ACID FUNCTIONALIZATION OF SBA-15 MESOPOROUS CATALYST FOR GLYCEROL ESTERIFICATION TO MONOGLYCERIDE

by

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Lilis Hermida

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LIST OF SYMBOLS

Symbols	Descriptions	Unit
A	Pre-exponential factor	(L mol^{-1} $g_{cat}^{-1}h^{-1}$)
C	Conversion of lauric acid	Dimensionless
C_{FA0}	Initial fatty acid concentration	(mol L^{-1})
C_{G0}	Initial glycerol concentration	(mol L^{-1})
Df	Dilution factor	Dimensionless
E_A	Activation energy	(cal mol^{-1})
k_s	Specific rate of reaction	(L mol^{-1} h^{-1})
M	Molar ratio of glycerol and fatty acid	Dimensionless
N_A	Initial numbers of moles	(mol)
R	Gas constant	(cal $mol^{-1}K^{-1}$)
r_{FA}	Rate of esterification reaction	(mol $g^{-1}_{cat}h^{-1}$)
R_{SD}	Ratio of peak area of ester to peak area of internal standard in the standard references	Dimensionless
R_{SP}	Ratio of peak area of ester to peak area of internal standard in the sample	Dimensionless
S	Monoglyceride selectivity	Dimensionless
T	Absolute reaction temperature	(K)
t	Reaction time	(h)
W	Catalyst weight	(g)
X_{FA}	Monoglyceride yield	Dimensionless
X_{FA0}	Initial fatty acid conversion	Dimensionless
X_{G0}	Initial glycerol conversion	Dimensionless

LIST OF ABBREVIATIONS

a. u	Arbitrary unit
ANOVA	Analysis of variance
BET	Brunauer-Emmett-Teller
BJH	Barrett-Joyner-Halenda
C12TAB	Dodecyl trimethylammonium bromides
C16TAB	Hexadecyl trimethylammonium bromides
CITES	Chloromethyltriethoxysilane
CSPTMS	2-(4-chlorosulfonylphenyl)-ethyltrimethoxy silane
DOE	Design of experiment
EDX	Energy dispersive X-ray
FAME	Fatty acid methyl ester
FESEM	Field emission scanning electron microscopy
FID	Flame ionization detector
FSM	Folded sheet mesoporous materials
FT-IR	Fourier transformed infrared
H_2O	Water
HCl	Hydrochloric acid
HMS	Hexagonal mesoporous silica
IUPAC	International union of pure and applied chemistry
MCM	Mobil crystalline of matter
MeOH	Methanol
MG	Monoglycerides
MMSs	Mesoporous molecular sieves

MPMDS	3-mercaptopropiyl(methyl)dimethoxy silane
MPTMS	3-mercaptopropyltrialkoxylane
MSU	Michigan state university material
MTES	Methyltriethoxysilane
MTMS	Methyl-trimethoxysilane
NaOH	Sodium hydroxide
NH_3TPD	Temperature programmed desorption of ammonia
P123	Pluronic 123
PTES	Phenyl triethoxysilane
PTMS	Propyl-trimethoxysilane
PUFA	Polyunsaturated fatty acid
RSM	Response surface methodology
SBA-12	Santa barbara amorphous no.12
SBA-15	Santa barbara amorphous no.15
SBA-15SO_3H	SBA-15 functionalized with propylsulfonic acid
SBA-15SZ	SBA-15 functionalized with sulfated zirconia
SEM	Scanning electron microscopy
SS	Sum of square
TCP	Tri-block copolymer
TEM	Transmission electron microscopy
TEOS	Tetraethylorthosilicate
TGA	Thermal gravimetric analysis
TLCT	True liquid crystal template
TMOH	Tetramethyl- ammonium hydroxide
TMOS	Tetramethylorthosilicate

TMS	Transition metal oxide mesoporous molecular sieve
TPD	Temperature – programmed desorption
VIH	Vapour-induced internal hydrolysis
VTES	Vinyltriethoxysilane
XRD	X-ray diffraction
C_{12} A	n-dodecylamine

FUNGSIONALISASI ASID TERHADAP MANGKIN SBA-15 MESO LIANG UNTUK PENGESTERAN GLISEROL KEPADA MONOGLISERIDA

ABSTRAK

Bagi mengeksploitasi aliran gliserol, penukaran bahan ini kepada monogliserida dijalankan dalam penyelidikan ini. Monoglycerida telah dihasilkan melalui pengesteran gliserol dengan asid laurik dengan menggunakan bahan meso liang Santa Barbara No. 15 (SBA-15) yang berfungsikan asid sebagai mangkin disebabkan oleh luas permukaan dan diameter liang yang besar, serta ketahanan hidrotermal. Mangkin SBA-15 berfungsikan asid ini disintesis dengan cara mencantumkan dua jenis asid yang berlainan, iaitu asid propil sulfonik dan zirkonia tersulfat ke atas SBA-15. SBA-15 yang dicantumkan asid propilsulfonik (SBA-15SO_3H) disediakan dengan cara menjalankan reflux campuran daripada SBA-15, toluena kering dan trimerkaptopropil trimetoksi silana (MPTMS) pada 105 ^oC, diteruskan dengan rentapan sokhlet selama 24 jam untuk menghasilkan kumpulan propil tiol. Mangkin SBA-15SO_3H dihasilkan dengan cara pengoksidaan kumpulan propil tiol ini kepada bentuk asid sulfonik. Sementara itu, SBA-15 yang difungsikan zirkonia tersulfat (SBA-15SZ) disediakan dengan cara menjalankan tindak balas SBA-15 dengan larutan zirkonium klorida dan urea pada 90 ^oC untuk menghasilkan SBA-15ZrO_2. Mangkin SBA-15SZ dihasilkan dengan cara menjalankan tindak balas SBA-15ZrO_2 ini dengan larutan H_2SO_4 pada 30 ^oC. Dua jenis mangkin ini telah dicirikan dengan beberapa teknik analisis iaitu analisis permukaan, denyut ammonia serapan kimia, termo program penyahjerapan (TPD) ammonia, pembelauan sinar X (XRD), mikroskopi penghantaran elektron (TEM), mikroskopi imbasan elektron (SEM), mikroskopi imbasan electron pancaran medan (FESEM), spektroskopi infra

merah transformasi fourier (FT-IR) and analisis thermograviti (TGA), dan telah diuji bagi menentukan mangkin yang sesuai untuk tindak balas pengesteran gliserol dengan asid laurik pada 160 ^{o}C selama 6 jam pada nisbah bilangan mol gliserol/asid laurik 4 : 1. Mangkin SBA-15SO_3H yang memberikan penukaran asik laurik (73 %) dan kepilihan monogliserida (68 %) telah didapati sebagai mangkin yang paling sesuai untuk tindak balas ini kerana mempunyai kepekatan tapak asid yang lebih tinggi. Kajian pengoptimuman proses persediaan mangkin SBA-15SO_3H merangkumi kesan jumlah MPTMS (1 – 5 ml) dan masa refluks (4-20 jam). Proses pengoptimuman ini dijalankan dengan menggunakan uji kaji faktorial peringkat tiga 3^2 bagi mendapatkan mangkin SBA-15SO_3H yang memberikan penukaran asid laurik dan kepilihan monogliserida yang paling tinggi, dan pada masa yang sama untuk menilai keadaan di antara parameter-parameter yang saling bertindak balas. Keadaan optimum bagi menyediakan mangkin SBA-15SO_3H adalah dengan menggunakan 3-merkap topropil trimetoksi-silana (MPTMS) sebanyak 1 ml per gram SBA-15 dan masa refluk selama 20 jam bagi mendapatkan penukaran asid laurik (95%) dan kepilihan monogliserida (70%) yang paling tinggi untuk tindak balas pengesteran gliserol pada 160 ^{o}C, pada nisbah bilangan mol gliserol/asid laurik 4 : 1 dan tanpa kehadiran pelarut. Tambahan pula, kajian penggunaan semula mangkin yang ditemukan pada keadaan optimum (SBA-15SO_3H) telah dijalankan sehingga empat pusingan tindak balas dengan menggunakan mangkin dan keadaan tindak balas pengesteran gliserol yang sama. Mangkin SBA-15SO_3H telah mengekalkan prestasi pemangkinannya ke atas empat pusingan tindak balas tanpa mengalami penyahaktifan yang ketara. Pengesteran gliserol oleh mangkin SBA-15SO_3H didapati memenuhi model kinetik peringkat kedua dengan tenaga keaktifan 40.6 kJ/mol yang mana lebih rendah daripada yang dicatatkan di literatur.

ACID FUNCTIONALIZATION OF SBA-15 MESOPOROUS CATALYST FOR GLYCEROL ESTERIFICATION TO MONOGLYCERIDE

ABSTRACT

In order to exploit the glycerol stream, its transformation into monoglyceride was carried out in the present study. Monoglyceride was produced through glycerol esterification with lauric acid using acid functionalized Santa Barbara no.15 (SBA-15) mesoporous material as catalyst due to high surface area, large pore diameter and hydrothermal stability. The acid functionalized SBA-15 catalysts were synthesized by incorporating two different acid sites, i.e. propylsulfonic acid and sulphated zirconia, on the SBA-15. The SBA-15 incorporated with propylsulfonic acid (SBA-15SO_3H) was prepared by refluxing a mixture of SBA-15, dry toluene, trimercaptopropyl trimethoxysilane (MPTMS) at 105 ^oC, followed by soxhlet extraction for 24 h to propylthiol groups. The SBA-15SO_3H catalyst was obtained by oxidation of the thiol group (-SH) to sulfonic acid form (–SO_3H). Meanwhile, SBA-15 incorporated with sulfated zirconia (SBA-15SZ) was prepared by reacting SBA-15 with solution of zirconiumoxychloride and urea at 90 ^oC to create SBA-15ZrO_2. The SBA-15SZ catalyst was obtained by reacting SBA-15ZrO_2 with H_2SO4 solution at 30 ^oC. The two types of catalysts were characterized by a number analytical techniques i.e. surface analysis, pulse chemisorption and temperature programmed desorption (TPD) of ammonia, X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), field emission scanning electron microscopy (FESEM), energy dispersive X-ray (EDX), fourier transformed infrared (FT-IR), thermal gravimetric analysis (TGA). Then, the two types of catalysts were tested to determine the suitable catalyst for the glycerol

esterification with lauric acid at 160 ^{o}C for 6 h with glycerol/lauric acid molar ratio of 4 : 1. The SBA-15SO_3H catalyst giving lauric acid conversion of 73 % and monoglyceride selectivity of 68% was found to be suitable catalyst for the glycerol esterification due to the higher acid site concentration. Furthermore, optimization study on the preparation process of SBA-15SO_3H catalysts covered the effect of MPTMS amount (1 – 5 ml) and reflux time (4 -20 h). Optimization was assessed using 3^2 three levels factorial design of experiment to obtain the catalyst giving the highest lauric acid conversion and monoglyceride selectivity, and to evaluate the interaction between the synthesis parameters at the same time. The optimum conditions obtained to prepare SBA-15SO_3H catalyst were the use of 1 ml MPTMS per g SBA-15 and a reflux time of 20 h to give the best lauric acid conversion of 95 % and monoglyceride selectivity of 70 % in the reaction glycerol esterification at 160 ^{o}C using glycerol/lauric acid molar ratio of 4 : 1 in the solvent free condition. Moreover, reusability study of catalyst found under optimum condition (SBA-15SO_3H(1)) was carried out for up to four cycles of reaction using the same catalyst and reaction condition. It was found that the SBA-15SO_3H (1) catalyst relatively maintained its catalytic performance over four cycles of reaction without significant deactivation. In addition, kinetic model of the glycerol esterification using SBA-15SO_3H(1) catalyst followed a second order kinetic model with the activation energy of 40.6 kJ/mol which was lower than that reported in the literature.

CHAPTER ONE

INTRODUCTION

1.1 Introduction to glycerol

Glycerol is also called glycerine or 1,2,3-propanetriol. It has three hydrophilic hydroxyl groups that are responsible for its solubility in water and its hygroscopic nature. It is a colorless, odorless, sweet-tasting and syrupy liquid. It boils with decomposition at 290 ^{o}C, melts at 18 ^{o}C, and is miscible with water and ethanol (Perry and Green, 1997). Major applications of glycerol include (Miller-Klein Associates, 2006):

1 Food and drink:

Glycerol is a raw material to manufacture mono- and di-glycerides for use as emulsifier and to manufacture polyglycerol esters for shortening. Glycerol is used as a filler and sweetener in low-fat food products such as cookies and also used as a humectant and sweetener in a wide range of products.

2 Pharmaceuticals

Glycerol is used as a lubricant and humectant in pharmaceutical preparation, such as suppositories, cough syrups and expectorants.

3 Personal care products:

Glycerol is used in wide range of personal care products as an emollient, humectants, solvent and lubricant; including skin care, hair care, toothpastes, shaving creams and soaps

4 Polymer

Glycerol is used as a raw material to produce polyether polyols (for polyourethane foams and other flexible foams) and to produce alkyd resins for paints

and coatings. Glycerol is also used as a plasticizer in cellophane.

Glycerol was a co-product of soap making, produced by heating fats in the presence of ash as early as 2800 BC. Since the late 1940s, glycerol synthesis has been carried out using a raw material of epichlorohydrin, a petrochemical precursor. Glycerol is also co-product generated during production of biodiesel (fatty acid methyl/ethyl ester) via transesterification of a triglyceride (vegetable oil, animal fat etc) with alcohol (methanol or ethanol) in the presence of a catalyst (basic, acidic enzymatic, etc), as shown in Figure 1.1. For every 9 kg of biodiesel produced, a crude glycerol is formed as a by-product of about 1 kg. Purification of the crude glycerol to reach purity levels at least 98% is attempted by most of the biodiesel producers for sale in the commodity glycerol market (Demirbas, 2003; Bournay *et al*., 2005).

Biodiesel is emerging as a green fuel because it is biodegradable and completely non-toxic, meaning spillages represent far less of a risk than fossil diesel spillages. After the energy crisis in 1970, it has received considerable attention to be developed as an alternate energy resource. The global biodiesel market is predicted to reach 37 billion gallons by 2016, growing at an average annual rate of 42% (Fuji-Keizai USA, 2007)

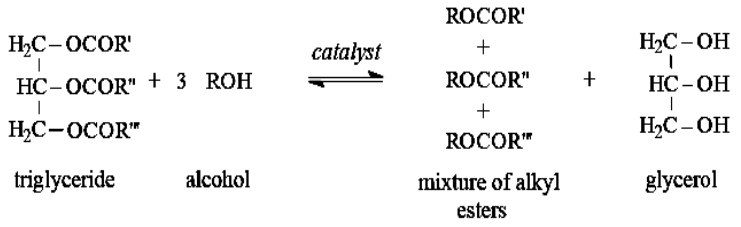

Figure 1.1 Transesterification of triglyceride with alcohol in the presence of catalysts to produce biodiesel and the glycerol as co-product.

The increase of biodiesel production is followed by an excess of glycerol generated to the extent that the old epichlorohydrin process for glycerol synthesis is no longer economical. The illustration of worldwide glycerol supply and demand is depicted in Figure 1.2. (Paris, 2007). The global glycerol market was only about 1,094,000 MT in 2001. Currently, the market increases rapidly to around 2,528,000 MT in 2010, while the global glycerol demand is only about 1,412,000 MT. Therefore, oversupply of glycerols is approximately 1,116,000 MT.

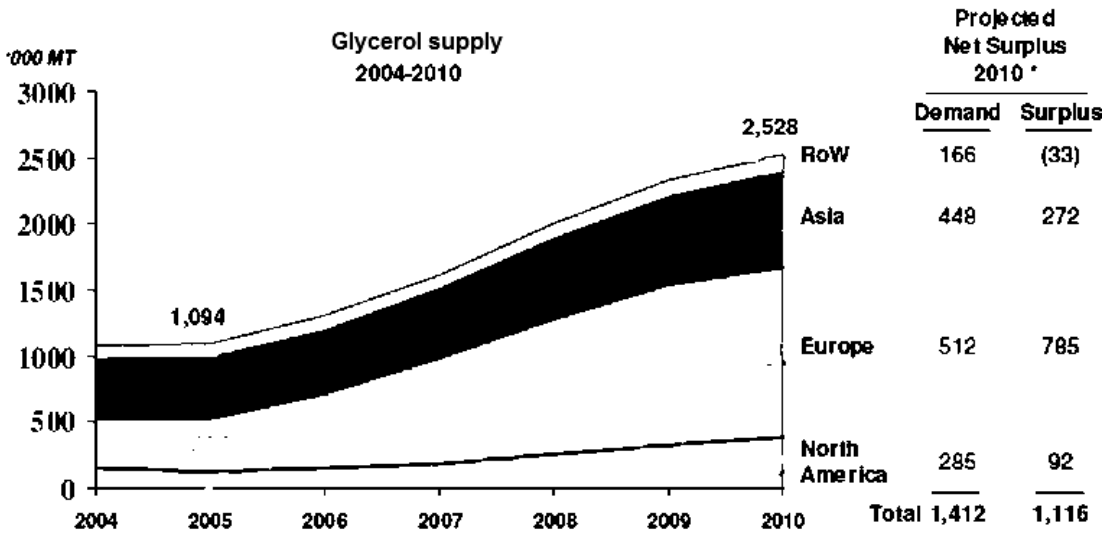

Figure 1.2 Projection of worldwide glycerol supply and demand (Paris, 2007)

The oversupply of glycerol will reduce its price. As reported by Miller-Klein Associates (2006), from the 1970s to the last few years, prices of high purity natural glycerol were quite stable, i.e. from about US$1200 per tonne to US$1800 per tonne. Increasing in the market quantities of glycerol resulted in the prices beginning to drop into a relatively inelastic market. The prices were then around US$600 per tonne in 2006 and falling. The value of crude glycerol has also diminished. Currently, crude glycerol prices are quoted at US$0 - US$70 per tonne in the US.

Zero value to the crude glycerol is attached by most biodiesel producers, and at least some producers have to pay for transport to a purification unit. It is assumed that crude glycerol has a negative value in the future.

In order to exploit the glycerol streams and improve the economic viability of the biodiesel industries, it is proposed to develop an innovative transformation of glycerol into monoglyceride as valuable product. The monoglyceride finds significant applications as safe and biodegradable emulsifiers in industry (Garti *et al*., 2000). As emulsifier, monoglyceride prices are from about US$1.12 per kilogram to US$1.24 per kilogram in 2010 (Hangzhou Fuchun Food Additive Co., Ltd., 2010)

1.2 The use of monoglyceride

Monoglyceride is the largest group of fatty acid partial esters of commercial significance. Due to the presence of two hydroxyl groups in hydrophilic part and and an aliphatic lipophilic chain in its structure, it acts as an important non-ionic surfactant (surface active substances) of low HLB (hydrophilic-lipophilic balance) value, especially valuable as benign and environmentally friendly "water in oil" emulsifier. Monoglyceride or mixture with di-glyceride accounts for about 75% of the worldwide emulsifier production (Sagalowiz, 2006). The global production of emulsifier is estimated at approximately 200,000 - 250,000 metric tons per year (Krog, 1997; Moonen *et al.,* 2004). The US requires about 100 million kilogram annually (Birbaun, 1981). Monoglyceride has various applications in different fields such as in the food industry, in cosmetics, pharmaceutical formulations, drug delivery systems, oil well drilling, textile, packaging, plastic processing, and construction materials.

In food industry, monoglyceride is widely used in bakery products, margarines, dairy products, and confectionery because of its emulsifying, stabilizing, and conditioning properties (James *et al.*, 1982).

Monoglyceride as non-ionic surface active substances is also used in cosmetics to clean and care the human skin and hair (Boyxen *et al*., 2001). It is found that the combination of fatty acid partial glyceride (mixtures of mono-, diglyceride) and monoglyceride sulphates have high dermatological compatibility with optimal refatting properties required for treatment of the human skin and hair.

In pharmaceutical formulations, monolaurin or glycerol monolaurate, a type of monoglyceride, is widely used as antimicrobial compound with inhibitory activity against the production of pro-inflammatory cytokines (Fu *et al*., 2006). Besides, it can inhibit mucosal signalling and the innate and inflammatory response to HIV-1. This opens a promising new avenue for the development of effective interventions to block Human Immunodeficiency Virus-1 (HIV-) mucosal transmission (Li *et al*., 2009).

Two common monoglycerides, i.e. monosterin and monoolein has been used for drug delivery system. Drug delivery is a method or process of administering a pharmaceutical compound to achieve a therapeutic effect in humans or animals. Drug delivery technologies are patent protected formulation technologies that modify drug release profile, absorption, distribution and elimination for the benefit of improving product efficacy and safety, as well as patient convenience and compliance. In drug

delivery system, monoglyceride is used in terms of protection of drug and controlled release of drug. Peptidic drugs such as desmopressin, lysine-vasopresin, and somatostatin incorporated into system of monoolein/water protected the drugs from enzymatic degradation (Shadale *et al.*, 1998). Monoolein is used to prevent the labile drug such as cefuroxin and cezafolin from hydrolysis and oxidation, respectively. The monoglyceride is also used to prevent insulin from aggregating (Shadle *et al.*, 1999). Drug release from monoglyceride that has gel cubic phase follows a square root of time law, indicating that the release is diffusion controlled. For example, release of drug such as bupivacaine from monoglyceride is sustained over periodes of more than 24 h (Shah *et al*., 2001). In addition, emulsified cubic phase (ECP) particles of monoglyceride loaded with insulin enabled the serum glucose concentration in diabetic rats for more than 6 h after oral administration. When using insulin in an aqueous solution, the serum glucose concentration is not controlled (Chung *et al.*, 2002).

Boring into the earth for oil and gas production typically involves rotating a toolhead bit fastened to the end of string of drill pipe with the string being driven by surface engine. A fluid called "drilling mud" containing lubricating composition such as monoglyceride is injected into the hole at the point of the bit to clean the bit, take up debris from the well and stabilize the formation walls in contact with the drilling mud, as well as to prevent drilling string sticking. The advantages of monoglyceride as lubricating composition in the well drilling are generally nontoxic to marine life, environmentally acceptable, easy to prepare, and capable of being disposed of at the drill site without costly disposal procedures (David *et al.*,2005).

In plastic processing, monostearin, a kind of monoglyceride, is used as lubricant in rigid plastic materials such as polyvinylchloride to improve heat stability of the plastic material (Rosen *et al.,* 1982).

1.3 Monoglycerides as a product line from glycerol.

Glycerol is usually used for commercial production of monoglyceride through transesterification of glycerol with fat (triglyceride) or with fatty acid methyl ester (FAME) using homogeneous basic catalyst. Besides that, monoglyceride is also produced industrially via esterification of glycerol with fatty acid using homogeneous acid catalyst. The transesterification and esterification reactions are illustrated in Figure 1.3, Figure 1.4 and Figure 1.5, showing that the reactions are reversible and consist of several stepwise reactions. Monoglyceride are known to be the main reaction product, but diglyceride and triglyceride are also found in the final equilibrium state. As emulsifier, monoglyceride is far better-quality compared to diglyceride while the presence of triglyceride is undesirable (Lin *et al.,* 1999).

Strong homogeneous catalysts of 10 mol % of 1,5,7-tri-azabicyclo(4.4.0)de-5-ene, 1,2,3-tricyclohexylguanidine or 1,3-decyclohexyl-2-n-octylguanidine was used in transesterification of methyl stearate and tristerin with glycerols (Noureddini *et al.*, 1998). The reaction was carried out at 110 ^{o}C and 16 mbar and gave a conversion of about 80% with selectivity around 50 – 60 % for monoglyceride. In order to obtain a high yield of monoglyceride in the transesterification process, a high temperature, in the range of 493 – 523 K is usually required (Sonntag, 1982).

However, the use of high temperature leads to the development of unwanted flavors and a dark color. Besides, the high-temperature chemical process is not

suitable for the production of heat–sensitive monoglycerol containing PUFA (polyunsaturated fatty acid), which has nutritional value applied for functional food, pharmaceutical and the like (Damstrup *et al.*, 2005).

Several enzyme-catalyzed transesterification reactions at much lower temperature (below 80^{o}C) without or using solvent were investigated (Bellot *et al*., 2001; Kaewthong *et al.*, 2004). Solvents such as *n*-hexane, *n*-heptane, dioxane, acetonitrile, acetone, isooctane, 2-methyl-2-propanol (*tert*-butanol), 2-methyl-2-butanol (*tert*-pentanol), or mixtures of some of them are usually used for lipase-catalyzed transestereification reactions (Yang *et al.*,2005). The results revealed that the enzyme-catalyzed processes were potential for monoglyceride production. However, an industrial-scale process of the enzyme-catalyzed processes is still unavailable due to a slow reaction rate and/or a relatively complex work-up of the reaction mixture.

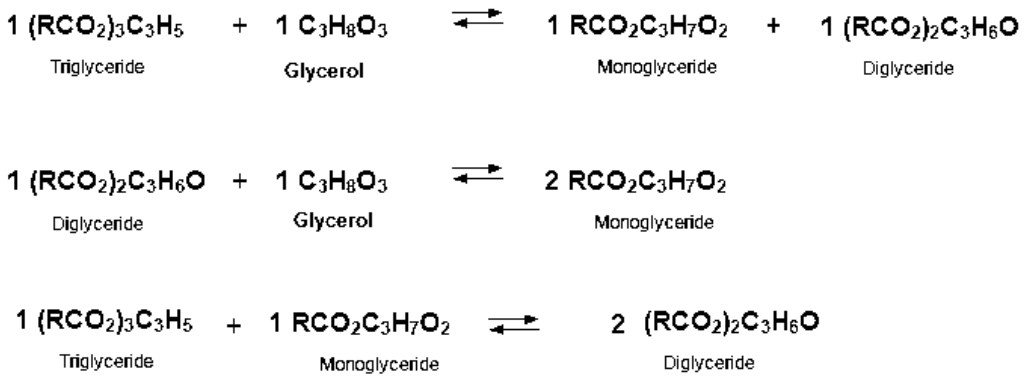

Figure 1.3 Transesterification of glycerols with fat (triglyceride) to produce monoglyceride as the main product (Noureddini *et al.*, 2004)

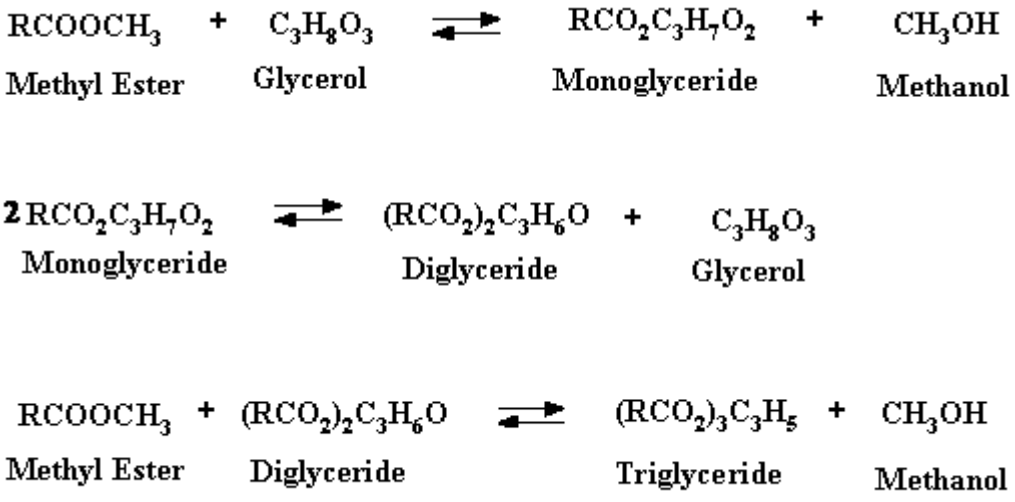

Figure 1.4 Transesterification of glycerols with fatty acid metyl ester (FAME) to produce monoglyceride, and the formation of di-glyceride and tri-glyceride as by-product (Negi *et al.*, 2006)

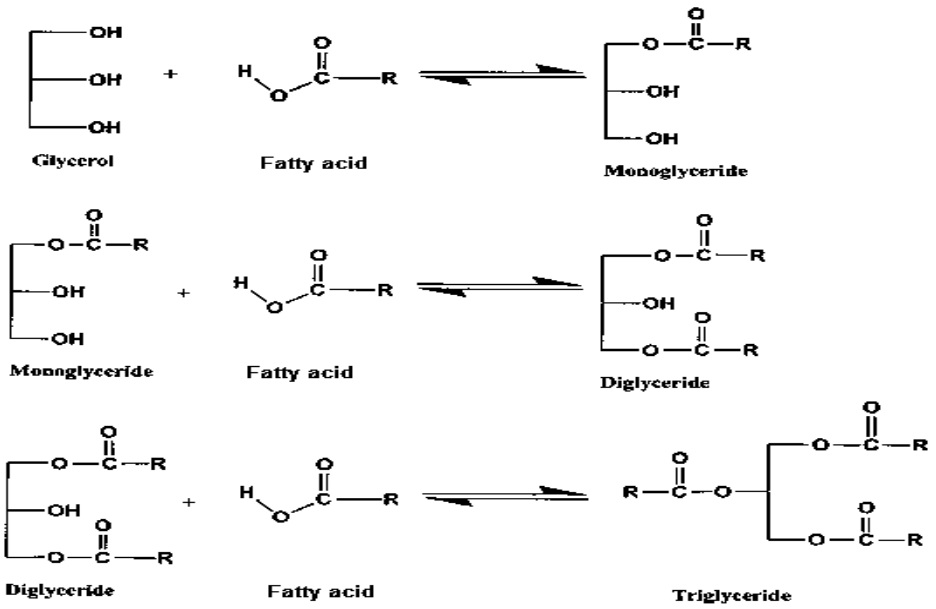

Figure 1.5 Esterification of glycerol with fatty acid to produce monoglyceride, and the formation of di-glyceride and tri-glyceride as by-products (Mbaraka *et al.*, 2006)

The esterification method is favorable for monoglyceride production in the industry (Moquin *et al.*, 2008). The esterification method using mineral acids (sulfuric acid) or organic acids (para-toluene sulfonic acid) is the most convenient method for monoglyceride production. However, the technology possesses severe drawbacks of environmental aspects. Besides that, side-reactions from degradation of the fatty acid such as oxidation, dimerisation or side-reactions from the glycerol such as polymerization, dehydration into acrolein, oxidation are favored by these catalysts (Pouilloux *et al.*, 2000). Hence, the use of solid acid catalysts offering ease of product separation and possibility for catalyst reuse should improve the direct esterification process.

1.4 Solid acid catalysts for esterification of glycerol

Acidic resin and zeolite have been used as solid acid catalysts in the esterification of glycerol with fatty acids (Aracil *et al.*, 1992; Heykants *et al*., 1996; Poulloux *et al.*, 1999). However, the acidic resins will be unstable at reaction temperatures above 150 °C, causing them to be unfavourable for the esterification reactions. Zeolite may exhibit high monoglyceride selectivity, but the activity and consequently monoglyceride yield are low (Heykants *et al*., 1996). This is due to the small pore diameter of around 8 Å, which makes them unsuitable for reactions involving bulky molecules like monoglyceride (Pariente *et al.*, 2003). This observation is consistent with that reported by Wilson *et al*.(2000).

The discovery of the M41S family of mesoporous molecular sieves such as Mobile Crystalline Matter No. 41 (MCM-41), Hexagonal Mesoporous Silica (HMS), and Santa Barbara No. 15 (SBA-15) offering pore sizes in the range from 20 Å to

100 Å opens up new possibilities for liquid-phase reactions using solid acid catalyst (Beck *et al.*, 1992). This is based on the fact that the effect of diffusion diminishes with an increase in the size of the pores (Pouilloux *et al*., 1999). This basic structural chemical feature is highly advantageous for the solid catalysts because they allow large molecules of the reactants to access the large internal surfaces where a high concentrations of active sites can be incorporated, thereby enhancing the catalytic activity (Perez-Pariente *et al.*,2003).

1.5 Problem statements

Mesoporous silica SBA-15 having surface area (500-1500 m^2/g), large pore size (50-100 Å) with narrow pore size distribution and thermal stability had been incorporated with sulfated zirconia or propylsulfonic acidon their surface to generate solid acid catalyst via direct synthesis or post synthesis route. Direct synthesis route usually involves the reaction between active source with tetraethylorthosilicate (TEOS) or Tetramathylorthosilicate (TMOS) in the presence of structure directing agents that cause the active site to be anchored to the pore walls. Meanwhile, the post synthesis route involves the modification of the mesoporous silica, usually after the surfactant removal. The solid catalyst exhibited high activity for esterification reactions such as reaction of fatty acid with methanol for biodiesel, cyclohexanol with acetic acid, and acetic acid with n-butanol, as well as for transesterification of triacetin with methanol. However, sulfated zirconia functionalized SBA-15 for the esterification of glycerols with lauric acid to monoglycerides has not been reported so far. Furthermore, a number of papers have been published on the use of SBA-15 functionalized with propylsulfonic acidvia direct synthesis route for esterification of glycerol with fatty acid. However to our knowledge, no work has been reported on

the use of SBA-15 functionalized with propylsulfonic acidvia post synthesis route for the glycerol esterification with lauric acid. Therefore, in this study, SBA-15 functionalized with organo sulfonic acid and with sulfated zirconia through post synthesis routes for the glycerol esterification were observed.

1.6 Objectives

1) To synthesize acid-functionalized SBA-15 catalysts by post synthesis method using different acidic sites, i.e. sulfated zirconia and propylsulfonic acidand then to identify the most suitable acid functionalized SBA-15 for esterification of glycerol with lauric acid.
2) To identify the optimum catalyst preparation conditions of the acid functionalized SBA-15 by studying the effects of the preparation condition on catalytic activities of the catalysts in the esterification glycerol esterification using 3^2 factorial design of experiment.
3) To observe reusability of the acid modified SBA-15 catalyst synthesized under optimum conditions, which catalyzed the esterification for up to 4 cycles of experimental run.
4) To identify and establish a suitable kinetic model of the esterification of glycerol with fatty acid catalyzed by the acid modified SBA-15 synthesized under optimum conditions.

1.7 Scope of study

In this study, the mesoporous material considered is SBA-15. The SBA-15 materials were then modified with sulfated zirconia and with propylsulfonic acid by post synthesis-grafting to SBA-15SZ and SBA-15SO_3H catalyst, respectively. The

parent SBA-15 and acid modified SBA-15 catalysts were characterized by a number of analytical techniques such as surface analysis, Fourier transformed-infrared (FT-IR), XRD, EDX and pulse chemisorptions of NH_3, followed by temperature programmed desorption (TPD) of NH_3. The catalysts were tested for the esterification of glycerol with lauric acid to monolaurin production in the solvent free conditions at 160 ^oC for 6 h using molar ratio lauric acid to glycerol 1: 4 to selec the most suitable acid modified SBA-15 catalyst.

Furthermore, preparation condition of the selected catalyst (SBA-15SO_3H(1)) was optimized using 3^2 factorial design accompanied with response surface analysis. In the optimization study, parameters considered were the effect of MPTMS amount (1, 3, 5 ml) and the effect of reflux time (4, 12, 20 h) in the post synthesis preparation condition. The catalytic behavior was measured in terms of lauric acid conversion and monolaurin selectivity.

Reusability study of SBA-15SO_3H(1) synthesized under optimum condition for the esterification of glycerols with fatty acid was also performed. Besides that, a kinetic study for the esterification reaction using SBA-15SO_3H(1) catalyst was studied to obtain its kinetic model and the activation energy was calculated using Arrhenius equation.

1.8 Thesis organization

This thesis consists of six chapters. Each chapter explains the important information of this research. Chapter One covers an introduction to glycerol, monoglyceride as product lines from glycerol and the importance of heterogeneous

catalyst involved in esterification of glycerol for monoglyceride. This chapter also provides the problem statement, objectives of the present studies, research scope and finally the description on the thesis organization.

Chapter Two focuses on literature review of the six main parts including mesoporous molecular sieves (MMSs), SBA-15, acid functionalized mesoporous silica, esterification of glycerol with fatty acid, optimization and kinetic study. Mesoporous molecular sieves section explains about general mechanism of mesoporous material formation and types of mesoporous molecular sieves materials. The section on SBA-15 gives details about the synthesis process of SBA-15 and synthesis approaches in improving the quality of SBA-15 materials, i.e. via post synthesis approaches and in-situ synthesis approaches. In acid functionalized mesoporous silica section, the explanations about mesoporous molecular sieves (MMSs) as catalyst supports, incorporation of sulfated zirconia on MMSs, MMSs functionalized with organosulfonic acid and acid functionalized mesoporous catalysts for esterification of glycerol with fatty acid reported in the literature are provided. Esterification of glycerol with fatty acid part reviews azeotropic esterification, esterification using an inert gas sparge, esterification under reduced pressure and factors influencing direct esterification of glycerol with fatty acid. The next part covers about optimization study using a statistical model built from a complete 3^2 factorial designs and finally, kinetic study was carried out.

Chapter Three fully explains the complete experimental works carried out, which consist of the preparation and characterization of parent SBA-15 and catalysts, i.e. SBA-15 functionalized with sulfated zirconia (SBA-15SZ), and functionalized

with propylsulfonic acid(SBA-15SO_3H), Then, procedures for characterization and catalytic activity test of the catalysts in the glycerol esterification are given in detail. Furthermore, the optimum preparation condition to prepare SBA-15SO_3H catalyst was identified by studying the effect of the catalyst preparation variables on their activity in the esterification of glycerols with lauric acid using the three levels of 3^2 factorial design of experiment. Then, reusability study of SBA-15SO_3H catalyst synthesized under the optimum condition for the esterification of glycerol with lauric acid was also evaluated, which was followed by kinetic study of the esterification using the catalyst to obtain the kinetic model.

Chapter Four covers all the results and explanation of the findings in the study. It is divided into four parts: (a) preliminary study on the synthesis of SBA-15, SBA-15 functionalized with propylsulfonic acid(SBA-15SO_3H) and SBA-15 functionalized with sulfated zirconia (SBA-15SZ) (b) design of experiment (DOE) for preparation of SBA-15SO_3H catalysts (c) reusability study of SBA-15 functionalized with propylsulfonic acid catalyst synthesized under the optimum condition (SBA-15SO_3H(1)) and (d) kinetic of the esterification of glycerol with lauric acid using SBA-15SO_3H(1) catalyst.

Chapter Five gives the conclusions to the findings made in the present study. It also provides some recommendations for future studies based on the results of the present study.

CHAPTER TWO

LITERATURE REVIEW

2.1 Mesoporous molecular sieves (MMSs)

M41S family of mesoporous molecular sieves having pore size in the range from 20 Å to 100 Å was disclosed for the first time in 1992 (Kresge *et al*., 1992). Since the initial reports, considerable scientific effort has been carried out to use the mesoporous molecular sieves (MMSs) as solid catalysts for liquid-phase reaction due to the effect of diffusion diminishes with an increase in the size of the pores (Pouilloux *et al.*, 1999). The basic structural chemical features of the MMSs allow large molecules of the reactants to access the large internal surfaces where a high concentration of active sites can be incorporated (Pariente *et al*., 2003).

The general mechanism of mesoporous material formation is shown in Figure 2.1. (Stucky *et al.*,1994). The surfactant molecules acting as the organic structure-directing templates usually form ordered complex structures in aqueous solution, either (1) by true liquid crystal template (TLCT) mechanism, or (2) by cooperative self-organization mechanism. In the true liquid-crystal template (TLCT) mechanism, a lyotropic liquid-crystalline phase is produced under the prevailing conditions (temperature, pH) as the concentration of the surfactant is so high, without requiring the presence of the silica precursor framework materials. Then, the siliceous framework polymerizes around these preformed surfactant aggregates in forming a supramolecular structure (a). Alternatively, the addition of the inorganic precursor to a solution of surfactant templates even at lower concentration, initiates a cascade of cooperative-assembly arrangements between the inorganic and organic species,

associated with hydrolysis of the inorganic species that gives growth to the supramolecular structure (Stucky *et al.*,1994).

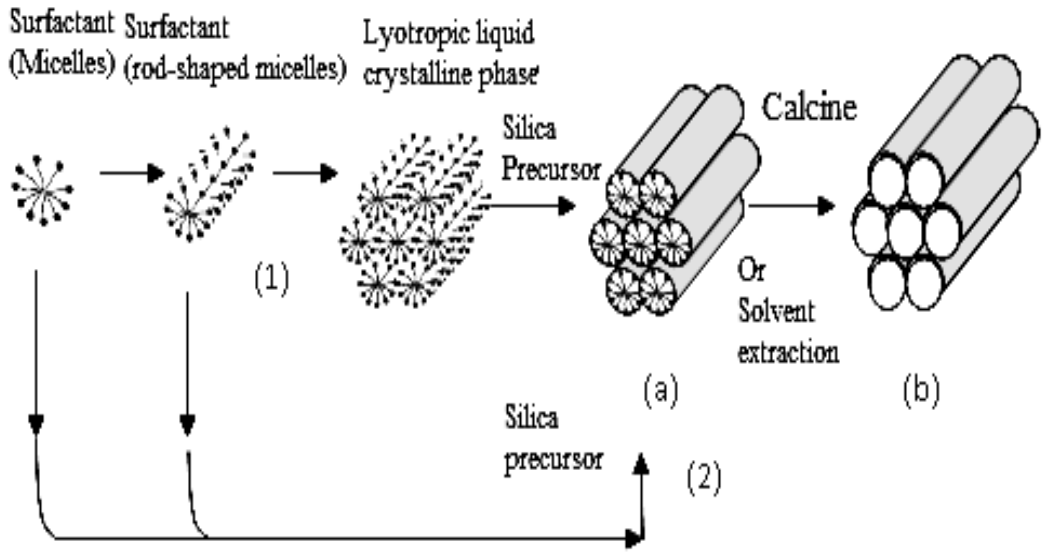

Figure 2.1 Mechanisms of mesoporous material formation (Stucky *et al.*,1994)

The interaction between the inorganic precursor and the surfactant micelles is generated via forces that include electrostatic, van der Waals, and hydrogen bonding. These interactions subsequently come to a decision of the textural characteristics of the final materials. Materials synthesized using an ionic surfactant generate MCM (Whitehurst, 1992; Stucky *et al.*, 1994; On *et al.*, 2003) while neutral and nonionic surfactants give rise to HMS (Tanev *et al.*, 1995; Bagshaw *et al.*, 1996; Pinnavaia *et a,l* 199) and SBA-15 (Kleitz *et al.*, 2005; Jin *et al.*, 2008) materials, respectively. The template in the mesopores of the as-synthesized mesoporous material is eliminated by either refluxing in a suitable solvent or calcining at high temperatures.

2.2 SBA-15

Hexagonal ordered SBA-15 silica having robustness in terms of the synthesis conditions, pore size adjustment capabilities and tailored particle morphology has been found enormously applicable in the fields of catalysis. In particularly, SBA-15 materials functionalized with active sites in the silica walls or on the inner surface were used as solid catalysts and exhibited facile catalytic properties (Reddy *et al*., 2007; Garg *et al*., 2009; Kureshy *et al*., 2009).

SBA-15 silica materials are usually synthesized in a high concentration of acidic medium, using non-ionic surfactant templates of poly (ethylene oxide-*b*-propylene oxide-*b*-ethylene oxide) triblock copolymer (EO_{20}–PO_{70}–EO_{20}, Pluronic 123 (P123) as the mesopore-directing agent and tetraethylorthosilicate (TEOS) as silica source. In the high concentration of acid solution, the hydrophilic EO moieties are expected to interact with the protonated silica by the $(S^0H^+)(X^-I^+)$ mechanism described as follows (Zhao et al.,1998):

First, alkoxylane species are hydrolyzed which is followed by partial oligomerization at the silica:

$$Si(OEt)_4 + nH_3O^+ \xrightarrow{hydrolysis\,pH<2} Si(OEt)_{4-n}(OH_2^+)_n + nEtOH \quad (2.1)$$

The EO moities of the surfactant in strong media associates with hydronium ions,

$$REO_m + yHX \xrightarrow{H_2O} REO_{m-y}\{(EO \bullet H_3O^+]_y \bullet\bullet\bullet yX^- \quad (2.2)$$

Where R = alkyl or poly(propylene oxide) and X = Cl^-, Br^-, I^-, NO_3, $H_ySO_4^{-2+y}$, $H_yPO_4^{-3+y}$.

Furthermore, these charge-associated EO units and the cationic silica are assembled together by a combination of electro-static, hydrogen bonding and van der Waals interactions, i.e. $REO_{m-y}[(EO) \bullet H_3O^+]_y \bullet\bullet\bullet yX^- \bullet\bullet\bullet I^+$, which can be designated as $(S^0H^+)(X^-I^+)$.

Coordination sphere expansion around the silicon atom by anion (e.g., Cl^-) coordination of the form $X^- \bullet Si - OH_2^+$ may take part in an important responsibility (Huo *et al.*, 1994a and 1994b). During the hydrolysis and condensation of the silica species, they are sometimes observed as intermediate mesophases, such as hexagonal, cubic, or lamellar mesostructures (Monnier *et al.*, 1993; Stucky *et al.*, 1994). Further condensation of the silica species and organization of the surfactant and inorganic species result in the formation of silica surfactant mesophase structure, and followed by the solidifying inorganic network (Huo *et al.*, 1994a and 1994b; Firouzi *et al.*, 1997). The mesoporous silica of SBA-15 is obtained after removal of the surfactant template framework either by calcination or by solvent extraction.

The characteristic feature of the SBA-15 material synthesized according to procedure described by Zhao *et al.* (1998) is that it has unique dual pore system formed by hexagonally arranged cylindrical mesopores with micropores (defined as pores of diameter below 2 nm) within the walls, which provide connectivity between large pores (Kruk *et al.*, 2000; Ryoo *et al.*, 2000; Galarneau *et al.*, 2003; Yang *et al.*, 2003), as illustrated in Figure 2.2 (Choi *et al.*, 2003). The origin of these micropores is ascribed to the hydrophilic nature of EO blocks of the template, which leads to the formation of the silica framework around the EO-blocks, in that way incorporating them in the pore walls (Kruk *et al.*, 2000; Ryoo *et al.*,

2000). After all, the EO blocks may be deeply occluded within the silica walls. Since EO-blocks of adjacent micelles may be highly entangled (Kramer *et al.*, 1998), the penetration of EO-blocks within the pore walls of as-synthesized SBA-15 may provide connectivity between the cylindrical micellar templates, and consequently, between the pores of the calcined materials. Such deep occlusion of EO blocks had been investigated using nuclear magnetic resonance (NMR) analysis (Melosh *et al*., 1999) and the evidence of microporous corona around the mesopores of SBA-15 had been shown by carbon and platinum replication experiments (Liu *et al.*, 2001; Shin *et al*., 2001), X-ray diffraction quanti tative measurements (Imperor-Clerc *et al*., 2000), N_2 sorption (Kruk *et al.*,2000; Ryoo *et al.*, 2000; Galarneau *et al*., 2001 and 2003) and neutron diffraction studies (Smarsky *et al.*, 2001). Based on these studies, SBA-15 framework has been categorized as an array of mesopore-micropore network instead of an array of uniform mesoporous network. Such a framework cannot be considered as a host for fabrication of nanowires and related areas of nanotechnology. Hence, it is noteworthy to create uniform mesopores of SBA-15 structure.

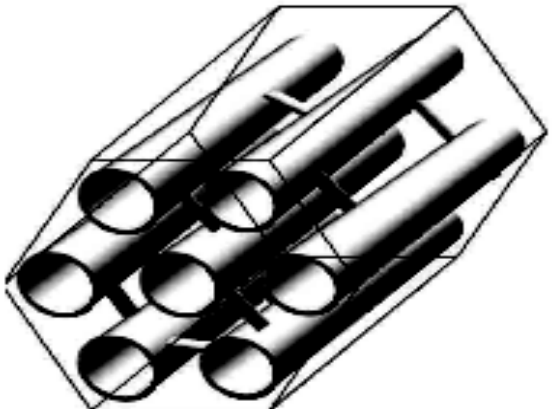

Figure 2.2 SBA-15 mesoporous material with interconnecting pore (Choi *et al.*, 2003)

In order to synthesize the uniform mesopores of SBA-15 structure or at least to reduce the micropores structure of the SBA-15, several attempts have been made, which involve post synthesis and in situ synthesis approaches.

2.2.1 **Post synthesis approaches**

There are several post synthesis approaches suggested to reduce the microporosity within the framework of SBA-15, such as the calcination of as-synthesizes SBA-15 at 1273 K and basic treatments which use hot water, ammonia aqueous solution at room temperature and at 100 ^{o}C .

Attempts to diminish the microporosity of as-synthesizes SBA-15 were carried out by Ryoo *et al.* (2000) using post synthesis approaches. The SBA-15 sample previously calcined at 823 K was heated to 973 K with the initial heating ramp of 2 K/min and kept at 973 K for 4 h. The sample was, then, calcined at 1073, 1173, and 1273 K using the same heating ramp and time. The evidence of the changes in porosity of the SBA-15 was confirmed by nitrogen adsorption studies. Data obtained from the nitrogen adsorption indicated that the microporosity within the framework of SBA-15 was retained using calcination at 1073 and 1173 K. On the other hand, the calcination at 1273 K resulted in a complete disappearance of the microporosity of SBA-15. This heat treatment was accompanied by a significant decrease in the specific surface area and pore volume and narrowing the pore size distribution.

Moreover, the porosity of SBA-15 sample calcined previously at 450 ^{o}C had been modified by suspending the sample in boiling water at 100 ^{o}C, in an aqueous ammonia (pH=11) solution at room temperature and in aqueous ammonia (pH=11) solution at 100 ^{o}C for 22 h (Escax et al., 2007). The result confirmed by N_2 sorption, TEM images and X-ray scattering measurements revealed that after a water treatment at 100 ^{o}C, the micropores were eliminated, while the overall porous volume was not significantly modified. Moreover, the micropores were not detected and the average diameter increased slightly when the treatment using ammonia at room temperature. While, after treatment with ammonia at 100 ^{o}C, both micropores and mesopores were affected and the presence of macropores was detected.

2.2.2 **In situ synthesis approaches**

Numerous one-in situ synthesis approaches to improve the porosity of SBA-15 materials were reported in the literatures, which involve variation of the synthesis conditions, addition of swelling agents, modifying in surfactant structure, modifying of silica source, and the like.

The preparation of SBA-15 material was varied in terms of the synthesis temperature ranging from 35 to 130 ^{o}C for 24 h (Galarneou *et al.*, 2000 and 2003). The evidence of micropores within the walls, providing connectivity between mesopores of SBA-15, was identified by examination of inverse platinum replicas of the SBA-15 structure, as proposed in the literature (Ryoo *et al*., 2000). It was found that SBA-15 synthesized between 35 and 60 ^{o}C showed micropores and no connection between mesopores. Moreover, micropores and connections between mesopores were present in the SBA-15 synthesized at around 100 ^{o}C, while if SBA-

15 synthesized at 130 ^{o}C showed no micropores but connections between mesopores, as shown in Figure 2.3.

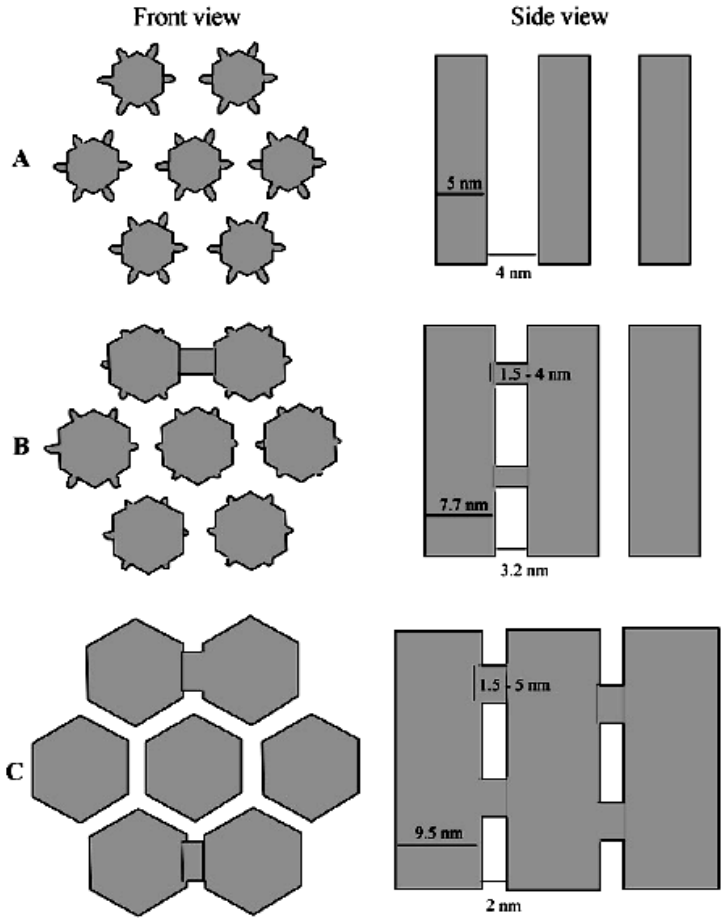

Figure 2.3 Representation of SBA-15 synthesized (A) : between 35 and 60 ^{o}C, (B) : around 100 ^{o}C, and (C) : at 130 ^{o}C (Galarneou *et al.*, 2003)

Furthermore, variation synthesis conditions for preparation of SBA-15 were studied by adjusting the proportion of 37 wt% HCl solution (21.9 -30.7 g), P123 (7.5 – 15.5 g), H_2O (240 – 300 g), TEOS (18 – 30 g) and synthesis temperature ranging from 40 – 60 ^{o}C (Abdullah *et al.*, 2007a and 2007b). It was found that the synthesis conditions at the proportion of 37 wt% HCl solution of 30.7 g, P123 of 11.5 g, H_2O

of 240 g and TEOS of 24 g at synthesis temperature of 60 ^{o}C, gave highly ordered SBA-15 with a surface area of 760 m^2/g, mostly in the mesoporous size range.

Klimova *et al*. (2006) studied the effect of varied synthesis conditions of SBA-15 preparation on textural and structural properties of the SBA-15 using a statistical model built from a full 2^3 factorial design of experiment. The factors of the synthesis condition varied were temperature of gel formation or hydrolysis-condensation stage (35 – 60 ^{o}C), temperature of the aging stage (60 – 80 ^{o}C) and time for the aging stage (24 – 48 h). The results revealed that the surface area, total pore volume, average pore diameter and unit-cell parameter of the SBA-15 increased with both gel formation and aging stage temperature increase. On the other hand, the micropores area and pore wall thickness decreased. The effect of the aging time was strong to the micropore area which decreased with the increase of aging time. The high quality of SBA-15 with total surface area of 906 m^2/g, micropore area of 134 m^2/g, total pore volume of 1.324 cm^3/g, average pore diameter of 68 Å and the pore wall thickness of 38 Å was achieved using the preparation conditions at gel formation stage temperature of 60 ^{o}C, aging stage temperature of 80 ^{o}C and aging stage duration 0f 48 h.

Several attempts were also carried out in the preparation of SBA-15,such as the use of low HCl concentration (0.1 M), adjusting SiO_2 : P123 molar ratio (45 -75) and varying silica sources, i.e. TEOS and sodium silicate, to obtain high quality of SBA-15 materials (Choi et al., 2003). The results revealed that synthesis conditions for SBA-15 using low concentration of HCl, low-cost sodium silicate instead of TEOS and thorough mixing of reactants, were suitable to obtain SBA-15 with an

excellent degree of mesoscopic order, tunable pore wall thickness and pore connectivity. This observation was consistent to that reported by Jo *et al*. (2009) who used water glass or commercial sodium silicate as a silica source. In the preparation of SBA-15, the silica source was mixed into HCl-surfactant solution under vigorous mixing for 0.5 h, followed by moderate mixing for 24 h to gel formation. At this condition, $\equiv SiO^-$ groups in the sodium silicate are immediately converted into $\sim SiOH_2^+$ without further polymerization. The silica species are then irreversibly polymerized by H_3O^+. The quality of the SBA-15 obtained, having surface area of 797 m^2/g, total volume of 1.02 cm^3/g and pore size diameter of 8.2 nm was excellent compared with the product from TEOS, which had surface area of 751 m^2/g, total volume of 0.95 cm^3/g and pore diameter of 7.9 nm.

Moreover, it was reported in another literature that a short time of gel formation stage, i.e. 2 h was adequate if sodium metasilicate ($Na_2SiO_3.9H_2O$) instead of TEOS was used to produce a highly ordered SBA-15 material with surface area of 885 m^2/g, total volume of 1.18 cm^3/g and micropore volume of 0.13 cm^3/g (Fulvio *et al.*, 2005).

Ultrasonic irradiation, a technique to promote the mixing of liquids at a microflow level within a short period, was also used to improve the quality of mesoporous silica and to shorten its preparation time (Gedanken *et al.*, 2001). The ultrasonic irradiation induces the passage of acoustic vibrations through liquid and improves a property because the continuous formation, growth and implosive collapse of bubbles within a liquid. This effect may enhance liquid–solid mass transfer and lead to a significant physicochemical change in the processed medium.