

CHAPTER II

LITERATURE REVIEW

Glycerol is a by-product from the biodiesel production process. One of the most interesting routes to convert glycerol to high value added products is catalytic dehydroxylation of glycerol to propylene glycol. For this experiment, MgO-Al₂O₃ mixed oxide supports were prepared by co-precipitation method and CuZnO/MgO-Al₂O₃ catalysts were prepared by incipient wetness impregnation method.

2.1 Properties of Glycerol

Glycerol or more correctly named 1, 2, 3 propanetriol (Figure 2.1) is a tri-basic alcohol. Glycerol has three hydroxyl groups that are responsible for its solubility in water and its hygroscopic nature. The glycerol backbone is central to all lipids known as triglycerides. Glycerol is sweet-tasting and generally considered non-toxic. Glycerol is a colorless, odorless, viscous liquid, derived from both natural and petrochemical feedstocks.

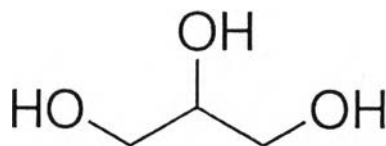


Figure 2.1 Structure of glycerol. (Pagliaro *et al.*, 2010).

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 refers 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 $18.2 \text{ }^{\circ}\text{C}$ and a boiling point of $290 \text{ }^{\circ}\text{C}$ under normal atmospheric pressure, accompanied by decomposition. At low temperatures, glycerol may form crystals which melt at $17.9 \text{ }^{\circ}\text{C}$. Overall, it possesses a unique combination of physical and chemical properties (Table 2.1), which are utilized in many thousands of commercial products. 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. 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 $20 \text{ }^{\circ}\text{C}$ (Raton, 2006)

Chemical formula	$\text{C}_3\text{H}_5(\text{OH})_3$
Molecular mass	$92.09382 \text{ g/mol}^{-1}$
Density	1.261 g/cm^{-3}
Viscosity	$1.5 \text{ Pa}\cdot\text{s}$
Melting point	$18.2 \text{ }^{\circ}\text{C}$
Boiling point	$290 \text{ }^{\circ}\text{C}$
Food energy	4.32 kcal/g
Flash point	$160 \text{ }^{\circ}\text{C}$ (closed cup)
Surface tension	64.00 mN/m^{-1}
Temperature coefficient	$-0.0598 \text{ mN}/(\text{mK})^{-1}$

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 (Raton, 2006)

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.

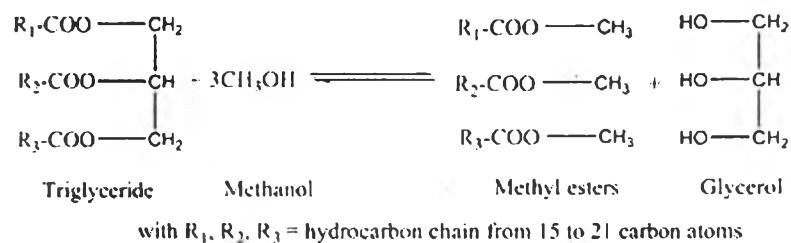


Figure 2.2 Overall reaction for production of biodiesel through vegetable oil methanolysis (Zhou *et al.*, 2008).

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

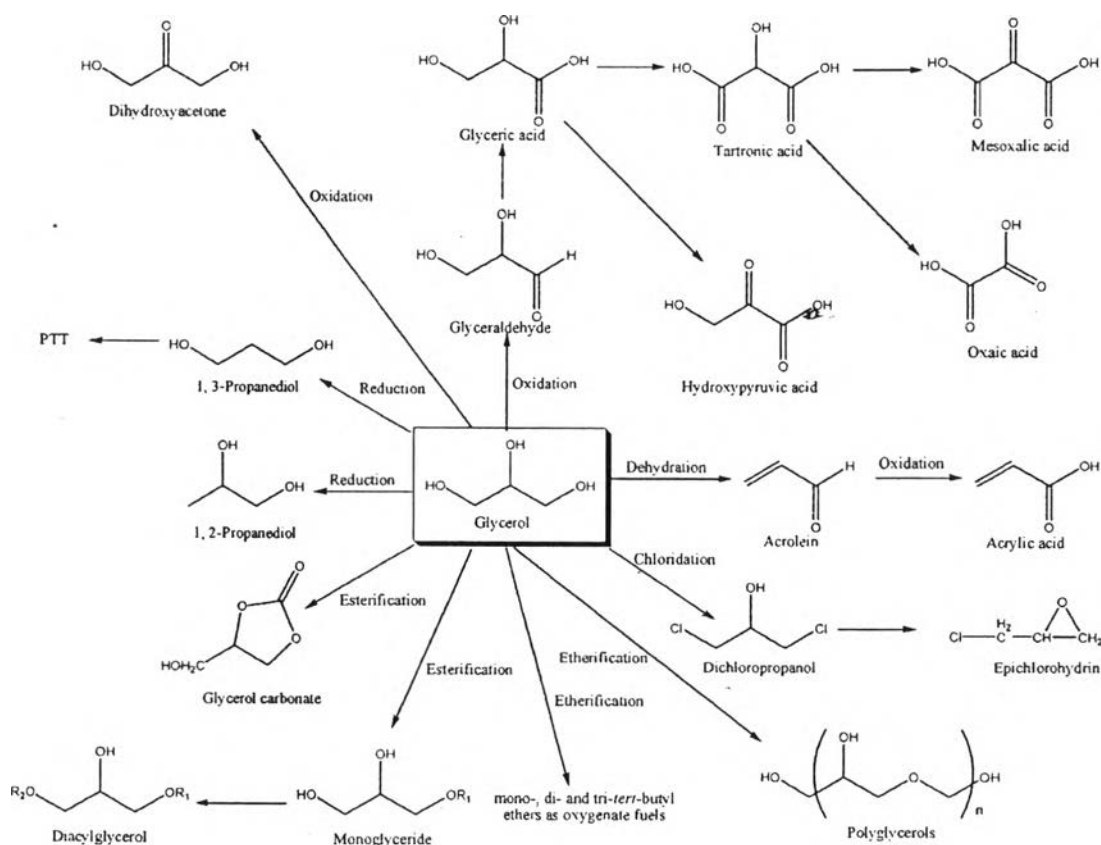


Figure 2.3 Commodity chemicals from glycerol (Zheng *et al.*, 2008).

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 product.

2.2 Properties of Propylene Glycol

Propylene glycol or 1,2 Propanediol, ($\text{CH}_3\text{CHOHCH}_2\text{OH}$) is a clear, colorless, viscous, practically odorless and tasteless liquid. Propylene glycol is aliphatic organic compound having two hydroxyl groups per molecule and has intermediate properties between alcohols, with a single hydroxyl group and glycerol with its three hydroxyl groups. Likewise, the solubility characteristics of this glycol tend to be between those of the simple alcohols and glycerol. The physical properties of propylene glycol are given in Table 2.3 below.

Table 2.3 Physical properties of propylene glycol

Boiling point, °C	187.3
Flash Point (Open Cup), °C	107
Freezing Point, °C	-60*
Heat of Vaporization at 1 atm, cal/g	165
Refractive Index, n _D ²⁰	1.4329
Specific Gravity at 20/ 4 °C	1.0363
Specific Heat at 25 °C, cal/g	0.59
Surface Tension at 25 °C, dynes/cm	0.37
Vapor Pressure at 20 °C, mmHg	0.05
Viscosity at 20 °C, cps	60.5

* Sets to glass below this temperature

Several physical properties of propylene glycol are directly related to important industrial applications.

2.2.1 Uses of Propylene Glycol

Since propylene glycol can undergo chemical reactions on one or both hydroxyl groups, it is important as chemical intermediate with a 4% annual growth in the market size. The current global market for 1,2-propanediol is roughly 2 million tonnes annually. Propylene glycol plays a significant role in industry due to its wide range of practical applications. It is found in such diverse products and applications as thermoset plastics, clothing, latex paints, glass and enamel surface cleaners, automotive antifreeze/coolants, heat transfer fluids, aircraft deicing fluids, natural gas treatment, chemical process fluids, hydraulic fluids, paper and packaging, adhesives, plasticizers, pesticides, printing inks, cosmetics, pharmaceuticals, foods and electronics. All of these applications utilize propylene glycol, either as an integral part of the product or as a facilitator in their production. The major industrial applications of propylene glycol are shown in Figure 2.4.

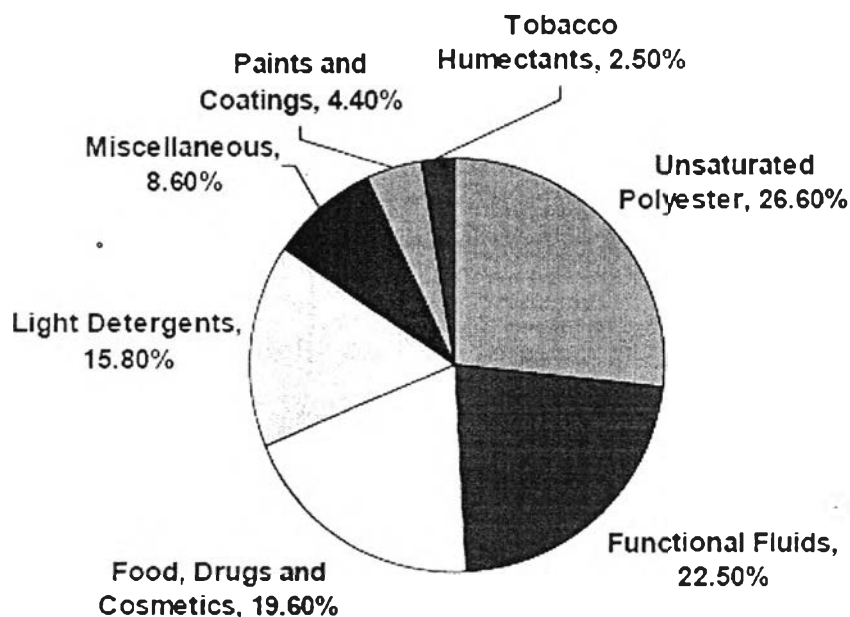


Figure 2.4 Distribution of various uses of propylene glycol (*Dasari., 2006*).

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*). Furthermore, 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*).

2.3 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.

1,3-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 2.5.

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).

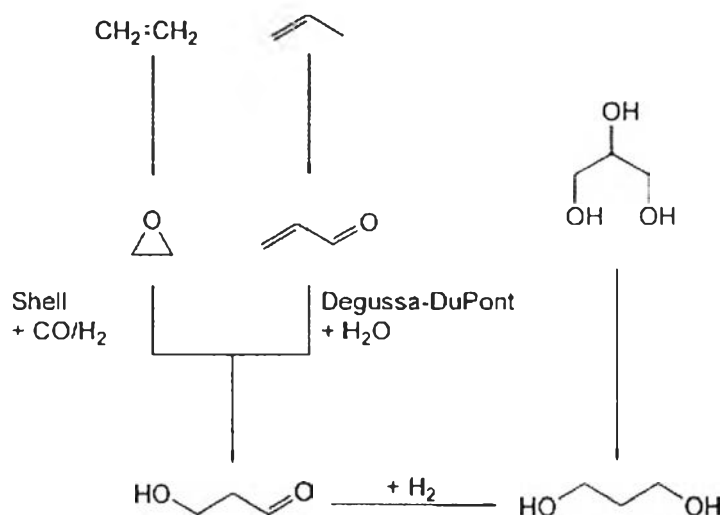


Figure 2.5 Different routes to 1,3-propanediol starting from ethene, propene or glycerol (Behr *et al.*, 2008).

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.

2.3.1 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 2.6). 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 catalyzed by osmium compounds, the classical route based on propylene oxide is still widely used.

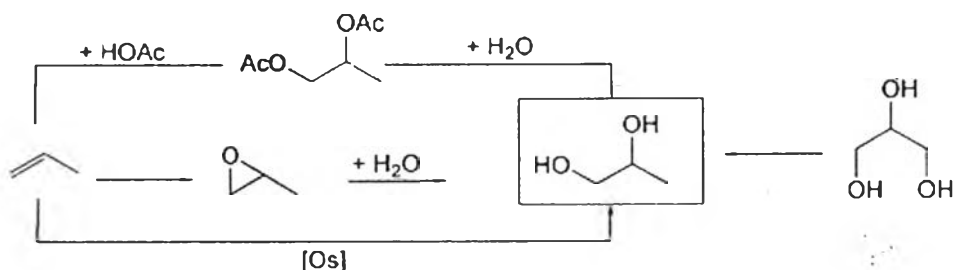


Figure 2.6 Comparison of the reaction routes to 1,2-propanediol starting from propene or glycerol (Behr *et al.*, 2008).

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 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 section.

2.3.1.1 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. 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* (Behr *et al.*, 2008).

2.3.1.2 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 H₂ 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).

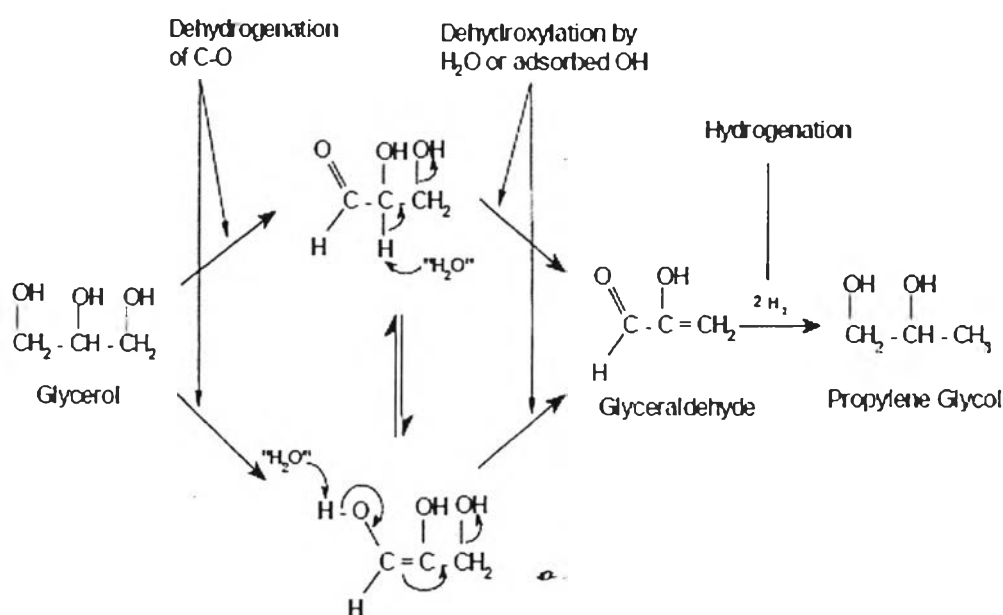


Figure 2.7 Reaction mechanism for conversion of glycerol to propylene glycol proposed by Montassier *et al.* (1991)

2.3.1.3 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 H₂ 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 2.7.

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 H₂ pressure for 90 hours. Among the various catalysts (Cu, Pd, Rh), supports (ZnO, C, Al₂O₃), solvents (H₂O, sulfolane, dioxane), and additive such as tungstic acid (H₂WO₄), the best selectivity (100%) to 1,2-propanediol was obtained when using CuO/ZnO catalysts.

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 2.8).

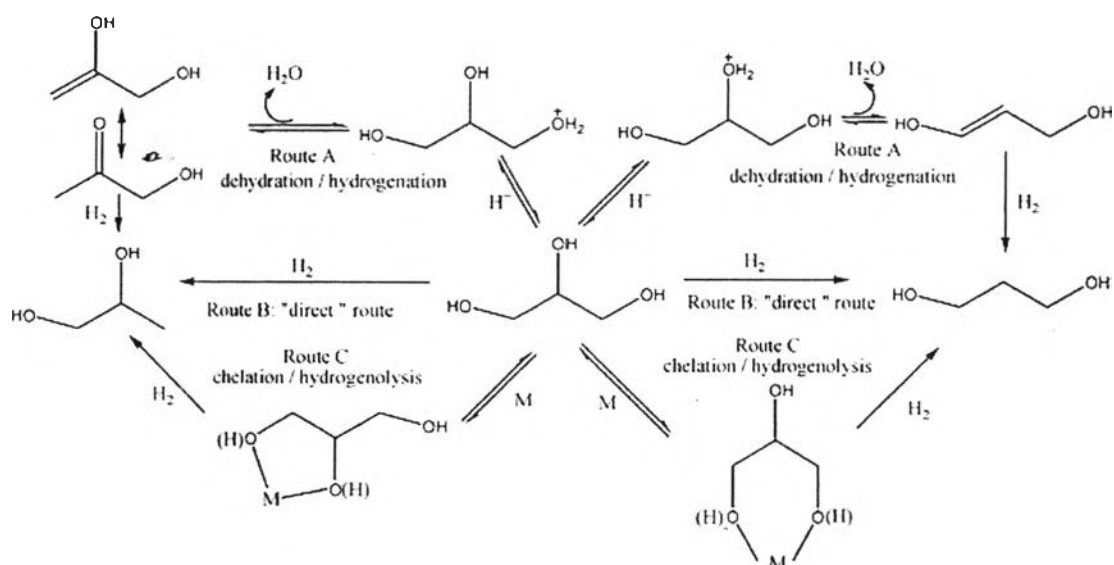


Figure 2.8 Possible reaction routes for catalytic hydrogenolysis of glycerol proposed by Chaminand *et al.* (2004).

The diols can be formed *via* several routes. The tungstic acid can favor 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 H₂WO₄ 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 selected by a diol and thus modifies the selectivity of the hydrogenolysis (route C).

Table 2.4 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 Davison	Raney Nickel	49.5	26.1	52.7
Grace Davison	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 2.4. 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 2.9.

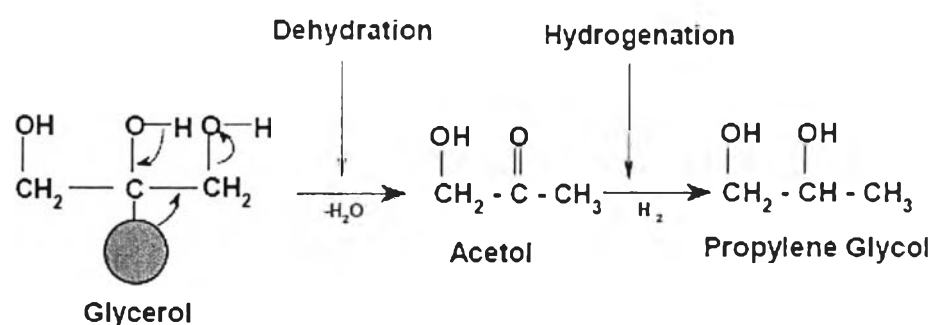


Figure 2.9 Proposed reaction mechanism for conversion of glycerol to propylene glycol (Dasari *et al.*, 2005).

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 H₂) than other metal–acid bifunctional catalyst systems such as zeolites, sulfated zirconia, H₂WO₄, and liquid H₂SO₄. 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 2.10.

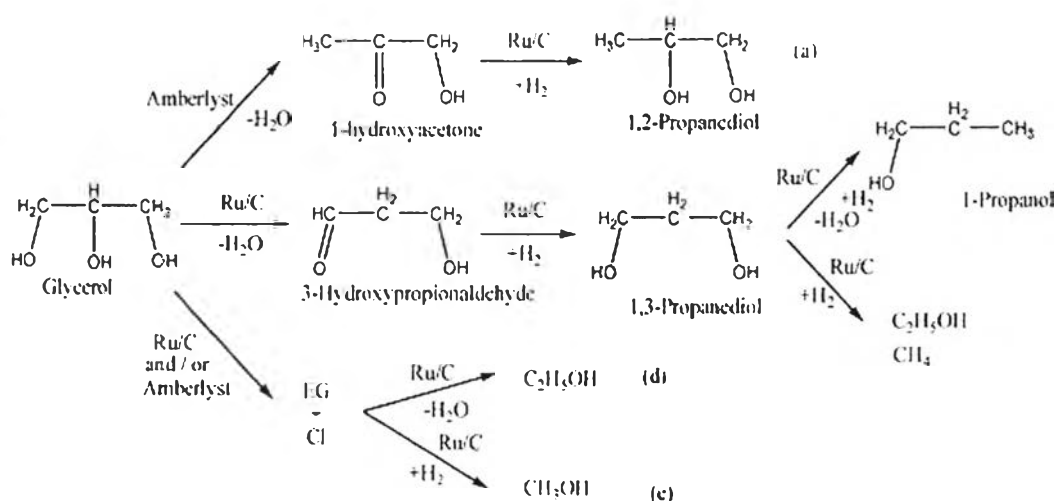


Figure 2.10 Reaction scheme of glycerol hydrogenolysis and degradation reactions (Miyazawa *et al.*, 2006).

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 + H₂SO₄ 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 H₂ 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 2.11, where the two proposed dehydrated intermediates were acetol (1-hydroxyacetone) and glycidol (3-hydroxy-1,2-epoxypropane).

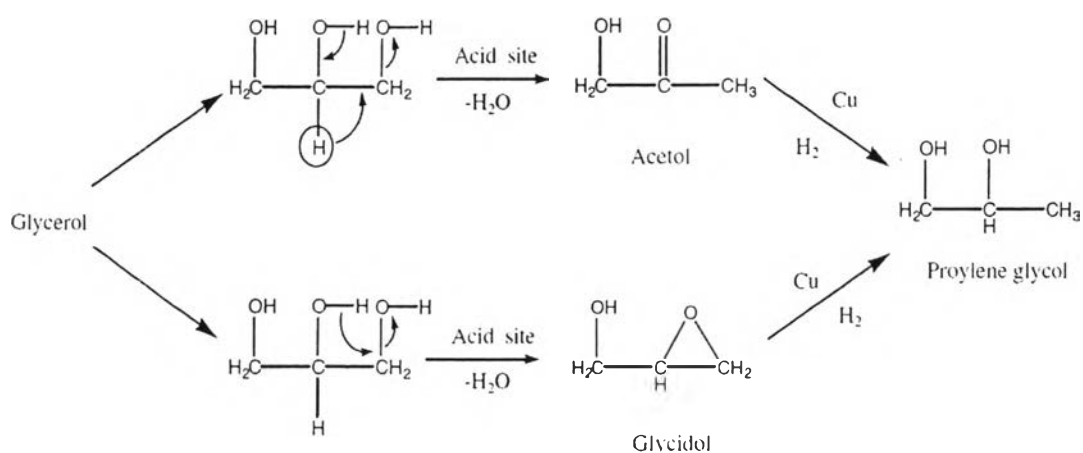


Figure 2.11 Proposed bifunctional glycerol hydrogenolysis reaction pathways (Wang *et al.*, 2007).

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/SiO₂, Ru/NaY, Ru/ γ -Al₂O₃, Ru/C, and Ru/TiO₂, the TiO₂ supported catalyst showed high activity giving the highest conversion of glycerol (90%); however, Ru/TiO₂ catalyst favored the production of ethylene glycol over 1,2-propanediol under the tested conditions (180 °C, 5 MPa). In contrast, Ru/SiO₂ 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

$\text{Ru}/\text{SiO}_2 > \text{Ru}/\text{NaY} > \text{Ru}/\gamma\text{-Al}_2\text{O}_3 > \text{Ru}/\text{C} > \text{Ru}/\text{TiO}_2$. 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-aldolization of glyceraldehyde 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 $\gamma\text{-Al}_2\text{O}_3$ 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 2.12.

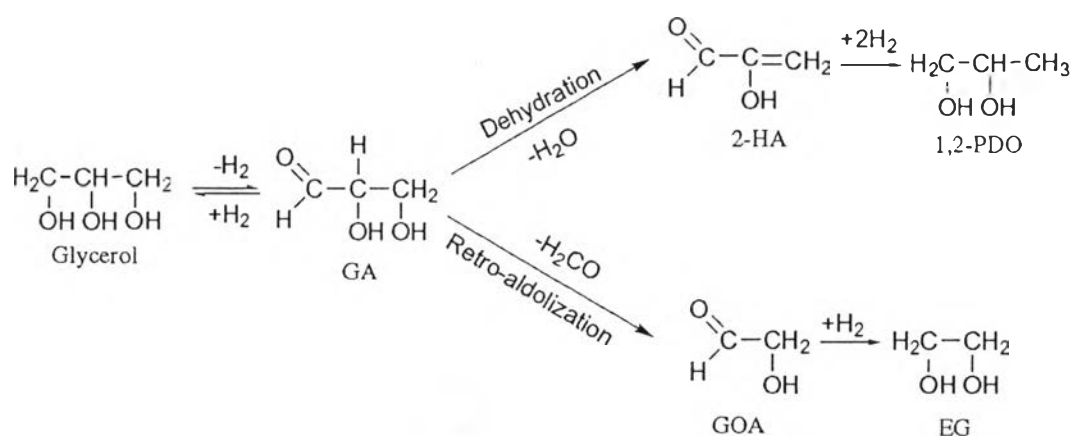


Figure 2.12 Reaction route for the hydrogenolysis of glycerol to glycols (Feng *et al.*, 2008). GA=glyceraldehyde, 2-HA=2-hydroxyacrolein, 1,2-PDO=1,2-propanediol, GOA=glycolaldehyde, and EG=ethylene glycol

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.

Dehydration-hydrogenolysis of glycerol into 1,2-propanediol at ambient hydrogen pressure was investigated (Akiyama *et al.*, 2009). Glycerol was

converted into 1,2-PDO through the dehydration into hydroxyacetone, followed by the dehydrogenation into 1,2-PDO (Figure 2.13). The yield of 1,2-PDO was limited up to 80% at a constant temperature of 190 °C because of a trade-off problem between the dehydration and the hydrogenation. The dehydration needs relatively high reaction temperatures, whereas the hydrogenation favors low temperature and high hydrogen concentration. So, they developed an efficient process in order to increase the yield of 1,2PDO.

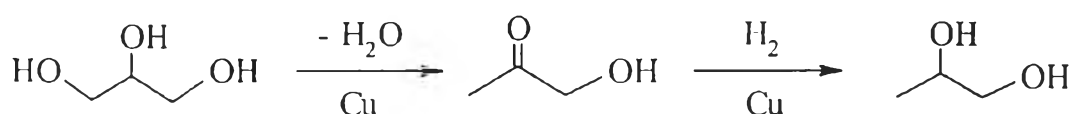


Figure 2.13 Proposed reaction for conversion of glycerol to 1,2-PDO (Akiyama *et al.*, 2009).

The reactor with the catalyst bed was placed in an electric furnace under the stable condition in a way that the temperature on the top surface of the catalyst bed is higher than that on the bottom. The result shown that glycerol was converted into 1,2-PDO with the yield higher than 96% due to the gradient temperature of the catalyst. This indicates that hydroxyacetone is sequentially hydrogenated to 1,2-PDO in the hydrogenolysis of glycerol.

Zhu *et al.* (2013) studied hydrogenolysis of glycerol to 1,3-propanediol (1,3-PDO) over zirconia supported bifunctional catalysts containing Pt and heteropolyacids using $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ (HSiW), $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (HPW) and $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ (HPMo) as active compounds. The result of this study indicate that heteropolyacids modified Pt/ZrO₂ catalysts were effective in glycerol hydrogenolysis to 1,3-PDO due to the enhanced acidity. Pt-HSiW/ZrO₂ obtained the highest selectivity to 1,3-PDO compared to Pt-HPW/ZrO₂ and Pt-HPMo/ZrO₂, which was probably related to the high Brønsted acid sites and good thermal stability. The 1,3-PDO yield was proportional to the concentration of the Brønsted acid sites, whereas the 1,2-PDO yield was proportional to the concentration of Lewis acid sites. The reaction pathways have been proposed (Figure 2.14) that PDOs formation proceeds via

Sitthisa *et al.* (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 *et al.* (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.

Chirddilok *et al.* (2009) reported that the CuZnO/Al₂O₃ catalyst showed the best catalytic activity compared with Cu/Al₂O₃ 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 *et al.* (2011) concluded that the CuZnO/Al₂O₃ 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 CuZnO/ Al₂O₃ (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 *et al.* (2012) concluded that the catalytic dehydroxylation of glycerol to propylene glycol using CuZnO/ Al₂O₃ catalyst using refined glycerol as feed-stock gave higher catalytic activity than technical grade glycerol. The ICP-EOS results indicated that the cause of catalyst deactivation was

the concentration of impurities in the feedstocks. The higher amount of impurity (especially Na and K) the lower catalytic activity.

Wongpraphairoat *et al.* (2013) studied catalytic dehydroxylation of glycerol to propylene glycol over CuZnO base catalysts: Effects of supports. The result showed that CuZnO/Al₂O₃ gave the highest catalyst activity because of its largest surface area and the highest copper dispersion. CuZnO/MgO exhibited the highest performance in terms of stability and the regenerated CuZnO/MgO gave the glycerol conversion as high as the fresh catalyst.

Paengsri *et al.* (2014) investigated the catalytic dehydroxylation of glycerol to propylene glycol over CuZnO/MgO catalysts. The result showed that co-precipitated catalyst exhibited higher catalytic activity than the impregnated catalyst. The NaOH containing glycerol feedstock did not affect the stability of catalysts and also increase the catalytic activity due to the enhancement of catalyst basicity in the presence of MgO. Furthermore, the small amount of MgO did not modify the electronic effect of Cu and Zn species in the catalysts.

2.4 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 media.

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/SiO₂) + solid acids catalysts (Miyazawa *et al.*, 2006a,b, 2007) and a ruthenium-doped acidic heteropoly salt Cs_{2.5}H_{0.5}[PW₁₂O₄₀] (Alhanash *et*

et al., 2008) were reported for hydrogenolysis of glycerol. In these conditions, 1,2-PDO formed via a dehydration and hydrogenation routine (Figure 2.15).

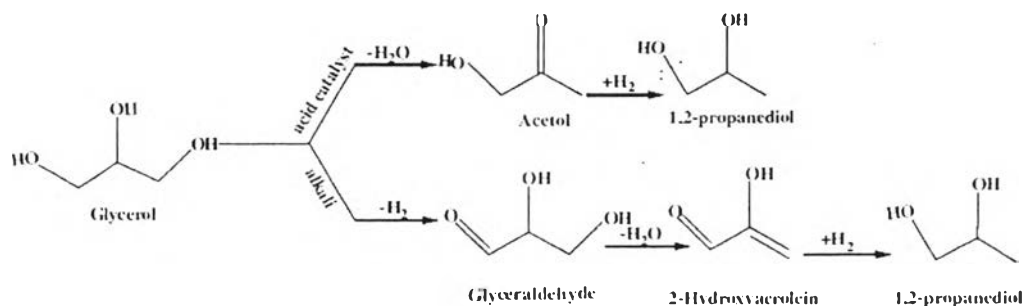


Figure 2.15 Hydrogenolysis of glycerol to 1,2-PDO (Yuan *et al.*, 2010).

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/SiO₂) + 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, 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, Al₂O₃, 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 (Al₂O₃, 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.

Selective hydrogenolysis of glycerol to 1,2-propanediol over Cu–MgO catalysts is reported (Balaraju *et al.*, 2012). A series of Cu–MgO catalysts with varying Cu content were prepared by a co-precipitation method. The activity results showed that Cu content on MgO has a significant role in glycerol conversion as well as formation of 1,2-propanediol. 20 wt% of Cu content on MgO is identified as an optimum Cu content. The catalyst is equally active even with crude glycerol and glycerol containing alkali salts as impurity. It was indicated that well dispersed Cu species and accessible basic sites of MgO are the essential requirements for high glycerol hydrogenolysis activity.

Selective hydrogenolysis of glycerol to propylene glycol on MgO–Al₂O₃ dispersed Cu catalysts was investigated (Wang *et al.*, 2012). Cu/MgO–Al₂O₃ catalysts were prepared by an impregnation method using ethanol as solvent instead of water. The results showed that density of the basic sites for the dispersed Cu catalysts increased with increasing the MgO contents in the basic supports. These catalysts catalyzed glycerol hydrogenolysis to propylene glycol with a high selectivity (>90%) at 200⁰C and 6.0 MPa H₂. Researchers propose a synergetic effect that the basic sites at the interfaces between the Cu sites and the supports assist the cleavage of α -C–H bonds of glycerol on the Cu surfaces leading to the faster dehydrogenation of glycerol to glyceraldehyde, a kinetically-relevant step in glycerol hydrogenolysis to propylene glycol.

2.5 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. The methods that have found wide use (including industrial use) are impregnation and co-precipitation.

In the last two decades, the greatest progress has been made in the sol-gel preparation of dispersed single component and multicomponent systems by the hydrolysis of solutions of metal alkoxides and in the synthesis of new, so-called mesophasemesoporous materials (Pakhomov and Buyanov, 2005).

2.5.1 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).

2.5.2 Co-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 counter ions from the precipitate yield the final solid. The resultant architecture of the co-precipitated 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 co-precipitation offers an improved alternative to co-precipitation. A limitation for co-precipitation is that the support and metal oxide precursors are unlikely to share similar solubility (i.e., solubility products). Consequently, drop wise 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 drop wise to an excess of precipitating agent, this approach ensures that a strict ratio of precursors is maintained throughout the course of batch wise addition and leads to better co-precipitate homogeneity.

2.5.3 Sol-Gel Method

The sol-gel process involves first the formation of a sol followed by that of a gel. A sol, which is a liquid suspension of solid particles ranging in size from 1 nm to 1 micron, can be obtained by the hydrolysis and partial condensation of a precursor such as an inorganic salt or a metal alkoxide. The further condensation of sol particles into a three-dimensional network produces a gel, which is a material with a solid encapsulating a solvent. Alternatively, a gel can be produced by destabilizing a solution of preformed sols.

In either case the materials are referred to aquasol (or aquagel) when water is used as a solvent, and alcosol (or alcogel) when alcohol is used. The encapsulated liquid can be removed from a gel by either evaporative drying or drying with supercritical extraction (supercritical drying for short). The resulting solid products are known as a xerogel and an aerogel, respectively. The four key steps in taking a precursor to a particular product from via sol-gel preparation: formation of a gel, aging of a gel, removal of solvent, and heat treatment are showed in Figure 2.16.

The precursor in a sol-gel preparation can either be a metal salt/alkoxide dissolved in an appropriate solvent or a stable colloidal suspension of preformed sols. Metal alkoxides have been the most extensively used because they

are commercially available in high purity and their solution chemistry has been documented. Alkoxides have the following advantages over inorganic precursors (Pakhomov and Buyanov, 2005):

- (i) high purity of the precursor and final products;
 - (ii) reliable control of the process parameters determining the final structure of the alkogel and its properties;
 - (iii) uniformity of the chemical, physical, and morphological properties of the product;
 - (iv) mixing of the components at the molecular level;
 - (v) possibility of preparing samples at low temperatures;
 - (vi) possibility of introducing a variety of components in one step;
- and
- (vii) possibility of controlling the reaction kinetics and stabilizing metastable systems.

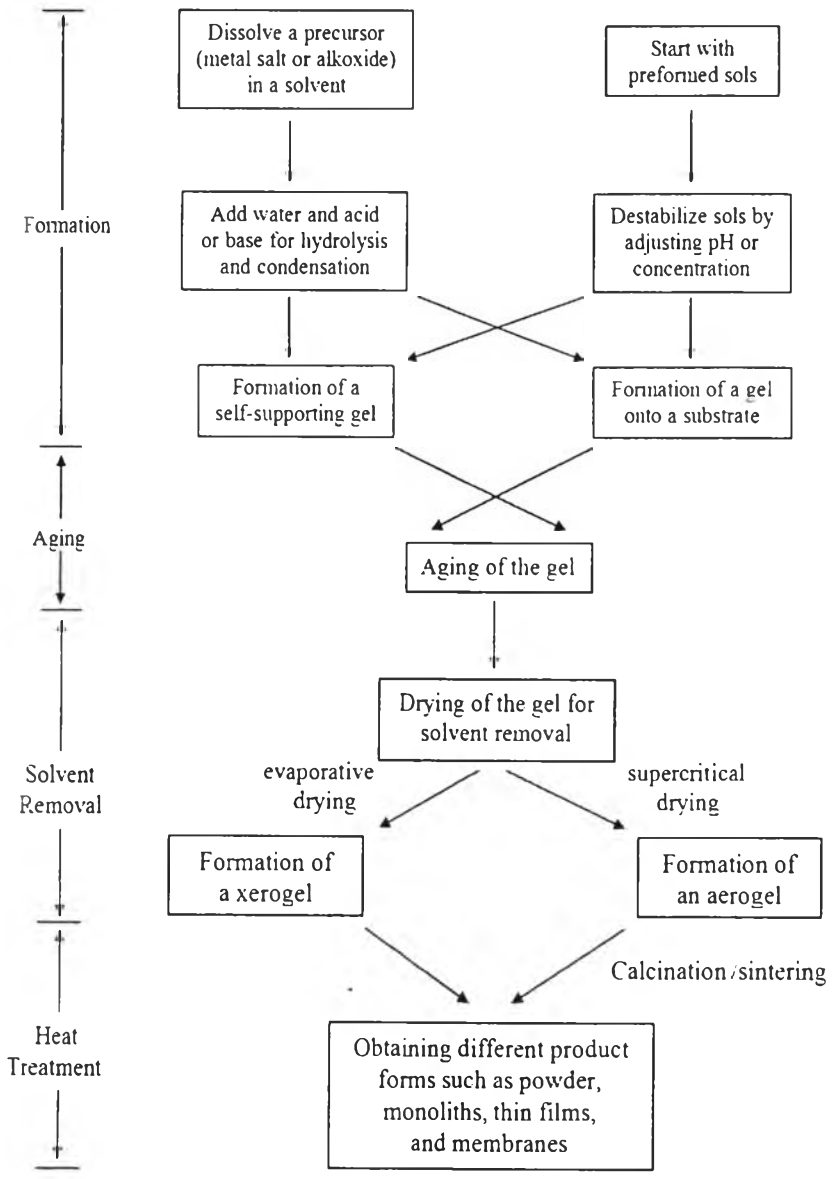


Figure 2.16 Schematic diagram showing the various steps of a sol-gel process (Ertl et al., 1999).

2.6 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.

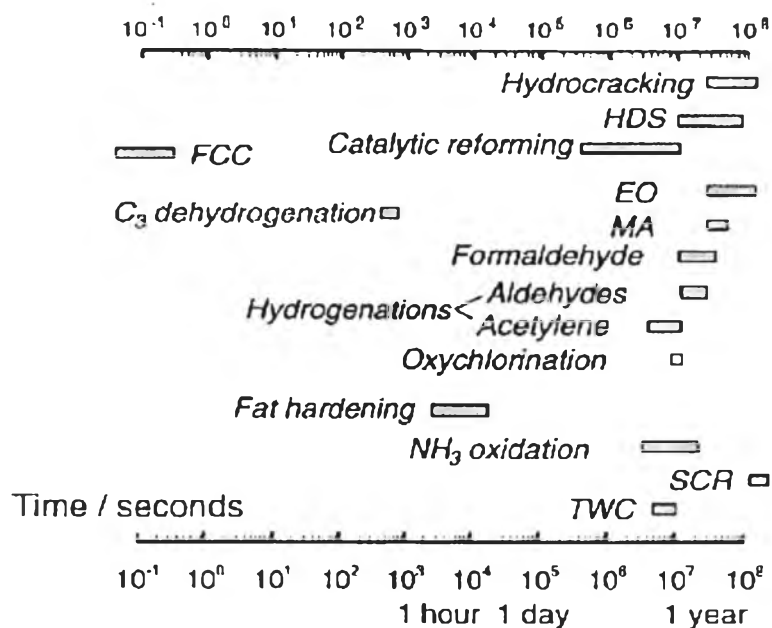


Figure 2.17 Time scale of deactivation of various catalytic processes (Moulijn *et al.*, 2001).

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

Table 2.5 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

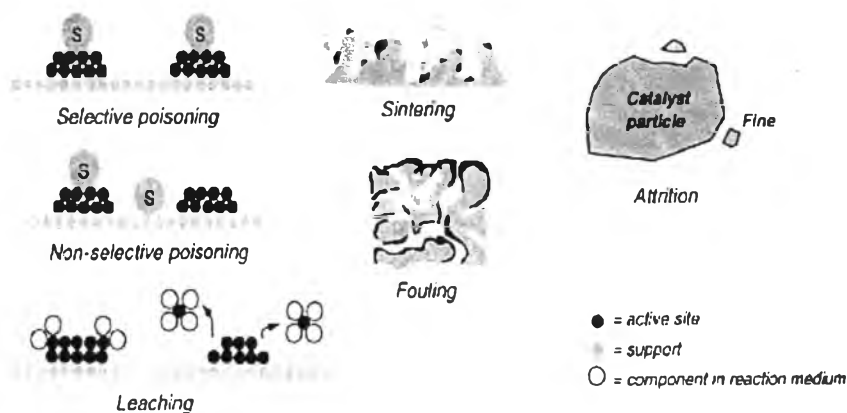


Figure 2.18 Major types of deactivation in heterogeneous catalysis (Moulijn *et al.*, 2001).

2.6.1 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.

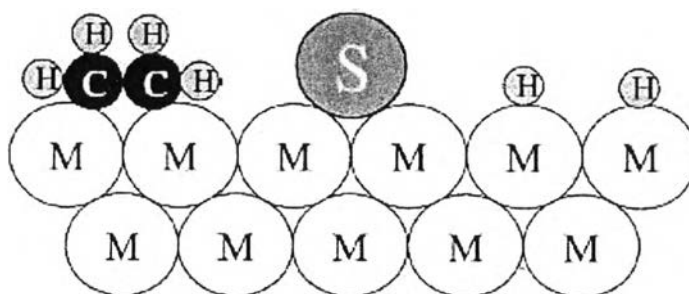


Figure 2.19 Conceptual model of poisoning by sulfur atoms of a metal surface during ethylene hydrogenation (Bartholomew, 2001).

Table 2.6 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 $\text{SO}_4^{2-} < \text{SO}_2 < \text{H}_2\text{S}$.

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 2.20, 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.

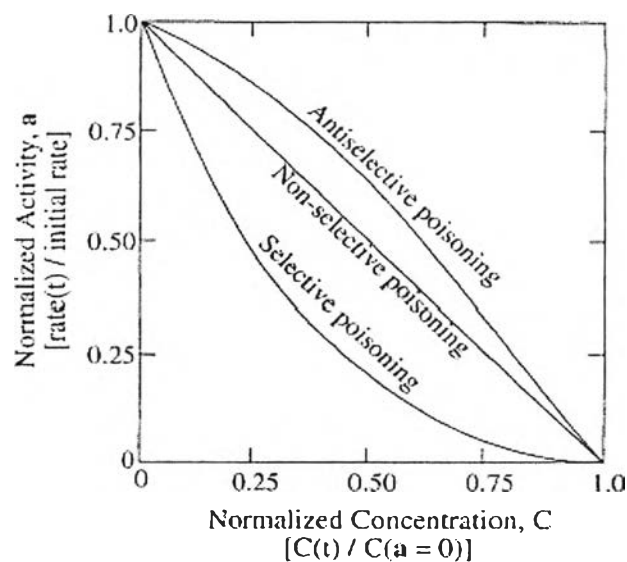


Figure 2.20 Three kinds of poisoning behavior in terms of normalized activity vs. normalized poison concentration (Bartholomew, 2001).

2.6.2 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) 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.

2.6.3 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 2.20. 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.

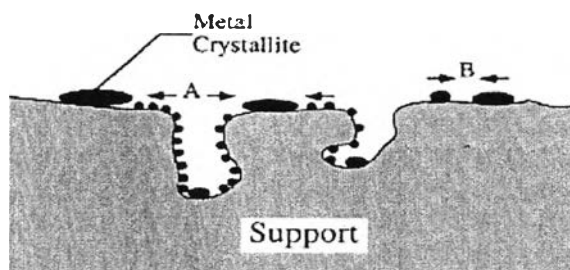


Figure 2.21 Two conceptual models for crystallite growth due to sintering by (A) atomic migration or (B) crystallite migration (Bartholomew, 2001).

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)

Table 2.7 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 ₂ O 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

Temperature, atmosphere, metal type, metal dispersion, promoter impurities and support surface area, texture and porosity, are the principal parameters affecting rates of sintering and re-dispersion (Table 2.7). 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.

2.6.4 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.

2.6.5 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 latter case is irreversible.