No.:	17/176,222		
Filed:	February 16, 2021	Group Art Unit:	1736
Entitled:	A CO TO CO_2 COMBUSTION PROMOTER		
		Conf. No.:	3640

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

DECLARATION OF NATALIE P. HERRING Ph.D. UNDER 37 C.F.R. 1.132

I, declare:

1. I, Natalie P. Herring, Ph.D., hold the position of Director of Technology at G. W. Aru, LLC.
2. I hold a Bachelor of Science in Chemistry from The College of William and Mary and a Ph.D. in Chemistry from Virginia Commonwealth University. I have previously held a position as a Catalyst Development Scientist at Johnson Matthey. A true and accurate copy of my Curriculum Vitae and publication list is provided herewith as Exhibit 1.
3. I have been a scientist in the fields of Fluid Catalytic Cracking (FCC) for over 7 years. My work focuses on the research and development of catalysts for FCC applications. My research and experience in these fields are evident in the publications appended in my Curriculum Vitae.
4. I have reviewed the Non-Final Office Action mailed on April 7, 2021 in the 17/176,222 application (the '222 application hereafter). In particular, I note that the Office Action:
    a. Alleges that the term "microsphere" is indefinite
    b. Implies that "microspheroidal" and "eggshell" are synonymous

c. Contends that the Yaluris application (US 2005/0042158; "Yaluris" hereafter) describes an eggshell particle in Example 4-5.

5. I disagree with each of these positions.

6. *"Microsphere" is a well understood term within the field.* "Microsphere" is defined as spherical particles having a diameter of 1 micron to 1,000 microns (1 mm). In my professional experience, this term is well-understood to have this meaning by those of ordinary skill in the art.

7. *"Eggshell" and "microsphere" are not synonymous.* As detailed in the accompanying Exhibits 3-5, "eggshell" is defined as a particle structure having chemically distinct inner and outer layers, and when a catalyst is present, having a higher concentration of the catalyst in the outer layer. In my professional experience, this term is well-understood to have this meaning by those of ordinary skill in the art. While a single particle, such as those described in the '222 application could certainly be both a microsphere and an eggshell particle, these two terms describe different physical aspects of a particle and are in no way interchangeable or equivalent.

8. *Yaluris does not describe an eggshell particle.* Yaluris' Example 4 describes the formation of a base material, which is then impregnated in Example 5 with a platinum solution. To someone familiar with chemistry, it is understood that the base material formed in Example 4 of Yaluris will ***necessarily*** comprise pores and that impregnating the base material will according to the methods of Example 5 ***necessarily*** result in the platinum being found homogenously throughout the base material particles.

9. Porous particles generally are known for use in FCC processes and as combustion promoters. The spray drying technic described in Yaluris is understood to form such porous particles. The pores in such particles are measurable on the scale of nanometers (10^{-9} m) that extend throughout and into the center of each particle. When such particles are impregnated as described in Yaluris, the impregnating material will penetrate throughout the pores and be present in a homogeneous distribution throughout the particles.

10. It is physically impossible for the method described in Examples 4 and 5 of Yaluris to form an eggshell particle, as there is no mechanism in place to prevent capillary effects from forcing the platinum solution to penetrate throughout the entire depth of the pores of the particle.

11. I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that wilful false statements and the like are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such wilful false statements may jeopardize the validity of the application or any patents issued thereon.

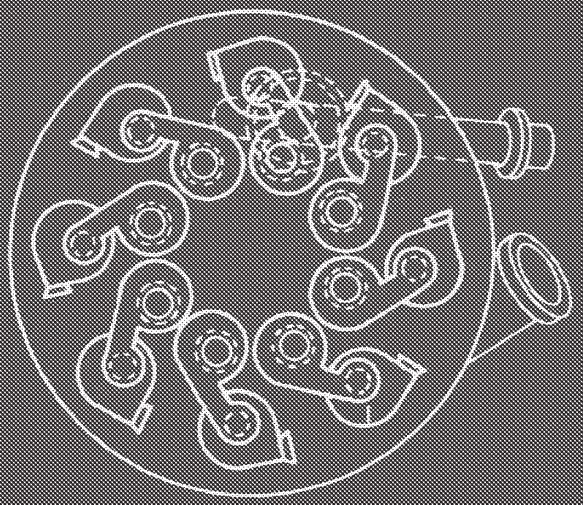
Date: July 3, 2021

Respectfully submitted,

Natalie P. Herring, Ph.D.

CHEMICAL INDUSTRIES/1

FLUID CATALYTIC CRACKING WITH ZEOLITE CATALYSTS



Paul B. Venuto
E. Thomas Habib, Jr.

[147]. A number of studies emphasizing the effect of HDT severity on FCC process variables, crackability, yields/selectivity, and product quality have been reported [99, 130, 142, 147, 152]. Hydrotreating catalysts are designed to accept large amounts of deposited metals (i.e., act as a metals sink), thereby preventing contamination of the FCC catalyst, the performance of which is much more sensitive to metals [142].

VII. PROPERTIES AND CHARACTERIZATION OF FCC CATALYSTS

A. Background and Scope

As noted in Table 1, synthetic silica-alumina was introduced as a cracking catalyst about 1940 and, in one modification or another, dominated the cracking catalyst field until the early 1960s and the introduction of the zeolites [13, 17, 18]. However, over the decade of the 1950s, and particularly during the latter half, only incremental improvements in selectivity and regenerability of the amorphous catalysts (e.g., via silica-magnesia variations [128, 154, 155]) were achieved, and it remained for the zeolite catalysts to truly revolutionize the cracking catalyst field.

Plank and Rosinski (see the series of patents issued to Mobil Oil [156-161]) discovered that incorporation of a minor proportion of zeolite (such as rare-earth cation exchanged X or Y synthetic faujasite) in a matrix such as silica-alumina, silica, or silica-clay, produced compositions of matter that, over more than a decade, have met, to a large extent, the most severe requirements [13, 17, 18] for successful cracking catalysts, including:

1. High activity (allowing economic throughput rates)
2. Reasonable activity stability (resistance to time-dependent deactivation by coke)
3. High selectivity to gasoline vs coke and dry gas
4. Thermal and hydrothermal stability (ruggedness to withstand the regenerator environment)
5. Accessibility (sufficient diffusivity and internal porosity to allow small, economic reactor volumes)
6. Attrition resistance
7. Resistance to poisons (metals, nitrogen, etc.)
8. Acceptably low cost

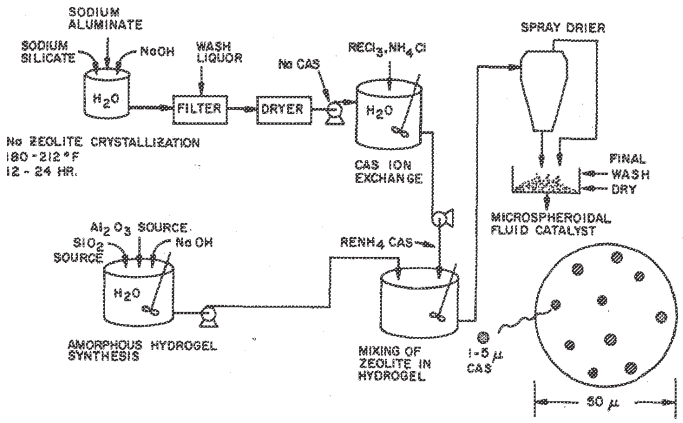


FIG. 13. Simplified conceptual scheme for manufacture of commercial fluid cracking catalyst (XZ-25). Modified after flow sheets in Koffler [181].

In this section we attempt to focus on highlights of the zeolite cracking catalysts, limiting our discussion of the amorphous silica-alumina type to selected comparisons only, as these have been well described by Sittig [10], Voge [11], and others [45, 122, 128, 162-180].

B. Manufacture of FCC Catalysts

As visualized in Fig. 13, the major operations in the manufacture of a commercial zeolite cracking catalyst [182] may include synthesis and ion exchange of the zeolite component, preparation of the amorphous gel, intimate admixture of the zeolite in the gel matrix, and spray drying.

Manufacture of zeolites commercially involves combination of readily available, inexpensive, raw materials, including a silica source, an alumina source, and a strong base such as sodium hydroxide [13, 181, 183, 184]. These materials, in proper stoichiometric ratios, molarity, and state (i.e., solution or colloidal

since not all deposited metals are equally effective in producing coke and hydrogen [12]. On a weight basis, nickel shows four times the coke- and hydrogen-forming tendency of vanadium [29, 224], and similar relative responses for both metals on amorphous silica-alumina have been reported [221]. Cimbalo, Foster, and Wachtel [28] define "effective metals" (in the contaminant sense) as (4 [ppm Ni] + [ppm V]) X "fraction effectiveness" which, in turn, is a function of feed type and throughput, catalyst type, age and history, and unit inventory and makeup rate [28, 29]. As an example, for systems where daily makeup rates ranges from 0.5 to 3.0% of inventory, the "fraction effectiveness" varied from about 0.21 to 0.32 [28]. Iron (which is commonly scale or "tramp" metal) and most other metals are not considered significant catalyst contaminants.

Freshly deposited metals are more active than "older" metals that have been subjected to numerous cycles in the FCC regenerator/reactor circuit [102]. Upon exposure to such repeated cycles of oxidation/reduction, the poisoning effects of metals contaminants are diminished, but those on zeolites lose their effectiveness more slowly than those on amorphous catalysts [28]. Grane, Conner, and Masologites [221], in a study of metals-poisoned silica-alumina, suggested that the repeated shift from oxidizing to reducing environment in going from regenerator to reactor may influence the oxidation state of the metals or cause sintering (and loss of surface area) with consequent deactivation. Morozov et al. [225] observe that, for a given feedstock, a greater metals buildup may occur on fluid catalysts than on bead types, because with the latter there is removal of significant amounts of surface metals by attrition. Montgomery [102] observes that sulfur in FCC feed may tend to sulfide—and thereby activate—the metals on a cracking catalyst. On the other hand, it has been observed that zeolite catalysts have excellent metals resistance, particularly in short contact time operation [92, 226]; this may occur because metal oxides on the circulating catalyst are not retained in the reaction zone long enough to become sufficiently sulfided to show strong dehydrogenation activity [92, 226].

7. The Role of the Matrix

The role of the matrix in composite catalysts has been discussed in some detail by several authors [13, 101, 125]. Matrices encompass a broad range of SiO_2-Al_2O_3 gels, clays, Al_2O_3, and other siliceous materials, and may be expected to vary in different catalysts [227]. Natural, chemically treated, and calcined clay have also been specified [158] as possible constituents. Although most fundamental studies have been conducted on zeolites alone, Oblad [13] points out that a fair amount of catalyst mechanistic patterning may also be true for matrix-zeolite blends.

In a sense, the matrix protects the small (~1 to 5 μm), relatively fragile zeolite crystallites, building the composite up to a ~50 μm microsphere and providing shape and bulk for fluidization [76] and minimizing mechanical attrition (see Fig. 13). Eastwood, Plank, and Weisz [101] observe that the high surface area matrix surrounding and diluting the zeolite crystals acts as a heat carrier or "sink," facilitating heat transfer during regeneration and cracking. The stability of the composite to high severity steaming is also enhanced [13, 101]. Some matrices may act as "sodium sinks," allowing solid-solid sodium ion exchange, thus improving stability of the zeolite particles [13, 101], i.e.,

$$\text{RE NaY} + \text{H-Gel} \rightarrow \text{RE HY} + \text{Na-Gel}$$

$$\text{RE NaY} + \text{Al-Gel} \rightarrow \text{RE AlY} + \text{Na-Gel}$$

Although it is true that matrices have catalytic properties of their own [13], the much greater zeolite activity permits a relatively small amount of molecular sieve to dominate the catalytic behavior of the composite [13, 158]. In fact, a synergistic effect has been described [13, 100] wherein enhancement of zeolite activity occurs (in that the same conversion can be obtained for a smaller amount of zeolite when incorporated in the matrix). The requirement for a matrix to possess—and retain— adequate porosity to maintain full accessibility to feed molecules and regeneration gases is critical [13, 76, 127, 185].

E. Performance Characteristics and Physiochemical Characteristics of FCC Catalysts

1. Some Aspects of Fluidization Dynamics

It is because solid fluid catalyst particles have the capacity to exhibit liquid-like flow properties when aerated that makes possible the high catalyst circulation rates utilized in FCC units. In fact, if the degree of slippage between the gases and solids is sufficient, the system can very closely parallel the dynamics of a true fluid system [10, 92], even to the extent of permitting flow across a (slide) valve. When a gas flows upward through a bed of solid particles at low velocity, it flows through the interstices without moving the bed. Such a situation is called a fixed bed. If the velocity (and pressure drop) are increased, a point will be reached where the pressure drop equals the weight of the bed and the gas will begin to lift the solids. The particles will

move apart and the bed will expand in volume, becoming more loosely packed. As the gas velocity is further increased, the pressure drop remains essentially constant (equal to the weight of the bed) because the interstices open up to decrease the resistance to flow. Finally, a point is reached where the particles no longer touch. Gas bubbles begin to form, and the particles begin to move relative to each other in a turbulent manner. For FCC catalyst, the points of incipient bed lifting and incipient bubble formation occur at gas velocities of about 0.01 and 0.1 ft/sec, respectively [80]. For gas velocities at or higher than the point of incipient bubbling, the solid particles are described as a fluidized dense bed.

Further increase in the gas velocity results in larger bubbles. If the bed is narrow, the bubbles can become as wide as the vessel, and alternate rising layers of gas and solids will form. This is called slugging, and as the slugs of solids rise, individual particles fall through the gas layer and the solid slug eventually disintegrates. At very high velocities the terminal velocity of solid particles is exceeded and the particles are carried along with the gas. Such a regime is called a dilute phase with pneumatic transport of solids [228]. The various states of an aerated bed are illustrated in Fig. 18.

Whenever a fluidized bed is used, some of the particles—particularly the smaller ones (fines)—are entrained and carried out with the gas. To overcome this difficulty, cyclonic collectors (somewhat analogous to centrifuges) are employed. The gas/solids mixture enters the cylinder tangentially, gas is removed overhead from the middle, and the solids are displaced toward the wall and funneled downward toward diplegs (see Figs. 9 and 10). Key cyclone performance variables include inlet velocity, component geometry, particle size/density, and gas viscosity [63, 82-84, 88].

In a fluidized dense bed there are two ranges of gas holdup times: One for the gas that goes through the bed in bubbles and another, much longer one, for the gas that proceeds through the interstices between the particles. The gas in the bubbles tends to have poor contacting with the solids, while the gas in the interstices has good contacting. This is less of a problem if the bubbles can be made smaller. Smaller particles result in smaller bubbles but also result in more entrainment and poor cyclone efficiency. However, a small amount of smaller particles (fines) added to the coarser particles produces bubbles nearly as small as if all the particles were small. The amount of fines required to achieve this effect is that needed to coat all the large particles with fines [80].

Schatz, Owen, and Snyder [229], in riser pilot-plant studies of dilute phase fluid transport, measured catalyst concentrations and

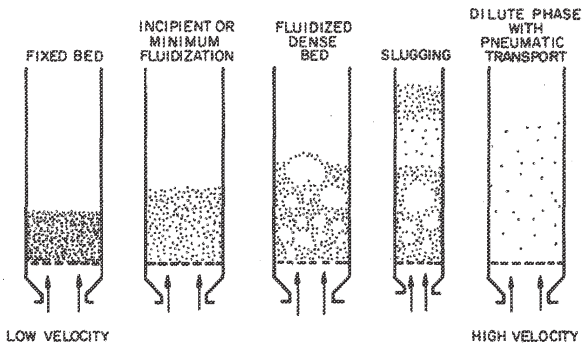


FIG. 18. The various states of an aerated bed. The gas velocity is increasing from left to right. If the vessel diameter is large enough, the slugging regime may not occur and increasing gas velocity will result in a smooth transition from dense bed to dilute phase. After Kunii and Levenspiel [228].

deviations from ideal plugflow for gas and catalyst. Saxton and Worley [63] conducted fundamental studies on the nature of fluidization in risers; they observed that local densities greater than 60 lb/ft^3 occurred near the riser walls, and that densities less than 3 lb/ft^3 occurred near the riser center line, indicating local velocities as much as twice the superficial vapor velocities of 35 to 75 ft/sec. General information on fluidization and pneumatic transport of solids can be found in Refs. 10, 80, 82, 84, 228, and 230.

2. Properties of Equilibrium FCC Catalysts

Table 8 gives a representative comparison of the properties of fresh and equilibrium zeolite and amorphous FCC catalysts as reported by Baker and Blazek [124]. The 0.20 to 0.25% carbon on the equilibrium catalysts is the residual level remaining after regeneration. Note the relatively low sodium levels and the sharply higher levels of iron, and the appearance of contaminant metals such as nickel and vanadium on the equilibrium catalysts. Bass [231] reports that clay-based catalysts surprisingly often have titanium

TABLE 8

Comparison of Properties of Fresh and Equilibrium FCC Catalysts[a]

	Amorphous high alumina		Zeolite XZ-2	
	Fresh	Equilibrium	Fresh	Equilibrium
Chemical analysis (dry basis), wt%				
Alumina[b]	28	21.5	31	25.4
Carbon	0	0.20	0	0.25
Sulfate	0.7	0.1	0.3	0.1
Sodium	0.03	0.02	0.04	0.04
Iron (ppm)	300	3900	700	3700
Metals (ppm of V + Ni + Cu)	0	162	0	259
Physical properties				
Surface area, m^2/g	415	140	335	97
Pore volume, cm^3/g	0.88	0.43	0.60	0.45
Average bulk density, g/cm^3	0.39	0.70	0.52	0.68
Particle size, micromesh sieves, wt%				
0 to 20 μm	2	0	2	0
0 to 40 μm	17	8	19	6
0 to 80 μm	68	69	75	75
Average particle size, μm	65	63	62	62
Catalytic activity				
Microactivity, vol% conversion	60[c]	59[c]	85	73
Carbon factor	1.0	1.1	0.6	0.6
Hydrogen factor	1.0	1.1	0.2	0.7

[a]Data from Ref. 124 for same commercial unit.

[b]Equilibrium values are lower due to presence of some residual low alumina of long age.

[c]After 24 hr/1050° F/60 psig, 100% steam.

inclusions in local concentrations far greater than levels indicated by bulk chemical analysis. Typical rare-earth element distributions and levels were discussed earlier. With the use of a scanning electron microscope/energy dispersive x-ray analyzer, Bass has also been able to distinguish the presence of plate-like kaolin clay, granular gel, and crystalline zeolite in the interior of lightly ground cracking catalyst powder [231].

Surface areas are sharply lower (by a factor of ~3 to 3.5) in equilibrium vs fresh catalyst; likewise, there is a drop in pore volume and an increase in bulk density. Letzsch [227] suggests that, in some cases, the initial loss in surface area with catalyst use may in large part be due to the collapse of small matrix pores and some zeolite regions which were not properly stabilized (i.e., had high residual sodium or inadequate rare-earth exchange levels).

For both amorphous and zeolite catalysts, the 0 to 20 μm fraction disappears and the 0 to 40 μm fraction is greatly lowered in the equilibrium catalysts compared to the fresh. This reflects the observation [62] that the finest part of the fresh catalyst added to a fluid unit is often lost on the first one or two cycles of operation, before it has much chance to do the work of cracking. Efficient regenerator cyclones will minimize fines loss and makeup required for catalyst activity maintenance. Beyond the immediate loss of fresh catalyst fines, most catalyst losses result from attrition to particles below the size range retained by the cyclones [62]; attritional losses are aggravated by excessive steam or air velocities. However, as indicated earlier, a distribution or gradation of particle sizes is required to maintain proper fluidization dynamics and cyclone efficiency [62]. Edgar [232] has demonstrated (from lab simulations and scanning electron-micrograph studies) that fresh FCC catalysts are not subject to thermal shock and fracture from rapid vaporization of volatiles when added to hot (1200° F+) regenerators.

Conversions are higher, and carbon producing (CPF) and hydrogen factors are lower for the zeolite, as expected. CPF is a useful guide to the degree of contamination of a catalyst, and is the ratio of coke yield for a given catalyst to that for a standard clean silica-alumina catalyst at the same conversion level [28]. The hydrogen factor—defined as the ratio of moles of H_2/moles of C_1+ moles of C_2's—increases with metals level.

Other data summaries on properties of fluid zeolitic catalysts have been reported [106, 107], as well as inspections for TCC bead catalysts [101, 105, 128, 131], silica-magnesia [128, 155, 174], etc.

This is an open access article published under an ACS AuthorChoice License, which permits copying and redistribution of the article or any adaptations for non-commercial purposes.

CHEMICAL REVIEWS

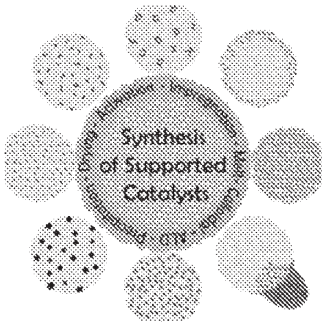
Review

pubs.acs.org/CR

Recent Developments in the Synthesis of Supported Catalysts

Peter Munnik, Petra E. de Jongh, and Krijn P. de Jong*

Inorganic Chemistry and Catalysis, Debye Institute for Nanomaterials Science, Utrecht University, Universiteitsweg 99, 3584 CG Utrecht, The Netherlands



CONTENTS

1. Introduction 6687
2. Catalyst Requirements 6688
3. Precipitation 6689
3.1. Coprecipitation 6689
3.1.1. "Greener" Coprecipitation Methods 6691
3.2. Deposition Precipitation 6691
3.2.1. Gold Catalysts 6692
4. Impregnation and Drying 6693
4.1. Impregnation 6693
4.1.1. Pore Filling 6694
4.2. Adsorption 6694
4.2.1. Outer and Inner Sphere Complex Formation 6695
4.2.2. Metal Distribution 6697
4.3. Drying 6699
4.3.1. Drying of Strongly or Weakly Adsorbing Species 6699
4.3.2. Metal Redistribution at the Nanoscale 6700
4.3.3. Alternative Drying Methods 6701
4.4. Activation 6702
4.4.1. Formation of the Active Phase 6702
4.4.2. Chelating Additives and Other Organic-Containing Precursors 6704
4.4.3. Plasma Activation 6705
5. Emerging Techniques 6706
5.1. Melt Infiltration 6706
5.2. Colloidal Synthesis 6708
5.3. Atomic Layer Deposition 6710
5.3.1. ALD for Nanoparticle Stabilization 6711
6. Conclusion and Outlook 6713
Author Information 6713
Corresponding Author 6713
Notes 6713
Biographies 6713
Acknowledgments 6714
References 6714

1. INTRODUCTION

Heterogeneous catalysis, whereby a gas- or liquid-phase reaction is performed over a solid catalyst, is at the heart of the modern energy and chemical industries. Most chemical processes, both established[1−3]and emerging,[4−7] are performed using functional nanomaterials as catalysts. Moreover, upcoming fields such as nanoelectronics and energy conversion and storage are based upon the application of similar nanomaterials. The catalytic activity for these materials often resides with metal (oxide, sulfide) surface sites, and efficient use of the metals and space available requires small particles, located on a mostly inert support to enhance the thermal stability of the catalyst. The field of catalyst synthesis, also known as catalyst preparation or catalyst manufacturing, aims at establishing the desired composition and structure of these materials.

Market studies in 2013 have estimated the total sales of catalysts to be between $15 and $19 billion per year, and to rise 4−5% per year.[8,9] Moreover, the added value catalysts create in the conversion of feedstocks to products such as fuels and chemicals is much larger. Studies have estimated that the cost of the catalyst only represents between 0.1% and 1% of the final product margin, meaning that the total value the catalysis-based industry creates can be estimated to be on the order of trillions of dollars per year.[10,11] Even so, catalyst synthesis has often been regarded as an art rather than a science, although an exponential increase in the number of scientific papers on supported catalysts testifies to the increased ability to rationally synthesize active, selective, and stable catalysts.[12] Despite this, many of the fundamental mechanisms concerning catalyst synthesis are as yet not fully understood. For example, a recent review highlights the lack of knowledge on the mechanisms and rates of particle formation in supported catalyst synthesis.[13] Moreover, heterogeneous catalysts for a wide variety of reactions, such as biomass conversion, (de)hydrogenation and oxidation, the Fischer−Tropsch synthesis, ammonia synthesis, deNO_x, hydrodesulfurization, and others, encounter challenges during preparation, activation, and operational use. While very small metal particles are generally desired, the formation of poorly reducible compounds such as transition-metal silicates, aluminates, and titanates often prevents complete reduction of the precursor to the active phase, so that the costly metal is not fully utilized. Alternatively, the particles may be in close proximity to each other, resulting in significant particle growth during operation. During the synthesis of bimetallic or promoted systems, phase segregation or preferential deposition may result in separated phases or one metal covered by the other where an alloy was desired, while macroscopic nonuniform distributions may prevent optional use of the catalyst.

Received: August 29, 2014
Published: June 19, 2015

Downloaded via 73.216.154.207 on April 7, 2021 at 19:03:25 (UTC).
See https://pubs.acs.org/sharingguidelines for options on how to legitimately share published articles.

 © 2015 American Chemical Society

DOI: 10.1021/cr500486u
Chem. Rev. 2015, 115, 6687−6718

In this review, we describe recent developments in the synthesis of supported catalysts reported over the past 5−10 years. First, the main requirements of solid catalysts are discussed. Next, recent developments of the two main preparation methods used in industry, precipitation and impregnation, are highlighted. In both of these methods, a metal precursor, mostly an inorganic salt, is the starting point to deposit the active metal onto the support. With precipitation techniques, metal particle growth is induced by supersaturation of the precursor solution, resulting in nucleation and growth of metal particles. This can happen in conjunction with the formation of the support (coprecipitation) or on an existing support (deposition precipitation). With impregnation techniques, the support is contacted with a precursor solution. Low loadings, often for precious metals, are achieved by adsorption of the precursor molecules onto surface groups of the support (ion adsorption) or through the exchange of ions in, for example, zeolites (ion exchange), after which excess precursor is removed. When higher loadings are required, the washing step is skipped and the support is directly dried, so that all precursor ends up on the support (impregnation and drying). Impregnation can be performed to incipient wetness, whereby only the pores of the support are filled with precursor solution, to prevent deposition on the external surface of the catalyst grains and to limit waste. Besides progress in understanding these traditional methods, emerging preparation techniques are discussed in this review. Precursors with low melting points can be heated and contacted directly with the support, such that capillary forces suck up the precursor upon melting (melt infiltration). Particles can also be formed in solution (colloidal route) controlled through use of stabilizing agents or ligands, after which the formed particles are deposited on a support. Vapor deposition involves gaseous metal atoms, clusters, or organics selectively reacting with support surface groups. Finally, we provide an outlook on the anticipated developments in the field of supported catalyst synthesis.

2. CATALYST REQUIREMENTS

Catalysts come in a wide variety to accommodate the large differences in operating conditions, feedstocks, and products, and the catalytically active metals can be deposited on a range of supports, which are generally highly porous and can vary in size from small powders to centimeter-sized pellets. In each case, high activities and selectivities toward the desired products are required. Moreover, the stability of the catalyst is highly important, and processes such as the irreversible growth of particles or poisoning of the active sites have to be prevented.[14] The performance and stability of the catalyst are determined by what we refer to as the "DNA" of the catalyst, that is, the density, nature, and accessibility of the active sites, with the accessibility largely determined by the support pore architecture.

The density of active sites is important to the activity primarily through the number of particles on the support connected to the metal loading. Since industrial reactors are generally limited in size for practical reasons, it is often desirable to use a high density of active sites (high metal loading) to maximize the activity per unit volume. The local particle density, and therefore the distance between particles, can also be important for the stability of the catalysts. Maximizing the spacing between Cu particles proved highly beneficial for the stability of methanol catalysts.[15] Similarly, reducing the size of aggregates of cobalt nanoparticles on silica gel in Fischer−Tropsch catalysts has been shown to improve catalyst stability.[16]

The nature of the active sites has a direct bearing on the surface-specific activity, often referred to as the turnover frequency (TOF), and the catalyst selectivity. This nature is determined by the composition (i.e., type of metal and promoters or bimetallics), size, and shape of the nanoparticles. Reduction of the size of the nanoparticles increases the amount of surface sites per unit weight of metal and generally results in more active catalysts. For structure-sensitive reactions favored by specific surface sites, such as low-coordination sites found on defects, corners, steps, or edges, reduction of the particle size may enhance the TOF.[17] However, maximum weight-based activities at a certain particle size have also been reported. In the dehydrocyclization of *n*-heptane over Pt catalysts, a large increase in TOF was observed with decreasing particle size from 4 to 1.5 nm, whereas further reduction in size resulted in a large decrease.[18] The TOF of Fischer−Tropsch cobalt catalysts was found to be constant for particles larger than 6 nm, while below 6 nm it steeply decreased.[19,20]

The nature of the metal(s) and the support can also influence the catalyst stability. For example, small Ag particles displayed a much higher adhesion energy when supported on reduced CeO_2 compared to MgO,[21] and 4 nm bimetallic PtRh particles exhibited higher thermal stability compared to monometallic Pt particles.[22] The initial particle size might play a role as well, since 2 nm Pt nanoparticles in polymer electrolyte membrane fuel cells were found to be very unstable, while 5 nm particles exhibited almost no deactivation.[23] Similarly, 3−4 nm Ni particles on silica gel used in the methanation reaction exhibited rapid particle growth resulting in particles up to 100 nm in size, whereas 8−9 nm initial particles remained of a size similar to the pore diameter (10 nm) of the silica gel support.[24]

Accessibility of active sites calls upon control of the catalyst porosity. This is key for the rate of mass transfer of reactants to and products from the active sites, and affects activity by diffusion rates, selectivity by the extent of secondary reactions, and stability via processes such as coke formation and poisoning. In academia, fine powder grains are often used to ensure good accessibility of the active sites to prevent mass-transfer limitations. However, small grains cause a large pressure drop over a catalyst bed of significant height. Therefore, catalyst support bodies or pellets a few millimeters in size are often used in industry. For these relatively large bodies, the macroscopic distribution of the active sites becomes important, and a useful tool to estimate the degree of mass-transfer limitations in a catalytic system is the Thiele modulus φ:

$$\varphi = \frac{V_p}{A_p}\sqrt{\frac{k_r}{D_e}} \tag{1}$$

where V_p is the volume of the pellet, A_p is the external surface area of the pellet, k_r is the first-order rate constant, and D_e is the effective diffusion coefficient. A φ greater than 0.3 is an indication that diffusion of the reactant through the pores is rate limiting. Thus, for large catalyst bodies, a homogeneous distribution of the active phase is only preferential for relatively slow catalytic reactions, providing reactants time to diffuse to the active sites. If the reaction is fast or if secondary reactions are problematic, a different macroscopic distribution of the active phase might be preferred, such as an eggshell distribution

DOI: 10.1021/cr500486u
Chem. Rev. 2015, 115, 6687−6718

or an egg-white distribution if the catalyst is prone to attrition. If the reactants contain poisons, an egg-yolk distribution may be favorable so that the poison can be captured at the edge of the catalyst body, where few active sites are present (Figure 1).

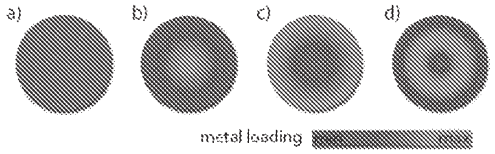


Figure 1. Different types of macroscopic metal distributions across a support body: (a) homogeneous distribution, (b) egg-yolk distribution, (c) eggshell distribution, (d) egg-white distribution (red, high concentration of metal; blue, low concentration of metal).

Common support materials consist of refractory oxides such as SiO_2, Al_2O_3, or TiO_2. These materials exhibit high specific surface areas, high porosities, and high thermal and mechanical stability and come in a variety of pore sizes, while they are mostly chemically inert. Carbon is also widely used, while zeolites are often applied in many oil-refining and petrochemical applications. Recently, an increasing variety of ordered mesoporous materials have been used as model supports.[25] Finally, metal organic frameworks are showing an increased use as catalysts or as support for metal (oxide) nanoparticles.[26] To maintain activity as well as for practical reasons, the support requires a high mechanical strength and the macroscopic bodies should be resistant to attrition if the catalyst is vigorously agitated such as in fluid bed or slurry bed reactors.

Oxidic supports are commonly produced via sol−gel chemistry, in which a metal precursor (usually a silicate dissolved in water, sometimes a metal alkoxide in an organic solvent) is polymerized in solution, forming polysilicate species. Further condensation leads to the formation of small particles, links between particles, and eventually the formation of a gel. Parameters such as the pH, temperature, growth time, and presence of salts are important to determine the morphology of the oxides formed. Also the drying procedure and further thermal treatment are critical to determine the final porosity of the carrier.[27] The surface of oxidic supports generally contains a significant concentration of hydroxyl groups, which act as adsorption sites for metal complexes and are key to many interactions between the metal precursor and the support. Depending on the type of support and the pH of the aqueous solution, these groups can become protonated or deprotonated.[28] For each support, in water there exists a pH for which the net charge of these surface groups is zero, so that the net particle charge can be considered nil. Above this pH, more groups are deprotonated and the surface is negatively charged, whereas, below the point of zero charge (PZC), the surface is positively charged due to protonation. Table 1 shows the PZC for several important supports. An extensive list can be found elsewhere.[29]

Oxidic supports can often (partly) dissolve in acidic or alkaline media. This can have a negative effect on the resulting catalyst, such as with the impregnation of aqueous cobalt nitrate on γ-alumina.[30] Partial dissolution of the alumina resulted in loosely bound cobalt particles after drying and thermal treatment, giving rise to attrition during Fischer−Tropsch synthesis and thus contamination of the product stream. However, partial dissolution can also be beneficial. During deposition precipitation of nickel on silica, partial dissolution of the silica has been proposed to facilitate the deposition of a nickel silicate phase, forming small homogeneous particles during subsequent thermal decomposition.[31] Thus, the solubility of the support may play a role in the synthesis of heterogeneous catalysts, although it is rarely considered explicitly.

Table 1. Point of Zero Charge for Several Important Supports in Aqueous Solution[29]

support	PZC range	support	PZC range
SiO_2	2−4	γ-Al_2O_3	8−9
oxidized activated carbon	2−4	activated carbon	8−10
TiO_2	5−7		

3. PRECIPITATION

Precipitation can be induced by a change in conditions such as temperature, pH, or evaporation, and has long been used to produce supported catalysts. Controlled precipitation from a precursor solution follows the principles of nucleation and growth. An initial nucleation boom of tiny crystallites followed by growth without the formation of new nuclei can result in small and quite monodisperse particles. This concept is known as "burst nucleation" and is not only important for precipitation but also key in the synthesis of colloids and can play a role in the synthesis of catalysts via impregnation.

3.1. Coprecipitation

In coprecipitation, salts of the active metal and support are dissolved and mixed such that nucleation and growth of a combined solid precursor of the active metal and support is obtained in a single step. Very high metal loadings of 70 wt % and higher can be achieved while maintaining small particle sizes, and as such, it is the most convenient way to produce catalysts with a high metal weight to volume ratio. Small particles are formed even at these high loadings by creating a very high degree of supersaturation, so that all components nucleate at a high rate and at the same time. This is often realized by mixing two concentrated solutions, the components of which result in an insoluble material when combined. Highly soluble metal nitrates, chlorides, or sulfides can be mixed with basic reagents such as alkali carbonates or hydroxides so that metal carbonates or hydroxides are formed. The low solubility of these compounds causes most of the precursor to precipitate. During coprecipitation, great care has to be taken to prevent local fluctuations in the conditions caused by, for example, temperature gradients, insufficient mixing, or concentration gradients, which can cause additional nucleation events, different or inhomogeneous growth patterns, or the precipitation of different phases. New techniques such as spray-drying and continuous consecutive precipitation can help overcome these practical problems.[32,33]

Coprecipitation can be utilized to produce catalysts such as nickel alumina for steam reforming[34] or iron copper potassium for Fischer−Tropsch synthesis,[35] while most recent systematic studies that have led to increased fundamental insight focused on $Cu/ZnO/Al_2O_3$ catalysts for methanol synthesis. The active sites for this catalyst are metallic copper step sites which are in close contact with Zn.[1] Molar Cu/Zn ratios of 70:30 are most common, while the molar Al_2O_3 content is generally below that of Zn, and preparation is done by combining copper, zinc, and aluminum nitrates and precipitated using alkali (bi)-

DOI: 10.1021/cr500486u
Chem. Rev. 2015, 115, 6687−6718

carbonates.[36] After precipitation and aging, washing steps are necessary to remove residual nitrates and sodium or potassium, which can cause particle sintering and agglomeration during further thermal treatment, leading to a loss of surface area. Titration experiments have shown that precipitation is preferably performed at constant pH. When the pH is slowly increased, sequential precipitation results, whereby Cu is first precipitated followed by Zn.[37] Baltes et al. systematically studied the precipitation at different pH values (4.5−10) and temperatures (30−70 °C), while keeping the subsequent treatments the same (1 h of aging, calcination at 300 °C).[38] The precipitation conditions had little effect on the Cu/Zn/Al ratio, which was similar in all precipitated samples, and close to that of the initial solution (60:30:10). However, large differences were observed in the Brunauer−Emmett−Teller (BET) and Cu(0) surface areas after reduction at 300 °C in H_2 (Figure 2). The lowest Cu(0) surface areas were found at a very

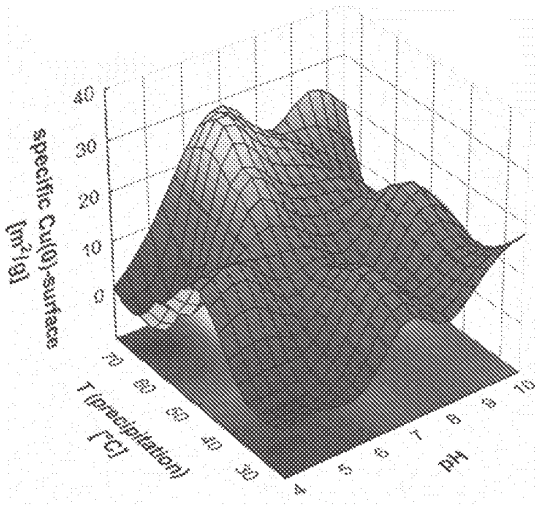


Figure 2. Influence of the pH and temperature during the precipitation of Cu/Zn/Al catalysts on the final specific Cu(0) surface area. After precipitation, all catalysts were aged for 1 h, calcined at 300 °C, and reduced at 300 °C. The final properties of the catalyst were highly dependent on the conditions during precipitation. In general, a higher temperature and a pH between 6 and 7 during precipitation resulted in catalysts with the highest metallic copper surface areas. Adapted with permission from ref 38. Copyright 2008 Elsevier.

low pH, where X-ray diffraction (XRD) revealed large CuO crystallites and ZnO diffraction lines after calcination. High Cu(0) surface areas were generally found at higher precipitation temperatures, with a maximum at a pH of 6−7 at a temperature of >60 °C, in agreement with the results of previous studies. Under these conditions, small CuO particles and some residual zincian malachite, $(Cu,Zn)_2(CO_3)(OH)_2$, were reported after calcination.[38]

Zincian malachite has previously been reported to be the desired precursor for the formation of active methanol catalysts.[39] The crystalline phase is formed during the aging process after initial precipitation, which generally forms an amorphous product due to the fast kinetics of the precipitation process (Figure 3). The resulting zincian malachite consists of thin needles 5−15 nm in width, and forms the general

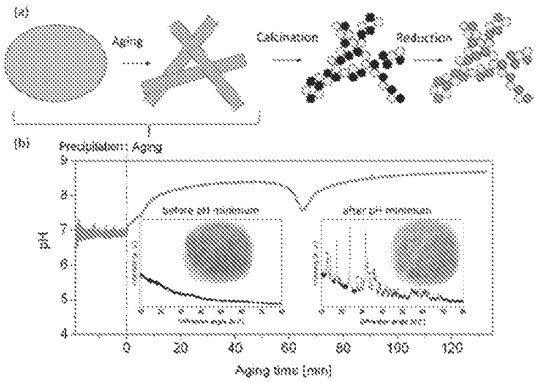


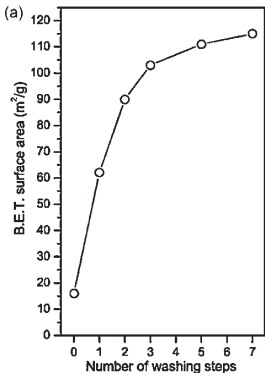
Figure 3. (a) Cartoon of the steps during coprecipitation of Cu/ZnO catalysts. During precipitation, an amorphous material is obtained, which is turned into a crystallite phase during aging. A subsequent calcination step forms small CuO and ZnO particles, the former of which can be reduced. (b) Evolution of the pH during precipitation and aging of a typical Cu/ZnO sample, along with the associated change in color and crystallinity during aging (inset). Adapted with permission from ref 39. Copyright 2012 Royal Society of Chemistry.

mesostructure of the catalyst. By incorporation of Zn, close Cu−Zn interactions enable the formation of small Cu particles during subsequent calcination and reduction.[40] Zander et al. analyzed the aging process of Cu/Zn (molar ratio 70:30) in detail with in situ energy-dispersive XRD (EDXRD) and UV−vis measurements.[39] The precipitate was formed at pH 7 at 65 °C, close to the previously found optimum, and immediately spray-dried to allow separation of the precipitation and aging steps. Subsequently, the aging step was studied in a pH range between 5 and 8, and at temperatures between 50 and 70 °C. Two mechanisms were found for the formation of high Zn incorporation into zincian malachite. At pH > 7, a sodium zinc salt precipitated along with a low Zn content zincian malachite, followed by slow dissolution of the sodium zinc salt and incorporation of the Zn into the zincian malachite during aging. At pH between 5 and 6.5, direct co-condensation of copper and zinc caused direct formation of the zincian malachite, resulting in the highest amount of Zn incorporation (29.2%), close to the total amount added.[40] A study on different precipitation agents for Cu/Zn/Al precipitated at pH 6 and aged for 2 h showed little difference in the obtained crystalline phases and final BET surface area among sodium, potassium, and ammonium carbonate precipitating agents, although use of sodium hydroxide provided a notably lower surface area.[41]

After aging, the zincian malachite precursor is converted into CuO and ZnO particles by a calcination step. Stepwise calcination at 100 °C intervals from 200 to 700 °C showed the best result was usually obtained at 300 °C.[38] At this point, most of the copper was present in the form of small CuO particles, while some degree of zincian malachite was still present. Although decomposition of these last traces was possible at higher temperatures, this also resulted in a sharpening of the CuO XRD diffraction line, corresponding to larger CuO particles due to sintering at the increased temperature. Other studies on Cu/Zn/Al coprecipitates also reported an increase in CuO particle size upon increasing the severity of the calcination procedure. Increasing the calcination time at 350 °C from 1 to 3 h increased the CuO particle size

DOI: 10.1021/cr500486u
Chem. Rev. 2015, 115, 6687−6718

(a)



(b)

Number of washing steps	Calcination gas composition	Calcination gas flow (h^{-1})	B.E.T. surface area (m^2/g)	CuO crystallite size (nm)
0	Air	0	70	12
7	Air	0	100	9
0	Air	$1 \cdot 10^3$	105	8.8
0	N_2	$1 \cdot 10^3$	110	8
0	N_2	$12 \cdot 10^3$	120	7
0	1% NO/N_2	$1 \cdot 10^3$	115	7.6
0	1% NO/N_2	$12 \cdot 10^3$	120	7.2

Figure 4. Evolution of the BET surface area of $Cu/ZnO/Al_2O_3$ catalysts obtained by different washing and calcination treatments after coprecipitation: (a) Na_2CO_3 used as the precipitating agent, followed by calcination in stagnant air, (b) $(NH_4)HCO_3$ used as the precipitating agent, followed by different numbers of washing steps and calcination treatments. Adapted with permission from ref 47. Copyright 2013 Elsevier.

from 3.0 to 3.7 nm, which increased further to 5.0 nm at 400 °C.[42] Similarly, increasing the calcination temperature from 400 to 700 °C brought about a gradual increase from 5.3 to 15.8 nm, highlighting the importance of a relatively mild activation treatment.[43]

Although water is normally used as the solvent for precipitation techniques, high Cu surface areas have been obtained in a solvent mixture of ethylene glycol and water at a ratio of 4:1.[44] Cu/Zn/Al at a ratio of 3:3:1 was precipitated at pH 5 and 70 °C, aged for 2 h, and calcined at 350 °C. It was postulated that the ethylene glycol works as a surfactant that adsorbs on the surface of growing crystallites, thereby inhibiting further growth so that small particles and high surface areas are obtained. However, mixing other polar solvents with water, such as ethanol, tetrahydrofuran, and 1,4-dioxane, had a negative effect on the Cu surface area.

Microwave irradiation has been investigated as an alternative heat source during the precipitation and aging process of Cu/Zn/Al at a molar ratio of 64:32:4 at pH 7.5−8.[45] Although microwave irradiation had little effect on the precipitation process, aging at 70−90 °C using microwave irradiation showed an increased incorporation of Zn compared to regular aging at the same temperature, eventually leading to smaller CuO particles after activation.

3.1.1. "Greener" Coprecipitation Methods. Coprecipitation methods generally require numerous washing steps after precipitation to wash out residual nitrates, sodium, potassium, and other compounds to prevent sintering and agglomeration of particles during thermal treatment. This produces large amounts of wastewater contaminated with nitrates, and although this is undesired, precursor salts based on sulfate or chloride instead of nitrate introduce poisons for the methanol catalyst. To circumvent this, metal formates have been investigated as a precursor replacement.[46] Titration experiments revealed that copper and zinc formates have a higher tendency to simultaneously precipitate, increasing the homogeneity of the metal distribution in the precipitate. In the absence of nitrates, formation of zincian malachite is not possible, and instead, a phase with the general formula $(Cu_{1-x}Zn_x)_2(OH)_3HCO_2$ was formed. Investigation of the crystal structure revealed a maximum Zn incorporation into the precursor phase of around 20% ($x = 0.2$), somewhat lower compared to the 20−30% generally found in zincian malachite when using nitrate precursors. Upon coprecipiatation of Cu/Zn from formate precursors, 12 nm CuO particles were found, somewhat larger than present in conventional systems. However, this was attributed to the lack of Al_2O_3 in the sample and relatively lower amount of Zn. Even so, the catalyst showed a relatively good activity, possible due to the good interaction of the Cu and Zn phases, showing formates are promising nitrate substitutes.

Alternatively, altering the calcination treatment has been shown to circumvent the need for a multitude of washing steps to remove residual nitrates altogether.[47] Cu/Zn/Al catalysts with a molar ratio of 55:30:15 were precipitated using Na_2CO_3 or $(NH_4)HCO_3$ at a pH of 7 and a temperature of 70 °C and aged for 2 h. If no washing was performed, a very low BET surface area of 15 m^2/g was found after calcination in stagnant air for the sample precipitated with Na_2CO_3 (Figure 4). This increased significantly with each washing step, to a maximum of 115 m^2/g after seven steps, illustrating the importance of removing nitrates and sodium to prevent agglomeration of the resulting copper particles. When $(NH_4)HCO_3$ was used as the precipitating agent, the values varied from 70 to 100 m^2/g after calcination in stagnant air depending on the number of washing steps. However, if the calcination was performed in a high flow of N_2, 120 m^2/g was obtained without performance of a single washing step. Moreover, although washing is normally needed to remove sodium from the sample, by using $(NH_4)HCO_3$, the need for a washing step was circumvented altogether, albeit at less than quantitative precipitation of copper. Alteration of the thermal treatment step has been rarely studied for precipitated catalysts, in contrast to catalysts prepared by impregnation and drying, which is discussed in detail in section 4.4.

3.2. Deposition Precipitation

Similar to coprecipitation, deposition precipitation concerns deposition from a precursor solution through a change of pH, temperature, or evaporation, so that metal compounds are formed with a low solubility, often metal hydroxides. In the case of deposition precipitation, this is done in the presence of an existing support, and the concentration of the new compound is increased gradually to prevent formation of bulk phases in solution. Preferential precipitation on the support can be

DOI: 10.1021/cr500486u
Chem. Rev. 2015, 115, 6687−6718

achieved because introduction of the support in the solution causes either a reduction of the surface free energy of tiny nuclei or stabilization of the precipitate, decreasing the energy barrier for nucleation. Hence, conditions exist where nucleation can only occur on the support and not in the bulk solution, so that the support surface functions as a seed for nucleation.[31]

Nucleation of the metal species is generally induced by changing the pH so compounds with a low solubility are formed. When this is done by injection of the precipitant (e.g., alkaline solution), great care has to be taken to prevent local concentrations exceeding the critical supersaturation, which would cause bulk precipitation. Because of this, homogeneous deposition precipitation methods are often preferred, whereby precipitation is induced homogeneously throughout the reaction vessel. This can be achieved by adding urea (at room temperature), which when heated to 90 °C will slowly decompose, resulting in the formation of OH^-, thereby slowly enhancing the pH upon decomposition. Other popular precipitation techniques include the direct reduction of solvated metal ions to the metal[48] or a gradual reduction of the pH by slow removal of ligands such as ammonia via evaporation.[49]

Classically, deposition precipitation was developed to produce catalysts with metal loadings that exceed those obtained by impregnation which is limited by solubility;[50] however, few recent studies in this respect are noted. In one, hexachloroplatinic acid was used as a precursor to deposit up to 60 wt % Pt on a high surface area carbon black via deposition of $PtCl_x(OH)_y(H_2O)_z$ species formed by the decomposition of urea.[51] Increasing the urea/Pt molar ratio from 0 to 80 showed a decrease in size of the Pt particles from 5 to 2 nm (Figure 5)

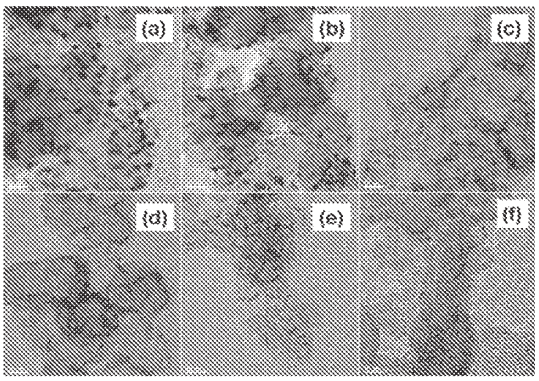


Figure 5. TEM images of 60 wt % Pt/C before reduction, showing the size of the Pt nanoparticle complexes dependent on the amount of urea used during deposition: (a) no urea, (b–f) urea/Pt molar ratio of (b) 5, (c) 10, (d) 20, (e) 40, and (f) 80. Scale bar 10 nm. Adapted from ref 51. Copyright 2009 American Chemical Society.

before reduction. Note that deposition was also possible without addition of urea, suggesting not only precipitation but also adsorption of Pt complexes played a role (see section 4.2). It was postulated that the observed reduction in size was mainly due to electrostatic charge effects: at a higher pH, obtained by more urea addition, Pt complexes with a more negative charge were formed, so that their growth was limited by repulsion. The reduction step was also important for the final metal particle size. When reduction was performed by addition of $NaBH_4$ at room temperature, the high reduction potential of $NaBH_4$ resulted in large particles and agglomerates. When ethylene glycol was added at room temperature instead, small monodispersed Pt particles were obtained by in situ formation of acetaldehyde at 120 °C, which functioned as a reducing agent. A separate study focused on the initial pH of the solution for the production of 40 wt % PtRu (equal molar ratio) on carbon black.[52] Through addition of NaOH, the initial solution was varied between pH 3 and pH 10 before the temperature was raised to 90 °C to start decomposition of urea (urea/PtRu molar ratio of 20). The metal particle size varied from 3.6 nm at pH 3–4 to 2.6 nm at pH 9–10 after reduction in a flow of H_2.

Cobalt has been deposited on silica gel and carbon nanofiber (CNF) supports using deposition precipitation starting from an aqueous solution of cobalt nitrate and urea.[53] At a 15 wt % loading of cobalt, the resulting material consisted of mainly cobalt hydrosilicates on silica, whereas on CNF a weak interaction with the precursor resulted in limited nucleation on the support, with both materials exhibiting large cobalt particles after reduction (40 and 25 nm, respectively). Uniform deposition was more successful when cobalt carbonate and a high initial pH were used instead, and precipitation was induced by evaporation of ammonia at 90 °C, slowly lowering the pH. Using this method, much smaller particles of 8 and 13 nm size were obtained for CNF and silica, respectively. Similar results were obtained in a separate study on Co/TiO_2 at loadings varying between 4 and 24 wt %. Although some small 2 nm particles were found using urea and cobalt nitrate, large unsupported particles were observed, resulting in an average of 20 nm particles at 4 wt % Co and 50 nm at 24 wt % on titania. Deposition precipitation onto titania of cobalt carbonate by evaporation of ammonia resulted in a homogeneous distribution of 9 nm particles at 4 wt % Co, growing only to 15 nm for the sample prepared at 24 wt %.[54] These results show the interaction of the precursor and the support is important to the method of deposition precipitation; when the interaction is too strong, such as with cobalt nitrate and silica, mixed metal–support phases are formed, whereas a too weak interaction, such as with cobalt nitrate and CNF or TiO_2, results in large, unsupported particles. In all reported cases, deposition precipitation of cobalt carbonate by evaporation of ammonia resulted in a more optimal interaction.

3.2.1. Gold Catalysts. Recently, deposition precipitation has frequently been used for the preparation of finely dispersed gold particles at relatively low loadings. A facile and common proceeding starts with an aqueous solution of $HAuCl_4$ to arrive at 0.5–2 wt % loading.[55] The pH of the solution is raised using NaOH, followed by addition of the support under vigorous stirring, and heating to 70 °C. In general, not all gold is deposited from solution, and an investigation on the effects of pH during deposition for Au/TiO_2 revealed the uptake of gold was maximum at a pH around 6, close to the PZC of the TiO_2 support.[56,57] However, this resulted in the formation of large Au particles, while a good compromise between particle size and uptake was obtained at pH 9. This technique has been applied to deposit Au on a variety of supports such as a hydrotalcite,[58] diamond,[59] SiO_2/TiO_2,[60] and Al_2O_3.[61] However, several studies on the mechanism argue that it is technically not a deposition precipitation.[56,62−65] Moreau et al. proposed that electrostatic adsorption takes place at a pH below the PZC for gold deposited on titania, while above the PZC a neutral $Au(OH)_3{\cdot}H_2O$ species adsorbs on two TiO^- surface sites.[65] Cellier et al. compared anion adsorption at pH 3 to deposition precipitation at pH 7 on two titania supports.[64] In both cases,

DOI: 10.1021/cr500486u
Chem. Rev. 2015, 115, 6687–6718

evidence of gold chloride complexes on the surface of the support was obtained, suggesting $AuCl_{4-x}(OH)_x^-$ complexes had reacted with surface OH groups to form surface species, rather than forming a precipitate of the type $Au(OH)_xCl_{3-x}$. Moreover, when titania with a higher surface area was used, a higher Au loading was achieved, corroborating the mechanism of surface adsorption rather than precipitation. It has been argued that an adsorption equilibrium explains why not all Au precipitates from solution, although finite solubility of a precipitate offers an alternative explanation.

Zanella et al. already postulated a similar mechanism of gold surface complexation for the NaOH "deposition precipitation" method in 2002, and compared it with the more conventional deposition precipitation method using urea to slowly raise the pH for the preparation of a Au/TiO_2 catalyst with a nominal loading of 8 wt % Au.[63] Precipitation of all gold in solution was achieved using the urea deposition precipitation method, whereas a maximum Au loading of only 3 wt % was obtained using the NaOH method, suggesting the two involve different deposition pathways. Further study suggested that $AuCl(OH)_3^-$, the dominant species at pH 8, reacts with the surface hydroxyl species in the NaOH method.[66] For the urea deposition method, a gold–urea or gold–urea derivative complex formed with a high N content, although the exact nature of the complex was not reported. It was postulated that initially some $AuCl_{4-x}(OH)_x^-$ anions adsorbed on the positively charged support surface hydroxyl groups at low pH, which serve as nucleation sites for the precipitation of the gold–urea complex species in the first hour. These form relatively large particles, which fragment into smaller particles upon aging as the pH rises further (Figure 6).

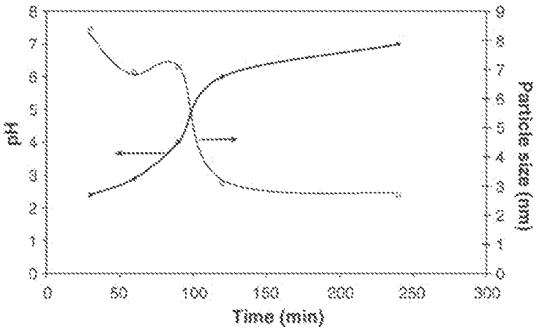


Figure 6. Time evolution of the pH and the Au particle size estimated by TEM during the preparation of 8 wt % Au/TiO_2 prepared by deposition precipitation using urea. Adapted with permission from ref 66. Copyright 2005 Elsevier.

The urea deposition precipitation method was further used to deposit Au on Al_2O_3, TiO_2, ZrO_2, and CeO_2 at loadings between 1 and 7 wt %.[67] In each case, small particles of around 2 nm size were found by transmission electron microscopy (TEM) analysis, and the synthesis was readily scaled up to 50 g without compromise. Moreover, it was concluded that, at a loading of 1 wt %, which was found to be below the absorption capacity of the supports investigated, all the gold was initially adsorbed by the support as $AuCl_{4-x}(OH)_x^-$ species. This first adsorption step was then rapidly followed by a change of speciation by adsorbed gold–urea complex formation, so that again this technically is not a deposition precipitation. Using this method, 1 wt % AuPd bimetallic particles were deposited on TiO_2 and Al_2O_3 with different Au/Pd ratios and very good incorporation of Pd into the Au particles.[68−70]

A thermodynamic model has been proposed to rationalize the cluster size of Au particles during deposition precipitation using urea.[71] A key part of the model is the dependency of the interfacial energy on the electrostatic interaction between the nanoparticles and support, which was related to the PZC of the support and the pH of the solution. The experimental data of 2 wt % Au deposited at a pH of 8 on different supports (Al_2O_3, PZC = 8; TiO_2, PZC = 6; SiO_2, PZC = 4) showed a decrease in particle size from 2.3 to 1.6 nm with decreasing support PZC. Even though further thermal treatments such as drying and calcination were not taken into account, and the authors acknowledged that the model provides only some qualitative trends, while the interactions involved are likely more complicated, the experimental results were in fair agreement with model predictions.

4. IMPREGNATION AND DRYING

4.1. Impregnation

Impregnation and drying is a frequently used preparation method among others due to its simple execution and low waste streams. The first step is contacting a metal precursor solution with a porous support. Common precursors include inorganic metal salts, such as metal sulfates, carbonates, chlorides, nitrates, or acetates, and organic metal complexes, such as metal acetylacetonates. The most commonly used solvent for inorganic salts is water because of the high solubility of many precursors, whereas organic solvents are mainly used for organometallic precursors. To prevent premature deposition of the metal precursor in bulk solution, concentrations below (super)saturation are required.

Two main impregnation methods are distinguished, namely, wet impregnation (WI), whereby an excess amount of solution is used, and pore volume impregnation (PVI), in which an amount to just fill the pore volume of the support is used. The latter method is also known as incipient wetness impregnation (IWI) or dry impregnation (DI), because the impregnated material keeps a dry character at a macroscopic scale. Uptake of the liquid into the pores of the support occurs due to the capillary pressure difference Δp across a hemispherical meniscus in a pore with radius r_p according to the Young–Laplace equation[72]

$$\Delta p = (2\gamma_{lv}/r_p)\cos\theta \quad (2)$$

where γ_{lv} is the surface tension between the liquid and vapor interface and θ is the wetting angle between the solid and the liquid. If $\theta < 90°$, the liquid is considered as wetting and will penetrate the support spontaneously, which is the case with water in combination with most oxidic supports. If the liquid is nonwetting ($\theta > 90°$), the capillary pressure becomes negative and an external pressure is needed to force the liquid into the pores. This can occur for hydrophobic supports such as carbon materials, for which a less polar solvent such as ethanol or 2-propanol may be more appropriate, although this usually comes at the expense of a lower precursor solubility. From eq 2 it is clear the pressure difference depends inversely on the pore size, so that liquid is preferentially sucked up by the smallest pores. The rate at which the liquid fills the pores is generally fast and is often not considered critical for catalyst synthesis. According to the Washburn equation,[73] infiltration of a wetting liquid into

DOI: 10.1021/cr500486u
Chem. Rev. 2015, 115, 6687–6718

a porous body of a few millimeters can occur in seconds to minutes, as has been experimentally verified.[74] However, when the support is prewetted with the same solvent before loading of the precursor via wet impregnation, capillary forces do not play a role and the only driving force for the precursor to enter the support is diffusion, which can take significantly longer.[75]

4.1.1. Pore Filling. Although pore filling occurs rapidly, whether all pores are filled after impregnation to incipient wetness has been questioned. Inhomogeneous MnO_2 and Fe distributions have been observed after calcination on SBA-15 and MCM-41, respectively, and attributed to inhomogeneous filling during impregnation.[76,77] Direct imaging of the impregnated precursor solution is difficult, due to evaporation and decomposition induced by a high-intensity beam of an electron microscope. A first visualization of SBA-15 impregnated with a nickel nitrate hexahydrate solution was done by Sietsma et al. using cryo-TEM.[78] Frozen to −197 °C, many pores were found empty after impregnation (Figure 7), which

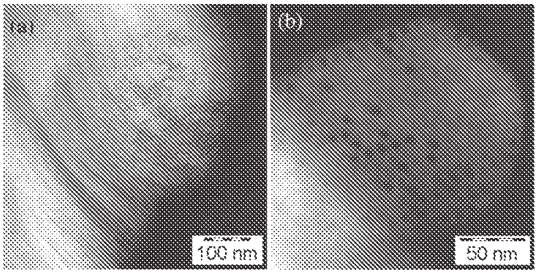


Figure 7. Cryo-HAADF-STEM (cryogenic high-angle annular dark field scanning transmission electron microscopy) images of the SBA-15 pore volume impregnated with an aqueous nickel nitrate solution and frozen to −196 °C, showing several pores remained empty after impregnation. Adapted from ref 78. Copyright 2008 American Chemical Society.

was attributed to the relatively low hydroxyl density of SBA-15 compared to that of regular silica, resulting in incomplete wetting. However, it is also possible N_2 physisorption underestimated the total pore volume of the SBA-15, so that there was not enough liquid to fill all the pores. A more detailed cryo-TEM tomography study was performed by Eggenhuisen et al. on SBA-15 impregnated with cobalt nitrate or nickel nitrate solutions.[79] Although a few empty pores were found mainly on the external edge of the support particles, the majority were filled, and it was concluded that impregnation does lead to an almost homogeneous and complete pore filling. More quantitative measurements on larger samples by differential scanning calorimetry (DSC) have also provided evidence on the complete filling of porous supports (Figure 8).[80] Due to the downward shift in the melting point of liquid confined in nanopores, a distinction was possible between extraporous and intraporous liquid in the material. Incipient wetness impregnation of several ordered mesoporous silicas and silica gels with several solutions, including a eutectic nickel nitrate solution, resulted in fillings between 90% and 100%.

The two-solvent impregnation method, also known as the double-solvent technique, offers an alternative to ensure no material ends up at the outer surface of the support particle.[76] In this method, the support is first dispersed in an apolar solvent such as pentane or cyclohexane. Subsequently, an

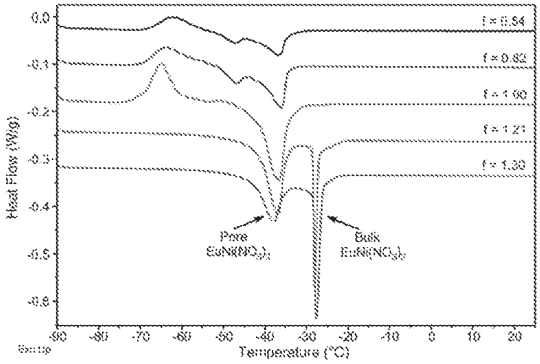


Figure 8. DSC measurements during the heating of a silica gel with 16 nm pores filled with a eutectic nickel nitrate solution ($EuNi(NO_3)_2$). The maximum filled fraction f is defined by $f = V_{EuNi(NO_3)_2}/V_{SiO_2\ pores}$. Due to confinement, the solution in the pores melts (endothermic peak) at a lower temperature compared to the extraporous or bulk solution. Even at a filling of 1.00, no bulk melting was detected, indicating all of the impregnation solution was located inside the pores. Adapted from ref 80. Copyright 2009 American Chemical Society.

aqueous solution containing the metal precursor is added. Due to the favorable wetting properties of the aqueous solvent, i.e., the aqueous phase has a lower contact angle θ, it replaces the apolar solvent in the mesopores of the support. However, inhomogeneous distributions inside the catalyst grains are often reported after drying and calcination when using this method,[81−84] which is at least partly influenced by the choice of the apolar solvent. Van der Meer et al. studied pentane, hexane, heptane, and cyclohexane as apolar solvents for the production of Co_3O_4/SBA-15 from an aqueous solution of cobalt nitrate, followed by drying and calcination.[84] Use of cyclohexane resulted in large aggregates of cobalt particles a few hundred nanometers in size, whereas pentane resulted in relatively small aggregates several tens of nanometers in size. It was proposed that the aggregate size is influenced by the size of the aqueous droplets that form in the alkane phase, which is influenced by the interfacial tension between the polar and apolar solvents. This was lowest for pentane, resulting in the smallest droplets and subsequent aggregates.[85] Comparison of nickel actetate and nickel nitrate on MCM-41 (Ni loading of 1 and 5 wt %) showed more homogeneous distributions were obtained using nickel acetate, suggesting the thermal treatment after impregnation plays a significant role in the distribution of the precursor.[82] In this case, it was postulated that nickel acetate exhibited stronger adsorption on the support surface, thereby limiting redistribution, whereas nickel nitrate redistributed during further treatment due to a weak interaction with the support, as will be discussed in the following sections. Also note that organic material present during subsequent thermal treatments can greatly affect the final dispersion of the catalyst, as discussed in section 4.4.1.

4.2. Adsorption

In general, adsorption of metal ions from aqueous solution onto a support plays an important role when low metal loadings are applied. Electrostatic adsorption requires the pH of the solution to be different from the PZC of the support to create adsorption sites in the form of charged surface hydroxyl

DOI: 10.1021/cr500486u
Chem. Rev. 2015, 115, 6687−6718

groups. This ability of support surface hydroxyl groups in water to become protonated or deprotonated also allows them to function as a pH buffer. When a γ-alumina with a surface area of 200 m^2/g, pore volume of 0.5 mL/g, and surface hydroxyl density of 8 groups/nm^2 is impregnated to incipient wetness with an acidic solution of pH 3, only 1 of 5000 surface groups become protonated so that the surface will be negligibly charged. However, the pH of the solution will rise from 3 to that close to the PZC charge of the γ-alumina, about 8−9.[86] Therefore, adsorption is often low upon incipient wetness impregnation, especially with high precursor concentrations, and when adsorption is desired, wet impregnation is generally applied. It should be noted that the change in pH of the impregnating solution upon impregnation to incipient wetness is often not considered, even though many transition metals are hydrolyzed at high pH, which may result in premature precipitation of metal hydroxides.

Varying names are used for adsorption techniques, such as strong electrostatic adsorption (SEA), ion adsorption (IA), and equilibrium deposition filtration (EDF). All these methods are based on the same general principle. To achieve adsorption, wet impregnation is performed with a large excess of solution, a low concentration of the precursor, and a predetermined pH. The modes of deposition can be globally divided into two main modes of adsorption. Outer sphere complex formation concerns nonspecific, Coulombic or electrostatic interactions of the precursor with the support, whereby the support surface charge is compensated by a layer of charged metal ion complexes in solution. Inner sphere complex formation occurs when support surface groups become directly involved in binding the complex, e.g., when a surface oxygen or hydroxyl group enters the first coordination sphere of the metal complex. A detailed review on the fundamentals of adsorption can be found elsewhere.[87]

4.2.1. Outer and Inner Sphere Complex Formation. Adsorption via outer sphere complex formation concerns mainly electrostatic interactions, and has been formulated into a relatively simple model.[88] In general, multivalent ions preferentially adsorb over monovalent ions.[89] This type of adsorption is highly pH dependent; at a pH at the PZC, the net charge of the surface is zero and very limited or no adsorption takes place. Anions are adsorbed at a pH below the PZC, while cations are adsorbed when the pH is higher. Care should be taken not to use extreme pH values, whereby the high ionic strength of the solution diminishes the adsorption equilibrium constant, so that adsorption is actually reduced instead of improved. Moreover, support dissolution can be significant especially at a pH very different from the PZC of the support.

Recently, Regalbuto et al. used palladium, copper, cobalt, ruthenium, and nickel ammine complexes to obtain silica-supported catalysts at loadings between 1 and 3 wt %.[90] After deposition at a pH of 12, the catalysts were dried and directly reduced. Small particles between 1 and 3 nm in size were found, and calculations showed that these metal loadings were close to the maximum obtainable by electrostatic adsorption for the used silica with a surface area of 180 m^2/g and a PZC of 4.0. It was postulated that the maximum loading mainly depends on the surface area of the support. A follow-up study focused on SBA-15 supports with different surface areas.[91] Ammine complexes were used to deposit Pd nanoparticles of 1.3 nm size at a relatively high loading of 8.7 wt % on 1000 m^2/g SBA-15, and 1.9 nm Pt particles were synthesized on SBA-15 with a 600 m^2/g surface area with a loading of 9.2 wt %, showing high surface areas were indeed beneficial for adsorption. Co particles were also synthesized using this method, but larger particles of 7 nm size at a loading of 5.1 wt % resulted. This was attributed to particle growth that occurred during the high reduction temperature of 800 °C needed to reduce the strongly adsorbing cobalt complexes, whereas the Pt and Pd catalysts were reduced at 350 °C or lower. Moreover, dissolution of the silica support was already observed at pH 9, and 25% of the SBA-15 silica was dissolved after 1 h at pH 10, the optimum pH for the uptake of metal cations. This led to a large increase in pore diameter and pore volume; however, this was not considered a problem due to the relatively thick walls of SBA-15. It was suggested to minimize the contact time to reduce this effect.

Recent studies have focused on adsorption on high surface area carbon supports to obtain high metal loadings. Hexachloroplatinate was deposited on several carbon xerogels with a BET surface area of 650 m^2/g (at pH 11, PZC = 9.4), while platinum tetrammine was deposited on oxidized carbon (at pH 2.5, PZC = 2.4).[92] The maximum loading of hexachloroplatinate was found to be 9.2 wt %, while that of platinum tetrammine was only 4 wt %, and scaled linearly with the mesoporous surface area of the support. It was hypothesized that the platinum ammine complexes, which retain two hydration sheaths, were too large to enter the micropores of the carbon, which was not a problem for the smaller hexachloroplatinate. In each case, small Pt particles between 1.1 and 1.3 nm in size were obtained. In another study, 2 nm Pt particles at a very high loading of 28 wt % were obtained on a carbon black material with a 1500 m^2/g surface area using hexachloroplatinate at high pH.[93] Regalbuto et al. have shown for support material with a lower surface area that high loadings can be achieved by successive impregnation and reduction steps. On carbon xerogel with a surface area of about 600 m^2/g, hexachloroplatinate was deposited at loadings of 7.5, 15.0, and 22.3 wt % for the first, second, and third steps, respectively.[94] Thus, it appeared the adsorbed metal ions formed small particles during reduction, thereby fully regenerating the adsorption sites, as has also been observed during atomic layer deposition (see section 5.3). Moreover, the particle size did not increase significantly upon additional treatments, but stayed constant at 2.0 nm, resulting in an increased particle density upon multiple deposition cycles.

Although short contact times (1 h) resulted in outer sphere complex formation, a longer contact time between platinum tetrammine and oxidized carbon at low pH gave rise to reduction of Pt concurrent with oxidation of the carbon surface.[93] Similarly, when trying to deposit cobalt on a carbon support at high pH, it was found that the cobalt ammine complex was completely converted to Co_3O_4 after 1 h, which did not occur on silica.[95] Reductive ammination of the precursor took place, forming different precipitates depending on the pH (CoO at pH 9.2, Co_3O_4 at pH 9.8, and $Co(OH)_4^{2-}$ at pH > 11 when NH_4OH was used as the base), so that the process is better described as a deposition precipitation. Moreover, at higher pH the cobalt ammine reacted to $[Co(NH_3)_5Cl]Cl_2$, which did not adsorb at all.[96] Nonetheless, particles of 5 nm size were obtained at a Co loading of 6.7 wt % at a pH of 10.

While in each of the previously discussed studies diluted slurries of a powdered support in a large excess of solvent were used, it was recently shown that significant adsorption is also possible during incipient wetness impregnation, in a modified method called charge-enhanced dry impregnation (CEDI).[97]

DOI: 10.1021/cr500486u
Chem. Rev. 2015, 115, 6687−6718

To overcome the buffering effect and charge of the support, very high or low pH values were required (Figure 9). While

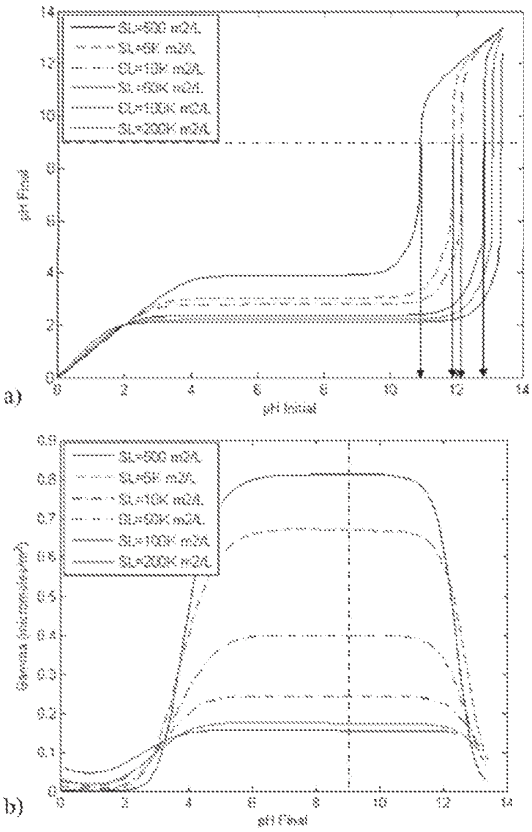


Figure 9. Estimation of the pH needed to obtain maximum cation adsorption for a material with PZC = 2: (a) difference in the initial pH of the solution and the final pH caused by buffering of the support, dependent on the surface loading (SL, defined as the amount of support surface area present in the slurry per liter), (b) cation uptake, dependent on the final pH and surface loading. The dashed blue line in (b) shows maximum uptake around a final pH of 9. In (a), it can be seen that, to obtain this final pH, the slurry should be at an initial pH of 9 for very low SL (a highly diluted slurry), whereas at high SL, such as is the case for incipient wetness impregnation, an initial pH of 13 can be required (the SL at incipient wetness for a material with a surface area of 200 m^2/g and pore volume of 1 mL/g is 200K m^2/L). Adapted from ref 97. Copyright 2013 American Chemical Society.

dissolution of the support could be an issue at such extreme pH, it was reasoned that the buffering effect of the support would result in relatively fast pH equilibration, so that the pH drops to a value where the surface is charged but dissolution is less problematic. Using this method, 2 wt % Pt was deposited on carbon (PZC = 2, pH 13), silica (PZC = 4, pH 13), and alumina (PZC = 8, pH 1). Small particles between 1.5 and 3 nm in size were obtained, much smaller compared to those from a conventional dry impregnation whereby the pH of the impregnating solution was not optimized. Thus, CEDI provides the advantage of obtaining high dispersions without high amounts of wastewater, albeit at relatively low metal loadings.

The principles of strong electrostatic adsorption have also been used to selectively deposit metals on specific surface sites. Using the difference in PZC between Co_3O_4 (PZC = 8) and TiO_2 (PZC = 4), manganese was selectively deposited on cobalt in a Co_3O_4/TiO_2 catalyst by using $KMnO_4$ at a pH of 1, whereby the TiO_2 was negligibly charged.[98] Scanning transmission electron microscopy–electron energy loss spectroscopy (STEM–EELS) showed MnO was located preferentially on the Co_3O_4 (Figure 10), while samples prepared by conventional incipient wetness impregnation whereby the pH was not regulated resulted in MnO dispersed all over the TiO_2 support.[99] However, reduction of the catalyst resulted in migration of the MnO in both cases to the Co/TiO_2 interface, which appeared to be thermodynamically favorable. Similar results were obtained for $MnO/Co/SiO_2$ and $MnO/Rh/SiO_2$, where MnO was preferentially adsorbed on Co_3O_4 or Rh_2O_3, respectively, However, no MnO migration was observed after reduction on the silica support.[100,101]

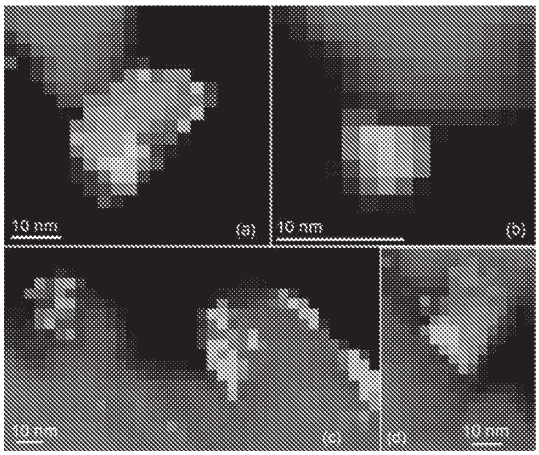


Figure 10. STEM–EELS map for $Mn/Co/TiO_2$. Strong electrostatic adsorption resulted in manganese (green) deposited on the cobalt (red) after calcination (a), which moved to the cobalt titania (blue) interface after reduction (b). By deposition via IWI, MnO was present on the TiO_2 support after calcination (c), which after reduction also migrated to the Co/TiO_2 interface (d). Adapted with permission from ref 99. Copyright 2010 Wiley.

Inner sphere complex formation concerns a chemical adsorption, whereby metal complexes are covalently coordinated to the hydroxyl groups (Figure 11). Because a charged complex is bonded to the support, this is generally compensated through the release or accumulation of protons by the support for a positive or negative metal complex, respectively, leading to a change in the pH of the impregnating solution. Therefore, to optimize procedures whereby inner sphere complex formation occurs, it is often important to actively regulate the pH during the equilibration procedure. In addition, adsorption can occur at a pH similar to the PZC, as described for Au on Al_2O_3 or TiO_2 (see section 3.2.1). The exact nature of adsorption depends on the support, precursor, and conditions, and often both inner and outer sphere complex formation can occur simultaneously.

In a series of papers, Lycourghiotis et al. investigated the method of adsorption on titania (PZC = 6.5, BET surface area

DOI: 10.1021/cr500486u
Chem. Rev. 2015, 115, 6687–6718

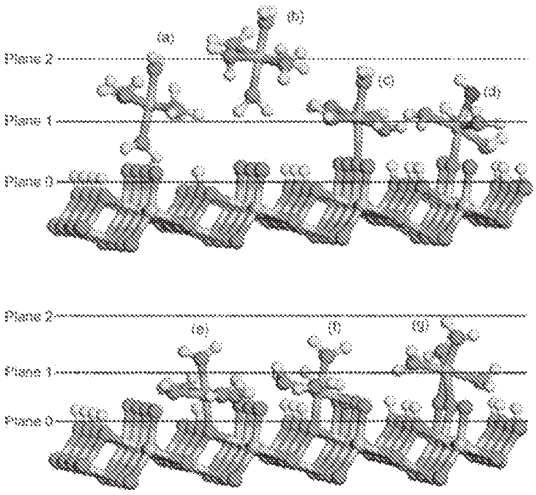


Figure 11. Schematic representation of various deposition possibilities of $Co(H_2O)_6^{2+}$ on (101) anatase: (a) hydrogen bonding, (b) outer sphere complex formation via electrostatic adsorption, (c) inner sphere complex formation via monosubstitution of a H_2O ligand with a terminal surface oxygen atom, (d) monosubstitution with a hydrolyzed compound, (e) formation of a monosubstituted complex with a bridging surface oxygen, (f) formation of a disubstituted complex with one bridging and one terminal surface oxygen, (g) formation of a disubstituted complex with two terminal oxygen groups (Ti in gray, H in yellow, O in red, Co in pink, and oxygen of the hydrolyzed group in blue). Adapted with permission from ref 102. Copyright 2009 Wiley.

50 m^2/g) supported chromium, molybdenum, tungsten, cobalt, and nickel at various pH values ranging from below to above the PZC.[102−106] It was found that CrO_4^{2-}, $HCrO_4^-$, and CrO_7^{2-} mainly adsorb through electrostatic forces to form outer sphere complexes, at a maximum of 1 wt % at pH 4.5.[105] However, the other metals all showed some form of covalent bonding of the metal precursor complex and the titania support. Mo and W complexes showed the highest adsorption of 3 and 10 wt %, respectively, at pH 4. Mainly mononuclear MoO_4^{2-} and WO_4^{2-} species were observed, whereby the complexes were formed via hydrogen bonds or substitution of one or two oxygen ligands with terminal oxygen groups of the titania. Polymeric species were also found in both cases when high initial concentrations and low pH were used, which adsorbed mainly through electrostatic forces. $Co(H_2O)_6^{2+}$ and $Ni(H_2O)_6^{2+}$ species preferentially adsorbed as mononuclear species, whereby one water ligand was replaced by a surface oxygen group, at a maximum of about 2 wt % at pH 7.5. In addition, one or more water ligands not bonding with the support could be hydrolyzed.

The knowledge of the type of species adsorbed at different pH values has allowed for the rational synthesis of supported catalysts. In the synthesis of 1.5 wt % MoO_3/TiO_2 catalysts, it was found that deposition at a constant pH of 6 resulted in much better dispersed catalysts as determined by XPS, which showed a Mo/(Mo + Ti + O) ratio of 2.2 compared to 1.3 for the catalyst prepared at pH 9.[107] It was postulated that the disubstituted MoO_4^{2-} that formed at pH 6, whereby two oxygen ligands of the precursor are replaced with terminal oxygen groups of the TiO_2, was more stable to sintering during subsequent calcination compared to the monosubstituted species which dominated at pH 9. Studies on Co/Al_2O_3 and Mo/Al_2O_3 illustrated the technique is not always easy, as deposition of large crystals or too strongly interacting species which were difficult to reduce also occurred depending on the conditions.[108,109] Nonetheless, Kordulis et al. showed Co/Mo (2 wt %/17 wt %) bimetallic catalysts can be synthesized on an Al_2O_3/SiO_2 mixed support. Co-adsorption of ammonium heptamolybdate and cobalt nitrate at pH 5 resulted in the selective deposition of MoO_4^{2-} on the positively charged alumina, while the silica was negatively charged. Alternatively, Co was preferentially deposited on the silica surface, which resulted in fewer irreducible Co/Al_2O_3 sites. The resulting catalyst was over 10% more active for the hydrodesulfurization of thiophene compared to a similar one prepared via regular impregnation.

In the synthesis of 1 wt % Ni/SiO_2 catalysts using nickel ethylenediamine (en) complexes from nickel nitrate and ethylenediamine, the NiO species were controlled via different graftings of the nickel precursor complex.[110] Both $Ni(en)(H_2O)_4$ and $Ni(en)_2(H_2O)_2$ were grafted onto the support via replacement of two H_2O ligands with surface hydroxyl groups. After calcination, grafted $Ni(en)(H_2O)_4$ gave rise to nickel phyllosilicate formation, eventually resulting in large nickel particles after reduction. However, grafted $Ni(en)_2(H_2O)_2$ brought about isolated Ni^{2+} ions after calcination, resulting in very small particles after reduction. This was attributed to the lack of free H_2O ligands in the adsorbed complex, so that it no longer reacted with other complexes or silicon-containing species.

4.2.2. Metal Distribution. Adsorption also plays a significant role in the metal distribution across macroscopic support grains or pellets.[111,112] Although the pore filling with liquids of larger bodies occurs within a few seconds or minutes, adsorption on support sites often slows penetration of the precursor significantly. After short equilibration times, it is possible that metal precursor complexes are mostly adsorbed in the outer shell of the support body, resulting in an eggshell distribution. The details of an eggshell distribution will strongly depend on the equilibrium between adsorbed and solvated species. A longer equilibration time leads to diffusion of the metal complex toward the center of the catalyst body due to concentration gradients if the adsorption is at least to some extent reversible, so that eventually the system will converge to a homogeneous distribution. Addition of a second component that adsorbs more strongly than the precursor can result in egg-white or egg-yolk distributions (Figure 1). The additional component adsorbs in the outer shell, leaving no sites available for the metal precursor complex, which diffuses inward where more adsorption sites are available. Although this has been known for a long time, the subsequent drying step is also reported to have a large impact on the distribution, and direct monitoring of the distribution during impregnation is now possible by advanced spectroscopic techniques that have recently been developed.[113]

Using Raman spectroscopy, the impregnation of 3 mm γ-Al_2O_3 pellets (PZC = 9) with ammonium heptamolybdate (AHM) solutions at pH 5 or 9, leading to 15 wt % Mo, was followed over time.[114] Because of the equilibrium between heptamolybdate and monomolybdate, $Mo_7O_{24}^{6-}$ was the predominant species at pH 5, while at pH 9 mainly MoO_4^{2-} was found. Upon impregnation with the solution at pH 9, close to the PZC of the γ-Al_2O_3, the surface was minimally charged

DOI: 10.1021/cr500486u
Chem. Rev. 2015, 115, 6687−6718

and almost no interaction took place between the precursor and support, which led to a homogeneous MoO_4^{2-} distribution across the pellet after 10 min. With an impregnation solution of pH 5, the γ-Al_2O_3 was positively charged, and electrostatic adsorption of $Mo_7O_{24}^{6-}$ took place at the outer edges of the surface. At the same time, the buffering effect of γ-Al_2O_3 resulted in an increase in the pH and MoO_4^{2-} formation, which more easily diffused toward the inside of the pellet. Moreover, $(NH_4)_3[Al(OH)_6Mo_6O_{18}]$ precipitated on the external surface, preventing a large part of the Mo from diffusing into the pellet altogether. When a γ-Al_2O_3 with a lower PZC of 8 was used, areas of high Mo concentrations were found throughout the pellet at long equilibration times with diagonally offset Raman spectroscopy and X-ray absorption tomography.[115,116] These were attributed to the formation of $Al(OH)_6Mo_6O_{18}^{3-}$ species throughout the support due to the lower buffering capacity of the alumina with PZC = 8 instead of 9 as in the previous study. This was mitigated by co-impregnation of a species that forms stable complexes with Mo^{6+}, such as citrate or H_3PO_4, which resulted in homogeneous distributions after a sufficient time for equilibration.[114,116]

The concentration of the precursor has also been found important, which can be explained by the limited adsorption capacity of a support surface. For $Co(H_2O)_6^{2+}$ complexes impregnated on alumina, little interaction is expected between the positive complex and the protonated or neutral surface hydroxyls. Nonetheless, impregnation of a 3.85 mm γ-Al_2O_3 pellet with a low concentration (0.2 M) of $Co(NO_3)_2$ took 4 h for equilibration, as followed with ^1H magnetic resonance imaging (MRI),[117] while in a different study impregnation of a 3 mm γ-Al_2O_3 pellet with a higher concentration (1.35 M) of $Co(NO_3)_2$ solution showed a homogeneous distribution already after 5 min.[118] Bergwerff et al. further studied the impregnation of 0.2 M Co^{2+} by varying the pH and citric acid concentration using ^1H MRI.[119] If no citric acid was added, a homogeneous distribution was obtained after 160 min at pH 1. Addition of citric acid at pH 1 did not lead to the formation of cobalt citrate complexes, so that competitive adsorption between $Co(H_2O)_6^{2+}$ and free citric acid resulted in more rapid transport of Co^{2+} to the center of the 3.85 mm pellet, producing egg-yolk catalysts after 90 min of equilibration (Figure 12). At pH 5 and 9, cobalt citrate complexes formed which strongly adsorbed on the surface of the γ-Al_2O_3, resulting in eggshell distributions of varying degrees even after 48 h. However, addition of extra citrate to these solutions again resulted in competitive adsorption, so that the Co^{2+} complexes migrated toward the center more rapidly.

Nickel combined with ethylenediamine showed similar results. Upon impregnation of a 3 mm γ-Al_2O_3 pellet with 0.5 M $Ni(H_2O)_6^{2+}$ and en at different Ni/en molar ratios (0, 1, 2, and 3), homogeneous $Ni(H_2O)_6^{2+}$ and $Ni(en)_3^{2+}$ distributions were found after 5 min for Ni/en ratios of 0 and 3, respectively.[120] At other ratios, $Ni(en)_x(H_2O)_{6-2x}^{2+}$ complexes formed which strongly adsorb, resulting in eggshell formations after 5 min, and a 2 h equilibrium period was necessary to obtain homogeneous distributions. On a 3.85 mm pellet, 5 min was not sufficient to obtain a homogeneous distribution upon impregnation of a 0.5 M $Ni(H_2O)_6^{2+}$ solution.[121] This relatively slow equilibration of weakly interacting species was attributed to partial hydrolysis and subsequent redissolution of nickel nitrate. While the PZC and surface area of this pellet were similar to those of the pellet used in the previous study, the difference might be attributed to the lower pore volume of the pellet, so that the amount of surface area per volume of impregnating solution doubled, allowing for more interaction with the support. Regardless, after 1 h a homogeneous distribution was found. Combined with ethylenediaminetetraacetic acid (EDTA) at a molar ratio of Ni/EDTA of 6 at pH 1 or 6, slight eggshell formations were found due to the formation and electrostatic adsorption of $Ni(EDTA)^{2-}$ and $Ni(EDTA\text{-}H)^{-}$ complexes in the external shell, while the remaining $Ni(H_2O)_6^{2+}$ was homogeneously distributed throughout the rest of the pellet. Equilibration was faster at pH 1, for which less hydrolysis of $Ni(H_2O)_6^{2+}$ species occurred. This difference in equilibration time based on pH was even more pronounced for $Cr(H_2O)_6^{3+}$ complexes, where very defined eggshell profiles were formed at pH 4.5 due to hydrolysis of the precursor, while uniform distributions were obtained at pH 1.[122] When CrO_4^{2-} complexes were used as the precursor, the roles were reversed. Strong electrostatic adsorption at low pH led to egg-white structures, while high pH led to limited interaction and therefore a homogeneous distribution. In this case, citric acid was found to limit hydrolysis of the Cr^{3+} complexes, while it also caused reduction of Cr^{6+} to Cr^{3+}, so that in most cases homogeneous distributions were obtained.

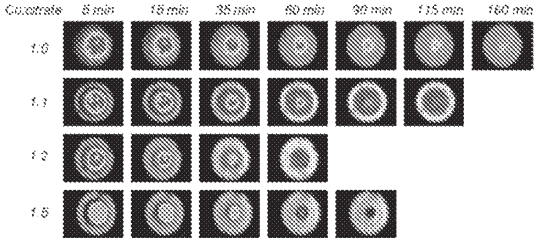


Figure 12. 2D ^1H MRI images recorded on an Al_2O_3 extrudate after impregnation with 0.2 M $Co(NO_3)_2$(aq) at pH 1 with different molar ratios of cobalt to citrate. The blue color indicates a low cobalt concentration, yellow indicates a medium cobalt concentration, and red indicates a high cobalt concentration. The higher the amount of citric acid, the faster cobalt migrated to the inside of the pellet, resulting in more concentrated egg yolks, while the eggshells with only medium cobalt concentrations (yellow) became larger. Adapted with permission from ref 119. Copyright 2008 Wiley.

In the previous study, competitive adsorption was also studied using H_3PO_4. This led to egg-yolk catalysts upon co-impregnation with Cr^{6+} species.[122] Another example of competitive adsorption is Cl^- and $PdCl_4^{2-}$. Five minutes after impregnation, all $PdCl_4^{2-}$ had hydrolyzed to $PdCl_2(OH)_2^{2-}$ at the edge of the γ-Al_2O_3 pellet due to the basic surface OH groups, regardless of the Cl^- concentration and pH.[123] After 2 h, egg-white distributions were obtained at pH 1 because many sites at the edge of the pellet were protonated followed by adsorption of Cl^-, so that the $PdCl_2(OH)_2^{2-}$ moved deeper into the pellet for adsorption on free sites. At pH 5, Cl^- adsorption was less favorable so that eggshell distributions were still detected. After 96 h each of the four main distributions (Figure 1) could be obtained depending on the conditions used. An egg-white distribution was obtained by strong and competitive Cl^- adsorption at low pH, which was limited to the outer shell of the pellet at low Cl^- concentration, while at higher Cl^- concentration more competitive adsorption resulted in an egg-yolk profile. At higher pH and low Cl^- concentration,

DOI: 10.1021/cr500486u
Chem. Rev. 2015, 115, 6687−6718

limited competitive adsorption resulted in an eggshell catalyst, while increasing the Cl^- concentration resulted in a more homogeneous distribution.

4.3. Drying

The drying step has long been known to have a strong influence on the final catalyst.[112,124] Drying can be separated into three main stages, the increasing rate, constant rate, and falling rate periods. The increasing rate period concerns the time it takes for the system to attain the equilibrium drying temperature, which is slightly lower than the temperature set on the drying oven because evaporation is an endothermic process, but a pseudo steady state is generally achieved relatively rapidly. In the constant rate period, drying mainly occurs on the external surface of the drying grain or pellet. The system is in what is called a pendular state, whereby a continuous liquid exists throughout the particle, such that the solvent can be transported toward the external surface of the catalyst grain via capillary forces. If the precursor has a weak interaction with the support, it may be transported toward the external surface along with the solvent, resulting in a concentration buildup on the external rim of the support. As a consequence of the resulting concentration gradient, back-diffusion toward the inside of the grain can occur. At a certain time, the amount of solvent has been reduced to such an extent that capillary flow toward the external surface of the catalyst grain can no longer keep up with the rate of drying, and the drying front moves inward. As this happens, the drying rate slows as transport via the vapor is slower than via the liquid, and the liquid inside the pores becomes discontinuous, called the funicular state, so that isolated patches of liquid can form, and macroscopic redistribution at this stage becomes very limited.

As the solvent is removed during drying, the concentration of the precursor will rise, and once it reaches the critical supersaturation, precipitation will take place. Moreover, a chemical change of the precursor induced by dehydration, temperature, or a gas atmosphere can result in precipitation. As systems likely go through severe macroscopic redistribution across the catalyst grain or pellet during drying, precipitation can be important for the final macroscopic distribution of the active phase. It should be noted that many organic molecules such as citric acid or EDTA have previously been reported to change the viscosity of the impregnating solution.[125] This was recently shown in the preparation of 1−20 wt % Fe catalysts on α-Al_2O_3 by Torres et al., who compared the effect of iron nitrate and ammonium iron citrate on the iron distribution of the final catalysts.[126] Iron particles of around 20 nm were found regardless of the precursor at loadings of 5 and 10 wt % Fe. However, iron nitrate resulted in high local loadings, while other parts of the support remained empty, whereas ammonium iron citrate led to a homogeneous distribution. This was attributed to the formation of a gel-like phase for the citrate precursor, thereby preventing redistribution. Addition of ethylene glycol (EG) in the preparation of 20 wt % Ni/MCM-41 catalysts prepared from nickel nitrate has been shown to prevent redistribution of nickel to the external surface during thermal treatment, which happened to a great extent when EG was not co-impregnated.[127] However, few other recent studies have been performed on the effects of the viscosity, although the addition of organic molecules has been used extensively to obtain a higher metal dispersion, which is discussed in the section on activation (4.4.1).

4.3.1. Drying of Strongly or Weakly Adsorbing Species. Since drying concerns movement of solvated species on a large scale, it is important to consider the degree of adsorption of the metal species in solution. Recently, Liu et al. modeled the effects of drying on porous bodies with different metal profiles after impregnation.[75] Although 0.25 M nickel nitrate was used as a case study, the developed methodology presented was not limited to specific active components or supports, and the interaction between the two could be parametrically varied. By varying the strength of adsorption of nickel nitrate to the support, and varying the nickel nitrate distribution after impregnation from homogeneous to eggshell, the effect of drying was studied. For a high adsorption strength, drying had little effect on the distribution, so that the main determining factor for the distribution was the impregnation step. A homogeneous distribution after impregnation remained homogeneous after drying, while eggshell distributions remained largely unchanged when the adsorption strength was high.

Recent improvements in spectroscopic techniques have enabled imaging of distributions after impregnation and drying, providing experimental evidence of the limited effect of drying on strongly adsorbing species. UV−vis and IR microspectroscopy showed nickel ethylenediamine complexes (0.5 M) with one or two en ligands grafted on γ-alumina did not redistribute during drying, whereas nonadsorbing $Ni(en)_3^{2+}$ migrated toward the outside of the support.[120] Strongly adsorbing Pd species (0.1 M $PdCl_4^-$ solution) on alumina were studied with UV−vis microspectroscopy, and were also found to retain the distribution they had obtained during impregnation after drying.[123] Using magnetic resonance imaging, cobalt nitrate at low concentration (0.2 M, pH 4) was found to adsorb sufficiently strongly to a γ-alumina surface to retain its eggshell distribution obtained during impregnation after drying.[128] Thus, these studies confirm that, for strongly adsorbing species, the drying step does not alter the macroscopic distribution of the precursor to a large degree.

For weakly adsorbing species and high concentrations, convection and back-diffusion during the drying step become very important. In the model of Liu et al., when the adsorption strength of nickel nitrate was reduced to a moderate value and assuming a homogeneous distribution after impregnation, drying could result in severe redistribution of the 0.25 M nickel nitrate solution on γ-alumina depending on the conditions.[75] Drying at 70 °C resulted in an almost homogeneous distribution. However, increasing the drying temperature to 300 °C resulted in eggshell distributions, because back-diffusion of nickel nitrate was not fast enough to compensate for the high drying rate. Similar results were obtained upon alteration of the humidity of the drying air; at 0.5% humidity, drying was relatively fast, resulting in an eggshell distribution, while drying in 10% humidity resulted in an almost homogeneous distribution. Finally, the size of the support pellet had a great influence on the distribution. A pellet diameter of 1 mm resulted in a moderate eggshell distribution whereby the concentration of nickel nitrate in the shell was 1.5 times higher than in the center of the pellet. For a 10 mm pellet, the concentration in the shell was almost 3 times higher compared to that in the center. The model was recently extended to a 3 mm γ-alumina pellet impregnated with nickel nitrate concentrations ranging from 0.005 to 4.0 M (Figure 13), and many of the results were compared to experimental data.[129,130] A very low nickel nitrate concentration (0.005 M)

DOI: 10.1021/cr500486u
Chem. Rev. 2015, 115, 6687−6718

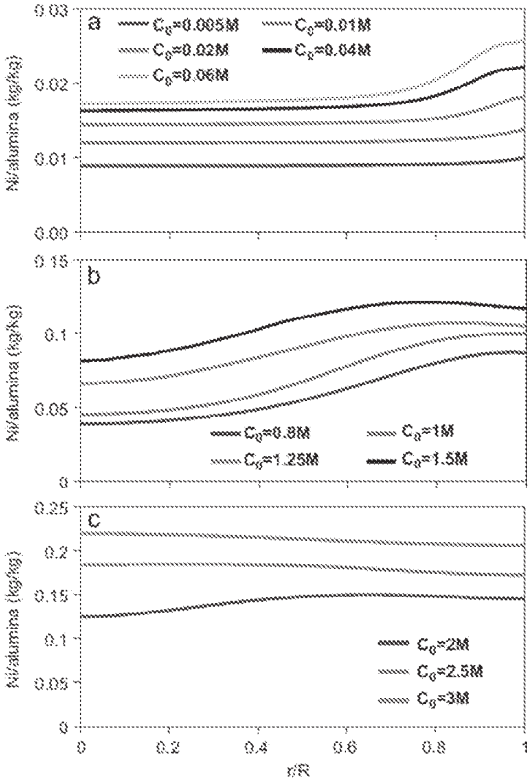


Figure 13. Simulated effect of the initial $Ni(NO_3)_2$(aq) concentration on the final metal profile across a 3 mm γ-Al_2O_3 pellet after drying at 80 °C, starting from a homogeneous distribution after impregnation: (a) low metal loadings, (b) moderate metal loadings, (c) high metal loadings. The loading of nickel is plotted as a function of the normalized radial distance r/R, whereby r is the distance from the center of the pellet and R is the pellet radius. Adapted with permission from ref 130. Copyright 2012 Elsevier.

resulted in homogeneous distributions after drying at 80 °C because most of the nickel nitrate remained adsorbed on the γ-alumina. At a slightly higher concentration (0.06 M), the amount of nickel nitrate exceeded the adsorption capacity of the support, and an eggshell distribution was obtained due to convective redistribution toward the edge of the pellet. Although back-diffusion gave rise to partial mitigation of this redistribution, the system entered the falling rate period relatively rapidly, so that film breakage occurred and material was no longer transported across large distances. At even higher concentrations (3 M), the precursor was also initially transported toward the outer edge of the pellet, but the concentration was so high that film breakage did not occur, so that sufficient back-diffusion time resulted in a homogeneous distribution. It should be noted that, in these model systems, only the solvent water was removed, leaving the nickel nitrate hexahydrate, which melts in its own crystal water above 56 °C, intact. Nonetheless, good agreement was found between the model predictions and real experiments, suggesting macroscopic distribution occurs mainly during the removal of the solvent, not removal of the crystal water of metal nitrates.

An interesting consequence of these considerations is that precursor material present on the external surface of the catalyst grain or pellet does not necessarily mean it will be deposited there during drying. If material remains on the external surface during impregnation, capillary flow can still pull it in when part of the pore volume becomes accessible again due to (partial) evaporation of the solvent, assuming the material on the external surface is still dissolved or can be molten. The latter case closely resembles melt infiltration, which will be discussed in detail in section 5.1.

Other experimental evidence on redistribution of the precursor during drying has been reported in recent years. Impregnation of a basic AHM solution (1.8 M, pH 9) onto γ-alumina resulted in little interaction with the support, so that redistribution toward the external portion of the pellet resulted in eggshell distributions.[131] Alternatively, addition of H_3PO_4 to an impregnation of γ-alumina with AHM resulted in surface adsorption of PO_4^{3-}, so that the support surface was not significantly charged even at pH 2, together with complex formation of the form $H_xP_2Mo_5O_{23}^{6-x-}$.[116] While normally AHM would adsorb to the alumina surface at this low pH, the negatively charged complex only weakly interacted with the PO_4 surface groups, so that redistribution of the complexes also resulted in eggshell distributions. As mentioned earlier, weakly interacting $Ni(en)_3$ complexes redistributed during drying, resulting in eggshell profiles.[120] Clearly, weakly interacting species can migrate over macroscopic distances during the drying step.

4.3.2. Metal Redistribution at the Nanoscale. Macroscopic distributions can be largely avoided by reducing the grain size of the support. This is often done in academia to rule out the effect of macroscopic distributions on the catalyst performance. However, even though support grains might be homogeneously distributed on the macroscale, inhomogeneities are frequently reported on the nanoscale. The active metal is often located in large clusters or aggregates, while a large part of the support remains empty. These aggregates can be much larger than the average pore diameter, and the nanoparticles often form an intricate network throughout the pore structure.[132] Moreover, the crystallites inside these aggregates have been observed to have an overall crystallographic alignment, suggesting they are closely linked to each other or were at some point during their synthesis.[133] Methods to prevent this include modification of the support or co-impregnation of organic molecules.[134,135] However, recent studies revealed these inhomogeneous distributions can be circumvented by careful control of the drying step.

Using Stöber silica spheres impregnated with nickel nitrate solutions, Banerjee et al. used environmental TEM to study the distribution of the nickel phases during preparation. It was shown that inhomogeneous distributions obtained after in situ drying of an aqueous solution largely remained after calcination and reduction, while use of ethanol as a solvent resulted in more homogeneous distributions, which was attributed to the lower surface tension of ethanol.[136] Munnik et al. used a silica gel (38−75 μm grains) impregnated with a 4.2 M aqueous cobalt nitrate solution, close to saturation, and opted for drying in a N_2 flow in a fluidized bed reactor at different temperatures instead of the often-practiced stagnant drying in a muffle oven, followed by calcination at 350 °C in a N_2 flow.[16] While all of the samples displayed uniform cobalt distributions on the macroscale, drying at 25 °C followed by calcination resulted in 8 nm cobalt oxide particles clustered together in aggregates of

DOI: 10.1021/cr500486u
Chem. Rev. 2015, 115, 6687−6718

40 nm size. Increasing the drying temperature gradually reduced the aggregate size until at 100 °C the 8 nm particles were homogeneously distributed over the support and no aggregates were found. However, a further increase of the drying temperature to 150 °C resulted again in aggregate formation, up to 80 nm in size (Figure 14). This behavior was

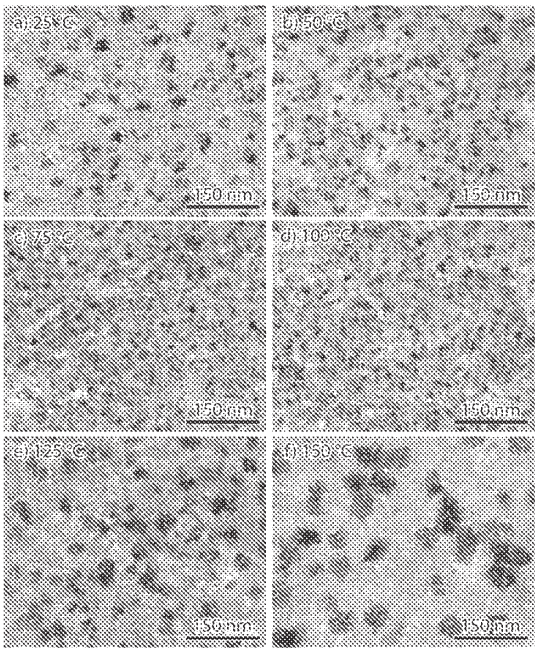


Figure 14. TEM images of calcined Co_3O_4/SiO_2 after drying treatments in a N_2 fluidized bed at different temperatures: (a) 25 °C, (b) 50 °C, (c) 75 °C, (d) 100 °C, (e) 125 °C, (f) 150 °C. Different extents of cobalt aggregation (black) were observed on the silica support (gray) depending on the drying temperature. The size of the primary cobalt oxide nanoparticles was ~9 nm in all cases. Adapted from ref 16. Copyright 2014 American Chemical Society.

further studied by performing a calcination in a gas flow of 1% NO/N_2 after the drying treatment, which resulted in immobilization of the cobalt nitrate precursor via cobalt hydroxynitrate formation, so that further redistribution after drying was not possible.[137] After drying at 25 °C and calcination in a NO/N_2 gas flow, 3−4 nm cobalt oxide particles were found in large irregularly shaped aggregates up to 200 nm in size. Increasing the drying temperature reduced the size of the aggregates, until at 100 °C a homogeneous distribution of 3−4 nm cobalt particles was obtained.[138] A further increase of the temperature resulted in 8 nm cobalt particles in increasingly large aggregates. It was postulated that aggregation originated from two separate mechanisms. At low temperature, precipitation of a cobalt nitrate species occurred when the concentration reached supersaturation. If the drying rate is low, nucleation of this species is relatively slow so that growth becomes very significant, resulting in large cobalt nitrate islands, while other areas on the support become depleted. Raising the temperature increased the drying rate, so that the nucleation rate increased and smaller islands were formed, eventually resulting in a homogeneous distribution at 100 °C. This behavior shows a resemblance to what is observed in the drying of colloidal wet films[139,140] and suggests that at low temperature aggregate formation is mainly a physical process. At temperatures above 100 °C, nucleation and growth of cobalt oxide due to decomposition of cobalt nitrate was found to occur during drying. As this mainly occurred in the presence of a large amount of water, either in liquid or vapor form, the cobalt nitrate was highly mobile and nucleation and growth of cobalt oxide resulted in increasingly larger aggregates.[138]

The effect of precursor−support interactions was also investigated for a γ-alumina support. While stagnant drying in a muffle oven between 60 to 120 °C always resulted in 8 nm cobalt particles located in 30−60 nm aggregates after calcination in a N_2 flow, drying in a fluidized bed between 25 and 100 °C resulted in the 8 nm particles being uniformly distributed throughout the support after calcination.[138] At 150 °C, aggregates of 30−40 nm size were found, somewhat smaller than on silica. Thus, it appeared that the increased support−precursor interactions of the γ-alumina inhibited aggregate formation. Moreover, although drying in stagnant air always resulted in aggregates, drying using a N_2 flow resulted in uniform distributions, showing the importance of rapid removal of water during the drying process. It should be noted that fast drying can have a negative effect on the macroscopic distribution across catalyst grains when precipitation occurs without sufficient time for back-diffusion, as mentioned in the previous section and observed for silica with larger pores of 23 nm.

Aggregate formation due to a long retention time of water vapor has also been used for the synthesis of nanocast materials. Starting from iron nitrate, large iron oxide aggregates up to 2000 nm in size were synthesized on an ordered mesoporous silica support by covering up the sample container during a heat treatment to 150 °C.[141] Similar results were found for cobalt, nickel, indium, manganese, cesium, and chromium oxides when starting from the respective metal nitrates, showing the importance of the water pressure during drying and decomposition of metal nitrate hydrates in general.

4.3.3. Alternative Drying Methods. While drying is most often performed in stagnant air in a regular muffle oven, other alternatives besides fluidized bed drying are available that alter the rate of drying or the drying process, and so influence the distribution of the active metal phase. In freeze-drying the precursor is frozen after impregnation, followed by sublimation of the immobilized solvent at reduced temperature and pressure. Eggenhuisen et al. performed freeze-drying on SBA-15 impregnated with nickel or cobalt nitrate by freezing in liquid nitrogen and drying at −55 °C under reduced pressure.[79] Using cryo-TEM tomography to visualize the dried samples, it was shown that freeze-drying resulted in homogeneous distributions of cobalt nitrate after drying, whereas inhomogeneous distributions were obtained after conventional drying at 60 °C (Figure 15). This difference in nanoscale distribution was largely maintained after a thermal activation was performed, illustrating the drying step is highly important for the final metal distribution at the nanoscale. The method was also shown to work on a silica gel for cobalt nitrate and nickel nitrate.[24,142] However, freezing the precursor required great care.[142] When a liquid is confined in nanometer-sized pores, the freezing and melting points can be greatly depressed. While a 4.2 M cobalt nitrate solution froze at about −30 °C, confinement in a silica gel with 8 nm pores caused a freezing point depression to −90 °C. Thus, to properly freeze and dry

DOI: 10.1021/cr500486u
Chem. Rev. 2015, 115, 6687−6718

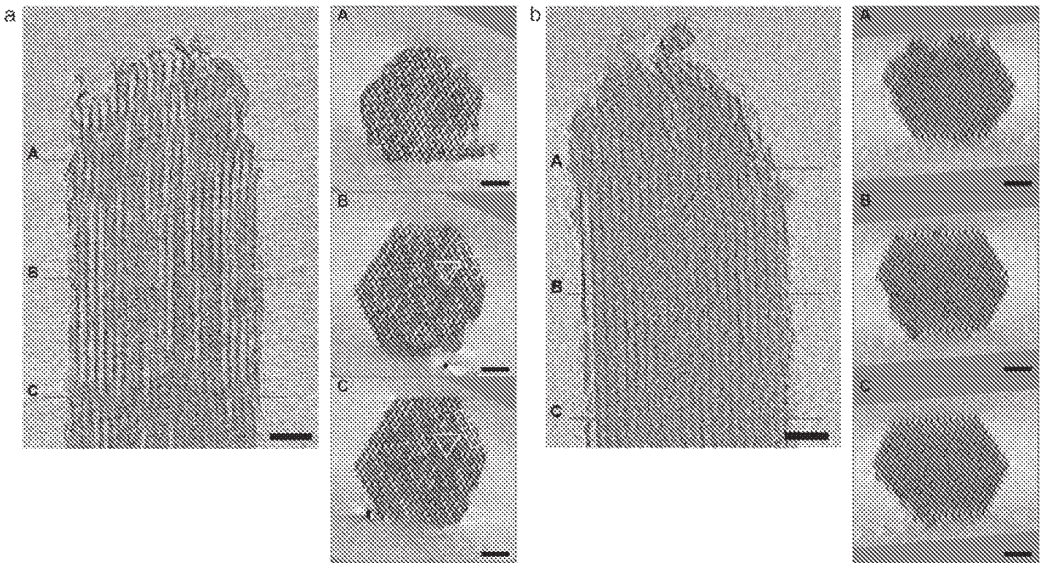


Figure 15. Cryo-TEM tomography results of $Co(NO_3)_2$ salt distribution in mesoporous SBA-15 after different drying treatments: (a) dried at 60 °C in a muffle oven, showing an inhomogeneous distribution after drying (triangles and rectangles in (B) and (C) indicate examples of pores with inhomogeneous fillings), (b) dried by freeze-drying, showing a homogeneous distribution after drying. All scale bars are 50 nm. Lines A, B, and C indicate the positions of the cross-sections. Bright dots and lines are empty pores; dark areas are filled pores. Adapted from ref 79. Copyright 2013 American Chemical Society.

the impregnated sample, a temperature of −90 °C or lower should be applied. Therefore, although liquid nitrogen temperatures were sufficient to freeze the confined precursor, −45 °C was not sufficient to solidify the precursor, and redistribution was observed over the macroscopic catalyst grains, creating distinct eggshell distributions.

Microwave drying provides another alternative. It has the potential to speed up drying drastically due to the volumetric heating of the material, removing the need for heat transport from the outer edge of the particle toward the center. Liu et al. studied microwave drying on 3 mm pellets impregnated with different concentrations of nickel nitrate solutions from 0.1 to 2 M.[130] In all cases, homogeneous macroscopic distributions across the pellet were obtained. Moreover, the drying step was completed in a relatively short amount of time. It was proposed that uniform drying reduced convection so that more homogeneous distributions were obtained.

4.4. Activation

In the activation step the deposited metal precursor is converted into the active phase. Generally, this is done by a calcination step, resulting in the metal oxides, followed by a reduction if metallic particles are required. Next to metals, common active phases include metal oxides or metal sulfides.

4.4.1. Formation of the Active Phase. The activation treatment leads to the formation of nanoparticles, and often has a large influence on the final particle size. Moreover, although most treatments remain below the melting point of the active materials, the temperatures used can easily exceed the Hüttig temperature ($T_{Hüttig} = 0.3T_{melt}$), around which defect sites on metal particles become mobile, or even the Tammann temperature ($T_{Tammann} = 0.5T_{melt}$), whereby surface atoms become mobile, which can lead to particle growth via migration and coalescence of the particles or via Ostwald ripening.

Although direct reduction of many precursors can lead to well-dispersed catalysts, direct reduction is often highly exothermic and can lead to mixed metal−support phases. Moreover, it can produce a pyrophoric catalyst that needs to be passivated, often making it impractical for use on an industrial scale. Therefore, a calcination procedure is usually performed to form the pure metal oxide particles before further treatment such as reduction. Both the heating rate and air flow during calcination have been shown to be highly important for the preparation of 23 wt % Co/γ-Al_2O_3 catalysts for the Fischer−Tropsch synthesis. Heating rates between 0.1 and 1 °C/min resulted in similarly active catalysts; however, higher heating rates of 4 and 8 °C/min significantly reduced the activity when calcined to 250 °C.[143] Air flows of 1 $m^3/(kg_{Co(NO_3)_2}\cdot h)$, roughly corresponding to a gas hourly space velocity (GHSV) of 2000 h^{-1}, and higher during calcination resulted in similar catalysts with a cobalt surface area of 11 m^2/g; however, at lower flows cobalt surface areas as low as 6 m^2/g were obtained. In a separate study, flows higher than the above-mentioned 1 $m^3/(kg_{Co(NO_3)_2}\cdot h)$ were used to investigate the gas composition and calcination temperature in the synthesis of 20 wt % Co/γ-Al_2O_3.[144] Although calcination at temperatures between 150 and 500 °C for 10 h showed almost complete decomposition of the cobalt nitrate regardless of the temperature, dispersions of around 9% were found at 150 °C, whereas at 400 °C this was slightly lower (7.5%). Upon testing the gas composition, only 50% steam/air produced lower cobalt dispersions, whereas little difference was observed between N_2 and air.

Sietsma et al. studied the calcination of nickel nitrate on SBA-15 (24 wt % Ni).[145] After drying at 120 °C, the precursor was found only inside the pores of the SBA-15 support, in the form of 9 nm crystallites of $Ni_3(NO_3)_2(OH)_4$, similar to the pore size of the support. Thermal decomposition of this phase

DOI: 10.1021/cr500486u
Chem. Rev. 2015, 115, 6687−6718

in stagnant air resulted in severe redistribution and large particles on the external surface of the support (Figure 16). In a

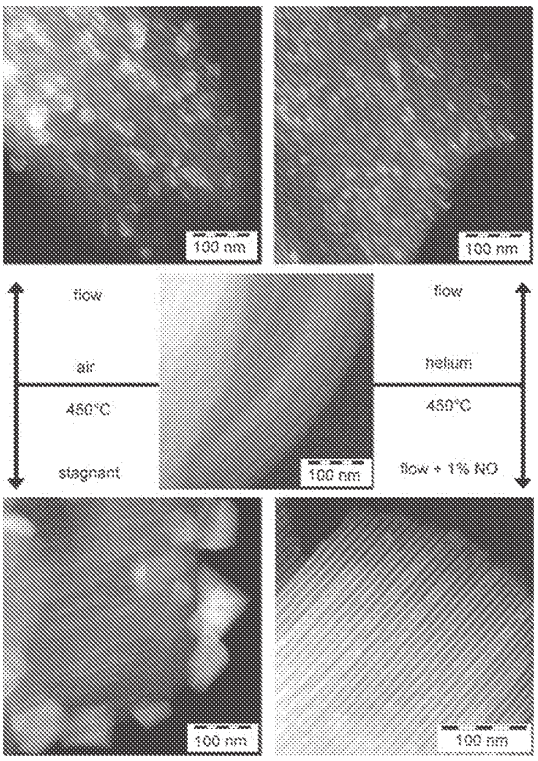


Figure 16. HAADF-STEM (high-angle annular dark field scanning transmission electron microscopy) images of Ni/SBA-15 after drying at 120 °C (center) and after calcination in different gas atmospheres at 450 °C. After drying, nanowires of basic nickel nitrate were observed exclusively inside the mesopores of SBA-15. Calcination in stagnant air resulted in large NiO crystals on the external surface of the support particle. Calcination in air or helium flow gave rise to smaller NiO particles, while calcination in 1% NO led to very small particles of about 4 nm. Adapted with permission from ref 145. Copyright 2007 Wiley.

flow of air, the particle size was decreased, and a further improvement was obtained in a flow of He, suggesting decomposition in a flow and an O_2-free environment was beneficial for the metal dispersion. The highest dispersion was obtained in a flow of 1% NO/He, which resulted exclusively in small 4 nm NiO particles inside the mesopores of the support. Further investigation on Ni/SBA-15 showed that addition of NO_2 or O_2 to the gas stream, both decomposition products of $Ni_3(NO_3)_2(OH)_4$, was detrimental for the metal dispersion and resulted in large particles and migration toward the external surface of the SBA-15 particles.[78] Moreover, NO concentrations as low as 0.1 vol % were already enough to reduce the NiO particle size from 11 to 4 nm at a GHSV of 24 500 h^{-1}. Reduction of the GHSV at a NO concentration of 1 vol % showed little impact until a GHSV of 7000 h^{-1}, while further reduction resulted in gradually larger particles.[146] Additional IR, MS, and isotopic labeling studies revealed that NO scavenges oxygen radicals from the nitrate during decomposition.[147] It was proposed that when a nitrate group becomes unstable during the thermal treatment, NO reacts with the formed oxygen radical, thereby shifting the equilibrium toward NiO and so creating a NiO nucleus. As this occurs at lower temperatures and because a larger number of nuclei are present, many small particles result, and extensive sintering or migration is prevented. If NO is not present during decomposition, oxygen radicals will combine to form O_2. This was proposed as the rate-determining step, and moreover was postulated to be catalyzed by the formed NiO so that nucleation would start an autocatalytic process, causing the entire $Ni_3(NO_3)_2(OH)_4$ crystallite to rapidly decompose, resulting in large particles.

Wolters et al. further investigated the decomposition of scandium, manganese, iron, cobalt, nickel, copper, and zinc nitrates impregnated onto silica gel and SBA-15 at metal loadings between 6 and 16 wt %.[148] After impregnation with the 3 M metal nitrate solution, the samples were dried in a desiccator at room temperature to prevent premature decomposition of the nitrates, followed by thermal treatment in Ar or 1% NO/Ar at 1 °C/min. For all metals, addition of NO was found to lower the decomposition temperature significantly by about 50 °C. However, for Sc, Mn, Fe, and Zn, no crystalline phases were detected by XRD after decomposition in either Ar or NO/Ar flow. For Co, Ni, and Cu, addition of NO resulted in rapid hydrolysis of the metal nitrate to its respective metal hydroxynitrate, which resulted in significantly lower metal oxide particle sizes of 5, 4, and 7 nm after decomposition, respectively, compared to averages of 10, 12, or 23 nm obtained in air. By varying the pore size of the ordered mesoporous support between 2.5 and 10 nm, it was shown that the formed nickel hydroxynitrate crystallites obtained after drying were of a size similar to that of the pores, and that the size of the final NiO particles obtained after calcination depended on the original size of these crystallites.[149] Quick X-ray absorption spectroscopy on cobalt nitrate impregnated on silica at a Co loading of 10 wt % also revealed rapid formation of cobalt hydroxynitrate below 100 °C in the presence of 5% NO/He, which further decomposed to Co_3O_4 between 110 and 170 °C.[150] Furthermore, temperature-programmed calcination on cobalt nitrate melt infiltrated (see section 5.1) on γ-Al_2O_3, followed by drying at 85 °C in air, revealed the hydrolysis of cobalt nitrate during a NO thermal treatment and subsequent improved particle size after decomposition also occurred on γ-Al_2O_3.[151] However, the resulting increase in cobalt specific surface area of up to 33% for catalysts prepared using NO was less compared to the increase with silica. Using temperature-programmed reduction−X-ray absorption fine structure (TPR−XAFS) spectroscopy,, Jacobs et al. also observed that the effect of NO on the dispersion is larger on silica compared to γ-alumina, and attributed this to the strong interaction between γ-alumina and cobalt nitrate, which already results in relatively small particles.[152] Therefore, it was postulated that the effect of NO would work best on supports such as silica that exhibit a weak interaction with the precursor.

Further study on the decomposition of copper nitrate impregnated on SBA-15 and silica gel (18 wt % Cu) confirmed the formation of copper hydroxynitrate at temperatures below 100 °C in the presence of 2 vol % NO, which subsequently decomposes directly into CuO at 200 °C, leading to small 6−8 nm particles.[153] However, when NO was not present, a higher copper dispersion was obtained in air flow with GHSV as low as 250 h^{-1}. Although large 30 nm CuO crystallites were detected

DOI: 10.1021/cr500486u
Chem. Rev. 2015, 115, 6687−6718

by XRD, N_2O chemisorption for the reduced catalyst revealed a relatively high Cu surface area of 90 m^2/g_{Cu}, indicating small particles dominated. From diffuse reflectance infrared Fourier transform (DRIFT) measurements during calcination, it was concluded that the high dispersion originated from the mobilization of copper nitrate anhydride, which rapidly redispersed over the support surface anchored by silanol groups, ultimately resulting in very small CuO particles. The large CuO particles were the result of a small amount of poorly dispersed copper hydroxynitrate which formed even in the absence NO. Such premature hydrolysis during the initial stages of the thermal treatment may be largely avoided by vacuum-drying at room temperature. When this was performed on SBA-15 impregnated with a 4 M copper nitrate solution for 12 h, no large crystallites were found after calcination at 500 °C in a N_2 flow (GHSV = 1000 h^{-1}).[15]

4.4.2. Chelating Additives and Other Organic-Containing Precursors. Organic precursors or additives are frequently used for the synthesis of supported catalysts, in particular for hydrodesulfurization (HDS) catalysts such as alumina-supported CoMoS, NiMoS, CoWS, and NiWS. For these catalysts the active phase consists of MoS_2 or WS_2 slabs decorated with Co or Ni atoms located at the edges, which are commonly prepared by co-impregnation of the metal precursors followed by drying, calcination, and sulfidation. However, under standard conditions, sulfidation of cobalt or nickel occurs prior to that of molybdenum or tungsten, resulting in undesired Co_9S_8 or Ni_2S_3 phases. Chelating agents are used among others to retard sulfidation of cobalt and nickel, so that they are only sulfidized after MoS_2 or WS_2 phases have formed and the cobalt or nickel can be efficiently deposited at the edges of the slabs. For CoMoS catalysts, a moderately strong chelating agent such as nitrilotriacetic acid (NTA) offers sufficient retardation,[154] whereas NiMoS catalysts require slightly stronger complexing agents such as EDTA.[155] Because tungsten is sulfidized at a higher temperature than molybdenum, formation of CoWS and NiWS catalysts generally requires even stronger complexing agents.[156,157]

More recently, research has focused on the use of chelating agents for the preparation of cobalt Fischer–Tropsch catalysts. In an extensive study, 5 wt % Co/SiO_2 catalysts were prepared by incipient wetness impregnation of cobalt nitrate and NTA, EDTA, or *trans*-1,2-diaminocyclohexane-*N*,*N*,*N*′,*N*′-tetraacetic acid (CyDTA) at equal nitrate/chelate molar ratios and a pH of 9–10 to ensure chelation of Co^{2+}(aq).[158] After impregnation, samples were dried at 120 °C, calcined in stagnant air at 450 °C, and reduced at 500 °C. A correlation was found between the cobalt dispersion and the complex formation constant of the chelating agent, showing increasingly smaller particles going from no chelate to NTA to EDTA to CyDTA. However, for EDTA and CyDTA, the particles were difficult to reduce due to the formation of cobalt silicates. Glycine, citric acid, aspartic acid, and triethylenetetramine-*N*,*N*,*N*′,*N*′,*N*″,*N*″-hexaacetic acid (TTHA) were tested in a separate study, but exhibited lower Co dispersion compared to NTA.[159] The catalytic activity of Co was correlated to the complex formation constants of the organic additives with Co^{2+} in a volcano-type plot (Figure 17), suggesting a moderately strong complexing agent offers the best compromise of obtaining small yet reducible particles. Further investigation on NTA showed a Co^{2+}/NTA molar ratio of 1 resulted in the highest dispersion, and that a calcination temperature of 450 °C was optimal.[160]

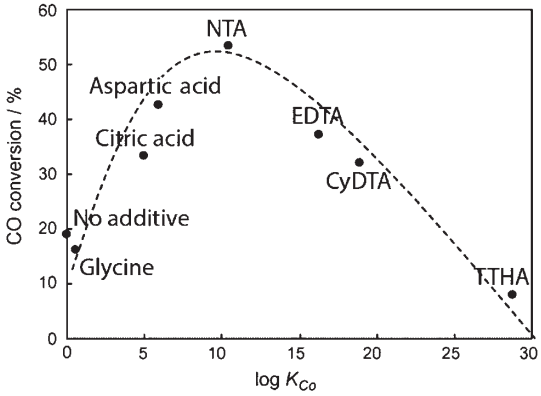


Figure 17. Relationship between the CO conversion in the Fischer–Tropsch synthesis of reduced Co catalysts and the complex formation constant of the organic acids and chelating agents used during the catalyst preparation. The CO conversion was proportional to the dispersion after reduction, which exhibited a similar relationship with log K_{CO}. Adapted with permission from ref 160. Copyright 2009 Elsevier.

Due to the presence of chelating agents, the concentration of the impregnation solution and thereby the resulting metal loading are relatively low. To cope with this challenge, a stepwise impregnation was proposed, whereby silica was first impregnated with the chelating agent (NTA or CyDTA) and dried at 120 °C, after which cobalt nitrate was impregnated with weight loadings up to 20 wt %. At these loadings both NTA- and CyDTA-prepared catalysts exhibited very good reducibility and similar activities.[161] Further investigation of the 20 wt % Co catalyst with a Co/chelate ratio of 4 showed only one-fourth of the CyDTA was complexed with Co^{2+} in the dried material, resulting in the suppressed particle growth of Co_3O_4 during calcination through stabilization of small cobalt clusters that served as nuclei.[162]

Glycols are a popular alternative to improve the dispersion of cobalt catalysts. Borg et al. prepared γ-alumina- and α-alumina-supported catalysts with Co loadings of 12, 20, and 30 wt % by impregnation with cobalt nitrate and different ratios of water/ethylene glycol as the solvent.[135] After impregnation, samples were dried at 110 °C and calcined in air at 300 °C. On both supports, Co_3O_4 particles became smaller upon increasing the amount of ethylene glycol relative to water, from 16 nm to as low as 4 nm, and addition of EG resulted in more uniform particle distributions. The authors postulated that EG works as a surfactant, resulting in better wetting of the support, although the impact of EG on the drying and calcination steps was not excluded in this work. This glycol method was subsequently used to prepare a wide range of particle sizes on γ-, δ-, θ-, and α-aluminas.[163,164]

The difference between straight chains (ethylene glycol, diethylene glycol (DEG), triethylene glycol (TEG)) or branched (glycerol, pentaerythritol) glycols has been investigated for the preparation of 10 and 20 wt % Co/SiO_2 catalysts at different Co/glycol molar ratios between 0 and 1.[165,166] After impregnation, the samples were dried at 120 °C and calcined in stagnant air at 450 °C. A reduction in crystallite size from 35 to 10 nm was observed; however, the resulting Co_3O_4 crystallite sizes did not depend on the specific glycol, but rather on the atomic ratio of carbon to Co^{2+} (Figure 18), while no further

DOI: 10.1021/cr500486u
Chem. Rev. 2015, 115, 6687–6718

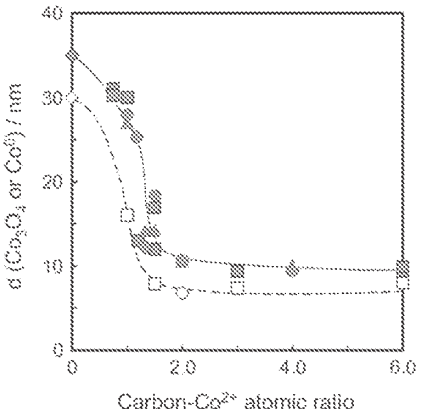


Figure 18. Impact of the amount of atomic carbon relative to Co^{2+} present in the impregnating solution for the preparation of 20 wt % Co/SiO_2. Closed symbols represent Co_3O_4 measurements after calcination and open symbols metallic Co after reduction. Key: circles, EG; triangles, DEG; squares, TEG. Adapted with permission from ref 165. Copyright 2011 Elsevier.

improvement was found above a carbon/Co ratio of 2. FTIR investigation of TEG samples suggested a polymer-complex-like species was formed during calcination through ester polymerization of TEG with its derivatives, thereby preventing excessive growth of particles. Other sugar additives have been used with mixed success. Co-impregnation of sorbitol for the preparation of 10 wt % Co/SiO_2 samples has led to poorly reducible cobalt,[167] while addition of sucrose did not change the reducibility of 6−8 wt % Co/SiO_2.[168] In the latter case, the catalysts were also promoted with Ru or Re, suggesting a reduction promotor may be necessary when using sugar-derived additives.

Organic precursors are a popular alternative to inorganic metal salts. Cobalt nitrate and acetate have been compared for the preparation of 10 wt % Co/SiO_2 catalysts by incipient wetness, drying at 90 °C, and calcination at 400 °C.[169] Cobalt nitrate exhibited an endothermic calcination, favoring the formation of agglomerated 20 nm Co_3O_4 crystallites, while acetate decomposed exothermically during calcination, resulting in the formation of cobalt silicates, which hamper reduction. Comparison of cobalt nitrate, acetate, and chloride for the synthesis of 20 wt % $Co/AlPO_4$ by impregnation, drying at 110 °C, and calcination at 500 °C showed similar results, while cobalt chloride gave rise to very large 35−160 nm crystallites.[170] Nickel nitrate and acetate have been compared for the deposition of 1 or 5 wt % Ni/MCM-41 by the two-solvent impregnation. After drying at 90 °C and calcination in an air flow at 500 °C, nickel acetate was shown to produce smaller NiO particles compared to nickel nitrate, while only a limited amount of nickel silicate was found.[82] Wet impregnated nickel glycinate on γ-alumina at a nickel loading of 15 or 28 wt % resulted in 5−30 nm nickel particles after drying at 80 °C and calcination at 500 °C in an argon flow.[171] Using the glycinate precursor, both hexagonal close-packed (hcp) and face-centered cubic (fcc) Ni phases were detected, whereas normally fcc is the dominant phase. Incipient wetness impregnation of γ-alumina has been performed with nickel ethylenediamine nitrate or nickel nitrate hexahydrate (14−15 wt % Ni), followed by drying at 100 °C, calcination at 500 °C, and reduction at 500 °C.[172] The Ni(en) precursor resulted in a metallic nickel surface area of 13 m^2/g_{cat}, whereas nickel nitrate resulted in 6 m^2/g_{cat}. Moreover, Ni(en) did not lead to formation of nickel aluminate, whereas this was found in significant amounts for nitrate samples. These results show that although organic precursors can result in smaller particles, the conditions during thermal treatment and the nature of the support have a large influence on the formation of mixed metal−support phases which are difficult to reduce, which was more severe for cobalt than for nickel precursors.

4.4.3. Plasma Activation. Although thermal activation treatments are conventionally used to decompose and reduce the metal precursors, cold plasma techniques are receiving increased attention. Especially glow discharge plasma is of interest, due to its ability to provide reduced catalysts when working with noble-metal precursors without the need for a reducing agent. In glow discharge plasma, the sample is loaded into a special reactor, followed by evacuation of the reaction chamber to around 100 Pa. After this the gas is introduced, often H_2, Ar, or N_2, and a voltage is applied to generate the plasma. Using this method, 2−3 wt % Pt, Pd, Ag, or Au was prepared on TiO_2, γ-Al_2O_3, or HZSM-5 following impregnation with an aqueous solution of H_2PtCl_6, $PdCl_2$, $AgNO_3$, or $HAuCl_4$.[173] Directly after impregnation, Ar glow discharge plasma was performed to produce the reduced materials. The treatment led to Pd, Pt, and Ag particles of 2, 4, and 6 nm size, respectively, a factor of 2−3 smaller compared to those of samples reduced in H_2 at 300 °C. A systematic study on 2 wt % Pt/TiO_2 revealed it took 60 min to fully reduce the sample, and even O_2 usage led to a net reducing plasma, although some oxides were also formed. Ar glow discharge plasma has also been used to produce 3.5 wt % Pd/γ-Al_2O_3 after impregnation and drying at 110 °C.[174] Compared to a regular calcination and reduction treatment at 500 °C, a factor of 2 smaller particles were obtained (3.2 vs 7.5 nm). One weight percent Ir/γ-Al_2O_3 was prepared after impregnation with H_2IrCl_6 followed by Ar glow discharge plasma.[175] Even after annealing at 600 °C in Ar, only 1 nm particles were found, while conventional reduction in H_2 resulted in 3 nm particles. AuPd bimetallic particles on SBA-15 have also been prepared using this method by incipient wetness impregnation of $HAuCl_4$ and $Pd(NO_3)_2$ at a total metal loading of 4 wt %.[176] After impregnation, Ar glow discharge plasma was used to decompose the precursors. The resulting material exhibited nanoparticles with Pd-rich shells and Au cores, whereas conventionally prepared samples contained homogeneous PdAu alloy particles, showing the potential for producing tailored bimetallics.

Succession of N_2 and H_2 plasmas has also been used after impregnation and drying. Unpromoted and Pt-promoted 15 wt % Co/γ-Al_2O_3 catalysts were prepared by impregnation and drying at 100 °C.[177] Even though a H_2 plasma was used, X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) data showed that the cobalt nitrate decomposed not into metallic Co but rather into Co_3O_4, suggesting the type of gas only plays a minor role; however, no crystallinity was detected by XRD. Upon subsequent thermal reduction, 6−7 nm Co particles were obtained related to improved reducibility of the plasma-treated sample as compared to a conventionally calcined sample that led to 10 nm particles. Unpromoted and Ru-promoted 10 wt % Co/SiO_2 catalysts have also been prepared via this method after impregnation and drying at 90 °C.[178] It was found that the

DOI: 10.1021/cr500486u
Chem. Rev. 2015, 115, 6687−6718

resulting Co_3O_4 particles depended on the power used during glow discharge. At 60 V, 8.5 nm particles formed, with good reducibility and performance in the Fischer–Tropsch reaction. Particles as small as 5.7 nm were found after treatment at 120 V; however, this was accompanied by formation of cobalt silicate, which led to catalysts with lower activity. It was proposed that the plasma promotes crystal nucleation, so that a relatively high nucleation to growth ratio can be achieved, resulting in relatively small particles. Slightly smaller nickel particles have also been reported in 8 wt % Ni/MgO–Al_2O_3 materials after impregnation and drying at 110 °C.[179]

Glow discharge plasma has also been used as an additional pretreatment step to improve catalysts. Five weight percent Ni/γ-Al_2O_3 has been prepared by impregnation and drying at 110 °C, followed by decomposition in Ar plasma and a subsequent thermal calcination step.[180] An improved stability was found during the dry reforming of methane, which was attributed to a stronger metal–support interaction induced by the plasma treatment. A similar improved interaction was also suggested for the production of up to 2 wt % Pt/TiO_2 by including an Ar glow discharge plasma step between drying and thermal calcination.[181] In the above-mentioned studies, the plasma treatment lasted between 1 and 2 h. This is shorter than most conventional thermal activation procedures and a potential benefit of cold plasma techniques. However, to our knowledge, no studies have been performed on the minimum duration of the plasma treatment needed for completeness and of the decomposition or the penetration power of the treatment for applications in larger catalyst bodies or pellets.

Other cold plasma techniques have been investigated. Dielectric barrier discharge (DBD) plasma under atmospheric conditions was used in the synthesis of 20 wt % Co/SiO_2 after incipient wetness impregnation and drying at 100 °C.[182] However, the resulting catalyst exhibited similar activity in the Fischer–Tropsch synthesis compared to conventionally calcined catalysts, and TEM images showed 50 nm aggregates were formed in the DBD method, so more research is needed to make this a viable alternative. Microwave plasma has been used for the preparation of 5 or 10 wt % Ni/CeO_2 by wet impregnation and drying at 100 °C.[183] Catalysts prepared with a power of 250 W exhibited a dispersion similar to that of samples conventionally prepared by calcination. The samples formed by microwave plasma exhibited a greatly increased stability, which was again attributed to enhanced metal–support interactions. However, during the microwave treatment, a large decrease in support surface area and a large increase in pore diameter were observed, which did not occur during conventional thermal calcination. This was attributed to removal of residual carbon that remained after synthesis of the CeO_2 support. However, this may significantly influence the formed phase.

5. EMERGING TECHNIQUES

5.1. Melt Infiltration

In melt infiltration, a metal or metal precursor salt is physically mixed with the support structure, and subsequently heated above the melting temperature of the metal (salt). This results in the melt being sucked into the pores of the support by capillary forces, whereby an important condition is that the melt and decomposition temperatures should be sufficiently different. As such, this preparation method exhibits many similarities to impregnation and drying (section 4), and similar physical principles of support wetting and capillary pressure and flow are important.[184] In specific cases melt infiltration can provide an attractive alternative due to the relatively simple procedure and no need for solvent. Besides melt infiltration, the method is known by other names such as the solid–solid method, solid-state impregnation, and the solvent-free method.

Melt infiltration for the synthesis of catalysts has been mostly performed with transition-metal nitrate hydrates. These exhibit low melting points since melting occurs as dissolution in their own crystal water, generally between 50 and 100 °C (Table 2),

Table 2. Example of Melting Temperatures of Several Metal Precursors[185]

precursor	T_{melt}[a] (°C)	precursor	T_{melt}[a] (°C)
$Co(NO_3)_2{\cdot}6H_2O$	55	$Fe(NO_3)_3{\cdot}9H_2O$	47
$Ni(NO_3)_2{\cdot}6H_2O$	56	$Ag(NO_3)$	210
$Cu(NO_3)_2{\cdot}3H_2O$	114	$Fe(acac)_2$	190
$Cr(NO_3)_3{\cdot}9H_2O$	66	$(NH_4)_2Cr_2O_7$	n/a[b]

[a]It is noted that many metal nitrates start to lose part of the crystal water at temperatures slightly above the melting temperature. [b]Decomposes before melting.

while use of metal precursors without crystal water is generally less successful. For example, physical mixing of MCM-41 and $Ni(NO_3)_2{\cdot}6H_2O$ followed by heating to 500 °C caused infiltration of the nickel nitrate into the pores of the support, resulting in small NiO particles.[82] However, when nickel acetate and MCM-41 were physically mixed, no infiltration was observed during thermal treatment, and all of the acetate remained outside the pores. Care has to be taken to prevent decomposition of the precursor prior to entrance into the pores. Physical mixing of a hydrated $Fe(NO_3)_3$ salt (hydration not specified) and MCM-41, followed by heating to 400 °C at 5 °C/min and further heating to 700 °C, resulted in sharp XRD patterns related to crystallites over 40 nm in size present on the external surface of the MCM-41 primary particles.[186] It is likely that the high-temperature ramp applied caused decomposition of the iron nitrate before it completely filled the mesopores of the support. However, many small particles were also observed, indicating melt infiltration was partly successful. One millimole of $Co(NO_3)_2{\cdot}6H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$, $Ce(NO_3)_3{\cdot}6H_2O$, or $Cr(NO_3)_3{\cdot}9H_2O$ physically mixed with 0.15 g of SBA-15 or KIT-6 and heated to 500 °C at a rate of 1 °C/min resulted in large interconnected networks inside the pores of the support, which formed porous single-crystal networks after removal of the silica.[187] A similar procedure attempted with $Pb(NO_3)_2$ and $(NH_4)_2Cr_2O_7$ revealed these precursors did not infiltrate the silica supports, which was explained by decomposition of the precursor without melting. Physical mixing of $Ce(NO_3)_3{\cdot}6H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$, or $Co(NO_3)_2{\cdot}6H_2O$ with SBA-15 at lower loadings (0.3 mmol for 0.1 g) followed by calcination to 450 °C did not result in large interconnected networks but rather in small 4–7 nm particles.[188] This suggests the loading may be relevant for the formation of large crystals, or that there was a significant difference between the interconnectivity of the used SBA-15 supports.

In the previous studies, infiltration and decomposition of the metal nitrate hydrate precursors was performed in a single step. However, when decomposition starts while infiltration is still ongoing, it is possible that material decomposes on the external surface of the support, or that the formed metal oxide nuclei are continuously supplied with additional metal nitrate hydrate,

DOI: 10.1021/cr500486u
Chem. Rev. 2015, 115, 6687–6718

causing the grow of large crystals forming a network throughout the pores of the support. As this is undesirable for catalysis, the infiltration and decomposition step should ideally be separated. In a detailed study, three different SBA-15's, MCM-41, and a silica gel were melt infiltrated with $Co(NO_3)_2{\cdot}6H_2O$ by heating to 60 °C in a sealed Teflon-lined autoclave for 24 h.[189] Afterward, XRD did not detect any crystalline material, suggesting all the $Co(NO_3)_2{\cdot}6H_2O$ was taken up by the pores of the support. In contrast, when the same procedure was performed in an open crucible, sharp $Co(NO_3)_2{\cdot}4H_2O$ peaks were observed indicative of partial decomposition of $Co(NO_3)_2{\cdot}6H_2O$, which then remained on the external surface of the support. After calcination in a flow of N_2, large Co_3O_4 particles were found on the external surface when an open crucible was used for infiltration, while no such particles were observed after melt infiltration in a closed autoclave. Making use of the difference in melting point between intraporous (5−20 °C) and extraporous (53 °C) $Co(NO_3)_2{\cdot}6H_2O$, the maximum loading was studied by DSC.[189] Up to a loading of 1.4 $g_{Co(NO_3)_2{\cdot}6H_2O}/g_{SBA\text{-}15}$, only intraporous $Co(NO_3)_2{\cdot}6H_2O$ was observed, whereas, above this, both extraporous and intraporous $Co(NO_3)_2{\cdot}6H_2O$ was found (Figure 19). This amount corresponded to a pore filling

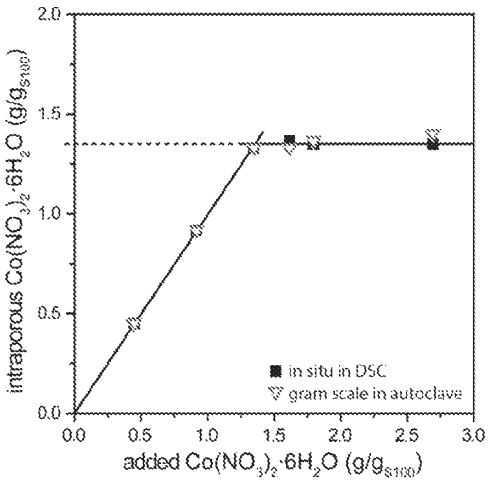


Figure 19. Amount of intraporous $Co(NO_3)_2{\cdot}6H_2O$ per gram of SBA-15 as a function of the amount added in the physical mixture. Squares indicate preparation in situ in DSC measurement cups, while triangles indicate preparation ex situ in a closed autoclave at 60 °C. Up to 1.4 g of added $Co(NO_3)_2{\cdot}6H_2O$ was all found inside the pores after melt infiltration, whereas further addition did not increase the intraporous loading. Adapted from ref 189. Copyright 2010 American Chemical Society.

of 75% assuming the density of crystalline $Co(NO_3)_2{\cdot}6H_2O$. However, due to the lack of an XRD signal, it was proposed that the $Co(NO_3)_2{\cdot}6H_2O$ was not crystalline but rather an amorphous phase with a lower density, so that a close to 100% filling was more likely. This methodology of melt infiltration in an autoclave was subsequently utilized to produce a variety of highly loaded Co/SiO_2 (20 wt %) and Ni/SiO_2 (21 wt %) catalysts by using calcination in N_2 or 1% NO/N_2 gas flows,[24,142] and a similar method was used to form a bimetallic Co/Rh catalyst on γ-Al_2O_3 (20 and 1 wt %, respectively).[151]

Also Cu−Ce bimetallic materials have been synthesized using melt infiltration. $Cu(NO_3)_2{\cdot}2.5H_2O$ and $Ce(NO_3)_3{\cdot}6H_2O$ were first mixed at 120 °C in a closed vial, after which silica hollow spheres were added for infiltration followed by calcination at 550 °C.[190] The molar ratio between the copper and ceria nitrates was varied, while in each case the total salt volume was kept below the pore volume of the support. However, when Cu/Ce ratios higher than 1 were used, large $Cu(NO_3)_2{\cdot}2.5H_2O$ crystals were detected after infiltration, suggesting extraporous $Cu(NO_3)_2{\cdot}2.5H_2O$ was still present. This was also observed after calcination, where large 100 nm CuO crystallites were detected. When the ratios were reversed, no extraporous salt was found. Another similar study successfully prepared Cu−Ce/SBA-15 using melt infiltration, which exhibited better mixing between copper and ceria compared to that with wet impregnation.[191]

Besides metal nitrates, acetylacetonate (acac) precursors have also been used for melt infiltration. $Mo(acac)_3$ and $Fe(acac)_3$ were used to prepare Fe/KIT-6, Mo/KIT-6, and Mo−Fe/KIT-6 at loadings between 0.3 and 1.5 wt % by physically mixing the salt and support and heating to 500 °C for 5 h.[192] However, this may have caused a large amount of pores to be blocked, as a reduction in BET surface area from 600 to 60 m^2/g was observed accompanied by a reduction in pore volume from 0.8 to 0.15 mL/g, suggesting the melting point and decomposition temperature of these precursors are too close to each other for an efficient melt infiltration procedure. $Pt(acac)_2$ has also been introduced into an Al-SBA-15 material by physical mixing, followed by a thermal treatment at 100 °C for 24 h, 180 °C for 0.5 h (5 °C/min), and 400 °C for 6 h (10 °C/min).[193] A homogeneous distribution of the 1 wt % Pt was obtained, with small 1 nm particles similar to those in the preparation by wet impregnation. However, 180 °C is close to the boiling point of $Pt(acac)_2$, so that this form of solid-state impregnation concerns vapor deposition rather than melt infiltration.

Due to the absence of solvent that needs to be removed and the increased viscosity of molten metal salts compared to aqueous solutions, melt infiltration can have an effect on the distribution of the active phase during the loading step. For example, although the surface tensions of a cobalt nitrate solution and molten $Co(NO_3)_2{\cdot}6H_2O$ at 60 °C were found to be similar, the viscosity of the melt was over 10 times higher.[194] Melt infiltration of a 2.7 mm silica pellet by $(NO_3)_2{\cdot}6H_2O$ at 60 °C for 30 s resulted in penetration of the outer 0.1−0.2 mm, whereas solution impregnation resulted in a homogeneous distribution. Similarly, melt infiltration of $Ni(NO_3)_2{\cdot}6H_2O$ into a 3 mm alumina pellet for 2−5 min, followed by cooling to room temperature, resulted in distinct eggshells as determined by micro X-ray fluorescence (micro-XRF), while infiltration over 10 or 30 min, or an aging step at 65 °C, resulted in more homogeneous distributions.[195] Some inhomogeneities did remain, attributed to the precipitation of nickel tetrahydrate on the alumina, which has a higher melting point.

The absence of additional solvent can limit redistribution during subsequent thermal steps if enough time is allowed for a homogeneous distribution during melt infiltration. As described in section 4.3.3, freeze-drying of a 4 M aqueous solution of cobalt nitrate inside the pores of the silica gel required temperatures below −90 °C to freeze.[142] At −45 °C, the material was not completely frozen and extensive redistribution was observed in the form of eggshell catalysts and large aggregates. However, when $Co(NO_3)_2{\cdot}6H_2O$ was melt infiltrated, a freezing temperature of only −20 °C was required

DOI: 10.1021/cr500486u
Chem. Rev. 2015, 115, 6687−6718

to solidify the confined precursor. Thus, when freeze-drying was performed at −45 °C, a homogeneous distribution was obtained after melt infiltration (Figure 20). A more

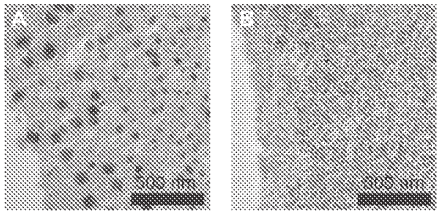


Figure 20. TEM images of Co_3O_4/SiO_2 prepared via incipient wetness impregnation (A) and melt infiltration (B) followed by freeze-drying at −45 °C and calcination in N_2 flow at 350 °C. The impregnated sample was not fully solidified, resulting in severe aggregation and redistribution of the metal nitrate toward the external surface of the silica grain, whereas the melt-infiltrated sample exhibited a homogeneous distribution due to the fully frozen precursor. Adapted with permission from ref 142. Copyright 2013 Elsevier.

homogeneous distribution was also obtained after drying of Co/SiO_2 with large pores in a N_2 flow at 150 °C, which resulted in eggshell catalysts after incipient wetness impregnation but in homogeneous distributions after melt infiltration.[138]

5.2. Colloidal Synthesis

Colloidal synthesis provides unique opportunities to control the size, shape, and composition of nanoparticles in the liquid phase and has been reviewed previously.[196,197] The nanoparticles are generally formed by stepwise induction of a change in conditions in an otherwise homogeneous solution of the metal precursor. This results in a nucleation burst, followed by growth of the nanoparticles from the remaining precursor in solution. Ligands present in the solution play an essential role in stabilizing the nanoparticles against aggregation, coalescence, and growth, while they may also influence the shape of the nanoparticles.[198] Even though the synthesis of colloidal nanoparticles has been studied extensively also for catalysis[199] (see also reviews on electrocatalysis,[200] the oxygen reduction reaction,[201] or size and shape selectivity[202]), few studies focus on deposition of the preformed particles on a support, even though this step is crucial for obtaining active and stable heterogeneous catalysts. Moreover, different colloidal synthesis methods and the variety of stabilizing ligands that have to be removed before or after deposition make generalization of the available literature difficult. Here we do not repeat earlier reviews on nanoparticle synthesis but rather focus on recent studies that address the challenge of deposition of nanoparticles on a support.

Wet impregnation is commonly applied to deposit the colloids onto a support due to the relatively low nanoparticle concentrations in colloidal solutions necessary to prevent aggregation and precipitation. It can take a long time for all particles to migrate into the pores of the support because diffusivity of colloidal nanoparticles is relatively slow, which can be stimulated through use of sonication. The drying step can have a large influence on the distribution of the nanoparticles when particles are not strongly bound to the support, as has been demonstrated for the drying of colloidal wet films.[140] Significant redistribution toward the external surface of the grains is possible since evaporation of the solvent in porous bodies usually occurs on the external surface (see section 4.3). Even so, few studies report the distribution of nanoparticles at the nanoscale and even less the macroscopic distribution across support grains. Co nanoparticles deposited on SBA-15 by wet impregnation followed by extensive washing resulted in aggregation of particles in some areas, while other areas of the support remained empty.[203] Similarly, iron oxide particles of 2−10 nm size deposited by wet impregnation on γ-Al_2O_3 showed similarly inhomogeneous distributions with particles aggregated and preferentially deposited on the external surface of the support.[204] The same particles deposited on MCM-41 with a pore size of 3 nm exhibited homogeneous distributions, but were exclusively deposited on the external surface, not surprising considering the relatively small pore size in relation to the size of the nanoparticles. However, eggshell catalysts have also been observed on carbon model supports with pore sizes larger than the colloidal particles. Focused ion beam scanning electron microscopy (FIB-SEM) on a model carbon support with pore sizes between 75 and 250 nm impregnated with 15−30 nm Pd particles revealed almost exclusively eggshell distributions.[205] Penetration of the pores was possible when a vacuum impregnation was performed; however, the resulting metal distribution remained inhomogeneous.

Deposition of nanoparticles often relies on electrostatic interactions, van der Waals interactions, or polar bonds involving the stabilizing ligands of the particles on one hand, and the support surface groups on the other hand. Electrostatic interactions have been shown to play an important role in 4 nm Pd colloids stabilized with poly(vinylpyrrolidone) (PVP).[206] These were found to be negatively charged between pH 2 and pH 8. When deposited by a wet impregnation at pH 3 on differently treated CNFs with PZCs ranging from 2.2 to 7.7, a maximum uptake (3.9 wt %) occurred for CNFs with high PZCs, whereas supports with a PZC around 2−3 exhibited almost no uptake (0.5 wt %). Thus, the supports with a low PZC and concomitant high surface oxygen content that were negatively charged at pH 3 repelled the negatively charged colloids, whereas the high PZC carbon supports with low oxygen content attracted the colloids. The uptake of PtO_2 colloidal particles prepared by the polyol method and stabilized by glycolate exhibited a similar dependency on the carbon support.[207,208] Uptake of PtO_2 nanoparticles varied greatly from 1.5 to 19 wt %. However, since deposition of the oxidic particles was performed at pH 9−10, electrostatic interaction was unlikely. It was proposed that the particles adsorbed preferentially on carbene-type or surface defect sites. Moreover, similar to the Pd metal particles, uptake was improved by removing oxygen groups from the support, which were thought to weaken the adsorption strength.

Kimura et al. found the adsorption capacity of TiO_2 for Pt colloids stabilized with PVP to be very high, good for Al_2O_3 and MgO, and poor on SiO_2.[209] However, adsorption on TiO_2 was not dependent on the pH of the solution between pH 2 and pH 10, suggesting nonspecific interactions (van der Waals or polar) played an important role. At high loadings (10 wt %), an increase in particle size was observed, suggesting the support did not directly bind with all particles at these high loadings, leading to aggregation. Similar results have been reported for other Pd and Pt particles, which started to form aggregates at higher loadings.[210] Moreover, extra addition of the used stabilizing agent hexadecyl(2-hydroxyethyl)-dimethylammonium dihydrogen phosphate reduced the uptake of the metal nanoparticles likely due to competitive adsorption,

DOI: 10.1021/cr500486u
Chem. Rev. 2015, 115, 6687−6718

suggesting the adsorption of ligands was competing with the surface deposition of nanoparticles.

Immobilization of Au_{11}^{3+} particles with 0.8 nm diameter stabilized with triphenylphosphine (TPP) has been found to depend on the solvent.[211] The highest uptake on silica was observed when pure dichloromethane (DCM) was used, whereas a gradual decrease in uptake occurred upon mixing with ethanol. It was proposed that the binding with the TPP ligands occurred via weak interactive forces between the permanent dipole of the silica OH surface groups and the induced dipole within the ligand layer. At increasing ethanol concentration, the attractive force between the two became weaker due to the increased electrical permittivity caused by ethanol. However, although uptake was less when a DCM/ethanol mixture was used, smaller particle sizes were also obtained, which was attributed to a more homogeneous distribution due to the weaker interaction in the presence of ethanol. The stability of Au particles also depends on the stabilizing ligand. When the electrostatic stabilizer tetrakis-(hydroxypropyl)phosphonium chloride (THPC) was used, smaller particles were deposited on a carbon support compared to those deposited when poly(vinyl alcohol) (PVA), a steric stabilizer, was used.[212] However, when Pd was subsequently added from a Na_2PdCl_4 solution in the presence of PVA and H_2, THPC-stabilized particles exhibited more extensive growth compared to the PVA-stabilized particles.

The charge of the stabilizing agent also plays a large role. For the deposition of 10 nm Ag particles stabilized with 3-mercatopropionic acid (MPA) onto γ-Al_2O_3, the pH of the impregnating solution influenced the final particle size.[213] At pH 3.7, MPA was negatively charged, causing repulsion between nanoparticles, whereas attraction with the positively charged support caused direct deposition of the nanoparticles. However, at a pH of 2.9, MPA was almost negligibly charged, causing particles to assemble together due to hydrogen bonding and resulting in average particles of 26 nm after calcination at 550 °C (Figure 21).

After deposition of the particles on the support, care has to be taken to remove the stabilizing and structure-directing ligands or surfactants. Thermal decomposition of the ligands is most common. However, depending on the ligand, this can require high temperatures at which sintering of the metal particles becomes significant. For example, for nickel particles

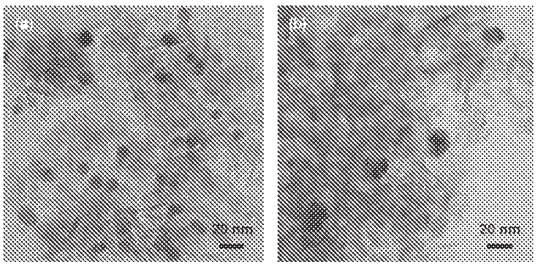


Figure 21. TEM images of Ag particles deposited on γ-Al_2O_3 at different pH values, followed by calcination at 550 °C and reduction at 200 °C: (a) pH 3.7, (b) pH 2.9. At pH 3.7 the originally 10 nm Ag colloids are unchanged after deposition due to the electrostatic repulsion of the MPA ligands, whereas at pH 2 severe sintering occurs due to the negligible charge of MPA at this pH. Adapted from ref 213. Copyright 2009 American Chemical Society.

capped with a mixture of oleic acid, trioctylamine, and trioctylphosphine deposited on SiO_2, activation at 150 and 350 °C in H_2 was not sufficient to remove all the ligands.[214] Even at 500 °C not all ligands were removed, while at this temperature particles exhibited significant sintering, growing from 5.3 to 20 nm.

Alternatively, the ligands may be extracted using solvents after deposition. In this case, the particles should exhibit a high affinity for the support to prevent excessive redistribution, or a solvent other than the solvent during deposition may be used. This was first demonstrated on 3 nm gold colloids capped with PVA after aqueous deposition on TiO_2.[215] A conventional thermal treatment was compared to aqueous solvent extraction. Refluxing in water at 90 °C for 60 min resulted in removal of 20% PVA, and no gold was found in the washing solution, while the particle size showed a minor increase from 3.0 to 4.8 nm. After a calcination treatment at 300 °C, all PVA was removed; however, the particle size increased to 6.1 nm. Further removal of ligands using the washing treatment was difficult; nonetheless, the washed material was 5 times more active in the CO oxidation reaction. Although this cannot be explained solely from the particle size difference between the two methods, it shows washing may be beneficial compared to thermal treatment even if not all ligands can be removed. Copper particles capped with cetyltrimethylammonium bromide (CTAB) were successively deposited on a γ-alumina via a similar method.[216] The 4.6 nm copper particles were impregnated using an aqueous solution, followed by washing with ethanol to remove the CTAB. After subsequent activation at 300 °C in H_2, only a minor increase in particle size to 5.2 nm was observed. However, the ligand removal was not quantified, nor was potential loss of copper during washing commented on. Unfortunately, the removal of ligands after deposition of the colloidal metal nanoparticles is rarely studied in detail, even though it is crucial to obtain active catalysts and deserves more attention.

Microemulsions provide a different way to produce finely dispersed colloidal nanoparticles, whereby nanoparticles are synthesized in the aqueous cores of the surfactant reverse micelles. Deposition of these nanoparticles can often be done by destabilizing the microemulsion in the presence of a support by addition of, for example, THF. However, the resulting supported metal dispersion can suffer compared to that of the nanoparticles in solution. Moreover, synthesis of reverse micelle Co_3O_4 particles directly in contact with a γ-Al_2O_3 support resulted in large amounts of cobalt aluminate, which gave rise to cumbersome catalyst activation.[217] A study on neutral (sodium bis(2-ethylhexyl) sulfosuccinate, AOT) or ionic (poly(oxyethylene) (8) octylphenyl ether, TT) surfactants for the production of Co_3O_4 particles showed the particle size was only slightly influenced by the surfactant.[218] However, a great improvement in dispersion was observed when the silica support was first silylated. This resulted in a decrease in Co particle size from 16 to 6.5 nm (TT) or from 15 to 5 nm (AOT) after reduction. It was concluded that the increased interaction between the hydrophobic silylated support and the micelles reduced the degree of aggregation in the liquid medium, thereby improving the dispersion and possibly the distribution.

Although investigation on the kinetics of particle formation is difficult and rarely attempted, Finke et al. elucidated the kinetics of Pt nanoparticle formation from a H_2PtCl_6 solution in the presence of γ-Al_2O_3 for the synthesis of 1 wt % Pt/

DOI: 10.1021/cr500486u
Chem. Rev. 2015, 115, 6687−6718

Al_2O_3.[219] By using the hydrogenation activity of Pt, the nanoparticle formation was inferred from the simultaneous hydrogenation reaction of cyclohexene with hydrogen. Through use of a high-precision pressure transducer, real-time information on the loss in H_2 pressure provided unique kinetic data on the nanoparticle formation, assuming the reaction was structure insensitive. H_2PtCl_6 was first impregnated using ethyl acetate as the solvent, dried at room temperature in vacuum, and subsequently added to a solution of cyclohexene in ethanol. By applying a H_2 pressure at 22 °C, the Pt precursor was reduced to Pt(0), forming supported nanoparticles which immediately started to convert cyclohexene to cyclohexane. The rate-determining step was assumed to be formation of the growing nanoparticle, so that the catalyzed reaction was used as a probe for the rate of formation. Further study suggested a sigmoidal growth behavior that fit a two-step mechanism for nanoparticle formation of slow nucleation and autocatalytic surface growth first discovered for nanoparticle formation in solution.[220] Because of the good fit to the two-step mechanism, it was proposed that many of the insights obtained for nucleation and growth in solution also hold in the presence of a support.

A more detailed study was subsequently performed for the synthesis of 1 wt % Ir/γ-Al_2O_3 catalysts.[221] Similarly, [Ir(1,5-COD)Cl]$_2$ was first deposited on γ-alumina using ethyl acetate and dried, followed by formation of the Ir nanoparticles in acetone at 22 °C under hydrogen pressure, which was monitored by the hydrogenation reaction of cyclohexene. Again, the system showed an excellent fit to the two-step mechanism of nucleation followed by autocatalytic surface growth, producing 3 nm iridium particles with a relatively narrow particle size distribution. Further investigation showed nucleation occurred bimolecularly from the precursor in solution, followed by rapid capture of the nuclei by the γ-Al_2O_3 surface and further autocatalytic growth of the supported particles.[222,223] However, when a 5-fold decrease of the Ir(1,5-COD)Cl/γ-Al_2O_3 precatalyst was used, a different growth behavior was observed, resulting in iridium particles of 1.7 nm with a relatively broad particle size distribution.[224] This led to the proposal of a four-step mechanism (Figure 22), whereby Ir(0) nuclei are first formed, which subsequently grow autocatalytically from additional precursor in solution to form larger Ir(0)$_n$ clusters, but can also aggregate. These larger aggregated clusters can again grow autocatalytically from the precursor in solution, but will likely not aggregate with other nuclei due to their limited mobility when they are deposited on the support surface. The new model showed an excellent fit with experimental data; however, whether the individual steps occur in solution or on the support surface was not reported, and the reason for the change from a two-step to a four-step mechanism at lower concentration is subject to further research.

Finally, it is noted that in recent years colloidal techniques have been used for synthesizing a porous support shell around preformed nanoparticles. While these are relevant for catalysis and catalyst preparation, their discussion is beyond the scope of the present review, and they have recently been reviewed elsewhere.[225−227]

5.3. Atomic Layer Deposition

Atomic layer deposition (ALD) has shown increased use for the preparation of catalysts.[228] ALD, also known as atomic layer epitaxy (ALE) or molecular layering, is based on the irreversible

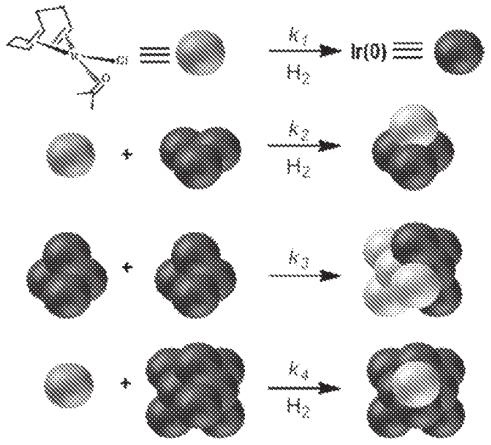


Figure 22. Schematic representation of the four-step mechanism for nanoparticle formation and agglomeration. Ir(1,5-COD)Cl is first reduced to Ir(0) nuclei, which subsequently grow autocatalytically by addition of more Ir(1,5-COD)Cl to form Ir(0)$_n$. Two such Ir(0)$_n$ clusters can aggregate to form one larger cluster, while further growth of such large clusters is limited to autocatalytic growth via addition of Ir(1,5-COD)Cl. Adapted from ref 224. Copyright 2014 American Chemical Society.

and self-limiting reaction between molecules in the gas phase and a surface, so that a uniform monolayer is formed. In general, it entails reaction of a vapor-phase metal precursor with support surface groups such as terminal hydroxyls, followed by purging and a second reaction, often with oxygen or hydrides of the nonmetal elements such as water, ammonia, or hydrogen sulfide, for the formation of metals and metal oxides, nitrides, or sulfides. This second reaction also regenerates surface sites, often in the form of hydroxyl groups, so that multiple ALD cycles can be performed successively to deposit more material in a layer by layer fashion to produce increasingly thick films.[229] The technique principally deposits sequential (mono)layers of material; however, transition metals and especially noble metals tend to agglomerate to form small particles even after one cycle due to the stable metal−metal bonds.

Early detailed studies on atomic layer deposition for catalyst preparation mainly concerned 2,2,6,6-tetramethyl-3,5-heptanedionato (thd) ligands for precursors such as Cu(thd)$_2$,[230] Pd(thd)$_2$,[230,231] and Rh(thd)$_2$[231] while acac precursors such as Ni(acac)$_2$,[232] Co(acac)$_2$,[233] Co(acac)$_3$,[233,234] Cr(acac)$_3$,[235] and VO(acac)$_2$[236] were also used. Selective adsorption on SiO_2 and Al_2O_3 surfaces occurred via an exchange reaction between surface OH groups and ligands, although recently steric hindrance was found to play a role in the deposition of Co(acac)$_2$ and Co(acac)$_3$.[237] The remaining acac or thd ligands were decomposed in oxygen, hydrogen, or water vapor. Multiple cycles were mainly used for Co and Ni, which exhibited a linear increase in metal loading along with an increase in particle size for one to ten cycles. Multiple cycles of $VO(OC_3H_9)_3$ on silica were less successful, because the V-catalyzed decomposition of the $VO(OC_3H_9)_3$ precursor complex caused uncontrolled deposition in later cycles.[238]

ALD can be an efficient deposition method for the production of finely dispersed metal particles for catalysis due to the self-limiting deposition reaction, allowing for a homogeneous distribution even in highly porous and

DOI: 10.1021/cr500486u
Chem. Rev. 2015, 115, 6687−6718

heterogeneous support bodies, which would not be possible with other, non-self-limiting methods. However, the actual penetration depth of the gas is highly dependent on the support material and partial pressure of the precursor. For example, on a very low density silica aerogel, ZnO was deposited from $Zn(C_2H_5)_2$ homogeneously penetrating hundreds of micrometers,[239] while a copper layer formed by $[Cu(^{S}Bu\text{-}Me\text{-}amd)]_2$ penetrated only up to 10 μm due to the 2 orders of magnitude lower partial pressure of the Cu precursor.[240] Similar results were also obtained for deposition of Pt on carbon aerogel from (methylcyclopentadienyl)trimethylplatinum ($MeCpPtMe_3$).[241] It was postulated that, next to diffusion, adsorption−desorption equilibrium of the precursor and reaction product molecules also plays an important role depending on the support.

Feng et al. used silica with a grain size between 75−200 μm as a support for deposition of Pd.[242] Prior to Pd deposition, the silica was first coated by a 0.5 nm thick layer of Al_2O_3 using trimethylaluminum (TMA), or ZnO using diethyl zinc at 200 °C, while water was used to decompose the precursors. Subsequently, 1.5−2.5 wt % Pd was deposited by one or two cycles of palladium hexafluoroacetylacetonate ($Pd(hfac)_2$) and formalin (formaldehyde and methanol in water). On the basis of a time-dependent deposition study, it was concluded that diffusion of the precursor into the support was the limiting step for these materials and conditions. On the Al_2O_3-coated silica, 1−2 nm Pd particles were found distributed uniformly across the support particles by scanning electron microscopy−energy-dispersive X-ray (SEM−EDX) spectroscopy, while no particles were detected on ZnO, suggesting an alloy formation. Using up to 25 cycles, it was found that the Pd particle size increased almost linearly from 1.1 to 2.9 nm on Al_2O_3-coated silica.[243] Moreover, an induction time was observed for the uptake of Pd, which increased after several cycles. It was postulated that when $Pd(hfac)_2$ is deposited, Al(hfac)* species are formed which are not removed during subsequent formalin exposure, and thus are poisoning the surface.[244] The formalin treatment only removed hfac ligands on the Pd and replaced them with hydrogen adatoms, which formed new nucleation sites for further Pd cycles, resulting in an increased Pd uptake as particles became larger due to an increasing amount of nucleation sites for additional $Pd(hfac)_2$. A similar growth behavior was observed on MgO and TiO_2 layers; however, no Pd particles were observed on pure silica, suggesting a limited reactivity of the Si−OH hydroxyl groups with $Pd(hfac)_2$.[243]

A study of the deposition of Pt on γ-Al_2O_3, TiO_2, and $SrTiO_3$ using $MeCpPtMe_3$ and H_2 or N_2 cycles showed the Pt precursor can be adsorbed on oxidic supports at temperatures as low as 100 °C, and is decomposed at 200 °C in H_2 or 300 °C in N_2 to form metallic Pt particles.[245] Even though a prolonged time was necessary for adsorption of $MeCpPtMe_3$ at 100 °C, at 300 °C premature decomposition resulted in Pt deposition throughout the reactor. During decomposition of the precursor in H_2 or N_2, mobile Pt species formed that aggregated into small clusters, forming Pt particles of 1−2 nm. The hydroxyl groups during these treatments were also regenerated, so that additional cycles may be performed. It was observed that the $MeCpPtMe_3$ precursor preferentially adsorbs on surface hydroxyl groups and not on metallic Pt, and that the Pt particle size did not increase much upon subsequent cycles. When O_2 was used to decompose the precursor, PtO formed, which interacted with $MeCpPtMe_3$ via reductive adsorption, resulting in an increase in Pt particle size. However, this only occurred when $MeCpPtMe_3$ already occupied most of the surface hydroxyls, and was less noticeable for high surface area supports under the used conditions. Pt on silica gel (30−75 μm grain size) has also been prepared while keeping the substrate at 325 °C.[246] Even though the previous study mentioned 300 °C as an upper temperature, homogeneous distributions were reported on cross-sectioned silica particles. Three, five, or ten cycles of Pt precursor and O_2 were used to deposit 1.6, 2.3, or 12 wt % Pt, respectively, with particle sizes between 1 and 2.5 nm.

Mixed PtRu particles on Al_2O_3 were synthesized using alternating cycles of $MeCpPtMe_3$ and (2,4-dimethylpentadienyl)(ethylcyclopentadienyl)ruthenium (Ru(DER)), decomposing the precursor with oxygen in between. Two cycles of Ru(DER)/O_2 were followed by one cycle of $MeCpPtMe_3/O_2$ and one cycle of Ru(DER)/O_2 for a final 1:1 molar ratio, and resulted in 1−2 nm particles with good mixing of Ru and Pt as determined by EXAFS analysis.[247] PtPd bimetallic particles have also been synthesized using ALD on SiO_2 covered with Al_2O_3 or TiO_2 supports, creating 1−2 nm particles.[248] However, as soon as a reduction treatment was performed, the particles rearranged to a Pt core/Pd shell nanostructure independent of the deposition sequence.

Although most studies have been performed on noble-metal nanoparticles, non-noble-metal particles can also be synthesized. Co_3O_4 was deposited on Al_2O_3-coated and uncoated silica gel to 25 wt % using bis(cyclopentadienyl)cobalt and ozone.[249] Using ALD, the particle size was reduced 2-fold compared to that obtained with incipient wetness impregnation, from 10−11 to 5−6 nm. However, IWI-prepared catalysts were more active for the Fischer−Tropsch reaction. This was attributed to retarded reduction of Co_3O_4 to Co for catalysts prepared by ALD, which was mitigated somewhat by Pt addition.

5.3.1. ALD for Nanoparticle Stabilization. Next to the active metal, a method has been developed in which an additional oxidic support layer was deposited by an extra step during ALD, referred to as ABC atomic layer deposition.[250] The nature of Pd deposition from $Pd(hfac)_2$ was especially suitable for this. In step A, $Pd(hfac)_2$ was adsorbed on Al_2O_3, whereby some hfac ligands dissociated and adsorbed on the alumina to prevent total coverage of Pd. Next, step B entailed ALD of TMA, which did not adsorb on the Pd precursor but did decompose the Al(hfac)* species, and deposited a new layer of alumina on the support. In step C, the adsorbed TMA was decomposed by water, creating new surface sites for Pd adsorption in the next ABC cycle while keeping the existing adsorbed Pd(hfac) intact, so that further growth of these particles was not possible (note $Pd(hfac)_2$ was decomposed by formalin, not water). This resulted in a very narrow size distribution of 1 nm particles for up to 15 cycles and 6.6 wt % Pd.[243] However, this method is only possible if the precursor in step A does not adsorb on all sites, and reactants in step B and C do not react with the precursor from step A but do create new adsorption sites.

Deposition of a covering and stabilizing layer after synthesis of the supported metal particles has been completed is also possible. Feng et al. deposited Pd by ALD on an Al_2O_3-covered silica gel, and subsequently coated this with additional Al_2O_3 by several ALD cycles using TMA and water at 200 °C.[251] The resulting catalysts were tested in the decomposition of methanol, and showed significantly more active catalysts after 1−16 Al_2O_3 ALD cycles. This was attributed to more stable catalysts already after one cycle; whereas the uncoated catalyst

DOI: 10.1021/cr500486u
Chem. Rev. 2015, 115, 6687−6718

exhibited particle growth from 1.4 to 2.3 nm, the Al_2O_3-coated catalysts did not exhibit any particle growth. When more than 16 cycles were used, the activity greatly decreased, attributed to coverage of the entire Pd particle by Al_2O_3. It was found that initial Al_2O_3 cycles preferentially adsorbed on the Pd edge, step, and corner sites, whereas the catalytic activity comes from Pd(111), which was left unchanged. Further investigation showed that the Pd remained accessible because CH_3 species were adsorbed on Pd after the first ALD cycle, blocking it for further adsorption of TMA in the subsequent cycle, and therefore preventing formation of a monolayer (Figure 23).[252]

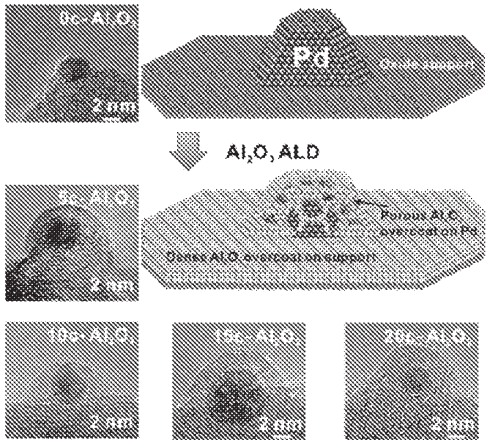


Figure 23. Schematic representation of the deposition of a porous alumina layer on Pd particles supported on an oxidic support, and TEM images of spherical alumina-supported Pd particles with different numbers of Al_2O_3 layers deposited on top, represented by the number of cycles (*x*c). An increasingly thick layer was observed with increasing cycles; however, the particles remained accessible for catalysis. Adapted from ref 252. Copyright 2012 American Chemical Society.

One study showed that, even after 45 ALD cycles with a resulting Al_2O_3 layer of 8 nm thickness, the Pd was still largely accessible and very resistant to coking and sintering in the dehydrogenation of ethane to ethylene at 650 °C.[253,254]

The principle of blocking part of the nanoparticle by adsorption of a specific molecule so that a porous rather than solid layer is formed was further investigated on Pd deposited on θ-Al_2O_3 by ALD.[255] After investigation of several blocking agents, octadecanethiol was chosen due to its relatively strong binding to the Pd particles and relatively large 2 nm length, while it does not react with TMA and therefore should remain on the surface of the Pd nanoparticles during ALD deposition of Al_2O_3. CO adsorption after 21 cycles showed that Pd remained accessible when the blocking agent was used during ALD, whereas unprotected nanoparticles were completely covered in the sample prepared without octadecanethiol.

Coating of 1.7 nm Pt particles deposited by ALD on mesoporous silica has also been performed. A total of 10, 20, 30, or 40 cycles of TMA and ethylene glycol were performed for layers of 1, 2, 3, or 4 nm thickness, respectively.[256] After 20 cycles, all Pt was found to be covered. However, an oxidation step at 400 °C in air created porosity in the Al_2O_3 layer. The resulting material had a Pt dispersion of 38%, significantly lower than that of the original material (65%) (Figure 24). However, when the materials were exposed to a temperature of 800 °C,

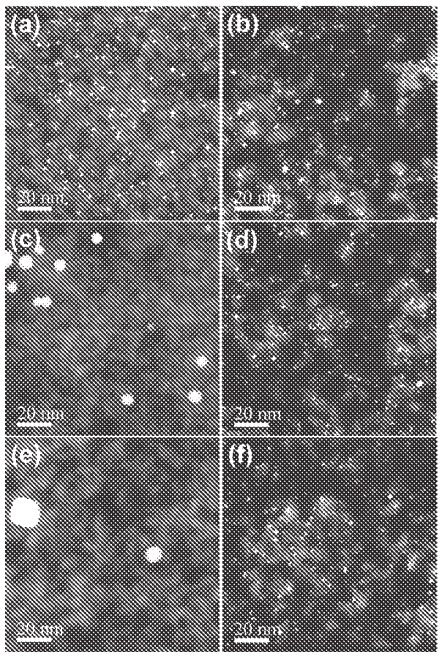


Figure 24. HAADF-STEM (high-angle annular dark field scanning transmission electron microscopy) images of Pt/silica catalysts after calcination for 4 h at 400 (a, b), 600 (c, d), and 800 (e, f) °C. The uncoated catalyst exhibited significant sintering, especially at higher temperatures (a, c, e), whereas the Al_2O_3-coated catalyst prepared using 40 ALD cycles exhibited negligible particle growth (b, d, f). Adapted from ref 256. Copyright 2011 American Chemical Society.

the uncoated Pt catalyst exhibited significant sintering and a reduced dispersion of 4%, whereas the Pt sample coated with 20 cycles of Al_2O_3 exhibited much better stability and 27% dispersion. When 40 cycles were used, sintering was even almost nil.

It should be noted that ALD of a stabilizing layer can also be realized on existing materials which have not been created by ALD. For example, ALD was used to deposit an Al_2O_3 layer on a 3 nm Cu/γ-Al_2O_3 catalyst prepared by incipient wetness impregnation of copper nitrate.[257] After reduction, the catalyst exhibited 86 μmol/g surface Cu sites. After deposition of an Al_2O_3 layer by 45 cycles of TMA and water, no Cu surface sites were found. However, a thermal treatment at 700 °C in air created porosity in the layer, resulting in 23 μmol/g Cu surface sites. During the liquid-phase hydrogenation of furfural, this catalyst did not exhibit any particle growth, whereas the uncoated catalyst showed particle growth from 3 to 5 nm after catalysis. A similar improvement in nanoparticle stability was obtained for a Cu/SiO_2 material coated by application of 30 cycles of TMA and water, followed by calcination at 700 °C in air.[258] Prior to the alumina coating, the catalyst displayed 34 μmol/g Cu surface sites. After coating, no sites were detected, whereas 15 μmol/g surface sites were recovered after accessibility was recreated by calcination at 700 °C. To image the pores in the alumina overcoat, a layer of NbO_x was applied by 20 alternating ALD cycles of $Nb(OCH_2CH_3)_5$ and H_2O, which was previously shown to provide a uniform 1 nm thick niobia layer in the pores of SBA-15.[259] Using STEM–EELS, the

DOI: 10.1021/cr500486u
Chem. Rev. 2015, 115, 6687–6718

penetration depth of NbO_x was found to be significantly larger after calcination of the overcoat at 700 °C, indicating the presence of pores before NbO_x deposition.[258]

Similar deposition of a protective layer by ALD on preformed material is playing an increasingly important role, for example, for the stabilization of photocathodes for the photoelectrochemical water reduction. In particular, Cu_2O is an attractive p-type oxide for photoelectrochemical hydrogen production; however, it is unstable in water. Recently, it was shown that protective Al-doped zinc oxide and titanium oxide layers deposited by ALD provided a stabilizing effect.[260] Similarly, alumina ALD has been performed to coat $LiCoO_2$ for lithium ion battery electrodes, which also exhibited improved stability after extensive charge−discharge cycling compared to the untreated material.[261]

6. CONCLUSION AND OUTLOOK

In this review, we have summarized the progress in conventional and new techniques for the synthesis of supported catalysts that has been obtained in recent years. Detailed studies of coprecipitation have provided new insights into the precipitation mechanism and effect of subsequent thermal activation treatments, while alternative precursors, precipitating agents, and thermal treatments provide promising alternatives for "greener" coprecipitation methods. Deposition precipitation is used to produce highly loaded metal catalysts, but shows an increased usage for the preparation of low-loaded, highly dispersed (noble)-metal catalysts. However, research has revealed that the physicochemical processes that take place at low loadings resemble adsorption rather than precipitation.

Impregnation and drying remains the most studied preparation technique. Detailed study of impregnated ordered materials has shown complete pore filling with aqueous solutions and oxidic supports, and an enhanced understanding of adsorption on support surfaces has improved the ability to rationally synthesize well-dispersed supported metal catalysts. The development of microspectroscopic tools enabled the study of (the development of) gradients and chemical speciation in macroscopic catalyst bodies during impregnation and drying processes, whereas models have been developed and experimentally verified that predict the distribution of the metal precursor across catalyst grains for both high and low precursor loadings. In addition, the development of the nanoscale metal distribution, which has been a long-standing challenge in the synthesis of catalysts, was recently studied. Thermal decomposition of the metal salt precursor, in particular the role of the gas composition or use of chelating agents, has also been systematically studied to elucidate the effects on particle size and particle distribution.

Besides these, several new or rejuvenated approaches were noticed. First, melt infiltration is a promising and facile technique for the preparation of catalysts with high metal loadings that bears many similarities to impregnation and drying, and as such could benefit from the extensive knowledge obtained recently on this method. Second, the synthesis of colloids in solution leads to unique control over particle size, shape, and composition and yields extensive literature. However, deposition of the formed colloids onto a support is critical but has been less studied. Third, the kinetics of particle growth in the presence of a support have been studied in real time for the first time using in situ catalytic measurements of the emerging catalyst. Fourth, atomic layer deposition is showing promise especially for deposition of nanoparticles, but also for deposition of a stabilizing layer onto supported catalysts, for which further insight into the stabilizing effect and ability to obtain porous layers is desired.

On the basis of literature described in this review, it is clear that single (monometallic) particle properties can be largely controlled. To further advance the field of catalyst preparation, more detailed studies on the kinetics of particle formation[13] for each of the preparation methods, as well as systematic studies to control the collective properties of the nanoparticles,[15] and the controlled formation of bimetallic and core−shell particles,[262] are greatly desired. To achieve this, the development of in situ spectroscopic and microscopic techniques will be critical. In particular, X-ray-based techniques[263] and liquid-cell TEM[264] offer possibilities to study the genesis of particles in real time, while other advanced electron microscopy techniques such as cryo-TEM[79] and electron tomography[265] offer information on the distribution of the precursor at different stages during preparation. Furthermore, surface science studies provide increased understanding of the influence of support hydroxylation and the preparation method,[266,267] while X-ray[268] and microbalance[269,270] techniques offer increasingly accurate information on the adsorption of complexes on flat surfaces. Model supports are also essential since 2D model supports provide an excellent platform to study morphological and compositional changes of nanoparticles,[271] while 3D model supports are excellent to study the synthesis,[79] distribution, and stability[272] of metal nanoparticles in a more realistic environment, and other synthesis methods such as electrodeposition allow for precise control of the material.[273] Combination of these and other techniques will provide key insights to further the rationalization of the synthesis of supported catalysts.

AUTHOR INFORMATION

Corresponding Author

*E-mail: K.P.deJong@uu.nl.

Notes

The authors declare no competing financial interest.

Biographies



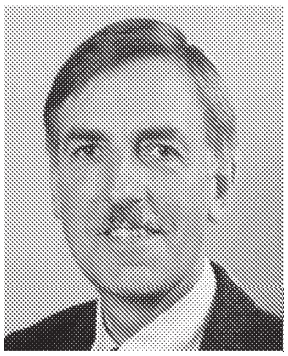
Peter Munnik received his M.Sc. at Utrecht University in 2010. During his studies, he successfully completed an internship at the University of Syndey, Australia, and graduated cum laude with his thesis on the decomposition of supported transition-metal nitrates. Thereafter, he became a Ph.D. student in the Inorganic Chemistry and Catalysis group at Utrecht University under the supervision of K. P. de Jong and P. E. de Jongh, focusing on the synthesis−structure−performance

DOI: 10.1021/cr500486u
Chem. Rev. 2015, 115, 6687−6718

relationships of supported metal catalysts. He graduated cum laude in 2014 and is presently employed by Shell Global Solutions.



Petra E. de Jongh received her Ph.D. in photoelectrochemistry from Utrecht University in 1999, and worked for 5 years as a senior scientist and project leader at Philips Research Laboratories. Since 2004, she has been a member of the Inorganic Chemistry and Catalysis group of the Debye Institute for Nanomaterials Science at Utrecht University, where she was appointed Chair of Inorganic Nanomaterials in 2014. Her present research interest is supported nanoparticles and nanoporous materials, and the impact of nanosizing and confinement, especially for applications in heterogeneous catalysis and energy storage and conversion.



Krijn P. de Jong received his B.Sc. (1976), M.Sc. (1978), and Ph.D. (1982) in chemistry, all cum laude, at Utrecht University. In 1987, he also obtained an M.Sc. degree in chemical engineering from Twente University. From 1982 to 1997, he was with Shell Research working on catalyst preparation, heavy oil conversion, environmental processes, zeolite catalysis, and synthesis gas production and conversion. In 1997, he was appointed as Professor of Inorganic Chemistry and Catalysis at Utrecht University. His current research interests are catalyst synthesis, electron tomography of nanostructured catalysts, hydrocarbon conversions over zeolites, catalysts for liquid-phase catalysis, and conversion of synthesis gas to fuels and chemicals.

ACKNOWLEDGMENTS

PM acknowledges financial support from NWO-TOP-700.57.341, PEdJ from NWO-VICI-016.130.344 and KPdJ from the European Research Council, ERC Advanced Grant no. 338846.

REFERENCES

(1) Behrens, M.; Studt, F.; Kasatkin, I.; Kühl, S.; Hävecker, M.; Abild-Pedersen, F.; Zander, S.; Girgsdies, F.; Kurr, P.; Kniep, B.-L.; Tovar, M.; Fischer, R. W.; Nørskov, J. K.; Schlögl, R. *Science* **2012**, *336*, 893.
(2) Babich, I. V.; Moulijn, J. A. *Fuel* **2003**, *82*, 607.
(3) Brown, D. E.; Edmonds, T.; Joyner, R. W.; McCarroll, J. J.; Tennison, S. R. *Catal. Lett.* **2014**, *144*, 545.
(4) Torres Galvis, H. M.; Bitter, J. H.; Khare, C. B.; Ruitenbeek, M.; Dugulan, A. I.; de Jong, K. P. *Science* **2012**, *335*, 835.
(5) Besson, M.; Gallezot, P.; Pinel, C. *Chem. Rev.* **2014**, *114*, 1827.
(6) Huber, G. W.; Iborra, S.; Corma, A. *Chem. Rev.* **2006**, *106*, 4044.
(7) Guo, X.; Fang, G.; Li, G.; Ma, H.; Fan, H.; Yu, L.; Ma, C.; Wu, X.; Deng, D.; Wei, M.; Tan, D.; Si, R.; Zhang, S.; Li, J.; Sun, L.; Tang, Z.; Pan, X.; Bao, X. *Science* **2014**, *344*, 616.
(8) Transparency Market Research. Refinery (FCC, Hydrocracking, Catalytic Reforming), Synthesis, Polymer & Environmental Catalyst Market—Global Industry Analysis by Material (Zeolites, Metal, Others), by Type (Homogenous & Heterogeneous), Catalyst Regeneration (Off-Site & On-Site), Size, Share, Growth, Trends and Forecast 2012–2018, 2013. www.transparencymarketresearch.com/global-refinery-catalyst-market.html (accessed on January 2, 2015).
(9) Freedonia Group. World Catalysts, 2013. www.freedoniagroup.com/world-catalysts.html (accessed on January 2, 2015).
(10) Rabo, J. A. *Stud. Surf. Sci. Catal.* **1993**, *75*, 1.
(11) De Jong, K. P. *CatTech* **1998**, *2*, 87.
(12) Schwarz, J. A.; Contescu, C.; Contescu, A. *Chem. Rev.* **1995**, *95*, 477.
(13) Mondloch, J. E.; Bayram, E.; Finke, R. G. *J. Mol. Catal. A* **2012**, *355*, 1.
(14) Bartholomew, C. H. *Appl. Catal.* **2001**, *212*, 17.
(15) Prieto, G.; Zečević, J.; Friedrich, H.; de Jong, K. P.; de Jongh, P. E. *Nat. Mater.* **2013**, *12*, 34.
(16) Munnik, P.; de Jongh, P. E.; de Jong, K. P. *J. Am. Chem. Soc.* **2014**, *136*, 7333.
(17) Van Santen, R. A. *Acc. Chem. Res.* **2009**, *42*, 57.
(18) Lundwall, M. J.; Mcclure, S. M.; Wang, X.; Wang, Z.; Chen, M.; Goodman, D. W. *J. Phys. Chem. C* **2012**, *116*, 18155.
(19) Bezemer, G. L.; Bitter, J. H.; Kuipers, H. P. C. E.; Oosterbeek, H.; Holewijn, J. E.; Xu, X. D.; Kapteijn, F.; van Dillen, J. A.; de Jong, K. P. *J. Am. Chem. Soc.* **2006**, *128*, 3956.
(20) Den Breejen, J. P.; Radstake, P. B.; Bezemer, G. L.; Bitter, J. H.; Frøseth, V.; Holmen, A.; de Jong, K. P. *J. Am. Chem. Soc.* **2009**, *131*, 7197.
(21) Farmer, J. A.; Campbell, C. T. *Science* **2010**, *329*, 933.
(22) Cao, A.; Veser, G. *Nat. Mater.* **2010**, *9*, 75.
(23) Holby, E. F.; Sheng, W.; Shao-Horn, Y.; Morgan, D. *Energy Environ. Sci.* **2009**, *2*, 865.
(24) Munnik, P.; Velthoen, M.; de Jongh, P. E.; de Jong, K. P.; Gommes, C. J. *Angew. Chem., Int. Ed.* **2014**, *53*, 9493.
(25) Li, W.; Yue, Q.; Deng, Y.; Zhao, D. *Adv. Mater.* **2013**, *25*, 5129.
(26) Corma, A.; García, H.; Llabrés i Xamena, F. X. *Chem. Rev.* **2010**, *110*, 4606.
(27) Pierre, A. C.; Pajonk, M. *Chem. Rev.* **2002**, *102*, 4243.
(28) Hiemstra, T.; Venema, P.; Riemsdijk, W. *J. Colloid Interface Sci.* **1996**, *184*, 680.
(29) Kosmulski, M. *J. Colloid Interface Sci.* **2011**, *353*, 1.
(30) Barradas, S.; Caricato, E. A.; van Berge, P. J.; van de Loosdrecht, J. *Stud. Surf. Sci. Catal.* **2002**, *143*, 55.
(31) Burattin, P.; Che, M.; Louis, C. *J. Phys. Chem. B* **1998**, *102*, 2722.
(32) Kaluza, S.; Schröter, M. K.; Naumann d'Alnoncourt, R.; Reinecke, T.; Muhler, M. *Adv. Funct. Mater.* **2008**, *18*, 3670.
(33) Kaluza, S.; Behrens, M.; Schiefenhövel, N.; Kniep, B.; Fischer, R.; Schlögl, R.; Muhler, M. *ChemCatChem* **2011**, *3*, 189.
(34) Villacampa, J. I.; Royo, C.; Romeo, E.; Montoya, J. A.; Del Angel, P.; Monzón, A. *Appl. Catal., A* **2003**, *252*, 363.
(35) Shroff, M. D.; Kalakkad, D. S.; Coulter, K. E.; Kohler, S. D.; Harrington, M. S.; Jackson, N. B.; Sault, A. G.; Datye, A. K. *J. Catal.* **1995**, *156*, 185.

DOI: 10.1021/cr500486u
Chem. Rev. 2015, 115, 6687–6718

(36) Behrens, M.; Schlögl, R. *Z. Anorg. Allg. Chem.* **2013**, *639*, 2683.
(37) Behrens, M.; Brennecke, D.; Girgsdies, F.; Kissner, S.; Trunschke, A.; Nasrudin, N.; Zakaria, S.; Idris, N. F.; Hamid, S. B. A.; Kniep, B.; Fischer, R.; Busser, W.; Muhler, M.; Schlögl, R. *Appl. Catal., A* **2011**, *392*, 93.
(38) Baltes, C.; Vukojevic, S.; Schuth, F. *J. Catal.* **2008**, *258*, 334.
(39) Zander, S.; Seidlhofer, B.; Behrens, M. *Dalton Trans.* **2012**, *41*, 13413.
(40) Behrens, M. *J. Catal.* **2009**, *267*, 24.
(41) Simson, G.; Prasetyo, E.; Reiner, S.; Hinrichsen, O. *Appl. Catal., A* **2013**, *450*, 1.
(42) Zhang, X.; Zhong, L.; Guo, Q.; Fan, H.; Zheng, H.; Xie, K. *Fuel* **2010**, *89*, 1348.
(43) Kowalik, P.; Konkol, M.; Kondracka, M.; Próchniak, W.; Bicki, R.; Wiercioch, P. *Appl. Catal., A* **2013**, *452*, 139.
(44) Budiman, A.; Ridwan, M.; Kim, S. M.; Choi, J.-W.; Yoon, C. W.; Ha, J.-M.; Suh, D. J.; Suh, Y.-W. *Appl. Catal., A* **2013**, *462*−*463*, 220.
(45) Li, Z.; Yan, S.; Fan, H. *Fuel* **2013**, *106*, 178.
(46) Behrens, M.; Kissner, S.; Girsgdies, F.; Kasatkin, I.; Hermerschmidt, F.; Mette, K.; Ruland, H.; Muhler, M.; Schlögl, R. *Chem. Commun.* **2011**, *47*, 1701.
(47) Prieto, G.; de Jong, K. P.; de Jongh, P. E. *Catal. Today* **2013**, *215*, 142.
(48) De Jong, K. P.; Geus, J. W. *Appl. Catal.* **1982**, *4*, 41.
(49) Lok, C. M. *Stud. Surf. Sci. Catal.* **2004**, *147*, 283.
(50) Bitter, J. H.; van der Lee, M. K.; Slotboom, A. G. T.; van Dillen, J. A.; de Jong, K. P. *Catal. Lett.* **2003**, *89*, 139.
(51) Fang, B.; Chaudhari, N. K.; Kim, M.-S.; Kim, J. H.; Yu, J.-S. *J. Am. Chem. Soc.* **2009**, *131*, 15330.
(52) Kim, M.-S.; Lim, S.; Chaudhari, N. K.; Fang, B.; Bae, T.-S.; Yu, J.-S. *Catal. Today* **2010**, *158*, 354.
(53) Bezemer, G. L.; Radstake, P. B.; Koot, V.; van Dillen, J. A.; Geus, J. W.; de Jong, K. P. *J. Catal.* **2006**, *237*, 291.
(54) Eschemann, T. O.; Bitter, J. H.; de Jong, K. P. *Catal. Today* **2014**, *228*, 89.
(55) Moreau, F.; Bond, G. C. *Appl. Catal., A* **2006**, *302*, 110.
(56) Moreau, F.; Bond, G.; Taylor, A. *J. Catal.* **2005**, *231*, 105.
(57) Moreau, F.; Bond, G. C. *Catal. Today* **2007**, *122*, 215.
(58) Fang, W.; Chen, J.; Zhang, Q.; Deng, W.; Wang, Y. *Chemistry* **2011**, *17*, 1247.
(59) Martin, R.; Navalon, S.; Delgado, J. J.; Calvino, J. J.; Alvaro, M.; Garcia, H. *Chemistry* **2011**, *17*, 9494.
(60) Lim, S. H.; Phonthammachai, N.; Zhong, Z.; Teo, J.; White, T. J. *Langmuir* **2009**, *25*, 9480.
(61) Yazid, H.; Adnan, R.; Farrukh, M. A.; Hamid, S. A. *J. Chin. Chem. Soc.* **2011**, *58*, 593.
(62) Souza, K. R.; de Lima, A. F. F.; de Sousa, F. F.; Appel, L. G. *Appl. Catal., A* **2008**, *340*, 133.
(63) Zanella, R.; Giorgio, S.; Henry, C. R.; Louis, C. *J. Phys. Chem. B* **2002**, *106*, 7634.
(64) Cellier, C.; Lambert, S.; Gaigneaux, E. M.; Poleunis, C.; Ruaux, V.; Eloy, P.; Lahousse, C.; Bertrand, P.; Pirard, J.-P.; Grange, P. *Appl. Catal., B* **2007**, *70*, 406.
(65) Moreau, F.; Bond, G. C. *Catal. Today* **2007**, *122*, 260.
(66) Zanella, R.; Delannoy, L.; Louis, C. *Appl. Catal., A* **2005**, *291*, 62.
(67) Hugon, A.; El Kolli, N.; Louis, C. *J. Catal.* **2010**, *274*, 239.
(68) Hugon, A.; Delannoy, L.; Krafft, J.; Louis, C. *J. Phys. Chem. C* **2010**, *114*, 10823.
(69) Ward, T.; Delannoy, L.; Hahn, R.; Kendell, S.; Pursell, C. J.; Louis, C.; Chandler, B. D. *ACS Catal.* **2013**, *3*, 2644.
(70) Cárdenas-Lizana, F.; Gómez-Quero, S.; Hugon, A.; Delannoy, L.; Louis, C.; Keane, M. A. *J. Catal.* **2009**, *262*, 235.
(71) Murzin, D. Y.; Simakova, O. A.; Simakova, I. L.; Parmon, V. N. *React. Kinet. Mech. Catal.* **2011**, *104*, 259.
(72) Van Honschoten, J. W.; Brunets, N.; Tas, N. R. *Chem. Soc. Rev.* **2010**, *39*, 1096.
(73) Washburn, E. W. *Phys. Rev.* **1921**, *17*, 273.
(74) Haneveld, J.; Tas, N. R.; Brunets, N.; Jansen, H. V.; Elwenspoek, M. *J. Appl. Phys.* **2008**, *104*, 014309.
(75) Liu, X.; Khinast, J. G.; Glasser, B. J. *Chem. Eng. Sci.* **2008**, *63*, 4517.
(76) Imperor-Clerc, M.; Bazin, D.; Appay, M.; Beaunier, P.; Davidson, A. *Chem. Mater.* **2004**, *16*, 1813.
(77) Moreno, M. S.; Weyland, M.; Midgley, P. A.; Bengoa, J. F.; Cagnoli, M. V.; Gallegos, N. G.; Alvarez, A. M.; Marchetti, S. G. *Micron* **2006**, *37*, 52.
(78) Sietsma, J. R. A.; Meeldijk, J. D.; Versluijs-Helder, M.; Broersma, A.; van Dillen, J. A.; de Jongh, P. E.; de Jong, K. P. *Chem. Mater.* **2008**, 2921.
(79) Eggenhuisen, T. M.; Friedrich, H.; Nudelman, F.; Zečević, J.; Sommerdijk, N. A. J. M.; de Jongh, P. E.; de Jong, K. P. *Chem. Mater.* **2013**, *25*, 890.
(80) Eggenhuisen, T. M.; van Steenbergen, M. J.; Talsma, H.; de Jongh, P. E.; de Jong, K. P. *J. Phys. Chem. C* **2009**, *113*, 16785.
(81) Cornu, C.; Bonardet, J. L.; Casale, S.; Davidson, A.; Ambramson, S.; Andre, G.; Porcher, F.; Grcic, I.; Tomasic, V.; Vujevic, D.; Koprivanac, N. *J. Phys. Chem. C* **2012**, *116*, 3437.
(82) Marceau, E.; Che, M.; Čejka, J.; Zukal, A. *ChemCatChem* **2010**, *2*, 413.
(83) Boubekr, F.; Davidson, A.; Casale, S.; Massiani, P. *Microporous Mesoporous Mater.* **2011**, *141*, 157.
(84) Van der Meer, J.; Bardez-Giboire, I.; Bart, F.; Albouy, P.; Wallez, G.; Davidson, A. *Microporous Mesoporous Mater.* **2009**, *118*, 183.
(85) Van der Meer, J.; Bardez-Giboire, I.; Mercier, C.; Revel, B.; Davidson, A.; Denoyel, R. *J. Phys. Chem. C* **2010**, *114*, 3507.
(86) Park, J.; Regalbuto, J. R. *J. Colloid Interface Sci.* **1995**, *175*, 239.
(87) Bourikas, K.; Kordulis, C.; Lycourghiotis, A. *Catal. Rev.* **2006**, *48*, 363.
(88) Hao, X.; Spieker, W. A.; Regalbuto, J. R. *J. Colloid Interface Sci.* **2003**, *267*, 259.
(89) Agashe, K.; Regalbuto, J. R. *J. Colloid Interface Sci.* **1997**, *185*, 174.
(90) Jiao, L.; Regalbuto, J. R. *J. Catal.* **2008**, *260*, 329.
(91) Jiao, L.; Regalbuto, J. R. *J. Catal.* **2008**, *260*, 342.
(92) Lambert, S.; Job, N.; Dsouza, L.; Pereira, M.; Pirard, R.; Heinrichs, B.; Figueiredo, J.; Pirard, J.; Regalbuto, J. R. *J. Catal.* **2009**, *261*, 23.
(93) Hao, X.; Barnes, S.; Regalbuto, J. R. *J. Catal.* **2011**, *279*, 48.
(94) Job, N.; Lambert, S.; Chatenet, M.; Gommes, C. J.; Maillard, F.; Berthon-Fabry, S.; Regalbuto, J. R.; Pirard, J.-P. *Catal. Today* **2010**, *150*, 119.
(95) Dsouza, L.; Jiao, L.; Regalbuto, J. R.; Miller, J.; Kropf, A. *J. Catal.* **2007**, *248*, 165.
(96) Dsouza, L.; Regalbuto, J. R.; Miller, J. *J. Catal.* **2008**, *254*, 157.
(97) Zhu, X.; Cho, H.; Pasupong, M.; Regalbuto, J. R. *ACS Catal.* **2013**, *3*, 625.
(98) Feltes, T. E.; Espinosa-Alonso, L.; de Smit, E.; D'Souza, L.; Meyer, R. J.; Weckhuysen, B. M.; Regalbuto, J. R. *J. Catal.* **2010**, *270*, 95.
(99) Feltes, T. E.; Zhao, Y.; Klie, R. F.; Meyer, R. J.; Regalbuto, J. R. *ChemCatChem* **2010**, *2*, 1065.
(100) Zhao, Y.; Feltes, T. E.; Regalbuto, J. R.; Meyer, R. J.; Klie, R. F. *Catal. Sci. Technol.* **2011**, *1*, 1483.
(101) Liu, J.; Tao, R.; Guo, Z.; Regalbuto, J. R.; Marshall, C. L.; Klie, R. F.; Miller, J. T.; Meyer, R. J. *ChemCatChem* **2013**, *5*, 3665.
(102) Petsi, T.; Panagiotou, G. D.; Garoufalis, C. S.; Kordulis, C.; Stathi, P.; Deligiannakis, Y.; Lycourghiotis, A.; Bourikas, K. *Chem.—Eur. J.* **2009**, *15*, 13090.
(103) Panagiotou, G. D.; Petsi, T.; Bourikas, K.; Kordulis, C.; Lycourghiotis, A. *J. Catal.* **2009**, *262*, 266.
(104) Panagiotou, G. D.; Petsi, T.; Bourikas, K.; Kalampounias, A. G.; Boghosian, S.; Kordulis, C.; Lycourghiotis, A. *J. Phys. Chem. C* **2010**, *114*, 11868.
(105) Petsi, T.; Panagiotou, G. D.; Bourikas, K.; Kordulis, C.; Voyiatzis, G. A.; Lycourghiotis, A. *ChemCatChem* **2011**, *3*, 1072.

DOI: 10.1021/cr500486u
Chem. Rev. 2015, 115, 6687−6718

(106) Bourikas, K.; Stavropoulos, J.; Garoufalis, C. S.; Kordulis, C.; Petsi, T.; Lycourghiotis, A. *Chem.—Eur. J.* **2011**, *17*, 1201.
(107) Bourikas, K.; Vakros, J.; Fountzoula, C.; Kordulis, C.; Lycourghiotis, A. *Catal. Today* **2007**, *128*, 138.
(108) Zacharaki, I.; Kontoyannis, C. G.; Boghosian, S.; Lycourghiotis, A.; Kordulis, C. *Catal. Today* **2009**, *143*, 38.
(109) Li, H.; Li, M.; Chu, Y.; Liu, F.; Nie, H. *Fuel* **2014**, *116*, 168.
(110) Sun, K.-Q.; Marceau, E.; Che, M. *Phys. Chem. Chem. Phys.* **2006**, *8*, 1731.
(111) Lee, S. Y.; Aris, R. *Catal. Rev.: Sci. Eng.* **1985**, *27*, 207.
(112) Neimark, A. V.; Kheifez, L. I.; Fenelonov, V. B. *Ind. Eng. Chem. Prod. Res. Dev.* **1981**, 439.
(113) Espinosa-Alonso, L.; Beale, A. M.; Weckhuysen, B. M. *Acc. Chem. Res.* **2010**, *43*, 1279.
(114) Bergwerff, J. A.; Visser, T.; Leliveld, B. R. G.; Rossenaar, B. D.; de Jong, K. P.; Weckhuysen, B. M. *J. Am. Chem. Soc.* **2004**, *126*, 14548.
(115) Zandbergen, M. W.; Jacques, S. D. M.; Weckhuysen, B. M.; Beale, A. M. *Angew. Chem., Int. Ed.* **2012**, *51*, 957.
(116) Gibson, E. K.; Zandbergen, M. W.; Jacques, S. D. M.; Biao, C.; Cernik, R. J.; Brien, M. G. O.; Di Michiel, M.; Weckhuysen, B. M.; Beale, A. M. *ACS Catal.* **2013**, *3*, 339.
(117) Bergwerff, J. A.; Lysova, A. A.; Espinosa-Alonso, L.; Koptyug, I. V.; Weckhuysen, B. M. *Angew. Chem., Int. Ed.* **2007**, *46*, 7224.
(118) Van de Water, L. G. A.; Bezemer, G. L.; Bergwerff, J. A.; Versluijs-Helder, M.; Weckhuysen, B. M.; de Jong, K. P. *J. Catal.* **2006**, *242*, 287.
(119) Bergwerff, J. A.; Lysova, A. A.; Espinosa-Alonso, L.; Koptyug, I. V.; Weckhuysen, B. M. *Chem.—Eur. J.* **2008**, *14*, 2363.
(120) Espinosa-Alonso, L.; de Jong, K. P.; Weckhuysen, B. M. *J. Phys. Chem. C* **2008**, *112*, 7201.
(121) Espinosa-Alonso, L.; Lysova, A. A.; de Peinder, P.; de Jong, K. P.; Koptyug, I. V.; Weckhuysen, B. M. *J. Am. Chem. Soc.* **2009**, *131*, 6525.
(122) Zandbergen, M. W.; Beale, A. M.; Weckhuysen, I. B. M. *ChemCatChem* **2012**, *4*, 217.
(123) Espinosa-Alonso, L.; de Jong, K. P.; Weckhuysen, B. M. *Phys. Chem. Chem. Phys.* **2010**, *12*, 97.
(124) Lekhal, A.; Glasser, B. J.; Khinast, J. G. *Chem. Eng. Sci.* **2001**, *56*, 4473.
(125) Van Dillen, J. A.; Terorde, R.; Lensveld, D.; Geus, J.; de Jong, K. P. *J. Catal.* **2003**, *216*, 257.
(126) Torres Galvis, H. M.; Koeken, A. C. J.; Bitter, J. H.; Davidian, T.; Ruitenbeek, M.; Dugulan, A. I.; de Jong, K. P. *Catal. Today* **2013**, *215*, 95.
(127) Qju, S.; Zhang, X.; Liu, Q.; Wang, T.; Zhang, Q.; Ma, L. *Catal. Commun.* **2013**, *42*, 73.
(128) Lysova, A. A.; Bergwerff, J. A.; Espinosa-Alonso, L.; Weckhuysen, B. M.; Koptyug, I. V. *Appl. Catal., A* **2010**, *374*, 126.
(129) Liu, X.; Khinast, J. G.; Glasser, B. J. *Ind. Eng. Chem. Res.* **2010**, *49*, 2649.
(130) Liu, X.; Khinast, J. G.; Glasser, B. J. *Chem. Eng. Sci.* **2012**, *79*, 187.
(131) Bergwerff, J. A.; Jansen, M.; Leliveld, B. R. G.; Visser, T.; de Jong, K. P.; Weckhuysen, B. *J. Catal.* **2006**, *243*, 292.
(132) Arslan, I.; Walmsley, J. C.; Rytter, E.; Bergene, E.; Midgley, P. A. *J. Am. Chem. Soc.* **2008**, *130*, 5716.
(133) Borg, Ø.; Walmsley, J. C.; Dehghan, R.; Tanem, B. S.; Blekkan, E. A.; Eri, S.; Rytter, E.; Holmen, A. *Catal. Lett.* **2008**, *126*, 224.
(134) van de Loosdrecht, J.; Datt, M.; Visagie, J. L. *Top. Catal.* **2013**, *57*, 430.
(135) Borg, Ø.; Dietzel, P. D. C.; Spjelkavik, A. I.; Tveten, E. Z.; Walmsley, J. C.; Diplas, S.; Eri, S.; Holmen, A.; Rytter, E. *J. Catal.* **2008**, *259*, 161.
(136) Banerjee, R.; Crozier, P. A. *J. Phys. Chem. C* **2012**, *116*, 11486.
(137) Wolters, M.; Munnik, P.; Bitter, J. H.; de Jongh, P. E.; de Jong, K. P. *J. Phys. Chem. C* **2011**, *115*, 3332.
(138) Munnik, P.; Krans, N. A.; de Jongh, P. E.; de Jong, K. P. *ACS Catal.* **2014**, *4*, 3219.
(139) Stannard, A.; Martin, C. P.; Pauliac-Vaujour, E.; Moriarty, P.; Thiele, U. *J. Phys. Chem. C* **2008**, *112*, 15195.
(140) Stannard, A. *J. Phys.: Condens. Matter* **2011**, *23*, 083001.
(141) Sun, X.; Shi, Y.; Zhang, P.; Zheng, C.; Zheng, X.; Zhang, F.; Zhang, Y.; Guan, N.; Zhao, D.; Stucky, G. D. *J. Am. Chem. Soc.* **2011**, *133*, 14542.
(142) Eggenhuisen, T. M.; Munnik, P.; Talsma, H.; de Jongh, P. E.; de Jong, K. P. *J. Catal.* **2013**, *297*, 306.
(143) Van de Loosdrecht, J.; Barradas, S.; Caricato, E. A.; Ngwenya, N. G.; Nkwanyana, P. S.; Rawat, M.; Sigwebela, B. H.; van Berge, P. J.; Visagie, J. L. *Top. Catal.* **2003**, *26*, 121.
(144) Borg, Ø.; Blekkan, E. A.; Eri, S.; Akporiaye, D.; Vigerust, B.; Rytter, E.; Holmen, A. *Top. Catal.* **2007**, *45*, 39.
(145) Sietsma, J. R. A.; Meeldijk, J. D.; den Breejen, J. P.; Versluijs-Helder, M.; van Dillen, J. A.; de Jongh, P. E.; de Jong, K. P. *Angew. Chem., Int. Ed.* **2007**, *46*, 4547.
(146) Sietsma, J. R. A.; Friedrich, H.; Broersma, A.; Versluijs-Helder, M.; Jos van Dillen, A.; de Jongh, P. E.; de Jong, K. P. *J. Catal.* **2008**, *260*, 227.
(147) Wolters, M.; Daly, H.; Goguet, A.; Meunier, F. C.; Hardacre, C.; Bitter, J. H.; de Jongh, P. E.; de Jong, K. P. *J. Phys. Chem. C* **2010**, *114*, 7839.
(148) Wolters, M.; Andrade, I. C. A. C.; Munnik, P.; Bitter, J. H.; de Jongh, P. E.; de Jong, K. P. *Stud. Surf. Sci. Catal.* **2010**, *175*, 69.
(149) Wolters, M.; van Grotel, L. J. W.; Eggenhuisen, T. M.; Sietsma, J. R. A.; de Jong, K. P.; de Jongh, P. E. *Catal. Today* **2011**, *163*, 27.
(150) Hong, J.; Marceau, E.; Khodakov, A. Y.; Griboval-Constant, A.; La Fontaine, C.; Briois, V. *Chem.—Eur. J.* **2012**, 2802.
(151) Becker, H.; Turek, T.; Güttel, R. *Catal. Today* **2013**, *215*, 8.
(152) Jacobs, G.; Ma, W.; Davis, B. H.; Cronauer, D. C.; Jeremy Kropf, A.; Marshall, C. L. *Catal. Lett.* **2010**, *140*, 106.
(153) Munnik, P.; Wolters, M.; Gabrielsson, A.; Pollington, S. D.; Headdock, G.; Bitter, J. H.; de Jongh, P. E.; de Jong, K. P. *J. Phys. Chem. C* **2011**, *115*, 14698.
(154) Coulier, L.; de Beer, V. H. J.; van Veen, J. A. R.; Niemantsverdriet, J. W. *Top. Catal.* **2000**, *13*, 99.
(155) Coulier, L.; de Beer, V. H. J.; van Veen, J. A. R.; Niemantsverdriet, J. W. *J. Catal.* **2001**, *197*, 26.
(156) Kishan, G.; van Veen, J. A. R.; Niemantsverdriet, J. W. *Top. Catal.* **2004**, *29*, 103.
(157) Kishan, G.; Coulier, L.; de Beer, V. H. J.; van Veen, J. A. R.; Niemantsverdriet, J. W. *J. Catal.* **2000**, *196*, 180.
(158) Mochizuki, T.; Hara, T.; Koizumi, N.; Yamada, M. *Appl. Catal., A* **2007**, *317*, 97.
(159) Mochizuki, T.; Hara, T.; Koizumi, N.; Yamada, M. *Catal. Lett.* **2007**, *113*, 165.
(160) Koizumi, N.; Mochizuki, T.; Yamada, M. *Catal. Today* **2009**, *141*, 34.
(161) Mochizuki, T.; Hongo, D.; Satoh, T.; Koizumi, N.; Yamada, M. *Catal. Lett.* **2008**, *121*, 52.
(162) Koizumi, N.; Ibi, Y.; Hongo, D.; Hamabe, Y.; Suzuki, S.; Hayasaka, Y.; Shindo, T.; Yamada, M. *J. Catal.* **2012**, *289*, 151.
(163) Rane, S.; Borg, Ø.; Yang, J.; Rytter, E.; Holmen, A. *Appl. Catal., A* **2010**, *388*, 160.
(164) Rane, S.; Borg, Ø.; Rytter, E.; Holmen, A. *Appl. Catal., A* **2012**, *437*−*438*, 10.
(165) Koizumi, N.; Suzuki, S.; Niiyama, S.; Ibi, Y.; Shindo, T.; Yamada, M. *Appl. Catal., A* **2011**, *395*, 138.
(166) Koizumi, N.; Suzuki, S.; Niiyama, S.; Shindo, T.; Yamada, M. *Catal. Lett.* **2011**, *141*, 931.
(167) Hong, J.; Marceau, E.; Khodakov, A. Y.; Griboval-Constant, A.; La, C.; Briois, V.; Chernavskii, P. A. *Catal. Today* **2011**, *175*, 528.
(168) Girardon, J. S.; Quinet, E.; Gribovalconstant, A.; Chernavskii, P.; Gengembre, L.; Khodakov, A. Y. *J. Catal.* **2007**, *248*, 143.
(169) Girardon, J. S.; Lermontov, A. S.; Gengembre, L.; Chernavskii, P. A. *J. Catal.* **2005**, *230*, 339.
(170) Bae, J. W.; Kim, S.-M.; Kang, S.-H.; Chary, K. V. R.; Lee, Y.-J.; Kim, H.-J.; Jun, K.-W. *J. Mol. Catal. A* **2009**, *311*, 7.

DOI: 10.1021/cr500486u
Chem. Rev. 2015, 115, 6687−6718

(171) Rodríguez-González, V.; Marceau, E.; Beaunier, P.; Che, M.; Train, C. *J. Solid State Chem.* **2007**, *180*, 22.
(172) Marceau, E.; Löfberg, A.; Giraudon, J.-M.; Négrier, F.; Che, M.; Leclercq, L. *Appl. Catal., A* **2009**, *362*, 34.
(173) Zou, J.-J.; Zhang, Y.; Liu, C.-J. *Langmuir* **2006**, *22*, 11388.
(174) Liang, X.; Liu, C.; Kuai, P. *Green Chem.* **2008**, *10*, 1318.
(175) Zhao, Y.; Pan, Y.; Xie, Y.; Liu, C. *Catal. Commun.* **2008**, *9*, 1558.
(176) Chen, Y.; Wang, H.; Liu, C.-J.; Zeng, Z.; Zhang, H.; Zhou, C.; Jia, X.; Yang, Y. *J. Catal.* **2012**, *289*, 105.
(177) Chu, W.; Wang, L. N.; Chernavskii, P. A.; Khodakov, A. Y. *Angew. Chem., Int. Ed.* **2008**, *47*, 5052.
(178) Hong, J.; Chu, W.; Chernavskii, P. A.; Khodakov, A. Y. *J. Catal.* **2010**, *273*, 9.
(179) Yu, X.; Zhang, F.; Wang, N.; Hao, S.; Chu, W. *Catal. Lett.* **2013**, *144*, 293.
(180) Zhu, X.; Huo, P.; Zhang, Y.; Cheng, D.; Liu, C. *Appl. Catal., B* **2008**, *81*, 132.
(181) Zou, J.-J.; He, H.; Cui, L.; Du, H.-Y. *Int. J. Hydrogen Energy* **2007**, *32*, 1762.
(182) Huang, C.; Bai, S.; Lv, J.; Li, Z. *Catal. Lett.* **2011**, *141*, 1391.
(183) Odedairo, T.; Chen, J.; Zhu, Z. *J. Phys. Chem. C* **2013**, *117*, 21288.
(184) De Jongh, P. E.; Eggenhuisen, T. M. *Adv. Mater.* **2013**, *25*, 6672.
(185) *Handbook of Chemistry and Physics*, 92nd ed.; CRC Press: Boca Raton, FL, 2012.
(186) Schüth, F.; Wingen, A.; Sauer, J. *Microporous Mesoporous Mater.* **2001**, *45*, 465.
(187) Yue, W.; Zhou, W. *Chem. Mater.* **2007**, *19*, 2359.
(188) Tang, C.; Zhang, H.; Sun, C.; Li, J.; Qi, L.; Quan, Y.; Gao, F.; Dong, L. *Catal. Commun.* **2011**, *12*, 1075.
(189) Eggenhuisen, T. M.; den Breejen, J. P.; Verdoes, D.; de Jongh, P. E.; de Jong, K. P. *J. Am. Chem. Soc.* **2010**, *132*, 18318.
(190) Li, X.; Quek, X.-Y.; Michel Ligthart, D. A. J.; Guo, M.; Zhang, Y.; Li, C.; Yang, Q.; Hensen, E. J. M. *Appl. Catal., B* **2012**, *123−124*, 424.
(191) Tang, C.; Sun, J.; Yao, X.; Cao, Y.; Liu, L.; Ge, C.; Gao, F.; Dong, L. *Appl. Catal., B* **2014**, *146*, 201.
(192) Boulaoued, A.; Fechete, I.; Donnio, B.; Bernard, M.; Turek, P.; Garin, F. *Microporous Mesoporous Mater.* **2012**, *155*, 131.
(193) Medina-Mendoza, A. K.; Cortés-Jácome, M. A.; Toledo-Antonio, J. A.; Angeles-Chávez, C.; López-Salinas, E.; Cuauhtémoc-López, I.; Barrera, M. C.; Escobar, J.; Navarrete, J.; Hernández, I. *Appl. Catal., B* **2011**, *106*, 14.
(194) Iglesia, E.; Soled, S. L.; Baumgartner, J. E.; Reyes, S. C. *J. Catal.* **1995**, *153*, 108.
(195) Liu, X.; Khinast, J. G.; Glasser, B. J. *Ind. Eng. Chem. Res.* **2014**, *53*, 5792.
(196) Tao, A. R.; Habas, S.; Yang, P. *Small* **2008**, *4*, 310.
(197) Casavola, M.; Buonsanti, R.; Caputo, G.; Davide, P. *Eur. J. Inorg. Chem.* **2008**, 837.
(198) Park, J.; Joo, J.; Kwon, S. G.; Jang, Y.; Hyeon, T. *Angew. Chem., Int. Ed.* **2007**, *46*, 4630.
(199) Jia, C.-J.; Schüth, F. *Phys. Chem. Chem. Phys.* **2011**, *13*, 2457.
(200) You, H.; Yang, S.; Ding, B.; Yang, H. *Chem. Soc. Rev.* **2013**, *42*, 2880.
(201) Guo, S.; Zhang, S.; Sun, S. *Angew. Chem., Int. Ed.* **2013**, *52*, 8526.
(202) An, K.; Somorjai, G. A. *ChemCatChem* **2012**, *4*, 1512.
(203) Gross, A. F.; Diehl, M. R.; Beverly, K. C.; Richman, E. K.; Tolbert, S. H. *J. Phys. Chem. B* **2003**, *107*, 5475.
(204) Hondow, N.; Fuller, R. O. *J. Colloid Interface Sci.* **2014**, *417*, 396.
(205) Witte, P. T.; Boland, S.; Kirby, F.; van Maanen, R.; Bleeker, B. F.; de Winter, D. A. M.; Post, J. A.; Geus, J. W.; Berben, P. H. *ChemCatChem* **2013**, *5*, 582.
(206) Zhu, J.; Zhao, T.; Kvande, I.; Chen, D.; Zhou, X.; Yuan, W. *Chin. J. Catal.* **2008**, *29*, 1145.
(207) Kvande, I.; Zhu, J.; Zhao, T.-J.; Hammer, N.; Rønning, M.; Raaen, S.; Walmsley, J. C.; Chen, D. *J. Phys. Chem. C* **2010**, *114*, 1752.
(208) Muthuswamy, N.; de la Fuente, J. L. G.; Ochal, P.; Giri, R.; Raaen, S.; Sunde, S.; Rønning, M.; Chen, D. *Phys. Chem. Chem. Phys.* **2013**, *15*, 3803.
(209) Kimura, K.; Einaga, H.; Teraoka, Y. *Catal. Today* **2011**, *164*, 88.
(210) Witte, P. T.; Berben, P. H.; Boland, S.; Boymans, E. H.; Vogt, D.; Geus, J. W.; Donkervoort, J. G. *Top. Catal.* **2012**, *55*, 505.
(211) Liu, Y.; Tsunoyama, H.; Akita, T.; Tsukuda, T. *J. Phys. Chem. C* **2009**, *113*, 13457.
(212) Villa, A.; Wang, D.; Su, D.; Veith, G. M.; Prati, L. *Phys. Chem. Chem. Phys.* **2010**, *12*, 2183.
(213) Mori, K.; Kumami, A.; Tomonari, M.; Yamashita, H. *J. Phys. Chem. C* **2009**, *113*, 16850.
(214) Rinaldi, R.; Porcari, A. D. M.; Rocha, T. C. R.; Cassinelli, W. H.; Ribeiro, R. U.; Bueno, J. M. C.; Zanchet, D. *J. Mol. Catal. A* **2009**, *301*, 11.
(215) Lopez-Sanchez, J. A.; Dimitratos, N.; Hammond, C.; Brett, G. L.; Kesavan, L.; White, S.; Miedziak, P.; Tiruvalam, R.; Jenkins, R. L.; Carley, A. F.; Knight, D.; Kiely, C. J.; Hutchings, G. J. *Nat. Chem.* **2011**, *3*, 551.
(216) Lin, J.-H.; Guliants, V. V. *ChemCatChem* **2011**, *3*, 1426.
(217) Fischer, N.; Minnermann, M.; Baeumer, M.; van Steen, E.; Claeys, M. *Catal. Lett.* **2012**, *142*, 830.
(218) Martínez, A.; Prieto, G. *Catal. Commun.* **2007**, *8*, 1479.
(219) Mondloch, J. E.; Yan, X.; Finke, R. G. *J. Am. Chem. Soc.* **2009**, *131*, 6389.
(220) Watzky, M. A.; Finke, R. G. *J. Am. Chem. Soc.* **1997**, *119*, 10382.
(221) Mondloch, J. E.; Wang, Q.; Frenkel, A. I.; Finke, R. G. *J. Am. Chem. Soc.* **2010**, *132*, 9701.
(222) Mondloch, J. E.; Finke, R. G. *J. Am. Chem. Soc.* **2011**, *133*, 7744.
(223) Mondloch, J. E.; Finke, R. G. *ACS Catal.* **2012**, *2*, 298.
(224) Kent, P.; Mondloch, J. E.; Finke, R. G. *J. Am. Chem. Soc.* **2014**, *136*, 1930.
(225) Li, G.; Tang, Z. *Nanoscale* **2014**, *6*, 3995.
(226) An, K.; Somorjai, G. A. *Catal. Lett.* **2014**, 233.
(227) Ma, Z.; Dai, S. *ACS Catal.* **2011**, *1*, 805.
(228) Stair, P. C. *Top. Catal* **2012**, *55*, 93.
(229) Miikkulainen, V.; Leskelä, M.; Ritala, M.; Puurunen, R. L. *J. Appl. Phys.* **2013**, *113*, 021301.
(230) Molenbroek, A. M.; Haukka, S.; Clausen, B. S. *J. Phys. Chem. B* **1998**, *102*, 10680.
(231) Lashdaf, M.; Hatanpää, T.; Krause, A. O. I.; Lahtinen, J.; Lindblad, M.; Tiitta, M. *Appl. Catal., A* **2003**, *241*, 51.
(232) Lindblad, M.; Peter, L.; Suntola, T. *Catal. Lett.* **1994**, *27*, 323.
(233) Backman, L. .; Rautiainen, a; Lindblad, M.; Krause, A. O. I. *Appl. Catal., A* **2000**, *191*, 55.
(234) Backman, L. B.; Rautiainen, A.; Krause, A. O. I.; Lindblad, M. *Catal. Today* **1998**, *43*, 11.
(235) Haukka, S.; Lakomaa, E.; Suntola, T. *Appl. Surf. Sci.* **1994**, *75*, 220.
(236) Keränen, J.; Auroux, a; Ek, S.; Niinistö, L. *Appl. Catal., A* **2002**, *228*, 213.
(237) Backman, L. B.; Rautiainen, A.; Lindblad, M.; Krause, A. O. I. *Appl. Catal., A* **2009**, *360*, 183.
(238) Keranen, J.; Guimon, C.; Iiskola, E.; Auroux, A.; Niinisto, L. *J. Phys. Chem. B* **2003**, *107*, 10773.
(239) Kucheyev, S. O.; Biener, J.; Wang, Y. M.; Baumann, T. F.; Wu, K. J.; van Buuren, T.; Hamza, A. V.; Satcher, J. H.; Elam, J. W.; Pellin, M. J. *Appl. Phys. Lett.* **2005**, *86*, 083108.
(240) Kucheyev, S. O.; Biener, J.; Baumann, T. F.; Wang, Y. M.; Hamza, A. V.; Li, Z.; Lee, D. K.; Gordon, R. G. *Langmuir* **2008**, *24*, 943.
(241) King, J. S.; Wittstock, A.; Biener, J.; Kucheyev, S. O.; Wang, Y. M.; Baumann, T. F.; Giri, S. K.; Hamza, A. V.; Baeumer, M.; Bent, S. F. *Nano Lett.* **2008**, *8*, 2405.

DOI: 10.1021/cr500486u
Chem. Rev. 2015, 115, 6687−6718

(242) Feng, H.; Elam, J. W.; Libera, J. A.; Setthapun, W.; Stair, P. C. *Chem. Mater.* **2010**, *22*, 3133.
(243) Lu, J.; Stair, P. C. *Langmuir* **2010**, *26*, 16486.
(244) Goldstein, D. N.; George, S. M. *Appl. Phys. Lett.* **2009**, *95*, 143106.
(245) Setthapun, W.; Williams, W. D.; Kim, S. M.; Feng, H.; Elam, J. W.; Rabuffetti, F. A.; Poeppelmeier, K. R.; Stair, P. C.; Stach, E. A.; Ribeiro, F. H.; Miller, J. T.; Marshall, C. L. *J. Phys. Chem. C* **2010**, *114*, 9758.
(246) Li, J.; Liang, X.; King, D. M.; Jiang, Y.-B.; Weimer, A. W. *Appl. Catal., B* **2010**, *97*, 220.
(247) Christensen, S. T.; Feng, H.; Libera, J. L.; Guo, N.; Miller, J. T.; Stair, P. C.; Elam, J. W. *Nano Lett.* **2010**, *10*, 3047.
(248) Lei, Y.; Liu, B.; Lu, J.; Lobo-Lapidus, R. J.; Wu, T.; Feng, H.; Xia, X.; Mane, A. U.; Libera, J. A.; Greeley, J. P.; Miller, J. T.; Elam, J. W. *Chem. Mater.* **2012**, *24*, 3525.
(249) Cronauer, D. C.; Elam, J. W.; Kropf, A. J.; Marshall, C. L.; Gao, P.; Hopps, S.; Jacobs, G.; Davis, B. H. *Catal. Lett.* **2012**, *142*, 698.
(250) Lu, J.; Stair, P. C. *Angew. Chem., Int. Ed.* **2010**, *49*, 2547.
(251) Feng, H.; Lu, J.; Stair, P. C.; Elam, J. W. *Catal. Lett.* **2011**, *141*, 512.
(252) Lu, J.; Liu, B.; Greeley, J. P.; Feng, Z.; Libera, J. A.; Lei, Y.; Bedzyk, M. J.; Stair, P. C.; Elam, J. W. *Chem. Mater.* **2012**, *24*, 2047.
(253) Lu, J.; Fu, B.; Kung, M. C.; Xiao, G.; Elam, J. W.; Kung, H. H.; Stair, P. C. *Science* **2012**, *335*, 1205.
(254) Fu, B.; Lu, J.; Stair, P. C.; Xiao, G.; Kung, M. C.; Kung, H. H. *J. Catal.* **2013**, *297*, 289.
(255) Ray, N. A.; Van Duyne, R. P.; Stair, P. C. *J. Phys. Chem. C* **2012**, *116*, 7748.
(256) Liang, X.; Li, J.; Yu, M.; McMurray, C. N.; Falconer, J. L.; Weimer, A. W. *ACS Catal.* **2011**, *1*, 1162.
(257) O'Neill, B. J.; Jackson, D. H. K.; Crisci, A. J.; Farberow, C. A.; Shi, F.; Alba-Rubio, A. C.; Lu, J.; Dietrich, P. J.; Gu, X.; Marshall, C. L.; Stair, P. C.; Elam, J. W.; Miller, J. T.; Ribeiro, F. H.; Voyles, P. M.; Greeley, J.; Mavrikakis, M.; Scott, S. L.; Kuech, T. F.; Dumesic, J. A. *Angew. Chem., Int. Ed.* **2013**, *52*, 13808.
(258) Alba-Rubio, A. C.; O'Neill, B. J.; Shi, F.; Akatay, C.; Canlas, C.; Li, T.; Winans, R.; Elam, J. W.; Stach, E. A.; Voyles, P. M.; Dumesic, J. A. *ACS Catal.* **2014**, *4*, 1554.
(259) Pagán-Torres, Y. J.; Gallo, J. M. R.; Wang, D.; Pham, H. N.; Libera, J. A.; Marshall, C. L.; Elam, J. W.; Datye, A. K.; Dumesic, J. A. *ACS Catal.* **2011**, *1*, 1234.
(260) Paracchino, A.; Laporte, V.; Sivula, K.; Grätzel, M.; Thimsen, E. *Nat. Mater.* **2011**, *10*, 456.
(261) Scott, I. D.; Jung, Y. S.; Cavanagh, A. S.; Yan, Y.; Dillon, A. C.; George, S. M.; Lee, S.-H. *Nano Lett.* **2011**, *11*, 414.
(262) Calderone, V. R.; Shiju, N. R.; Curulla-Ferré, D.; Chambrey, S.; Khodakov, A. Y.; Rose, A.; Thiessen, J.; Jess, A.; Rothenberg, G. *Angew. Chem., Int. Ed.* **2013**, *52*, 4397.
(263) Filez, M.; Poelman, H.; Ramachandran, R. K.; Dendooven, J.; Devloo-Casier, K.; Fonda, E.; Detavernier, C.; Marin, G. B. *Catal. Today* **2014**, *229*, 2.
(264) Evans, J. E.; Jungjohann, K. L.; Browning, N. D.; Arslan, I. *Nano Lett.* **2011**, *11*, 2809.
(265) Zečević, J.; de Jong, K. P.; de Jongh, P. E. *Curr. Opin. Solid State Mater. Sci.* **2013**, *17*, 115.
(266) Sterrer, M.; Freund, H.-J. *Catal. Lett.* **2013**, *143*, 375.
(267) Xu, Y.; Yang, J.; Demura, M.; Hara, T.; Hirano, T.; Matsushita, Y.; Tanaka, M.; Katsuya, Y. *Appl. Catal., A* **2014**, *478*, 165.
(268) Park, C.; Fenter, P.; Sturchio, N.; Regalbuto, J. *Phys. Rev. Lett.* **2005**, *94*, 076104.
(269) Blanchard, J.; Hervier, A.; Costentin, G.; Regalbuto, J.; Louis, C.; Boujday, S. *Catal. Today* **2014**, *235*, 245.
(270) Hervier, A.; Blanchard, J.; Costentin, G.; Regalbuto, J.; Louis, C.; Boujday, S. *Chem. Commun.* **2014**, *50*, 2409.
(271) Thüne, P. C.; Weststrate, C. J.; Moodley, P.; Saib, A. M.; van de Loosdrecht, J.; Miller, J. T.; Niemantsverdriet, J. W. *Catal. Sci. Technol.* **2011**, *1*, 689.
(272) Prieto, G.; Shakeri, M.; de Jong, K. P.; de Jongh, P. E. *ACS Nano* **2014**, *8*, 2522.
(273) Stephens, I. E. L.; Bondarenko, A. S.; Perez-Alonso, F. J.; Calle-Vallejo, F.; Bech, L.; Johansson, T. P.; Jepsen, A. K.; Frydendal, R.; Knudsen, B. P.; Rossmeisl, J.; Chorkendorff, I. *J. Am. Chem. Soc.* **2011**, *133*, 5485.

DOI: 10.1021/cr500486u
Chem. Rev. 2015, 115, 6687−6718

PTO/SB/06 (09-11)
Approved for use through 1/31/2014. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

PATENT APPLICATION FEE DETERMINATION RECORD Substitute for Form PTO-875	Application or Docket Number 17/176,222	Filing Date 02/16/2021	☐ To be Mailed

ENTITY: ☐ LARGE ☑ SMALL ☐ MICRO

APPLICATION AS FILED - PART I

	(Column 1)	(Column 2)			
FOR	NUMBER FILED	NUMBER EXTRA		RATE ($)	FEE ($)
☐ BASIC FEE (37 CFR 1.16(a), (b), or (c))	N/A	N/A		N/A	
☐ SEARCH FEE (37 CFR 1.16(k), (i), or (m))	N/A	N/A		N/A	
☐ EXAMINATION FEE (37 CFR 1.16(o), (p), or (q))	N/A	N/A		N/A	
TOTAL CLAIMS (37 CFR 1.16(i))	minus 20 =	*		x $50 =	
INDEPENDENT CLAIMS (37 CFR 1.16(h))	minus 3 =	*		x $240 =	
☐ APPLICATION SIZE FEE (37 CFR 1.16(s))	If the specification and drawings exceed 100 sheets of paper, the application size fee due is $310 ($155 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s).				
☐ MULTIPLE DEPENDENT CLAIM PRESENT (37 CFR 1.16(j))					
* If the difference in column 1 is less than zero, enter "0" in column 2.				TOTAL	

APPLICATION AS AMENDED - PART II

		(Column 1)		(Column 2)	(Column 3)			
AMENDMENT	07/07/2021	CLAIMS REMAINING AFTER AMENDMENT		HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA		RATE ($)	ADDITIONAL FEE ($)
	Total (37 CFR 1.16(i))	* 23	Minus	** 22	= 1		x $50 =	50
	Independent (37 CFR 1.16(h))	* 2	Minus	*** 3	= 0		x $240 =	0
	☐ Application Size Fee (37 CFR 1.16(s))							
	☐ FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))							
							TOTAL ADD'L FEE	50

		(Column 1)		(Column 2)	(Column 3)			
AMENDMENT		CLAIMS REMAINING AFTER AMENDMENT		HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA		RATE ($)	ADDITIONAL FEE ($)
	Total (37 CFR 1.16(i))	*	Minus	**	=		x $0 =	
	Independent (37 CFR 1.16(h))	*	Minus	***	=		x $0 =	
	☐ Application Size Fee (37 CFR 1.16(s))							
	☐ FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))							
							TOTAL ADD'L FEE	

* If the entry in column 1 is less than the entry in column 2, write "0" in column 3.	LIE
** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20".	/SHARON D HARRIS/
*** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, enter "3".	
The "Highest Number Previously Paid For" (Total or Independent) is the highest number found in the appropriate box in column 1.	

This collection of information is required by 37 CFR 1.16. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
17/176,222	02/16/2021	Guido William ARU	071816-091960USC1	3640

53143 7590 08/13/2021

RONALD I. EISENSTEIN
NIXON PEABODY LLP
Exchange Place, 53 State Street
BOSTON, MA 02109

EXAMINER	
SOLIMAN, HAYTHAM	

ART UNIT	PAPER NUMBER
1736	

NOTIFICATION DATE	DELIVERY MODE
08/13/2021	ELECTRONIC

Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

Notice of the Office communication was sent electronically on above-indicated "Notification Date" to the following e-mail address(es):

bostonpatent@nixonpeabody.com
ipairlink@nixonpeabody.com

Office Action Summary	**Application No.** 17/176,222	**Applicant(s)** ARU, Guido William	
	Examiner HAYTHAM SOLIMAN	**Art Unit** 1736	**AIA (FITF) Status** Yes

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --

Period for Reply

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE 3 MONTHS FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133). Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

Status

1)☑ Responsive to communication(s) filed on 2/16/2021.

☐ A declaration(s)/affidavit(s) under **37 CFR 1.130(b)** was/were filed on _____.

2a)☑ This action is **FINAL.** 2b) ☐ This action is non-final.

3)☐ An election was made by the applicant in response to a restriction requirement set forth during the interview on _____; the restriction requirement and election have been incorporated into this action.

4)☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

Disposition of Claims*

5) ☑ Claim(s) 1-23 is/are pending in the application.

5a) Of the above claim(s) _____ is/are withdrawn from consideration.

6) ☐ Claim(s) _____ is/are allowed.

7) ☑ Claim(s) 1-23 is/are rejected.

8) ☐ Claim(s) _____ is/are objected to.

9) ☐ Claim(s) _____ are subject to restriction and/or election requirement

* If any claims have been determined allowable, you may be eligible to benefit from the **Patent Prosecution Highway** program at a participating intellectual property office for the corresponding application. For more information, please see http://www.uspto.gov/patents/init_events/pph/index.jsp or send an inquiry to **PPHfeedback@uspto.gov.**

Application Papers

10)☐ The specification is objected to by the Examiner.

11)☐ The drawing(s) filed on _____ is/are: a)☐ accepted or b)☐ objected to by the Examiner.

Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).

Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).

Priority under 35 U.S.C. § 119

12)☑ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

Certified copies:

a)☑ All b)☐ Some** c)☐ None of the:

1.☐ Certified copies of the priority documents have been received.

2.☑ Certified copies of the priority documents have been received in Application No. 17043031.

3.☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).

** See the attached detailed Office action for a list of the certified copies not received.

Attachment(s)

1) ☐ Notice of References Cited (PTO-892)

2) ☑ Information Disclosure Statement(s) (PTO/SB/08a and/or PTO/SB/08b) Paper No(s)/Mail Date 07/07/2021.

3) ☐ Interview Summary (PTO-413) Paper No(s)/Mail Date _____.

4) ☐ Other: _____.

DETAILED ACTION

Claim Rejections - 35 USC § 102

The following is a quotation of the appropriate paragraphs of 35 U.S.C. 102 that form the basis for the rejections under this section made in this Office action:

> A person shall be entitled to a patent unless –
>
> (a)(1) the claimed invention was patented, described in a printed publication, or in public use, on sale, or otherwise available to the public before the effective filing date of the claimed invention.

Claims 1-6, 8, 9, 12, 14, 15, 16-19, and 21-23 are rejected under 35 U.S.C. 102(a)(1) as being anticipated by Yaluris et al. (US 2005/0042158).

As an initial matter, in the remarks dated 07/07/2021 ("Remarks"), the Applicant noted that the terms "microsphere" and "eggshell" are not interchangeable. See Remarks at p8. It appears that the Applicant is distinguishing between the two terms in that "microsphere" relates to the shape of the claimed particles while "eggshell" relates to the distribution of the claimed "one or more Group VIII noble metals" in the claimed microsphere. Along with other references, the Applicant points to pages 6688-99 of Munnik et al. ("Recent Developments in the Synthesis of Supported Catalysts") to support this distinction. See Remarks at p9. Munnik teaches that an eggshell distribution is a "macroscopic distribution" that is resulted from the adsorption of a metal precursor "in the outer shell of the support body." See Munnik at section 4.2.2. The Office will adopt this interpretation of both terms.

With regards to **claims 1-6, 9, 12, 14, 16, 17 and 23**, Yaluris teaches particles that minimize the content of harmful gasses present in regenerator units during the regeneration of spent FCC catalysts. See, e.g., ¶0022-24. The particles are microsphere with a dimension capable of passing through a No. 200 screen (*i.e.*, 74 microns). ¶0083.

Yaluris teaches that the particles are porous in that they are mixed and sprayed with a solution that is adjusted to not exceed the water pore volume of the powder. ¶0085.

The particles have alumina and silica support and are shaped as microspheroidal, contains cerium oxide, and is impregnated with platinum. Examples 4 and 5. Since the support is porous (*i.e.*, because it has a pore volume, it must be porous, see ¶0085), and since platinum is impregnated via spray a platinum solution onto the support, it is inevitable that some of the platinum solution is adsorbed into the support's pores. As such, according to the adopted definition of "eggshell" above, Yaluris anticipates the claimed invention.

With regards to **claims 8, 18, 19, 21 and 22**, the claims are product by process claims. When the examiner has found a substantially similar product as in the applied prior art, the burden of proof is shifted to the applicant to establish that their product is patentably distinct and not the examiner to show the same process as making. *In re Brown.* 173 USPQ 685, *In re Fessman*, 180 USPQ 324 and *In re Marosi*, 218 USPQ 289.

Even though these are product-by-process claims, it is noted that Yaluris teaches the claimed process steps (see Examples).

With regards to **claim 15**, Yaluris teaches that the particles contain palladium. See claim 1.

Claim Rejections - 35 USC § 103

The following is a quotation of 35 U.S.C. 103 which forms the basis for all obviousness rejections set forth in this Office action:

> A patent for a claimed invention may not be obtained, notwithstanding that the claimed invention is not identically disclosed as set forth in section 102, if the differences between the claimed invention and the prior art are such that the claimed invention as a whole would have been obvious before the effective filing date of the claimed invention to a person having ordinary skill in the art to which the claimed invention pertains. Patentability shall not be negated by the manner in which the invention was made.

Claims 10, 11, 13, and 15 are rejected under 35 U.S.C. 103 as being unpatentable over Yaluris et al. (US 2005/0042158).

With regards to **claims 10 and 11**, the teachings of Yaluris are as set forth above. Yaluris teaches that the particles have an attrition index of from 0 to 15, which overlaps with the claimed range and thus renders it obvious. See MPEP 2144.05 (I).

With regards to **claims 13 and 15**, the teachings of Yaluris are as set forth above. Yaluris teaches that the noble metal utilized in their particles can be a mixture of palladium and platinum. See ¶0051 and claim 1. As such, it would have been obvious to one of ordinary skill in the art to include both pt and pd in carrying out the exemplified embodiments of Yaluris.

Claim 7 is rejected under 35 U.S.C. 103 as being unpatentable over Yaluris et al. (US 2005/0042158) in view of Vaarkamp et al. (US 2006/0204420).

With regards to **claim 7**, the teachings of Yaluris are as set forth above. Yaluris teaches that the metal support (*i.e.*, the alumina containing component) may be crystalline or amorphous, but is silent with regards to containing gamma or theta alumina.

Vaarkamp teaches particles for minimizing the emission of harmful gasses during regeneration of FCC catalysts. See, e.g., abstract and ¶0006. Vaarkamp states that it is known in the art that porous gamma alumina is used as part the promoter, ¶0011, and teaches that the support maybe crystalline or amorphous and can be gamma or theta alumina. ¶0033. As such, one of ordinary skill in the art would have found it obvious to modify Yaluris' invention by using gamma or theta alumina as the support

Claims 20 is rejected under 35 U.S.C. 103 as being unpatentable over Yaluris et al. (US 2005/0042158) in view of Loganathan et al. (US 2015/0352525).

With regards to **claim 20**, the teachings of Yaluris are as set forth above. Yaluris teaches that the microsphere particle has surface area of 135 m2/g (Example 5), with a particle size of 74 microns (¶0083).

Yaluris is silent with regards to the porous particles including gamma alumina and with regards to the claimed pore volume.

Loganathan teaches a CO oxidation promoter additive for use in the regeneration of an FCC catalyst. See abstract and background of the invention sections. The promoter has a gamma alumina with a pore volume of from 0.3 to 0.6 cm3/g, which overlaps with the claimed invention. See MPEP 2144.05.I. Loganathan teaches that such a support allows it's shaping into microspheres having high density and low attrition strength without employing any alumina based dispersants like aluminum chlorohydrate, hydroxy nitrate or phosphate. ¶ 0066-67. As such, it would have been obvious to one of ordinary skill in the art at the time of the invention to modify the teachings of Yaluris to include Loganathan's gamma alumina with a pore volume that overlaps with the claimed invention to allow for shaping the microspheres without using alumina based dispersants.

Response to Arguments

Applicant's arguments filed on 07/07/2021 ("Remarks") have been fully considered. The arguments regarding the rejection under 35 U.S.C. 112(b) are withdrawn in light of the amendments and arguments presented in the Remarks. However, Applicant's arguments regarding the rejection under 35 U.S.C. 102 are not persuasive.

The Examiner clarified the Office's position regarding the distinction between the claimed terms "microsphere" and "eggshell" above. In essence, the former relates to the structure of the claimed particles while the latter refers to the distribution of claimed "one or more Group VIII noble metals" in the microsphere particles.

Regarding Yaluris et al. (US 2005/0042158), the Applicant argues that "*Yaluris does not disclose eggshell particles*" Remarks at p9 (emphasis in original). To support this argument, Applicant asserts that "Yaluris does not contain a single reference to 'eggshell,' 'gradient,' or 'coating' and uses the term 'layer' only in reference to layers of material applied to trays, not particles." *Id.* at 9-10. This argument is unpersuasive.

Yaluris teaches that the support is porous (*i.e.*, because it has a pore volume, it must be porous, see ¶0085). Yaluris also teaches that platinum is impregnated via spray a platinum solution onto the support. As such, it is inevitable that some of the platinum solution is adsorbed onto the support's pores yielding an "eggshell" distribution within Yaluris' microsphere particles. Accordingly, Applicant's arguments are unpersuasive.

Still, Applicant points to a declaration by Dr. Herring ("Declaration") and concludes that "Yaluris fails to disclose, explicitly or inherently, any eggshell particles according to instant claim 1." Remarks at p11. The Declaration states:

> To someone familiar with chemistry, it is understood that the base material formed in Example 4 of Yaluris will ***necessarily*** comprise pores and that impregnating the base material will according to the method of Example 5 ***necessarily*** result in the platinum being found homogenously throughout the base material particles.

Declaration at ¶8 (emphasis in original).

This portion from the Declaration further supports the rejection of claim 1. Claim 1 requires "<u>one or more Group VII noble metals</u>" to be distributed in the microsphere particle. The distribution is defined in the claim where it states, "...such that a high

concentration of the one or more Group VIII noble metals is present in the outer region of the microsphere sized porous particle as compared to the concentration of the one or more Group VII noble metal in the centre of the microsphere sized porous particle." Because the claim allow for only one noble metal, and since Yaluris' support "necessarily" porous, and further since Yaluris sprays the support with platinum solution, it is inevitable that the pores of the support will include platinum solution is adsorbed into it.

Munnik et al. further supports this conclusion. It states under section 4.2.2. Metal Distribution:

> Adsorption also plays a significant role in the metal distribution across macroscopic support grains or pellets. **Although the pore filling with liquids of larger bodies occurs within a few seconds or minutes**, adsorption on support sites often slows penetration of the precursor significantly. After short equilibration times, it is possible that metal precursor complexes are mostly adsorbed in the outer shell of the support body, resulting in an eggshell distribution.

Munnik at p6697 (emphasis added).

In other words, because the Declaration makes it clear that Yaluris base material "will ***necessarily*** comprise pores," (Declaration at ¶8), and because filling these pores with liquid results "in an eggshell distribution," (Munnik at p6697), then Yaluris' microsphere particle must have an eggshell distribution as required by the claimed invention. Thus, the claimed invention is anticipated by the teachings of Yaluris.

Applicant's arguments regarding the obviousness rejections are based on the unpersuasive argument that Yaluris does not anticipate the independent claim, and thus are found unpersuasive, too.

Conclusion

THIS ACTION IS MADE FINAL. Applicant is reminded of the extension of time policy as set forth in 37 CFR 1.136(a).

A shortened statutory period for reply to this final action is set to expire THREE MONTHS from the mailing date of this action. In the event a first reply is filed within TWO MONTHS of the mailing date of this final action and the advisory action is not mailed until after the end of the THREE-MONTH shortened statutory period, then the shortened statutory period will expire on the date the advisory action is mailed, and any extension fee pursuant to 37 CFR 1.136(a) will be calculated from the mailing date of the advisory action. In no event, however, will the statutory period for reply expire later than SIX MONTHS from the mailing date of this final action.

Any inquiry concerning this communication or earlier communications from the examiner should be directed to HAYTHAM SOLIMAN whose telephone number is (571)270-7192. The examiner can normally be reached on M-F 8:00-500.

Examiner interviews are available via telephone, in-person, and video conferencing using a USPTO supplied web-based collaboration tool. To schedule an interview, applicant is encouraged to use the USPTO Automated Interview Request (AIR) at http://www.uspto.gov/interviewpractice.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Stanley Silverman can be reached on 5712721358. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see https://ppair-my.uspto.gov/pair/PrivatePair. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free). If you would like assistance from a USPTO Customer Service Representative or access to the automated information system, call 800-786-9199 (IN USA OR CANADA) or 571-272-1000.

/HAYTHAM SOLIMAN/
Primary Examiner, Art Unit 1736

Search Notes	Application/Control No.	Applicant(s)/Patent Under Reexamination
	17/176,222	ARU, Guido William
	Examiner	Art Unit
	HAYTHAM SOLIMAN	1736

CPC - Searched*		
Symbol	**Date**	**Examiner**
B01J23/8926, B01J37/0236, B01J21/12, B01J8/26, B01J23/42, C01B32/50, B01J35/1019, B01J37/0221, B01J35/1038, B01J23/44, B01J35/08, B01J21/04, B01J35/1014, B01J8/1827, C10G11/04, B01J21/08, B01J37/088, B01J23/63, B01J35/008	04/04/2021	/HS/
Updated above search	08/10/2021	/HS/

CPC Combination Sets - Searched*		
Symbol	**Date**	**Examiner**

US Classification - Searched*			
Class	**Subclass**	**Date**	**Examiner**
208	120.35	04/04/2021	/HS/
	Updated above search	08/10/2021	/HS/

* See search history printout included with this form or the SEARCH NOTES box below to determine the scope of the search.

Search Notes		
Search Notes	**Date**	**Examiner**
Searched EAST	04/04/2021	/HS/
Preformed Inventor Search	04/04/2021	/HS/
Preformed USPC and CPC search	04/04/2021	/HS/
Preformed Assignee search	04/04/2021	/HS/
Considered IDS and ISR of sister app # 17043031	04/04/2021	/HS/
Updated above search	08/10/2021	/HS/

/HAYTHAM SOLIMAN/ Primary Examiner, Art Unit 1736	

Search Notes	Application/Control No.	Applicant(s)/Patent Under Reexamination
	17/176,222	ARU, Guido William
	Examiner	Art Unit
	HAYTHAM SOLIMAN	1736

Interference Search			
US Class/CPC Symbol	US Subclass/CPC Group	Date	Examiner

/HAYTHAM SOLIMAN/ Primary Examiner, Art Unit 1736	

Doc code: IDS
Doc description: Information Disclosure Statement (IDS) Filed

PTO/SB/08a (02-18)
Approved for use through 11/30/2020. OMB 0651-0031
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (**Not for submission under 37 CFR 1.99)**		
	Application Number	17176222
	Filing Date	2021-02-16
	First Named Inventor	Aru, Guido William
	Art Unit	1736
	Examiner Name	Soliman, Haytham
	Attorney Docket Number	071816-091960USC1

U.S.PATENTS						
Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1					
If you wish to add additional U.S. Patent citation information please click the Add button.						

U.S.PATENT APPLICATION PUBLICATIONS						
Examiner Initial*	Cite No	Publication Number	Kind Code[1]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1					
If you wish to add additional U.S. Published Application citation information please click the Add button.						

FOREIGN PATENT DOCUMENTS								
Examiner Initial*	Cite No	Foreign Document Number[3]	Country Code[2] ¡	Kind Code[4]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear	T[5]
	1							☐
If you wish to add additional Foreign Patent Document citation information please click the Add button								

NON-PATENT LITERATURE DOCUMENTS			
Examiner Initials*	Cite No	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc), date, pages(s), volume-issue number(s), publisher, city and/or country where published.	T[5]

EFS Web 2.1.18

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /H.S/

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	17176222
	Filing Date	2021-02-16
	First Named Inventor	Aru, Guido William
	Art Unit	1736
	Examiner Name	Soliman, Haytham
	Attorney Docket Number	071816-091960USC1

	1	Microspheres Online. "12 Essential Properties of Microspheres - Detailed Guide to Achieve Results." Retrieved from web 2021-04-20. URL: <https://www.microspheres.us/properties-of-microspheres/>. 7 pages. (2020)	☐
	2	MUNNIK et al. "Recent developments in the synthesis of supported catalysts." Chemical Reviews 115(14): 6687-6718 (2015)	☐
	3	PAPAGEORGIOU et al. "Preparation of Pt/γ-Al2O3Pellets with Internal Step-Distribution of Catalyst: Experiments and Theory." Journal of Catalysis 158(2): 439-451 (1996)	☐
	4	RUSSO et al. "Intraparticle Modeling of Non-Uniform Active Phase Distribution Catalyst." ChemEngineering 4(2): 24 pp. 1-15 (2020)	☐
	5	VENUTO et al. "Fluid catalytic cracking with zeolite catalysts." Marcel Dekker, Inc. New York. Pages 30-31, 42-47 (1979)	☐

If you wish to add additional non-patent literature document citation information please click the Add button

EXAMINER SIGNATURE

Examiner Signature	/HAYTHAM SOLIMAN/	Date Considered	08/10/2021

*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through a citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

[1] See Kind Codes of USPTO Patent Documents at www.USPTO.GOV or MPEP 901.04. [2] Enter office that issued the document, by the two-letter code (WIPO Standard ST.3). [3] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. [4] Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [5] Applicant is to place a check mark here if English language translation is attached.

EFS Web 2.1.18

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /H.S/

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	17176222
	Filing Date	2021-02-16
	First Named Inventor	Aru, Guido William
	Art Unit	1736
	Examiner Name	Soliman, Haytham
	Attorney Docket Number	071816-091960USC1

CERTIFICATION STATEMENT

Please see 37 CFR 1.97 and 1.98 to make the appropriate selection(s):

☐ That each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(1).

OR

☐ That no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing the certification after making reasonable inquiry, no item of information contained in the information disclosure statement was known to any individual designated in 37 CFR 1.56(c) more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(2).

☐ See attached certification statement.

☒ The fee set forth in 37 CFR 1.17 (p) has been submitted herewith.

☒ A certification statement is not submitted herewith.

SIGNATURE

A signature of the applicant or representative is required in accordance with CFR 1.33, 10.18. Please see CFR 1.4(d) for the form of the signature.

Signature	/Nicole D. Kling/	Date (YYYY-MM-DD)	2021-07-07
Name/Print	Nicole D. Kling	Registration Number	71,959

This collection of information is required by 37 CFR 1.97 and 1.98. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 1 hour to complete, including gathering, preparing and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

EFS Web 2.1.18

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /H.S/

Privacy Act Statement

The Privacy Act of 1974 (P.L. 93-579) requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C. 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether the Freedom of Information Act requires disclosure of these record s.

2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.

3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.

4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).

5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.

6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).

7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.

8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspections or an issued patent.

9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

EFS Web 2.1.18

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /H.S/

UNITED STATES PATENT AND TRADEMARK OFFICE

USPTO Automated Interview Request (AIR)

Oct 15 2021

This paper requesting to schedule and/or conduct an interview is appropriate because:

This submission is requested to be accepted as an authorization for this interview to communicate via the internet. Recognizing that Internet communications are not secure, I hereby authorize the USPTO to communicate with the undersigned concerning scheduling of the interview via video conference, instant messaging, or electronic mail, and to conduct the interview in accordance with office practice including video conferencing.

Name(s):
Nicole D. Kling

S-signature:
/NIcole Kling/

Registration Number:
71959

U.S. Application Number:
17176222

Confirmation Number:
3640

E-mail Address:
nkling@nixonpeabody.com

Phone Number:
+1 6174706866

Proposed Time of Interview:
10-25-2021 1:00 PM ET

Alternative Proposed Time(s) of Interview:
10-27-2021 10:00 AM ET

Alternative Proposed Time(s) of Interview:
10-27-2021 11:00 AM ET

Prefered Interview Type:
Telephonic

I am the applicant or applicant's representative for this application.

Topic for Discussion:
103 rejection, teachings of cited art

uspto UNITED STATES PATENT AND TRADEMARK OFFICE

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	17/176,222	ARU, Guido William
	Examiner	**Art Unit**
	HAYTHAM SOLIMAN	1736

CPC							
Symbol						**Type**	**Version**
B01J	/	23	/	8926		F	2013-01-01
C01B	/	32	/	50		I	2017-08-01
B01J	/	8	/	1827		I	2013-01-01
B01J	/	8	/	26		I	2013-01-01
B01J	/	21	/	04		I	2013-01-01
B01J	/	21	/	08		I	2013-01-01
B01J	/	21	/	12		I	2013-01-01
B01J	/	23	/	42		I	2013-01-01
B01J	/	23	/	44		I	2013-01-01
B01J	/	23	/	63		I	2013-01-01
B01J	/	35	/	008		I	2013-01-01
B01J	/	35	/	08		I	2013-01-01
B01J	/	35	/	1014		I	2013-01-01
B01J	/	35	/	1019		I	2013-01-01
B01J	/	35	/	1038		I	2013-01-01
B01J	/	37	/	0221		I	2013-01-01
B01J	/	37	/	0236		I	2013-01-01
B01J	/	37	/	088		I	2013-01-01
C10G	/	11	/	04		I	2013-01-01

CPC Combination Sets							
Symbol					**Type**	**Set**	**Ranking**	**Version**
	/		/					

NONE		Total Claims Allowed:	
(Assistant Examiner)	(Date)	22	
/HAYTHAM SOLIMAN/ Primary Examiner, Art Unit 1736	03 November 2021	O.G. Print Claim(s)	O.G. Print Figure
(Primary Examiner)	(Date)	1	2

U.S. Patent and Trademark Office — Part of Paper No.: 20211103

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	17/176,222	ARU, Guido William
	Examiner	**Art Unit**
	HAYTHAM SOLIMAN	1736

INTERNATIONAL CLASSIFICATION				
CLAIMED				
C10G	/	11	/	00

NON-CLAIMED				
	/		/	

US ORIGINAL CLASSIFICATION	
CLASS	**SUBCLASS**
208	120.35

CROSS REFERENCES(S)						
CLASS	**SUBCLASS (ONE SUBCLASS PER BLOCK)**					

NONE		**Total Claims Allowed:**	
(Assistant Examiner)	(Date)	22	
/HAYTHAM SOLIMAN/ Primary Examiner, Art Unit 1736	03 November 2021	O.G. Print Claim(s)	O.G. Print Figure
(Primary Examiner)	(Date)	1	2

U.S. Patent and Trademark Office — Part of Paper No.: 20211103

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	17/176,222	ARU, Guido William
	Examiner	**Art Unit**
	HAYTHAM SOLIMAN	1736

☑ Claims renumbered in the same order as presented by applicant ☐ CPA ☐ T.D. ☐ R.1.47

CLAIMS															
Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original

NONE (Assistant Examiner)	(Date)	**Total Claims Allowed:** 22	
/HAYTHAM SOLIMAN/ Primary Examiner, Art Unit 1736 (Primary Examiner)	03 November 2021 (Date)	O.G. Print Claim(s) 1	O.G. Print Figure 2

U.S. Patent and Trademark Office — Part of Paper No.: 20211103

Search Notes	Application/Control No.	Applicant(s)/Patent Under Reexamination
	17/176,222	ARU, Guido William
	Examiner	Art Unit
	HAYTHAM SOLIMAN	1736

CPC - Searched*		
Symbol	**Date**	**Examiner**
B01J23/8926, B01J37/0236, B01J21/12, B01J8/26, B01J23/42, C01B32/50, B01J35/1019, B01J37/0221, B01J35/1038, B01J23/44, B01J35/08, B01J21/04, B01J35/1014, B01J8/1827, C10G11/04, B01J21/08, B01J37/088, B01J23/63, B01J35/008	04/04/2021	/HS/
Updated above search	08/10/2021	/HS/
Updated above search	11/03/2021	/HS/

CPC Combination Sets - Searched*		
Symbol	**Date**	**Examiner**

US Classification - Searched*			
Class	**Subclass**	**Date**	**Examiner**
208	120.35	04/04/2021	/HS/
	Updated above search	08/10/2021	/HS/
	Updated above search	11/03/2021	/HS/

* See search history printout included with this form or the SEARCH NOTES box below to determine the scope of the search.

/HAYTHAM SOLIMAN/ Primary Examiner, Art Unit 1736	

Search Notes	Application/Control No.	Applicant(s)/Patent Under Reexamination
	17/176,222	ARU, Guido William
	Examiner	Art Unit
	HAYTHAM SOLIMAN	1736

Search Notes		
Search Notes	**Date**	**Examiner**
Searched EAST	04/04/2021	/HS/
Preformed Inventor Search	04/04/2021	/HS/
Preformed USPC and CPC search	04/04/2021	/HS/
Preformed Assignee search	04/04/2021	/HS/
Considered IDS and ISR of sister app # 17043031	04/04/2021	/HS/
Updated above search	08/10/2021	/HS/
Updated above search	11/03/2021	/HS/

Interference Search			
US Class/CPC Symbol	**US Subclass/CPC Group**	**Date**	**Examiner**
208	120.35	11/03/2021	/HS/

/HAYTHAM SOLIMAN/ Primary Examiner, Art Unit 1736	

Applicant-Initiated Interview Summary	Application No. 17/176,222	Applicant(s) ARU, Guido William		
	Examiner HAYTHAM SOLIMAN	Art Unit 1736	AIA (First Inventor to File) Status Yes	Page 1 of 1

All Participants (applicant, applicants representative, PTO personnel)	Title	Type
HAYTHAM SOLIMAN	Primary Examiner	Telephonic
Natalie Herring Ph.D.	Inventor	
Nicole D. Kling	Agent of Record	

Date of Interview: 25 October 2021

Issues Discussed:

35 U.S.C. 102

Applicant argued that the distinction between the closest prior art of record and the claimed invention is that the concentration (i.e., m/v) of the noble metal as oppose to merely its mass, is not uniform throughout the claimed promoter. The Applicant asserted that the closest prior art of record is at best silent regarding this feature. The Examiner agreed. In a later call, the Applicant agreed to cancel claim 23 via an examiner amendment.

☑ Attachment

/HAYTHAM SOLIMAN/ Primary Examiner, Art Unit 1736	

Applicant is reminded that a complete written statement as to the substance of the interview must be made of record in the application file. It is the applicants responsibility to provide the written statement, unless the interview was initiated by the Examiner and the Examiner has indicated that a written summary will be provided. See MPEP 713.04
Please further see:
MPEP 713.04
Title 37 Code of Federal Regulations (CFR) § 1.133 Interviews, paragraph (b)
37 CFR § 1.2 Business to be transacted in writing

Applicant recordation instructions: The formal written reply to the last Office action must include the substance of the interview. (See MPEP section 713.04). If a reply to the last Office action has already been filed, applicant is given a non-extendable period of the longer of one month or thirty days from this interview date, or the mailing date of this interview summary form, whichever is later, to file a statement of the substance of the interview.

Examiner recordation instructions: Examiners must summarize the substance of any interview of record. A complete and proper recordation of the substance of an interview should include the items listed in MPEP 713.04 for complete and proper recordation including the identification of the general thrust of each argument or issue discussed, a general indication of any other pertinent matters discussed regarding patentability and the general results or outcome of the interview, to include an indication as to whether or not agreement was reached on the issues raised.

Interview Agenda for USSN 17/176,222
Scheduled for October 25, 2021 at 1 pm Eastern

Attendees:

Nicole D. Kling	Applicant's Representative, Agent of Record
Natalie Herring Ph.D.	Director of Technology and Business Development at G.W. Aru

Points of Discussion

1. Introduce Dr. Herring; Overview of combustion promoter technology

2. The Yaluris inventors have physically characterized their particles and describe the "palladium is present in the form of highly dispersed PdO species"

    a. See Alexeev et al. Characterization of Pd-based FCC CO/NOx control additives by in situ FTIR and extended X-ray absorption fine structure spectroscopies. Catalysis Today, 2007, 127, 176–188.

    "EXAFS results indicate that in a freshly prepared Pd^{n+} /Ce^{n+} / Na^{+} /γ-Al_2O_3 sample, similar to materials used commercially as FCC NOx additives, palladium is present in the form of ***highly dispersed*** PdO species."

3. The Munnik reference is not applicable to Yaluris

    a. The relevant compositions are physically distinct in size and chemical makeup. Those physical distinctions are known to affect absorption.

    b. The relevant compositions are made by methods with different impregnation conditions.

4. The present invention provides unexpected results

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

NOTICE OF ALLOWANCE AND FEE(S) DUE

53143 7590 11/17/2021

RONALD I. EISENSTEIN
NIXON PEABODY LLP
Exchange Place, 53 State Street
BOSTON, MA 02109

EXAMINER
SOLIMAN, HAYTHAM

ART UNIT	PAPER NUMBER
1736	

DATE MAILED: 11/17/2021

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
17/176,222	02/16/2021	Guido William ARU	071816-091960USC1	3640

TITLE OF INVENTION: CO TO CO2 COMBUSTION PROMOTER

APPLN. TYPE	ENTITY STATUS	ISSUE FEE DUE	PUBLICATION FEE DUE	PREV. PAID ISSUE FEE	TOTAL FEE(S) DUE	DATE DUE
nonprovisional	SMALL	$600	$0.00	$0.00	$600	02/17/2022

THE APPLICATION IDENTIFIED ABOVE HAS BEEN EXAMINED AND IS ALLOWED FOR ISSUANCE AS A PATENT. PROSECUTION ON THE MERITS IS CLOSED. THIS NOTICE OF ALLOWANCE IS NOT A GRANT OF PATENT RIGHTS. THIS APPLICATION IS SUBJECT TO WITHDRAWAL FROM ISSUE AT THE INITIATIVE OF THE OFFICE OR UPON PETITION BY THE APPLICANT. SEE 37 CFR 1.313 AND MPEP 1308.

THE ISSUE FEE AND PUBLICATION FEE (IF REQUIRED) MUST BE PAID WITHIN THREE MONTHS FROM THE MAILING DATE OF THIS NOTICE OR THIS APPLICATION SHALL BE REGARDED AS ABANDONED. THIS STATUTORY PERIOD CANNOT BE EXTENDED. SEE 35 U.S.C. 151. THE ISSUE FEE DUE INDICATED ABOVE DOES NOT REFLECT A CREDIT FOR ANY PREVIOUSLY PAID ISSUE FEE IN THIS APPLICATION. IF AN ISSUE FEE HAS PREVIOUSLY BEEN PAID IN THIS APPLICATION (AS SHOWN ABOVE), THE RETURN OF PART B OF THIS FORM WILL BE CONSIDERED A REQUEST TO REAPPLY THE PREVIOUSLY PAID ISSUE FEE TOWARD THE ISSUE FEE NOW DUE.

HOW TO REPLY TO THIS NOTICE:

I. Review the ENTITY STATUS shown above. If the ENTITY STATUS is shown as SMALL or MICRO, verify whether entitlement to that entity status still applies.

If the ENTITY STATUS is the same as shown above, pay the TOTAL FEE(S) DUE shown above.

If the ENTITY STATUS is changed from that shown above, on PART B - FEE(S) TRANSMITTAL, complete section number 5 titled "Change in Entity Status (from status indicated above)".

For purposes of this notice, small entity fees are 1/2 the amount of undiscounted fees, and micro entity fees are 1/2 the amount of small entity fees.

II. PART B - FEE(S) TRANSMITTAL, or its equivalent, must be completed and returned to the United States Patent and Trademark Office (USPTO) with your ISSUE FEE and PUBLICATION FEE (if required). If you are charging the fee(s) to your deposit account, section "4b" of Part B - Fee(s) Transmittal should be completed and an extra copy of the form should be submitted. If an equivalent of Part B is filed, a request to reapply a previously paid issue fee must be clearly made, and delays in processing may occur due to the difficulty in recognizing the paper as an equivalent of Part B.

III. All communications regarding this application must give the application number. Please direct all communications prior to issuance to Mail Stop ISSUE FEE unless advised to the contrary.

IMPORTANT REMINDER: Maintenance fees are due in utility patents issuing on applications filed on or after Dec. 12, 1980. It is patentee's responsibility to ensure timely payment of maintenance fees when due. More information is available at www.uspto.gov/PatentMaintenanceFees.

PART B - FEE(S) TRANSMITTAL

Complete and send this form, together with applicable fee(s), by mail or fax, or via EFS-Web.

By mail, send to: Mail Stop ISSUE FEE
Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450

By fax, send to: (571)-273-2885

INSTRUCTIONS: This form should be used for transmitting the ISSUE FEE and PUBLICATION FEE (if required). Blocks 1 through 5 should be completed where appropriate. All further correspondence including the Patent, advance orders and notification of maintenance fees will be mailed to the current correspondence address as indicated unless corrected below or directed otherwise in Block 1, by (a) specifying a new correspondence address; and/or (b) indicating a separate "FEE ADDRESS" for maintenance fee notifications.

CURRENT CORRESPONDENCE ADDRESS (Note: Use Block 1 for any change of address)

53143 7590 11/17/2021

RONALD I. EISENSTEIN
NIXON PEABODY LLP
Exchange Place, 53 State Street
BOSTON, MA 02109

Note: A certificate of mailing can only be used for domestic mailings of the Fee(s) Transmittal. This certificate cannot be used for any other accompanying papers. Each additional paper, such as an assignment or formal drawing, must have its own certificate of mailing or transmission.

Certificate of Mailing or Transmission

I hereby certify that this Fee(s) Transmittal is being deposited with the United States Postal Service with sufficient postage for first class mail in an envelope addressed to the Mail Stop ISSUE FEE address above, or being transmitted to the USPTO via EFS-Web or by facsimile to (571) 273-2885, on the date below.

(Typed or printed name)
(Signature)
(Date)

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
17/176,222	02/16/2021	Guido William ARU	071816-091960USC1	3640

TITLE OF INVENTION: CO TO CO2 COMBUSTION PROMOTER

APPLN. TYPE	ENTITY STATUS	ISSUE FEE DUE	PUBLICATION FEE DUE	PREV. PAID ISSUE FEE	TOTAL FEE(S) DUE	DATE DUE
nonprovisional	SMALL	$600	$0.00	$0.00	$600	02/17/2022

EXAMINER	ART UNIT	CLASS-SUBCLASS
SOLIMAN, HAYTHAM	1736	208-120350

1. Change of correspondence address or indication of "Fee Address" (37 CFR 1.363).

❑ Change of correspondence address (or Change of Correspondence Address form PTO/SB/122) attached.

❑ "Fee Address" indication (or "Fee Address" Indication form PTO/SB/47; Rev 03-09 or more recent) attached. **Use of a Customer Number is required.**

2. For printing on the patent front page, list
(1) The names of up to 3 registered patent attorneys or agents OR, alternatively,
(2) The name of a single firm (having as a member a registered attorney or agent) and the names of up to 2 registered patent attorneys or agents. If no name is listed, no name will be printed.

1_____
2_____
3_____

3. ASSIGNEE NAME AND RESIDENCE DATA TO BE PRINTED ON THE PATENT (print or type)

PLEASE NOTE: Unless an assignee is identified below, no assignee data will appear on the patent. If an assignee is identified below, the document must have been previously recorded, or filed for recordation, as set forth in 37 CFR 3.11 and 37 CFR 3.81(a). Completion of this form is NOT a substitute for filing an assignment.

(A) NAME OF ASSIGNEE (B) RESIDENCE: (CITY and STATE OR COUNTRY)

Please check the appropriate assignee category or categories (will not be printed on the patent) : ❑ Individual ❑ Corporation or other private group entity ❑ Government

4a. Fees submitted: ❑Issue Fee ❑Publication Fee (if required) ❑Advance Order - # of Copies _____

4b. Method of Payment: *(Please first reapply any previously paid fee shown above)*

❑ Electronic Payment via EFS-Web ❑ Enclosed check ❑ Non-electronic payment by credit card (Attach form PTO-2038)

❑ The Director is hereby authorized to charge the required fee(s), any deficiency, or credit any overpayment to Deposit Account No. _____

5. **Change in Entity Status** (from status indicated above)

❑ Applicant certifying micro entity status. See 37 CFR 1.29

❑ Applicant asserting small entity status. See 37 CFR 1.27

❑ Applicant changing to regular undiscounted fee status.

NOTE: Absent a valid certification of Micro Entity Status (see forms PTO/SB/15A and 15B), issue fee payment in the micro entity amount will not be accepted at the risk of application abandonment.
NOTE: If the application was previously under micro entity status, checking this box will be taken to be a notification of loss of entitlement to micro entity status.
NOTE: Checking this box will be taken to be a notification of loss of entitlement to small or micro entity status, as applicable.

NOTE: This form must be signed in accordance with 37 CFR 1.31 and 1.33. See 37 CFR 1.4 for signature requirements and certifications.

Authorized Signature _____ Date _____

Typed or printed name _____ Registration No. _____

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
17/176,222	02/16/2021	Guido William ARU	071816-091960USC1	3640

53143 7590 11/17/2021

RONALD I. EISENSTEIN
NIXON PEABODY LLP
Exchange Place, 53 State Street
BOSTON, MA 02109

EXAMINER	
SOLIMAN, HAYTHAM	
ART UNIT	PAPER NUMBER
1736	

DATE MAILED: 11/17/2021

Determination of Patent Term Adjustment under 35 U.S.C. 154 (b)
(Applications filed on or after May 29, 2000)

The Office has discontinued providing a Patent Term Adjustment (PTA) calculation with the Notice of Allowance.

Section 1(h)(2) of the AIA Technical Corrections Act amended 35 U.S.C. 154(b)(3)(B)(i) to eliminate the requirement that the Office provide a patent term adjustment determination with the notice of allowance. See Revisions to Patent Term Adjustment, 78 Fed. Reg. 19416, 19417 (Apr. 1, 2013). Therefore, the Office is no longer providing an initial patent term adjustment determination with the notice of allowance. The Office will continue to provide a patent term adjustment determination with the Issue Notification Letter that is mailed to applicant approximately three weeks prior to the issue date of the patent, and will include the patent term adjustment on the patent. Any request for reconsideration of the patent term adjustment determination (or reinstatement of patent term adjustment) should follow the process outlined in 37 CFR 1.705.

Any questions regarding the Patent Term Extension or Adjustment determination should be directed to the Office of Patent Legal Administration at (571)-272-7702. Questions relating to issue and publication fee payments should be directed to the Customer Service Center of the Office of Patent Publication at 1-(888)-786-0101 or (571)-272-4200.

PTOL-85 (Rev. 02/11)

OMB Clearance and PRA Burden Statement for PTOL-85 Part B

The Paperwork Reduction Act (PRA) of 1995 requires Federal agencies to obtain Office of Management and Budget approval before requesting most types of information from the public. When OMB approves an agency request to collect information from the public, OMB (i) provides a valid OMB Control Number and expiration date for the agency to display on the instrument that will be used to collect the information and (ii) requires the agency to inform the public about the OMB Control Number's legal significance in accordance with 5 CFR 1320.5(b).

The information collected by PTOL-85 Part B is required by 37 CFR 1.311. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 30 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, Virginia 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, Virginia 22313-1450. Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

Privacy Act Statement

The Privacy Act of 1974 (P.L. 93-579) requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether disclosure of these records is required by the Freedom of Information Act.
2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.
3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.
4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).
5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.
6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).
7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.
8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspection or an issued patent.
9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

Notice of Allowability	Application No. 17/176,222	Applicant(s) ARU, Guido William	
	Examiner HAYTHAM SOLIMAN	Art Unit 1736	AIA (FITF) Status Yes

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address--

All claims being allowable, PROSECUTION ON THE MERITS IS (OR REMAINS) CLOSED in this application. If not included herewith (or previously mailed), a Notice of Allowance (PTOL-85) or other appropriate communication will be mailed in due course. **THIS NOTICE OF ALLOWABILITY IS NOT A GRANT OF PATENT RIGHTS.** This application is subject to withdrawal from issue at the initiative of the Office or upon petition by the applicant. See 37 CFR 1.313 and MPEP 1308.

1. ☑ This communication is responsive to 08/13/2021.
   ☐ A declaration(s)/affidavit(s) under **37 CFR 1.130(b)** was/were filed on _____.

2. ☐ An election was made by the applicant in response to a restriction requirement set forth during the interview on _____; the restriction requirement and election have been incorporated into this action.

3. ☑ The allowed claim(s) is/are 1-22 . As a result of the allowed claim(s), you may be eligible to benefit from the **Patent Prosecution Highway** program at a participating intellectual property office for the corresponding application. For more information, please see **http://www.uspto.gov/patents/init_events/pph/index.jsp** or send an inquiry to **PPHfeedback@uspto.gov.**

4. ☑ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

   Certified copies:

   a) ☑ All b) ☐ Some* c) ☐ None of the:

   1. ☐ Certified copies of the priority documents have been received.
   2. ☑ Certified copies of the priority documents have been received in Application No. 17043031 .
   3. ☐ Copies of the certified copies of the priority documents have been received in this national stage application from the International Bureau (PCT Rule 17.2(a)).

   * Certified copies not received: _____ .

Applicant has THREE MONTHS FROM THE "MAILING DATE" of this communication to file a reply complying with the requirements noted below. Failure to timely comply will result in ABANDONMENT of this application.
THIS THREE-MONTH PERIOD IS NOT EXTENDABLE.

5. ☐ CORRECTED DRAWINGS (as "replacement sheets") must be submitted.
   ☐ including changes required by the attached Examiner's Amendment / Comment or in the Office action of Paper No./Mail Date _____ .

   Identifying indicia such as the application number (see 37 CFR 1.84(c)) should be written on the drawings in the front (not the back) of each sheet. Replacement sheet(s) should be labeled as such in the header according to 37 CFR 1.121(d).

6. ☐ DEPOSIT OF and/or INFORMATION about the deposit of BIOLOGICAL MATERIAL must be submitted. Note the attached Examiner's comment regarding REQUIREMENT FOR THE DEPOSIT OF BIOLOGICAL MATERIAL.

Attachment(s)

1. ☐ Notice of References Cited (PTO-892)
2. ☐ Information Disclosure Statements (PTO/SB/08), Paper No./Mail Date _____.
3. ☐ Examiner's Comment Regarding Requirement for Deposit of Biological Material _____.
4. ☑ Interview Summary (PTO-413), Paper No./Mail Date. 20211103.
5. ☑ Examiner's Amendment/Comment
6. ☑ Examiner's Statement of Reasons for Allowance
7. ☐ Other _____.

/HAYTHAM SOLIMAN/
Primary Examiner, Art Unit 1736

DETAILED ACTION

EXAMINER'S AMENDMENT

An examiner's amendment to the record appears below. Should the changes and/or additions be unacceptable to applicant, an amendment may be filed as provided by 37 CFR 1.312. To ensure consideration of such an amendment, it MUST be submitted no later than the payment of the issue fee.

Authorization for this examiner's amendment was given in an interview with Dr. Nicole Kling on 11/4/2021.

The application has been amended as follows:

Claim 23 is now cancelled.

Reasons for Allowance

The following is an examiner's statement of reasons for allowance:

The claimed invention requires the concentration, *i.e.*, mass/volume, as opposed to the amount, i.e., mass, of the claimed noble metal is change from the outer region of the claimed promoter to its inner region. The closest prior art of record is silent regarding this feature, and as such it does not anticipate or render it obvious.

Any comments considered necessary by applicant must be submitted no later than the payment of the issue fee and, to avoid processing delays, should preferably accompany the issue fee. Such submissions should be clearly labeled "Comments on Statement of Reasons for Allowance."

Conclusion

Any inquiry concerning this communication or earlier communications from the examiner should be directed to HAYTHAM SOLIMAN whose telephone number is (571)270-7192. The examiner can normally be reached M-F 8:00-500.

Examiner interviews are available via telephone, in-person, and video conferencing using a USPTO supplied web-based collaboration tool. To schedule an

interview, applicant is encouraged to use the USPTO Automated Interview Request (AIR) at http://www.uspto.gov/interviewpractice.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Stanley Silverman can be reached on 5712721358. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

Information regarding the status of published or unpublished applications may be obtained from Patent Center. Unpublished application information in Patent Center is available to registered users. To file and manage patent submissions in Patent Center, visit: https://patentcenter.uspto.gov. Visit https://www.uspto.gov/patents/apply/patent-center for more information about Patent Center and https://www.uspto.gov/patents/docx for information about filing in DOCX format. For additional questions, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free). If you would like assistance from a USPTO Customer Service Representative, call 800-786-9199 (IN USA OR CANADA) or 571-272-1000.

/HAYTHAM SOLIMAN/
Primary Examiner, Art Unit 1736

Attorney Docket No. 071816-091960USC1 PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:	Guido William ARU *et al.*	Confirmation No.:	3640
Application No.:	17/176,222	Art Unit:	1736
Filing Date:	February 16, 2021	Examiner:	Haytham SOLIMAN
For:	A CO TO CO2 COMBUSTION PROMOTER		

VIA EFS-WEB
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

GENERAL TRANSMITTAL & CERTIFICATE OF EFS SUBMISSION

Pursuant to 37 C.F.R. § 1.8(a)(1)(i)(C) I hereby certify that the following documents are being submitted to the Patent and Trademark Office via the Office Electronic Filing System in accordance with § 1.6(a)(4) on **December 6, 2021;**

1. **General Transmittal & Certificate of EFS Submission (1 pg.);**
2. **Issue Fee Transmittal (1 pg.);**
3. **Declaration (1 pg.); and**
4. **Fee Transmittal (1 pg.)**

AUTHORIZATION TO CHARGE/CREDIT DEPOSIT ACCOUNT

The Director of the USPTO is hereby authorized to charge any fee deficiencies associated with the instant filing, **except excess claims fees**, and credit any overpayments to NIXON PEABODY LLP Deposit Account No. **50-0850**, from which the undersigned is authorized to withdraw.

Customer No.: 53143

Date: December 6, 2021

Respectfully submitted,

/NICOLE D. KLING/

NICOLE D. KLING (Reg. No. 71,959)
RONALD I. EISENSTEIN (Reg. No. 30,628)
NIXON PEABODY LLP
Exchange Place – 53 State Street
Boston, MA 02109-2835
Tel. (617) 345-1013/6054
Fax (617) 345-1300
Email: bostonpatent@nixonpeabody.com

4833-4902-4040.1

Electronic Patent Application Fee Transmittal	
Application Number:	17176222
Filing Date:	16-Feb-2021
Title of Invention:	CO TO CO2 COMBUSTION PROMOTER
First Named Inventor/Applicant Name:	Guido William ARU
Filer:	Nicole Dian Kling/Ali Yamakaitis
Attorney Docket Number:	071816-091960USC1
Filed as Small Entity	
Filing Fees for Utility under 35 USC 111(a)	

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Basic Filing:				
Pages:				
Claims:				
Miscellaneous-Filing:				
Petition:				
Patent-Appeals-and-Interference:				
Post-Allowance-and-Post-Issuance:				
UTILITY APPL ISSUE FEE	2501	1	600	600

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Extension-of-Time:				
Miscellaneous:				
		Total in USD ($)		**600**

DECLARATION UNDER 37 CFR §1.63 FOR UTILITY APPLICATION USING AN APPLICATION DATA SHEET

TITLE OF INVENTION:

A CO TO CO_2 COMBUSTION PROMOTER

As the below named inventor, I hereby declare that:

This Declaration is directed to:

- ▪ United States application 17/176,222 filed February 16, 2021, which claims priority to PCT international application number **PCT/US2019/024742** filed on **March 29, 2019**.
- ▪ I have reviewed the Amendment filed July 7, 2021.
- ▪ I have reviewed the Examiner's Amendment mailed November 17, 2021.

The above-identified application was made or authorized to be made by me.

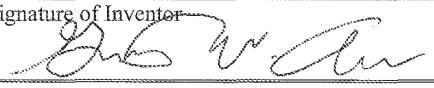
I believe that I am the original inventor or an original joint inventor of a claimed invention in the application.

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, §1.56(a).

I hereby further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further, that these statements were made with the knowledge that any willful false statements and the like so made in this declaration are punishable by fine or imprisonment of not more than 5 years, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

LEGAL NAME OF INVENTOR	LAST NAME	FIRST NAME	MIDDLE NAME
	ARU	**GUIDO**	**WILLIAM**

Signature of Inventor	Date:
	DECEMBER 3, 2021

Electronic Acknowledgement Receipt	
EFS ID:	44438559
Application Number:	17176222
International Application Number:	
Confirmation Number:	3640
Title of Invention:	CO TO CO2 COMBUSTION PROMOTER
First Named Inventor/Applicant Name:	Guido William ARU
Customer Number:	53143
Filer:	Nicole Dian Kling/Ali Yamakaitis
Filer Authorized By:	Nicole Dian Kling
Attorney Docket Number:	071816-091960USC1
Receipt Date:	06-DEC-2021
Filing Date:	16-FEB-2021
Time Stamp:	12:44:23
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	yes
Payment Type	DA
Payment was successfully received in RAM	$600
RAM confirmation Number	E2021B6C44482954
Deposit Account	
Authorized User	
The Director of the USPTO is hereby authorized to charge indicated fees and credit any overpayment as follows:	

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Transmittal Letter	2021-12-06-EFS_Transmittal_071816-091960USC1.pdf	116877 567f9c4d99904f0e22fb62da028737917119 87e3	no	1
Warnings:					
Information:					
2	Oath or Declaration filed	2021-12-06_Declaration_071816-091960USC1.pdf	989995 0a5a21d92eda57b773453723a6f3f56227f7 af39	no	1
Warnings:					
Information:					
3	Issue Fee Payment (PTO-85B)	2021-12-06_Issue_Fee_Transmittal_071816-091960USC1.pdf	1621239 c098f599b2531a010c52557be25aa29b0d1 516a2	no	1
Warnings:					
Information:					
4	Fee Worksheet (SB06)	fee-info.pdf	37983 8a2724d9ea44a596521157f14a20f52fe422 95eb	no	2
Warnings:					
Information:					
		Total Files Size (in bytes):	2766094		

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

PART B - FEE(S) TRANSMITTAL

Complete and send this form, together with applicable fee(s), by mail or fax, or via EFS-Web.

By mail, send to: Mail Stop ISSUE FEE
Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450

By fax, send to: (571)-273-2885

INSTRUCTIONS: This form should be used for transmitting the ISSUE FEE and PUBLICATION FEE (if required). Blocks 1 through 5 should be completed where appropriate. All further correspondence including the Patent, advance orders and notification of maintenance fees will be mailed to the current correspondence address as indicated unless corrected below or directed otherwise in Block 1, by (a) specifying a new correspondence address; and/or (b) indicating a separate "FEE ADDRESS" for maintenance fee notifications.

CURRENT CORRESPONDENCE ADDRESS (Note: Use Block 1 for any change of address)

53143 7590 11/17/2021

RONALD I. EISENSTEIN
NIXON PEABODY LLP
Exchange Place, 53 State Street
BOSTON, MA 02109

Note: A certificate of mailing can only be used for domestic mailings of the Fee(s) Transmittal. This certificate cannot be used for any other accompanying papers. Each additional paper, such as an assignment or formal drawing, must have its own certificate of mailing or transmission.

Certificate of Mailing or Transmission

I hereby certify that this Fee(s) Transmittal is being deposited with the United States Postal Service with sufficient postage for first class mail in an envelope addressed to the Mail Stop ISSUE FEE address above, or being transmitted to the USPTO via EFS-Web or by facsimile to (571) 273-2885, on the date below.

(Typed or printed name)
(Signature)
(Date)

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
17/176,222	02/16/2021	Guido William ARU	071816-091960USC1	3640

TITLE OF INVENTION: CO TO CO2 COMBUSTION PROMOTER

APPLN. TYPE	ENTITY STATUS	ISSUE FEE DUE	PUBLICATION FEE DUE	PREV. PAID ISSUE FEE	TOTAL FEE(S) DUE	DATE DUE
nonprovisional	SMALL	$600	$0.00	$0.00	$600	02/17/2022

EXAMINER	ART UNIT	CLASS-SUBCLASS
SOLIMAN, HAYTHAM	1736	208-120350

1. Change of correspondence address or indication of "Fee Address" (37 CFR 1.363).

☐ Change of correspondence address (or Change of Correspondence Address form PTO/SB/122) attached.

☐ "Fee Address" indication (or "Fee Address" Indication form PTO/SB/47; Rev 03-09 or more recent) attached. **Use of a Customer Number is required.**

2. For printing on the patent front page, list
(1) The names of up to 3 registered patent attorneys or agents OR, alternatively,
(2) The name of a single firm (having as a member a registered attorney or agent) and the names of up to 2 registered patent attorneys or agents. If no name is listed, no name will be printed.

1 NIXON PEABODY LLP
2 RONALD I. EISENSTEIN
3 NICOLE D. KLING

3. ASSIGNEE NAME AND RESIDENCE DATA TO BE PRINTED ON THE PATENT (print or type)

PLEASE NOTE: Unless an assignee is identified below, no assignee data will appear on the patent. If an assignee is identified below, the document must have been previously recorded, or filed for recordation, as set forth in 37 CFR 3.11 and 37 CFR 3.81(a). Completion of this form is NOT a substitute for filing an assignment.

(A) NAME OF ASSIGNEE: COCHISE TECHNOLOGY, LLC

(B) RESIDENCE: (CITY and STATE OR COUNTRY): Conifer, CO (US)

Please check the appropriate assignee category or categories (will not be printed on the patent) : ☐ Individual ☒ Corporation or other private group entity ☐ Government

4a. Fees submitted: ☒ Issue Fee ☐ Publication Fee (if required) ☐ Advance Order - # of Copies _____

4b. Method of Payment: *(Please first reapply any previously paid fee shown above)*

☒ Electronic Payment via EFS-Web ☐ Enclosed check ☐ Non-electronic payment by credit card (Attach form PTO-2038)

☒ The Director is hereby authorized to charge the required fee(s), any deficiency, or credit any overpayment to Deposit Account No. 50-0850

5. **Change in Entity Status** (from status indicated above)

☐ Applicant certifying micro entity status. See 37 CFR 1.29

☐ Applicant asserting small entity status. See 37 CFR 1.27

☐ Applicant changing to regular undiscounted fee status.

NOTE: Absent a valid certification of Micro Entity Status (see forms PTO/SB/15A and 15B), issue fee payment in the micro entity amount will not be accepted at the risk of application abandonment.
NOTE: If the application was previously under micro entity status, checking this box will be taken to be a notification of loss of entitlement to micro entity status.
NOTE: Checking this box will be taken to be a notification of loss of entitlement to small or micro entity status, as applicable.

NOTE: This form must be signed in accordance with 37 CFR 1.31 and 1.33. See 37 CFR 1.4 for signature requirements and certifications.

Authorized Signature /NICOLE D. KLING/ Date 2021-12-06

Typed or printed name NICOLE D. KLING Registration No. 71,959

PTOL-85 Part B (08-18) Approved for use through 01/31/2020 OMB 0651-0033 U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	ISSUE DATE	PATENT NO.	ATTORNEY DOCKET NO.	CONFIRMATION NO.
17/176,222	01/18/2022	11224864	071816-091960USC1	3640

53143 7590 12/28/2021

RONALD I. EISENSTEIN
NIXON PEABODY LLP
Exchange Place, 53 State Street
BOSTON, MA 02109

ISSUE NOTIFICATION

The projected patent number and issue date are specified above.

Determination of Patent Term Adjustment under 35 U.S.C. 154 (b)
(application filed on or after May 29, 2000)

The Patent Term Adjustment is 0 day(s). Any patent to issue from the above-identified application will include an indication of the adjustment on the front page.

If a Continued Prosecution Application (CPA) was filed in the above-identified application, the filing date that determines Patent Term Adjustment is the filing date of the most recent CPA.

Applicant will be able to obtain more detailed information by accessing the Patent Application Information Retrieval (PAIR) WEB site (http://pair.uspto.gov).

Any questions regarding the Patent Term Extension or Adjustment determination should be directed to the Office of Patent Legal Administration at (571)-272-7702. Questions relating to issue and publication fee payments should be directed to the Application Assistance Unit (AAU) of the Office of Data Management (ODM) at (571)-272-4200.

INVENTOR(s) (Please see PAIR WEB site http://pair.uspto.gov for additional inventors):

Guido William ARU, Conifer, CO;

APPLICANT(s) (Please see PAIR WEB site http://pair.uspto.gov for additional applicants):

COCHISE TECHNOLOGY, LLC, Conifer, CO;

The United States represents the largest, most dynamic marketplace in the world and is an unparalleled location for business investment, innovation, and commercialization of new technologies. The USA offers tremendous resources and advantages for those who invest and manufacture goods here. Through SelectUSA, our nation works to encourage and facilitate business investment. To learn more about why the USA is the best country in the world to develop technology, manufacture products, and grow your business, visit SelectUSA.gov.

IR103 (Rev. 10/09)

AO 120 (Rev. 08/10)

TO:	Mail Stop 8 Director of the U.S. Patent and Trademark Office P.O. Box 1450 Alexandria, VA 22313-1450	REPORT ON THE FILING OR DETERMINATION OF AN ACTION REGARDING A PATENT OR TRADEMARK

In Compliance with 35 U.S.C. § 290 and/or 15 U.S.C. § 1116 you are hereby advised that a court action has been filed in the U.S. District Court District of Maryland on the following

☐ Trademarks or ☑ Patents. (☐ the patent action involves 35 U.S.C. § 292.):

DOCKET NO.	DATE FILED	U.S. DISTRICT COURT
1:22-cv-2636	10/13/22	District of Maryland

PLAINTIFF	DEFENDANT
G. W. Aru, LLC, and Cochise Technology, LLC	W. R. Grace & Co.-Conn.

	PATENT OR TRADEMARK NO.	DATE OF PATENT OR TRADEMARK	HOLDER OF PATENT OR TRADEMARK
1	11,224,864	1/18/2022	Cochise Technology, LLC
2			
3			
4			
5			

In the above—entitled case, the following patent(s)/ trademark(s) have been included:

DATE INCLUDED	INCLUDED BY ☐ Amendment ☐ Answer ☐ Cross Bill ☐ Other Pleading	
PATENT OR TRADEMARK NO.	DATE OF PATENT OR TRADEMARK	HOLDER OF PATENT OR TRADEMARK
1		
2		
3		
4		
5		

In the above—entitled case, the following decision has been rendered or judgement issued:

DECISION/JUDGEMENT

CLERK	(BY) DEPUTY CLERK	DATE

Copy 1—Upon initiation of action, mail this copy to Director **Copy 3—Upon termination of action, mail this copy to Director**
Copy 2—Upon filing document adding patent(s), mail this copy to Director **Copy 4—Case file copy**