



(51) International Patent Classification:
B01J 23/02 (2006.01) *C07C 11/02* (2006.01)
C07C 1/24 (2006.01)

(74) Agents: **WILSON SONSINI GOODRICH & ROSATI**
et al.; c/o Cobalt Technologies, Inc., 650 Page Mill Road,
Palo Alto, California 94304 (US).

(21) International Application Number:
PCT/US2015/014943

(81) Designated States (unless otherwise indicated, for every
kind of national protection available): AE, AG, AL, AM,
AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY,
BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM,
DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT,
HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR,
KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG,
MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM,
PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC,
SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN,
TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(22) International Filing Date:
8 February 2015 (08.02.2015)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/945,683 27 February 2014 (27.02.2014) US

(71) Applicants: **COBALT TECHNOLOGIES, INC.**
[US/US]; 500 Clyde Avenue, Mountain View, California
94043 (US). **CLARIANT CORPORATION** [US/US];
1600 West Hill Street, Louisville, Kentucky 40210 (US).

(84) Designated States (unless otherwise indicated, for every
kind of regional protection available): ARIPO (BW, GH,
GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ,
TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU,
TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE,
DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU,
LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK,
SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ,
GW, KM, ML, MR, NE, SN, TD, TG).

(72) Inventors: **WRIGHT, Michael E.**; 500 Clyde Avenue,
Mountain View, California 94043 (US). **MEYER, An-
drew D.**; 500 Clyde Avenue, Mountain View, California
94043 (US). **HOU, Connie**; 1600 West Hill Street, Louis-
ville, Kentucky 40210 (US). **LUGMAIR, Claus G.**; 1600
West Hill Street, Louisville, Kentucky 40210 (US).
VOLPE, Anthony F., Jr.; 1600 West Hill Street, Louis-
ville, Kentucky 40210 (US). **LOWE, David M.**; 1600
West Hill Street, Louisville, Kentucky 40210 (US).
SHVAREVA, Tatiana Y.; 1600 West Hill Street, Louis-
ville, Kentucky 40210 (US).

Published:

— with international search report (Art. 21(3))

(54) Title: REGIOSELECTIVE DEHYDRATION OF TERMINAL ALCOHOLS

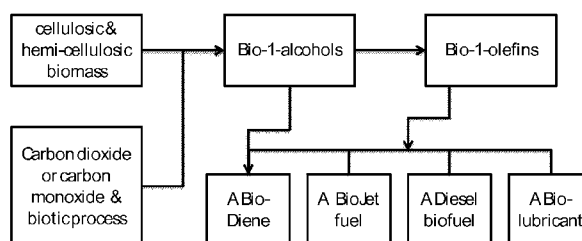


FIG 1

(57) Abstract: The present invention relates to the preparation of a dehydration catalyst and a method and apparatus for dehydrating 1-alcohols to 1-alkenes with high regiospecificity. The 1-alkenes are useful in preparing copolymers with ethylene and high flash-point diesel and jet fuels, which are useful to civilian and military applications. Furthermore, the 1-butene may be converted to 1,3-butadiene which is useful in preparing synthetic rubbers. Some linear C₄ diols can be dehydrated directly to a 1,3-butadiene.

REGIOSELECTIVE DEHYDRATION OF TERMINAL ALCOHOLS

CROSS-REFERENCE TO RELATED APPLICATIONS

[01] This application claims the benefit of U.S. Provisional Application No. 61/945,683, filed February 27, 2014, which is incorporated herein by reference in its entirety.

FIELD OF THE INVENTION

[02] The invention generally relates to conversion of terminal alcohols to the corresponding terminal alkenes with high regioselectivity at high conversion. The terminal alkenes are useful in the preparation of fuels, plastics, and for creating chemical intermediates for many commercial products.

BACKGROUND

[03] α -Olefins are useful intermediates in preparing diesel and jet/turbine fuels. In the case of 1-butene it is a very useful precursor to 1,3-butadiene, which in turn is used to make synthetic rubber. They are also useful in preparing poly- α -olefins (PAOs) and copolymers with ethylene to form low-density plastics. For α -olefins made from petroleum resources, there exist several well-known processes for ethylene oligomerization that afford α -olefins such as 1-butene, 1-hexene, 1-octene, and so forth, and that after a distillation and purification process can yield a single pure terminal olefin. The Shell Higher Olefin Process ("SHOP") is perhaps the best known to those skilled in the art of ethylene oligomerization.

[04] Obtaining α -olefins from renewable and sustainable resources requires a significantly different approach. Since alcohols can be produced in large scale by fermentation processes, they can be an attractive feedstock for α -olefin preparation provided that they can be dehydrated in high yield, which requires achieving high regioselectivity at high alcohol conversion. A problem that is particular to selective α -olefin synthesis is the competing isomerization reaction that produces the thermodynamically favored internal olefin(s) if a pathway is kinetically available. For example, dehydration of 1-butanol often produces a mixture of 1-butene (~33 mol%) and 2-butenes (~67 mol% total, as a mixture of cis and trans isomers) where the 2-butenes are a result of 1-butene isomerization to the more thermodynamically stable 2-butenes [Yori et al. *Applied Catalysis* **1988**, *41*, pp 1-11].

[05] Bio-1-butanol in particular has a rich history of successful large-scale commercial production since the discovery by Louis Pasteur in 1863 of bacteria that could ferment sugars to a mixture of acetone, 1-butanol, and ethanol (ABE). Since Pasteur's initial discovery of the ABE process, many advances have been made in the fermentation process to optimize bio-1-butanol production and to reduce ethanol and acetone co-production. Most notable are the successful efforts using non-engineered bacteria that have led to commercial plants that produce bio-1-butanol operating for decades.

[06] Since fermentations are carried out in aqueous medium, separation of the fermentation products of interest from the multi-component mixture ("fermentation broth") of water, bacteria, media components, and other metabolic byproducts is energy- and time-intensive. In the case of bio-1-butanol, several methods have been reported for isolating the butanol component. In addition to simple distillation, one method that has found commercial success is use of a sparging gas (*e.g.*, carbon dioxide or steam) that carries the more volatile bio-1-butanol/water azeotrope away from the fermentation broth. Other more academic approaches involve pervaporization. In these cases, a selective-membrane material is used that permits bio-1-butanol to pass through, thus leaving the bacteria and water behind. Regardless of the method, it is evident to those skilled in the art that removing the last traces of impurities and water are costly in energy and time. The available methods vary significantly in capabilities. However, water and impurities are a direct and unavoidable consequence of bio-alcohol fermentation processing. Ruwet et al. (Bull. Soc. Chim. **1987**, 96, 281-292) discuss the problems in using a wet ABE bio-1-butanol feed in a dehydration reaction to afford a mixture of olefins. More recently, D'Amore et al. (US2008/0015395 A1) reported extreme difficulty in dehydrating aqueous solutions of 1-butanol using a variety of acid catalysts to afford a mixture of olefins and other oxygenated products (*e.g.* ethers), including high amounts of unreacted 1-butanol. An improved method is needed to prepare terminal olefins efficiently from a solution containing bio-1-alcohols and water as a major impurity.

[07] Kaizik et al. at Evonik Oxeno GmbH (US2012/0136190 A1) describe the use of a solid alumina catalyst that is primarily of a mesoporous nature. In this work 3-methyl-1-butanol was dehydrated with moderately high selectivity to the corresponding 3-methyl-1-butene provided conversions were kept below 88% and the reaction temperature was also maintained at 270 °C, or below. Furthermore, even at a somewhat low alcohol conversion (39-87%), the weight hourly space velocity (WHSV) was less than 0.6 h⁻¹. No data were presented for the use of alcohol feeds containing steam (*i.e.* water) for the disclosed catalyst

system and process. It is well known that the presence of water can have a significant adverse effect on the performance of catalysts of this type.

[08] Other alternative catalysts include silica and alumina solid phase catalysts as well as standard mineral acid catalysts. D'Amore et al. (US 2009/0030239) disclose the contact of water and alcohols with acid catalysts to afford a mixture of alkene products. Mixtures are typical products of acid-catalyzed dehydration and previous work in the field discloses that complicated mixtures of alkene products are formed. The lack of regioselectivity for terminal olefin occurs when isomerization to the more thermodynamically stable internal olefin occurs. In some cases the internal olefins can be formed directly via an acid catalyzed mechanism, typically denoted as an *EI* elimination mechanism.

[09] For those skilled in the art it is known that the catalytic dehydration of terminal alcohols can occur over a solid phase catalyst; however, the dehydrations described differ from the regioselective formation of 1-alkenes (*e.g.*, bio-1-alkenes) made from α -alcohols (*e.g.*, bio-1-alcohols) and are not compatible with the impurities (*e.g.*, water) commonly found in bio-1-alcohol feeds produced by fermentation processes and/or potentially other biological procedures. It is well understood in the art that water contained in the alcohol feed deactivates the catalyst and/or leads to a loss of regioselectivity to form the 1-alkene product. Since water is a common co-product in making bioalcohols, there exists a significant limitation in the art to regioselectively form bio-1-alkenes.

[10] Work in 2005 specifically pointed out the shortcomings of using γ -alumina to dehydrate 1-alcohols. The study (Makgoba et al. *Applied Catalysis A: General* **2005**, 297(2), 145-150) showed that γ -alumina exhibited a significant loss in regioselectivity for conversion of 1-alcohols to 1-alkenes as a function of time on stream (TOS) leading to production of internal olefins. In this particular case the conversion rate of alcohols to alkenes remained relatively constant over time; the regioselectivity declined over time.

[11] Currently available dehydration methods form a mixture of alkenes (regioisomers), including internal alkenes. For example, 1-butanol when dehydrated by typical solid phase catalysts like untreated commercially available γ -alumina (*e.g.* Strem Chemicals) at 380 °C using a WHSV of 0.5, we found in the laboratory that a mixture of 1-butene (~70%) and 2-butenes (~30%) is formed. Other examples, such as the dehydration of isobutanol (Taylor et al. *Topics Catal.* **2010**, 53, pp 1224–1230), afford regioisomers as well as products of skeletal rearrangements (*e.g.*, to 2-butene).

[12] Internal alkenes are far less effective in Ziegler-Natta polymerization chemistry and are not of direct use in preparing high-flashpoint diesel and jet fuels and for making lubricants. The type of alkene feed can also affect other oligomerization processes useful in preparing fuels. Thus, for utilizing a bio-1-alcohol (*e.g.*, bio-1-butanol) as feedstock, it is highly desirable to have a selective dehydration process that affords rapid and high conversion to the terminal-olefin (*e.g.*, bio-1-butene) and is accompanied by no carbon skeletal rearrangement (*e.g.*, to isobutylene). Furthermore, retaining high regioselectivity for a long time on stream is a desirable attribute in commercial applications.

BRIEF SUMMARY OF THE INVENTION

[13] A catalyst system and process are provided that can convert a feed of terminal alcohol containing from about 0.1 wt% to about 90 wt% water to a product stream containing the respective terminal olefin and water. In some embodiments, the terminal olefin is produced with about 90% to about 99% regiochemical selectivity. In some embodiments, a single pass over the catalyst system affords a chemical conversion of greater than about 95%. In some embodiments, the terminal olefin is produced employing WHSV values greater than 1 hr⁻¹, *e.g.*, greater than 1 and less than 10 h⁻¹, or about 1.01 hr⁻¹ to about 10 hr⁻¹. In some embodiments of the methods disclosed herein, at least one solid phase catalyst is maintained at a temperature of about 220 °C to about 440 °C, with the feed a solution containing terminal alcohol and water at a pressure of about 1 psig to about 1000 psig to produce a 1-alkene in high regioselectivity at high terminal alcohol conversion. In one embodiment, bio-*n*-butanol that is obtained from a fermentation broth (*e.g.*, after removal of minor acidic contaminants and addition of water) can be dehydrated to bio-1-butene in a yield of greater than about 90%, or greater than 95%, or greater than 98%.

[14] Catalyst compositions disclosed herein contain an inorganic support modified by a Ca⁺² compound as one preferred embodiment. In one embodiment modification may be accomplished via treatment of the support with the calcium compound dissolved in a solvent. In some embodiments Ca⁺² is the modifier and the Ca⁺² compound is calcium acetate (Ca(OAc)₂). The solvent may be water, or an organic solvent, or a mixture of the two. In a preferred embodiment, a solvent is used that is capable of completely dissolving the Ca⁺² compound used for preparation of the catalyst. In some embodiments, an "Incipient Wetness Impregnation Process" (IWP) is used for catalyst preparation. In one embodiment, the catalyst composition includes Ca⁺² (as wt% of the modified inorganic support) at about 0.8 to about 3.0 wt%. In one embodiment, γ -alumina is used as the

inorganic support. In some embodiments, γ -alumina is modified with binder, physically formed (e.g. extruded) to a preselected shape (e.g., rods), heat-treated (e.g., calcined), and then modified with Ca^{+2} as noted above in this paragraph. Calcium imparts an increase in reaction rate when compared to Group 1 metals such as sodium and potassium when used at similar wt% loading values. Furthermore, calcium provides an increase in selectivity for the terminal alkene product over use of Group 1 metals at high and comparable terminal olefin conversion.

[15] Promoter (e.g. Group 2 metal) modified and heat-treated (e.g., calcined) catalysts can be further modified by treatment with at least one organosilane to create new catalysts that are especially useful for the dehydration of 1-alcohols mixed with high wt% of steam. The promoter-organosilane-modified alumina catalysts afford high regioselectivity in forming 1-alkene and can perform for extended periods of time on stream with little loss in regioselectivity.

[16] Methods disclosed herein for producing terminal olefins include using the preferred calcium or calcium-organosilane modified alumina catalysts in isothermal continuous flow reactors or in a series of one or more adiabatic reactors where some of the heat necessary for the dehydration reaction is carried into the reactor in the form of steam. This creates a very water rich gas phase in the reactor making some embodiments of the current invention beneficial for commercial applications.

[17] Some embodiments of the invention generally relate to fuels (e.g., alternative and/or renewable fuels), and the production of 1-alkenes (e.g., bio-1-alkenes) that can be utilized directly or, by further processing, to prepare a drop-in and full performance diesel fuel (e.g., diesel biofuel), jet (e.g., biojet) fuel, lubricant (e.g., biolubricant), 1,3-butadiene (e.g., bio-1,3-butadiene), or other chemical products and/or intermediates useful in the production of commercial products. Embodiments also include such processes starting from cellulosic and/or hemicellulosic biomass material, as are shown schematically in FIG 1. 1-Alcohols can also be generated by feeding a carbon-source of carbon dioxide and/or carbon monoxide to at least one biological organism. Typically the biological organism is suspended in water or it may be attached to at least one support system and then placed in contact with water and a carbon source.

[18] In one aspect, methods are provided for dehydrating a 1-alcohol to a 1-alkene. In some embodiments, the method includes contacting and heating a 1-alcohol with at least one catalyst that includes a calcium-modified inorganic support at a WHSV of about 1.01 hr^{-1} to about 10 hr^{-1} , wherein the 1-alcohol is in a mixture with about 1 ppm to about 93

wt% water, thereby producing the corresponding 1-alkene with greater than about 90% regioselectivity.

[19] In some embodiments of the methods disclosed herein, the 1-alcohol is a C₄ to C₆ 1-alcohol. In one embodiment, the 1-alcohol is 1-butanol. The 1-alkene produced in some embodiments of the methods disclosed herein may be 1-butene. In some embodiments of the methods disclosed herein, the 1-alcohol is 1-butanol, 1-pentanol, 1-hexanol, 3-methyl-1-butanol, 2-methyl-1-butanol, 4-methyl-1-pentanol, 3-methyl-1-pentanol, or 2-methyl-1-pentanol.

[20] In some embodiments of the methods disclosed herein, the 1-alcohol is a bio-1-alcohol. For example, in some embodiments, the bio-1-alcohol may be a C₄ to C₆ 1-alcohol, *e.g.*, bio-1-butanol. The 1-alkene produced in some embodiments of the methods disclosed herein may be bio-1-butene.

[21] In some embodiments of the methods disclosed herein, the 1-alcohol is an alcohol of general formula R¹R²CH(CH₂)₂OH, where R¹ and R² are independently H or a C₁ to C₂₀ alkyl radical, or contain one or more aromatic rings containing exclusively carbon or a mixture of carbon and heteroatoms, or a nitrile, alkene, or ketone functional group, or a combination thereof. In some embodiments, the 1-alcohol is an alcohol of general formula HO(CH₂)_n(CH₃) with n being any integer from 1 to 22.

[22] In some embodiments, the regioselectivity of 1-alkene production is greater than about 95%. In some embodiments, the regioselectivity of 1-alkene production is about 90% to about 99%. In some embodiments, the 1-alkene produce includes ≤ about 5% unreacted 1-alcohol.

[23] In some embodiments, water is present in the catalytic reaction mixture at about 15 wt% to about 70 wt%, or about 10 wt% to about 70 wt%.

[24] In some embodiments, the inorganic support includes γ-alumina or zinc aluminate.

[25] In some embodiments, the catalyst is further modified by treatment with at least one organosilane, such as a chlorosilane. In one embodiment, the organosilane is diphenyldiethoxysilane.

[26] In some embodiments of the methods, at least one purge gas is provided, *e.g.*, nitrogen and/or argon.

[27] In some embodiments, the reaction mixture is heated to a temperature of about 200° C to about 440° C. In some embodiments, the temperature is about 300° C to about 420° C.

[28] In some embodiments, the method further includes separating water from 1-alkene product. In some embodiments, the method includes contacting the 1-alkene product from which water has been removed with a second catalyst, to form oligomers. In some embodiments, the second catalyst may be a Ziegler-Natta catalyst, a mesoporous oligomerization catalyst, or another catalyst that is capable of producing oligomers from 1-alkenes. In various embodiments, the oligomers may be used to produce a diesel fuel (*e.g.*, with a flashpoint of about 38 to about 100 °C, a Cetane rating of about 45 to about 60, and aromatic content of less than about 0.5 wt%), a jet fuel (*e.g.*, with a flashpoint of about 38 to about 100 °C, a cold flow viscosity of less than about 8.0 cSt at -20 °C, and aromatic content of less than about 0.5 wt%), or a lubricant (*e.g.*, with a viscosity of about 1 to about 10,000 cSt at 25 °C).

[29] In one embodiment, 1-butene produced in a method as disclosed herein (*e.g.*, from 1-butanol) may be used to produce 1,3-butadiene, for example, by contacting the 1-butene with a catalyst that includes Bi, Mo and Fe in a molar ratio of 1:1:0.5-1.25, and including a $\text{Bi}_3\text{FeMo}_2\text{O}_{12}$ phase and $\text{Fe}_2(\text{MoO}_4)_3$ phase.

[30] In some embodiments, the method includes contacting and heating a 1-alcohol with at least one catalyst that includes a calcium-modified inorganic support, thereby producing the corresponding 1-alkene with greater than about 90% regioselectivity. Optionally, the 1-alcohol is in a mixture with about 1 ppm to about 93 wt% water. Optionally, the catalyst is contacted with the 1-alcohol at a WHSV of greater than 1 (*e.g.*, about 1.01 hr^{-1} to about 10 hr^{-1}). Optionally, the catalyst is further modified by treatment with at least one organosilane.

[31] In some embodiments, the method includes contacting and heating a 1-alcohol with at least one catalyst that includes an inorganic support that is modified by a Group 2 element and at least one organosilane, thereby producing the corresponding 1-alkene with greater than about 90% regioselectivity. For example, the Group 2 element may include at least one of Mg, Ca, Ba, and Sr. Optionally, the 1-alcohol is in a mixture with about 1 ppm to about 93 wt% water. Optionally, the catalyst is contacted with the 1-alcohol at a WHSV of greater than 1 (*e.g.*, about 1.01 hr^{-1} to about 10 hr^{-1}).

[32] In another aspect, a catalyst composition is provided for producing 1-alkenes from 1-alcohols with high regioselectivity. In some embodiments, the catalyst compositions herein include an inorganic support that is modified with a promoter, *e.g.*, at least one Group 2 element, and at least one organosilane. In some embodiments, the catalyst includes at least one Group 2 element, for example, at least one of Mg, Ca, Ba, and Sr. In

one embodiment, the Group 2 element is Ca. In one embodiment, the organosilane is diphenyldiethoxysilane. In some embodiments, the inorganic support includes γ -alumina or zinc aluminate.

[33] In another aspect, a catalyst composition is provided for use in the methods described herein, that is prepared by: a) modifying an inorganic support with at least one Group 2 element to produce a first modified inorganic support, wherein the first modified inorganic support comprises said at least one Group 2 element; b) heat-treating (*e.g.*, calcining) the first modified inorganic support to produce a calcined (*e.g.*, heat-treated) first modified inorganic support; c) contacting the heat-treated (*e.g.*, calcined) first modified inorganic support with at least one organosilane to produce a second modified inorganic support, wherein the second modified inorganic support comprises said at least one Group 2 element and said at least one organosilane, or a fragment thereof; and d) heat-treating (*e.g.*, calcining) the second modified inorganic support to produce the catalyst composition.

BRIEF DESCRIPTION OF THE DRAWINGS

[34] FIG. 1 illustrates an overall process for synthesizing bio-1-alcohols with conversion through dehydration reactions to produce bio-1-olefins and/or a bio-diene. The bio-1-olefins are useful for the synthesis of a bio-diene, or a biojet fuel, or a diesel biofuel, or a bio-lubricant.

[35] FIG. 2 illustrates a high level process diagram for the modification of an inorganic support by contacting the support with a solution (202) containing at least one promoter (*e.g.*, Group 2 compound) to afford a dehydration catalyst (206) after removal of the solvent followed by a calcination.

[36] FIG. 3 illustrates a high level process diagram for the modification of a Group 2 modified inorganic support (206) by treatment with an organosilane solution (*e.g.* IWP) (301) containing at least one organosilane to afford a silanized dehydration catalyst (304) after removal of the IWP solvent with or without further calcination.

[37] FIG. 4 illustrates a high level process diagram for the dehydration of at least one 1-alcohol, with or without additional steam (402) input, to the 1-alkene (406) with high regioselectivity. Recycle of the water product and additional input (if used) is depicted using physical separation (407) and a purification (408) device.

[38] FIG. 5 illustrates a high level process diagram for the dehydration of at least one 1-alcohol, with or without additional steam (502) input, to the 1-alkene (509) with high

regioselectivity and using more than one reactor vessel. Recycle of the water product and additional input (if used) is depicted using physical separation (508) and a purification (510) device.

[39] FIG. 6 illustrates one possible chemical description and pathway for the conversion of 1-alcohols to 1-alkenes using 1-butanol as a chemical example.

[40] FIG. 7 illustrates a high level process diagram for the regioselective conversion of at least 1-alcohol to the corresponding 1-alkene and then conversion of said 1-alkene to fuels (713 and 714).

[41] FIG. 8 illustrates a high level process diagram for the removal of contaminants from the input (806) stream prior to contact with the dehydration catalyst of this invention. Regeneration of 802 is possible using solution 805.

[42] FIG. 9 is a graph showing the performance (*i.e.* 1-butanol/dibutyl ether conversion vs. 1-butene regioselectivity) of Catalyst 8 and comparative Catalysts 6 and 7 using a feed of 88 wt% 1-butanol, 2 wt% heptane, and 10 wt% water. Run #1 is fresh catalyst, prior to Run #2 the catalyst was aged by heating 60 hours at 400 °C with a continuous feed of 93 wt% water and 7 wt% 1-butanol, and prior to Run #3 an additional 60 h (*i.e.* total 120 hours) of aging at 400 °C under a continuous feed of 93 wt% water and 7 wt% 1-butanol. For each run the performance of Catalyst 8 was evaluated at four temperatures: 340 °C, 360 °C, 380 °C, and 400 °C. The performance of comparative Catalyst 6 was evaluated at three temperatures: 360 °C, 380 °C, and 400 °C for each run. Comparative Catalyst 7 was evaluated at four temperatures: 340 °C, 360 °C, 380 °C, and 400 °C in Run #1 and Run 2, and at three temperatures 360 °C, 380 °C, and 400 °C in Run #3. The lowest 1-butanol conversion is always at the lowest temperature and conversion increases with temperature.

[43] FIG. 10 is a graph showing the performance (*i.e.* 1-butanol/dibutyl ether conversion vs. 1-butene regioselectivity) of Catalyst 9 and comparative catalysts 10 and 11 using a feed of 88 wt% butanol, 2wt% heptane, and 10 wt% water. Run #1 is fresh catalyst, prior to Run #2 the catalyst was aged by heating 60 hours at 400 °C with a continuous feed of 93 wt% water and 7 wt% 1-butanol, and prior to Run #3 an additional 60 h (*i.e.* total 120 hours) of aging at 400 °C under a continuous feed of 93 wt% water and 7 wt% 1-butanol. For each run the catalyst performance was evaluated at four temperatures: 340 °C, 360 °C, 380 °C, and 400 °C. The lowest 1-butanol conversion is always at 340 °C and conversion increases with temperature.

[44] FIG. 11 is a graph showing the performance (*i.e.* 1-butanol/dibutyl ether conversion vs. 1-butene regioselectivity) of Catalyst 12, Catalyst 13, Catalyst 14, Catalyst 15, Catalyst

16, and Catalyst 17. The performance of Catalysts 12, 13, and 14 was evaluated at four temperatures: 340 °C, 360 °C, 380 °C, and 400 °C. The performance of Catalysts 15 and 16 was evaluated at three temperatures: 340 °C, 380 °C, and 400 °C, and the performance of Catalyst 17 was evaluated at two temperatures: 380 °C, and 400 °C. The lowest 1-butanol conversion is always at the lowest temperature and conversion increases with temperature.

[45] FIG. 12 is a graph showing the performance (*i.e.* 1-butanol/dibutyl ether conversion vs. 1-butene regioselectivity) of Catalyst 9, Catalyst 18, and Catalyst 19 using a feed of 88 wt% butanol, 2wt% heptane, and 10 wt% water. Run #1 is fresh catalyst, prior to Run #2 the catalyst was aged by heating 60 hours at 400 °C with a continuous feed of 93 wt% water and 7 wt% 1-butanol, and prior to Run #3 an additional 60 h (*i.e.* total 120 hours) of aging at 400 °C under a continuous feed of 93 wt% water and 7 wt% 1-butanol. For each run the performance of Catalyst 9 was evaluated at four temperatures: 340 °C, 360 °C, 380 °C, and 400 °C. The performance of Catalysts 18 and 19 was evaluated at three temperatures: 360 °C, 380 °C, and 400 °C in Run #1 and four temperatures: 340 °C, 360 °C, 380 °C, and 400 °C in Run # 2 and #3. The lowest 1-butanol conversion is always at the lowest temperature and conversion increases with temperature.

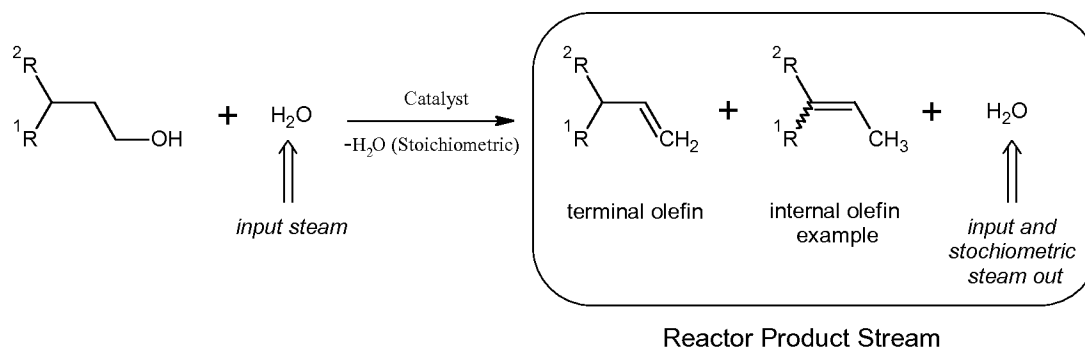
[46] FIG. 13 is a graph showing the performance (*i.e.* 1-butanol/dibutyl ether conversion vs. 1-butene regioselectivity) of Catalyst 20, Catalyst 21, and Catalyst 22 using a feed of 88 wt% butanol, 2 wt% heptane, and 10 wt% water. Catalyst performance was evaluated at four temperatures: 340 °C, 360 °C, 380 °C, and 400 °C. The lowest 1-butanol conversion is always at 340 °C and conversion increases with temperature.

[47] It is to be understood that the foregoing general description and the following detailed description are exemplary and explanatory only and are not to be viewed as being restrictive of the invention, as claimed. Further advantages of this invention will be apparent after a review of the following detailed description of the disclosed embodiments, which are illustrated schematically in the accompanying drawings and in the appended claims.

DETAILED DESCRIPTION

[48] Methods and catalyst compositions are provided herein for conversion of terminal alcohols to olefins, with high regiochemical selectivity for terminal olefins. In methods disclosed herein, a mixture that contains at least one terminal alcohol and water is contacted with a solid phase catalyst, which produces a product stream containing a terminal olefin

with high selectivity (*e.g.*, >90%) and an amount of water equal to the input water (*e.g.*, steam) plus the stoichiometric amount of water (*e.g.*, steam) produced from the dehydration reaction, shown schematically below:



[49] Typically, the catalytic reaction is performed at an elevated temperature (*e.g.*, from about 220 °C to about 440 °C). Preferred catalysts used in the methods described herein include but are not limited to Ca^{+2} -modified inorganic supports, such as Ca^{+2} -modified γ -alumina and can include an organosilane component. In some embodiments, Ca^{+2} is present at about 0.8 to about 3.0 wt% of the modified inorganic support.

[50] Catalyst systems and methods of use are provided that effect highly specific regioselective dehydration of 1-alcohols (*e.g.*, bio-1-alcohols) in water-containing mixtures, with retention of selectivity over extended periods of use, commonly reported as Time On Stream (TOS). In some embodiments, dehydration of 1-butanol (*e.g.*, bio-1-butanol) using the catalyst compositions and methods described herein provides 1-butene (*e.g.*, bio-1-butene) in greater than 80% yield, and, in some embodiments, 90-99% regioselectivity for 1-butene (*e.g.*, bio-1-butene) or 90-99% regioselectivity. In some embodiments, the catalyst can be used continuously for at least 1 to 3 months, or about 6 months and in some embodiments, up to about 12 months, or up to about 18 months, or up to about 24 months or up to about 30 months, or about 36 months, or up to 48 months while producing terminal olefin (*e.g.*, bio-1-olefin) without significant loss in regioselectivity for the terminal olefin.

[51] The terms “terminal alkene,” “1-alkene,” “ α -olefin,” “terminal olefin,” and “1-olefin” are used interchangeably herein to refer to an alkene with a double bond between the terminal carbon (carbon at the end of a hydrocarbon chain) and the adjacent carbon in the hydrocarbon chain.

[52] The terms “internal alkene,” and “internal olefin,” are used interchangeably herein to refer to an alkene which is not terminal, i.e., the carbon-carbon double bond, is not at the end of the hydrocarbon chain. A “2-alkene” is one example of an “internal alkene”.

[53] A “linear terminal alkene” refers to a terminal alkene with a double bond that can undergo isomerization to an “internal alkene.” For example isobutylene cannot be isomerized by movement of the double bond to form an “internal alkene,” and the same can be said for propylene since only a terminal olefin can be made from dehydrating 1-propanol.

[54] A “bio-1-olefin” or “bio-1-alkene” refers to a terminal olefin produced from a biologically (*e.g.*, via microbial fermentation process) produced terminal alcohol. In some embodiments, a bio-1-olefin is produced from a terminal alcohol that has been produced in a microbial fermentation process from cellulosic biomass (*e.g.*, lignocellulosic biomass) as a starting material.

[55] A “1-alcohol” or “terminal alcohol” or “*n*-alcohol” refers, interchangeably, to an alcohol with a hydroxyl group attached to a terminal, primary carbon in the hydrocarbon chain (*i.e.*, a $-\text{CH}_2\text{OH}$ group). Not all terminal alcohols when dehydrated can be isomerized and lead to a non-regioselective product. For example, isobutanol is a terminal alcohol that can afford only one regioisomer alkene product in the absence of a carbon-carbon bond rearrangement. By definition in this description then isobutanol can afford only one regioisomer; hence, the dehydration of isobutanol to isobutylene is NOT considered a regioselective dehydration since it is the only alkene product that can be formed (based on hydrogen migrations/movements).

[56] A “bio-1-alcohol” refers to a terminal alcohol that is produced biologically (*e.g.*, via microbial fermentation). In some embodiments, the terminal alcohol is produced in a microbial fermentation process from cellulosic biomass (*e.g.*, lignocellulosic biomass) as a starting material.

[57] “Bio-*n*-butanol” or “bio-1-butanol” refers to *n*-butanol that is produced biologically (*e.g.*, via microbial fermentation). In some embodiments, the bio-1-butanol is produced in a microbial fermentation process from cellulosic biomass (*e.g.*, lignocellulosic biomass) as a starting material.

[58] “Biofuel,” “biolubricant,” or “bio-1,3-butadiene” refers to a fuel, a lubricant, or 1,3-butadiene, respectively, that is produced from at least one biologically-produced starting molecule or at least one starting molecule in which at least one carbon atom is derived from a biological material, for example, cellulosic (*e.g.*, lignocellulosic) biomass. Also the

direct biological conversion of carbon dioxide and/or carbon monoxide is considered also defined as a viable route to bio-1-alcohols. In one embodiment, a biofuel, biolubricant, or bio-1,3-butadiene may be produced from a bio-1-alkene that is produced by dehydration of a bio-1-alcohol as described herein.

[59] “Regioselectivity” refers to selective formation of one olefin product over another. For example, formation of 90 mol-% terminal (1-olefin) and 10 mol-% internal (*e.g.*, 2-olefin) would be described as 90% regioselectivity for the terminal olefin product.

[60] “Incipient Wetness Impregnation Process” (IWP) is a technique that is used to modify a support material by treating the solid material with a predetermined amount of a solution containing at least one desired modifier (*e.g.*, calcium acetate), sufficient to wet the solid surface and fill the pore-volume, this followed by removal of some or all of the solvent (*e.g.*, by some method of evaporation) thus depositing the modifier uniformly on the support material.

[61] “Weight Hourly Space Velocity” (WHSV) is derived by dividing the weight of alcohol feed delivered per hour by the weight of catalyst used. For example, if 1.5 kg/hr of terminal alcohol are fed to a reactor containing 500 grams of catalyst, the WHSV is 3.0. The alcohol feed rate, in units of WHSV, is independent of the amount of water, or other components that may be in the feed, or co-fed to the catalyst bed.

[62] “Ph” herein refers to a phenyl (C₆H₅-) group.

[63] “Et” herein refers to an ethyl (CH₃CH₂-) group.

[64] “Ac” herein refers to an acetyl (CH₃C(O)-) group, therefore “OAc” refers to the acetate, or acetato, group.

[65] One preferred embodiment for the dehydration catalysts disclosed herein is an inorganic support modified by contact with a Ca⁺² compound. One embodiment is to deliver the calcium compound as a solution to the inorganic support using incipient wetness impregnation. Other embodiments can deliver a calcium compound by spraying a calcium solution on to inorganic support while the latter is carried on a belt system or is mixed in a rotating drum. Vapor phase deposition is also a possible method of depositing promoters on an inorganic support. Solvents used to prepare the solution may be aqueous, or an organic, or a mixture thereof. Nonlimiting examples of calcium-containing compounds that may be used for production of the catalysts described herein include Ca(OAc)₂, Ca(OEt)₂, calcium citrate, calcium borohydride, calcium acetylacetonate, calcium L-ascorbate, calcium *bis*(2,2,6,6-tetramethyl-3,5-heptanedionate), calcium carbonate, calcium citrate, calcium cyanamide, calcium 2-ethylhexanoate, calcium D-gluconate, calcium hydroxide,

calcium isopropoxide, calcium methoxide, calcium oxalate, calcium oxalate hydrate, calcium propionate, calcium *bis*(triphenylsilanoxy), and hydrates or solvates for any of those listed above. Other calcium and Group 2 compounds, or Group 1 compounds, or Group 3, or Group 4, or rare earth compounds may be employed for this purpose as promoters.

[66] In one embodiment, alumina (*e.g.*, γ -alumina) is used as the inorganic support. Other inorganic supports such as ZnAl_2O_4 can be used in the catalyst compositions provided herein. γ -Alumina is a preferred embodiment of the present invention and can be in the form of particles, or shaped extrudates, or other shaped bodies. In some embodiments, γ -alumina carriers that may be used include, but are not limited to, Clariant Actisorb 100-1, Clariant Actisorb 100-3, Clariant Actisorb 100-4, or Clariant Actisorb 100-4B, or Saint-Gobain Norpro SA6176 (1/8-inch pellets, bimodal pore size distribution 7 & 500 nm, surface area of 250 m^2/g), or Clariant T-374A. The γ -alumina can be formulated into and used as various shapes, some being complex three-dimensional motifs designed to retain or increase surface area, add mechanical strength, and/or reduce back pressure in the reaction apparatus. Any suitable commercial carrier may, optionally, be thermally treated according to one, or more than one, temperature program prior to modification with a promoter.

[67] In some embodiments, a Ca^{+2} compound is dissolved in one or more solvent(s) to create a solution, the Ca^{+2} solution is placed in contact with the carrier (*e.g.*, γ -alumina), and the solvent(s) is then removed, *e.g.*, with heat and/or reduced pressure. Those experienced in the methods of surface modification know that one technique to accomplish this is referred to as an incipient wetness impregnation process (IWP). IWP is typically followed by a drying or calcination process for some time, as shown schematically in FIG 2. The inorganic support (200) is added to vessel 201 and then addition of the IWP solution 202 is done in such a way as to provide even distribution. This can be done, for example, by contacting 202 by a spraying method. Mechanical mixing in apparatus 203 can also be used facilitate even distribution of the promoter solution. The wetted material in 203 is then heated to remove some or all of the IWP solvent. This material 204 can be further heated in a second apparatus (205) to provide drying or calcination of the catalyst. The drying or calcination can be carried out in vessel 203 or 205 at temperatures of about 100 °C to about 900 °C, or about 200 °C to 600 °C for a time period of about 1 h to about 8 h, or about 2 h to 6 h. The removal of the solvent can be done in air or under an inert atmosphere. In one embodiment the wetting solution is removed under a reduced pressure. The catalyst

removed from **204** or **205** can be sized by sifting or other methods common to solid phase catalyst processing, thus producing finished catalyst **206**. The concentration of Ca^{+2} in the solution is predetermined in such a way that a targeted amount of Ca^{+2} is deposited on the alumina surface. In some embodiments, the Ca^{+2} deposited in the range of about 0.8 to about 2.0 wt% or about 1.0 to 1.7 wt% of the total catalyst {weight of Ca^{+2} /(weight of inorganic support + weight of Ca^{+2}) x 100 = wt%}. Delivery of the calcium can also be made using other techniques such as, non-incipient wetness impregnation or, for example, vapor deposition followed by calcination in air or under an inert atmosphere. A preferred embodiment of this invention is to carry out all said modifications on the final shape or sized support material.

[68] In a preferred embodiment, the promoter-doped (e.g. Ca^{+2}) inorganic support (e.g., γ -alumina) can be further modified by treatment with an organosilane. Treatment with organosilane provides a catalyst with improved stability for the dehydration of 1-alcohols. In some embodiments, the organosilane can be delivered to the inorganic support (e.g., a Ca^{+2} modified γ -alumina carrier) using IWP, as shown in a high level and general view in FIG 3. In this embodiment the calcium-modified inorganic support **206** is treated with the IWP solution **301** in such a way as to provide even distribution. This can be accomplished by spraying the organosilane or organosilane solution **301** while mechanically mixing the promoted carrier in vessel **302**, the mixing process can greatly facilitate achieving an even distribution of the organosilane however is not always necessary. The wetted material in apparatus **302** is then heated to remove some or all of the IWP solution and/or can be transferred to vessel **303** for further drying under ambient or reduced pressure. The catalyst (**304**) can be formulated, shaped, and sized by sifting or other methods common to solid phase catalyst processing. A preferred embodiment of the invention is to use a shaped or sized support (e.g. **206**) in the modification process, hence, the catalyst **304** is already in the proper physical state (e.g. shape or particle distribution).

[69] The organosilane solution **301** used to modify the carrier by IWP can be made using water, an organic solvent, or a mixture of water and an organic solvent with or without additional additives. In the preferred embodiment the solvent is selected so that sufficient organosilane is soluble in the chosen solvent to deliver the required amount of organosilane to the solid by incipient wetness. Typical concentrations of the organosilane when used in a IWP solvent are about 0.05 to about 3 wt%, about 0.1 to about 0.2 wt%, about 0.15 to 1.5 wt%, or 0.3 to 1.3 wt%. In another embodiment, the organosilane can be delivered in neat form, for example, as a liquid or in the vapor phase. Contact time for the

neat organosilane or organosilane-IWP solution with modified carrier may be about 5 min to about 6 h, about 1 h to about 6 h, or about 2 h to about 4 h, thus allowing for complete dispersion and reaction, at or about ambient temperature (e.g., about 20 °C to about 30 °C). Solvent(s) removal is accomplished by the application of heat and/or reduced pressure. The typical final temperature reached is about 40 °C to 200 °C, or about 300 °C, or about 400 °C. Removal of the solvent(s), if used, can be done in air or under an inert atmosphere (e.g., nitrogen or argon).

[70] Typical organosilanes for use in the catalyst preparation methods disclosed herein include, but are not limited to, chlorosilanes, for example, Ph_2SiCl_2 and Ph_3SiCl . Alternatively, organosilanes such as Ph_3SiOEt and $\text{Ph}_2\text{Si}(\text{OEt})_2$ can also be used to create a silanized-dehydration catalyst. Furthermore, R_3SiX , R_2SiX_2 , and RSiX_3 organosilanes can be used in this invention where R is a mixture of aryl and alkyl radicals and where X represents a leaving group. The R-groups can be the same or a combination of alkyl, aryl, or organic functionalized substituents. Typical leaving groups include, but are not limited to halide, alkyl carboxylate (e.g. acetate), alkoxy (e.g. methoxy), or alkyl di- (e.g., oxalate) and tri-carboxylates (e.g., citrate). Example 4, *infra*, exemplifies use of Ph_2SiCl_2 dissolved in hexanes (i.e. a common solvent sold commercially that is comprised of six-carbon hydrocarbons) to prepare “Catalyst 4,” which was subsequently employed for dehydration of bio-1-butanol (TABLE 1).

[71] In some embodiments of the invention water soluble organosilanes are employed in the silanization process (defined as the treatment of the support with an organosilane solution and calcining). For these embodiments, the requirement is that the organosilane be soluble in water at levels of up to about 3 wt%. The water solubility can be achieved by the use of hydrogen bonding groups attached to the silicon atom (e.g. $\text{PhSi}(\text{OH})_3$) or by incorporation of a hydrogen bonding group or a dipolar functional group to one or more of the groups attached to the silicon atom. Examples could include an alkyl amine, ether, epoxide, or other dipolar or hydrogen bonding functional groups. Solubility of the organosilane can be increased by heating of water solution to about 40 °C, or about 50 °C, or about 60 °C, or to at least 90 °C.

[72] The effect and benefit of silanization is dependent upon the carrier used, alcohol feed, and the wt% of water content added or contained in the alcohol feed. Typically, reaction conditions employing high water concentrations (>50 wt%) in the feed have shown the greatest benefit from silanization of the catalyst and afford very stable dehydration catalysts. Silanization of calcium promoted, or Group 1, or Group 2, or other promoted

modified aluminas provides a catalyst that provides enhanced stability, which is reflected in retention of regioselective 1-alkene production as described and defined herein. The process of silanization can be applied to γ -aluminas or other inorganic supports (e.g. zinc aluminate) modified with Group 3, or Group 4, or Group 5, or Group 6, or Group 7, or Group 8, or Group 9, or Group 10 metals.

[73] Catalyst products **206** and **304** may be left as powders, for example, in the range of about 10 to about 1000 microns, or about 50 to about 200 microns, or they can be pelletized or shaped using techniques common to those skilled in the art. In some embodiments, pellets and shaped particles may lead to advantages in controlling the pressure drop across the catalyst reactor bed. This may be important where physical process requirements require long reaction tubes or where low head-pressures are desirable. Pellets may be any shape or size. In some embodiments, pellet diameters are about 1/16 in. diameter to about 1/4 in., with lengths about 1 to about 10 times the diameter, or about 2 to about 4 times the diameter. A preferred embodiment of the invention is to first complete shaping, or pelletizing, or crushing with size selection (e.g. sieving) of the support then carry out the addition of at least one promoter as described herein.

[74] In methods for dehydration of a 1-alcohol using the catalyst compositions disclosed herein, the water content in the initial 1-alcohol (e.g., bio-1-alcohol) mixture (alcohol-water mixture) that is fed to the catalyst can be from about 0.1 to about 93 wt%, about 1 to about 70 wt%, about 10 to about 50 wt%, about 15 to about 19 wt%, or about 17 wt%. The water in the alcohol feed can be contained in the alcohol-water mixture, or added using a second and separate feed, or may be a combination of the two {i.e., total water in feed = (alcohol + water mixture) + water feed}. In some embodiments, additional water is added to the alcohol-water mixture prior to contact with the catalyst, thereby producing an alcohol feed that contains about 30 to about 93 wt% of water, or about 45 to about 70 wt% of water. The use of high water content in the alcohol feed is especially well tolerated with catalysts prepared as disclosed herein. In some embodiments, the alcohol feed in contact with the catalyst (e.g., optionally including additional water added to the alcohol-water mixture prior to entering the reactor and/or water added separately into the reactor) includes about 1 to about 70 wt% water for optimum production of 1-alkene (e.g., bio-1-alkene). In some embodiments, the alcohol feed includes >90 wt% water. In some embodiments, the water content in the alcohol feed is about 1, about 5, about 10, about 15, about 20, about 25, about 30, about 35, about 40, about 45, about 50, about 55, about 60, about 65, about 70, about 75, about 80, about 85, or about 93 wt% or more. In some embodiments, the water

content in the alcohol feed is about 15 to about 20 wt%, about 15 to about 70 wt%, or about 50 to about 80 wt%. The alkene product stream of the reaction may contain an amount of water as described above in this paragraph (*e.g.*, 0.1 wt%) to about 93 wt%, or values or subranges described above that are greater than the stoichiometric amount of water that is produced in the dehydration reaction.

[75] Catalysts in this invention will dehydrate wet 1-alcohol (*e.g.*, bio-1-alcohol) mixtures that contain large amounts of water and, in addition, can have steam added prior to contact with the catalysts of this invention to afford high regioselectivity for the 1-alkene (*e.g.*, bio-1-alkene) dehydration product. Furthermore, some embodiments of this invention can maintain high regioselectivity for extended periods of time on stream, for example, 1 to 3 months, or 6 months, or 12 months, or 18 months, or 24 months, or 30 months, or 36 months, or 42 months, or as long as about 48 months.

[76] Catalysts of this invention will also dehydrate a 1-alcohol (*e.g.*, bio-1-alcohol) mixture that contains water at levels as low as 1 ppm to 1000 ppm where equal performance of catalyst to afford 1-alkene (*e.g.*, bio-1-alkene) is observed throughout the entire range of low water content and the catalyst can maintain high selectivity for extended periods of time on stream, for example, 1 to 3 months, or 6 months, or 12 months, or 18 months, or 24 months, or 30 months, or 36 months, or 42 months, or as long as about 48 months.

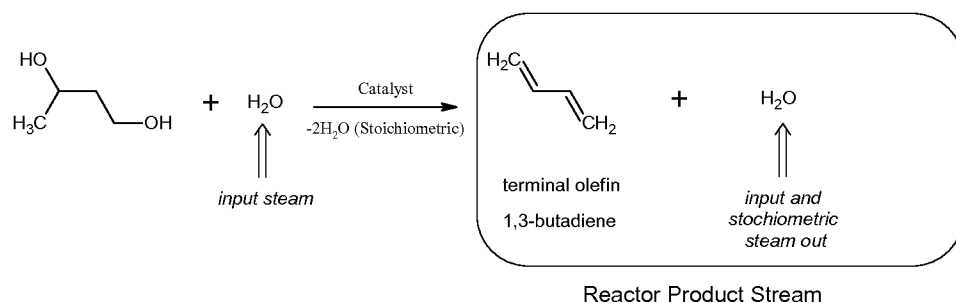
[77] An example of a catalytic 1-alcohol dehydration process as disclosed herein is shown schematically in FIG 4. A 1-alcohol (*e.g.*, bio-1-alcohol) feed **400** is introduced to the vaporization/mixing vessel (**401**) to which a water feed is added at some preselected amount. The output of **401** is transferred to vessel **403** which contains the dehydration catalyst (*e.g.*, **206** or **304** prepared above) at an elevated temperature, for example, about 200 °C to about 440 °C, or about 300 °C to about 420 °C. Optionally, a purge gas (*e.g.*, an inert gas such as argon and/or nitrogen) may be used to control dwell time in the reactor chamber. Temperature may be modified to optimize 1-alkene (*e.g.*, bio-1-alkene) production for a particular alcohol (*e.g.*, bioalcohol) feedstock. In some embodiments, the rate of 1-alcohol (*e.g.*, bio-1-alcohol) feedstock passage is about 0.1 to about 10 mass units of feedstock per mass unit of catalyst/h (*i.e.*, 0.1 to 10 WHSV), or 1.2 to 2.0 WHSV, or may be greater than 1 and less than 6 WHSV in some embodiments. Water content in the 1-alcohol (*e.g.*, bio-1-alcohol) feedstock in contact with the catalyst in the reactor **403** (water in the alcohol-water mixture entering the reactor, and optionally additional water added to the alcohol-water mixture and/or added separately into the reactor) is about 1 ppm (*i.e.*, 0.0001 wt%) to about 93 wt%. The output from apparatus **403** is fed to a cooling/condenser

system **404**. The output from **404** is transferred to a decanter where an aqueous solution **407** separates from the alkene product **405**. The isolated water product **407** (after decanting or distillation to create the isolated alkene **406**) may be optionally passed through a filter material, and/or one or more other unit operations **408** to remove traces of organic acids or other unwanted byproducts that may be produced during the dehydration reaction, thereby producing a purified water stream **402**. Optionally, the water stream **402** may be added to the alcohol feed in **401**.

[78] Non-limiting examples of 1-alcohols which may be selectively dehydrated to produce 1-alkenes with the catalyst compositions and methods disclosed herein include n-butanol, 1-pentanol, 3-methyl-1-butanol, 2-methyl-1-butanol, 1-hexanol, 4-methyl-1-pentanol, 3-methyl-1-pentanol, 2-methyl-1-pentanol. In some embodiments, the 1-alcohol is an alcohol of general formula $R^1R^2CHCH_2OH$, where R^1 and R^2 are independently H or a C_1 to C_{20} alkyl radical. In some embodiments, the 1-alcohol is an alcohol of general formula $HO(CH_2)_n(CH_3)$ with n being any integer from 1 to 22. In some embodiments, the 1-alcohol is a C_4 to C_6 alcohol.

[79] In some embodiments, the terminal 1-alcohols that may be selectively dehydrated to produce 1-alkenes with the catalyst compositions and methods disclosed herein may include at least one additional organic functional group. Non-limiting examples include aromatics (*e.g.*, with an aromatic ring that consists of carbon atoms or contains a mixture of carbon and heteroatoms), nitrile, alkene, or ketone.

[80] In some embodiments, terminal alcohols that contain one or more additional hydroxyl (alcohol) groups are used in the dehydration methods disclosed herein. Nonlimiting examples include 1,3-butanediol, 1,4-butanediol, 2,3-butanediol, 1,4-pentanediol, 1,3-pentanediol, 2,4-pentanediol, 1,6-hexanediol, 1,5-hexandiol, 2,4-hexanediol, 1,3-hexanediol. In one embodiment, an aqueous solution of 1,3-butanediol (*e.g.*, containing from about 5 to about 95 wt% of the diol) is dehydrated in a double dehydration to afford 1,3-butadiene, shown schematically below:



[81] The input steam is found to be useful in the double dehydration reactions that form a terminal olefin that is in conjugation with a second double bond (e.g. 1,3-butadiene). Conjugated dienes are generally more reactive and thus less stable. Dilution with solvent is commonly used to slow their decomposition/polymerization chemistry. The use of dilution is a well known practice to those skilled in the art of stabilizing reactive monomers (e.g. 1,3-butadiene).

[82] In some embodiments of the dehydration methods disclosed herein, the terminal alcohol and water are heated to about 300 °C to 400 °C and then contacted with the dehydration catalyst. In one embodiment, the catalyst is “**Catalyst 4**,” described *infra* in Example 4. The terminal alcohol dehydration methods disclosed herein may be operated in either isothermal or adiabatic configurations. The exiting product stream may be at a temperature of about 250 °C to about 350 °C. In embodiments of the dehydration methods disclosed herein, the final product stream may contain about 5 wt% terminal alcohol or less, or less than about 0.5 wt% terminal alcohol. Embodiments of the methods disclosed herein may produce the alkene product with about 90% to about 98% or greater regioselectivity for the terminal alkene.

[83] In a further embodiment, the dehydration method may include at least two reactors in sequence, with the same, similar, or better performance and yield as the single reactor system. Having the catalyst in more than one reactor for the instant invention can eliminate the need for external heating of the commercial reactors. Heating large commercial reactors in an isothermal manner can be cost prohibitive. In some embodiments, the product stream from the catalytic dehydration reaction (e.g., **403**) is then heated again to about 300 °C to 400 °C and contacted with a second reaction vessel containing dehydration catalyst. An example of a two-reactor process is shown schematically in FIG 5. The 1-alcohol feed **500** is added to the vaporization/mixing vessel **501** and a water feed is also added at some preselected amount. The output of **501** is

transferred to the first catalyst vessel **503** which contains the dehydration catalyst (*e.g.*, **206** or **304**, prepared as described above). The output from **503** is reheated in **504** and fed to a second catalyst vessel **505**. Vessel **503** and **505** typically do not have an external source of heat applied. The product stream from **505** is taken to a cooling/condenser system **506**. The output from **506** is transferred to a decanter where an aqueous solution **508** separates from the alkene product **507**. The product alkene **509** may be removed, and the aqueous solution **508** can be passed through a filter and/or one or more other unit operations **510** to remove traces of organic acids or other unwanted byproducts that can be produced during the dehydration reaction, thereby producing a purified water stream **502**. Optionally, the water stream **502** may be added to the alcohol feed in **501**. For those skilled in the art, this process is commonly denoted as an “adiabatic reactor” and, in some embodiments, provides the most economical and energy efficient means of dehydrating a terminal alcohol. In calculating a WHSV, the weight of alcohol feed per hour is divided by the weight of catalyst contained in both reactors. Thus in the system described above with two reactors, each separate reactor will appear to have a WHSV equaling twice that of the overall process WHSV (feed to process/total catalyst, where total catalyst is reactor 1 + reactor 2; assuming, for the explanatory case described here, that each of reactor 1 and reactor 2 is charged with the same amount of catalyst).

[84] In some embodiments of the methods disclosed herein, a device for separation of the 1-alkene product from water (*e.g.*, an aqueous solution that contains water and other components, for example, trace organic acids and/or other byproducts) is provided. For example, water may be separated from the alkene product stream by fractionation through a distillation column. Alternatively, physical separation of layers can be used when the alkene product contains a sufficiently high boiling point, for example, boiling at a temperature above about 30°C. In this case, separation may optionally be achieved with a decanter (**405/407** or **507/508**, as shown schematically in FIG 4 or FIG 5, respectively). The 1-alkene product will typically be the top layer formed upon condensation and is typically siphoned from the top of the decanter vessel with the separated aqueous layer (*i.e.*, typically bottom layer) drained (*e.g.*, continuously drained) from the bottom layer (*e.g.*, **407**, **508**). The separated aqueous layer (*e.g.*, **407**, **508**) can optionally be filtered to remove impurities and the water recycled for addition to the alcohol feed.

[85] In some embodiments the 1-alcohol/input steam is introduced to the catalyst reactor (*e.g.* **503**) at about 1 psig to 200 psig, or about 5 psig to 150 psig, or about 15 psig to 100 psig. The exit pressure from the catalyst reactor(s) can be controlled by at least one back

pressure regulator located on the exit side of the reactor. An increase in pressure can be useful although in some embodiments of the invention do not lead to an increase in the rate of dehydration (e.g. an increase in WHSV at a given temperature).

[86] Although not wishing to be bound by theory, the dehydration of terminal alcohols can be effectively modeled working on the assumption that a majority of the terminal alcohol, when contacted with the catalyst, very quickly converts to the ether product and produces water in an exothermic reaction. This reaction is shown schematically in FIG 6, using n-butanol as an example. As the reaction continues the dibutyl ether reacts with water to reform n-butanol which then undergoes a slower and likely concerted loss of water to form 1-butene. This two reaction model allows one to anticipate the effects of a change in the feed water content, reaction temperature, and/or WHSV. The isomerization of 1-butene to the respective 2-butene isomers (cis & trans) occurs at a much slower rate than 1-butene production and is not significantly impacted by changes in temperature or water content for preferred catalysts of this invention.

[87] In some embodiments a 1-alkene product produced as described herein can be utilized to make a drop-in diesel or jet fuel (e.g., biofuel) or a lubricant (e.g., biolubricant) in an energy-efficient manner. The term “drop-in” is used to indicate the new fuel prepared from the 1-alkene product can be used in commercial or military applications without the need for equipment changes or modifications. For example, the new fuels from this invention can meet the requirements of ASTM D1655 (via ASTM D7566), the standard for turbine fuels. Thus, the invention fuels can be fully compatible with existing petroleum fuel standards, be used in commercial aircraft, and therefore be considered “drop-in fuels”. In one embodiment, the methods taught herein may be utilized for conversion of n-butanol that is produced biologically, for example, in a microbial fermentation process (bio-1-butanol), containing small to large amounts of water, for example, water from the fermentation broth and optionally additional added water, to bio-1-butene with high regioselectivity and chemical conversion. The bio-1-butene in turn is useful in preparing products that are environmentally beneficial and reduce greenhouse gases compared to petroleum equivalents by virtue of the biological production of the alcohol and an energy efficient process of making the downstream products.

[88] An example of a method for making fuel products from a 1-alcohol starting material is shown schematically in FIG 7. The 1-alcohol feed **700** is added to the vaporization/mixing vessel **701** to which water feed **702** is added at some preselected amount. The output of **701** is transferred to the catalyst vessel **703** which contains the

dehydration catalyst (*e.g.*, **206** or **304**, prepared as described above). The output from **703** is fed to a cooling/condenser system (**704**). The output from **704** is transferred to a decanter where an aqueous solution **707** separates from the alkene product **705**. The aqueous solution **707** can be passed through a filter **708** and/or one or more unit operations to remove traces of organic acids or other unwanted byproducts that can be produced during the dehydration reaction, thereby producing a purified water stream **702**. Optionally, the water stream **702** may be added to the alcohol feed in **701**. The terminal alkene product **705** is feed to a dryer (**709**) (*e.g.*, by use of molecular sieves or similar inorganic drying agent). The output from **709** is fed to an oligomerization catalyst contained in apparatus **710** (*e.g.* Ziegler-Natta or mesoporous/zeolites) creating a product stream that is hydrogenated in vessel **711** using a hydrogenation catalyst (*e.g.* palladium supported on carbon) and source of hydrogen; these methods are well known in the art. The output from **711** is filtered to remove the hydrogenation catalyst (*e.g.*, a transition metal on a support) and fractionated in **712** to produce a heavy fuel cut (**714**, *i.e.*, diesel) and a light cut (**713**) which can be used as synthetic paraffinic kerosene (SPK) jet fuel meeting ASTM D7566 standards for blending with petroleum based fuels according to at least one ANNEX contained therein the most current approved ASTM D7566.

[89] In embodiments of the dehydration methods disclosed herein in which the 1-alcohol is produced biologically (bio-1-alcohol), contaminants (*e.g.*, organic contaminants) may be present in the alcohol-water mixture (*e.g.*, from fermentation broth), including but not limited to, esters, aldehydes, and/or ketones. Such contaminants can be tolerated in the dehydration reactions disclosed herein at various levels depending upon the 1-alcohol (*e.g.*, bio-1-alcohol) feedstock used. In some embodiments, up to about 5 wt%, or up to about 0.5 wt% may be tolerated, for example, when 1-butanol (*e.g.*, bio-1-butanol) is the 1-alcohol starting material.

[90] In some embodiments of the dehydration methods disclosed herein in which the 1-alcohol is produced biologically (bio-1-alcohol), acidic contaminants (*e.g.*, organic acids present in fermentation broth) may be removed by pretreatment of the alcohol (*e.g.*, bio-1-alcohol) mixture either in solution or in the gas phase. This can be accomplished, for example, by contacting the terminal alcohol (*e.g.*, bio-1-alcohol) mixture with a water solution containing an organic or inorganic base. Some examples include, but are not limited to, aqueous sodium bicarbonate or similar inorganic bases dissolved in water. In some embodiments, shown schematically in FIG 8, a solid phase reagent that is capable of absorbing H⁺ can be utilized. The alcohol feed (**800**) is passed through an acid scavenging

material **802** and then water **801** is added to the stream and placed in the vaporization/mixing chamber. The output **804** is now suitable for use in the regioselective dehydration reaction. The acid scavenging materials can be organic, inorganic, or a mixture thereof. Nonlimiting examples of a solid support that is capable of removing acidic (*e.g.*, acidic organic) components include poly(vinylpyridine) or related porous polymer-bound organic bases, which are well known to those skilled in the art of functionalized organic polymers. The functionalized organic polymers can be recharged by washing with an aqueous basic solution **805**, *e.g.*, about pH 7 or about pH 9 or greater. The exiting and used stream **806** can be treated with additional base and used again. After the scavenging material **802** is washed with **805**, pure water may be used to remove salts prior to restarting the feed **800**.

[91] In some embodiments of the methods disclosed herein, removal of final traces of water and oxygenated organics (*e.g.*, ethers, aldehydes, and/or aldol-type products) from the 1-alkene product can be accomplished by passing the alkene stream through a fixed bed of separation media, for example, activated alumina, molecular sieves, Celite, activated charcoal, size-exclusion type of media (*e.g.*, selective gas permeation membranes), or a combination thereof. For example, the media may be contained in a vessel shown schematically in FIG 7 as **709**. In some embodiments, reactivation of the fixed-bed materials may be possible by heating under a purge of hydrocarbon or inert gas while heating to temperature of about 50° to about 200° C, or about 100° C. In one embodiment, a series of membranes and/or bed of ionic-liquids that are well known for permitting selective passage of non-polar molecules and retaining more polar organics (*e.g.*, ethers and alcohols) can be used to dewater the 1-alkene product.

[92] The following examples are intended to illustrate, but not limit, the invention.

EXAMPLES

Example 1. Na-impregnated Strem gamma-alumina

[93] **Catalyst 1** was made by adding 1.5 wt% of NaOH onto Strem gamma-alumina by incipient wetness impregnation. The NaOH solution contained 0.06 g of NaOH dissolved in water to make 4 mL of solution. The clear solution was added to 4 g of Strem γ -alumina and mixed for about 5 min. The impregnated carrier was then dried at 200°C for 16 h to obtain the final catalyst.

Example 2. Na impregnated Actisorb 100-1

[94] Catalyst 2 was made by adding 0.6 wt% Na onto an alumina carrier, ActiSorb 100-1, by incipient wetness impregnation. The impregnation solution was prepared by dissolving Na_2CO_3 in water. The solution contained 0.003 g Na in 0.325 mL solution. The clear solution (0.325 mL) was added to 0.5 g of the carrier and mixed for about 5 min. The impregnated carrier was then calcined at 550 °C for 6 h to obtain the final catalyst.

Example 3. Ca impregnated ActiSorb 100-1

[95] Catalyst 3 was made by adding 1.1 wt% of Ca^{+2} onto Alumina (ActiSorb 100-1) by incipient wetness impregnation. The impregnation solution was prepared by dissolving $\text{Ca}(\text{OAc})_2$ in water. The solution contained 0.022 g of Ca^{+2} in 1.3 mL solution. The clear solution was added to 2 g of alumina and mixed for about 5 min. The impregnated carrier was then calcined at 550 °C for 6 h to obtain the final catalyst.

Example 4. Silanization on Ca^{2+} impregnated ActiSorb 100-1

[96] Catalyst 4 was prepared by adding 1.2 wt% of Ph_2SiCl_2 onto Catalyst 3 (prepared above) by incipient wetness impregnation. The Ph_2SiCl_2 in hexanes solution contained 0.00585 g of Ph_2SiCl_2 in 0.325 ml solution. The clear solution was added to 0.5 g of sample 3 and mixed for about 5 min. The impregnated catalyst was then dried at 120 °C for 16 h to obtain the final catalyst.

Example 5. Catalytic performance in 1-butanol dehydration reaction

[97] Catalyst examples 1-4 prepared above were tested in a fixed-bed test unit. In the test, a bio-1-butanol feed containing 2 wt% heptane (internal standard) was passed over a 200 mg catalyst bed at 1 atm and a WHSV of 0.5 or 1.26, while the bed temperature was controlled at five set points, 340, 360, 370, 380, and 400 °C. The products at the reactor outlet were monitored with an on-line gas chromatograph (GC). The lowest reaction temperature needed to achieve a 1-Butanol/dibutyl ether (DBE) conversion greater than 95% is shown in Table 1. The actual 1-Butanol/DBE conversion and the 1-Butene regioselectivity are shown for this process condition.

Table 1

Bio-1-butanol Dehydration Results.

	WHSV (h ⁻¹)	T (°C)	Feed	1-BuOH/DBE conversion	1-Butene regioselectivity
Catalyst 1	0.5	400	2 wt% heptane in bio-1-butanol	96.1	95.4
Catalyst 2	0.5	360	2 wt% heptane in bio-1-butanol	99.6	93.8
Catalyst 3	1.26	380	2 wt% heptane in bio-1-butanol	99.4	96.5
Catalyst 4	1.26	380	2 wt% heptane in bio-1-butanol	99.7	94.9

Example 6.

[98] **Comparative Catalyst 6** was prepared according to the procedure described in US Patent 4,234,752 A. Commercially available Strem gamma-alumina powder was placed in contact with an aqueous sodium hydroxide solution (2x the wt of the gamma-alumina, 5 wt% NaOH) for 2 h, isolated by filtration, and washed several times with water (total 4x the wt of gamma-alumina). **Comparative Catalyst 6** was dried at 200 °C for a period of 24 h and then used as a dehydration catalyst (see below).

Example 7

[99] **Comparative Catalyst 7** was prepared according to the procedure described in US Patent Application number 13/434,668. Commercially available Strem gamma-alumina powder (500 g) was placed in contact with an aqueous sodium hydroxide solution (2x the wt of the gamma-alumina, 5 wt% NaOH) for 2 h, isolated by filtration, and washed several times with water (total 4x the wt of gamma-alumina). This affords **Comparative Catalyst 6** (500 g) was dried at 200 °C for a period of 24 h. Next, this material was treated with diphenyldichlorosilane (3 g/L) and triethylamine (3 g/L) dissolved in a hexanes (total 1 L) solution. This material was washed with hexanes (1 L), then water (2 L), and dried at 200 °C for a period of 24 h. This afforded **Comparative Catalyst 7** and was used as a dehydration catalyst (see below).

Example 8

[100] This invention **Catalyst 8** was made by adding 2 wt% of Ca^{+2} onto Alumina (ActiSorb 100-1) by incipient wetness impregnation. The carrier was first calcined at 600 °C for 2h. The impregnation solution was prepared by dissolving $\text{Ca}(\text{OAc})_2$ in water. The solution contained 0.04 g of Ca^{+2} in 1.3 mL solution. The clear solution was added to 2 g of alumina and mixed for about 5 min. The impregnated carrier was then calcined at 550 °C for 6 h to obtain the final catalyst.

Example 9

[101] This invention **Catalyst 9** was made the same way as catalyst 8.

Example 10

[102] **Comparative Catalyst 10** was made by adding 0.8 wt% of Na onto Alumina (ActiSorb 100-1) by incipient wetness impregnation. The carrier was first calcined at 600 °C for 2h. The impregnation solution was prepared by dissolving Na_2CO_3 in water. The solution contained 0.016 g of Na in 1.3 mL solution. The clear solution was added to 2 g of alumina and mixed for about 5 min. The impregnated carrier was then calcined at 550 °C for 6 h to obtain the final catalyst.

Example 11

[103] **Comparative Catalyst 11** was made by adding 1.0 wt% of Na onto Alumina (ActiSorb 100-1) by incipient wetness impregnation. The carrier was first calcined at 600 °C for 2h. The impregnation solution was prepared by dissolving Na_2CO_3 in water. The solution contained 0.02 g of Na in 1.3 mL solution. The clear solution was added to 2 g of alumina and mixed for about 5 min. The impregnated carrier was then calcined at 550 °C for 6 h to obtain the final catalyst.

Example 12

[104] This invention **Catalyst 12** was made by adding 1 wt% of Ca onto Alumina (ActiSorb 100-1) by incipient wetness impregnation. The carrier was first calcined at 600 °C for 2h. The impregnation solution was prepared by dissolving $\text{Ca}(\text{OAc})_2$ in water. The solution contained 0.02 g of Ca^{+2} in 1.3 mL solution. The clear solution was added to 2 g of

alumina and mixed for about 5 min. The impregnated carrier was then calcined at 550 °C for 6 h to obtain the final catalyst.

Example 13

[105] **Catalyst 13** was prepared in a similar fashion as Catalyst 12 except that the carrier was Norpro SA 6176.

Example 14

[106] **Catalyst 14** was prepared in a similar fashion as Catalyst 12 except that the carrier was T-374A from Sud-Chemie.

Example 15

[107] **Catalyst 15** was prepared in a similar fashion as Catalyst 12 except that the carrier was ActiSorb 100-3. Prior to impregnation, the carrier was calcined at 600 °C for 2 h.

Example 16

[108] **Catalyst 16** was prepared in a similar fashion as Catalyst 12 except that the carrier was ActiSorb 100-4. Prior to impregnation, the carrier was calcined at 600 °C for 2 h.

Example 17

[109] **Catalyst 17** was prepared in a similar fashion as Catalyst 12 except that the carrier was ActiSorb 100-4A. Prior to impregnation, the carrier was calcined at 600 °C for 2 h.

Example 18

[110] This invention **Catalyst 18** was made by adding 1.3 wt% of Ca onto Alumina (ActiSorb 100-1) by incipient wetness impregnation. The carrier was first calcined at 600 °C for 2h. The impregnation solution was prepared by dissolving $\text{Ca}(\text{OAc})_2$ in water. The solution contained 0.026 g of Ca^{+2} in 1.3 mL solution. The clear solution was added to 2 g of alumina and mixed for about 5 min. The impregnated carrier was then calcined at 550 °C for 6 h to obtain the final catalyst.

Example 19

[111] This invention **Catalyst 19** was made by adding 1.5 wt% of Ca onto Alumina (ActiSorb 100-1) by incipient wetness impregnation. The carrier was first calcined at 600

°C for 2 h. The impregnation solution was prepared by dissolving $\text{Ca}(\text{OAc})_2$ in water. The solution contained 0.03 g of Ca^{+2} in 1.3 mL solution. The clear solution was added to 2 g of alumina and mixed for about 5 min. The impregnated carrier was then calcined at 550 °C for 6 h to obtain the final catalyst.

Example 20

[112] A solution of diphenyldiethoxysilane (7.69 g/L) in ethanol was prepared. A 1.3 mL portion of the silane solution was added to 2 g of the catalyst prepared in Example 19 by incipient wetness impregnation. The mixture was stirred for about 5 min. The catalyst was dried at 120 °C for 16 h to produce **Catalyst 20**.

Example 21

[113] A solution of diphenyldiethoxysilane (15.38 g/L) in ethanol was prepared. A 1.3 mL portion of the silane solution was added to 2 g of the catalyst prepared in Example 19 by incipient wetness impregnation. The mixture was stirred for about 5 min. The catalyst was dried at 120 °C for 16 h to produce **Catalyst 21**.

Example 22

[114] A solution of diphenyldiethoxysilane (30.77 g/L) in ethanol was prepared. A 1.3 mL portion of the silane solution was added to 2 g of the catalyst prepared in Example 19 by incipient wetness impregnation. The mixture was stirred for about 5 min. The catalyst was dried at 120 °C for 16h to produce **Catalyst 22**.

Example 23. Catalytic performance in 1-butanol dehydration reaction

[115] Catalyst examples 12-17 and 20-22 prepared above were tested in a fixed-bed test unit. In the test, a bio-1-butanol feed containing 2 wt% heptane (as internal standard) was passed over a 200 mg catalyst bed at 1 atm and a WHSV of 1.26, while the bed temperature was controlled at the set points named in the description of Figures 11 and 13. The products at the reactor outlet were monitored with an on-line gas chromatograph (GC). Conversion is defined as the combined conversion of 1-Butanol and dibutyl ether to butene products. 1-Butene selectivity is defined as the amount of 1-Butene formed divided by the sum of converted 1-Butanol and dibutyl ether. Representative results are shown in Table 2.

Example 24

[116] **Catalyst 24** was made by supporting 1.2 wt% Ca on an extruded (1/16 inch diameter) alumina carrier, ActiSorb 100-1, by incipient wetness impregnation. The carrier was calcined at 600 °C for 1 h in air prior to impregnation. The impregnation solution was prepared by dissolving Ca(OAc)₂ in water. The final solution contained 70.21 g of Ca(OAc)₂ in 1.30 L of water. The clear solution was added to 1.49 kg of the carrier and mixed for about 10 min. The impregnated carrier was then pre-dried at 120 °C for 30 min and then calcined at 500 °C for 1 h.

[117] A solution of diethoxydiphenylsilane in ethanol was prepared. 1.26 L of the impregnating solution containing 3.44 g of the silane was added to a 1.40 kg portion of the Ca-impregnated carrier. The mixture was stirred for about 10 min. The impregnated carrier was dried for 3 h at room temperature under vacuum and then at 120 °C for 1 h in air to obtain the final catalyst.

Example 25. Catalytic performance in 1-butanol dehydration reaction and hydrothermal stability

[118] Catalyst examples 8, 9, 18, 19, and 24 and Comparative examples 6, 7, 10, and 11 prepared above were tested in a fixed-bed test unit. Catalyst examples 6 – 11, 18, and 19 were prepared as powders and charged to the reactor to form the catalyst bed. Catalyst example 24 was crushed before charging to form the catalyst bed. In the test, a bio-1-butanol feed (88 wt%) containing 2 wt% heptane (as internal standard) and 10 wt% water was passed over a 200 mg catalyst bed at 1 atm and a WHSV of 1.26, while the bed temperature was controlled at the set points named in the descriptions of Figures 9, 10, and 12. The products at the reactor outlet were monitored with an on-line gas chromatograph (GC). After completion of the above tests the feed was switched to 7wt% 1-butanol in water. This feed was passed over the catalyst at WHSV = 1.4 at 400 °C for 60 h. After this hydrothermal treatment the feed was switched back to the 88 wt% 1-butanol feed and the performance was measured at the same five reaction temperatures. The catalysts were then subjected to another 60 h hydrothermal treatment as above followed by a third performance test with the 88 wt% 1-butanol feed. Representative results are shown in Table 2.

Table 2

Bio-1-butanol Dehydration Results.

	WHSV (h ⁻¹)	T (°C)	Aging time (h)	1-Butanol/DBE conversion	1-Butene selectivity
Example 6	1.26	380	no	89.4	95.9
			60	42.7	94.6
			120	41.1	93.6
Example 7	1.26	380	no	78.4	96.1
			60	77.3	95.5
			120	78.5	95.1
Example 8	1.26	380	no	82.8	96.9
			60	93.6	95.5
			120	95.1	94.9
Example 9	1.26	380	no	81.0	97.2
			60	92.6	96.1
			120	94.8	95.2
Example 10	1.26	380	no	95.6	95.1
			60	98.4	93.9
			120	98.8	93.2
Example 11	1.26	380	no	81.8	96.1
			60	87.4	95.4
			120	88.9	94.8
Example 12	1.26	360	no	98.8	96.4
Example 13	1.26	360	no	96.8	97.2
Example 14	1.26	360	no	99.0	93.5
Example 15	1.26	380	no	99.9	93.4
Example 16	1.26	380	no	99.9	95.3
Example 17	1.26	380	no	99.3	95.0
Example 18	1.26	380	no	99.4	94.6
			60	99.9	92.2
			120	100.0	91.0
Example 19	1.26	380	no	98.0	95.9
			60	99.6	94.1
			120	99.8	92.6
Example 20	1.26	380	no	93.0	96.2
Example 21	1.26	380	no	90.4	96.4
Example 22	1.26	380	no	95.1	95.5
Example 23	1.26	360	no	85.9	97.5
			60	98.1	95.1
			120	98.4	94.0

Example 26. Long-Term Isothermal Performance of Catalyst 24

[119] A 3/8 inch schedule 40, 316 SS (0.493 inch ID) tubular reactor, configured to operate isothermally with a downward flow, with essentially no pressure drop, and outlet at ambient atmospheric pressure, was charged with 7.4 g of **Catalyst 24** to give a catalyst bed 12 in deep, located between a 24 in bed of 3 mm glass beads upstream and a 4 in bed of inert silicon carbide granules downstream. A preheater/vaporizer immediately upstream of the reactor was used to ensure that the nominally 100% 1-butanol feed (no diluent) was completely vaporized prior to delivery to the top of the upstream bed of glass beads. The vaporized reactor effluent was analyzed by online gas chromatography.

[120] The conditions and results of testing **Catalyst 24** are reported in Table 3. The results are the mean value obtained over the duration of the run; “TOS” = “time on stream”, the duration of the run (in days); WHSV and T are in the same units as reported in Table 2; “Conversion” is the molar conversion of 1-butanol. Runs A, B, and C were conducted using the same catalyst charge and sequentially (therefore, the total time on stream was 19.5 days).

Table 3**Isothermal Performance of Catalyst 24**

Run	TOS	WHSV	T	Conversion	Molar C ₄ Selectivity			
					1-butene	<i>trans</i> -2-butene	<i>cis</i> -2-butene	DBE
A	11.6	2.14	375	0.955	0.94	0.01	0.02	0.02
B	4.0	2.16	386	0.987	0.95	0.01	0.03	0.00
C	3.9	1.57	387	0.996	0.94	0.02	0.04	0.00

[121] Where a range of values is provided, it is understood that each intervening value, to the tenth of the unit of the lower limit unless the context clearly dictates otherwise, between the upper and lower limits of that range is also specifically disclosed. Each smaller range between any stated value or intervening value in a stated range and any other stated or intervening value in that stated range is encompassed within the invention. The upper and lower limits of these smaller ranges may independently be included or excluded in the range, and each range where either, neither or both limits are included in the smaller ranges is also encompassed within the invention, subject to any specifically excluded limit in the stated range. Where the stated range includes one or both of the limits, ranges excluding either or both of those included limits are also included in the invention.

[122] Although the foregoing invention has been described in some detail by way of illustration and examples for purposes of clarity of understanding, it will be apparent to those skilled in the art that certain changes and modifications may be practiced without departing from the spirit and scope of the invention, which is delineated in the appended claims. Therefore, the description should not be construed as limiting the scope of the invention.

[123] All publications, patents, and patent applications cited herein are hereby incorporated by reference in their entireties for all purposes and to the same extent as if each individual publication, patent, or patent application were specifically and individually indicated to be so incorporated by reference.

CLAIMS

We claim:

1. A method for dehydrating a 1-alcohol to a 1-alkene, comprising:
contacting and heating a 1-alcohol with at least one catalyst that comprises a calcium-modified inorganic support at a WHSV of about 1.01 hr^{-1} to about 10 hr^{-1} ,
wherein said 1-alcohol is in a mixture with about 1 ppm to about 93 wt% water,
thereby producing the corresponding 1-alkene with greater than about 90% regioselectivity.
2. A method according to claim 1, wherein the 1-alcohol is a C_4 to C_6 1-alcohol.
3. A method according to claim 1, wherein said 1-alcohol is 1-butanol.
4. A method according to claim 3, wherein said 1-alkene is 1-butene.
5. A method according to claim 2, wherein said 1-alcohol is 1-butanol, 1-pentanol, 1-hexanol, 3-methyl-1-butanol, 2-methyl-1-butanol, 4-methyl-1-pentanol, 3-methyl-1-pentanol, or 2-methyl-1-pentanol.
6. A method according to claim 1, wherein said 1-alcohol is a bio-1-alcohol.
7. A method according to claim 6, wherein the bio-1-alcohol is a C_4 to C_6 1-alcohol.
8. A method according to claim 7, wherein said bio-1-alcohol is bio-1-butanol.
9. A method according to claim 8, wherein said 1-butene is bio-1-butene.
10. A method according to claim 1, wherein the 1-alcohol is an alcohol of general formula $\text{R}^1\text{R}^2\text{CH}(\text{CH}_2)_2\text{OH}$, where R^1 and R^2 are independently H or a C_1 to C_{20} alkyl radical, or contain one or more aromatic rings containing exclusively carbon or a mixture of carbon and heteroatoms, or a nitrile, alkene, or ketone functional group, or a combination thereof.
11. A method according to claim 1, wherein the 1-alcohol is an alcohol of general

formula $\text{HO}(\text{CH}_2)_n(\text{CH}_3)$ with n being any integer from 1 to 22.

12. A method according to claim 1, wherein the regioselectivity of 1-alkene production is greater than about 95%.
13. A method according to claim 1, wherein the regioselectivity of 1-alkene production is about 90% to about 99%.
14. A method according to claim 1, wherein said 1-alkene comprises $\leq$ about 5% unreacted 1-alcohol.
15. A method according to claim 1, wherein said water is present at about 10 to about 70 wt%.
16. A method according to claim 1, wherein said inorganic support comprises γ -alumina.
17. A method according to claim 1, wherein said catalyst is further modified by treatment with at least one organosilane.
18. A method according to claim 17, wherein said organosilane comprises a chlorosilane.
19. A method according to claim 1, further comprising providing at least one purge gas.
20. A method according to claim 19, wherein said purge gas comprises nitrogen and/or argon.
21. A method according to claim 1, wherein said heating comprises a temperature of about 200° C to about 440° C.
22. The method according to claim 21, wherein said heating comprises a temperature of about 300° C to about 420° C.

23. A method according to claim 1, further comprising separating water from said 1-alkene, thereby producing a dried 1-alkene product.
24. A method according to claim 23, comprising contacting said dried 1-alkene product with a second catalyst to form oligomers.
25. A method according to claim 24, wherein said second catalyst is selected from a Ziegler-Natta catalyst and a mesoporous oligomerization catalyst.
26. A method according to claim 24, further comprising using said oligomers to produce a diesel fuel.
27. A method according to claim 26, wherein said diesel fuel comprises a flashpoint of about 38 to about 100 °C, a Cetane rating of about 45 to about 60, and aromatic content of less than about 0.5 wt%.
28. A method according to claim 24, further comprising using said oligomers to produce a jet fuel.
29. A method according to claim 28, wherein said jet fuel comprises a flashpoint of about 38 to about 100 °C, a cold flow viscosity of less than about 8.0 cSt at -20 °C, and aromatic content of less than about 0.5 wt%.
30. A method according to claim 24, further comprising using said oligomer to produce a lubricant.
31. A method according to claim 30, wherein said lubricant comprises a viscosity of about 1 to about 10,000 cSt at 25 °C.
32. A method of making 1,3-butadiene, comprising contacting the 1-butene of claim 4 with a catalyst comprising Bi, Mo and Fe in a molar ratio of 1:1:0.5-1.25, and comprising a $\text{Bi}_3\text{FeMo}_2\text{O}_{12}$ phase and $\text{Fe}_2(\text{MoO}_4)_3$ phase.
33. A method for dehydrating a 1-alcohol to a 1-alkene, comprising:

contacting and heating a 1-alcohol with at least one catalyst that comprises a calcium-modified inorganic support, thereby producing the corresponding 1-alkene with greater than about 90% regioselectivity.

34. A method according to claim 33, wherein said 1-alcohol is in a mixture with about 1 ppm to about 93 wt% water.

35. A method according to claim 33, wherein the catalyst is contacted with the 1-alcohol at a WHSV of about 1.01 hr^{-1} to about 10 hr^{-1} .

36. A method according to claim 33, wherein said catalyst is further modified by treatment with at least one organosilane.

37. A method for dehydrating a 1-alcohol to a 1-alkene, comprising:
contacting and heating a 1-alcohol with at least one catalyst that comprises an inorganic support that is modified by a Group 2 element and at least one organosilane, thereby producing the corresponding 1-alkene with greater than about 90% regioselectivity.

38. A method according to claim 37 wherein the Group 2 element comprises at least one of Mg, Ca, Sr, and Ba.

39. A method according to claim 37, wherein said 1-alcohol is in a mixture with about 1 ppm to about 93 wt% water.

40. A method according to claim 37, wherein the catalyst is contacted with the 1-alcohol at a WHSV of about 1.01 hr^{-1} to about 10 hr^{-1} .

41. A catalyst composition for producing 1-alkenes from 1-alcohols with high regioselectivity, comprising:
an inorganic support that is modified with at least one Group 2 element and at least one organosilane.

42. A catalyst composition according to claim 41, wherein the Group 2 element comprises at least one of Mg, Ca, Sr, and Ba.

43. A catalyst composition according to claim 41, wherein the Group 2 element is Ca.

44. A catalyst composition according to claim 41, wherein the organosilane is diphenyldiethoxysilane.

45. A catalyst composition according to claim 41, wherein the inorganic support is γ -alumina or zinc aluminate.

46. A catalyst composition according to claim 41, produced by a method comprising:

a) modifying an inorganic support with at least one Group 2 element to produce a first modified inorganic support, wherein the first modified inorganic support comprises said at least one Group 2 element;

b) heat-treating the first modified inorganic support to produce a heat-treated first modified inorganic support;

c) contacting the heat-treated first modified inorganic support with at least one organosilane to produce a second modified inorganic support, wherein the second modified inorganic support comprises said at least one Group 2 element and said at least one organosilane, or fragment thereof; and

d) heat-treating the second modified inorganic support to produce the catalyst composition.

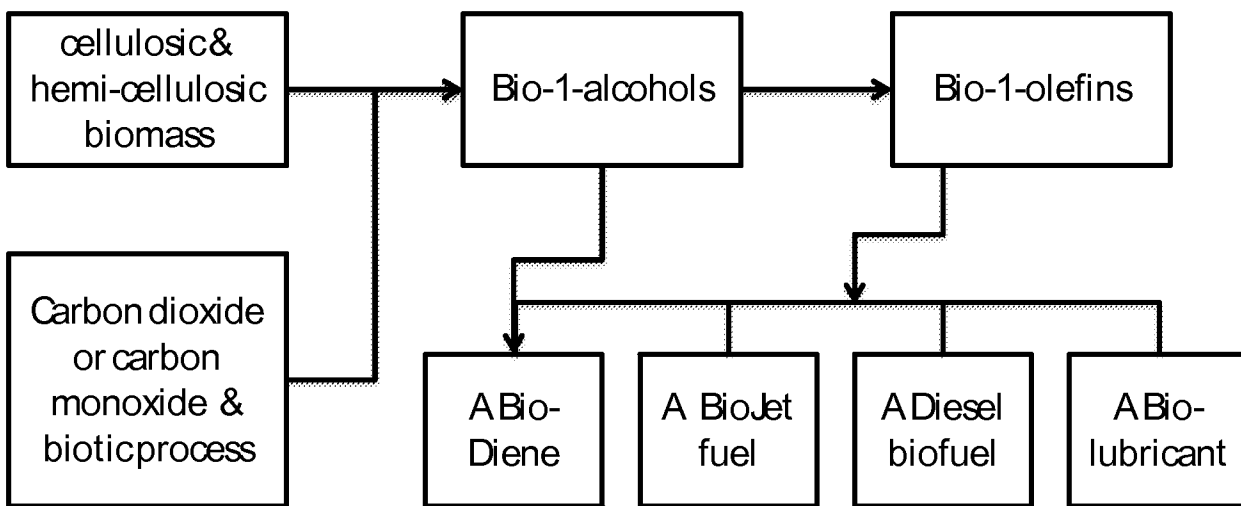


FIG 1

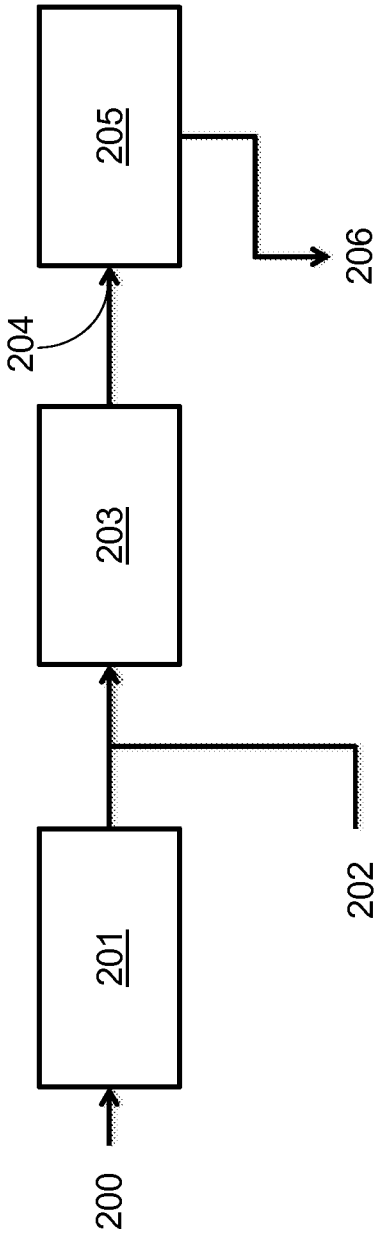


FIG 2

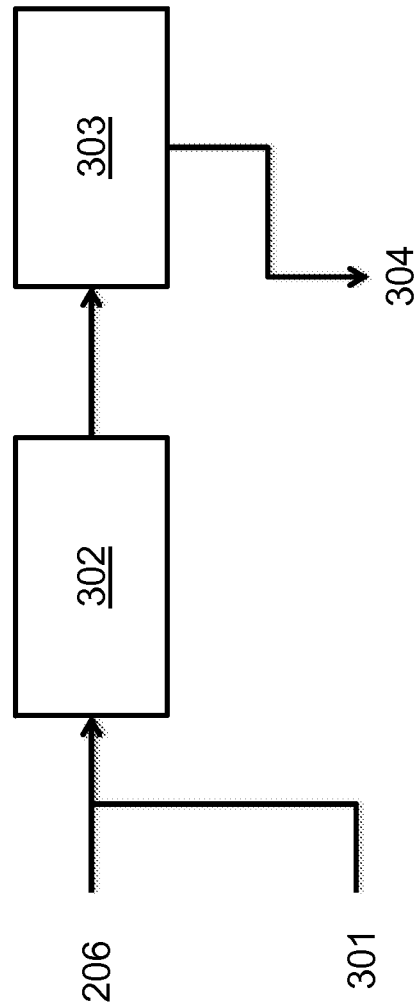


FIG 3

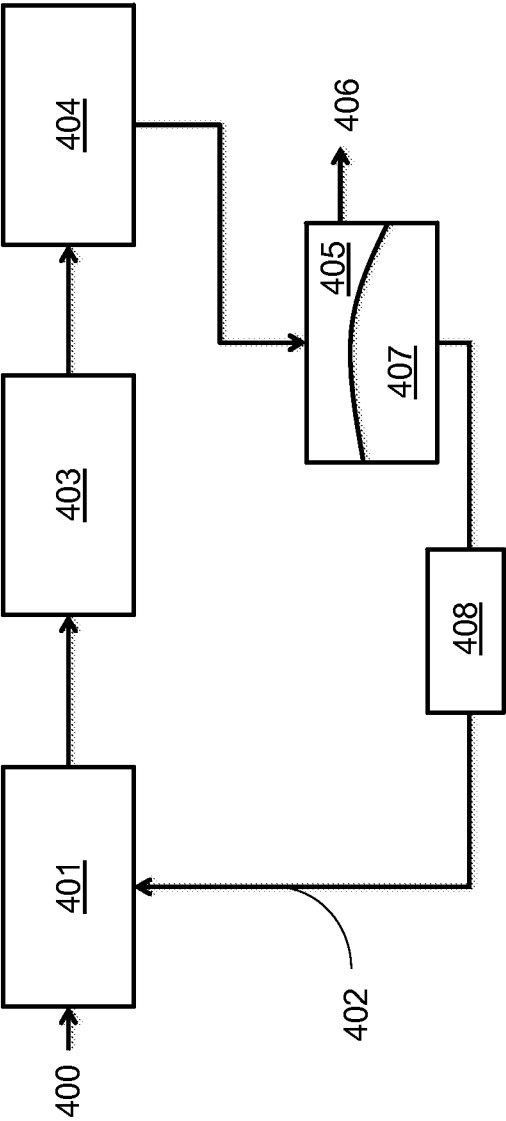


FIG 4

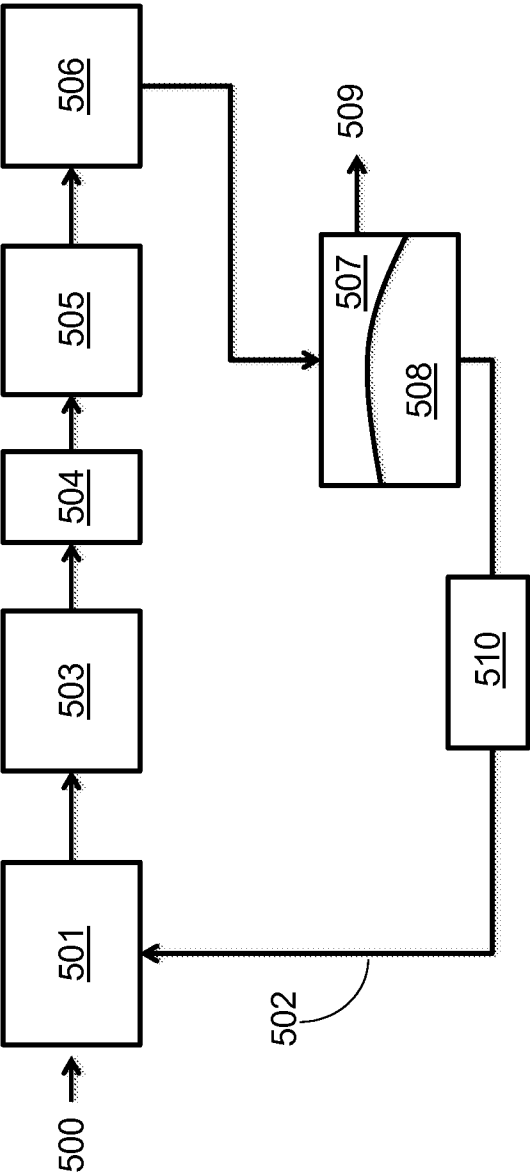


FIG 5

Chemical Model for the Dehydration of Terminal Alcohols

Chemical Reactions using n-butanol as a specific example:

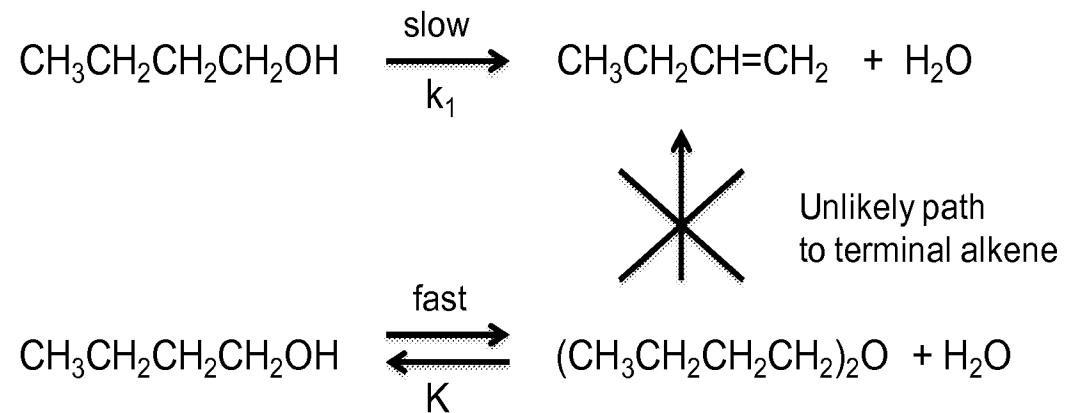


FIG 6

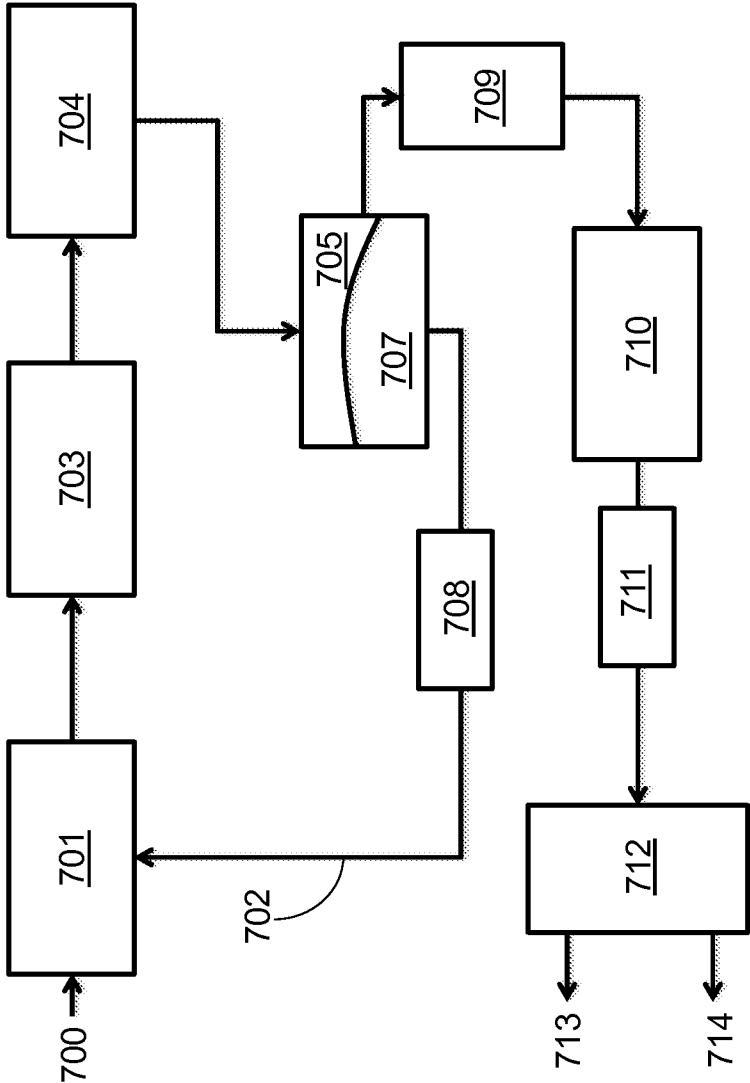


FIG 7

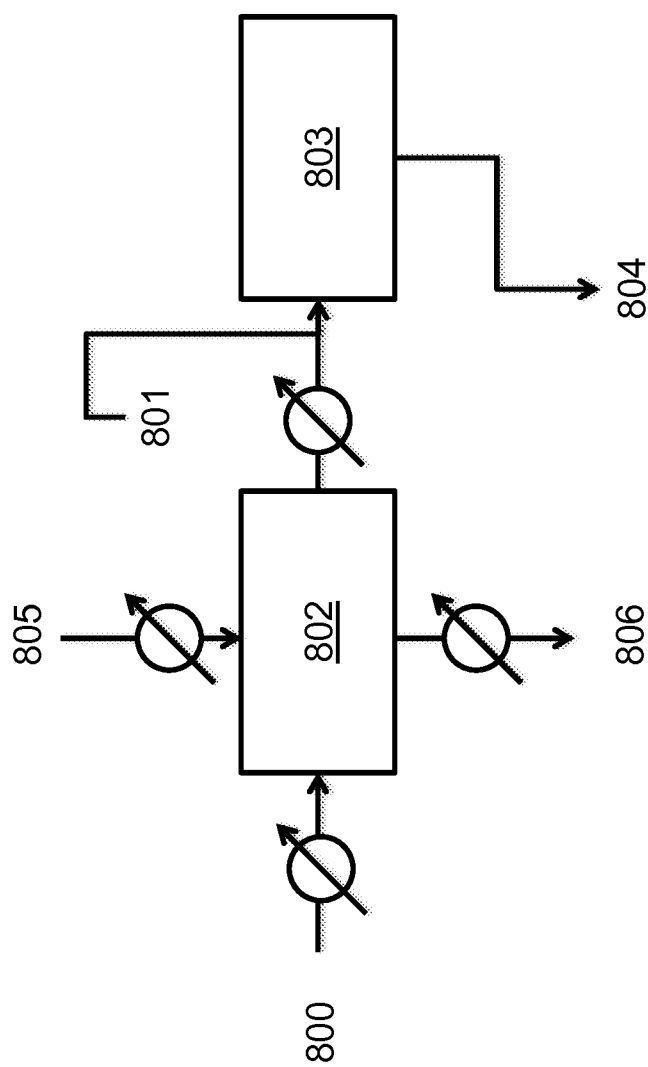


FIG 8

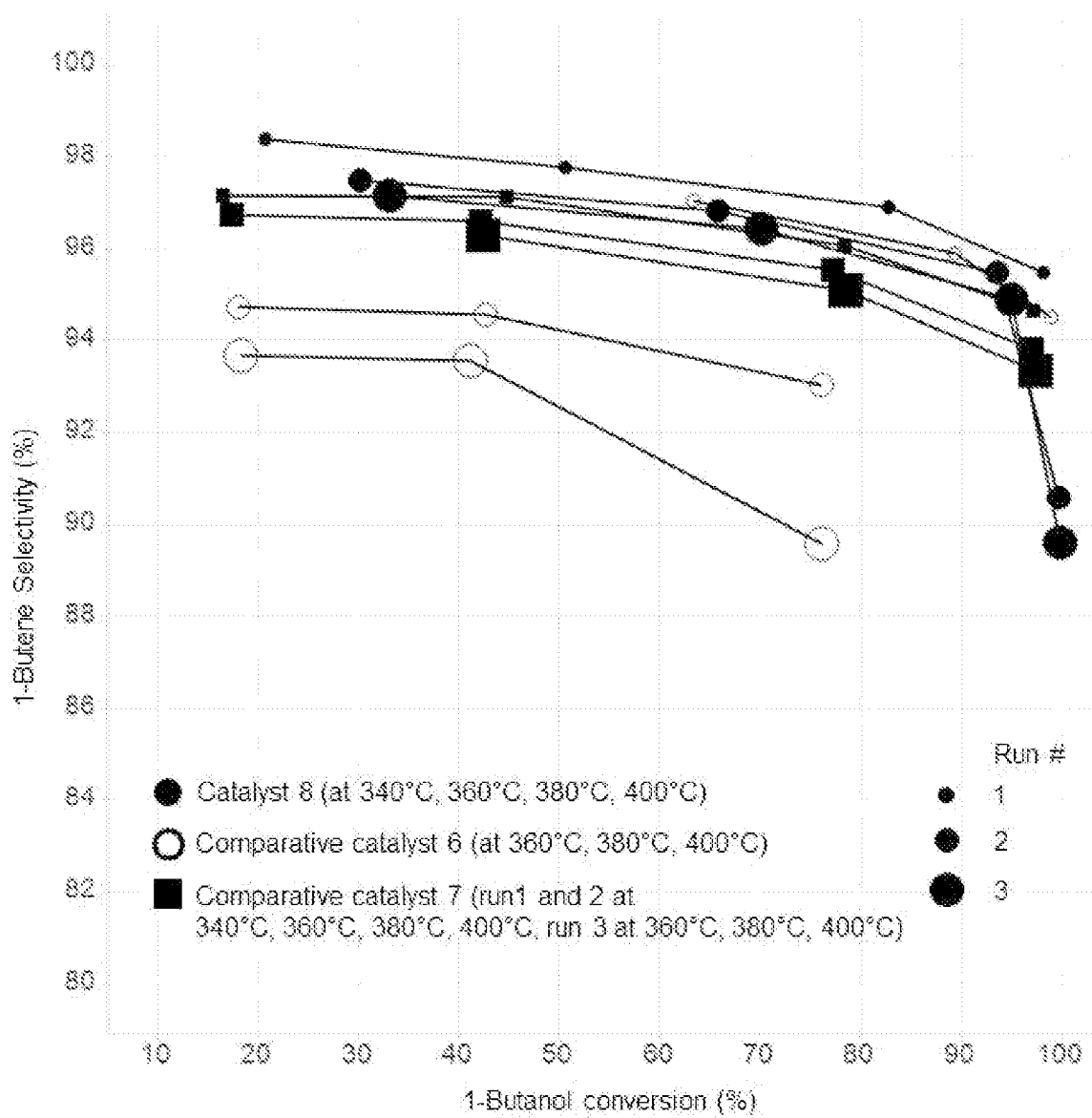


FIG 10

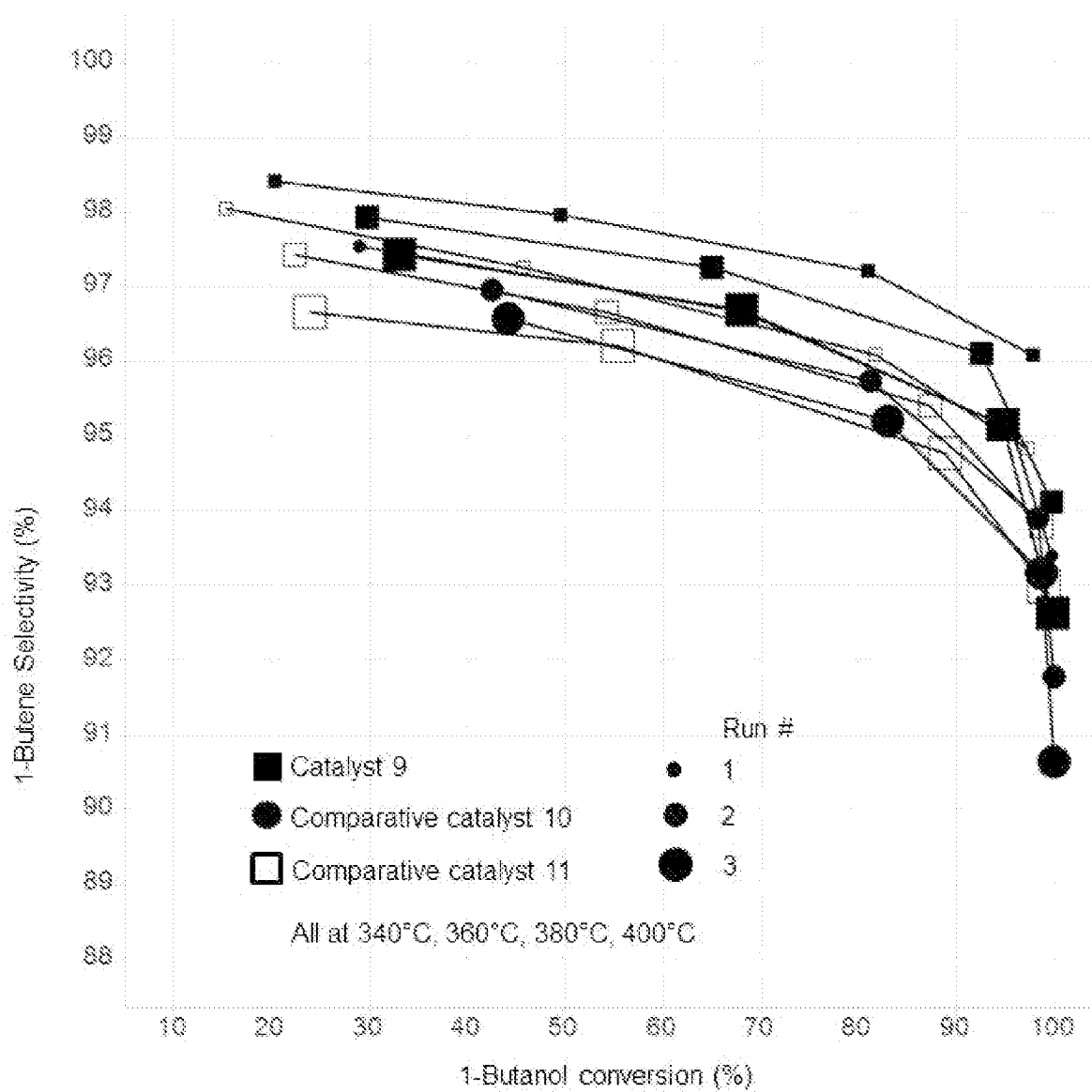
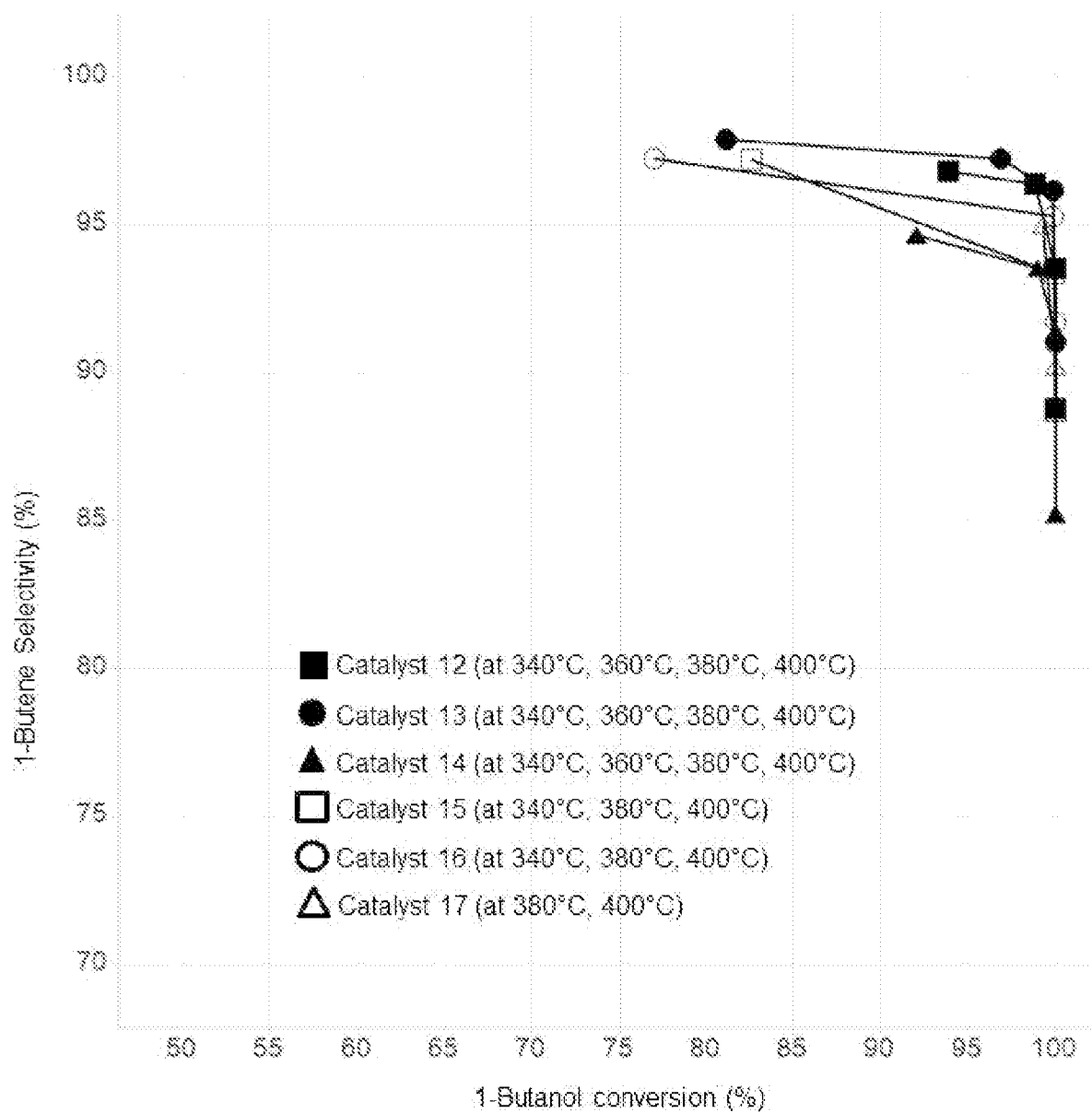


FIG 11



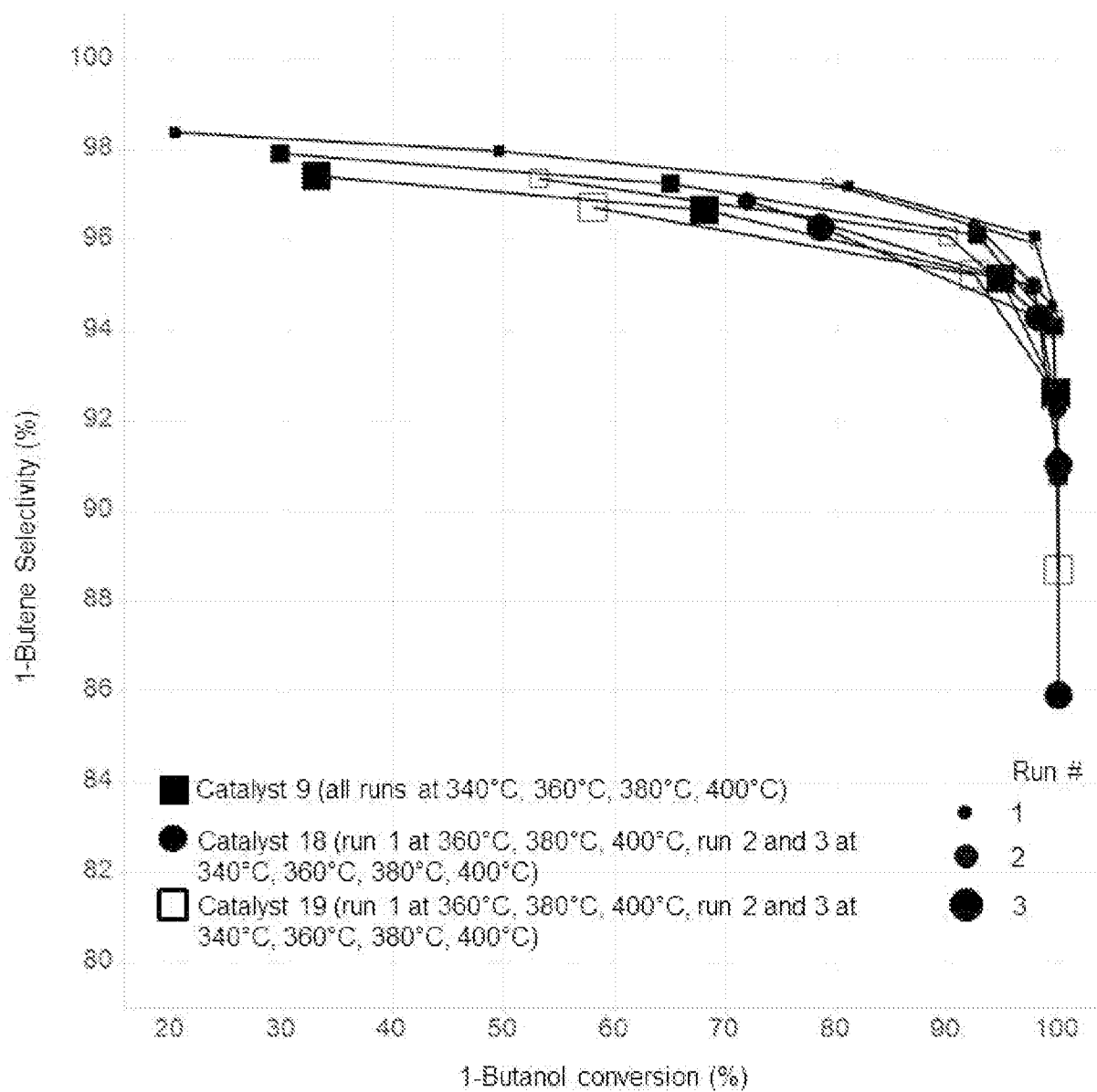
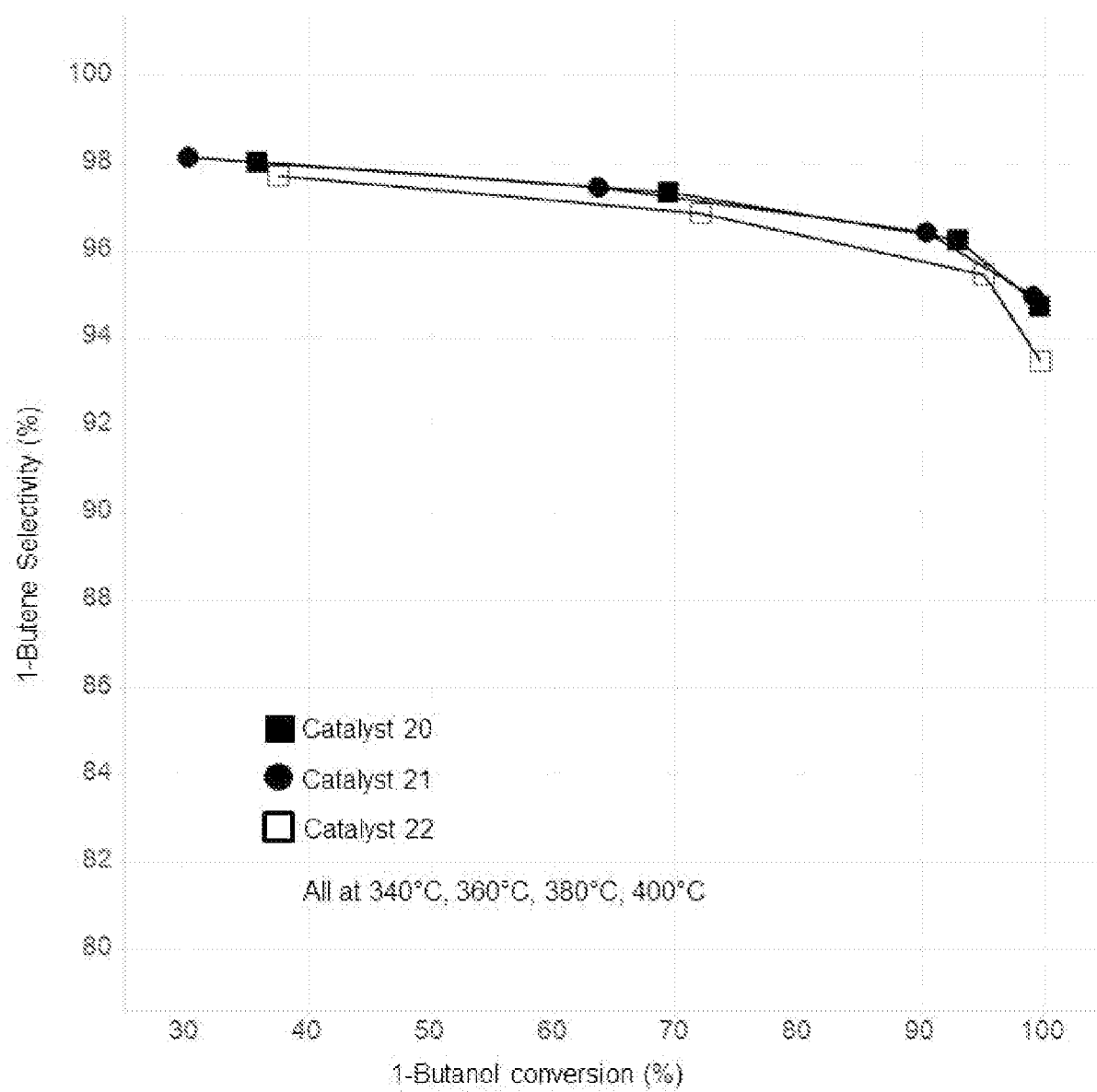


FIG 13



INTERNATIONAL SEARCH REPORT

International application No.

PCT/US15/14943

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - B01J 23/02; C07C 1/24, 11/02 (2015.01)

CPC - B01J 23/02; C07C 1/24, 11/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

-***-Continued Within the Next Supplemental Box-***-

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

PatSeer (US, EP, WO, JP, DE, GB, CN, FR, KR, ES, AU, IN, CA, INPADOC Data); Google Scholar; ProQuest; IP.com; dehydrating, 1-alcohol, 1-alkene, solid, calcium, modified, catalyst, regioselectivity, butane, butane, alumina, organosilane

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2012/0238788 A1 (WRIGHT, ME) 20 September 2012; paragraphs [0018]-[0023], [0032]-[0036]; claims 18, 20	1-46
Y	US 2008/0081909 A1 (DRENT, E et al.) 03 April 2008; paragraph [0061]	1-46
Y	WO 2013/106065 A1 (THE GOVERNMENT OF THE UNITED STATES OF AMERICA AS REPRESENTED BY THE SECRETARY OF THE NAVY) 18 July 2013; paragraphs [0033]-[0034]	27, 29
Y	US 2010/0099936 A1 (SHIN, CH et al.) 22 April 2010; paragraphs [0023], [0031], [0043]-[0044]	32
Y	US 2013/0245218 A1 (MOMAN, A et al.) 19 September 2013; paragraphs [0010]-[0011], [0013], [0037]-[0038]	44

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

17 April 2015 (17.04.2014)

Date of mailing of the international search report

29 APR 2015

Name and mailing address of the ISA/

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents
P.O. Box 1450, Alexandria, Virginia 22313-1450

Facsimile No. 571-273-3201

Authorized officer

Shane Thomas

PCT Helpdesk: 571-272-4300

PCT OSP: 571-272-7774