CHAPTER II
LITERATURE REVIEW

2.1 Properties of Glycerol

Glycerol (1,2,3-propanetriol, Figure 2.1) is a colorless, odorless, viscous liquid with a sweet taste, derived from both natural and petrochemical feedstocks. The name glycerol is derived from the Greek word for ''sweet,'' *glykys*, and the terms glycerin, glycerine, and glycerol tend to be used interchangeably in the literature. On the other hand, the expressions glycerin or glycerine generally refer to a commercial solution of glycerol in water of which the principal component is glycerol. Crude glycerol is 70–80% pure and is often concentrated and purified prior to commercial sale to 95.5–99% purity.

Glycerol is one of the most versatile and valuable chemical substances known to man. In the modern era, it was identified in 1779, by Swedish chemist Carl W Scheele, who discovered a new transparent, syrupy liquid by heating olive oil with litharge (PbO, used in lead glazes on ceramics). It is completely soluble in water and alcohols, is slightly soluble in many common solvents such as ether and dioxane, but is insoluble in hydrocarbons. In its pure anhydrous condition, glycerol has a specific gravity of 1.261 gmL^{-1}, a melting point of 18.2 ^{o}C and a boiling point of 290 ^{o}C under normal atmospheric pressure, accompanied by decomposition. At low temperatures, glycerol may form crystals which melt at 17.9 ^{o}C. Overall, it possesses a unique combination of physical and chemical properties (Table 2.1), which are utilized in many thousands of commercial products.2 Indeed, glycerol has over 1500 known end uses, including applications as an ingredient or processing aid in cosmetics, toiletries, personal care products, pharmaceutical formulations and foodstuffs.3 In addition, glycerol is highly stable under normal storage conditions, compatible with many other chemical materials, virtually non-irritating in its various uses, and has no known negative environmental effects (Pagliaro *et al.*, 2010).

Table 2.1 Physicochemical properties of glycerol at 20 °C. (Raton, 2006)

Chemical formula	$C_3H_5(OH)_3$
Molecular mass	92.09382 g/mol^{-1}
Density	1.261 g/cm^{-3}
Viscosity	1.5 Pa.s
Melting point	18.2 °C
Boiling point	290 °C
Food energy	4.32 kcal/g
Flash Point	160 °C (closed cup)
Surface tension	64.00mN/m^{-1}
Temperature coefficient	–0.0598 $mN/(mK)^{-1}$

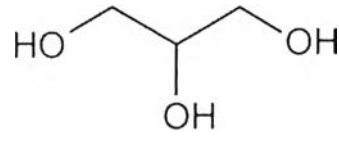

Figure 2.1 Structure of glycerol (Pagliaro *et al.*, 2010).

2.1.1 Types of Glycerol

Glycerol naturally occurs during the biodiesel production process and is specifically produced in the transesterification process. The glycerol produced at this stage is crude glycerol and is about 80% pure still containing contaminants like soap, methanol and water. In order to turn this crude glycerol into a usable state for existing or emerging uses, a purification process must take place. During this refinement process residual organic matter, water, salt, methanol, and odors are removed. There are many different types of glycerol grades ranging from crude glycerol, technical, yellow glycerol to refined glycerol. The specification of various glycerols is shown in Table 2.2

Table 2.2 Specification of glycerol feedstocks

Feedstocks	Glycerol (wt. %)	Methanol (wt. %)	MONG (wt. %)	Water (wt. %)	Ash (wt. %)
Refined glycerol	99.5	< 0.5	< 1	< 0.5	< 0.5
Yellow grade glycerol	80	< 1	< 20	< 1	< 0.1
Technical grade glycerol	> 80	< 1	< 2	< 10	< 7
Crude glycerol	50-60	2-5	<30	< 7	< 5

2.1.2 Industrial Production of Glycerol

Glycerol can be found naturally in the form of fatty acid esters and also as important intermediates in the metabolism of living organisms. Traditionally, glycerol is obtained as a by-product in four different processes: soap manufacture, fatty acid production, fatty ester production, and microbial fermentation. It can also be synthesized from propylene oxide.

Glycerol can be obtained from biomass *via* hydrolysis or methanolysis of triglycerides. The reactions for the direct transformation of vegetable oils and animal fats into methyl esters and glycerol have been known for over a century. However, it is only recently, following more than 10 years of research and development, that the transesterification of triglycerides, using rapeseed, soybean, and sunflower oils, has gained significance for its role in the manufacture of high quality biodiesel fuel.

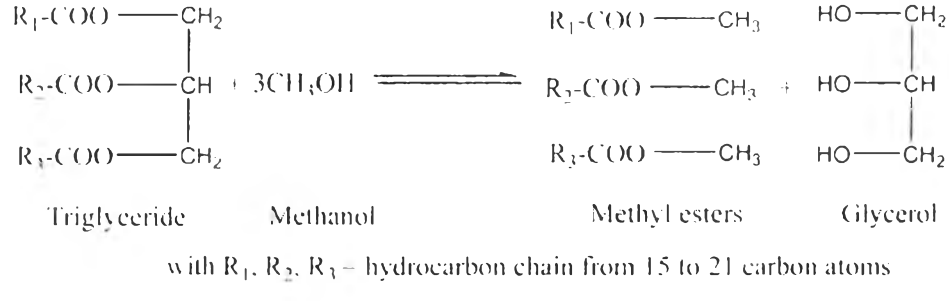

Figure 2.2 Overall reaction for production of biodiesel through vegetable oil methanolysis (Zhou *et al.*, 2008).

Glycerol is normally generated at the rate of 1 mol of glycerol for every 3 mol of methyl esters synthesized; approximately 10 wt% of the total product.

2.1.3 Commodity Chemicals Derived from Glycerol

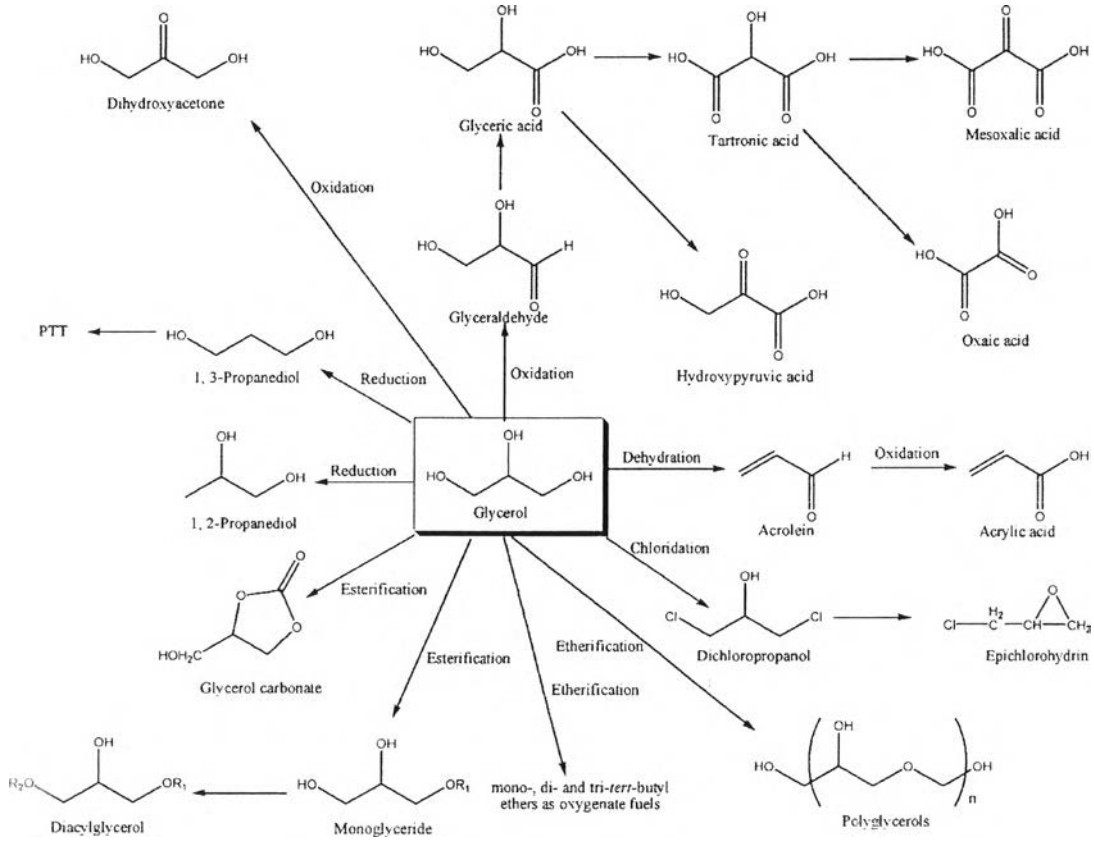

Figure 2.3 Commodity chemicals from glycerol (Zheng *et al.*, 2008).

The development of new applications for glycerol would be enthusiastically welcomed by the entire glycerol industry. The broadest-based opportunity for the effective consumption of glycerol will arise from its use as a primary chemical building block. Because of price and availability, many current uses of glycerol do not employ further transformation of its structure. Once it is recognized that a ready source of low cost glycerol is available from the biodiesel unit operation, glycerol could be positioned within the biorefinery as a primary renewable building block analogous to those of the petrochemical industry (methane, ethylene, BTX, etc.). As the price of glycerol drops and its availability rises, glycerol ceases to become an "additive" for a fragmented list of small volume products and

assumes a position as the starting point for the production of a smaller number of high volume materials. When the cost of a chemical drops, its range of industrial utility broadens, and the ability to absorb the cost of additional chemical transformations increases. Glycerol would transition from its current state as an advanced intermediate or chemical end product to a starting material for a large family of compounds. A number of opportunities for glycerol consumption have been identified and are summarized in Figure 2.3. (Zheng *et al.*, 2008)

The catalytic hydrogenolysis of glycerol to propanediols is one of the most attractive routes since it is a feasible and simple method that can convert the glycerol to high value-added products.

2.2 From Glycerol to Propanediols

Hydrogenolysis is 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. Through the selective hydrogenolysis of glycerol in the presence of metallic catalysts and hydrogen, glycerol can be converted to 1,2-propanediol and 1,3-propanediol, which are useful final products. Therefore, catalytic hydrogenolysis of glycerol is another alternative route to increase the profitability of biodiesel production plants as the products of glycerol hydrogenolysis can easily replace the chemical compounds, which at present are industrially produced mainly by using non-renewable sources.

1,2-propanediol (1,2-PDO) or propylene glycol, is an important medium-value commodity chemical with a 4% annual growth in the market size. The current global market for 1,2-propanediol is roughly 2 million tonnes annually. It is used for manufacturing high-performance unsaturated polyester resins, polyurethane foam systems, liquid detergents, pharmaceuticals, cosmetics, tobacco humectants, flavors and fragrances, personal care, paints, animal feed, antifreeze, etc. Traditionally, it is produced by the hydration of propylene oxide derived from propylene by either the chlorohydrin process or the hydroperoxide process. There has been a rapid expansion of the market for 1,2-propanediol as antifreeze and de-icing agents because of the growing concern over the toxicity of ethylene glycol-based products to humans and animals (Zhou *et al.*, 2008). 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 (Kenar, 2007).

1,3-propanediol (1,3-PDO) is also a high-value chemical that is an important compound in polymer production. 1,3-Propanediol is of interest as a reactant to prepare cyclic compounds and as a monomer for various types of polyesters, polyurethanes, polyethers. Polyesters prepared from 1,3-propanediol and terephthalic acid produce polyesters, known commercially as SORONA® from DuPont, or CORTERRA® from Shell, which has unique properties in terms of chemical resistance, light stability, elastic recovery, and dyeability (Zhou *et al.*, 2008). 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 as shown in Figure 2.4.

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, 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 heterogeneous, homogeneous or biocatalytic processes may become an attractive alternative (Behr *et al.*, 2008).

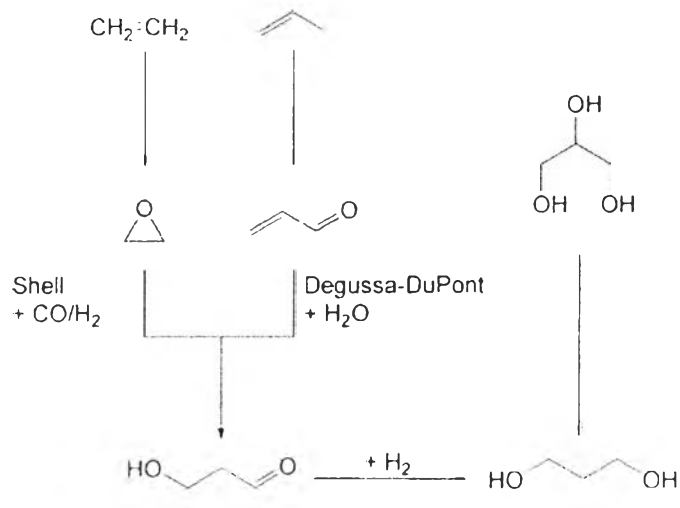

Figure 2.4 Different routes to 1,3-propanediol starting from ethene, propene or glycerol (Behr *et al.*, 2008).

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.

2.2.1 Production of 1,2-Propanediol from Glycerol

The present industrial way for manufacturing 1,2-propanediol (propylene glycol) is the hydrolysis of propylene oxide with water (Figure 2.5). After the reaction step, the mixture must be stripped and distilled to separate the product from water and the higher substituted polyols. Although there are further processes such as the acetoxidation of propene followed by hydrolysis or the direct hydroxylation catalysed by osmium compounds, the classical route based on propylene oxide is still widely used.

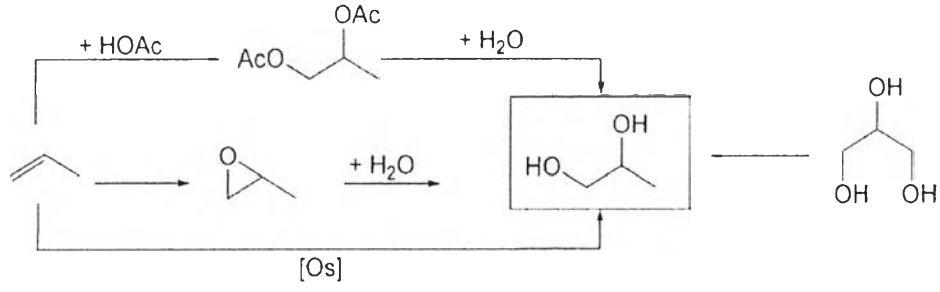

Figure 2.5 Comparison of the reaction routes to 1,2-propanediol starting from propene or glycerol (Behr *et al.*, 2008).

2.2.1.1 Type of the Catalysts to Convert Glycerol to 1,2-Propanediol

In particular, when 1,2-propanediol or its derivatives are applied in food, cosmetics or pharmaceutical products, the use of fossil raw materials is less favourable 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 section.

- *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. The aim of this project was the production of propylene glycol out of glycerol from the biodiesel industry at a factory in Europe. Cargill has already presented a process to obtain propylene glycol out of carbohydrates with *Escherichia coli* or *Thermoanaerobacterium thermosaccharolyticum* HG-8 (Behr *et al.*, 2008).

- *Homogeneous Catalyst*

In general the hydrogenolysis of glycerol by homogeneous catalysts leads to a variety of by-products such as propanol or ethers and to a mixture of 1,2- and 1,3-propanediol. The amount of different products depends on the mechanism of the product formation. 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, 1,3-propanediol and 1,2-propanediol were produced with 20% and 23% yield, respectively.

Schlaf *et al.* (2001) also described the catalytic hydrogenolysis of glycerol in sulfolane catalyzed by a homogeneous complex of ruthenium. The reaction proceeded under milder conditions at 110 °C and 5 MPa. But less than 5% yields of 1,2-PD and 1,3-PD were achieved. 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).

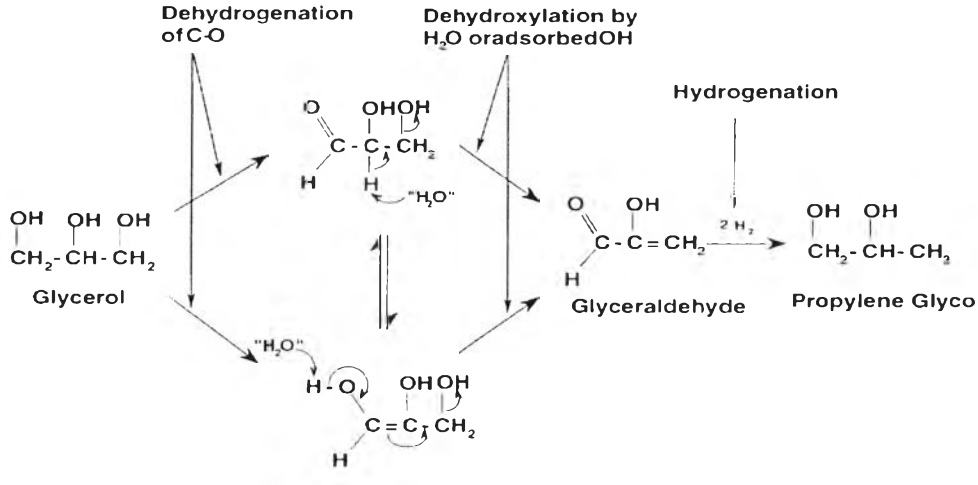

Figure 2.6 Reaction mechanism for conversion of glycerol to propylene glycol proposed by Montassier *et al.*

- *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 Ni, Ru, Rh and Ir catalysts. They found that mainly methane was produced, but when Raney Cu was used as a catalyst, 1,2-propanediol was the main reaction product. Raney Cu is known for its poor hydrogenolytic activity towards C–C bond but it is an efficient catalyst for C–O bond hydrogenation and dehydrogenation. A reaction mechanism

for conversion of glycerol to 1,2-propanediol proposed by Montassier *et al.* is shown in Figure 2.6.

Chaminand *et al.* (2004) studied the hydrogenolysis of glycerol in the presence of heterogeneous catalysts. Aqueous solutions of glycerol were hydrogenolysed at 180 °C and 8 MPa H_2 pressure for 90 hours. Among the various catalysts (Cu, Pd, Rh), supports (ZnO, C, Al_2O_3), solvents (H_2O, sulfolane, dioxane), and additive such as tungstic acid (H_2WO_4), the best selectivity (100%) to 1,2-propanediol was obtained when using CuO/ZnO catalysts.

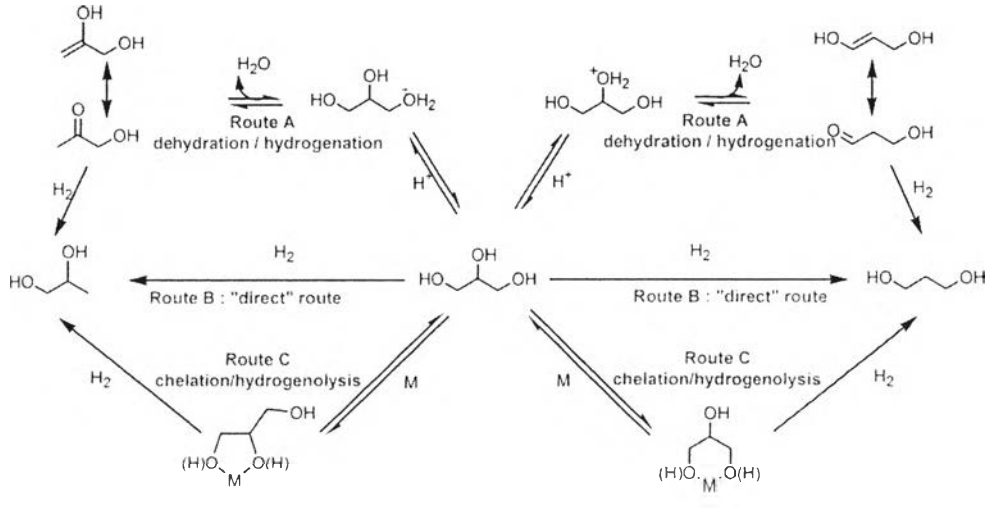

Figure 2.7 Possible reaction routes for catalytic hydrogenolysis of glycerol proposed by Chaminand *et al.* (2004).

To improve the selectivity to 1,3-propanediol the reaction was conducted with rhodium catalysts with tungstic acid added to the reaction medium. The best result in terms of conversion and selectivity to 1,3-propanediol (1,3-PDO/1,2-PDO = 2) was obtained by operating in sulfolane. A general mechanism can be proposed to explain the influence of the different parameters on the activity and selectivity of the reaction (Figure 2.7).

The diols can be formed *via* several routes. The tungstic acid can favour the dehydration route (route A) *via* protonation of the hydroxyl groups and loss of water. The keto group formed as intermediate can be easily reduced under the reaction conditions. However, the use of alternative acid (HCl) yielded low

conversion suggesting that the acidity of H_2WO_4 was not its dominant property for the considered reaction. Furthermore, the formation of a Rh–W catalyst cannot be excluded and can affect the selectivity and the activity of the hydrogenolysis. The addition of a second metal (Fe or Cu) in the reaction medium reduced the activity as if it poisoned the rhodium catalyst. Moreover, iron can be chelated by a diol and thus modifies the selectivity of the hydrogenolysis (route C).

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

Dasari *et al.* (2005) used the various types of commercial catalysts to study hydrogenolysis of a concentrated glycerol solution into propylene glycol under low pressure, as shown in Table 2.3. At temperatures above 200 °C and hydrogen pressure of 1.4 MPa, the selectivity to propylene glycol decreased due to excessive hydrogenolysis of the propylene glycol. The yield of propylene glycol increased with decreasing water content. Copper-chromite catalyst was identified as the most effective catalyst, yielding 73% of propylene glycol at moderate reaction conditions of 200 °C and 1.4 MPa. This result provides a very distinctive competitive advantage over traditional processes that use more severe reaction conditions.

A new reaction pathway for converting glycerol to propylene glycol via an intermediate was validated by isolating the acetol intermediate. In a two-step reaction process, the first step carried out at atmospheric pressure involves

the formation of 1-hydroxyacetone by the dehydration reaction while the hydrogenation second step requires a hydrogen partial pressure, as shown in Figure 2.8.

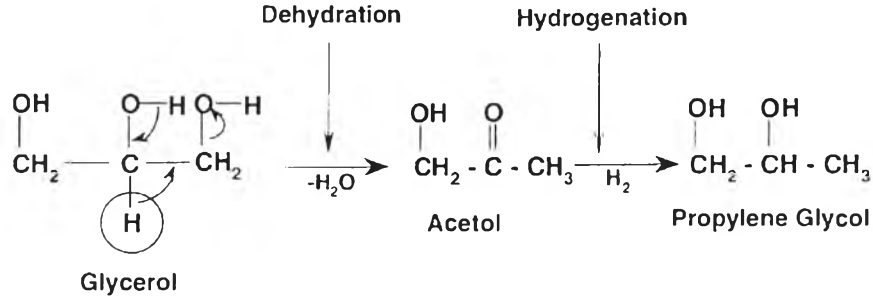

Figure 2.8 Proposed reaction mechanism for conversion of glycerol to propylene glycol (Dasari *et al.*, 2005).

Miyazawa *et al.* (2005, 2006) demonstrated that when active Ru, supported on carbon is used in combination with a cation exchange resin such as Amberlyst 15, it can exhibit higher activity in glycerol hydrogenolysis under mild reaction conditions (120 °C and 4 MPa or 8 MPa H_2) than other metal–acid bifunctional catalyst systems such as zeolites, sulfated zirconia, H_2WO_4, and liquid H_2SO_4. The Ru/C catalyst showed higher conversion than Rh/C, Pd/C, and Pt/C. However, the selectivity of cracking products was rather high over Ru/C, with the dehydration of glycerol to 1- hydroxyacetone being catalyzed by the acid catalysts. The subsequent hydrogenation of 1-hydroxyacetone on the metal catalysts gives 1,2-propanediol. Thus the addition of solid acid catalysts to Ru/C was effective in increasing the conversion and hydrogenolysis selectivity. A proposed reaction scheme for the hydrogenolysis of glycerol is shown in Figure 2.9.

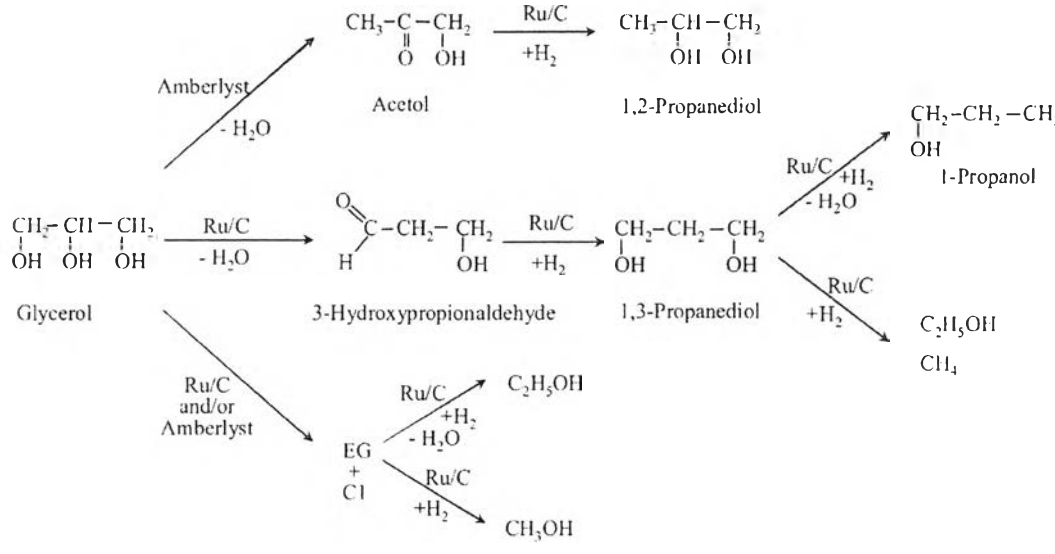

Figure 2.9 Reaction scheme of glycerol hydrogenolysis and degradation reactions (Miyazawa *et al.*, 2006).

During the hydrogenolysis reaction, the activity of the metal catalyst when combined with the cation exchange resin can be related to that of 1-hydroxyacetone hydrogenation over the metal catalysts. In addition, the OH group on Ru/C can also catalyze the dehydration of glycerol to 3-hydroxypropionaldehyde, which ultimately can be converted into 1,3-propanediol and other degradation products through subsequent hydrogenation. From these results Ru/C + H_2SO_4 showed lower activity than combined Ru/C+Amberlyst, suggesting that the solid acid was more effective for the hydrogenolysis of glycerol.

Wang *et al.* (2007) studied the hydrogenolysis of glycerol to propylene glycol over Cu/ZnO catalysts at 200 °C and 4.2 MPa H_2 pressure. Glycerol conversion and selectivity depend on Cu and ZnO particle sizes. Smaller ZnO and Cu domains led to higher conversion and propylene glycol selectivity, respectively. High propylene glycol selectivity (83.6%) was achieved at 22.5% glycerol conversion with Cu/ZnO atomic ratio of 1. These catalysts possess acid and hydrogenation sites required for bifunctional glycerol reaction pathways. The pathways may involve glycerol dehydration to dehydrated intermediates on acid sites of ZnO surfaces, followed by hydrogenation of the intermediates on Cu surfaces, as shown in Figure 2.10, where the two proposed dehydrated intermediates were acetol (1-hydroxyacetone) and glycidol (3-hydroxy-1,2-epoxypropane).

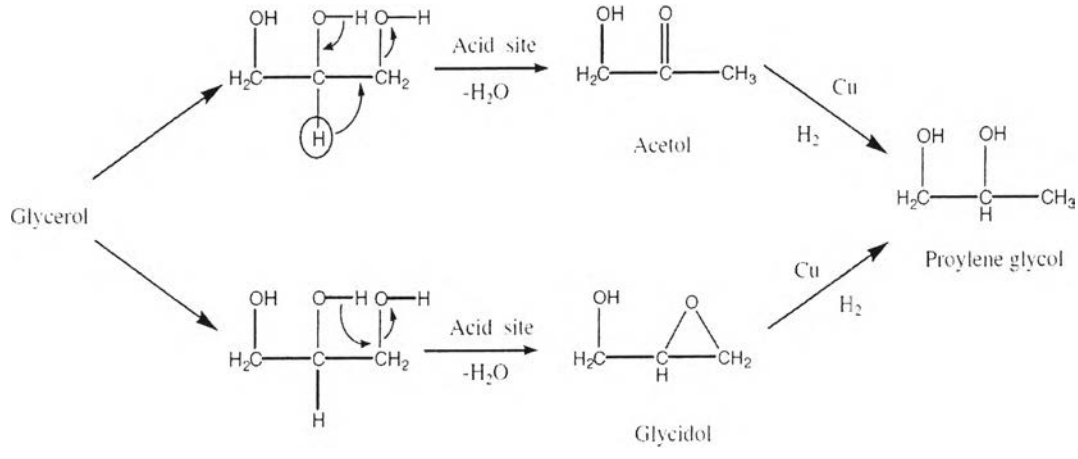

Figure 2.10 Proposed bifunctional glycerol hydrogenolysis reaction pathways (Wang *et al.*, 2007).

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 2.11.

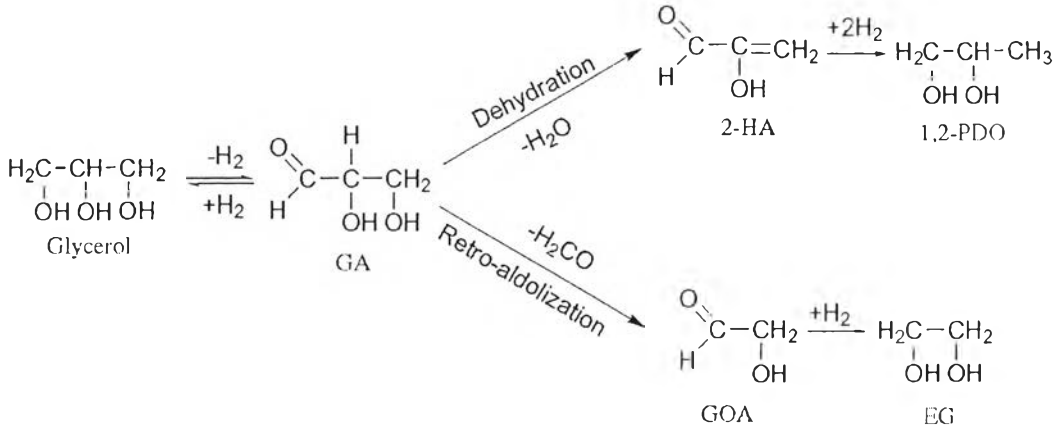

Figure 2.11 Reaction route for the hydrogenolysis of glycerol to glycols (Feng *et al.*, 2008). GA=glyceraldehyde, 2-HA=2-hydroxyacrolein, 1,2-PDO=1,2-propanediol, GOA=glycolaldehyde, and EG= ethylene glycol.

The reaction activity of TiO_2-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 *et al.* (2007) investigated the dehydroxylation reaction at 250 °C and 3.4 MPa H_2 pressure using 10% Cu/Al_2O_3 as a catalyst. The results showed that 100% conversion and 90% selectivity were obtained. However, the conversion dropped drastically after 6 h.

Swangkotchakorn *et al.* (2008) introduced ZnO into Cu/Al_2O_3 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.

Chirddilok *et al.* (2009) reported that the $Cu\text{-}ZnO/Al_2O_3$ catalyst showed the best catalytic activity compared with Cu/Al_2O_3 and Cu/ZnO catalysts. The presence of ZnO facilitates the reduction of Cu to the lower temperature. This behavior was attributed to the highly dispersed CuO species

present on the catalyst. The maximum activity was obtained for the catalyst calcined at 500 °C. When compared with the catalyst prepared by co-precipitation, the stability of the impregnated catalyst was lower than the co-precipitated catalyst. The BET surface area indicated that the high performance of the catalyst can be ascribed to the higher surface area, and the better performance of the co-precipitated catalyst might be attributed to the presence of CuO highly dispersed in spinel-like matrix.

Panyad, S. (2011) concluded that the Cu–ZnO/Al_2O_3 catalyst prepared by the IWI method exhibited the highest catalytic activity and stability as compared to the ones prepared by the SG and COP methods. The XRD, TPO and TPR results indicated that the causes of catalyst deactivation were the combination of coke formation and sintering of active copper metals. The Cu–ZnO/ Al_2O_3 (SG) catalyst exhibited the lowest stability in terms of the highest Cu leaching. It was found that coke formation and sintering of Cu had more influence in suppressing the catalytic activity, compared to the Cu leaching

Auttanat T. (2012) reported that the catalytic dehydroxylation of glycerol to propylene glycol using Cu–ZnO/ Al_2O_3 catalyst using refined glycerol as feedstock gave the higher catalytic activity than technical grade glycerol. The ICP-EOS results indicated that the cause of catalyst deactivation is the concentration of impurities in the feedstocks. The higher amount of impurity (especially Na and K) the lower catalytic activity.

2.2.1.2 Mechanism of Glycerol Hydrogenolysis to 1,2-PDO

It is popularly suggested that the mechanism of glycerol hydrogenolysis to 1,2-PDO varies in different reaction mediums.

In acidic conditions, glycerol hydrogenolysis undergoes in two separated steps, in which glycerol firstly dehydrates to acetol (catalyzed by acid active sites) and then the formed acetol hydrogenates to 1,2-PDO over the metal particles (Chaminand *et al.*, 2004; Dasari *et al.*, 2005; Wang and Liu, 2007).

On the other hand, this reaction proceeds consecutively in three steps in alkali solution. That is, glycerol firstly dehydrogenates to glyceraldehydes, followed with glyceraldehydes dehydrates to 2-hydroxyacrolein and 2-hydroxyacrolein hydrogenates to 1,2-PDO (Feng *et al.*, 2007, 2008). These

suggestions are summarized and illustrated in Figure 2.12. According to the reaction mechanism, hybrid Ru/C (or Rh/SiO_2) + solid acids catalysts (Miyazawa *et al.*, 2006, 2007) and a ruthenium-doped acidic heteropoly salt $Cs_{2.5}H_{0.5}[PW_{12}O_{40}]$ (Alhanash *et al.*, 2008) were reported for hydrogenolysis of glycerol.

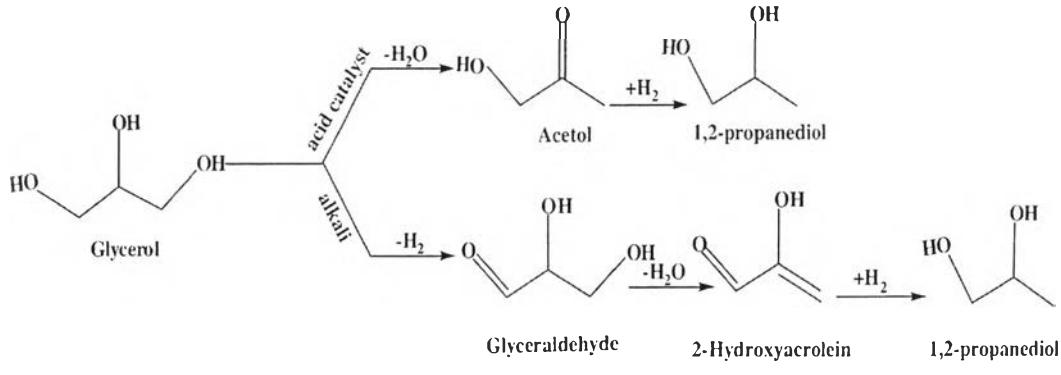

Figure 2.12 Hydrogenolysis of glycerol to 1,2-PDO (Yuan *et al.*, 2010).

At the same time, Pt/C and/or Ru/C catalyst plus alkali (NaOH or $Ca(OH)_2$) were also reported by Maris and Davis according to the alkali-catalyzed mechanism (Maris and Davis, 2007; Maris *et al.*, 2007). They found that the addition of alkali enhanced the reactivity of Pt to a greater extent than that of Ru and the main product was 1,2-PDO. But the added alkali such as NaOH promoted the cleavage of C–C bonds and the formation of lactate.

Besides the hybrid Ru/C (or Rh/SiO_2) + Amberlyst, Pt/C(or Ru/C) + NaOH catalyst, single Raney Ni, Pt/C, Pd/C, Ru/C and Ni/C were also reported for the hydrogenolysis of glycerol to 1,2-PDO. But the reported activity and selectivity of 1,2-PDO was low even under severe reaction conditions (Chaminand *et al.*, 2004).

According to the reaction mechanism of hydrogenolysis of glycerol to 1,2-PDO proposed above (1), we can deduce that a solid bifunctional catalyst consisting of metal and acidic (or basic) sites would be an alternate instead of the hybrid catalysts.

In Yuan *et al.*, 2009 work, hydrotalcite, MgO, Al_2O_3, H-ZSM5 and H-Beta supported Pt catalysts were prepared and tested for

hydrogenolysis of glycerol to 1,2-PDO. It was found that solid base (hydrotalcite and MgO) supported Pt catalysts exhibited the predominant activity and higher 1,2-PDO selectivity than that of solid acids (Al_2O_3, H-ZSM5 and H-Beta). Characterization results revealed that the alkaline strength of the catalyst contributed obviously to its activity for glycerol hydrogenolysis. At the same time, solid base supported catalysts also possess advantages in environmental friendly, easiness in separation and recycle. And the cleavage of C–C bonds in Pt/C + NaOH system was repressed efficiently.

2.3 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.

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.

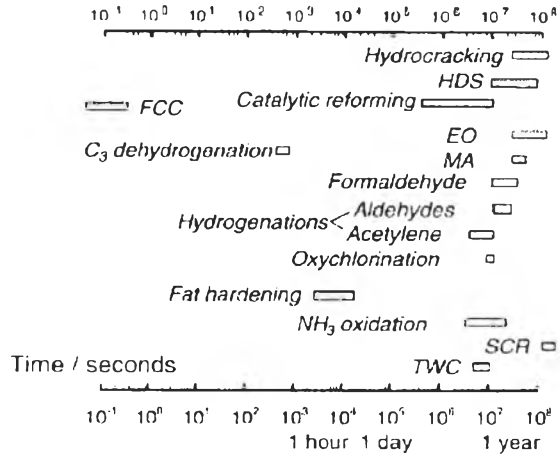

Figure 2.13 Time scale of deactivation of various catalytic processes (Moulijin *et al.*, 2001).

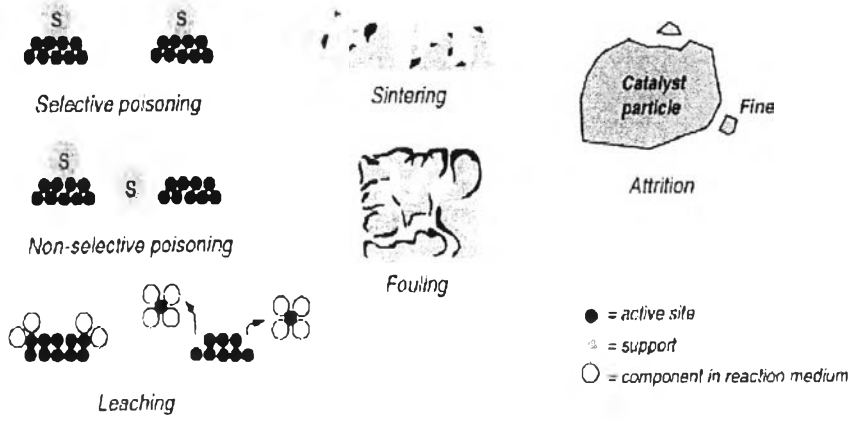

Figure 2.14 Major types of deactivation in heterogeneous catalysis (Moulijin *et al.*, 2001).

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 solid–solid reactions	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

2.3.1 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 and the catalytic activity were changed. 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.

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

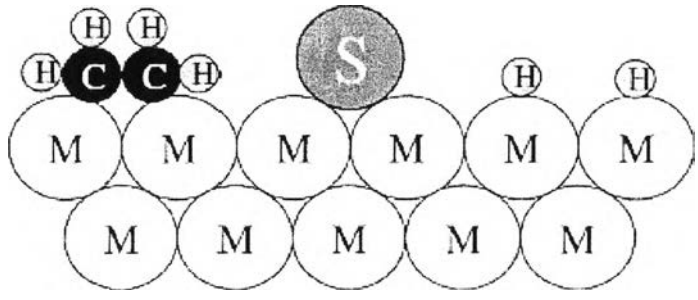

Figure 2.15 Conceptual model of poisoning by sulfur atoms of a metal surface during ethylene hydrogenation (Bartholomew, 2001).

The first group of poisons involve Group VA and V1A elements, including N, P, As and Sb (VA) and O, S, Se and Te (V1A). 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 2.17, 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".

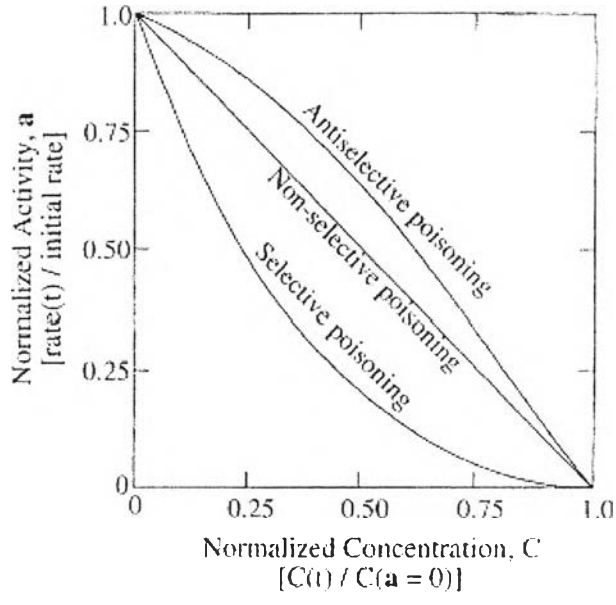

Figure 2.16 Three kinds of poisoning behavior in terms of normalized activity vs. normalized poison concentration (Bartholomew, 2001).

2.3.2 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.* (2001) reported 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.

2.3.3 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 2.18. 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.

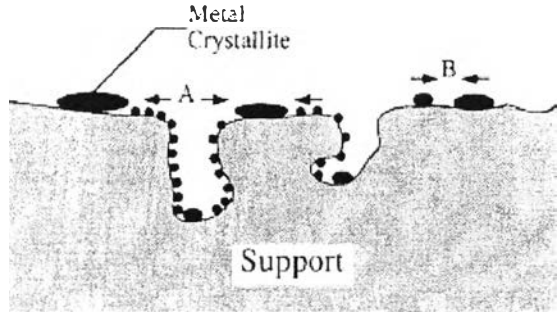

Figure 2.17 Two conceptual models for crystallite growth due to sintering by (A) atomic migration or (B) crystallite migration (Bartholomew, 2001).

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 re-dispersion (see Table 6). Sintering rates increase exponentially with temperature. Metals sinter relatively rapidly in oxygen and relatively slowly in hydrogen, although depending upon the support, metal re-dispersion can be facilitated by exposure at high temperature.

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 re-dispersion 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.

2.3.4 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.

2.3.5 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.

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 ≈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