# CHAPTER II

LITERATURE REVIEW

2.1 Glycerol

Glycerol and glycerin (e) are oftentimes used interchangeably, but glycerol is the preferred scientific terminology and refers to the pure trihydric alcohol, while glycerin (e) refers to the commercial products consisting of whatever grade or degree of purity (Kenar, 2007). Glycerol has been a well-known renewable chemical for more than two centuries. The Swedish chemist Carl Wilhelm Scheele discovered it in 1783 when treating natural oils with alkali materials. The name "glycerol" was given in 1811 by the chemist Michel Eugene Chevreul, who deduced this name from the Greek word "glykos" (= sweet) (Behr *et al.*, 2008).

The chemical structure for glycerol is $HOCH_2\text{-}CHOH\text{-}CH_2OH$ as shown in Figure 2.1. Glycerol consists of a chain of three carbon atoms with each of the end carbon atoms bonded to two hydrogen atoms (C-H) and a hydroxyl group (-OH), and the central carbon atom is bonded to a hydrogen atom (C-H) and a hydroxyl group (-OH).

Glycerol is viscous, colorless, odorless, and sweet taste. It is clear hygroscopic liquid, non-toxic, easily biodegradable, and pleasant taste which makes it an ideal ingredient in food, cosmetic, and pharmaceutical applications. Because glycerol has three hydroxyl groups (-OH), it is miscible in water and alcohols, but insoluble in ethers, chlorinated solvents, hydrocarbons, and oils.
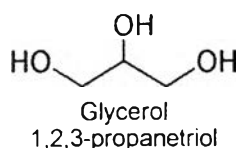
$C_3H_8O_3$
MW: 92.09
mp: 17.8 °C
bp_{760}: 290 °C (decomp).
Density @ 20 °C = 1.2375
Flash point 176 °C

Figure 2.1 Chemical structure and some properties of glycerol (Kenar, 2007).

2.2 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.
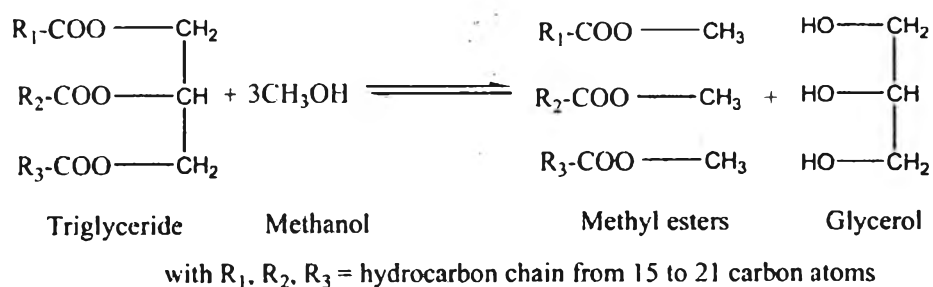
$$
\begin{array}{llll}
R_1\text{-COO}\text{---}CH_2 & & R_1\text{-COO}\text{---}CH_3 & HO\text{---}CH_2 \\
R_2\text{-COO}\text{---}CH + 3CH_3OH \rightleftharpoons & R_2\text{-COO}\text{---}CH_3 + & HO\text{---}CH \\
R_3\text{-COO}\text{---}CH_2 & & R_3\text{-COO}\text{---}CH_3 & HO\text{---}CH_2 \\
\text{Triglyceride} \quad \text{Methanol} & & \text{Methyl esters} & \text{Glycerol}
\end{array}
$$

with R_1, R_2, R_3 = hydrocarbon chain from 15 to 21 carbon atoms

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.

In recent years, the rapid development of biodiesel production has formed large quantities of glycerol as a by-product. The glycerol market will likely to be saturated because of limited utilization of glycerol at the present time. Finding new applications for glycerol will increase the economy of the whole biodiesel production process.

2.3 Glycerol Conversion into Valuable Chemicals

Using glycerol for the synthesis of value-added chemicals is of great industrial importance because, not only can glycerol be formed in large amounts during the biodiesel production, but also it is a nontoxic, edible, biosustainable and biodegradable compound.
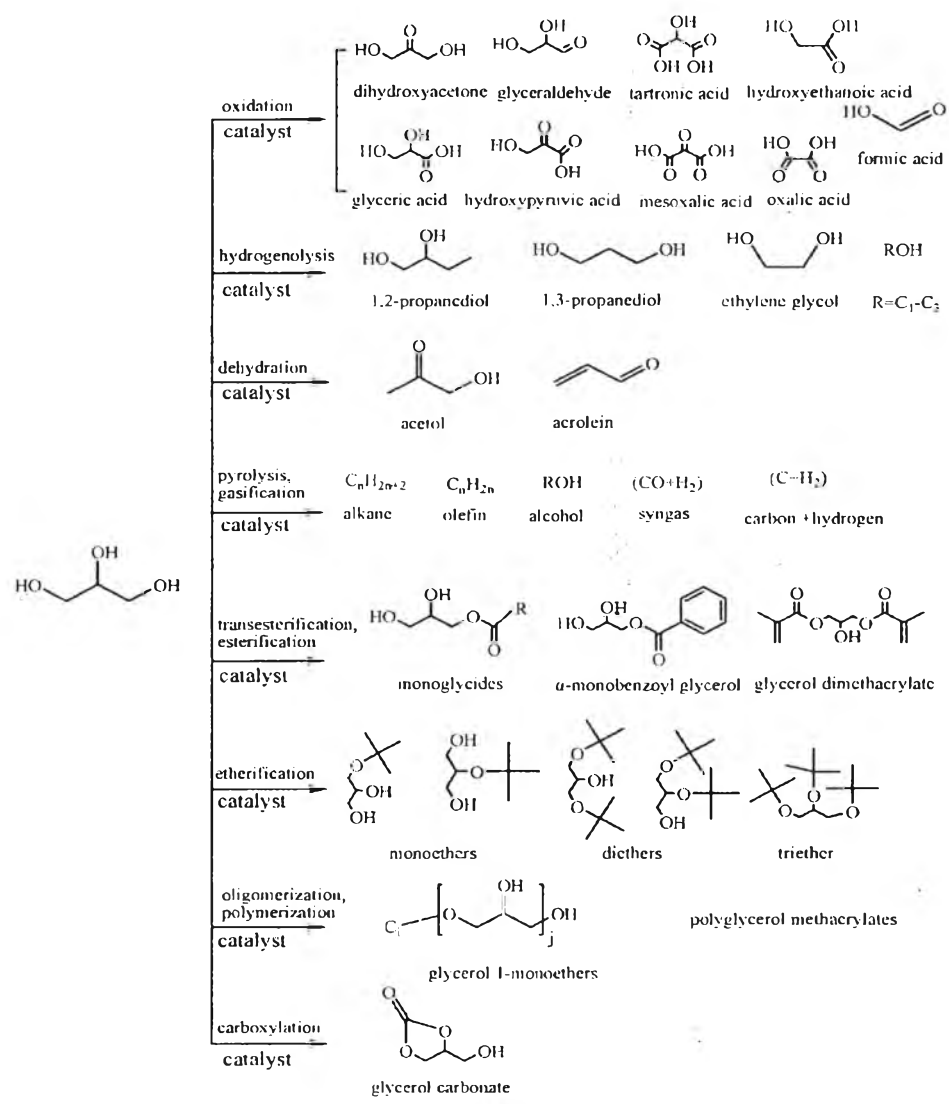

Figure 2.3 Processes of catalytic conversion of glycerol into useful chemicals (Zhou *et al.*, 2008).

In the past, most products were based on unmodified glycerol or simple modifications to glycerol molecules as the production of more complex chemical compounds were too costly. Now, the lower cost of glycerol can open many significant new markets in polymers, ethers, and other fine compounds. From a technical standpoint, glycerol's multifunctional structure and properties can be tailored by several different reaction pathways as shown in Figure 2.3. In the near future, the potential conversion of renewable resources into valuable commodity chemicals can facilitate the replacement of petroleum-based products. It is clear that a very large number of chemicals could be derived from glycerol. In this respect, catalysis represents a critical approach to green chemical technology in the activation and utilization of glycerol (Zhou *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.

2.4 Selective Hydrogenolysis of 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).
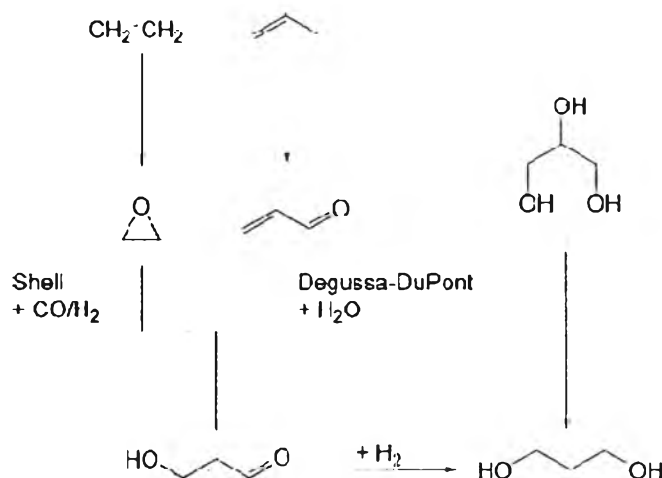

Figure 2.4 Different routes to 1,3-propanediol starting from ethene, propene or glycerol (Behr *et al.*, 2008).

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.

2.5 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.
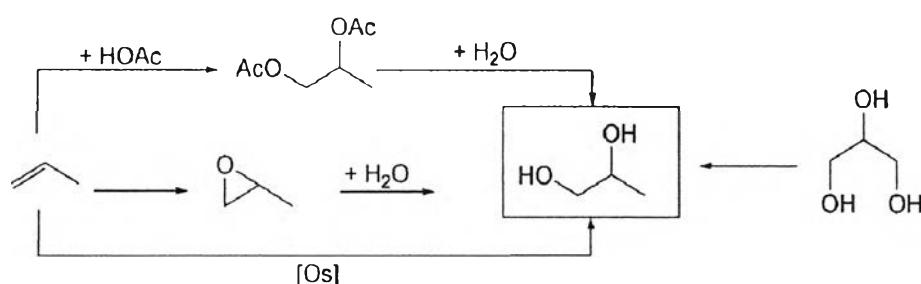

Figure 2.5 Comparison of the reaction routes to 1,2-propanediol starting from propene or glycerol (Behr *et al.*, 2008).

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.

2.5.1 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* or *Thermoanaerobacterium thermosaccharolyticum* HG-8 (Behr *et al.*, 2008).

2.5.2 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 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).
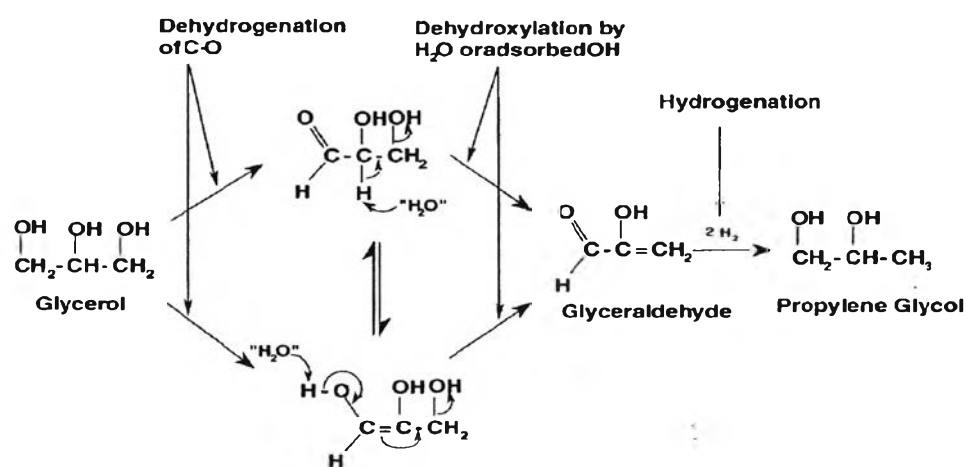

Figure 2.6 Reaction mechanism for conversion of glycerol to propylene glycol proposed by Montassier *et al.*

2.5.3 Heterogeneous Catalyst

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

Montassier *et al.* (1991) carried out the hydrogenolysis of glycerol at 260 °C and 30 MPa H_2 pressure in the presence of Raney 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.
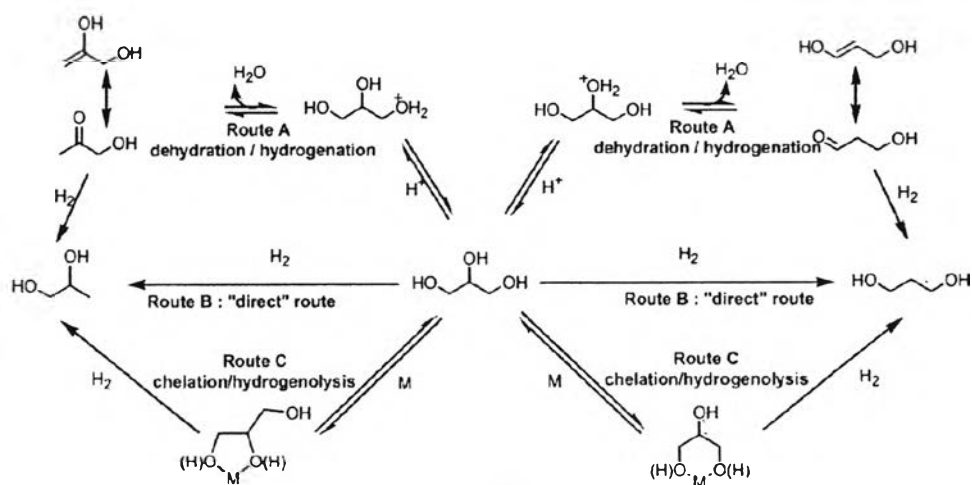

Figure 2.7 Possible reaction routes for catalytic hydrogenolysis of glycerol proposed by Chaminand *et al.* (2004).

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 2.1 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 2.1. 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.
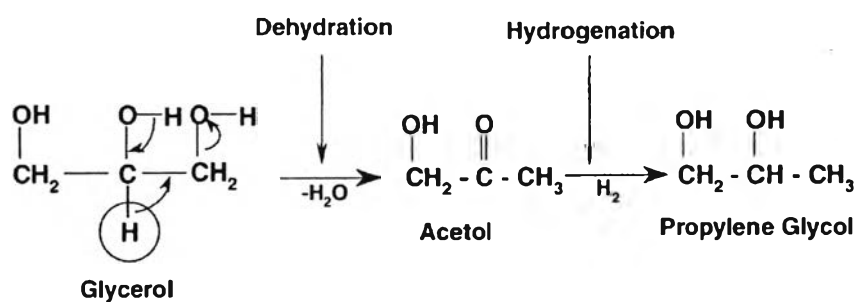

Figure 2.8 Proposed reaction mechanism for conversion of glycerol to propylene glycol (Dasari *et al.*, 2005).

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.
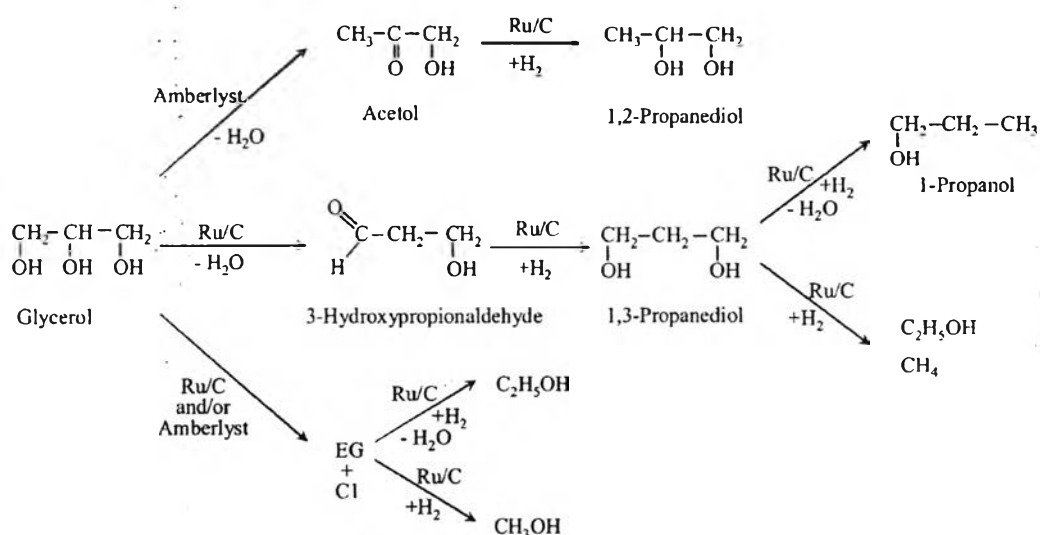

Figure 2.9 Reaction scheme of glycerol hydrogenolysis and degradation reactions (Miyazawa *et al.*, 2006).

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).
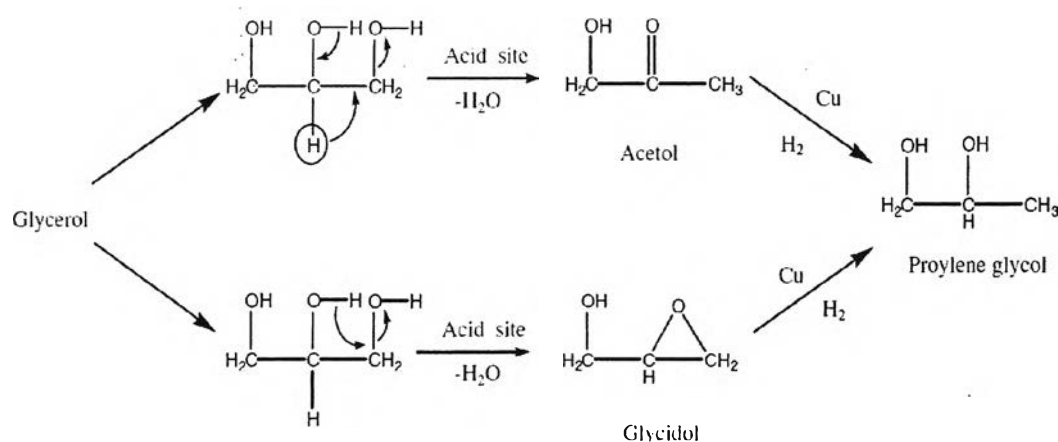

Figure 2.10 Proposed bifunctional glycerol hydrogenolysis reaction pathways (Wang *et al.*, 2007).

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/γ-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/γ-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 γ-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.
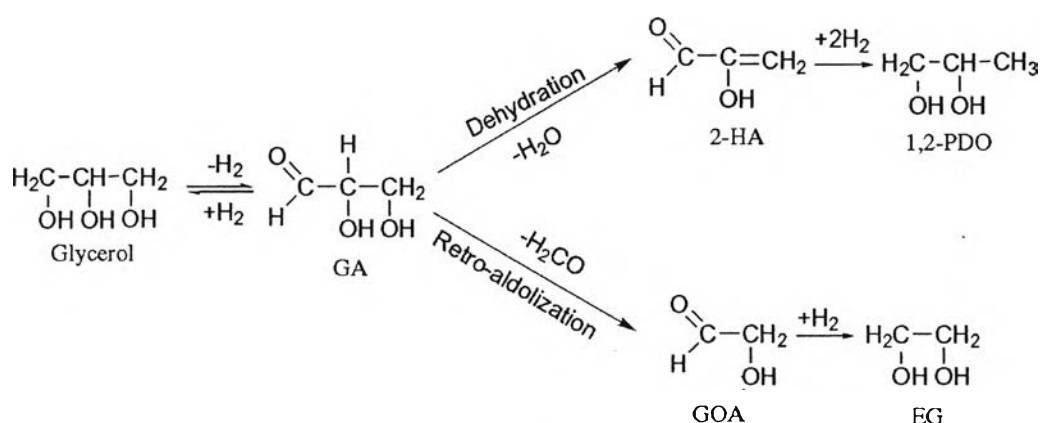

Figure 2.11 Reaction route for the hydrogenolysis of glycerol to glycols (Feng *et al.*, 2008).

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 $Cu-ZnO/Al_2O_3$ 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.

2.6 Preparation of Supported Metal Catalysts

Supported metal oxide comprises a large class of catalytic materials used in numerous industrial processes. There are conventional approaches to preparing these materials. 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 mesophase mesoporous materials (Pakhomov and Buyanov, 2005).

2.6.1 Impregnation

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

2.6.2 Precipitation

Co-precipitation differs from the other methods significantly. It is a method by which a solid is precipitated from a solution containing soluble precursors of both the support and surface oxides. Nucleation of the solid phase is initiated by mixing the solution with precipitating agent that either (1) change the solution pH and leads to precursor condensation to form oxide or hydroxides, or (2) " introduces additional ions into the system by which the solubility product for a certain precipitates is exceeded" (Schüth and Unger, 1997). Filtration and washing of 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.

Tanaka *et al.* (2003) optimized a composition of Cu-ZnO/Al$_2$O$_3$ catalysts prepared by the impregnation method for water gas shift reaction (WGSR) coupled with CO oxidation in the reformed gas. The optimum composition of the impregnated catalyst for high WGSR activity was 5 wt% Cu/5 wt% ZnO/Al$_2$O$_3$. The optimum loading amounts of Cu and ZnO in the impregnated catalyst were smaller than those in the co-precipitated catalyst. Its catalytic activity above 200 °C was comparable to that of the conventional co-precipitated Cu-ZnO/Al$_2$O$_3$ catalyst. However, the activity of the impregnated Cu-ZnO/Al$_2$O$_3$ catalysts was significantly lowered at 150 °C, whereas no deactivation was observed for the co-precipitated catalyst at the same temperature. It was found that deactivation occurred over impregnated catalysts with H$_2$O and/or O$_2$ in the reaction gas; it prevented CO adsorption on the surface.

2.6.3 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.
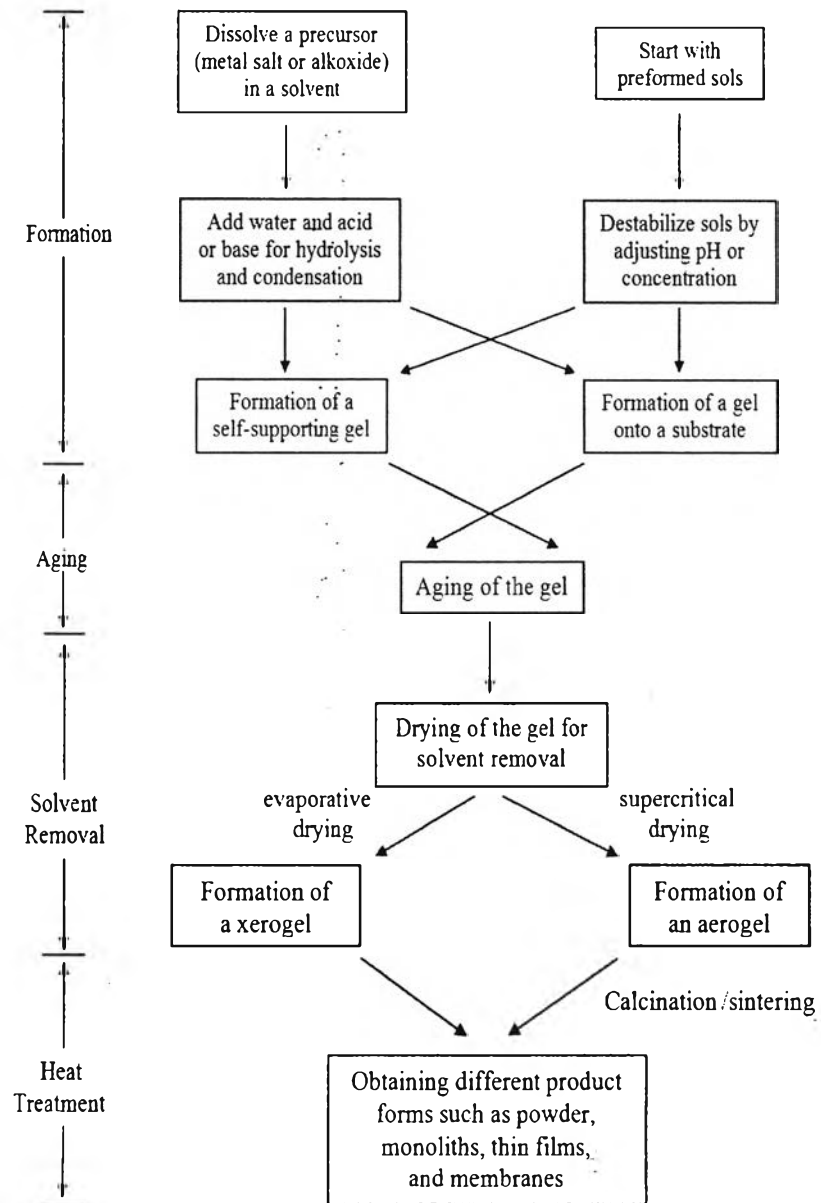

Figure 2.12 Schematic diagram showing the various steps of a sol-gel process (Ertl *et al.*, 1999).

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 2.12.

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.

Takeishi and Yamamoto (2007) patented the preparation method of copper alumina catalysts for dimethyl ether steam reforming (hydrogen production) by impregnation and sol-gel method. The results showed that, in an impregnation method in which a carrier made of alumina is impregnated in a catalyst metal solution to support a catalyst metal, a catalyst metal is supported only on the surface of a catalyst layer, showing poor dispersion. Furthermore, in the impregnation method, decrease in

reforming ability is a caused sometimes by sintering of an active metal by heat. In contrast, the catalyst prepared by sol-gel method has a feature that catalyst metal is highly dispersed and is not easily sintered. Furthermore, by inclusion of Mn, Fe, or Zn, Copper being active in dimethyl ether steam reforming reaction can be increasingly dispersed and highly active Cu and Cu^+ can be kept stable. By this, an excellent reforming ability can be obtained even at low temperatures such as 200 °C to 275 °C, at which a reaction does not occur easily with a normal catalyst. A catalyst prepared by a sol-gel method can have a large pore diameter without reducing the specific surface area by inclusion of Mn, Fe, and/or Zn. Pores of 80 Å to 200 Å are most suitable for dimethyl ether reforming and can provide an excellent reforming ability even at low temperatures.

2.7 Deactivation and Regeneration

The classic definition of a catalyst is a substance which alters the rate at which a chemical reaction occurs, but is itself unchanged at the end of the reaction. It is a practical reality, however, that catalysts deactivate over time.
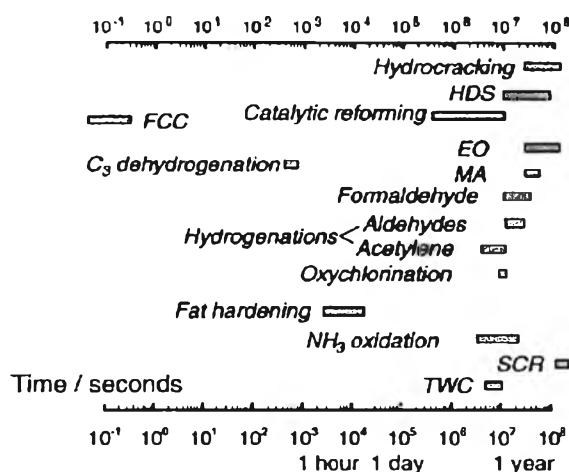

Figure 2.13 Time scale of deactivation of various catalytic processes (Moulijin *et al.*, 2001).

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 2.2 Mechanisms of catalyst deactivation (Bartholomew, 2001)

| Mechanism	Type	Brief definition/description
Poisoning	Chemical	Strong chemisorption of species on catalytic sites, thereby blocking sites for catalytic reaction
Fouling	Mechanical	Physical deposition of species from fluid phase onto the catalytic surface and in catalyst pores
Thermal degradation	Thermal	Thermally induced loss of catalytic surface area, support area, and active phase–support reactions
Vapor formation	Chemical	Reaction of gas with catalyst phase to produce volatile compound
Vapor–solid and	Chemical	Reaction of fluid, support, or promoter with solid–solid reactions catalytic phase to produce inactive phase
Attrition/crushing	Mechanical	Loss of catalytic material due to abrasion. Loss of internal surface area due to mechanical-induced crushing of the catalyst particle
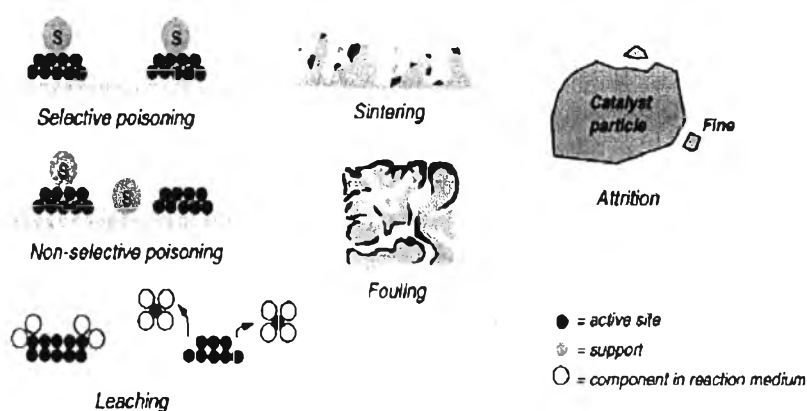
Figure 2.14 Major types of deactivation in heterogeneous catalysis (Moulijin *et al.*, 2001).

2.7.1 Poisoning

The activity of a catalyst is dictated by only a fraction of the total available surface. If those active sites react with a second chemical, then the nature of the surface 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.
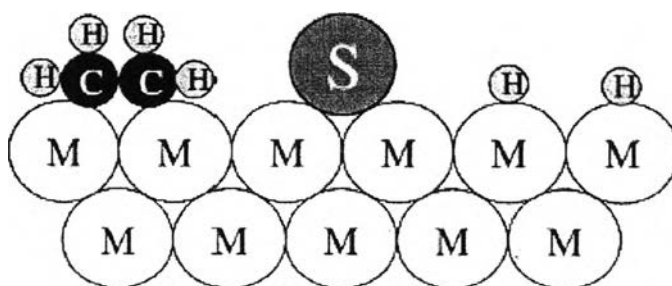

Figure 2.15 Conceptual model of poisoning by sulfur atoms of a metal surface during ethylene hydrogenation (Bartholomew, 2001).

Table 2.3 Common poisons classified according to chemical structure (Bartholomew, 2001)

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

The first group of poisons involve Group VA and VIA elements, including N, P, As and Sb (VA) and O, S, Se and Te (VIA). The elements poison metal catalysts by interaction through their S and P orbitals and the importance of the poisoning effect can be changed by changing the number of bonding electrons — for example, by oxidation or reduction. Thus, the poison efficiency of sulphur increases as $SO_4^{2-} < SO_2 < H_2S$.

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

Poisoning selectivity is illustrated in Figure 2.16, 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".
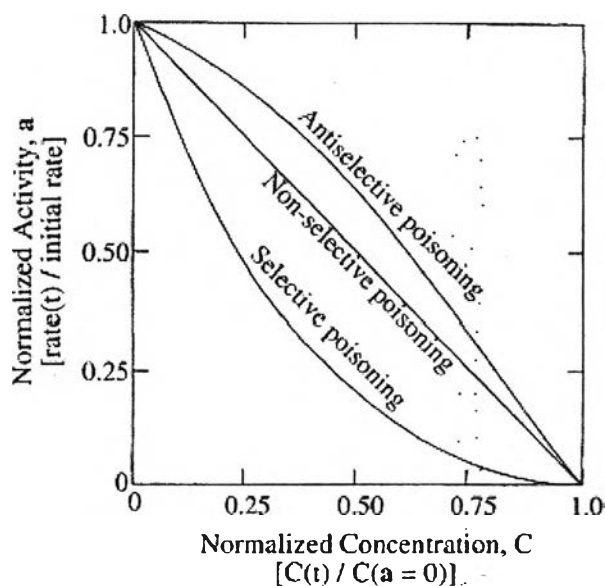

Figure 2.16 Three kinds of poisoning behavior in terms of normalized activity vs. normalized poison concentration (Bartholomew, 2001).

2.7.2 Fouling

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

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

All carbonaceous deposits may be removed by gasification or washing. The preferred route is gasification of coke with oxygen because of the efficiency and fastness, however, careful control of temperature is essential. On the other hand, washing is not a possibility often considered, but it can be effective in some case. Heck *et al.* (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.

2.7.3 Thermal Degradation

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

Three principal mechanisms of metal crystallite growth have been advanced:

(1) crystallite migration

(2) atomic migration

(3) vapor transport (at very high temperatures)

The processes of crystallite and atomic migration are illustrated in Figure 2.17. 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.
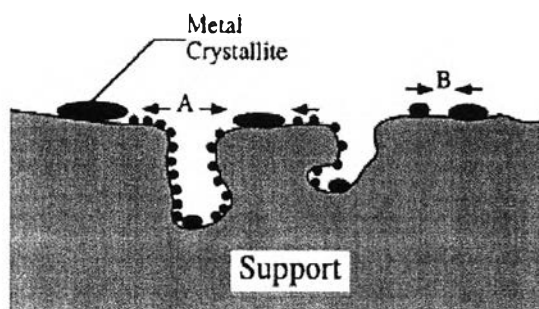
Figure 2.17 Two conceptual models for crystallite growth due to sintering by (A) atomic migration or (B) crystallite migration (Bartholomew, 2001).

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 2.4). Sintering rates increase exponentially with temperature. Metals sinter relatively rapidly in oxygen and relatively slowly in hydrogen, although depending upon the support, metal 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.

Table 2.4 Effects of important reaction and catalyst variables on sintering rates of supported metals based on GPLE data (Bartholomew, 2001)

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

2.7.4 Mechanical Deactivation

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

2.7.5 Corrosion/leaching

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

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

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

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

Zhu and Hofman (1996) studied deactivation of $Ni/SiO_2/Al_2O_3$ catalyst in hydrogenation of 3-hydroxypropanal (3-HPA) solution at temperature 45-80 °C and pressure 2.60-5.15 MPa. The experimental results showed that hydrogen concentration

in liquid phase and dissolution of nickel were not the reasons for the deactivation, on the contrary, the adsorption of by-products and some poison are the reasons for the loss of active site due to the blockage of the specific area (S_{meso}) from 117 m^2/g to 106 m^2/g and the mesopore radius (r_{meso}) from 1.9 nm to 2.2 nm.

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

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

Wang *et al.* (2007) studied deactivation and regeneration of titanium silicalite catalyst for epoxidation of propylene to produce 1,2-propanediol. After the

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

2.8 Criteria to Ensure Ideal Behaviors in Trickle-Bed Reactors

Trickle-bed reactors are regularly used in bench scale and pilot plant experiments to determine reaction kinetics and generate data for commercial scale-up. Depending on experimental conditions, these reactors sometimes cannot produce accurate data if the influences of three main factors—plug flow deviation, external wetting efficiency, and reactor wall effect—on reactor performance are not suitably minimized or eliminated. Therefore, it is highly desirable to operate a trickle-bed reactor at conditions at which these effects can be neglected so that reliable and repeatable data can be obtained (Mederos *et al.*, 2009).

Reducing the bed length will increase the deviation from plug flow towards more axial mixing. This is also described by the axial dispersion model, in which the dimensionless Peclet number, *Pe*, is used as parameter.

$$Pe = \frac{L_b}{d_p} Pe_p \qquad (1)$$

For a sufficiently close approach to ideal plug flow, Peclet number should exceed a certain value that depends on the degree of conversion (*x*) and on the reaction order

(*n*). Gierman refined the criterion of Mears and arrived at Equation (2), which can also be used for monoliths.

$$Pe > 8n \ln \left(\frac{1}{1-x}\right)$$ (2)

Evaluation of literature data on the correlation between the particle Peclet number, Pe_p (also referred to as the Bodenstein number) and the particle Reynolds number, Re_p for single-phase and trickle flow yielded Figure 2.18.
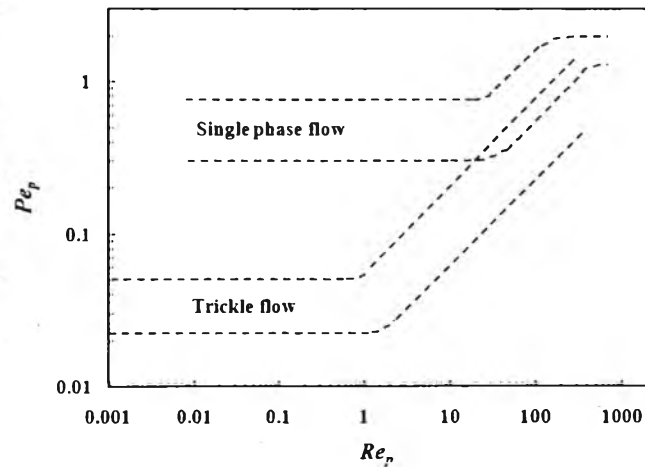

Figure 2.18 Relation between the Peclet particle and Reynolds particle numbers for single-phase and trickle flow (Ertl *et al.*, 2008).

Combining Equation (1) and (2) yields a criterion for the minimum ratio of the bed length (L_b) to the particle size (d_p):

$$\frac{L_b}{d_p} > \frac{8n}{Pe_p} \ln\left(\frac{1}{1-x}\right)$$ (3)

Taking particle Peclet number for the low Reynolds region of interest for laboratory-scale operation, it is possible to calculate the minimum reactor length for a

given reaction order, conversion and particle size. Alternatively, a maximum allowable particle diameter can be calculated for a reactor of given length.

In plug flow reactors, not only the reactor length but also the diameter (d_t) plays a role in its plug-flow performance. Close to the wall the packing density is lower than that in the interior because of the presence of a flat wall surface. To avoid the radial mixing effects, as a rule of thumb the following condition should be satisfied:

$$\frac{d_t}{d_p} > 10 \tag{4}$$

In ideal trickle-flow reactors, all particles in the catalyst bed take part in the overall reactor performance, since each is surrounded, "wetted", by the liquid phase that flows around it. Situations in which the liquid preferentially flows through a certain part of the bed, while the gas phase predominantly flows through another part, should be avoided. Gierman proposed the following criterion for the wetting number, W_{tr} for concurrent down flow operation:

$$W_{tr} = \frac{v_l u_l}{d_p^2 g} > 5 \times 10^{-6} \tag{5}$$

The main variables that dictate the uniformity of catalyst irrigation are the liquid velocity (u_l), the particle diameter (d_p) and the kinematic viscosity (v_l) of the liquid.

It will be clear that the particle size is a major factor to be considered in the application of small reactors. Obviously, catalysts in the commonly used form of extrudates of e.g. 1–3 mm in diameter can only be tested in a large reactor at the pilot-plant scale. Sometimes performance data are needed under conditions where internal diffusion gradients exist, to be able to predict industrial operation. A way to satisfy the criteria of small particle size and yet to use the full-size catalyst is to dilute the large catalyst particles with fine inert particles. A too dilute system, especially in the case of

equal sized particles, may lead to uneven distribution and bypassing of the catalyst. In general, samples should not be diluted more than 5–10-fold.