

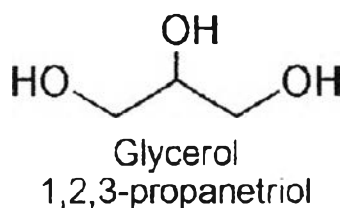


CHAPTER II LITERATURE REVIEW

2.1 Properties and Uses of Glycerol

Glycerol (1, 2, 3-propanetriol) is a colorless, odorless, viscous liquid with a sweet taste, derived from both natural and petrochemical feedstocks. The name glycerol originates 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 and glycerine generally refer to a commercial solution of glycerol in water, of which the principal component is glycerol. Crude glycerol is 70-80% pure and is often concentrated and purified prior to commercial sale to 95.5-99% purity (Pagliaro and Rossi, 2010). Moreover, Glycerol is low of toxicity, strongly hygroscopic (in an exothermic reaction), completely soluble in water and alcohol, and insoluble in hydrocarbon (Petsriprasit, 2009).

Glycerol has many common names such as glycerin, glycerine, glyceritol, glycy alcohol, 1, 2, 3-propanetriol, 1, 2, 3-trihydroxypropane and its chemical formula is $C_3H_5(OH)_3$. Glycerol is a trihydric alcohol, having two primary and one secondary hydroxyl groups, which are its potential reaction sites and the basis for glycerol’s usefulness as a chemical raw material. It has a molecular weight of 92.09, a density of 1.2375 (@ 20 °C), a melting point of 17.8 °C, a flash point of 176 °C and boiling point of 290 °C accompanied by decomposition (Petsriprasit, 2009).



$C_3H_8O_3$
MW: 92.09
mp: 17.8 °C
bp₇₆₀: 290 °C (decomp).
Density @ 20 °C = 1.2375
Flash point 176 °C

Figure 2.1 Glycerol properties (Kenar, *et al.*, 2007).

Glycerol can be used in various applications such as food industries, pharmaceuticals, personal care applications, botanical extracts, anti-freeze, and etc. In medical and pharmaceutical preparations, glycerol is used for improving smoothness and providing lubrication, and also acts as humectants, a hygroscopic substance keeping the preparation moist. Glycerol is also used to maintain texture because it can control water activity and prolongs shelf life in a host of applications. It is also widely used as a laxative, based on the same induced hyper osmotic effect, in cough syrups, elixirs and expectorants, toothpaste, mouthwashes, skin care products, shaving cream, hair care products, soaps and water-based personal lubricants.

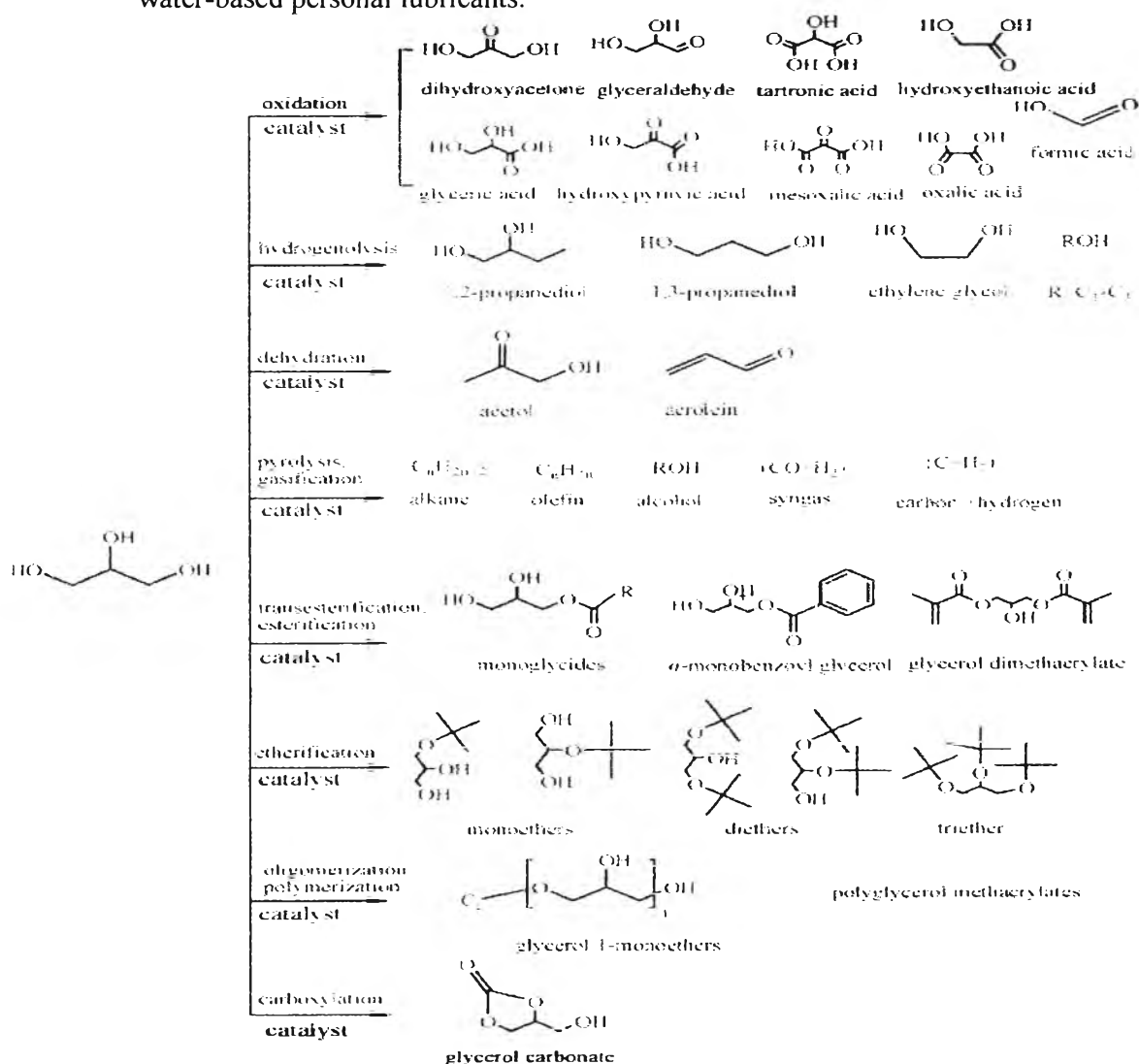


Figure 2.2 The conversion of glycerol into the useful products (Zhou, *et al.*, 2008).

In foods and beverages, glycerol serves as a humectant, solvent, and sweetener, and may help to preserve foods. It is also used as filler in commercially prepared low-fat foods (e.g., cookies), and as a thickening agent in liqueurs. Glycerol and water are used to preserve certain types of leaves.

Glycerol's utilizations in chemical industry cover a wide range of products and applications. Glycerol is the main starting material for nitroglycerine, which is used in the manufacture of dynamites and munitions. When reacted with dibasic acids, such as phthalic acid, it makes alkyd resins, an important class of chemicals used in coating and paints. Glycerol is also used as a levitating agent to reduce the particle size of a powder on grinding (Petsriprasit, 2009).

2.2 Properties and Uses of Polyglycerol

The viscosity of glycerol oligomers increases with chain length. The uses of higher polyglycerols (higher or equal to heptaglycerol) are restricted in food applications (EU Commission, 1998), where the desired polyglycerols are usually di- and triglycerol. A positive effect of increased chain length is decreased volatility, which reduces the evaporation of an added fragrance, e.g. in deodorants and mouthwashes (Solvay Chemicals, Inc., 2004). Other properties that follow chain length are increase of thermal stability and refractive index. In addition, the humectants property reduces with increase of the chain length (due to decrease of hydrophilicity).

Polyglycerols have a large number of applications. They are used as a starting material for the production of surfactants, cosmetics, food additives, and lubricants (Clacens, *et al.*, 2002). Also, polyglycerols can be used as reactants in the production of polyurethanes and polyesters (Solvay Chemicals, Inc, 2005). Recently, diglycerol derivatives were proposed as novel oligomeric liquid crystals (Nakamura, *et al.*, 2007).

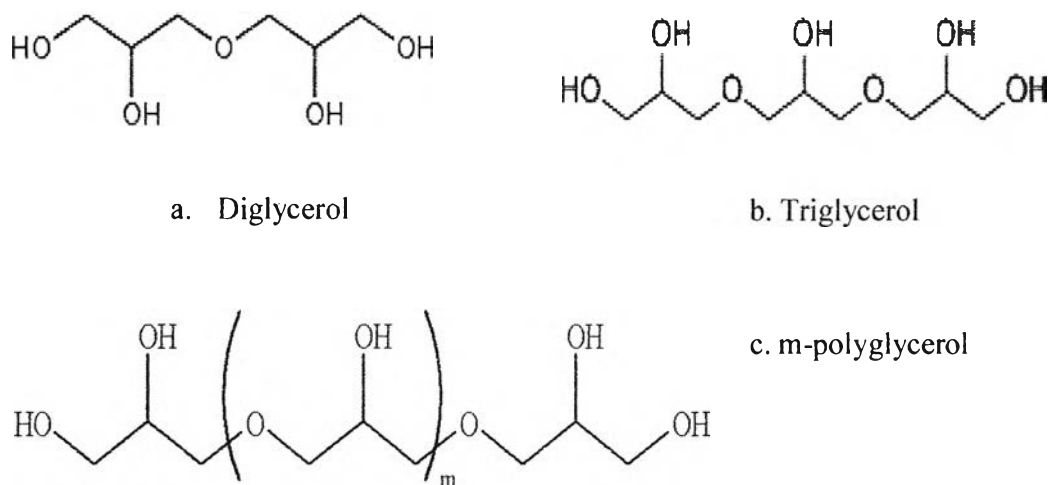


Figure 2.3 Structure formulas of diglycerol (a), triglycerol (b), glycerol polymer (c).

Even though the applications of polyglycerols are so numerous, as seen in the previous paragraphs, polyglycerol esters find much more widespread application.

Polyglycerol esters (PGE) are non-ionic surfactants that free from ethylene oxide and nitrosamines. They are biocompatible and biodegradable, and are allowed for food in many countries (Solvay Chemicals, Inc., 2008). The polyglycerol part, usually made up of a linear di- or triglycerol, is connected to the fatty acid part with an ester linkage. The length and shape of the fatty acid may vary. An important property of polyglycerol esters and surfactants is the hydrophilic-lipophilic balance (HLB); this ratio is simply calculated as the molar mass of the hydrophilic part divided by the molecule's molar mass. This ratio can be used to predict general behavior of a surfactant in a two-phase system (Acosta *et al.*, 2008).

Polyglycerol esters are used in several applications such as in cosmetics, in foods, pharmaceuticals and other industries. In cosmetics; they are used to emulsify, control viscosity, disperse and stabilize the final mixture. They are incorporated into hair styling gels, skin treatment gels, skin cleansers, baby creams, long-acting hand creams, moisturizing sunscreens, and sun-protective

sticks. In foods; they are used as emulsifying agents in the production of fine bakery, chewing gum, and in replacement of fats. Polyglycerol polyricinoleate (E476) is an emulsifier made from castor beans (rich in ricinoleic acid) which reduces the viscosity of chocolate and similar coatings and compounds. It is used at low levels (fractions of percents). By using (E476), the chocolate recipe has lower costs in terms of less cocoa butter but also gives the benefit of having less fat.

2.3 Glycerol with transesterification and esterification reaction

Monoglyceride and polyglycerol esters are the major products from transesterification and esterification reaction. In commercial process, basic catalysts such as potassium hydroxide and calcium oxide are normally used. Their applications are cosmetics, pharmaceuticals, food industries, synthetic lubricants, detergencies, and etc. Nowadays polyglycerol esters are so popular in surfactant applications because they are new marketable product and biodegradable for environmental friendly. For monoglyceride, it can be produced from these three commercial processes.

- Direct esterification of glycerol with fatty acid
- Transesterification of triglycerides with glycerol
- Glycerolysis of triglycerides

The product of direct esterification (shown in Figure 2.4) and transesterification (shown in Figure 2.5) is contained 40-60% of monoglyceride and 35-45% of diglyceride by using temperature at approximately 240 °C and resident time not exceed in half an hour. Moreover, from the basic catalysts, the purification section will include the neutralization step and removal of salt formations from the products.

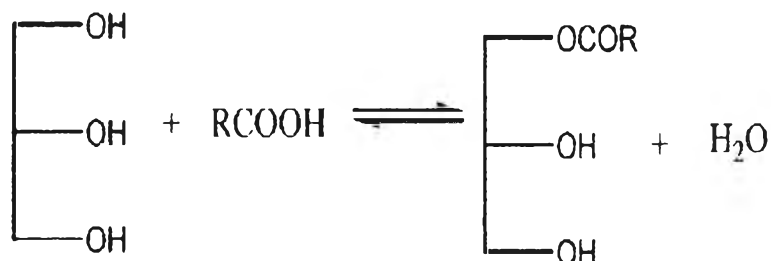


Figure 2.4 Reaction for direct esterification of glycerol with fatty acid (Zhou, *et al.*, 2008).

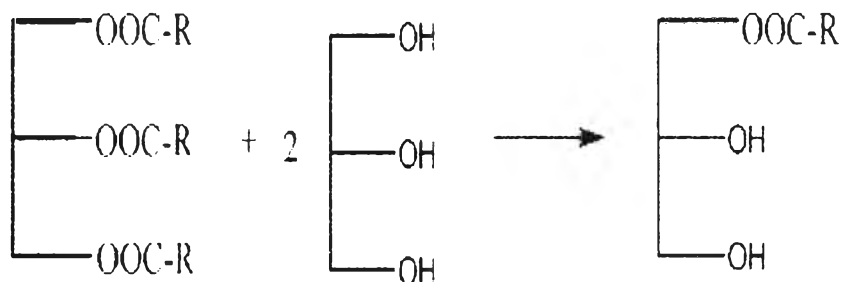


Figure 2.5 Reaction for transesterification of triglycerides with glycerol (Zhou, *et al.*, 2008).

2.4 Glycerol with Etherification Reaction

The obvious way of polymerizing glycerol is to simply add several glycerol molecules after each other, building arbitrarily long chains of polyglycerol. This kind of reaction is a condensation, or etherification, where one mole of water is created for every ether linkage formed. Etherification of glycerol may lead to a number of different products. Apart from getting linear polymer chains of varying lengths, one will get branched chains and to some extent also cyclic polyglycerols.

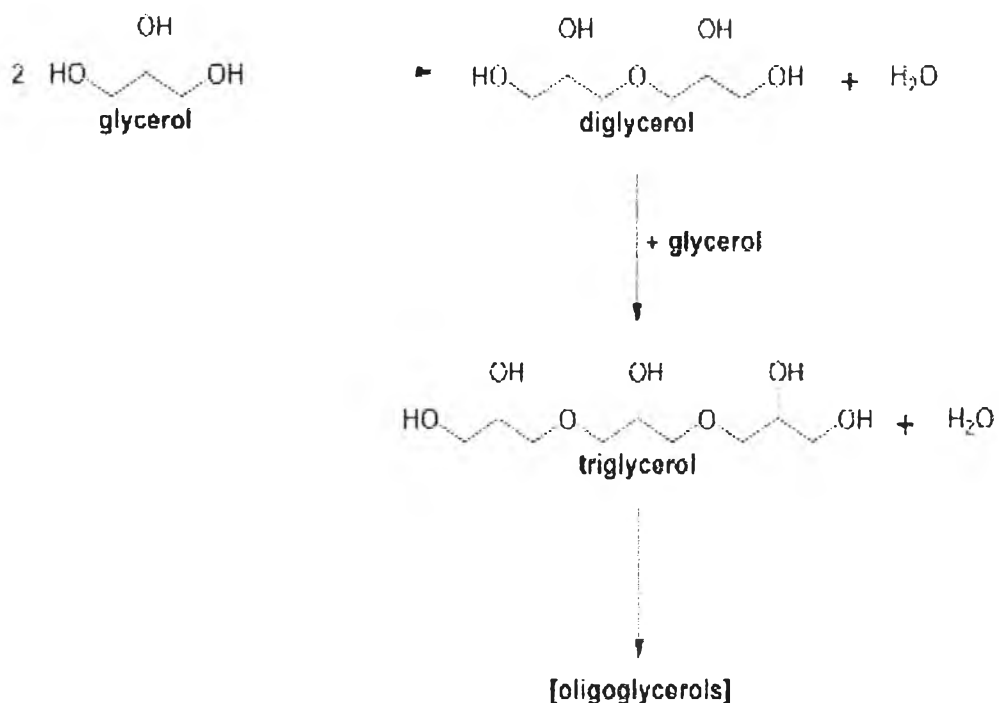


Figure 2.6 Condensation of glycerol to polyglycerols (Behr, *et al.*, 2007).

If the etherification is done in the presence of air, one will also likely get acrolein, the simplest aldehyde. Acrolein is clear or yellow liquid that evaporates quickly and burns easily. It has strong and unpleasant smell. It reacts quickly when exposed to other substances and used widely as an intermediate in the chemical industry. CO₂ or N₂ can be bubbled through the reaction mixture to prevent the formation of acrolein (Petsriprasit, 2009).

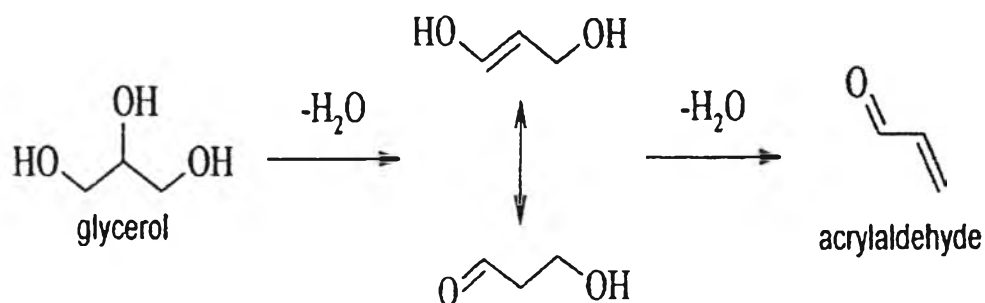


Figure 2.7 Dehydration of glycerol leading to the formation of acrylaldehyde, or acrolein (Petsriprasit, 2009).

Polymerization of glycerol is done with a specific linear polyglycerol as the intended product, most commonly, the linear di- and/or triglycerols. As the polyglycerol chain grows (by adding more glycerol units), the viscosity increases while the hydrophilicity decreases.

2.5 Etherification of Glycerol by Homogeneous Catalysis

The hindrances confronted on polymerization of glycerol using etherification reactions are involved with the reacting glycerol with epichlorohydrin in proper ratios to get the intended linear polyglycerol with high yields. The common solution of this problem was provided by Solvay, a large manufacturer of polyglycerols (Solvay Chemicals, Inc, 2005). The solution is to abandon the condensation route altogether.

The etherification reaction is followed by hydrolysis, neutralization, and finally purification of the product (Solvay Chemicals, Inc, 2005). This process is also described in detail in a patent by Jakobson and Siemanowski (1990).

However, this method of producing polyglycerols still has a drawback, which is the introduction of chlorinated reactants that can lead to hydrochloric acid and other chlorinated by-products. Unfortunately, it still seems not having a good way to polymerize glycerol homogeneously by simple condensation (etherification) without losing control of the final product's polyglycerol composition (Petsriprasit, 2009).

There is also a very old method provided by Seiden and Martin (1976), the composition of polyglycerol is controlled by quenching the reaction at a proper time with a base that neutralizes the catalyst (sulfuric acid). Then unreacted glycerol and cyclic diglycerol are removed by distillation.

Seiden and Martin (1976) also noticed the interesting fact that during the glycerol polymerization process, the initial rate of diglycerol formation is higher than that of the longer chain polymers. Moreover, they claimed that "the diglycerol content reaches its maximum concentration when about 50% of the glycerol has been polymerized". From that point onwards, the rate of diglycerol

formation is lower than the rate at which diglycerol is further polymerized. So the concentration of diglycerol decreases.

2.6 Etherification of Glycerol by Heterogeneous Catalysis

This field is quite new, at least academically, and it has been hard to find publications describing this matter. Much of the research is probably kept secret for commercial reasons.

Commercially, diglycerol is prepared by base hydrolysis of epichlorohydrin followed by distillation (Jakobson, 1986). But it is difficult to obtain diglycerols in a selective manner in homogenous system. Batch conversion requires fractional distillation to separate glycerol, diglycerols, and higher oligomers.

Seiden *et al.* (1976) studied process for preparing polyglycerol by heating glycerol under reduced pressure in the presence of sulfuric acid and glycerol ester. The condensation reaction was terminated by adding a neutralizing agent to the mixture. Then unreacted glycerol and cyclic diglycerol were removed by distillation. However, this process was complicated and products were relatively poor in color quality.

To overcome these drawbacks, attempts have been made to convert glycerol directly into the desired oligomers by using various bases, including hydroxides, carbonates, base porous solids, and oxides of several metals (Eshuis, *et al.*, 1997).

It was found that carbonates are more active than hydroxides, despite the weaker base character of the former (Garti, *et al.*, 1981). This behavior has been attributed to the better solubility of carbonates in glycerol and in the polymeric product at elevated temperatures.

Harris *et al.* (1992) reported that the fraction of the diglycerol and triglycerol is below or equal to 65% over sodium zeolites and sodium silicate. They suggested that there is no shape selectivity effect over these catalysts and likely the outer surface of the catalyst plays an important role in the case of NaA zeolite sample.

Clacens *et al.* (1998) reported that the heterogeneously catalyzed reaction using cesium ion exchanged zeolites gave a lower activity but higher of selectivity to di- and triglycerols than the homogeneously catalyzed reaction with Na_2CO_3 . Furthermore, the wide pore faujasite-type (FAU) zeolite X, ion-exchanged by Cs, exhibited a higher activity and selectivity than the medium-pore MFI-type zeolite ZSM-5, which was attributed to pore-size effects.

Hattori (1995) and Deka *et al.* (2000) found that the effect of alkali cations on the base strength of zeolites were in the order $\text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$. Therefore, attempts have been made to exchange Na^+ in the zeolite by Cs^+ in order to enhance the activity of the solid catalysts.

Barrault *et al.* (2002) demonstrated that solid and basic materials may replace the usual homogeneous catalyst with same activity and selectivity but without the formation of by-product and wastes. Further, in the presence of mesoporous solids with accurate pore size, more than 80% of yield was obtained and was selectively transformed to linear di- and triglycerol.

Lemke (2002) encountered that when potassium hydroxide or sodium hydroxide were replaced by calcium hydroxide during polymerization of glycerol. The formation of cyclic polyglycerols was extremely reduced. Thus, polyglycerols were prepared by mixing glycerol with calcium hydroxide catalyst. The temperature and pressure of this reaction were 230 °C and 150 mmHg, respectively. The polyglycerols in high yield with insignificant formation of cyclic polyglycerol were obtained.

Clacens *et al.* (2002) studied the selective synthesis, from glycerol and without solvent, of polyglycerols having a low polymerization degree (di- and triglycerol) in the presence of solid mesoporous catalyst. They studied the synthesis and impregnation of mesoporous solids with different basic elements for making them active, stable, and selective for the aim reaction. The results showed that impregnation method gave important activity, which must be correlated to important active species incorporation. The selectivity of the modified mesoporous catalysts, the best value to di- and triglycerol were obtained over solids prepared by cesium impregnation. The re-use of these cesium impregnated catalysts did not affect the selectivity to the di- and triglycerol fraction. In the

presence of magnesium and lanthanum containing catalysts, the glycerol dehydration to acrolein was very significant whereas this unwanted product was not formed when cesium was used as an impregnation promoter.

Barrault *et al.* (2004) studied synthesis and modification of catalysts. The catalysts prepared by the impregnation method showed the highest activity, but were subjected to metal leaching. The reaction was performed at 260 °C at atmospheric pressure under nitrogen atmosphere in the presence of 2 wt% of catalyst. Mesoporous solids modified by cesium impregnation or exchange led to the best selectivity and yield to (di-+tri-) glycerol (more than 90%). The exchanged catalysts were the most stable but the less ones; the impregnated catalysts can be reused without losing of their selectivity to (di-+tri-) glycerol.

Weckhuysen *et al.* (2008) observed that the reactivity of alkaline-earth oxides for glycerol conversion is in accordance with the basicity of the solids, that is $\text{BaO} \approx \text{SrO} > \text{CaO} \gg \text{MgO}$. However the authors also reported that CaO is active as BaO if applied in the form of colloidal particles.

Previous works showed that the homogeneous catalysts had a good activity but poor in selectivity. On the other side, heterogenous catalysts such as zeolite, ion exchanged mesoporous molecular sieves or other basic materials were not so good in activity but they had a high selectivity to diglycerol obtained at different glycerol conversion depending on the type of catalyst.

2.7 SBA-15

Since extensive leaching may threaten the reuse ability and the environmental sustainability of the heterogenous catalysts, pure solid seems not suitable for industrial applications. Therefore, it is important to investigate novel heterogenous basic catalysts that are both active and stable for the etherification reaction.

New chances have occurred in many areas of chemistry and material science since the discovery of mesoporous silica molecular sieves (Kresge, *et al.*, 1992). Because of its desirable features, e.g. tailorable pore size, high degree of structural ordering, ease of synthesis, larger pore size, thicker pore walls and

higher hydrothermal/thermal stability, SBA-15 has been widely studied in the last decade (Zhao, *et al.*, 1998).

SBA-15 is 2D hexagonally mesostructured silica molecular sieve, first reported by Zhao *et al.* (1998). The results suggested that SBA-15 has a highly ordered 2D hexagonal mesostructure with a very uniform pore-size distribution. SBA-15 materials prepared from P123 at 40-100 °C (hydrothermal temperature) have uniform pore sizes from ~6.5 to 10 nm. The pore-wall thickness is calculated to be 3.1-4.8 nm, much thicker than that of MCM-41 resulting in higher thermal and hydrothermal stability.

Albuquerque *et al.* (2008) studied the CaO supported on mesoporous silicas as basic catalysts for transesterification reactions. A new family of base catalysts has been prepared by impregnation and subsequent thermal treatment of calcium acetate supported on mesoporous SBA-15 silica. This support, as compared to MCM-41 and fumed silica, has proven to be more thermally resistant, and the interaction between CaO and silica is strong enough to prevent the lixiviation of the active phase in methanol.

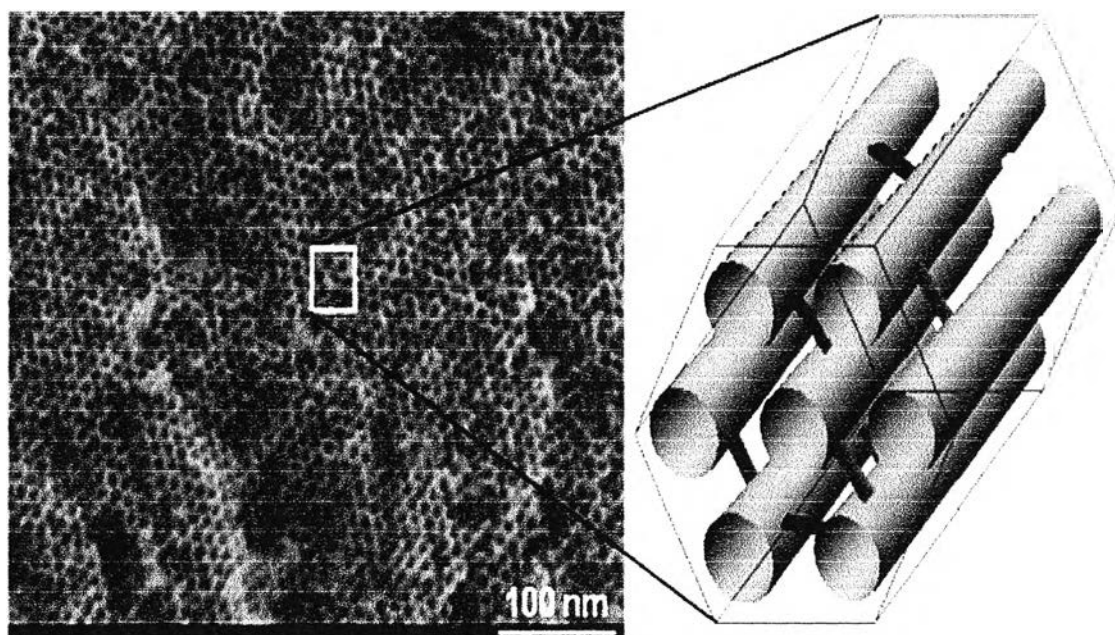


Figure 2.8 Ordered mesoporous silica SBA-15 (<http://nano/abstracts/kleitz.html>).

Li and Rudolph (2008) compared the catalytic activity of MgO-functionalized mesoporous materials in the transesterification of blended vegetable oil with ethanol. When the reaction was carried out at 220 °C for 5 h under continuous stirring in a batch reactor, SBA-15 impregnated with MgO was found to be the most effective, reaching a high conversion of 96%. They also concluded that SBA-15 impregnated with MgO is very promising catalyst for the transesterification of vegetable oil for biodiesel production and has potential as a heterogeneous catalyst for such reactions.

Nowadays, SBA-15 has achieved various applications in the fields of catalysis, adsorptions, separations, water purification, and advanced optical devices because of its unique physicochemical properties (Tuel, *et al.*, 2003).

2.8 Successive Ionic Layer Deposition (SILD)

Successive ionic layer deposition (SILD) is an aqueous method for depositing materials on a support through a series of chemical reactions. However, rather than plainly physically depositing small particles or atoms randomly onto a surface, SILD uses interactions between the support and ionic precursors to ultimately adhere the thin film to the support surface. The SILD procedure exploits the electric double layer effect to create a supported thin solid film in a layer-by-layer fashion. During each step of SILD, submonolayers of desired cations and anions are alternately and selectively adsorbed on a surface to produce SILD nanolayers with controlled composition and morphology. Low operating temperatures, simple equipment, and atmospheric pressure of the SILD process make it a comparatively low cost technology. Because SILD adheres the thin film to the support through electronic interactions between the support and the aqueous precursors, SILD may prove to become a powerful method for uniformly depositing oxide materials on a support such that they remain stable even at elevated temperatures (Gilbert, 2010).

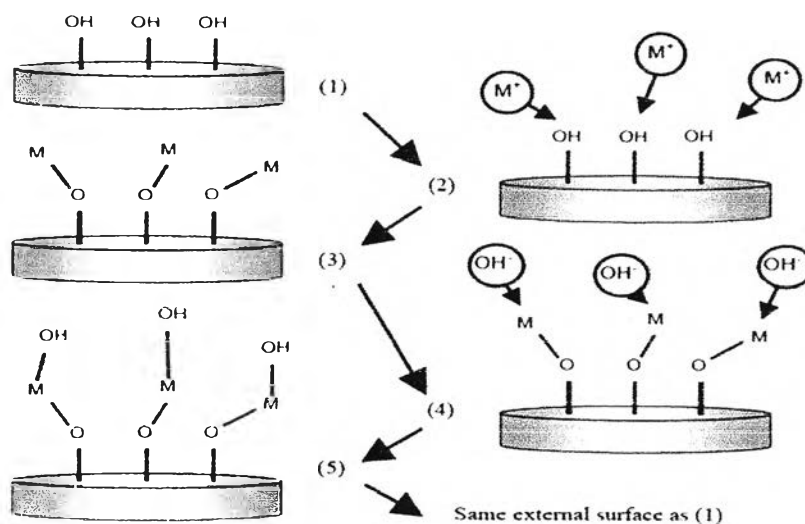


Figure 2.9 Illustration of the steps in the SILD cycle (Gilbert, 2010).

2.9 Quantification of Polyglycerol

Polyglycerols can be composed of cyclic polyglycerols and acrolein owing to side reactions and inadequate purification of the product. For this reason a responsive and reliable analytical method is needed to observe the purity of polyglycerols. Numerous chromatographic techniques such as Gas Chromatography/Mass Spectroscopy (GC/MS), Gas Liquid Chromatography (GLC), High Performance Liquid Chromatography (HPLC), Nuclear magnetic resonance (NMR), MALDI-TOF-MS, Gel Permeation Chromatography (GPC), Viscosimetry, VPO, and DSC have been employed (Petsriprasit, 2009).

Kumar *et al.* (1984) used high performance liquid chromatography (HPLC) with refractive index detector to find out the composition of polyglycerols. Carbohydrate analysis column with acetonitrile-water (85:15) were used to separate and define cyclic diglycerol and polyglycerol oligomers up to undecaglycerol and exhibit its utility in monitoring the preparation of polyglycerols. Hence, we can use HPLC as a tool for monitoring the creation of desired mixtures of polyglycerols and for analyzing polyglycerol esters straight through their polyglycerol moieties.

Roberts *et al.* (1998) used gas chromatography (GC) to examine the polyglycerol mixtures. The packed column was 3% OV-1 on gaschrom Q. and a linear programme was run from 100-300 °C at a rate 10 °C per minute. Gas chromatography/mass spectroscopy (GC/MS) was used to analyze the structural of polyglycerols. The capillary CP-SII 5CB column was run from 50-270 °C at rate 5 °C per minute. Both gas chromatography (GC) and gas chromatography/mass spectroscopy (GC/MS) samples were examined as the silyl derivatives by reacting polyglycerols products with a mixture of hexamethyldisilazane, trimethylsilylchloride and pyridine before the injection.

Lafosse *et al.* (1999) reported that liquid chromatography was used with evaporative light scattering detection and mass spectrometry. An aminopropyl-bond polymer and a porous graphitic carbon were packed in the columns to separate and define the isomeric diglycerols (*prim-prim*, *prim-sec*, and *sec-sec*). The *prim-prim* isomers were separated upon the porous graphite carbon packed column by using pure water as a mobile phase. The *prim-sec* and *sec-sec* isomers were separated upon the aminopropyl-bond polymer packed column by using acetonitrile-water (90:10) as a mobile phase. LC-MS was used to identify the quantities of other compounds.