CHAPTER II

LITERATURE REVIEW

2.1 Glycerol

Glycerol is a chemical with the formula $HOCH_2CH(OH)CH_2OH$, consisting of a chain of three carbon atoms with each of the end carbon atoms bonded to two hydrogen atoms (C–H) and a hydroxyl group (–OH), and the central carbon atom is bonded to a hydrogen atom (C–H) and a hydroxyl group (–OH).

Glycerol was discovered in 1783 by the Swedish chemist Carl Wilhelm Scheele when treating natural oils with alkali. The name "glycerol" was given in 1811 by the chemist Michel Eugene Chevreul, who deduced this name from the Greek word "glykos"(= sweet) (Behr *et al.*, 2008). Glycerol is also called glycerin or glycerine. Glycerol is the prefered scientific terminology and refers to the pure trihidric alcohol, whereas glycerin(e) refers to the comercial products consisting of whatever grade or degree of purity (Kenar, 2007).

Glycerol is a viscous sweet tasting, clear hygroscopic liquid with no odor, non-toxic, and easily biodegradable. It is miscible in water and alcohol, but insoluble in ether, chlorinated solvents, hydrocarbons, and oils. The chemical structure and some properties of glycerol are described in Table 2.1.

Table 2.1 Chemical structure and properties of glycerol

Chemical Sturcture	Property
	Molecular weight: 92.09
	Melting point (°C): 17.8
	Boiling point (°C): 290
	Density at 20°C: 1.2375
	Flash point (°C): 176

2.2 Production of Glycerol

Currently, the production of glycerol from fats and oils is carried out by saponification yielding glycerol and soaps (Figure 2.1, Y = ONa), by hydrolysis yielding glycerol and fatty acids (Figure 2.1, Y = OH), or by transesterification with methanol yielding glycerol and fatty acid methyl esters (Figure 2.1, Y = OCH₃). It can also be synthesized from propylene via the epichlorohydrin route.

$$
\begin{array}{ccccccc}
& O & & & & & O \\
& \| & & & & & \| \\
CH_2-O-C-R & & & CH_2-OH & & Y-C-R & \\
| & O & & | & & & O \\
& \| & & & & & \| \\
CH -O-C-R' & + & 3\,HY & \rightleftharpoons & CH-OH & + & Y-C-R' \\
| & O & & | & & & O \\
& \| & & & & & \| \\
CH_2-O-C-R'' & & & CH_2-OH & & Y-C-R'' &
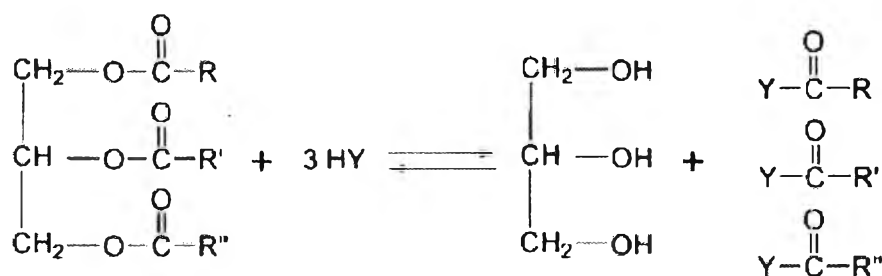\end{array}
$$

Figure 2.1 Synthesis of glycerol from fats and oils where Y is ONa, OH, or OCH₃ (Behr *et al.*, 2008).

Over the past couple decades, fatty acid methyl esters derived from vegetable oil and animal fat have been recognized as a potential diesel fuel extenders known as biodiesel. For every 9 kg of biodiesel produced, about 1 kg of glycerol is formed as a by-product (Dasari *et al.*, 2005). Obviously, the question arises how this additional glycerol can be used wisely. Finding new chemistry to convert the glycerol to high value-added products is being developed.

2.3 Reaction of Glycerol

In the past, glycerol is most commonly used without modification, or very basic structural modifications, as an additive material in food and cosmetic industry. At present, the potential conversion of renewable resources into valuable commodity chemicals can facilitate the replacement of petroleum-based products. From a technical standpoint, glycerol's multifunctional structure and properties can be

tailored by several different reaction pathways as shown in Figure 2.2. In this respect, catalysis represents a critical approach to green chemical technology in the activation and utilization of glycerol.
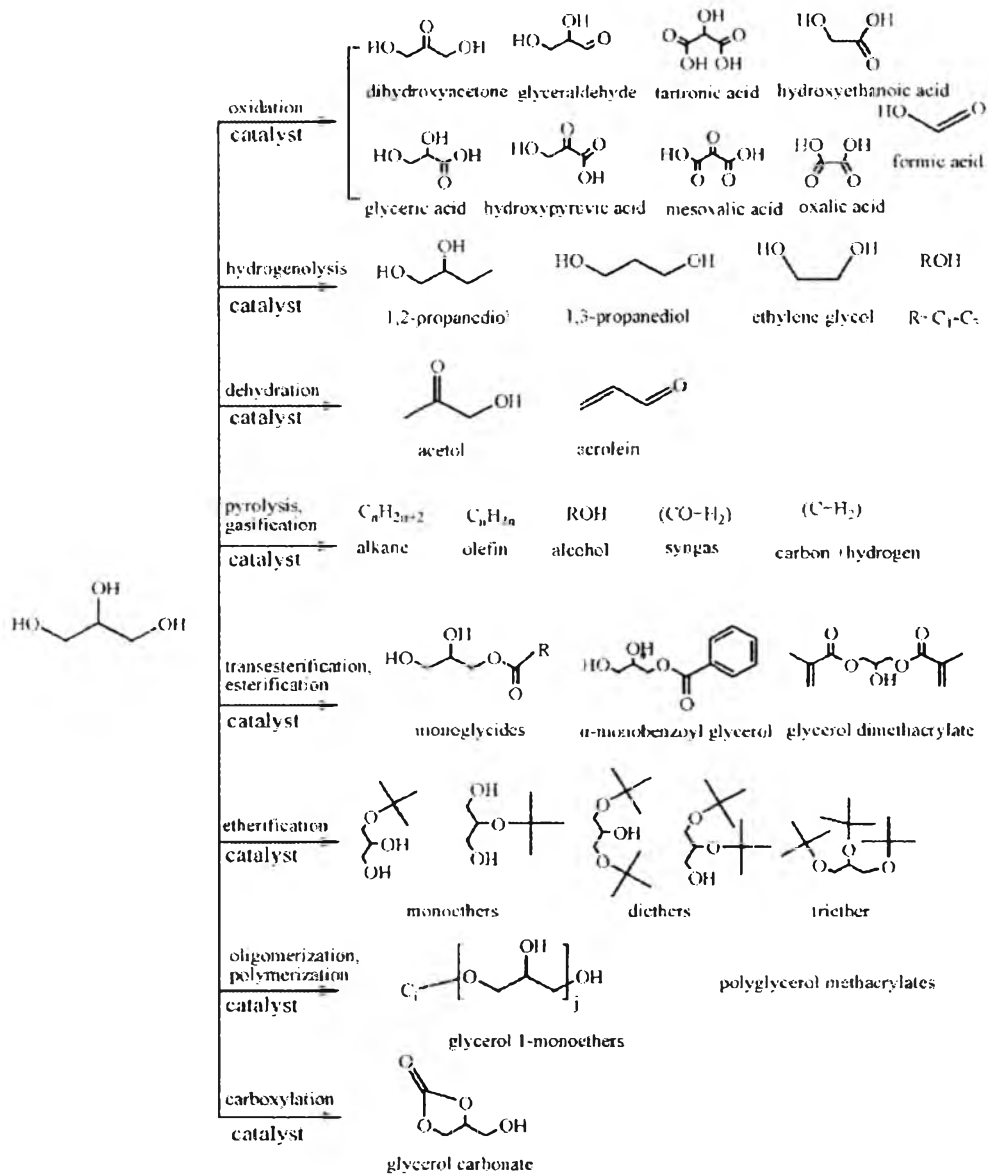

Figure 2.2 Processes of catalytic conversion of glycerol into useful chemicals (Zhou *et al.*, 2008).

The catalytic selective hydrogenolysis of glycerol to propanediol is one of the most attractive routes, since it is feasible and simple method that can convert the glycerol to high value-added products, such as 1,2-propanediol and 1,3-propanediol.

2.4 Propylene Glycol Uses and Market Data

Propanediols may refer to either of two isomeric organic chemical compounds: 1,2-propanediol and 1,3-propanediol. The 1,2-propanediol or propylene glycol, is an important medium-value commodity chemical. It is mainly used for manufacturing polyester resins, liquid detergents, pharmaceuticals, cosmetics, tobacco humectants, flavors and fragrances, personal care, paints, animal feed, antifreeze, etc. There has been a rapid expansion of the market for 1,2-propanediol as antifreeze and de-iceing agents because of the growing concern over toxicity of ethylene glycol-based products to human and animal. The current global market for 1,2-propanediol is roughly 2 million tonnes annually (Kenar, 2007). Recently, several major chemical producers, such as Dow, Cargill, Archer Daniels Midland, and Huntsman, have all announced plans to produce 1,2-propanediol from glycerol.

The 1,3-propanediol is also a high-value chemical that is mainly used in specialty polyester fibers, films, and coatings. The 1,3-propanediol is copolymerized with terephthalic acid to produce polyester SORONA® from DuPont, or CORTERRA® from Shell, which has unique properties in terms of chemical resistance, light stability, elastic recovery, and dyeability (Behr et al., 2008). The 1,3-propanediol is estimated to reach an overall market potential of 227 tonnes by 2020 (Kenar, 2007).

In the petrochemical industry, it has been known that 1,3-propanediol is more valuable than 1,2-propanediol; however, the selective hydrogenolysis of glycerol to 1,3-propanediol is still unsatisfactory. On the other hand, the production of 1,2-propanediol becomes more potential since the method is one-step and simple (Miyazawa et al., 2007). Therefore, the production of 1,2-propanediol from glycerol will be focused in this work. Following section is a description of the chemistry used to derive them from glycerol.

2.5 Selective Hydrogenolysis of Glycerol to Propanediol

The term "hydrogenolysis" refers to a catalytic chemical reaction that breaks a chemical bond in an organic molecule with the simultaneous addition of a hydrogen atom to the resulting molecular fragments (Zhou et al., 2008). Through the selective hydrogenolysis of glycerol in the presence of metallic catalysts and hydrogen, the commodity products—1,2-propanediol and 1,3-propanediol—could be obtained. Therefore, catalytic hydrogenolysis of glycerol is one route to improve economy of whole biodiesel production plants as the products of glycerol hydrogenolysis can easily replace the chemical compounds, which at present are industrially produced mainly by crude oil.

2.5.1 Production of 1,2-propanediol from Glycerol

The present industrial route for manufacturing 1,2-propanediol (propylene glycol) is the hydrolysis of propylene oxide with water, but the use of fossil raw materials is less favorable to the consumer acceptance, which leads to the demand of a renewable feedstock, such as glycerol. Glycerol can be converted to 1,2-propanediol using biocatalysts, homogeneous or heterogeneous catalysts, which are described in the following items.

2.5.1.1 Biocatalyst

A typical commercial example of a technology switch with respect to catalyst and feedstock was demonstrated by a joint venture of the chemical company Ashland Inc. and the food processor Cargill. Cargill has already presented a process to obtain propylene glycol from carbohydrates with *Escherichia coli* or *Thermoanaerobacterium thermosaccharolyticum* HG-8 (Behr et al., 2008).

2.5.1.2 Homogeneous Catalyst

In general, the hydrogenolysis of glycerol by homogeneous catalysts leads to a variety of by-products, such as propanol and ethers, and to a mixture of 1,2- and 1,3-propanediol. Earlier, Che et al. (1987) patented a one-step process for the catalytic hydrogenolysis of glycerol in water solution using syngas at 200°C and 32 MPa H_2 pressure in the presence of a homogeneous rhodium complex

catalyst (Rh(CO)$_2$(acac)) and tungstic acid. During the reaction, 1,2-propanediol and 1,3-propanediol were produced with 23% and 20% yield, respectively.

Schlaf *et al.* (2001) also described the catalytic hydrogenolysis of glycerol in sulfolane at 110°C and 5 MPa catalyzed by a homogeneous complex of ruthenium, and 5 % yields of 1,2-propanediol and 1,3-propanediol were obtained. Recently, the Shell Oil Company developed a process that uses homogenous palladium complex in a water–sulfolane mixture containing methane sulfonic acid. After a 10 h reaction, 1-propanol, 1,2-propanediol and 1,3-propanediol were detected in a ratio of 47 : 22 : 31 (Drent *et al.*, 2000).

2.5.1.3 Heterogeneous Catalyst

Carrying out over solid catalysts without the presence of dangerous solvents, it would become economically and environmentally attractive.

Montassier *et al.* (1991) carried out the hydrogenolysis of glycerol at 260°C and 30 MPa H$_2$ pressure in the presence of Raney nickel, ruthenium, rhodium, and iridium catalysts. They found that methane was mainly produced, but when Raney copper was used as a catalyst, 1,2-propanediol was the main reaction product. It is known as an efficient catalyst for carbon–oxygen bond hydrogenation and dehydrogenation. A reaction mechanism for conversion of glycerol to 1,2-propanediol proposed by Montassier *et al.* is shown in Figure 2.3.
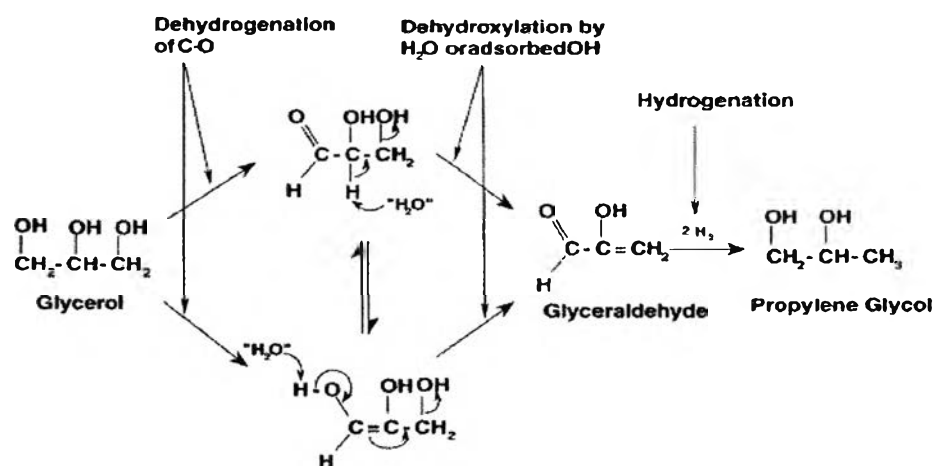

Figure 2.3 Reaction mechanism for conversion of glycerol to 1,2-propanediol proposed by Montassier *et al.* (1991).

Casale *et al.* (1993) patented a process for the hydrogenolysis of glycerol in the presence of Cu-ZnO/Al$_2$O$_3$ catalyst with an atomic ratio between the copper and zinc of 0.89. The molar ratio of hydrogen to glycerol was 4 to 1. The concentration of glycerol upon admission to the catalytic bed was 30 wt.% and operating pressure in the reactor was 15 MPa. The results of the tests are expressed in the Table 2.2.

Table 2.2 Summary of conversion rate and selectivity of products from hydrogenolysis of glycerol at various temperatures and space velocities (Casale *et al..* 1993)

Example	T (°C)	LHSV (h^{-1})	Conversion (%)	Selectivity (%)				
				PG	EG	AL	A	Gas
11	230	1.6	94.6	89	6.9	0.08	1.1	0.02
12	250	1.6	96.6	91	6.2	0.18	2.2	0.03
13	265	1.6	99.4	78	4.8	0.25	3.2	0.02
14	230	1	93.2	94	6.3	0	1.7	0
15	250	1	99.1	88	6.0	0	2.0	0.012
16	265	1	99.6	81	5.3	0.1	2.8	0.02

Note: PG: Propylene glycol, EG: Ethylene glycol, AL: Lactic acid, A: Alcohol, Gas: CH$_4$+CO$_2$+CO$_2$.

It was shown that the conversion rate increased as the temperature increased from 230 to 265°C, with a slight decrease in selectivity toward 1,2-propanediol. Moreover, it was noted that a change in space velocity did not appreciably change the test results. They also patented the same reaction process (Casale *et al.*, 1994) with the use of a ruthenium catalyst, with the activity of which was moderated by sulfides, in the presence of a base. It was shown that the desired product was unsatisfactory; however, because of large quantities of gaseous products, mainly methane was formed.

Schuster *et al.* (1997) studied the preparation of 1,2-propanediol from glycerol at 250°C and 25 MPa using a catalyst containing cobalt,

copper, magnesium, molybdenum, and an inorganic polyacid that can selectively produce 1,2-propanediol with yield up to 95%.

Chaminand *et al.* (2004) conducted the catalytic hydrogenolysis of glycerol over heterogeneous catalysts. The reaction was carried out at 180°C and 8 MPa H_2 pressure. Among the various catalysts (Cu, Pd, Rh), supports (ZnO, C, Al_2O_3), solvents (H_2O, sulfolane, dioxane), and additive (H_2WO_4), the CuO/ZnO catalyst showed the highest selectivity toward 1,2-propanediol. In sulfolane system, higher glycerol conversion and yield of 1,3-propanediol was observed. In view of these results, they proposed a general mechanism (Figure 2.4). The figure shows that H_2WO_4 can favor the dehydration route (route A, E1-like mechanism) via protonation of the hydroxyl groups with loss of water. The keto group formed as an intermediate can be easily reduced under these reaction conditions. However, when using acid (i.e. HCl), a low conversion was obtained, suggesting that the acidity of H_2WO_4 did not have a dominant effect on the reaction mechanism. At the same time, the formation of a Rh–W alloy cannot be excluded and can affect the selectivity and the activity of the glycerol hydrogenolysis reaction. Furthermore, they showed that the addition of a second metal (Fe or Cu) to the reaction medium reduced the activity of the Rh due to a poisoning effect. Moreover, iron can be chelated by a diol and consequently modifies the selectivity of the hydrogenolysis (route C).

Dasari *et al.* (2005) studied the low-pressure hydrogenolysis of a concentrated glycerol solution into 1,2-propanediol at moderate reaction conditions of 200°C and 1.4 MPa over the various types of commercial catalysts. Among of them, the copper–chromite was identified as the most effective catalyst, yielding 73% of 1,2-propanediol, as shown in Table 2.3.
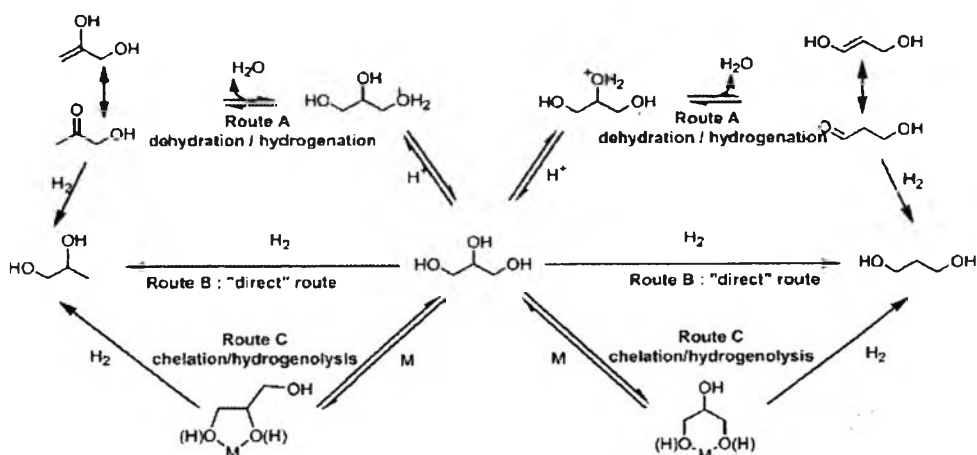
Figure 2.4 Possible reaction routes for catalytic hydrogenolysis of glycerol proposed by Chaminand *et al.* (2004).

Table 2.3 Summary of conversion of glycerol, yield, and selectivity of propylene glycol from glycerol over various metal catalysts (Dasari *et al.*, 2005)

Supplier	Description	Conversion	Yield	Selectivity
Johnson Matthey	5% Ru/C	43.7	17.5	40.0
Johnson Matthey	5% Ru/alumina	23.1	13.8	59.7
Degussa	5% Pd/C	5	3.6	72.0
Degussa	5% Pt/C	34.6	28.6	82.7
PMC Chemicals	10% Pd/C	8.9	4.3	48.3
PMC Chemicals	20% Pd/C	11.2	6.4	57.1
Grace Davision	Raney nickel	49.5	26.1	52.7
Grace Davision	Raney copper	48.9	33.8	69.1
Sud-Chemie	Copper	53	21.1	39.8
Sud-Chemie	Copper-chromite	54.8	46.6	85.0
Johnson Matthey	Ni/C	39.8	27.3	68.6
Alfa-Aesar	Ni/silica-alumina	45.1	29.1	64.5

Furthermore, the reaction mechanism for converting glycerol to propylene glycol was proposed via dehydration of glycerol to acetol and hydrogenation to 1,2-propanediol, as shown in Figure 2.5.
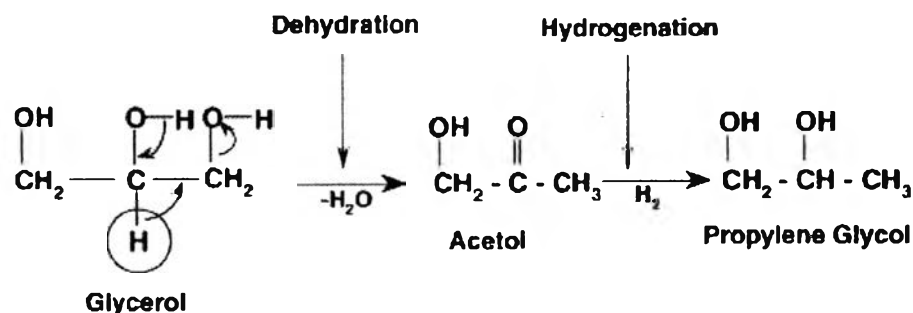
Figure 2.5 Reaction mechanism for conversion of glycerol to 1,2-propanediol proposed by Dasari *et al.* (2005).

Miyazawa *et al.* (2005) studied the hydrogenolysis of glycerol at 180°C under 8 MPa H_2 pressure using various noble metals (Ru/C, Rh/C, Pt/C, and Pd/C) and acid catalysts (an ion-exchange resin (Amberlyst15), H_2SO_4 (aq), and HCl (aq)). It was found that the Rh/C catalyst showed higher conversion than the others, and the combination of that catalyst with the Amberlyst15 exhibited higher activity. At high temperature, the low conversion is likely caused by the deactivation of Amberlyst, which can be degraded at 120°C. In addition, Ru/C + Amberlyst15 gave higher glycerol conversion than Ru/C at the low temperature of 120°C, on the other hand, Ru/C + Amberlyst15 had a much lower conversion than Ru/C at 200°C. This behavior can be explained by poisoning of the sulfur-containing compounds formed by Amberlyst decomposition. The regeneration of catalyst used in the glycerol reaction over Ru/C + Amberlyst15 was tested five times. The results showed that the conversion of glycerol remained almost constant. Furthermore, the reaction mechanism was shown in Figure 2.6.
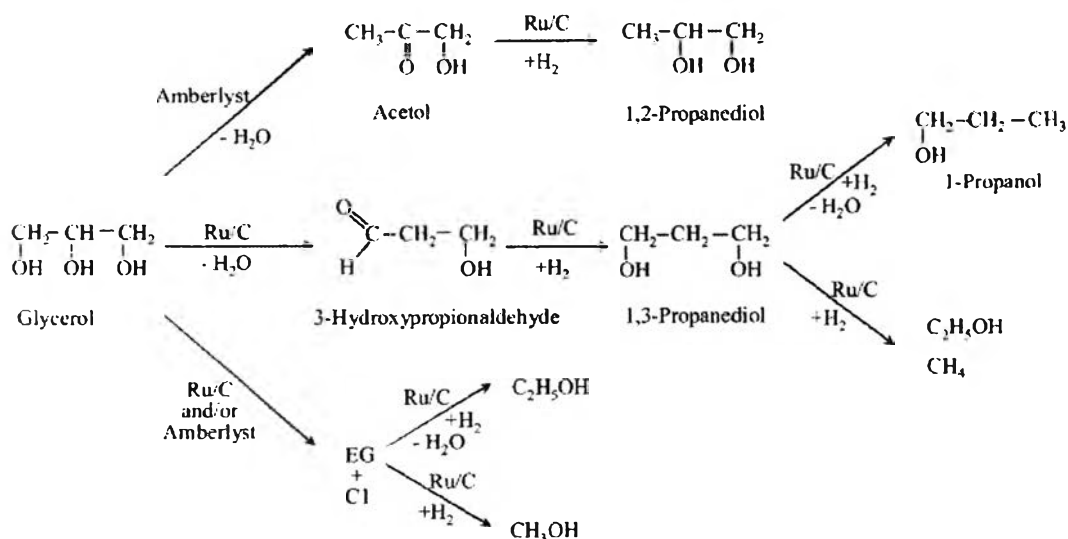
Figure 2.6 Schematic of glycerol hydrogenolysis and degradation reactions (Miyazawa *et al.*, 2006).

A weak point was then overcome by using an ion-exchange resin with higher heat resistance than the Amberlyst15, becoming available as Amberlyst70. The heat resistance of both resin types was investigated by temperature programmed desorption profile. Desorption of SO_2 started above 120°C, and the maximum was observed at about 175°C over Amberlyst15. On the other hand, in the case of Amberlyst70, SO_2 was not detected below 175°C, and desorption reached maximum at 225°C. It was demonstrated that the combination of Ru/C + Amberlyst70 exhibited the higher glycerol conversion, selectivity to 1,2-propanediol, and stability.

Wang *et al.* (2007) carried out the hydrogenolysis of glycerol to propylene glycol over Cu/ZnO catalysts at 200°C and 4.2 MPa. The reaction pathway was including glycerol dehydration to acetol and glycidol intermediates on acidic zinc oxide surfaces, followed by their hydrogenation on copper surfaces. A high propylene glycol selectivity (83.6%) was achieved at 22.5% conversion with atomic ratio of Cu/Zn of 1. The effect of particle size was also evaluated. Smaller zinc oxide and copper particle sizes led to higher glycerol conversion and propylene glycol selectivity.

Alhanash *et al.* (2008) studied the hydrogenolysis of glycerol to propanediols using multifunctional catalysis using heteropoly acid salt modified with ruthenium and rhenium at 150°C and low H_2 pressure of 0.5 MPa. It was found that Ru-doped (5%) acidic heteropoly salt $Cs_{2.5}H_{0.5}[PW_{12}O_{40}]$ (CsPW) is an active bifunctional catalyst, providing 96% selectivity to 1,2-propanediol at 21% glycerol conversion. The 5% Rh/CsPW catalyst, although less active, showed considerable selectivity to 1,3-propanediol (7.1%), with 1,2-propanediol being the main product (65%). The decrease in catalytic activity above 0.5 MPa H_2 pressure may be explained by reduction of W^{VI} in CsPW, which could lead to a decrease in catalyst acidity.

The effect of support and catalyst reduction temperature on the catalytic performance of Ru catalysts in the hydrogenolysis of glycerol was investigated (Feng *et al.*, 2008). The support material affected the metal particle size and the reaction route. Among the tested catalysts, including Ru/SiO_2, Ru/NaY, $Ru/\gamma-Al_2O_3$, Ru/C, and Ru/TiO_2, the TiO_2 supported catalyst showed high activity giving the highest conversion of glycerol (90%); however, Ru/TiO_2 catalyst favored the production of ethylene glycol over 1,2-propanediol under the tested conditions (180°C, 5 MPa). In contrast, Ru/SiO_2 showed the lowest activity, but resulted in much higher selectivity to 1,2-propanediol than that of ethylene glycol. It was well consistent with the mean Ru particle size of the catalyst in the order of Ru/SiO_2 > Ru/NaY > $Ru/\gamma-Al_2O_3$ > Ru/C > Ru/TiO_2. This indicated that the hydrogenolysis of glycerol was more active on small metal particles. The reaction route involved a reversible dehydrogenation of glycerol to glyceraldehyde, followed by dehydration and/or retro-aldorization of glyceroldehyde to 2-hydroxyacrolein and/or glycolaldehyde, and finally, the two glycol precursors are hydrogenated to 1,2-propanediol and ethylene glycol, respectively. Under the same reaction conditions, SiO_2 or $\gamma-Al_2O_3$ favored the dehydration route over the retro-aldolization route, leading to higher selectivity to 1,2-propanediol than that of ethylene glycol. In contrast, TiO_2 was in favor of the retro-aldolization route, resulting in higher selectivity to ethylene glycol. The reaction routes were shown in Figure 2.7.
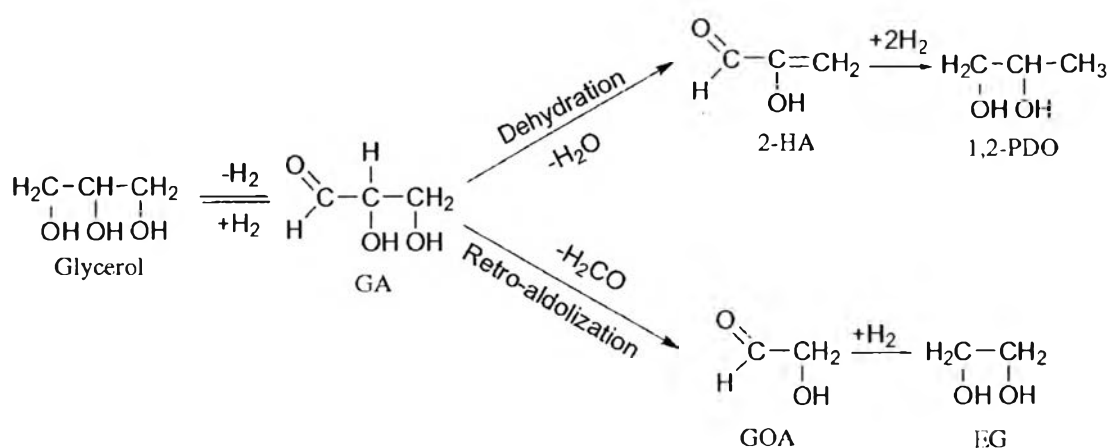
Figure 2.7 Reaction route for the hydrogenolysis of glycerol to glycols (Feng *et al.*, 2008).

The reaction activity of TiO₂-supported catalyst decreased with increasing catalyst reduction temperature, which was attributed to two reasons: (1) the growth in Ru particle size caused by heating treatment; and (2) the strong metal-support interaction (SMSI), which resulted in partial coverage of Ru metal particles by Ti_2O_3 species.

Sitthisa (2007) investigated the dehydroxylation reaction at 250°C and 3.4 MPa H₂ pressure using 10% Cu/Al₂O₃ as a catalyst. The results showed that 100% conversion and 90% selectivity were obtained. However, the conversion dropped drastically after 6 h. Swangkotchakorn (2008) introduced ZnO into Cu/Al₂O₃ catalyst and found that the addition of ZnO could prolong the stability of the catalyst by reducing the metal-support interaction to form aluminum copper, which may be the cause of catalyst deactivation. In addition, ZnO hindered the grain growth of CuO (El-Shobaky *et al.*, 1999), leading to higher dispersion of copper phase.

By analyzing the above cases, we found that various catalysts have been attempted for the reaction of glycerol to propylene glycol, among which heterogeneous copper-containing catalysts exhibit superior performances by enabling to hydro-dehydrogenation of carbon–oxygen bonds (Cant *et al.*, 1985). In addition, zinc oxide surfaces possess acid sites for glycerol dehydration (Wang *et al.*, 2007)

such that glycerol can be converted to reaction intermediates without the deactivation of catalyst according to the presence of aluminum copper. These considerations have led us to focus on Cu/ZnO catalysts.

After first making a selection among various basis materials when starting to prepare the catalyst, it also becomes necessary to choose proper support. It is well known that a small variation in the catalyst support can induce evident changes of surface structure and bring about different reaction performances.

Saito $et\ al.$ (1994, 1996) studied the role of metal oxides such as Ga_2O_3, Al_2O_3, ZrO_2 and Cr_2O_3 contained in Cu/ZnO-based ternary catalysts for methanol synthesis from CO_2 and H_2. The activities of methanol synthesis were different for the various catalysts, indicating the order of metal oxide was Ga_2O_3 > ZnO > Cr_2O_3 > ZrO_2 $\approx$ Al_2O_3 > SiO_2. The role of metal oxides can be classified into two categories: (1) Al_2O_3 or ZrO_2 improved the surface area of Cu, i.e., the dispersion of Cu particles in the catalyst, and (2) Ga_2O_3 and Cr_2O_3 increased the specific activity by optimizing the ratio of Cu^+/Cu^0 on the surface of Cu particles.

Francesco $et\ al.$ (2008) carried out the CO_2 hydrogenation to CH_3OH using Cu-ZnO/ZrO$_2$ catalysts. Characterization data indicated that ZnO promoted the dispersion and reactivity of metal copper to oxygen, while both ZnO and ZrO_2 support markedly enhance the surface CO_2 adsorption.

The activity of the various CuO species found in supported copper catalysts was studied during the complete oxidation of methane (Aguila $et\ al.$, 2008). Series of copper catalysts supported on ZrO_2, Al_2O_3, and SiO_2 with different metal concentration were investigated. It was found that the Cu species formed on ZrO_2 and Al_2O_3 are dependent on the metal loading/support's surface area ratio, and the activity of highly dispersed Cu is substantially higher than that of bulk CuO. In case of silica, only formation of bulk CuO was detected, accounting for the low activity of CuO/SiO$_2$. The activity of highly dispersed Cu species formed on ZrO_2 is higher than those formed over Al_2O_3, and it is not significantly affected by the formation of bulk CuO on the surface. On the contrary, the activity of copper species formed on alumina decreases continuously as the Cu loading is increased. Thus, for the range of copper loading studied in this work, the activity of the catalysts, per gram of loaded Cu, follows the sequence: CuO/ZrO_2 > CuO/Al_2O_3 >> CuO/SiO_2.

2.5.2 Production of 1.3-propanediol from Glycerol

There are two examples for the synthesis of 1,3-propanediol based on petrochemicals: the first one is the Shell process consisting of the hydroformylation of ethylene oxide to 3-hydroxypropanal followed by hydrogenation to 1,3-propanediol. The second is the Degussa–DuPont process based on the hydration of acrolein to 3-hydroxypropanal and further hydrogenation analogue to the Shell process (Figure 2.8).
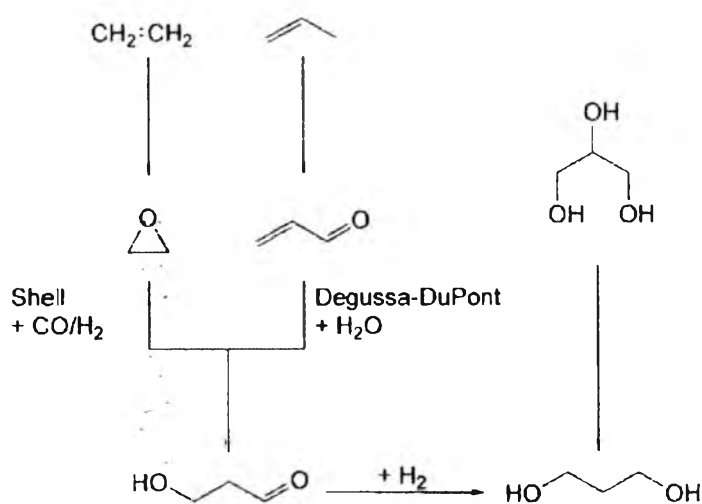

Figure 2.8 Different routes to 1,3-propanediol starting from ethene, propene or glycerol (Behr *et al.*, 2008).

Problems in the conventional processes are the high pressure applied in the hydroformylation and hydrogenation steps, as well as the use of aromatic solvents in the first and loss of acrolein due to extraction processes in the second example. The yields are around 80% in the first and about 40% in the second process (Behr *et al.*, 2008), so besides the demand of renewable sources like glycerol, there is also a huge interest in improving yields and overall selectivity of the processes applied. Therefore, the reaction from glycerol to 1,3-propanediol via biocatalyst, homogeneous, or heterogeneous catalysts may become an attractive alternative, which are described as follows.

2.5.2.1 Biocatalyst

Glycerol can be converted to 1,3-propanediol via 3-hydroxypropanal in a one-step enzymatic reaction in an aqueous solution at room temperature and ambient pressure with yields > 85% (Behr *et al.*, 2008). The fermentation of glycerol to synthesize 1,3-propanediol has been studied in detail for various bacterial strains of *Citrobacter*, *Enterobacter*, *Ilybacter*, *Klebsiella*, *Lactobacillus*, *Pelobacter*, and *Clostridium* (Yazdani *et al.*, 2007).

2.5.2.2 Homogeneous Catalyst

A typical advantage of homogeneous catalysts is their high selectivity, which can be explained by the well known mechanisms via organometallic species. Successful systems (Che *et al.*, 1987) to convert glycerol to 1,3-propanediol using homogeneous rhodium complex catalyst $Rh(CO)_2(acac)$ were developed, which led to a 20% selective conversion to 1,3-propandiol at 200°C and 32 MPa pressure.

Wang *et al.* (2003) described the selective production of 1,3-propanediol from glycerol using p-toluenesulfonic acid (Figure 2.9). The idea was to selectively transform the second hydroxyl group of glycerol into a tosyloxyl group (tosylation) and then to remove the transformed group by catalytic hydrogenolysis (detosyloxylation). This new approach involved three steps, namely acetalization, tosylation, and detosyloxylation. A yield of 1,3-propanediol was as high as 72%.

2.5.2.3 Heterogeneous Catalyst

Using hereterogeneous catalyst in the production of 1,3-propanediol from glycerol has not been satisfactory achieved.

Chaminand *et al.* (2004) studied the catalytic hydrogenolysis of glycerol in sulfolane system. It was found that high glycerol conversion (32%) was observed and the yield of 1,3-propanediol (4%) was twice that of 1,2-propanediol (2%). It was also noted that the presence of iron dissolved in the reaction medium can improve the selectivity to 1,3-propanediol.
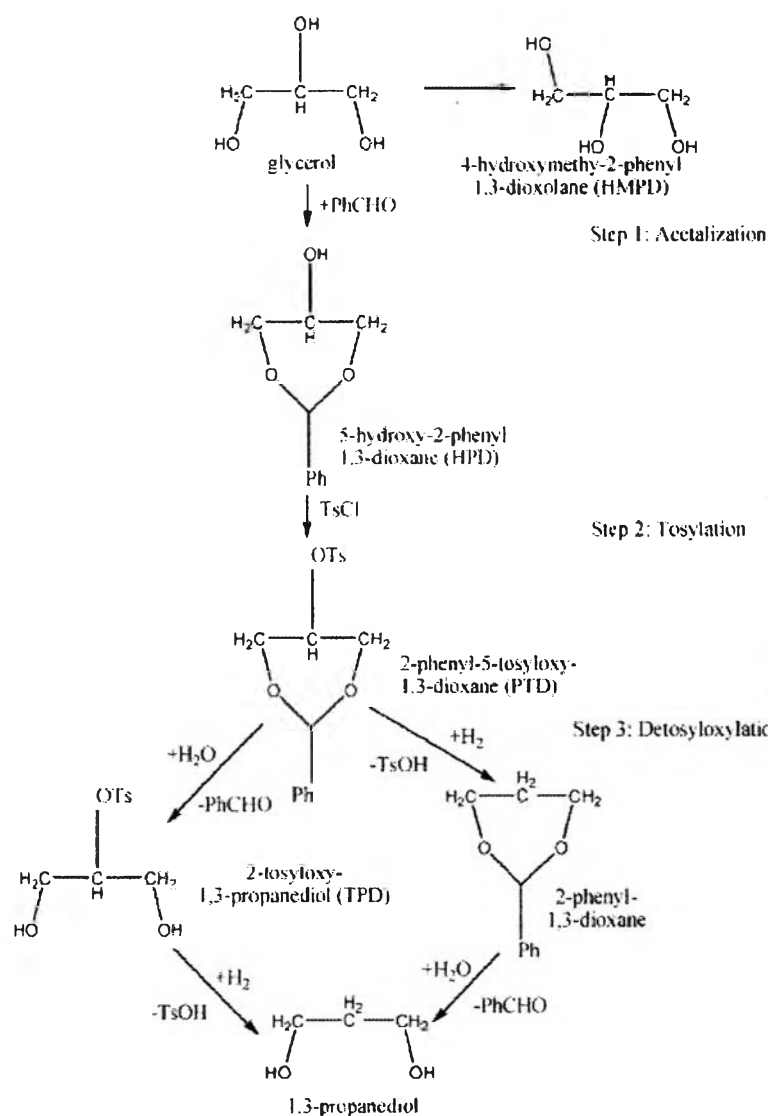
Figure 2.9 Conversion of glycerol to 1,3-propanediol via selective dehydroxylation in three steps (Wang et al., 2003).

Mizayawa et al. (2006) have proposed that 1,3-propanediol can be formed from dehydration of glycerol to 3-hydroxypropionaldehyde and subsequent hydrogenation over Ru/C catalyst, as shown in Figure 2.10.

Kurosaka et al. (2008) catalyzed glycerol hydrogenolysis using Pt/WO$_3$/ZrO$_2$ to yield 1,3-propanediol up to 24%. The sequence of catalyst preparation was also investiagated, and it was found that impregnation of WO$_3$ and then Pt on ZrO$_2$ was necessary to make effective catalyst. They suggested that the

active site for hydrogenolysis of glycerol to 1,3-propanediol may be Pt on WO_3 supported on ZrO_2.
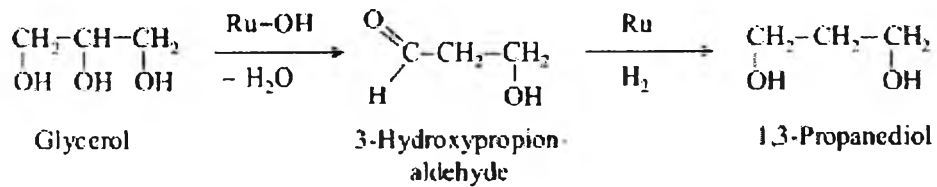
Figure 2.10 Proposed mechanism for conversion of glycerol to 1,3-propanediol via 3-hydroxypropionaldehyde (Miyazawa et al., 2006).

2.6 Preparation of Supported Metal Catalysts

Supported metal oxide comprises a large class of catalytic materials used in numerous industrial processes. There are conventional approaches to preparing these materials. In this section, the most common techniques for preparation of supported metal catalysts will be discussed, including impregnation, and co-precipitation.

2.6.1 Impregnation

Impregnation is a preparation technique in which a solution of the precursor of the active phase is brought in contact with the support. Two methodologies exist. In dry impregnation, also referred to as "pore volume impregnation", just enough liquid (solution of the precursors) is used to fill the pore volume of the support. In wet impregnation, the support is dipped into an excess quantity of solution containing the precursor(s) of the impregnated phase. In dry impregnation, the solubility of the catalyst precursors and the pore volume of the support determine the maximum loading available each time of impregnation. If a high loading is needed, successive impregnations (and heat treatments) may be necessary. When several precursors are present simultaneously in the impregnation solution, the impregnation is called "co-impregnation" (Anderson and García, 2005).

2.6.2 Precipitation

Co-precipitation differs from the other methods significantly. It is a method by which a solid is precipitated from a solution containing soluble precursors of both the support and surface oxides. Nucleation of the solid phase is initiated by mixing the solution with precipitating agent that either (1) change the solution pH and leads to precursor condensation to form oxide or hydroxides, or (2) " introduces additional ions into the system by which the solubility product for a certain precipitates is exceeded" (Schüth and Unger, 1997). Filtration and washing of counterions from the precipitate yield the final solid. The resultant architecture of the coprecipitated binary framework is more spatially distributed than a restrict supported metal oxide material prepared by the above methods. The distinct structure allows for better interaction between support and active species but also results in partial exclusion of the active species from the surface, rendering it inaccessible for catalysis. Surface density calculations for resulting materials thus overestimate actual value.

Inverse coprecipitation offers an improved alternative to co-precipitaton. A limitation for coprecipitaton is that the support and metal oxide precursors are unlikely to share similar solubilities (i.e., solubility products). Consequently, dropwise addition of a precipitating agent generates solids dominated by the more insoluble precursor during early stages and rich in the latter precursor at late stages. This gives rise to temporal-spatially inhomogeneous compositions. By contrast, inverse co-precipitation adds the precursor mixture dropwise to an excess of precipitating agent, this approach ensures that a strict ratio of precursors is maintained throughout the course of batchwise addition and leads to better co-precipitate homogeneity.

Tanaka *et al*. (2003) optimized a composition of $Cu/ZnO/Al_2O_3$ catalysts prepared by the impregnation method for water gas shift reaction (WGSR) coupled with CO oxidation in the reformed gas.The optimum composition of the impregnated catalyst for high WGSR activity was 5 wt.% Cu/5 wt.% ZnO/Al_2O_3. The optimum loading amounts of Cu and ZnO in the impregnated catalyst were smaller than those in the coprecipitated catalyst. Its catalytic activity above 200°C was comparable to that of the conventional coprecipitated $Cu/ZnO/Al_2O_3$ catalyst.

However, the activity of the impregnated Cu/ZnO/Al$_2$O$_3$ catalysts was significantly lowered at 150°C, whereas no deactivation was observed for the coprecipitated catalyst at the same temperature. It was found that deactivation occurred over impregnated catalysts with H$_2$O and/or O$_2$ in the reaction gas; it prevented CO adsorption on the surface.

2.6.3 Role of Calcination

Calcination (also known as annealing, thermolysis, or pyrolysis) exposes the as-prepared catalyst precursor to high temperatures for the final step in the formation of finished metal oxide catalysts. Although specifically referring only to heat treatment, calcination is commonly used to imply all the process variables associated with the furnace: composition of the gas phase atmosphere in contact with the catalyst (e.g., oxidizing, reducing, inert, functionalizing) and the thermal profile (e.g., ramp rate, hold temperatures, and hold times). The source of thermal energy is not considered critical and includes conversion and microwave ovens. The impact of gas pressure and thermal cooling rate are considered negligible.

There are several purposes for calcinations. If the support oxide is formed in a separate step before addition of the surface oxide, calcination may be used to lock in the support's surface aea, pore structure, and crystalline phase. The primary use of calcinations is to thermally decompose nonoxidic precursors, remove unwanted ligands, and oxidize the support and surface species. Precursor counterions consisting of hydrogen, carbon, or nitrogen often volatilize in the furnace and are swept away, leaving an impurity-free surface; counterions such as alkali and alkaline metals, halides, phosphates, and sulfides mostly remain on the surface and, if not washed, can participate as promoters or poisons in the final catalyst. Proper selection of gas composition permits control of the final oxidation state of the support and surface metal centers. After oxidation (or reduction) of the precursors, calcinations provides thermal energy to activate wetting and spreading as the Tammann temperature of the surface oxide is approached. Unfortunately, calcinations temperature is not the sole variable affecting wetting; even when the surface oxide has sufficient thermal energy, unfavorable surface free energies between support and

surface oxide can lead to poor dispersion. The thermal energy of calcinations also controls the crystalline phase and grain size of the support and surface oxides.

Calcination is one of the two main variables used to control surface density, the other is surface oxide concentration. At a constant calcination temperature, increasing the loading of surface oxide directly increases the surface density of that species. Perhaps lass intuitively, increasing calcinations temperature at a constant metal oxide loading can also increase surface density. Higher temperature would cause the support to crystallize, and as crystallization progresses, the pore walls of the support cannot withstand the growing internal stresses leading to pore collapse and the consequent loss of surface area.

Yahiro *et al.* (2006) studied the effect of calcination temperature on the catalytic activity for water-gas-shift (WGS) reaction was investigated for Cu/Al_2O_3 catalysts prepared by the impregnation method. The catalyst calcined at 1073 K, followed by the treatment in H_2 at 523 K, showed a high activity for WGS reaction. XRD and H_2-TPR measurements revealed that the catalyst calcined at 800°C contained both highly dispersed CuO and spinel $CuAl_2O_4$ particles. The former species was reduced by the treatment in H_2 at 523 K to yield the highly dispersed metallic copper which would act as catalytically active sites in WGS reaction.

Kim (2002) investigated the conversion as a function of temperature for complete oxidation of toluene over 15wt.% Cu/Al_2O_3 catalysts, prepared at different calcination temperatures. It was found that increasing the calcination temperature resulted in decreasing the conversion. It appeared that decreasing the conversion with increasing the calcinations temperature is associated with decreasing the specific surface area, which can resulted in losing the active sites.

2.7 Deactivation and Regeneration

The classic definition of a catalyst is a substance which alters the rate at which a chemical reaction occurs, but is itself unchanged at the end of the reaction. It is a practical reality, however, that catalysts deactivate over time. Catalyst life may be as short as few seconds, as in fluid catalytic cracking (FCC), or as long as several

years for ammonia synthesis but, inevitably, the catalyst will need regeneration or replacement.
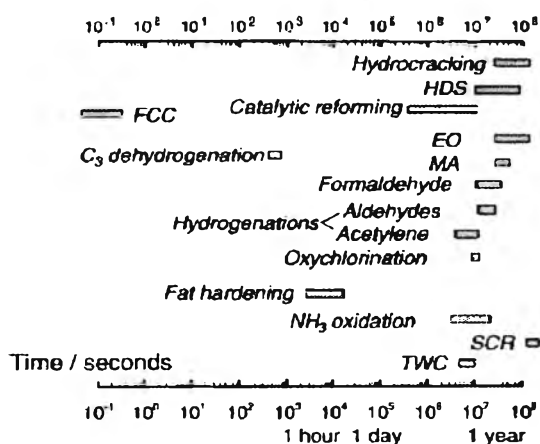

Figure 2.11 Time scale of deactivation of various catalytic processes (Moulijin *et al.*, 2001). ·

The efficiency of a catalyst is assessed in terms of the activity and selectivity of the catalyzed reaction and of catalyst life. The five main causes of deactivation are poisoning, fouling, thermal degradation (sintering, evaporation) initiated by the often high temperature, mechanical damage and corrosion/leaching by the reaction mixture.

Table 2.4 Mechanisms of catalyst deactivation (Bartholomew, 2001)

Mechanism	Type	Brief definition/description
Poisoning	Chemical	Strong chemisorption of species on catalytic sites, thereby blocking sites for catalytic reaction
Fouling	Mechanical	Physical deposition of species from fluid phase onto the catalytic surface and in catalyst pores
Thermal degradation	Thermal	Thermally induced loss of catalytic surface area, support area, and active

|		phase–support reactions
Vapor formation	Chemical	Reaction of gas with catalyst phase to produce volatile compound
Vapor–solid and	Chemical	Reaction of fluid, support, or promoter with solid–solid reactions catalytic phase to produce inactive phase
Attrition/crushing	Mechanical	Loss of catalytic material due to abrasion. Loss of internal surface area due to mechanical-induced crushing of the catalyst particle
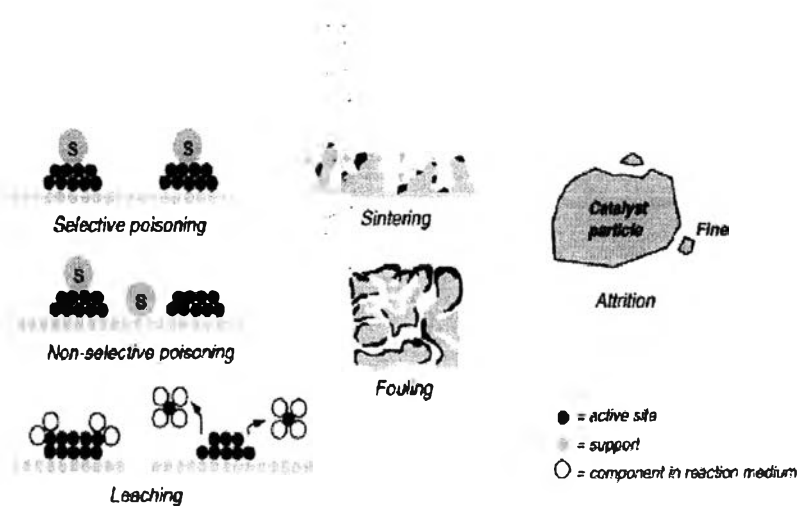
Figure 2.12 Major types of deactivation in heterogeneous catalysis (Moulijin *et al.*, 2001).

2.7.1 Poisoning

The activity of a catalyst is dictated by only a fraction of the total available surface. If those active sites react with a second chemical then the nature of the surface changes and the catalytic activity changes. If such changes are positive, the phenomenon is known as doping, if negative, as poisoning. A catalyst poison is a component such as a feed impurity that as a result of chemisorptions, the strong

interaction between a component of the feed or products and the active site, causes the catalyst to loss a substantial fraction of its activity.
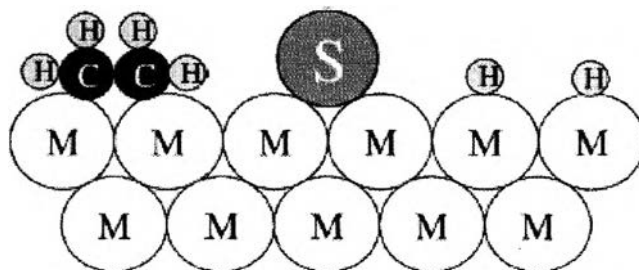

Figure 2.13 Conceptual model of poisoning by sulfur atoms of a metal surface during ethylene hydrogenation (Bartholomew, 2001).

Table 2.5 Common poisons classified according to chemical structure (Bartholomew, 2001)

Chemical type	Examples	Type of interaction with metals
Groups VA and VIA	N, P, As, Sb, O, S, Se, Te	Through s- and p-orbitals; shielded structures are less Toxic
Group VIIA	F, Cl, Br, I	Through s- and p-orbitals; formation of volatile halides
Toxic heavy metals and ions	As, Pb, Hg, Bi, Sn, Zn, Cd, Cu, Fe	Occupy d-orbitals; may form alloys
Molecules which adsorb with multiple bonds	CO, NO, HCN, benzene, acetylene, other unsaturated hydrocarbons	Chemisorption through multiple bonds and back bonding

The first group of poisons involve Group VA and VIA elements, including N, P, As and Sb (VA) and O, S, Se and Te (VIA). The elements poison

metal catalysts by interaction through their S and P orbitals and the importance of the poisoning effect can be changed by changing the number of bonding electrons — for example, by oxidation or reduction.Thus, the poison efficiency of sulphur increases as $SO_4^{2-} < SO_2 < H_2S$.

The second group of poisons is much harder to remove, since toxic heavy metals such as Pb, Hg, Cd, Cu, etc. may form alloys with the catalyst. The third group of poisons involves molecules that can chemisorb strongly to a catalyst and are entirely specific (Trimm, 2001).

Poisoning selectivity is illustrated in Figure 2.35, a plot of activity (the reaction rate normalized to initial rate) versus normalized poison concentration. "Selective" poisoning involves preferential adsorption of the poison on the most active sites at low concentrations. If sites of lesser activity are blocked initially, the poisoning is "anti-selective". If the activity loss is proportional to the concentration of adsorbed poison, the poisoning is "non-selective".
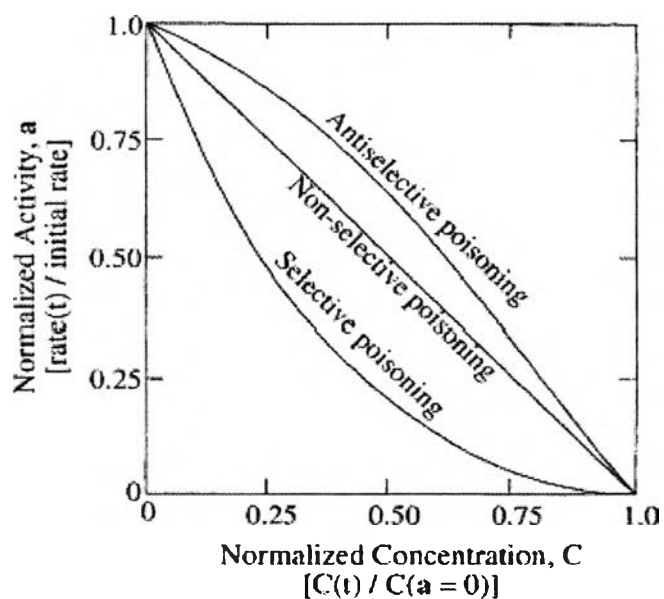

Figure 2.14 Three kinds of poisoning behavior in terms of normalized activity vs. normalized poison concentration (Bartholomew, 2001).

2.7.2 Fouling

Fouling is the physical (mechanical) deposition of species from the fluid phase onto the catalyst surface, which results in activity loss due to blockage of sites and/or pores. In its advanced stages it may result in disintegration of catalyst particles and plugging of the reactor voids.

The various forms of carbonaceous deposits, known collectively as coke which is a carbonaceous material of various compositions, often aromatic with high molecular weight and a typical composition of approximately CH, are by far the most common catalyst foulants.

All carbonaceous deposits may be removed by gasification or washing. The preferred route is gasification of coke with oxygen because of the efficiency and fastness, however, careful control of temperature is essential. On the other hand, washing is not a possibility often considered, but it can be effective in some case. Heck *et al.* (1994) report the effects of acid and alkali wash for organic abatement catalysts and for a platinum coated monolith. In the latter case, alkali washing removed most of the unwanted inorganic material. Washing may physically displace material or may result in a chemical reaction to form a soluble salt. The latter case is dealt with more thoroughly in the context of catalyst leaching.

2.7.3 Thermal Degradation

Thermal degradation is a physical process leading to catalyst deactivation because of sintering, chemical transformations, evaporation, etc. Thermally induced deactivation of catalysts results from (i) loss of catalytic surface area due to crystallite growth of the catalytic phase, (ii) loss of support area due to support collapse and of catalytic surface area due to pore collapse on crystallites of the active phase, and/or (iii) chemical transformations of catalytic phases to non-catalytic phases. The first two processes are typically referred to as "sintering".

Three principal mechanisms of metal crystallite growth have been advanced:

(1) crystallite migration

(2) atomic migration

(3) vapor transport (at very high temperatures)

The processes of crystallite and atomic migration are illustrated in Figure 2.36. Crystallite migration involves the migration of entire crystallites over the support surface followed by collision and coalescence. Atomic migration involves detachment of metal atoms from crystallites, migration of these atoms over the support surface and ultimately, capture by larger crystallites.

Sintering of metal particles resulting in loss of active surface area is an irreversible cause of catalyst deactivation. As a general rule, the rearrangement of most solids will start to occur at ca. 0.3–0.5 times the melting point of the material (Trimm, 2001)

Temperature, atmosphere, metal type, metal dispersion, promoters impurities and support surface area, texture and porosity, are the principal parameters affecting rates of sintering and redispersion (see Table 2.4). Sintering rates increase exponentially with temperature. Metals sinter relatively rapidly in oxygen and relatively slowly in hydrogen, although depending upon the support, metal redispersion can be facilitated by exposure at high temperature.
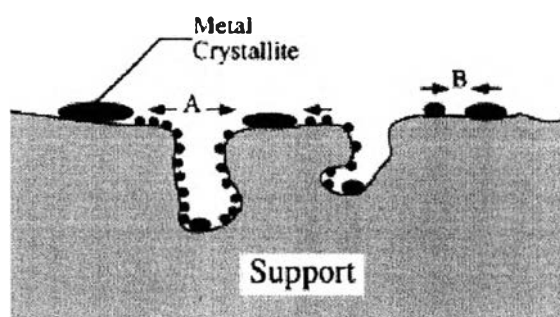

Figure 2.15 Two conceptual models for crystallite growth due to sintering by (A) atomic migration or (B) crystallite migration (Bartholomew, 2001).

In reducing atmosphere, metal crystallite stability generally decreases with decreasing metal melting temperature, i.e. in the order Ru > Ir > Rh > Pt > Pd > Ni > Cu > Ag, although this order may be affected by relatively stronger metal–support interactions. For noble metals, metal stability in air decreases in the order Rh > Pt > Ir > Ru. Promoters or impurities affect sintering and redispersion by either

increasing (e.g. chlorine and sulfur) or decreasing (e.g. oxygen, calcium and cesium) metal atom mobility on the support. Similarly, support surface defects or pores impede surface migration of metal particles, especially micropores and mesopores with pore diameters about the same size as the metal crystallite.

Table 2.6 Effects of important reaction and catalyst variables on sintering rates of supported metals based on GPLE data (Bartholomew, 2001)

Variable	Effect
Temperature	Sintering rates are exponentially dependent on T; E_{act} varies from 30 to 150 kJ/mol; E_{act} decreases with increasing metal loading; it increases in the following order with atmosphere: NO, O_2, H_2, N_2
Atmosphere	Sintering rates are much higher for noble metals in O_2 than in H_2 and higher for noble and base metals in H_2 relative to N_2; sintering rate decreases for supported Pt in atmospheres in the following order: NO, O_2, H_2, N_2
Metal	Observed order of decreasing thermal stability in H_2 is Ru > Ir $\approx$ Rh > Pt; thermal stability in O_2 is a function of (1) volatility of metal oxide and (2) strength of metal oxide–support interaction
Support	Metal–support interactions are weak (bond strengths of 5–15 kJ/mol); with a few exceptions, thermal stability for a given metal decreases with support in the following order: Al_2O_3 > SiO_2 > carbon
Promoters	Some additives decrease atom mobility, e.g. C, O, CaO, BaO, CeO_2, GeO_2; others increase atom mobility, e.g. Pb, Bi, Cl, F, or S; oxides of Ba, Ca, or Sr are "trapping agents" that decrease sintering rate

Pore size	Sintering rates are lower for porous vs. non-porous supports; they decrease as crystallite diameters approach those of the pores

2.7.4 Mechanical Deactivation

Mechanical strength is important in giving the catalyst resistance against crushing, e.g. during transport and loading of the catalyst in the reactor.

2.7.5 Corrosion/leaching

Leaching of catalyst in the reaction medium is the main cause of deactivation in liquid phase reactions. As far as metal catalysis is concerned, leaching of metal atoms depends upon the reaction medium (pH, oxidation potential, chelating properties of molecules) and upon bulk and surface metal properties (Besson and Gallezot, 2003)

From the observation, the three main causes of catalyst deactivation are fouling, poisoning, or thermal degradation. In fouling and poisoning, the phenomenon is often reversible while the lattes case is irreversible.

Arena (1992) studied several Ru/Al_2O_3 glucose hydrogenation catalysts in operating condition. The spent catalysts were tested to determine the cause of deactivation. From the experiments, the changes in physical properties of Al_2O_3 support due to the agglomeration of ruthenium were observed. The observation detected the existence of D-gluconic acid formation on the catalyst. However, the regeneration of the catalyst can be done by washing the strongly adsorbed acidic species out from the catalyst within basic medium.

Mallat *et al.* (1995) studied selective oxidation of cinnamyl alcohol to cinnamaldehyde with air over Bi-Pt/Alumina catalysts. The cause of deactivation was due to the formation of poison species during the initial adsorption of cinnamyl alcohol on surface Pt atom since the amount of hydrogen adsorbed on Pt decreased rapidly when cinnamyl alcohol was present. The other source of deactivation was from the byproducts and catalyst poison when oxidation reaction occurred. However, the decrease in active sites due to the geometric (block) effect of Bi promotion could

reduce the initial, destructive adsorption of cinnamyl alcohol and the chemisorption of bulky byproducts formed during reaction.

Zhu and Hofman (1996) studied deactivation of $Ni/SiO_2/Al_2O_3$ catalyst in hydrogenation of 3-hydroxypropanal (3-HPA) solution at temperature 45-80°C and pressure 2.60-5.15 MPa. The experimental results showed that hydrogen concentration in liquid phase and dissolution of nickel were not the reasons for the deactivation, on the contrary, the adsorption of by-products and some poison are the reasons for the loss of active site due to the blockage of the specific area (S_{meso}) from 117 m^2/g to 106 m^2/g and the mesopore radius (r_{meso}) from 1.9 nm to 2.2 nm.

Twigg and Spencer (2001) studied deactivation of supported copper metal catalysts for hydrogenation reactions. The major problems for deactivation are sintering and poisoning. Since copper has lower stability due to the low melting (1083°C) when it was compared to other metals such as nickel (1455°C) or iron (1535°C). Therefore, copper catalysts have strong tendency to thermal sintering via a surface migration process. Careful control of temperature is necessary, usually below 300°C. However, when catalysts were operated at low temperature, their surfaces were covered by the adsorption of poisons due to the thermodynamically favours. As a result, copper catalysts are extremely sensitive towards site-blocking poisons. On the contrary, the fouling of coke deposit is not considered as the cause of deactivation because copper has a very low activity for breaking C-O bonds or forming C-C bonds.

Besson et al. (2003) studied the catalytic hydrogenation of aqueous solution 3-hydroxypropanal (3-HPA) to produce 1,3-propanediol by using heterogeneous ruthenium catalysts at 40-60°C and 40 bar hydrogen. The ruthenium catalysts on titania supports was observed to be more stable at high temperature compare to SiO_2 support. By the experiments, 3 wt% Ru/TiO_2 P25 at LHSV = 2 h^{-1} gave the conversion of HPA 69.9% at 24 h and 67.3% after 100 h while 3.7% Ru/SiO_2 at LHSV = 1 h^{-1} exhibited high conversion of 99.8% at 24 h and decreased to 76.2% after an addition time of 75 h. Ruthenium catalysts supported on low surface area, non-porous TiO_2 XT90045 gave high stability, activity and selectivity compare to TiO_2 P25 because high molecular weight impurity do not deposit on the

low surface molecule. TEM also showed that decomposition of organic oligomers on the catalyst surface was the reason for the deactivation.

Wang *et al.* (2007) studied deactivation and regeneration of titanium silicalite catalyst for epoxidation of propylene to produce 1,2-propanediol. After the spent catalysts ware regenerated, the characterization from SEM, BET, XRD, FT-IR, 29Si MAS NMR and TGA were conducted. The results showed that the deposition on the external surface of ether, dimeric compound and oligomers as byproducts, and blockage of the channel of the catalyst from 1,2-propanediol and propylene glycol isopropyl ether as byproducts are the major reasons for the deactivation phenomenon. In addition, the calcination and washing with dilute hydrogen peroxide were highly effective regeneration methods to recover the catalytic activity since hydrogen peroxide can oxidize bulky by-products to form small molecular compounds which could easily diffuse out of the pore and the complete oxidation reaction of the organic compounds can occur at high temperature.