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Role of Precious Metal Catalysts

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1. Introduction

Precious metal catalysts have been used in many industries, such as refinery, petrochemicals, polymer, chemicals, pharmaceuticals, and environment, For example, automotive industry utilizes large amounts of precious metal catalysts as a part of auto exhaust gas purifier, because of their high activity and selectivity and stability under various reaction conditions. This article, introduces wide variety of applications on precious metal catalysts. We recognize that precious metal catalysts play very important role in our lives. Not only unique properties of precious metals but also advanced preparation technology allow us to use precious metal catalysts for wide range of applications. Principle of precious metal catalyst preparation is introduced, and various industrial applications of precious metal catalysts follow. Applications of precious metal catalysts were disclosed by some literatures. (Rylander 1967) (Bartholomew and Farrauto 2006)

2. Properties of precious metal catalysts

2.1 High activity and selectivity of precious metals in catalysis

Precious metal catalysts consist of highly dispersed nano-scale precious metal particles on supports with high surface area such as carbon, silica, and alumina. The nano scale metal particles easily adsorb hydrogen and oxygen in the atmosphere. The hydrogen or oxygen is very active due to its dissociative adsorption through *d*-electron of out of shell of precious metal atoms. Dissociatively adsorbed hydrogen and oxygen readily react with many substitutes at under the mild conditions. Although commercial plants are operated under heated and pressurized conditions, many hydrogenation and oxidation reactions proceed at room temperature. In such case, the product yield is relatively high because byproducts formation can be minimized under milder reaction conditions. For example, in hydrogenation of di-nitrotoluene to di-aminotoluene, reaction conditions of Ni catalyst requires 5 Mpa, 150 °C, and solvent such as methanol. However, such reaction with Pd/carbon proceeds under only 0.4 Mpa, and 90 °C without solvent. Quantity for Pd/carbon is one tenth of Ni catalyst.

Each precious metal catalyst shows unique characteristics, For instance, olefin hydrogenation can be accomplish with Pd/Al_2O_3 without hydrogenating aromatic bond at mild condition. In case of hydrogenation of phenol, Pd/Al_2O_3 gives produces cyclohexanone. Similarly, Pt/Al_2O_3 is highly selective to cyclohexane formation and Rh or Ru/Al_2O_3 gives cyclohexanol selectively. Furthermore, preparation technology of precious

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metal catalyst has been advanced in recent years based upon nano technology. As a result, energy saving, high productivity, production cost reduction were achieved. Precious catalyst is not almighty, low activity for hydrogenolysis of esters, low selectivity for selective oxidation in gas phase. However, many base metal catalysts changed to precious metal catalysts in history.

2.2 Stability

Precious metals are stable. They do not easily form oxides by oxidation. The oxides of precious metals are, on the other hand, relatively not stable. Precious metals do not easily dissolve in acid or alkaline solution. Thus for example, Pd/carbon can be used for hydrogenation of maleic acid in water which is acidic condition. However Ni catalyst cannot be used for the same reaction condition due to the leaching. Melting point of precious metals is higher than base metals. It corresponds to resistance to migration and sintering of precious metal catalysts. Because of high thermal stability, precious metal catalyst has been used as automotive exhaust gas purification catalysts.

2.3 Advance in catalyst preparation method

2.3.1 Control of metal particle size

Catalytic activity and selectivity largely depend upon metal particle size of metals of the catalysts for the some reactions. It is necessary to make sure if the development of reaction is influenced by metal particles size prior to selection of proper catalyst. (Bond 1968) Generally, hydrogenation and hydrogenolysis prefer to small particles, and oxidation prefers to large metal particles. However, there are many exceptions because of different carrier, preparation method and impurity of the catalysts. Smaller metal particles show high tolerance of sulfur poison because of high surface area for adsorption of sulfur. (Okada 1993) The size of metal can be controlled by selection of metal salts, conditions of impregnation and reduction conditions, including metal concentration and reduction temperature.

2.3.2 Metal distribution of catalysts: Ex. eggshell type

Diffusion of reactant to the catalyst surface controls reaction rate at mild condition. Hydrogen and oxygen penetrate into inside of micro pores in the catalysts. However, large molecules are difficult to diffuse into the smaller pores. BASF Catalysts., (Former Engelhard) developed and commercialized highly active hydrogenolysis catalyst which is eggshell type of Pd/carbon as a slurry type catalyst. The catalyst was applied for hydrogenolysis to produce aspartame. DuPont developed eggshell type of vinyl acetate catalyst. This is fixed-bed type catalyst, which is prepared by impregnation method using Pd and Au salt and SiO_2 carrier. Preparation of vinyl acetate catalysts consist of, 1) impregnation of metal solution, 2) metal fixation by alkaline, 3) keeping long times, 4) treated with reductive agent, 5) washing, 6) drying, 7) impregnate potassium acetate and 8) dry. Pd and Au deposited outer surface layer of the carrier, which is egg-shell type distribution. On the other hand, in case reduction is immediately employed after impregnation, Pd, and Au deposited more inner layer on the carrier. (DuPont 1977) Eggshell type catalysts have been applied for many other reactions, such as hydrogenation of polymer resin and hydrogenolysis of large molecular, and are expected to be used for other reactions as well. However, there is an example that highly dispersion, not eggshell type metal distribution, shows higher activity

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than eggshell type catalysts in the hydrogenation of benzoic acid under severe condition because of no diffusion control. (Grove 2002)

2.3.3 Unreduced catalysts

The reduced catalysts have been supplied commercially. Unreduced catalysts give higher activity for some hydrogenation reactions. Small particles are formed possibly due to some effect by solvent, which is in-situ reduction before the reaction starts. A combination of eggshell and unreduced catalyst also gives higher activity in hydrogenation at mild condition. But, unreduced catalysts cannot be used for dehydrogenation or oxidation. Unreduced $Pd(OH)_2$/carbon, called Pearlman's catalyst, is used widely in pharmaceuticals.

2.3.4 Bi-metalic catalysts

Bi-metalic Pd-Ru/carbon catalyst is highly active for hydrogenation and hydrogenolysis of 1,4-butyndiol. Rh-Ru/carbon shows high activity for hydrogenation of aromatics. (Rylander 1967) Adams catalyst, Pt-Ru shows highly active for aromatic nitrocompounds. (Bond 1964) Pt doped Pd/carbon gives excellent activity for debenzylation. (N.E.Chemcat 2002)

2.3.5 Modified catalysts: Doping

Modification effectively improves activity and selectivity of catalysts. Addition of alkaline or alkaline earth metal, such as Na, K, Ba, to Pd/carbon leads to high activity towards hydrogenation of aromatic nitro compounds because of electron transfer to Pd. Pd-Pt-Fe/carbon catalyst is commercialized for hydrogenation of di-nitrotoluene. Pd modified with Na is applied for selective hydrogenation of mesityl oxide to produce MIBK. Na prevents hydrogenation of carbonyl. Selective hydrodechlorination can be achieved by Pd/carbon modified Ag or Sn. Pd/Al_2O_3 modified with heavy metals, such as Pb, and Bi, is applied for hydrogenation of phenyl acetylene in styrene stream. Modification with heavy metals gives leads to high activity for liquid phase oxidation.

2.3.6 Control of migration and sintering

Pd-Au/SiO_2 is used for production of vinyl acetate by acetoxylation of ethylene. In case of Pd/ SiO_2 without Au addition, sintering is observed, which is caused through palladium acetate formation within a few days. Thus, Au addition prevents sintering of Pd by formation of solid solution with Pd. Fluorocarbon substitute, R-134a is introduced from R-114 by hydrodechlorination. Pd/carbon granular shows short life because of sintering in hydrogen chloride. Addition of small amounts of Re or Au to Pd/carbon gives lengthens catalyst life. (Asahi Glass 1989) High thermally stable catalysts have been developed for automotive exhaust catalysts. Precious metal loading amount was needed to be reduced. The technology by interaction with metal oxide such as ZrO_2, CeO_2, TiO_2, enables lower loading of precious metals.

2.3.7 Control of dissolution: Leaching

Although precious metal is stable for migration and/or dissolution, it occurs in acidic or alkaline condition with oxygen atmosphere. Pt ion is leached out from the catalyst a few %

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at reflux condition. Pd/Al_2O_3 is highly active and selective in hydrogenation of vinyl acetylene to butadiene in order to recover butadiene after extraction of butadiene. However, Pd is dissolved with acetylene by producing acetylide in short time. Pd_4Te/Al_2O_3 was developed to prevent leaching by acetylene, and the catalyst life was significantly improved. Pd_4Te is a chemical compound formed on the alumina carrier. The preparation is, at first Pd/Al_2O_3 is prepared, and secondary $TeCl_4$ is impregnated to Pd/Al_2O_3. Subsequently, the impregnated catalyst is heated at 500 °C. (JSR 1987) Pd is dissolved in acetoxylation of butadiene producing 1,4-butandiol because of acidic condition and presence of oxygen. Pd_4Te/carbon is developed by Mitsubishi Chemical and commercialized. (Mitsubishi Chemical 1973) Small particle of Au, less than 5 nm shows excellent oxidation and esterification activity. Methyl glycolate can be produced by ethylene glycol and methanol in slurry bed, of Au/TiO_2-SiO_2. This catalyst gives high activity, however Au leached out at oxidation condition. Addition of Pd to Au prevents dissolution. (Nippon Shokubai 2004)

3. History/background of precious metal catalyst development

3.1 Sulfuric acid

Industrial revolution started in England in 19th century. Demand of sulfuric acid as basic chemicals, especially producing sodium carbonate for Leblanc process, was increasing for the purpose of bleaching cotton cloth. The first catalytic process is oxidation of sulfur dioxide by Pt/asbestos which was developed by P. Philips in England in 1831. Lead chamber process replaced by catalytic process. That is the beginning of industrial catalysts. Ammonium sulfate for fertilizer production started using sulfuric acid and ammonia from coal distillation plant in the late of 1830s. Production of explosive cellulose nitrate from niter using sulfuric acid has started in Switzer-land in 1845. Novel developed dynamite which is nitro glycerol impregnated clay in 1866. Pt/asbestos had been used until finding V_2O_5 catalyst by BASF in 1915.

$$SO_2 + 1/2\,O_2 \rightarrow SO_3$$

3.2 Nitric acid

W. Ostwald found production of nitric acid by oxidation of ammonia with Pt-plate, and the nitric acid plant was commercialized in 1908. He received Novel prize in 1909. Nitric acid is very important to produce explosives. Ammonia was produced in coal furnace at the time. Commercialization of ammonia synthesis using nitrogen in the air by Haber and Boch was in 1913. Nitric acid was produced by CuO-MnO_2 or Fe_2O_3-Bi_2O_3 once. But since base metal catalysts show lower activity, Pt-Rh-gauze has been used now. Vaporized Pt is collected by Pd at downstream.

$$NH_3 + 5/4\,O_2 \rightarrow NO + 3/2\,H_2O$$

$$NO + 1/2\,O_2 \Leftrightarrow NO_2$$

$$2\,NO_2 \Leftrightarrow N_2O_4$$

$$3\,NO_2 + H_2O \Leftrightarrow 2\,HNO_3 + NO$$

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3.3 Acetic acid

Cellulose nitrate as fiber was replaced by cellulose acetate for flammability issue. Acetic acid, raw material of cellulose acetate was produced by oxidation of acetaldehyde which was produced hydration of acetylene by $HgSO_4$ in coal times. Coming petroleum time around after 1960s, acetaldehyde has started to be produced by oxidation of ethylene. The process was developed by Hoechst-Waker which uses $PdCl_2$ and $CuCl_2$ in homogeneous reaction.

$$CH_2{=}CH_2 + 1/2\,O_2 \rightarrow CH_3CHO \quad (PdCl_2\text{-}CuCl_2)$$

$$CH_3CHO + 1/2\,O_2 \rightarrow CH_3COOH \quad (Mn(AcO)_2$$

Most of acetic acid is produced by carbonylation of methanol in the world, which was developed by BP (Former Monsant) using Rh carbonyl complex. The product yield is more than 99%. Consumption of Rh is less than 1ppm.

$$CH_3OH + CO \rightarrow CH_3COOH$$

New development, called CATIVA process by BP, uses Ir and Ru carbonyl complex. The precursors are IrI_3 and RuI_3. Ru complex works as co-catalyst for Ir complex which consumption is said one tenth of Rh complex. In addition, Showa Denko in Japan developed direct acetic acid process from ethylene by gas phase Wacker process. The catalyst is Pd/ $H_4SiW_{12}O_{40}$-SiO_2. The process was commercialized once. (Showa Denko 1994)

$$C_2H_4 + H_2O + O_2 \rightarrow CH_3COOH + H_2O$$

Chiyoda Corporation has developed immobilized Rh complex with resin. It was made as fixed bed process producing acetic acid by carbonylation of methanol. The process was licensed to China. (Chiyoda Corporation 1993)

4. Refinery applications

4.1 Reforming

Due to increasing gasoline demand, reforming process, which produces gasoline with high octane number, was developed by Shell in 1949. The reactions are dehydrogenation of naphthene and isomerization of paraffin. The UOP reforming process is called "Platformer" because the catalyst constituent is Pt. At first, the catalyst life was short due to carbon deposition. In 1967, Chevron developed Pt-Re/Al_2O_3 bi-metalic catalyst which can be used almost 10 years with several times of regeneration. After that, continuous cyclic regeneration (CCR) process was developed by UOP and IFP. This process can produce gasoline with higher octane number due to higher aromatics yield under much severe condition or under low pressure. The catalyst is spherical Pt-Sn/Al_2O_3. More than three hundred plants including semi-regeneration process are running in the world.

4.2 Aromatization

To meet the demand of aromatics for in petrochemical industries, aromatization of n-hexane process was developed by Chevron. The catalyst for this application is Pt-F/L-zeolite which was improved by Idemitsu Kosan Co., Several plants in the world have been applying this technology.

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4.3 Removing aromatics

Removing aromatics from diesel fuel is necessary for environmental protection of atmosphere for more severe environmental protection. Many hydrotreating processes are developed, and consist of two series reactors of reactors. First reactor contains Ni-Mo/Al_2O_3 or Co-Mo /Al_2O_3 and the second contains Pt/Al_2O_3 or Pt/SiO_2-Al_2O_3. Bi-metalic catalyst was also developed because hydrogenation by Ni needs high temperature which occurs dehydrogenation to minimize the negative influence by sulfur. Pt-Pd/SiO_2-Al_2O_3 shows high activity even containing several tens ppm of sulfur. (Vaarkamp 2000)

4.4 Isomerization

Isomerization of butane and pentane is difficult by SiO_2-Al_2O_3. Bi-functional catalyst, Pt/SiO_2-Al_2O_3 with halogen can progress isomerization because the reaction occurs through dehydrogenation and hydrogenation by Pt and isomerization by acid. Jet fuel production, for example Hysomer process developed by Shell uses Pt/zeolite under hydrogen pressure. Japan Energy developed Pt-SiO_2/ZrO_2-Al_2O_3 for isomerization of naphtha. Small content of sulfur in naphtha deactivate this catalyst. Hybrid catalyst, consisting of Pt/SiO_2/ZrO_2-Al_2O_3 with addition of Pd/Al_2O_3 was developed to improve sulfur tolerance. The mechanism of sulfur tolerance is decomposition of sulfur compound by Pd is explained by Watanabe et al. (Watanabe 2005)

4.5 Hydrocracking

Gas oil or heavy gas oil is hydrocracked to produce gasoline. The typical cracking catalysts are Co-Mo/Al_2O_3 or Ni-W/SiO_2 or zeolite. Unicracking process licensed by UOP uses Pd/Y-zeolite producing jet fuel.

4.6 FCC additives

Fluid Catalytic Cracking (FCC) processes produce gasoline or diesel fuel from oil from heavier oil. FCC processes are operated in fluid bed with continuous regeneration processes for removal of deposited carbon. The size of catalyst is 70～100 μm ϕ composed SiO_2-Al_2O_3 and USY zeolite. Some additives improve stability and propylene yield. Pt/Al_2O_3 powder is also used to accelerate removal of deposited carbon.

5. Application in petrochemical

5.1 Hydropurification

Ethylene and propylene are important raw materials for many chemicals and polymers. Ethylene and propylene contain acetylene and dienes as impurities from cracker. Acetylenes and dienes are selectively hydrogenated to ethylene and propylene respectively with 0.02-0.2% Pd/Al_2O_3 in gas phase. These catalysts life is more than several years with carbon removal regeneration. Purification of butadiene in presence of 1-butene and 2-butene is employed under hydrogen by Pd/Al_2O_3 in liquid phase. Unsaturated C_4 and C_5 molecules are recycled to ethylene cracker after hydrogenation to increase ethylene yield. Small amount of phenyl acetylene as an impurity is removed as polystyrene applying by hydrogenation by Pd/Al_2O_3 or modified Pd/Al_2O_3. (Table-1)

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Stream	Removal	Catalysts	Phase	Remarks
Ethylene	Acetylene	0.01-0.02%Pd/Al_2O_3	Gas	
Propylene	Acetylene	0.1-0.2%Pd/SiO_2	Gas	
Butadiene	Vinyl acetylene	0.2%Pd-Te/Al_2O_3	Liquid	
1-Butene	Butadiene	0.5%Pd/Al_2O_3	Liquid	Addition of CO
2-Butene	Butadiene	0.1%Pd/Al_2O_3	Liquid	
C_4, C_5	Butene	0.3%Pd/Al_2O_3	Liquid	Return to cracker
Styrene	Phenyl acetylene	0.3%Pd/Al_2O_3	Gas	

Table 1. Hydropurification in ethylene plant

5.2 Hydrogenation of pyrolysis gasoline

Byproducts in liquid phase of ethylene cracker are aromatics and unsaturated compounds. In order to blend into gasoline, di-olefins are selectively hydrogenated to mono-olefin by Pd/Al_2O_3. Subsequent to the first reactor, Ni-Co/Al_2O_3 is utilized to remove mono olefins, sulfur, and nitrogen prior to production of benzene, toluene, and xylene before solvent extraction. Catalyst life of Pd/Al_2O_3 is generally several years with several times of regenerations. Every ethylene cracker equips this hydrogenation process.

5.3 Propylene

Propylene demand is increasing due to strong polypropylene market. Dehydrogenation of propane with Pt/Al_2O_3 is one of commercialized processes. Several plants apply this process.

$$CH_3CH_2CH_3 \rightarrow CH_2{=}CHCH_3 + H_2$$

5.4 Cyclohexane

Highly pure cyclohexane is intermediate of Nylon. It is produced by hydrogenation of benzene with Ni or Pt/Al_2O_3.

5.5 Oxo alcohol

2-Ethylhexanol, a raw material of di-octylphthalate (DOP), is used for vinyl chloride resin plasticizer. 2-Ethylhexanol is derived from n-butyl aldehyde is produced by hydroformylation of propylene with hydrogen and carbon monoxide by Rh complex catalyst. $RhH(CO)(PPh_3)_3$ with tri-phenylphosphine produces *n* and *i* butylaldehyde. Rh complex generates more than 10 of *n*/*i* ratio. (Table-2) In the same reaction, Co complex shows low *n*/*i* ratio. n-Butylaldehyde is separated by distillation from the boiling reactor. 2-Ethylhexanol is produced after condensation with NaOH and subsequent hydrogenation by Ni. (Fig. 1)

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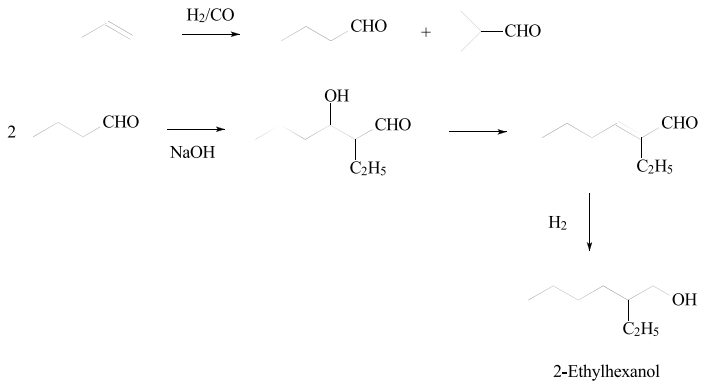

Fig. 1. 2-Ethylhexanol from propylene by hydroformylation

Catalyst	$RhH(CO)(PPh_3)_3$
Temp. °C	60～ 120
Pressure atm	1 ～50
Catalyst % Metal/Olefin	0.01～0.1
n / *i*	10 / 1
Conversion of Propylene %	30

Table 2. Hydroformylation by $RhH(CO)(PPh_3)_3$

6. Bulk chemicals

6.1 Ammonia

Fe-K catalysts have been used for last hundred years under various reaction conditions since Habar-Boch developed the catalyst. In addition, Ru-Cs/carbon graphite catalyst was developed by BP and Kellogge. (Czuppon 1993)

$$N_2 + 3/2\,H_2 \rightarrow 2\,NH_3$$

The process called KAAP process is commercialized. Two large plants are under operation in Trinidad and Tobago. Adsorption of nitrogen becomes weak due to electron transfer from Cs to Ru and Ru and from Ru to carbon graphite. The catalyst support, graphite is firstly, produced by thermal treatment of active carbon at 1,500 °C in argon, and in air at around 400 °C followed by subsequent thermal treatment at 1,700 °C in argon. Remaining catalyst preparation takes place as, impregnation of $RuCl_3$ solution to the graphite, reduction with hydrogen at 450 °C, drying, impregnation of Cs nitrate solution, and drying. (BP 1984)

6.2 Hydrogen peroxide

Hydrogen peroxide, H_2O_2, has widely been used as bleaching and oxidation agent for food, textile and paper. H_2O_2 has been producing by oxidation of hydroxyl alkyl anthraquinone after hydrogenation of alkyl anthraquinone by Pd. Small catalyst particles of Pd/Al_2O_3 or Pd/SiO_2 is generally used in slurry phase, and its alkaline modification prevents ring hydrogenation. Kemira process uses Pd black. Some fixed bed processes are commercialized.

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These catalysts form smooth surface because decomposition of hydrogen peroxide occurs by leaked fine catalyst particles after separation. Carbon monoxide in hydrogen stream is removed to less than 1 ppm by methanation with Ni or Ru/Al_2O_3 since small quantity of carbon monoxide poisons Pd catalyst at lower reaction temperature, e.g. 40 °C. (Fig. 2)

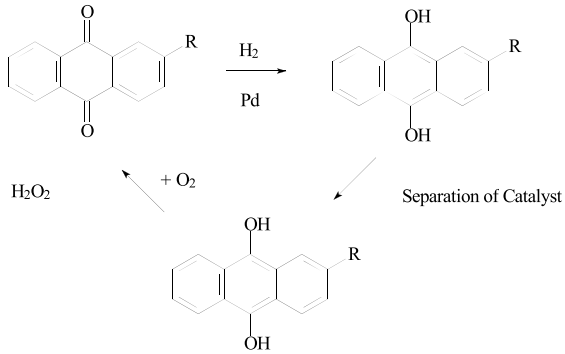

Fig. 2. Production of hydrogen peroxide by anthraquinone process

Direct hydrogen peroxide production, which is the process synthesize H_2O_2 from hydrogen and oxygen was developed by DuPont and commercialized several plants of paper plants in North America. This process uses Pd/carbon. HBr is used stabilizer of peroxide.

$$H_2 + O_2 \rightarrow H_2O_2$$

Head water has developed direct process at out of explosion range, e.g. H_2 3vol%, O_2 20vol% N_2 77vol% in H_2SO_4 solution with addition of small amount of NaBr and Pd-Pt/carbon black catalyst. The performance of this process is reported as 33% of the overall hydrogen conversion, 100% H_2O_2 selectivity with respect to hydrogen and 4.8% of hydrogen peroxide in a final liquid product at 45 °C and 10 MPa. (Headwater 2005)

6.3 Phenol

Phenol has been used as a raw material of phenol resin, nylon and others. Most phenol process uses cumene process in the world. Cumene is produced by alkylation of benzene with propylene by acid catalyst, such as H_3PO_4/Al_2O_3 or zeolite. Subsequently cumene hydroperoxide is produced by oxidation of cumene and phenol and acetone are converted from cumene hydroperoxide by sulfuric acid. In the step of phenol production, α-methyl styrene produced as byproducts is hydrogenated by Pd/Al_2O_3. Produced cumene by hydrogenation of α-methyl styrene is recycled to the feed. When α-methyl styrene demand increases, cumene hydroperoxide is hydrogenated to cumyl alcohol by Pd/Al_2O_3 and returned to stream to produce α-methylstyren more. Off gas treatment, such as oxidation of cumene, takes place by Pt/honeycomb catalyst at 350°C.

6.4 Aniline

Aniline has been produced by amination of phenol using Lewis acid such as Al_2O_3 and hydrogenation of nitrobenzene by Ni or Pd/carbon in slurry phase. Pd/carbon or modified Pd/carbon by Pt or Fe is used mainly for highly activity.

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6.5 Chlorine

Hydrogen chloride is produced as byproducts in TDI process, polycarbonate and other plants. It has to be neutralized by NaOH before disposal. Oxidation process for Cl_2 production was developed using acid resistant RuO_2/TiO_2-αAl_2O_3 by Sumitomo Chemical and was commercialized 3 plants. The commercialized Sumitomo fixed bed process is compact compare to Mitsui fluid bed process using Cr catalyst. In the preparation of RuO_2/TiO_2-αAl_2O_3, the carrier is firstly prepared by mixing α-Al_2O_3 and TiO_2 (100%rutile) powder followed by extrusion and calcination at 800 °C, Ru salt is impregnated on the prepared TiO_2-αAl_2O_3, and impregnated carrier is calcined. (Sumitomo Chemical 2004) Commercialized 2 plants are under operation with TDI plant and polycarbonate plant.

$$2\,HCl + 1/2\,O_2 \rightarrow Cl_2 + H_2O$$

6.6 1,4-butanediol

1,4-butanediol(1,4-BG) is used for production of polyester, polyurethane and others. Poly butylenes terephthalate (PBT) is used as engineering plastics for automotive and electronics. PBT is used as performance textile for sport wears and swimsuits, for instance, known spandex. 1,4-BG can be synthesized from butadiene by acetoxylation. The process is developed and commercialized by Mitsubishi Chemical. The catalyst is bi-metalic catalyst which is resistant to acetic acid. The first process was consisted of trickle bed reactor with Pd_4Te/carbon granular. The bi-metalic catalyst was prepared by, for example, charging active carbon granular into mixed solution of $PdCl_2$ and TeO_2 followed by drying and heating with methanol at 450 °C.(Mitsubishi Chemical 1973) (Tanabe 1981) (Ohno 2000)

Improved process use Pd_4Te/SiO_2 in fixed bed in up flow mode.

$$H_2C{=}CHCH{=}CH_2 + 2AcOH + 1/2O_2 \rightarrow AcO\text{-}CH_2CH{=}CHCH_2\text{-}OAc + H_2O$$

Di-acetoxybutene is hydrogenated to di-acetoxybutane by Pd/carbon and hydrolysis to 1,4-BG by acid ion exchange resin.

Dairen Chemical in Taiwan commercialized homogeneous process, which produces hydroxyfuran by hydroformylation with Rh hydride complex. Hydrogenation to 1,4-BG is conducted by Ni catalyst.(Fig.3)

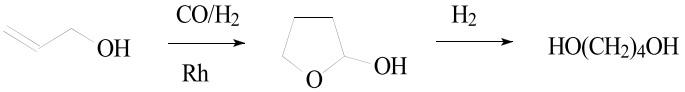

Fig. 3. Hydrofomylation of allylalcohol

6.7 MIBK

MIBK is widely used as a solvent. At first, diacetone alcohol is produced by condensation of acetone with $Ba(OH)_2$. And then, diacetone alcohol is dehydrated to mesityl oxide at second step. At last, mesityl oxide is hydrogenated to MIBK by Cu catalyst or Pd/carbon. Direct synthesis process of MIBK, Pd/acid ion exchange resin catalyst. The condensation and dehydration are with ion-exchange resin. Hydrogenation is done by Pd catalyst. The catalyst is prepared ion exchange of Pd salt and subsequently reduced by reductive agent. (Fig.4)

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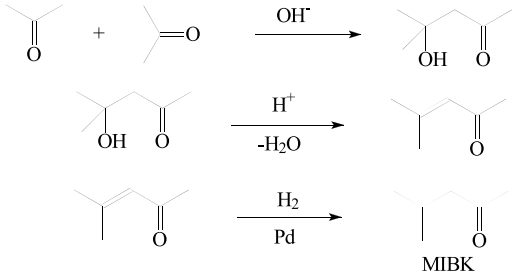

Fig. 4. MIBK production from acetone

6.8 Oxalic acid

Oxalic acid is used for hydration of starch, and it is a raw material of fertilizer and others. Di-methyl oxalate (DMO), an intermediate of oxalic acid, is synthesized from methanol and carbon monoxide. Methyl nitrate is produced at first under the mild condition without catalyst.

$$2\,CH_3OH + NO + 1/2\,O_2 \rightarrow 2\,CH_3ONO + H_2O$$

Carbon monoxide and methyl nitrate react to form DMO and NO by Pd/α-Al_2O_3. DMO is hydrated to oxalic acid. Produced NO is recycled in the system. For example, a reaction condition is at 0.2Mpa•G, and 110 ℃. (Yamamoto 2010) (Fig.5)

$$2\,CO + 2\,CH_3ONO \rightarrow (COOCH_3)_2 + 2\,NO$$

$$(COOCH_3)_2 + 4\,H_2O \rightarrow (COOCH_3)_2 \cdot 2\,H_2O + 2\,CH_3OH$$

$$\underline{2\,CH_3OH + 2\,NO + 1/2\,O_2 \rightarrow 2\,CH_3ONO + H_2O}$$

$$2\,CO + 3\,H_2O + 1/2\,O_2 \rightarrow (COOH)_2 \cdot 2\,H_2O$$

Fig. 5. Coupling of CO by methyl nitrate

Ethylene glycol (EG) can be produced from di-methyl oxalate by hydrogenolysis with Cu/SiO_2, e.g. at 3Mpa, 200 °C. China is expecting to produce EG form di-methyl oxalate using carbon monoxide which is originated from coal.

$$(COOCH_3)_2 + 4\,H_2 \rightarrow HOCH_2CH_2OH + 2\,CH_3OH$$

6.9 Di-methyl carbonate (DMC)

Di-methyl carbonate is a raw material of resin and others. DMC is expected to replace phosgene in production of polycarbonate and isocyanate. China started to use it diesel fuel additives. DMC is produced from methanol and carbon monoxide. Ube Ind. in Japan developed and commercialized a process applying oxy carbonylation of methanol by $PdCl_2$-$CuCl_2$/Al_2O_3 in gas phase. (Fig.6)

$$2\,CH_3OH + 2\,NO + 1/2\,O_2 \rightarrow 2\,CH_3ONO + H_2O$$

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$$CO + 2\,CH_3ONO \rightarrow (CH_3O)_2CO + 2\,NO$$

$$2\,CH_3OH + CO + 1/2\,O_2 \rightarrow (CH_3O)_2CO + H_2O$$

Fig. 6. Dimethyl carbonate by oxy carbonylation of methanol

6.10 γ -butyrolactone

γ-butyrolactone (GBL) used as a resin solvent and an intermediate of N-methylpyrrolidone can be produced from maleic anhydride. Maleic anhydride is hydrogenated to GBL by $Ru(AcAc)_3$ with trioctylphosphine in tetraglyme in homogeneous reaction. This process is commercialized by Mitsubishi Chemical. Reaction rate increases using succinic acid anhydride after hydrogenation by Pd/Al_2O_3. Conversion of succinic acid anhydride is 79.2%, Selectivity of GBL is almost 100% at 200 °C, 1.0MPa, 14 h.(Fig.7)

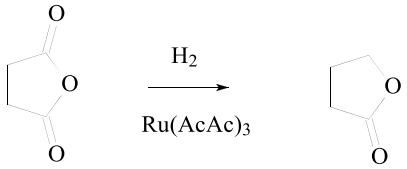


Fig. 7. Hydrogenation of succinic acid anhydride

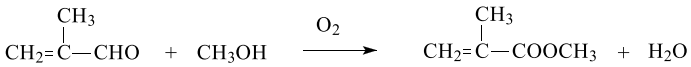
7. Polymer

7.1 Vinyl chloride

Poly vinyl chloride is used very widely such as pipe, sheet, film, housing material for stability. Vinyl chloride monomer (VCM) is produced by thermal decomposition of ethylene dichloride (EDC) which is produced by oxychlorination with $CuCl_2/Al_2O_3$. After decomposition of EDC, 2,000-4,000 ppm of acetylene is produced in HCl stream. Acetylene in hydrogen chloride atmospher is removed by hydrogenation with acid resistant catalyst which is Pd/α-Al2O3 or Pd/SiC in order to reduce chlorine consumption in recycled oxychlorination process. (Kaneka 1987)

7.2 Methyl methacrylate

Methylmethacrylate (MMA) demand has been increasing in Asia. It is a transparent polymer and is used as glass substitute. A few routes are known to produce MMA. Isobutene process is developed in Japan. MMA is produced by esterification of methacryl acid which is introduced two step oxidation through methacroleine from isobutene. Asahi Kasei Chemicals commercialized direct process from methacroleine and methanol by $Pd\text{-}Pb/SiO_2$ using slurry bed. Oxygen is fed from the bottom of the reactor as very fine bubbles. The catalyst is Pd_3Pb/SiO_2. (Asahi Kasei Chemicals 1996) The size of silica carrier containing alumina and magnesia is about 60μm. The catalyst is prepared by starting mixture of HCl solution of $PdCl_2$ and $Pb(NO_3)$, immediately the metal solution mixture is impregnated 1hr and then reduced by hydrazine.



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MMA processes from ethylene are summarized as Fig.8. Lucite commercialized carbomethoxylation by Pd phosphine complex. BASF process uses hydroformylation by Rh complex. (Fig.8)

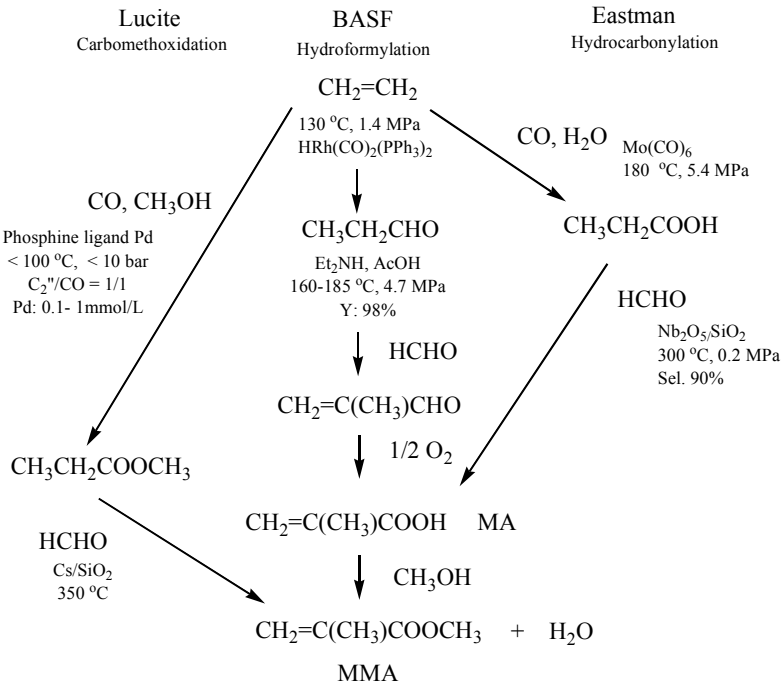

Fig. 8. MMA synthesis routs from ethylene

7.3 Toluene di-isocyanate

Toluene di-isocyanate (TDI) is used for polyurethane. TDI demand has been increasing due to the applications such as cushion of bed and sheet of car. TDI is produced from di-aminotoluene and phosgene. Di-aminotoluene is produced by hydrogenation of di-nitrotoluene with Pd/carbon or Pd-Pt-Fe/carbon in slurry bed.

7.4 Hydrogenated methaxylene diamine

Methaxylene diamine (MXDA) is used for heat resistant polyamide polymer. It is produced by ammoxidation of o-xylene with Fe catalyst. By Ru/Al_2O_3, a part of MXDA is hydrogenated to 1,3-di-amino cyclohexane which is highly heat resistant polymer material.

7.5 Cyclohexane di-methanol (CHDM)

Cyclohexane di-methyl is used heat resistant polyester resin. It is produced by hydrogenation of di-methylterephthalate. Pd or Ru/Al_2O_3 is used for hydrogenation of di-methyltrephthalate at first step, hydrogenolysis of cyclohexane di-methyl carboxylate is done by CuCrOx catalyst. (Fig.9)

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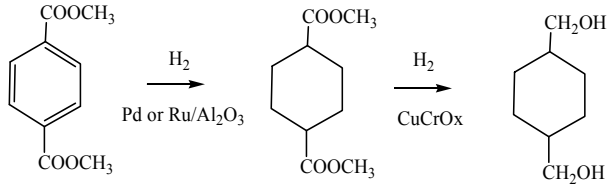

Fig. 9. DME synthesis from di-methyl trephthalate

7.6 Hydrogenated polymer

Hydrogenation of polymer is important to increase solubility to other polymer and transparency, which is applied such as adhesive for dipper. Hydrogenation of polybutene is conducted by Pd/Al_2O_3 in fixed bed. C_5, C_9 and terpentine resin are hydrogenated by Pd/Al_2O_3 and Pt/Al_2O_3. Hydroxypolybutadiene rubber is produced by hydrogenation with Ru/carbon prevention of hydrocracking of hydroxyl group. Nitril rubber and norbornene resin are hydrogenated with Rh complex in homogeneous phase. (Bayer 1980) Separation of catalyst from the system is very difficult. If the catalyst is very highly active, the loading quantity can be very small. Consequently, removal of catalyst is not necessary. (Shinohara 1997) It suggests that reaction system does not need filtration system like polymerization of polyethylene or polypropylene. Many resins are hydrogenated by precious metal catalysts. (Table-3)

Reactants	Catalysts	Reactor bed	Remarks
Polybutene	Pd/Al_2O_3	Fixed	
C_5 Petroleum resin	Pd/Al_2O_3	Fixed	
C_9 Petroleum resin	Pt/Al_2O_3	Fixed	
Hydroxy Polybutadiene Rubber	Ru/carbon	Slurry	
Nitril butadiene rubber	Pd/SiO_2	Slurry	
Norbornene resin	Ru complex	Homogeneous	
Terpentine resin	Pd/Al_2O_3	Fixed	Natural resin
Rosin	Pd/carbon	Fixed, Slurry	Hydrogenated rosin

Table 3. Commercialized hydrogenated resin

8. Synthetic fiber

8.1 Nylon

8.1.1 Inventa process

NO is produced by oxidation of ammonia with Pt-Rh gauze. NO is used for producing hydroxylamine which is reacted with cyclohexanone. NO is reduced by modified Pt carbon

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catalyst or Pt/carbon graphite in sulfuric acid solution at 40-60 °C. Anone oxime is converted to ε-caprolactam by Beckman rearrangement reaction. Cycrohexanone is produced by oxidation of cyclohexane or hydrogenation of phenol by Pd/carbon or Pd/Al_2O_3 in fixed bed reactor. (Fig.10)

$$4\,NH_3 + 5O_2 \rightarrow 4\,NO + 6\,H_2O$$

$$2\,NO + 3\,H_2 + H_2SO_4 \rightarrow (NH_2OH)_2 \cdot H_2SO_4$$

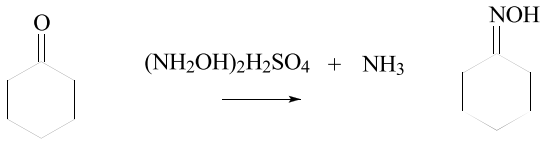

Fig. 10. Nylon-6 production route by Inventa process

8.1.2 DSM process

Ammonium nitrate is reduced by Pd/carbon or Pd-Pt/carbon in DSM process. Selectivity of Pd/carbon is higher than Pt/carbon. Mixed Pd/carbon and Pd-Pt/carbon gives highly activity and selectivity in H_3PO_4 aqueous solution with addition of GeO_2. Reaction temperature is 40-70 °C. The process is continuous slurry bed reactor installed swing filter system. Selectivity is effectively increased by small amount of halogen ion. (Fig.11)

$$H_3PO_4 \rightarrow H^+ + H_2PO_4^-$$

$$NO_3^- + 2\,H^+ + 3H_2 \rightarrow NH_3OH^+ + 2H_2O$$

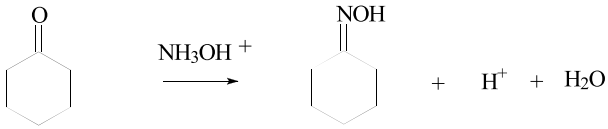

Fig. 11. Cyclohexanone oxime synthesis by DSM process

8.1.3 Snia viscosa process

Firstly toluene is oxidized to benzoic acid by metal acetate such as cobalt acetate in the aqueous phase. Subsequently, benzoic acid is hydrogenated to cyclohexane carboxylic acid by Pd/carbon in slurry bed. Hydrogenation condition is 170 °C, 1.0-1.7 Mpa. The production yield appears to be almost 100%. Cyclohexane carboxylic acid is reacted with $NOHSO_4$ and produces ε-caprolactam sulfate. (Fig.12)

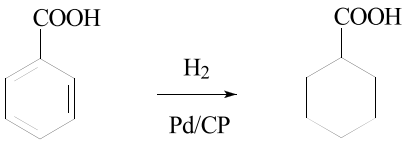

Fig. 12. Hydrogenation of benzoic acid

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8.1.4 Asahi Kasei process

Asahi Kasei Chemical commercialized selective hydrogenation of benzene to cyclohexene. A 60,000Mton/y plant started to operate in 1990. Selective hydrogenation of benzene to cyclohexene takes place in water with Ru black catalyst. Cyclohexene is hydrated to cyclohexanol by high silica containing MFI. The process was licensed to China. (Fig.13)

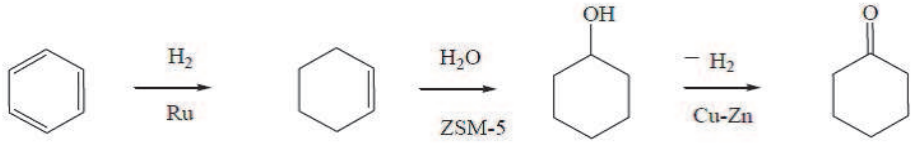

Fig. 13. Cyclohexanone production route by selective hydrogenation of benzene

8.1.5 Nylon 12

Nylon 12 is used as a hot melt adhesive. One of the Nylon 12 processes is hydrogenation of nitril compound. An intermediate of nylon-12, 12-Aminododecane acid is produced by hydrogenation of 11-cyanoundecane acid with Ru/SiC at 110-130 °C and 3.5 MPa, in mixed solvent of NH_4OH and n-propanol. Conv. 100%, Sel. 99.6%, yield of secondary amine is less than 0.4%. 11-cyanoundecane acid is produced by ammoxidation of cyclohexanone. (Ube Ind. 1976) (Fig.14)

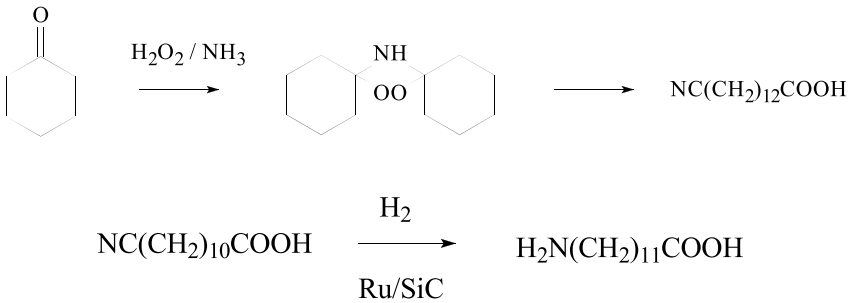

Fig. 14. Cyano undecane acid from cyclohexanone

8.2 Polyester

Most textile fiber has become polyester. Polyethylene terephthalate is produced ethylene glycol and terephthalic acid. Polyethylene terephthalate is very widely used to make bottles, for examples PET. Terephthalic acid is produced by oxidation of *p*-xylene introduced by isomerization of mixed xylene with ZSM-5 catalyst. Pt/ZSM-5 is used to convert ethyl benzene to *p*-xylene in hydrogen atmosphere. 4-carboxybenzaldehyde (4-CBA) is produced as a byproduct in oxidation of *p*-xylene by Co and Mn acetate in acetic acid solution. Producing pure terephthalic acid, 4-CBA is needed to remove to less than 25 ppm by hydrogenolysis by Pd/carbon granular in water solvent under severe condition. (Fig.15)

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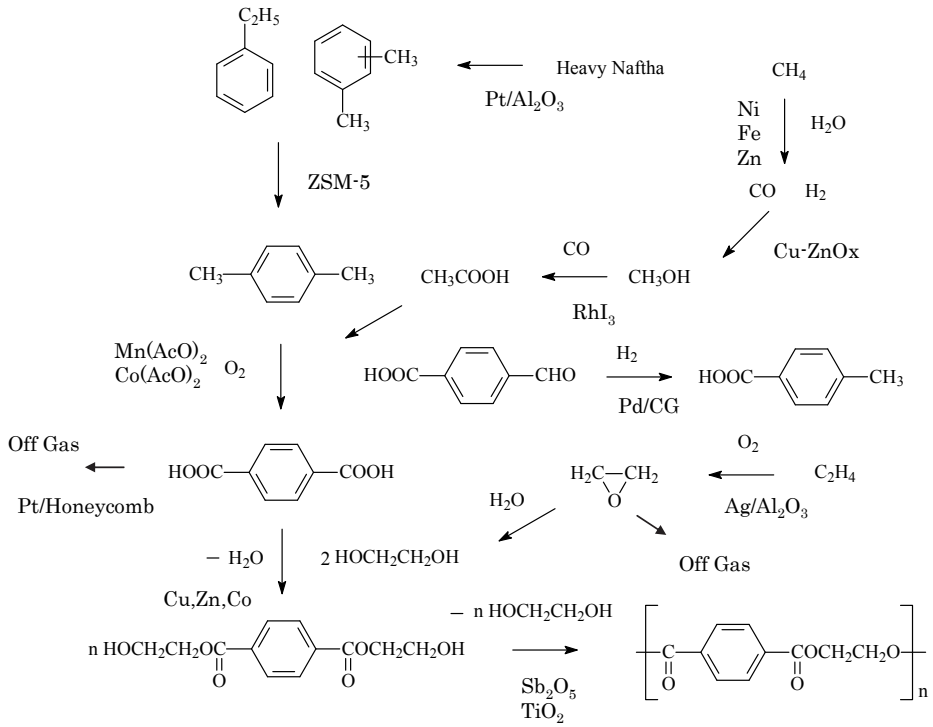

Fig. 15. Polyester production routs

8.3 Vinyl acetate

Vinylacetate is used for textile, paint, adhesive and others. Acetoxylation of ethylene in gas phase is commercialized developed by Bayer and ND (Millenium) with Pd-Au/SiO_2 or Pd-Au/alumina by multi tube reactor. Allylalcohol also commercialized by acetoxylation of propylene with Pd-Cu/SiO_2.

9. Gas production and purification

9.1 City gas

Producing city gas from coke oven gas contains hydrogen and carbon monoxide. Methanation is applied to produce methane by Ru/Al_2O_3 after removal of tar and sulfur compounds.

$$CO + 3\,H_2 \rightarrow CH_4 + H_2O$$

9.2 Purification of hydrogen

Removal of oxygen in hydrogen is proceeds with Pd/Al_2O_3. It is known as DEOXO process, and the catalyst was developed former Engelhard Ind., The technology has been used widely.

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The catalyst is applied for purification of He, Ar with addition of hydrogen. CO causes catalyst poisoning for hydrogenation. Thus, methanation using Ru/Al_2O_3 plays important role to converts CO to non-poisoning CH_4. Selective oxidation of CO in hydrogen process is also known. It called "Select oxo process" using Pt/Al_2O_3 modified with Co or Fe developed by former Engelhard. The principle is originated from the facile adsorption of CO on Pt compared to hydrogen. Oxygen addition leads to reaction with CO on the catalyst surface. The catalyst is used for purification of hydrogen for ammonia synthesis and fuel cell.

9.3 Purification of nitrogen

Pure nitrogen is essential in fabrication of semiconductor in atmospheric gas. Pure nitrogen gas is generally produced in cryogenic system from the air. But, small content of CO is difficult to remove from N_2 in cryogenic system. Pt or Pd/Al_2O_3 can oxidize CO to CO_2 at 100-150℃ before cryogenic system.

9.4 Carbon dioxide

Carbon dioxide is used for as a coolant and for carbonated drinks. Quality of food grade CO_2 is regulated by government. Hydrocarbons and CO and others are main impurities in off gas of CO_2 from oxidation plant such as ethylene oxide plant. CO_2 is purified to food grade by addition of small amount of oxygen by Pt and Pd/Al_2O_3.

9.5 Reductive gas

Hydrogen gas is produced by decomposition of NH_3, a mixed catalyst of Pt/Al_2O_3 and Rh/Al_2O_3 is used at 700 °C. Transfer of H_2 is difficult, however it is feasible to transport as liquid NH_3.

Reductive gas for annealing furnace is produced by combustion of butane with $Rh/\alpha\text{-}Al_2O_3$ at 800 °C.

10. Specialty chemicals

10.1 Dyestuff and organic pigment

Many dyestuffs are produced by hydrogenation of aromatic nitro compounds. Halo nitro compounds are hydrogenated to halo amino compound by Pt/carbon or sulfur modified Pt/carbon. Monochloro acetic acid using as a raw material of dyestuff is produced selective hydrodehalogenation from di-chlrolo and tri-chloro acetic acid with Pd/carbon pellet in fixed bed reactor. The di- and tri-chloro acetic acid are produced by chlorination of acetic acid. *p*-Methoxy aniline, which is an intermediate of printer ink, is produced from nitrobenzene by Bamberger rearrangement reaction using Pt/carbon in methanol solvent.

Intermediate of an important yellow organic pigment is di-chlorohydrazone (DCH). It is produced from o-chlorobenzene using Pt/carbon.

10.2 Rosin

Rosin is gathered or extracted from pine tree. Disproportionated rosin is used as an emulsion polymerization agent for butadiene rubber. Disproportionation of rosin is

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conducted with Pd/carbon without hydrogen. Hydrogenated rosin is very stable. It is used as pavement paint and used as one of the ingredients of chewing gum. Hydrogenated rosin is produced by hydrogenation using Pd/carbon at severe condition.

10.3 Antioxidant

Antioxidant for rubbers has been produced by reductive alkylation of di-phenyl amine with MIBK. Pt/carbon or sulfur modified Pt/carbon has been used for reductive alkylation.

10.4 Liquid crystal

Liquid crystal is produced by Suzuki coupling reaction. Suzuki coupling reaction is coupling halo compound and boron acid compound by Pd with alkali, for example $Pd(PPh_3)_4$ or Pd acetate in homogeneous reaction. 5CB (4-pentyl-4′-cyanobiphenyl) is typical liquid crystal compound is synthesized by Suzuki coupling reaction. (Fig.16) BND and PBD are produced by Suzuki coupling. (Fig.17)

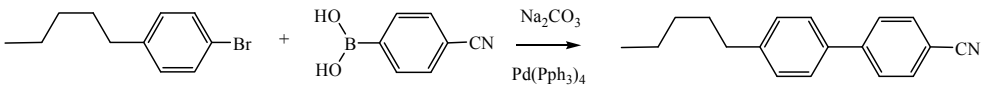

Fig. 16. 4CB synthesis by Suzuki coupling

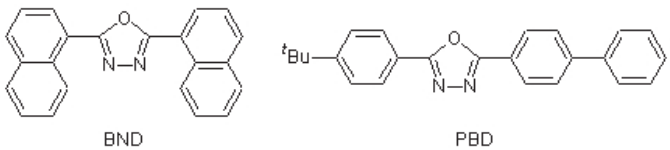

Fig. 17. Example of Liquid crystal produced by Suzuki coupling

Pd/carbon can be used instead of Pd complex. 4-Fluorobiphenyl acetic acid is produced by Pd/carbon.

10.5 Food industry

Sorbitol, known as a sweetener, is produced by hydrogenation of D-glucose. It is used for a moisturizing agent for ham and bacon, additive in teeth paste and others. Ru/carbon or Ni has been used as hydrogenation catalysts. Continuous process using Ru/carbon granular is developed. Succinic acid is produced by hydrogenation of maleic acid using Pd/carbon in slurry and fixed bed reactor.

Lecithin is hydrogenated to hydrogenated lecithin by Pd/carbon, which is used for food additives and cosmetics.

10.6 Synthetic perfume

Leaf alcohol (cis-3-hexene-1-ol) is produced by selective hydrogenation by Lindlar's catalyst which is 5%Pd-2.7%Pb/$CaCO_3$. (Fig.18)

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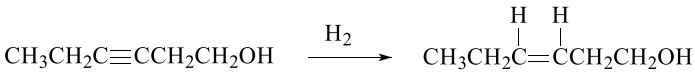

Fig. 18. Leaf alcohol synthesis by Lindlar's catalysts

Many synthetic perfumes are derivatives of isoprene. Acetylene compound is selectively hydrogenated by Lindlar's catalyst after ethynylation. Linalool is derived from isoprene. (Fig. 19) Many synthetic perfume, such as jasmine, are synthesized by using Lindlar 's catalyst.

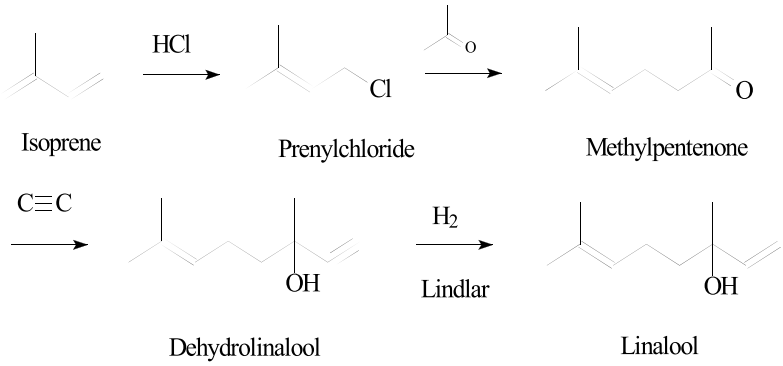

Fig. 19. Linalool synthesis by Lindlar's catalyst

10.7 Cosmetics

Squalene is extracted from liver of shark lives in deep sea. Squalene is hydrogenated with Pd/carbon to squarane which is used basic oil of cosmetics.

11. Medicines

11.1 Vitamin

Lindlar's catalyst was developed for producing vitamin A. (Fig.20)

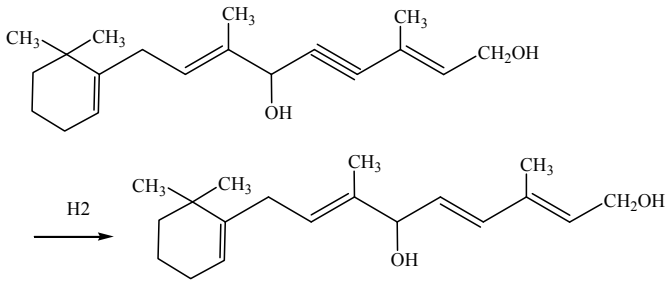

Fig. 20. Vitamin A synthesis by Lindlar's catalyst

Isophytol , an intermediate of vitamin E, is produced selective hydrogenation of carbonyl by Pd/carbon.

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11.2 Medicine for pain and fever

Acetaminophen has been widely used as medicine for pain and fever. *p*-Aminophenol is an intermediate of acetaminophen synthesized from nitrobenzene by hydrogenation in sulfuric acid solution or directly by Bamberger rearrangement reaction with Pt/carbon.

Ibuprofen, which shows small side effect, is produced from *i*-butyl benzene using Pd/carbon and $Pd(PPh_3)_4$. (Fig.21)

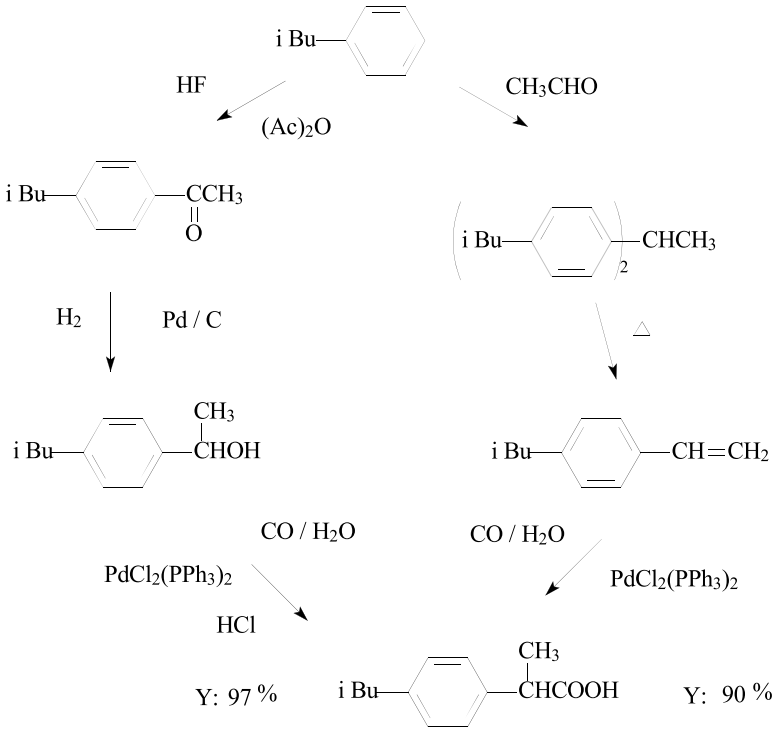

Fig. 21. Ibuprofen synthesis route by Pd

11.3 Hemostatic agent

Trans-ternexamic acid, used as a hemostatic agent, is produced by hydrogenation of nitril of *p*-cyanobenzoic acid with Pd/carbon at 100 °C and 5.0 Mpa, in NaOH aqueous solution. Consequently hydrogenation of aromatic conducts by Ru/carbon at the same condition.

11.4 Antibiotics

11.4.1 Di-hydroxystreptomycin

Streptomycin is hydrogenated to di-hydrostreptomycin which is more stable to alkaline and does not react with other carbonyl compounds. Hydrogenation is conducted by Adams PtO_2 in sulfuric acid solution. (Fig.22)

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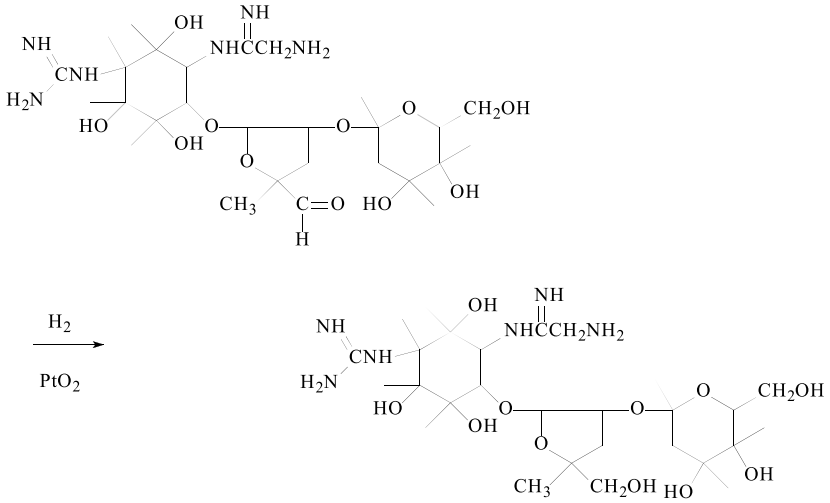

Fig. 22. Hydrogenation of streptmycin

11.4.2 Parasiticide

Wilkinson catalyst was discovered by Dr. Wilkinson in 1966. Wilkinson catalyst, $RhHCl_2(PPh_3)$ is used for hydrogenation of avermectin to produce ivermectin for parasiticide. This application is the largest use of Wilkinson catalyst. (Fig.23)

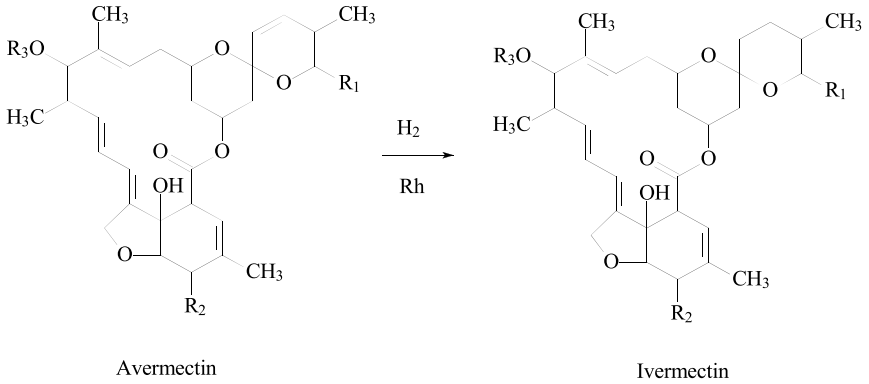

Fig. 23. Hydrogenation of avermectin

11.4.3 Tetracycline

Tetracycline type antibiotics are synthesized by Pd/carbon and Rh/carbon. Minocycline is produced by hydrodechlorination with Pd/carbon and employed enantio selective hydrogenation of methylene by Rh/carbon or Wilkinson Rh complex. (Fig. 24)

Doxycycline also produced through hydrodechlorination by Pd/carbon and hydrogenolysis by Rh/carbon.

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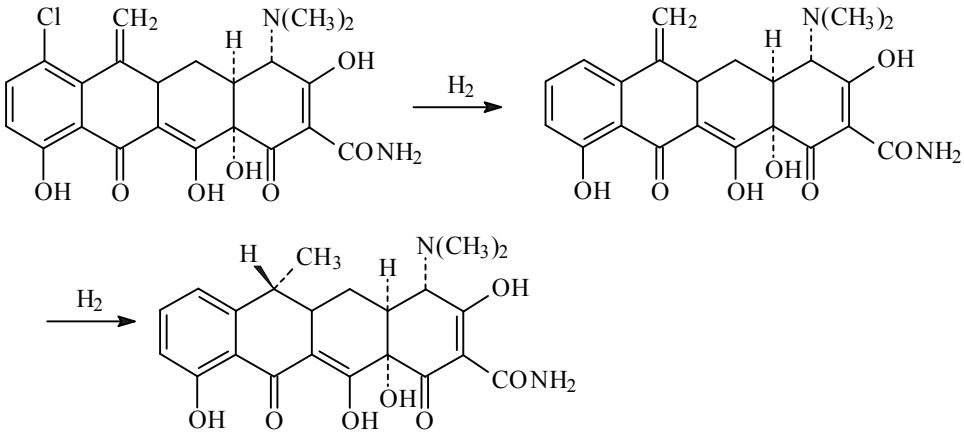

Fig. 24. Minocycline synthesis route

11.4.4 Carbapenem

Carbapenem antibiotics are produced by chiral Ru complex developed by Dr. Noyori.

β- lactam antibiotics were outstanding as next generation of antibiotics. It was intermediate of carbapenem antibiotics, 1β-methylcarboxylic acid. It is commercialized by chiral synthesis by Ru-BINAP. Target was synthesis of 4-acetoxy-2-azetizinone. Takasago International commercialized 40 ton/y of chiral 3-hydroxybutaneacid from α-acylaminomethyl acetic acid ester, at 50 °C, H_2 Press. 10Mpa, 20hrs, Yield is 99% ee, 95% de. (Fig.25) (Akutagawa 1987)

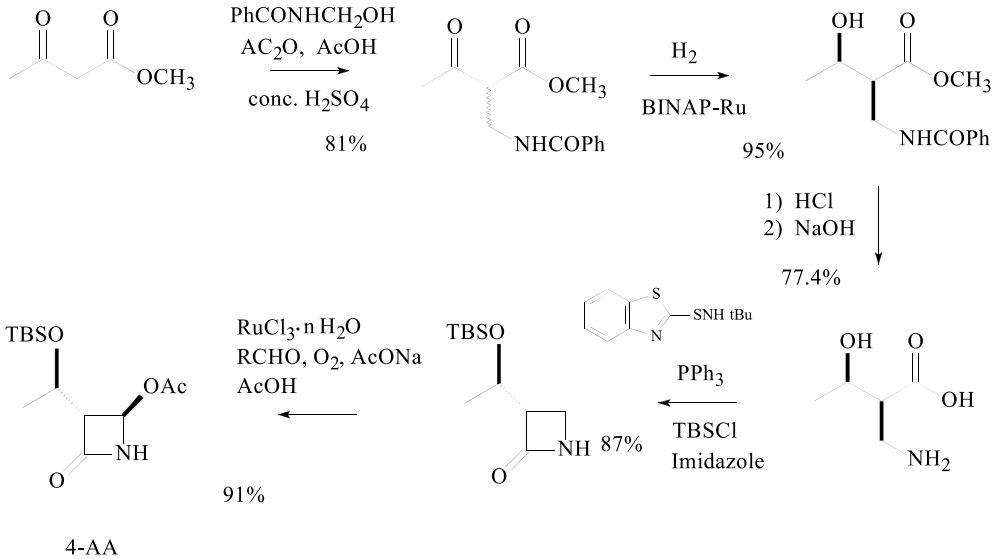

Fig. 25. 4-Acetoxy-2-azetizinone synthesis route

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11.5 L-Dopa

A part of former Monsant developed a drug uses in the treatment of Parkinson's disease.

L-Dopa [3-(3,4-dihydroxyphenyl)L-alanine] is synthesized by Rh complex with chiral bisphosphine ligand such as 1,4-diphenylphosphinobutane, at ～50 °C, and ～40psig. (Fig.26)

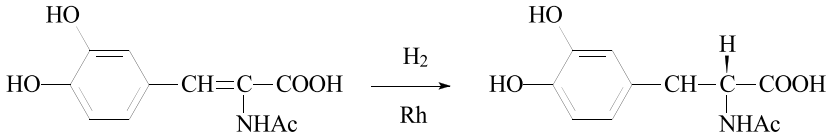

Fig. 26. L-Dopa synthesis

11.6 Indinavir (protease inhibitor)

Piperadine amide is one of the main intermediates of indinavir which is protease inhibitor developed by Merck. There are some synthesis routes to produce piperadineamide. One of synthesis routs is hydrogenation of piperadinecarboxylic acid t-butylamide hydrogenated by Pt/carbon and Ru/carbon and introduced rac-piperadine-2-carboxylic acid.

11.7 Anti-hypertensive

Many medicines are producing by Suzuki coupling using tetrakis-tri-phenyl Pd ($Pd(PPh_3)_4$) or Pd acetate for anti-hypertensive. (Table-4)

Name of medicine	Maker
Valsartan	Novartis
Losartan	Merk
Telmisartan	Boehringar-Ingelheim

Table 4. Example of anti-hypertensive medicine using Suzuki coupling

11.8 Other medicines

Suzuki coupling is applied for many anti-cancer medicines such as Vicenistatin. Negishi coupling is applied to produce anti-depressant. Many alkaloids are produced by the reaction using Pd complex.

11.9 Agricultural chemicals

Many agriculture chemicals are produced using Pt or Pd/carbon. Chloro pyridine is used for an intermediate of insecticide. Di- or tri chloropyridine which is over chlorination is hydrogenated to mono-chloro pyridine by Pd/carbon. Poly chloro amine is also hydrogenated to mono or di-chloroaniline by Pd-Sn/carbon. Reductive alkylation is general reaction to produce intermediates of herbicide by Pt/carbon. Heck carbonylation using $PdCl_2$ is applied for benzanilide type pesticide.

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12. Nuclear power plant

12.1 Reduction of Uranium

One of extraction method of Plutonium (Pu) from spent Uranium (U) is conducted using U^{4+}. Spent U contains Pu $^{4+}$ is reduced to Pu^{3+} and separated by U^{4+}. U^{4+} is produced from U^{6+} by hydrogenation with Pt/SiO_2 in PUREX process.

$$U(NO_3)_6 + 2\,H_2 \rightarrow U(NO_3)_4 + 2HNO_3$$

12.2 Recombiner

Operating nuclear reactors mainly function with boiling water reactor (BWR) and pressurized water reactor (PWR) in the world. In BWR, water (light water) is used as coolant, and moderator is warmed to approx. 200 °C and pressurized to 7 Mpa to make steam in nuclear furnace. Steam is directly sent to gas turbine and recycled after cooled by water. In PWR, operates at approx. 15 MPa, 300 °C of liquid water is produced as the first water which makes steam of the second water for gas turbine. The first water is recycled. Water and nitrogen are decomposed to ^{3}H, ^{6}N, ^{19}O and radioactive Kr, and Xe from fuel rod by neutron. Gas in condenser after gas turbine is separated and introduced to recombiner, which installed Pd or Pt catalyst, after heated. H_2 including T is reacted with O_2 and separated as liquid. Gas components are introduced to gas hold up tower until radioactivity becomes lower. (Fig.27)

$$H_2 + 1/2\,O_2 \rightarrow H_2O$$

$$T_2 + 1/2\,O_2 \rightarrow T_2O$$

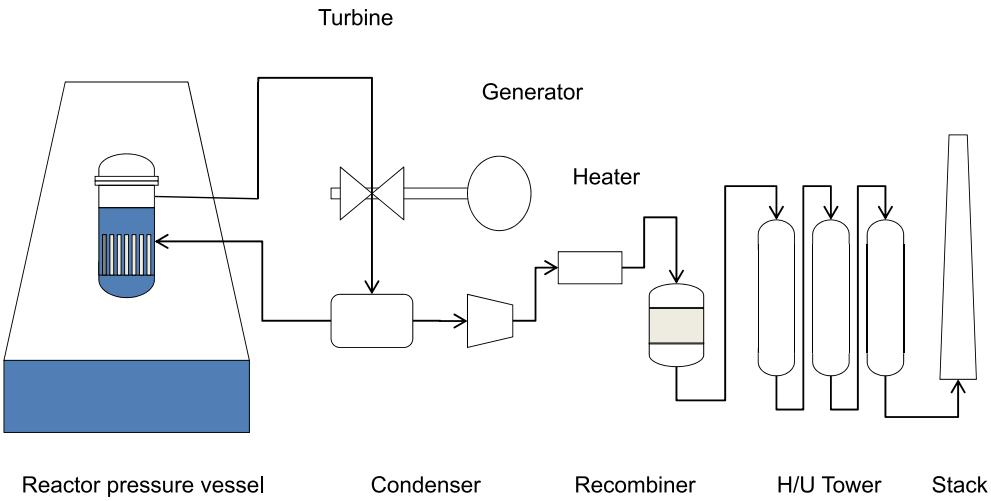

Fig. 27. Waste gas treatment in BWR

In PWR, the first water is recycled which is used warming the second water for gas turbine. Gas containing radioactive rare gases and H_2 containing T are purged and treated by recombiner, and treated gas holder as like as BWR (Fig.28)

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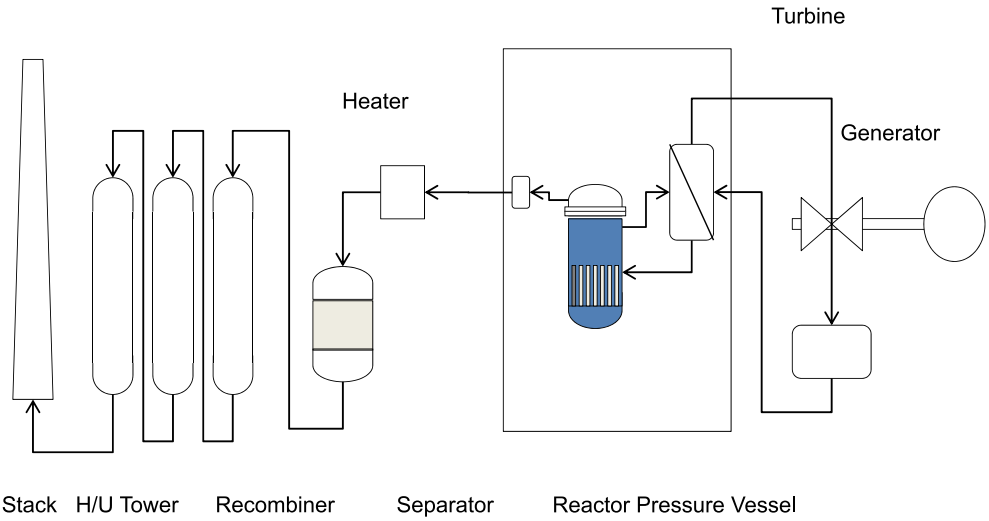
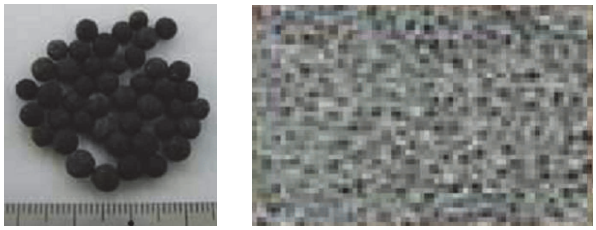


Fig. 28. Waste gas treatment in PWR

Pd/Al_2O_3 or Pt/metal form is used as a catalyst. Pd/Al_2O_3 sphere is charged SUS element. Water proof catalyst shows high activity for condensation of water. Pt/metal form is used as plate form, and charged 40 layers in the reactor. (Fig.29)



Pd/Al_2O_3 sphere Pt/metal form

Fig. 29. Recombiner catalysts

The example of reaction condition is described in Table-5.

		Inlet	Outlet
Gas Composition %	H_2	3.3%	< 1 ppm
	O_2	1.7%	
	Steam	Balance	Balance
Temp. °C		143	427

Press.0.12 MPa, S.V.: 1,500 hr^{-1}, O_2: Leak 0.5%

Table 5. Recombiner reaction condition

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12.3 Flammability control system (FCM)

Three Mile Island accident taught us introducing FCM which is countermeasure of accidental coolant loss by breakage of cooling pipe and/or others. When cooling system is out of order, steam and Zr, which is cover metal of fuel rods, react and produces H_2. And H_2 is potentially generated from fuel rods even after shut down of nuclear furnace. It may hydrogen explosion.

$$H_2O + 1/2\,Zr \rightarrow 1/2\,ZrO_2 + H_2$$

FCS is installed recombiner catalyst which is the same catalyst as waste gas treatment system. FCS is fixed outside or inside of the vessel as shown in Fig.30.

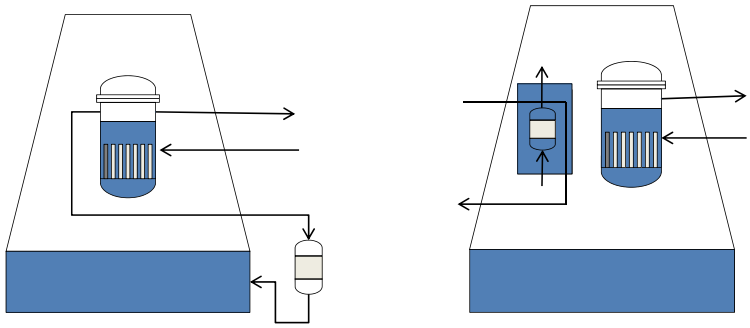

Fig. 30. FCS installed reactor

Radioactive I_2 are catalyst poison for Pd and Pt. I_2 adsorbent such as Ag/Al_2O_3 or Ag/zeolite are introduced. Such adsorbents are fixed on the front of the reactor.

13. Environment

13.1 VOC abatement

VOC (Volatile Organic Compounds) are removed by catalytic combustion system using Pt/honeycomb at lower than 350 °C. A lot of plants, not only chemical plants such as acrylic acid, maleic acid, phenol plants, but also printing, enamel wire, even food plant such as coffee plants, apply VOC removal. In case of high VOC content, heat recovery system equipped with Pt/honeycomb catalysts. The self combustion system after ignition without heating is running in some case. Off gas treatment of PTA plants and phenol plants use Pt/honeycomb, and generated heat during off gas treatment is recovered. In polyester film facilities, Pt/honeycomb reduce falling particle of organic compounds onto the film. Organic chloride compounds are completely oxidized by Pt/mordenite also.

13.2 Gas turbine off gas abatement

NOx can be reduced by adding water to fuel gas in gas turbine. NOx concentration can be reduced to 40 ppm from 150 ppm. However, addition of water increases CO from 10 ppm to 400 ppm because of lower flame temperature. In order to solve the problem, Pt/honeycomb is applied to oxidize CO completely. Since Pt/Al_2O_3 is poisoned by sulfur dioxide producing $Al_2(SO_4)_3$, sulfur resistant catalysts, Pt/TiO_2 are developed. Suggested reaction temperature and GHSV are 315-600 °C, and 200,000hr^{-1}, respectively. (Bartholomew 2006) (Fig.31)

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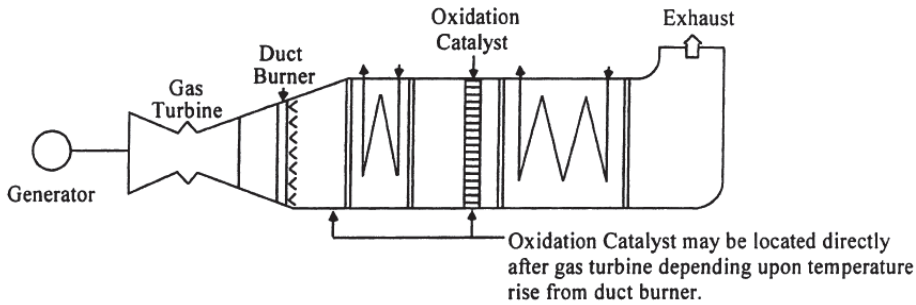

Fig. 31. Gas turbine installed CO oxidation catalyst

13.3 Low NOx burner

NOx is produced in the flame at high temperature. Production of NOx can be controlled by flam less combustion using Pd catalyst. Catalytica developed low NOx burner which consists of Pd/honeycomb layer and the combustion room without catalyst. Combustion gas is heated up to approx. 470 °C by burner. Catalytic combustion takes place in catalytic layer up to approx. 870 °C. At last, final combustion is conducted in flam less combustion room without catalyst. (Fig.32) NOx concentration of off gas is generally less than 5 ppm. Several plants with NOx burner system have been commercialized in USA. Ferrite type stainless containing Al honeycomb is selected for the honeycomb carrier instead of ceramics for prevention of heat destruction. (Shoji 1999) The system called Xonone Combustion System was developed by Catalytica Energy Co., NOx content is very low in the test results at power plant using gas engine. Small amount of NOx is produced at pre-burner, disclosed at Calfornia Air Resources Board Precertification Program in June 2002. (Table-6)

Off gas	Content ppm
NOx	1.13
CO	1.36
VOCs	0.16

Table 6. Power plant test result at O_2 15%

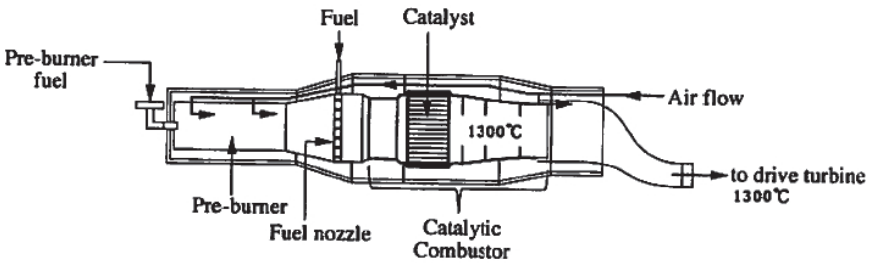

Fig. 32. Catalytic converter

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14. Auto exhaust catalyst

14.1 Pt consumption

50% of Pt, 60% of Pd, and 85% of Rh in production from mining per year are consumed for automotive exhaust purification catalysts. Recovery of metals from spent automotive exhaust catalyst is currently 15% for Pt and Pd, and 30% for Rh so far.

14.2 Gasoline engine

Three way catalysts that remove CO, HC and NOx from exhaust gas of gasoline engine are used in the world. Contaminants of automotive exhaust gas of gasoline engine are reduced almost 99% by the catalytic converter. Pt and Pd are especially effective for combustion of hydrocarbon and carbon monoxide. Rh is effective for NOx reduction under stoiciometric condition. For example Pd-Pt/honeycomb is fixed in front part and Pd-Rh or Pt-Rh/honeycomb is fixed in the rear part of the converter which is installed under driver floor. (Fig. 33)

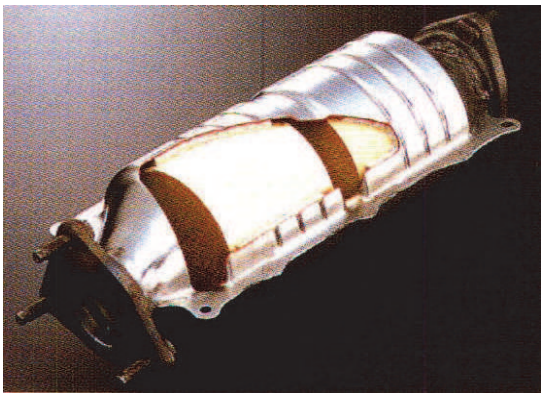

Fig. 33. Three way catalyst

Pt content cannot be reduced because of sintering which occurs at high temperature when reaches driving speed high. Some advanced technologies have been developed. Toyota Motor found Pt shows positive influence by strong interaction with metal oxide. Pt on CZY (CZY : 50%CeO_2, 46%ZrO_2, 4%Y_2O_3) does not show sintering at 800 °C, 5 hrs, and in the air. This is known as strong metal support interaction (SMSI). Pt is strongly fixed on oxide support by forming Pt oxide with carrier. By conducting XAFS analysis, Toyota Motor proved that Pt strongly bonds with carrier through surface oxygen atm. (Nagai 2007)

Daihatsu Motor developed heat resistant catalyst that consists of precious metal and peroveskite as support. PM is taken into lattice of peroveskite at oxidation atmosphere at high temperature. PM is out of lattice at reductive atmosphere at low temperature. Precious metal content of the catalyst can be reduced because sintering is significantly prevented. The catalysts are commercialized for light vehicle, and application of high exhaust gas temperature. The mechanism is investigated by XAFS study. (Daihatsu 2006) (Daihatsu 2008)

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14.3 Purification of diesel engine gas

NO_2 is found to be oxidizing agent for soot. NO is oxidized to NO_2 by Pt/Al_2O_3 / honeycomb at first converter, and then soot is combusted to CO_2 at soot trap filter which Pt coated pores of wall through honeycomb consisting of SiC as a heat resistant material.

$$NO + 1/2\,O_2 \rightarrow NO_2$$

$$C + 3/2\,NO_2 \rightarrow CO_2 + NO$$

$$NO + 1/2\,O_2 \rightarrow NO_2$$

$$2\,NO_2 + C \rightarrow CO_2 + NO$$

15. Amenity

15.1 Catalytic heater

Catalytic heaters, Pt coated on alumina or silica wool, are widely used in Northern Europe. Natural gas or LPG is used as a fuel. Flameless infrared light heats the room. Portable catalytic heaters are sold for outside leisure, for instance, for camping, fishing and others. Honeycomb type of catalytic heaters is several pieces of Pt/honeycomb connected in series. It generates far infrared light which convey heat in distance. Thus, it is very useful to apply for large room such as gymnasium. Cord less catalytic heater is used for soldering iron using LPG.

15.2 Closed type battery

Lead batteries are used as a power source for emergency light, telephone system and traffic light and others. Small amount of water is decomposed as hydrogen and oxygen during charging battery. Waterproof Pd/Al_2O_3 particles are charged in porous ceramic cage. Hydrogen and oxygen are converted to water and dropped back into battery. Water level can be kept same for the long time.

$$2\,H_2 + O_2 \rightarrow 2\,H_2O$$

15.3 Ozone decomposition

Aircraft have to take air into the cabin at high altitude where air contains more ozone. This ozone uptake potentially makes from passengers airplane sick. Ozone converter is installed in the every plane now. Ozone is decomposed by Pd/honeycomb catalyst.

$$2\,O_3 \rightarrow 3\,O_2$$

16. Space

Decomposition of hydrazine by Ir/Al_2O_3 is propulsion power for control of satellite position in the space. Thrusters are fixed at the several sides of satellite wall.

$$N_2H_4 \rightarrow N_2 + 2\,H_2$$

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17. Future

17.1 Fuel cell

17.1.1 Fuel cell system

Polymer electrolyte fuel (PEFC) is expecting to apply for residential and automotive use for at lower operation temperature. Target amount of Pt use is 0.5-0.7g/unit for residential use, 25-35 g/vehicle. Currently 5-10 times more of Pt is required. Since electric car cannot run long distance, fuel cell car is expected to be commercialized. Infrastructure of hydrogen supply remains as a technical challenge. (Table-7)

	Residential use	Automobile use
Power Capacity	0.7～1.0 kw	50 kw
Fuel	City gas, LPG, Kerocene	Hydrogen
Pt use amount	0.5～0.7 g/unit	25～35 g/car
Life of Cell	10 years	100,000 km

Table 7. Expecting performance of fuel cell

PEFC system for residential use equipped with purification, steam reforming, shift reaction, PROX, electrode and off gas treatment. It still appears to be complicated. (Fig.34)

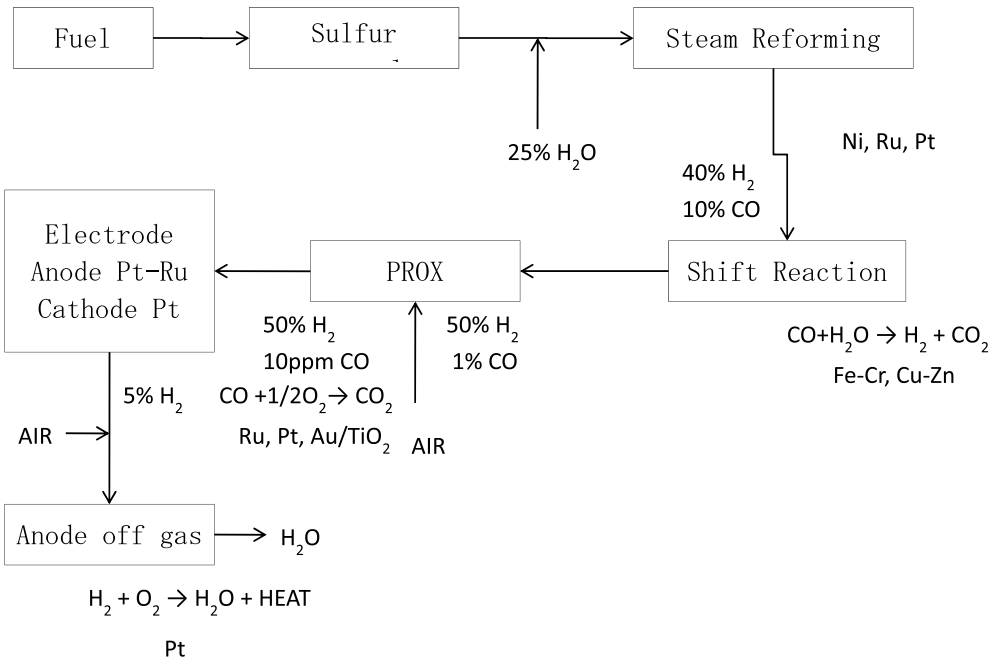

Fig. 34. Fuel Cell system flow

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17.1.2 Reforming and hydrogen purification

City gas can be a fuel for a fuel cell of residential use. Containing small amount of sulfur is removable by Fe or Ag/Al_2O_3. Ni or Pt/Al_2O_3 is used for steam reforming to produce hydrogen. Since containing CO impurity in hydrogen poisons catalyst, CO is needed to remove by shift reaction with Cu-Zn. Remaining 1% of CO is removed by preferential oxidation (PROX) to less than 10 ppm by using Ru, Pt, or Au/TiO_2. Ni/Al_2O_3 causes carbon formation in case of kerosene as fuel. Ru/ZrO_2 is developed to overcome the issue.

17.1.3 Electrode

Purified hydrogen is introduced to anode, however small amount of CO (10 ppm) is remain which is catalyst poison, therefore CO resistant Pt-Ru coated carbon is used. Air is fed to Cathode which is Pt coated carbon. Carbon is high temperature treated graphite, however carbon oxidation would not be overcome by produced hydrogen peroxide for long use. Reduction of amount of Pt and Ru loading is the most important target. An example of typical Pt/carbon and Pt-Ru/carbon electrode is shown in Table-8.

	Cathode	Anode
Pt content	50 %	27 %
Ru content	—	13 %
Moisture	< 5 %	< 5 %
BET surface area	320 m^2 /g	120 m^2/g
CO uptake	40 ml/g·Pt	40 ml/g·Pt+Ru
XRD crystal diameter	3 nm	6 nm

Table 8. Typical catalyst for electrode

17.1.4 Off gas

Off gas containing hydrogen is combusted to H_2O by Pt/honeycomb catalysts.

17.2 Dry reforming

Dry reforming instead of steam reforming is coming up to reduce CO_2 when syngas is produced from natural gas. Syngas can be used to produce F/T oil and methanol which can be further converted to propylene. Ni/Al_2O_3 can be used as same as steam forming catalyst, However, Ru/MgO shows stable performance with low carbon deposition. This system is operated in pilot plant scale in Niigata as a national project in Japan. (Chiyoda 2006)

$$CH_4 + CO_2 \rightarrow 2\,CO + 2\,H_2$$

17.3 Hydrogen transfer

Electric power generation by utilizing wind power is effective in South America and North islands. Organic hydride is effective material as a hydrogen carrier. For example, toluene is hydrogenated to methyl cyclohexane by Pt/Al_2O_3 by hydrogen produced electrolysis by

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wind power. Methyl cyclohexane is transported to consumption area by vessel, and hydrogen is taken from methylcyclohexane by dehydrogenation with Pt/Al_2O_3,. Dehydrogenated toluene is again, transports to strong wind area by vessel and recycled.

17.4 Biomass

17.4.1 Propanediol from glycerol

1,2 -propanediol can be synthesized from glycerol which is expected byproduct of bio-diesel oil production. Mixed catalyst with Ru/carbon and amberlyst gives higher activity than Ru/carbon alon. It presumes that hydroxyacetone is formed as an intermediate with ion-exchange resin, and hydrogenation undergoes by Ru/carbon. At last, 1,2-propanediol is formed.(Furizuno 2006)

17.4.2 Hydrogenolysis of glycerol to methanol

Oxford University has disclosed production of methanol from glycerol by hydrogenolysis. Conversion is 50% and selectivity is 80% by Ru/graphite at 2.0 Mpa, and 100 °C, 24 hrs. (Fig. 35) (ISIS Inovation 2009) Produced methanol can be used to synthesize FAME by transesterification.

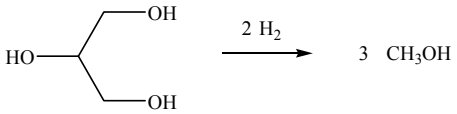

Fig. 35. Methanol by hydrogenolysis of glycerol

17.4.3 Hydrogen from glycerol

Hydrogen can be produced from diluted glycerol aqueous solution. Hydrogen is generated from 1-10wt% of glycerol at 220 °C and 2.9 Mpa by Pt/Al_2O_3. Conversion is 90% and selectivity is 90%. Small amount of alkanes are produced by Rh or Ni. (Boonyanuwat 2006)

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He graduated Akita University in Japan and worked in Evonik Degussa as project leader living in USA.

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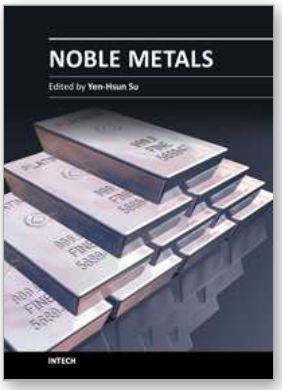

Noble Metals

Edited by Dr. Yen-Hsun Su

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This book provides a broad spectrum of insights into the optical principle, resource, fabrication, nanoscience, and nanotechnology of noble metal. It also looks at the advanced implementation of noble metal in the field of nanoscale materials, catalysts and biosystem. This book is ideal not only for scientific researchers but also as a reference for professionals in material science, engineering, nonascience and plasmonics.

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