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#### REVIEWS IN CHEMICAL ENGINEERING

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# **Reviews in Chemical Engineering**

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#### ABSTRACT

Due to increasing concerns about global warming and dwindling oil supplies, the world's attention is turning

to green processes that use s



Lilis Hermida, Hadis Amani, Samrand Saeidi, Ahmad Zuhairi Abdullah\* and Abdul Rahman Mohamed

# Selective acid-functionalized mesoporous silica catalyst for conversion of glycerol to monoglycerides: state of the art and future prospects

DOI 10.1515/revce-2016-0039 Received September 11, 2016; accepted January 11, 2017; previously published online May 3, 2017

Abstract: The quest for efficient and selective catalysts for conversion of glycerol monoglyceride is critical for the development of reliable methods for its synthesis. Thus, various types of catalyst and methods of catalyst manufacturing for conversion of glycerol to monoglycerides have been investigated. Acid-functionalized mesoporous catalysts are emerging as highly efficient catalysts for conversion of glycerol into monoglyceride. The incorporation of acid components into different mesoporous silicas for this application is reviewed in this work. The superiority of mesostructure catalysts in comparison to microporous catalysts has been elucidated in terms of accessibility to active sites, pore diffusion, thermal stability of the catalyst and catalyst reusability. Recent direction of novel acid-functionalized mesoporous catalysts development for this application is also critically reviewed.

**Keywords:** acid functionalization; mesoporous catalyst; reaction phenomena; selective esterification of monoglyceride; synthesis procedure.

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#### **1** Introduction

Presently, there is plenty of glycerol coming into the market from oleo-chemical and rapidly increasing biodiesel industries as it is the key co-product of these industries. Although this substance is currently abundantly produced, its application is rather limited (Karinen and Krause 2006, Demirel et al. 2007). Therefore, new glycerol usages as value-added products have to be continuously explored in order to achieve a more interesting economic return from the oleo-chemical and biodiesel industries (Deutsch et al. 2007).

One of the usages of glycerol is as a raw material for monoglyceride production. Monoglycerides are important food additives that are used as emulsifiers in food, pharmaceutical and cosmetic industries. These substances are composed of hydrophilic heads and hydrophobic tails. This composition gives them detergency characteristics. They also have high skin permeability, and thus, drug absorptions can occur relatively easy (Bossaert et al. 1999). Currently, commercial scale production of monoglyceride can be either through esterification of glycerol with fatty or through transesterification of glycerol with triglycerides (Formo 1954, Corma and Kumar 1998). In esterification of fatty acid with glycerol, strong acid catalysts, e.g. sulfuric acid, phosphoric acid or organic sulfonic acids such as Twitchell-type reagents, are required. However, this technology possesses severe drawbacks such as high energy requirement, poor environmental aspects and the eventual production of a mixture of mono-, di- and triglycerides (Nakamura et al. 2008). Monoglycerides have been considered as desirable products due to their emulsifying quality as compared to diglycerides and triglycerides (undesirable products) (Lin et al. 1999). In order to produce an acceptable monoglyceride product quality with about 90% purity, the resulting mixtures have to be separated by vacuum distillation technique, which is too expensive. Other methods of monoglyceride production include enzymatic alcoholysis of triglycerides and

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enzymatic esterification from glycerol and fatty acid. The major drawbacks of enzymatic processes are caused by their slow reaction rate and the use of non-reusable enzymes during the reaction. However, recent advances in enzyme immobilization have improved the feasibility of these processes. However, complex and costly product separation after the reaction remains a problem (Reetz et al. 1995, 1996).

The use of heterogeneous catalysts offers several advantages in the process design. It may improve the vield and selectivity of the desired product by designing specific solid catalysts for this particular process (Corma et al. 2005). There are several intrinsic advantages offered by heterogeneous catalysts over their homogeneous counterparts, i.e. ease of product separation and the potential of the catalyst to be reused and recycled, bi-functional phenomena involving reactant activation/spill-over between support and active phases and process advantages through reactor operation in a continuous flow rather than a batch configuration. Therefore, the development of new processes based on more selective heterogeneous acid catalysts can be considered as an interesting alternative from the economical perspective (Bancquart et al. 2001).

Acidic resins have been used as solid acid catalysts in esterification of fatty acid with glycerol for monoglyceride production (Pouilloux et al. 1999). Although these resins have good catalytic activity, they are also highly susceptible to swelling in organic solvents and will be unstable at elevated reaction temperatures (>150°C). Thus, they are practically unfavorable for the esterification reactions that are commonly performed at high temperature. Attempts to use zeolites have also been made for this particular application (Aracil et al. 1992, Sánchez et al. 1997, Alaba et al. 2016). Zeolites were considered as high selective catalysts for monoglyceride production, but after reusability test, their activity and yield related to monoglyceride dropped significantly (Heykants et al. 1997). This is due to their small pore diameter ( $\leq 8$  Å), which makes them unsuitable for liquid phase reactions involving bulky molecules like long fatty acids and monoglycerides (Wilson and Clark 2000). The other solid catalysts reported to face internal diffusion limitation in similar reactions are lead oxide, zinc chloride, cobalt chloride, tin chloride and sulfated iron oxide (Emtir et al. 1995, Guner et al. 1996).

The discovery of the M41S family of mesoporous molecular sieves with pore sizes in the range of 20 Å–100 Å (Beck et al. 1992) opens up new potentials for liquid-phase reactions using solid catalysts. This is because the effect of internal diffusion diminishes with an increase in pore size (Pouilloux et al. 1999). This basic structural chemical

feature is highly advantageous for solid catalysts because it allows larger reactant molecules to access the internal surfaces of the catalysts where high concentrations of active sites can be found (Pérez-Pariente et al. 2003). In this review paper, various preparation methods of acid-functionalized mesoporous silicas with their essential properties are critically discussed. Esterification of fatty acid with glycerol to produce monoglyceride is a particular concern in this review. This includes reaction pathway in homogeneous and heterogeneous reactions, kinetic model and the difference between performance of microporous and mesoporous catalysts. In addition, recent progresses of their application for the selective production of monoglycerides through esterification of fatty acid with glycerol and stability as well as reusability of the catalysts are also critically reviewed.

## 2 Esterification of fatty acid with glycerol for monoglyceride production

Esterification of fatty acid with glycerol is a condensation reaction of fatty acid and glycerol to give monoglyceride as an ester and water in the presence of either homogeneous or heterogeneous acid catalyst. Esterification is a reversible reaction, as can be seen in Figure 1. As such, the monoglyceride yield can be improved based on Le Chatelier's principle. The use of only the theoretical amount or a slight excess amount of the glycerol and the reaction with continuous water removal will promote the forward reaction. There are several methods that can be used for water removal, i.e. azeotropic esterification, esterification using an inert gas spurge and esterification under reduced pressure.

In azeotropic esterification, the theoretical amounts of glycerol and fatty acid are heated in the presence of refluxing solvent such as benzene, toluene, m-xylene, mesitylene, diethylbenzene and tetralin, which carries away the formed water during the reaction (Mantri et al. 2005a,b). The esterification was carried out in a



Figure 1: Esterification of fatty acid with glycerol to produce monoglyceride.

Brought to you by | Universiti Sains Malaysia (USM) Authenticated Download Date | 3/15/18 3:25 AM single-necked, round-bottom flask (100 ml) equipped with a Teflon-coated magnetic stirring bar and a Dean-Stark apparatus surmounted with a reflux condenser. The temperature of azeotropic esterification could be closely regulated by control of the solvent quantity.

Moreover, rate and degree of fatty acid esterification with glycerol can be improved by blowing an inert gas, such as nitrogen through the reaction mixture during the reaction (Nakamura et al. 2008). The esterification was carried out at in a two-necked flask (50 cm<sup>3</sup>) under atmospheric pressure, heated and stirred at 100°C in a N<sub>2</sub> flow of 10 cm<sup>3</sup>/min, so that water was effectively carried away by the gas stream. Díaz et al. (2000b, 2001a,b,c, 2003, 2005) used a steady flow N<sub>2</sub>, which was passed over the reaction mixture through one flask opening of a stirred four-opening flask. The water content in the flow was adsorbed by means of a glass elbow-shaped tube filled with zeolite A.

The reaction under reduced pressure offers the most efficient and practical method for esterification of polyhydric alcohols (Macierzanka and Szeląg 2004). In order to eliminate water that was formed during the reaction, Szelag et al. conducted the esterification of fatty acid with glycerol in a thermostatic reactor at 130-160°C equipped with a nitrogen tube, under stirring at 200 rpm and under reduced pressure (800 kPa) (Zwierzykowski 1998), while Aracil et al. carried out the esterification of oleic acid with glycerol in the presence of NaY zeolite using low working pressure that was maintained by a vacuum pump (Aracil et al. 1992). The elimination of water from the system in temperature range from 160 to 180°C was achieved, without significant variation in the viscosity of the reaction mixture or the reaction rate. We also previously reported the esterification of lauric acid with glycerol under reduced pressure using sulfated zirconia and propyl sulfonic acid-functionalized SBA-15 catalysts at various temperatures (140-160°C) (Hermida et al. 2010, 2011, 2012). On the other hand, according to Bossaert et al. (1999), the esterification could not be accommodated by flushing with nitrogen or under reduced pressure as water evaporation was facile at high surface area/volume. They carried out esterification of glycerol and lauric acids at 112°C in a round-bottom flask without flushing with nitrogen or under reduced pressure.

# 2.1 Catalysts for esterification of fatty acid with glycerol

In this section, the development of homogeneous and heterogeneous catalysts for esterification of fatty acid with glycerol will be overviewed. Some of the available data for various homogeneous acid catalysts such as sulfuric acid and toluene-sulfonic acid will be discussed. Studies on heterogeneous catalysts provide a thorough perspective on the possible application of microporous and mesoporous catalysts. Comparison of catalytic activities of microporous and mesoporous catalysts is made, and recent developments on the use of acid-functionalized mesoporous catalysts for esterification of fatty acid with glycerol are critically reviewed.

#### 2.1.1 Homogeneous catalyst

Homogeneous catalyst is the catalyst that operates in the same phase where the reaction occurs. In catalytic esterification of fatty acid with glycerol that occurs in liquid phase, sulfuric acid and p-toluene sulfonic acid can be employed as homogeneous catalysts. Richardson (1941) carried out esterification of stearic acid with glycerol catalyzed by sulfuric acid in the presence of dioxane solution as solvent to produce monoglyceride under a reflux for 3 h at 107°C. Water that was formed during the esterification was removed by passing the dioxane over a drying agent. After the esterification, the acid catalyst in mixture was neutralized with a small amount of alkali and the dioxane would be distilled out with the aid of a slow stream of nitrogen gas. Then glycerol could be separated from the mixture by gravity. The fatty acid conversion and monoglyceride yield that were achieved using this esterification technique were up to 91% and 90%, respectively.

Meanwhile, Gros and Feuge (1964) modified the Richardson's technique by using p-toluene-sulfonic acid as catalyst and acetonitrile as solvent to esterify oleic acid with glycerol for various reaction times between 2 and 6 h and at temperatures between 80 and 100°C. The maximum fatty acid conversion and monoglyceride yield of up to 81.4% and 67.7%, respectively, were achieved at a reaction time and temperature up to 6 h and 100°C. However, the final products of the reaction catalyzed either by sulfuric acid or p-toluene-sulfonic acid often appeared in dark color. Theories related to the color formation in the product have not been properly clarified (Abro et al. 1997). This could be due to other reactions occurring during the esterification such as the oxidation of fatty acid or polymerization, dehydration and oxidation of glycerol, as those reactions are favored by acid catalysts (Pouilloux et al. 1999). Attempts to improve and stabilize the color of the final esterification product were carried out by the addition of a small amount of hypophosphorus acid to the esterification system. Alternatively, the color of the esterification product could be removed by heating under

increasing amount of hypophosphorus acid up to 0.05% and 2% (based on product weight). Finally, hypophosphorus acid would be neutralized with a small amount of base.

#### 2.1.2 Heterogeneous catalyst

Although homogeneous catalyst generally shows excellent fatty acid conversion and monoglyceride selectivity, problems related to corrosion, handling, discolored products resulting from undesired reactions and difficulty of catalyst recycling are their limitations for industrial scale application. Heterogeneous catalyst is a catalyst in different phase from reactants or products, and it is usually in solid phase. Heterogeneous catalyst has obvious advantages over homogeneous catalyst in terms of ease of product separation from the reaction mixture and the possibility for catalyst reuse.

In catalytic esterification of fatty acid with glycerol, the choice of heterogeneous catalyst is important due to its role in controlling the fatty acid conversion and monoglyceride selectivity (Hermida et al. 2012). The properties of the heterogeneous catalyst are governed by acidity, pore size and surface area. Different types of heterogeneous catalyst have been employed for esterification of fatty acid with glycerol. These include microporous catalysts such as zeolites and gel resins (Da Silva-Machado et al. 2000a,b) and mesoporous catalysts such as propyl sulfonic acidfunctionalized MCM-41, HMS or SBA-15 catalyst; phenyl sulfonic acid-functionalized SBA-15 catalyst; and sulfated zirconia functionalized SBA-15 catalyst (Hermida et al. 2011). Microporous catalysts are heterogeneous catalysts that have average pore diameters of below 20 Å, while mesoporous catalysts are heterogeneous catalysts having average pore diameters in the range from 20 to 500 Å.

#### 2.1.2.1 Microporous catalyst

As mentioned in Section 2.1, the contribution of Bronsted sites protonation and hydroxyl groups especially on the adsorption of carboxylic acid is increased by the interaction with basic oxygen groups of zeolites. Zeolites are typical microporous catalysts. They are classified into several groups based on pore size, i.e. 6MR zeolites having effective pore size of 2.8 Å, 8MR zeolites having effective pore size of 4.2 Å, 10MR zeolites having effective pore size of 5.7 Å and 12MR zeolites having effective pore size of 7–7.4 Å (Xiao and Wei 1992). Meanwhile, gel resins such as Amberlyst 31 and K1481 are microporous catalysts with pore size typically up to 10 or 15 Å. Both catalysts were gel-type sulfonic acid-functionalized polymeric catalysts with different physical characteristics.

Table 1 summarizes the activity of different types of microporous catalysts in esterification of fatty acid with glycerol under different operating conditions. Heterogeneous catalysts such as various zeolites with different pore sizes (10MR and 12 MR zeolites), K10 (an acid-treated montmorillonite clay) and homogeneous catalyst of toluene-sulfonic acid were scrutinized in the esterification of lauric acid with glycerol without solvent at 102°C (Heykants et al. 1997). The reaction was carried out under reflux, and nitrogen flow was used to continuously remove water that formed. It was found that heterogeneous catalysts achieved higher monoglyceride selectivity compared to that of the homogeneous catalyst. This was

Table 1: Reaction conditions and kinetic model of esterification of fatty acid with glycerol using various catalysts.

Type of catalyst	Fatty acid (FA)	Glycerol/fatty acid molar ratio	Reaction pathway	Rate reaction expression	References
Na or K soaps	Lauric acid Myristic acid Palmitic acid Stearic acid	1:1	Consecutive reactions	$-r_{G} = k_{1}C_{G}$ $r_{Mono} = k_{1}C_{G} - k_{2}C_{Mono}$	Díaz et al. 2003
Zinc carboxylates	Lauric acid Myristic acid Palmitic acid Stearic acid	1:1	Consecutive reactions	$-r_{G} = k_{1}C_{G}$ $r_{Mono} = k_{1}C_{G} - k_{2}C_{Mono}$	Díaz et al. 2001a
Sulfated iron oxide	Oleic acid	1:1	Parallel reactions	$-r_{FA} = -(1/W)(dC_{FA}/dt)$ $=k_1C_6C_{FA}$	Guner et al. 1996
Zeolite (faujasite)	Oleic acid	1:3, 1:1 and 3:1	Parallel reactions	$-r_{FA} = -(1/W)(dC_{FA}/dt)$ $=k_1C_6C_{FA}$	Sánchez et al. 1997
HSO <sub>3</sub> SBA-15	Lauric acid	4:1	Parallel reactions	$-r_{FA} = -(1/W)(dC_{FA}/dt)$ $=k_1C_GC_{FA}$	Díaz et al. 2005

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Fatty acid	Microporous catalyst	Glycerol/fatty acid molar ratio	Reaction time (h)	Temperature (°C)	Conversion (%)	Selectivity (%)	References
Lauric acid	12MR zeolite	1:1	14	102	30	80	Heykants et al. 1997
	10MR zeolite		21		30	69	
Lauric acid	H-Beta zeolite	1:1	24	100	31	65	Da Silva-Machado et al. 2000b
	H-Y zeolite				30	58	
	H-Mordenite zeolite				25	53	
Lauric acid	H-Beta zeolite	1:1	10	100	32	68	Da Silva-Machado et al. 2000a
Oleic acid	Amberlyst 31 resin	6.3:1	24	90	54	90	Abro et al. 1997
	H-Y zeolite				5	67	
	Montmorillonite-Ti				10	71	

Table 2: Catalytic activity of acid-functionalized porous catalysts in the esterification of fatty acid with glycerol.

due to the presence of sorption effect of reactants in the pore of the heterogeneous catalyst in which the esterification occurred to consequently suppress consecutive esterification reactions for producing diglyceride and triglyceride (Heykants et al. 1997). Due to its homogeneous nature, there was no such sorption effect in the case of the homogeneous catalyst.

Furthermore, monoglyceride selectivity achieved by 12MR zeolite was higher than that by 10MR zeolite and the acid-treated montmorillonite clay. Da Silva-Machado et al. (2000b) also found that H-beta zeolite having pore diameter higher than that of H-Y and H-mordenite zeolites achieved higher lauric acid conversion and monoglyceride selectivity. Oleic acid conversion and monoglyceride selectivity of Amberlyst31 were higher than those of H-Y zeolite and Montmorillonite-Ti (Abro et al. 1997). These results provided evidence that esterification of fatty acid with glycerol to produce monoglyceride occurred in the internal pores of the microporous catalyst. The active sites can present in the internal pores or on the external surface of the microporous catalyst. The catalyst having larger pore sizes can allow bulky reactant molecules (fatty acids) to enter the pores and react with glycerol to produce monoglyceride (Da Silva-Machado et al. 2000b). Meanwhile, for microporous catalysts having smaller pore sizes, the esterification will mostly occur on the external surface of the catalyst. Such reaction could favorably form relatively bulkier molecules of diglyceride and triglyceride.

#### 2.1.2.2 Mesoporous catalyst

Bossaert et al. (1999) incorporated propyl sulfonic acid into HMS, MCM-41 mesoporous silica materials using various routes (post-synthesis grafting, post-synthesis coating and direct synthesis) to produce sylilated MCM-41-SO<sub>3</sub>, coated MCM-41-SO<sub>3</sub> and HMS-SO<sub>3</sub> mesoporous catalysts. The HMS-SO<sub>3</sub> had larger pore sizes than sylilated MCM-41-SO<sub>2</sub> and coated MCM-41-SO<sub>3</sub>. Subsequently, catalytic activities of the acid- functionalized mesoporous catalysts in the esterification of fatty acid with glycerol without solvent were compared with that of H-USY zeolite microporous catalyst. The H-USY catalyst had higher number of acidic sites than acid-functionalized mesoporous catalysts. The results are summarized in Table 2.

It should be noted that higher monoglyceride yield can be obtained for all acid-functionalized mesoporous catalysts in comparison with H-USY microporous catalyst. Furthermore, HMS-SO<sub>2</sub>H mesoporous catalyst was significantly more active than H-USY as tabulated in Table 2. These results indicate that esterification reaction catalyzed by H-USY microporous catalyst was strongly governed by the diffusion process within the pores. This was due to the fact that fatty acids are rather bulky molecules. It is estimated that molecular dimensions of lauric acid are from 1.8 Å to 17 Å, and those of oleic acid are from 4.6 Å to 21 Å as can be seen in Figure 2. Meanwhile, the H-USY microporous catalyst had an average pore size of about 13 Å. As such, the pore structure exhibited by the H-USY catalyst was rather insufficient for the fatty acid to access into the internal pores to allow the esterification



**Figure 2:** Molecular dimension of lauric and oleic acid to demonstrate different ability in accessing the internal pores during the esterification reaction.



**Figure 3:** Molecular representation of a monoglyceride molecule fitting in microporous catalysts of (A) 12MR zeolite, (B) 10MR zeolite (Heykants et al. 1997); copyright permission obtained from Department Interface Chemistry, Centrum voor Oppervlaktechemie en Katalyse, B-3001 Heverlee, Belgium.

reaction to occur. Molecular representations of a monoglyceride molecule fitting in various microporous catalysts are shown in Figure 2 (Heykants et al. 1997).

According to a previous research, the HMS-SO<sub>2</sub> mesoporous catalyst was considered as the most active among the acid-functionalized mesoporous silica catalysts, and its activity in the esterification using lauric acid was better than that of oleic acid. This was due to the higher average pore size of HMS-SO, mesoporous catalyst compared to sylilated MCM-41-SO<sub>2</sub> and coated MCM-41-SO<sub>2</sub> catalysts. Then, molecular dimensions of lauric acid are smaller than those of oleic acid as can be seen in Figure 3. The pore structure of HMS-SO<sub>3</sub> catalyst was suitable for the esterification involving the passage of lauric acid molecules within the internal pore structure. Thus, it could be concluded that the activity of the catalysts in the esterification was more influenced by good accessibility of the reactants to the active sites in the catalyst rather than the concentration of surface acidic groups.

# 2.2 Reaction pathways and kinetic models of esterification of fatty acid with glycerol

Reaction pathway is essential to be used for constructing kinetic model. The kinetic model is applied to predict the changes in the amount of specific product obtained during a reaction process. In order to obtain a better understanding on the reaction pathway, several researchers have undertaken various studies on glycerol esterification with different fatty acids and solid acid catalysts to produce monoglycerides (Zwierzykowski 1998, Macierzanka and Szeląg 2004). It is theoretically suggested that reaction pathway of esterification fatty acid with glycerol in the presence of sodium and potassium soaps under reduced pressure using glycerol/fatty acid molar ratio of 1 generated monoglyceride and co-products, i.e. diglyceride and triglyceride through irreversible consecutive reactions with monoglyceride and diglyceride as intermediate products. The monoglycerides formed are converted into diglycerides. Then, the diglycerides that formed are converted into triglyceride, as shown in Figure 4A (Zwierzykowski 1998). Meanwhile, Figure 4B shows another possible consecutive reaction with monoglyceride as an intermediate product for the esterification reaction as reported in the literature (Macierzanka and Szeląg 2004). The esterification



**Figure 4:** Consecutive reactions of the glycerol esterification: (A) as proposed by Zwierzykowski 1998 and (B) as proposed by

Macierzanka and Szeląg 2004.

Brought to you by | Universiti Sains Malaysia (USM) Authenticated Download Date | 3/15/18 3:25 AM was carried out in the presence of zinc carboxylate under reduced pressure using glycerol/fatty acid molar ratio of 1. In this reaction pathway, the formed monoglyceride is converted into diglyceride and triglyceride. On the basis of the consecutive character of the esterification reaction system, a kinetic model for monoglyceride formation to follow the first order with respect to glycerol is suggested, as shown in Equation (1) (Zwierzykowski 1998, Macierzanka and Szeląg 2004).

$$dC_{G}/dt = k_{1}C_{G}$$
(1)

Furthermore, it was previously reported that reaction pathways of esterification of oleic acid with glycerol with continuous water removal during the reaction can be modeled as irreversible parallel reactions, as shown in Figure 5. For the sake of clarity of representation, only 1,2-monoglyceride isomer is shown in the figure. The molar ratios of glycerol to oleic acid applied in the reaction were 1:1, 1:3 and 3:1 with reacting temperatures ranging from



**Figure 5:** Irreversible parallel reaction pathways of oleic acid esterification with glycerol under water removal condition during the reaction from Sánchez et al. (1997).

160 to 240°C using zeolite and sulfated iron oxide as catalysts (Guner et al. 1996, Sánchez et al. 1997). Kinetic model for the irreversible parallel reactions is suggested to follow a second order with respect to fatty acid and glycerol, as given in Equation (2). The observation was in agreement with the esterification of lauric acid with glycerol using a catalyst of propyl sulfonic acid-functionalized SBA-15, which has been previously reported (Hermida et al. 2011). The reaction orders reported in the open literatures can be summarized in Table 3. It can be concluded from the table that the reaction pathways of glycerol esterification with fatty acid can be modeled as consecutive reactions following the first-order kinetic model with respect to glycerol. Otherwise, they may also be irreversible parallel reactions following second-order kinetic model with respect to fatty acid and glycerol.

$$-r_{FA} = -(1/W) (dC_{FA}/dt) = kC_{G}C_{FA}$$
(2)

Also, the esterification reaction could proceed through an  $A_{AC}^2$  or  $A_{AL}^2$  mechanism (Heykants et al. 1997). In the  $A_{AC}^2$  mechanism, carboxylic acid is protonated, and then the protonated carboxylic acid undergoes a nucleophilic attack of the alcohol to produce ester and water. On the other hand, in an  $A_{AL}^2$  mechanism, alcohol is protonated. Furthermore, Corma et al. (1989) suggested that the mechanism using a zeolite as catalyst involved an extra stabilization of carboxylic acid on the zeolite surface. It was due to the presence of Bronsted sites protonation of especially hydroxyl groups of the carboxylic acid. However, more details about carboxylic acid on the zeolite surface are discussed in Section 2.1.2.1.

#### 3 Various methods for acid functionalization of mesoporous silica

The general mechanism of mesoporous material formation is shown in Figure 6. The surfactant molecules acting as the organic structure-directing templates usually

Table 3: Monoglyceride yield in the esterification of fatty acid with glycerol for different types of catalyst.

Catalyst	Reaction time (h)	Monoglyceride yield (%)	References
HMS-SO <sub>3</sub> H	10.2	52	Hermida et al. 2008
Silylated MCM-41-SO <sub>3</sub> H	24	53	Mbaraka 2005
Coated MCM-41-SO <sub>3</sub> H	24	47	El Kadib et al. 2013
H-USY	23.5	36	Bossaert et al. 1999
Silicotungstic acid nanoparticles on ionic liquid (STA-IL)	8	92	Isahak et al. 2014



**Figure 6:** Formation mechanism of straight mesopores in an ordered mesoporous material for use as catalyst (Corma and Kumar 1998); copyright permission obtained from Department of Chemistry, Universitat Politècnica de València (Valencia, Spain).

form ordered complex structures in an aqueous solution either by (1) 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, it occurs without the presence of the silica precursor framework materials. Then, the siliceous framework polymerizes around these preformed surfactant aggregates forming a supramolecular structure (a). Alternatively, the addition of an 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. This is associated with hydrolysis of the inorganic species, which causes the growth of a supramolecular structure.

The interaction between the inorganic precursor and the surfactant micelles occurs via hydrogen bonding, electrostatic and van der Waals forces. The nature of these interactions will subsequently influence the textural characteristics of final materials. If the synthesis process uses ionic surfactants, Mobil Composition of Matter (MCM) materials will be generated (Whitehurst 1992, Stucky et al. 1994, On et al. 2003). Meanwhile, while neutral and nonionic surfactants generally result in HMS (Tanev et al. 1994, Bagshaw et al. 1995, Tanev and Pinnavaia 1995, Bagshaw and Pinnavaia 1996, Zhang et al. 1996a, b, 1997, Prouzet and Pinnavaia 1997, Pinnavaia and Zhang 1998) and Santa Barbara Amorphous (SBA) materials (Zhao et al. 1998, Kleitz et al. 2005, Klimova et al. 2006, Jin et al. 2008, Abdullah et al. 2009), respectively. The template in the mesopores of the as-synthesized mesoporous materials is then eliminated by either refluxing them in a suitable solvent or through calcination at high temperature. Depending on the nature of the templates used, the assynthesized mesoporous materials usually have a narrow pore size distribution as well as long channels (b).

The incorporated active sites on the silica walls or the deposition of active species on the inner surface of the mesoporous materials are more frequently used to convert the MMSs into solid acid catalysts (Bossaert et al. 1999, Pouilloux et al. 1999). Solid acid catalysts can be described in terms of their Brønsted/Lewis acidity, the strength and number of these sites and the morphology of the support (typically in terms of surface area and porosity). The performance of the mesoporous catalysts in their chemical reaction can be influenced by the manipulation of these properties (Clark 2002).

In order to develop high-performance acid-functionalized mesoporous catalysts, researchers have investigated the several methods including incorporation of acid metals oxides into mesoporous silica, organo sulfonic acid-functionalized mesoporous silica, anchoring of perfluoroalkylsulfonic acid chains to mesoporous molecular sieves and dispersion of heteropoly acids on mesoporous silica (On et al. 2003). All these methods lead to materials with different physicochemical characteristics, which eventually affect the catalytic behaviors in the process.

#### 4 Incorporation of metals into mesoporous silica

#### 4.1 Incorporation of aluminum

Incorporations of aluminum (Al) atoms tetrahedrally coordinated within mesoporous silica through hydrothermal method have been investigated (Schmidt et al. 1994, Borade and Clearfield 1995, Luan et al. 1995b, Reddy and Song 1996). For the first time, the preparation of aluminosilicate MCM-41 was studied in 1992 (Beck et al. 1992). Sodium aluminate, as the Al source, was added to a solution containing  $C_{12}H_{25}$  (CH<sub>3</sub>)<sub>3</sub>NOH/CI (as a surfactant),

tetramethylammonium silicate (as a silica source), ultrasil silica and tetramethylammonium hydroxide. This mixture was then transferred into an autoclave and heated under stirring at 100°C for 24 h. Finally, the resulting solid product was calcined (Beck et al. 1992). This method is analogous to that used in the preparation of zeolites in which acid sites result from dissimilarity between the metal oxygen stoichiometry and the formal charge on the cations. The Al<sup>3+</sup> trivalent cations would then partially substitute Si<sup>4+</sup> within the framework. Thus, the framework containing aluminum cation would possess negative charge. This negative charge is balanced by a metal cation or a proton that represents a Lewis or a Brønsted acid site (Lewis 1966, Ward 1967, Kühl 1977, Venuto 1994), as shown in Figure 7. A Brønsted acid, similar to an acid defined by Arrhenius, is any hydrogencontaining species that is capable to release the protons. Conversely, a base is categorized by Brønsted as any species that can readily combine with protons (Brønsted 1923). Meanwhile, a Lewis acid site is defined by G.N. Lewis as any species that can accept an electron pair to form coordination bond (Lewis 1966). In contrast, the definition of a base is any species possessing a non-bonding electron pair that can be donated to form a coordination bond. Kosslick et al. (1997) detected the presence of bridging Brønstedhydroxy groups [Si-O(H)-Al] of the framework of Al-incorporated MCM-41 prepared by hydrothermal method. It was verified based on FTIR spectrum of ammonia-loaded samples that showed additional weak bands at 3,605 cm<sup>-1</sup>.

Lewis acid sites are also formed by extra-framework metal species. These sites exhibit a very broad distribution of acid strength. They can be detected by studying chemisorbed ammonia under FTIR that will show absorption band at 1,308 cm<sup>-1</sup>. Then, this band decreased almost



**Figure 7:** Representation of metal oxygen tetrahedral acid sites during incorporation of aluminum atoms tetrahedrally with mesoporous silica through hydrothermal method (Jeanvoine et al. 1998); copyright permission obtained from Institut Nancéien de Chimie Moléculaire, B.P. 239, 54506 Vandœuvre-lès-Nancy, France.

linearly when the sample was heated between 100 and 500°C. This finding is contrary to the observations made on zeolites, where desorption of ammonia from strong sites (1,330 cm<sup>-1</sup> vibration band) occurs between 350 and 450°C in a single step. The presence of the bridging Brønsted hydroxyl groups (Si-O(H)-Al) in mesoporous silica materials has also been reported by researchers (Janicke et al. 1994, Luo et al. 2003). Furthermore, Luan et al. (1995a) observed that the XRD pattern of the Al-MCM-41 framework indicated less uniform structure and the <sup>29</sup>Si MAS NMR results showed highly disordered on the mesoscale of the Al-MCM-41 compared with purely siliceous MCM-41. Corma et al. (1994) measured the acidity of aluminosilicate MCM-41 by adsorption-desorption of pyridine where both Brønsted and Lewis acid sites were detected. It was found that the acid strength of the aluminosilicate MCM-41 was relatively weaker than that in zeolites and more similar to that of amorphous silica-alumina materials. Bhagiyalakshmi et al. (2004) investigated Al-MCM-41 synthesized hydrothermally and found that H-beta zeolite was more acidic than Al-MCM-41.

The development of suitable Al incorporation methods into MMSs was recently attempted by Carrott et al. (2006). They intensively studied Al-MCM-41 and Al-MCM-48 using various aluminum sources via direct synthesis method at room temperature. The Al-MCM-41 materials prepared via direct synthesis at room temperature were compared with those prepared via conventional hydrothermal methods in terms of structural characteristics and acidity. Al-MCM-48 was also prepared through direct synthesis at room temperature and subsequently compared with Al-MCM-41 samples. They found that the Al-MCM-41 materials prepared via direct synthesis had uniform pore size and good hexagonal ordering, which were superior to the material prepared via hydrothermal methods (Russo et al. 2008). However, Al-MCM-48 was more active in the reaction (Carrott et al. 2006). Ordered mesopore structure with narrower pores and thicker walls was still observed in the Al-MCM-48 after a hydrothermal test (Russo et al. 2007).

Recent advances in the hydrothermal synthesis methods have enabled the synthesis of various acidic mesoporous materials through the incorporation of aluminum (Ajaikumar and Pandurangan 2007, Anuradha et al. 2007, Chandrasekar et al. 2007, Anunziata et al. 2008, Vinu et al. 2008). Jun and Ryoo (2000) incorporated aluminum into the mesoporous material (MCM-41 and MCM-48) via direct synthesis, post-synthesis grafting of the Al species with anhydrous AlCl<sub>3</sub> and post-synthesis impregnation with an aqueous solution of AlCl<sub>3</sub>. In the direct synthesis method, Al was incorporated into the mesoporous material by the addition of sodium

aluminate solution into the synthesis mixture. The grafting method involved the attachment of Al species onto the surface of pore walls via reaction with solution of anhydrous AlCl, in absolute ethanol, while the impregnation method involved slurrying the mesoporous silica in an aqueous solution of AlCl, for about 30 min at room temperature. They found that post-synthesis impregnation method was the most effective method. However, XRD patterns for aluminosilicate MCM-41 and MCM-48 prepared by the direct synthesis procedures indicated significant loss of structural order in comparison with the pure silica form. In a different study, Landau et al. (2001) grafted alumina multilayer on the walls of siliceous MCM-41 by using aluminum sec-butoxide solution in an anhydrous toluene followed by hydrolysis and calcination steps. Tetrahedral Al in the silica pore walls and clusters of a separate octahedral Al alumina phase were detected using <sup>27</sup>Al MAS NMR.

Meanwhile, post-synthesis methods involving the impregnation of Al onto SBA-15 and MCM-41 using trimethylaluminum (TMA) as aluminum sources have also been studied. Based on FTIR spectra of pyridine adsorbed on the mesoporous samples, it was identified that the Brønsted acid sites generated on Al-SBA-15 were more acidic than those on Al-MCM-41 (Sumiva et al. 2001). Several post-synthesis methods through which aluminum can be incorporated into the mesoporous wall with various Al sources have been developed. The methods are generally reported to produce Al-SBA-15 materials exhibiting well-enhanced Brønsted acidity without experiencing significant pore blocking (Kao et al. 2005, Baca et al. 2008, Cheralathan et al. 2008, Zukal et al. 2008). The aluminum incorporation methods within mesoporous molecular sieves are summarized in Table 4.

#### 4.2 Incorporation of zirconium

Zirconium or zirconia has been used as catalyst or catalyst support. However, its application is limited due to low surface area and weak acidity. In order to enhance catalytic activity, several methods have been attempted such as modification of zirconia with titania and tungstan to create titania zirconia (TiO<sub>2</sub>/ZrO<sub>2</sub>) and tungstated zirconia (WO<sub>2</sub>/ZrO<sub>2</sub>), respectively (Furuta et al. 2006, López et al. 2008). Treatment of zirconia with sulfuric acid has also been attempted to produce sulfated zirconia (SO $_{2}^{2}/ZrO_{2}$ ), which is a strong acid catalyst (Yadav and Nair 1999). Sulfated zirconia has been mostly studied as a solid acid catalyst, especially for isomerization, alkylation, esterification and acylation (Dijs et al. 2003, Hammache and Goodwin 2003, Melada et al. 2004, Cutrufello et al. 2005, Zane et al. 2006). However, it is not easy to control the textural properties of sulfated zirconia synthesized by a conventional method, and broad pore size distribution of large pores would be formed.

With the objective of developing a catalyst with narrow pore size distribution, sulfated zirconia supported on SBA-15 has been prepared by Hua et al. (2001) through post-synthesis method. They impregnated zirconium nitrate onto SBA-15, dried at 110°C, precalcined at 300°C for 3 h, then treated with  $H_2SO_4$  solution, filtered, dried and finally calcined at 650°C for 3 h to create the ( $SO_4^{-2}$ /ZrO<sub>2</sub>) modified SBA-15 (Hua et al. 2001). The modified SBA-15 had total number of acid sites close to that of the unsupported sulfated zirconia. However, the modified SBA-15 showed lower catalytic activity in comparison with the unsupported sulfated zirconia but still higher catalytic activity than zeolites. The sulfated zirconia supported on SBA-15 with higher catalytic activity ity than unsupported sulfated zirconia was successfully

Table 4: Mesoporous silica catalysts coordinated with aluminum oxide and prepared through various hydrothermal methods.

Mesoporous silica	Aluminum source	Functionalization method	References
MCM-41	Al(NO <sub>3</sub> ) <sub>3</sub>	Hydrothermal synthesis	Luo et al. 2003
MCM-41	Aluminum sulfate	Hydrothermal synthesis	Bhagiyalakshmi et al. 2004
MCM-41	Sodium aluminate	Hydrothermal synthesis	Carrott et al. 2006
MCM-48	Aluminum sulfate	Direct synthesis	Carrott et al. 2006
MCM-41	Aluminum sulfate	Direct synthesis	Carrott et al. 2006
MCM-41	NaAlO <sub>2</sub>	Hydrothermal synthesis	Anunziata et al. 2008
MCM-41	Aluminum sulfate	Hydrothermal synthesis	Ajaikumar and Pandurangan 2007
MCM-41	Aluminum sulfate	Hydrothermal synthesis	Anuradha et al. 2007
MCM-41	Al(O-sec-Bu) <sub>3</sub>	Post-synthesis grafting	Landau et al. 2001
SBA-15	Trimethylaluminum bromide	Posts-synthesis impregnation	Sumiya et al. 2001
SBA-15	Al(O- <sup>i</sup> Pr) <sub>3</sub>	Post-synthesis impregnation	Baca et al. 2008
SBA-15	Al <sub>2</sub> (OH) <sub>5</sub> Cl	Post-synthesis grafting	Zukal et al. 2008

synthesized by Chen et al. (2007). They used direct synthesis method using zirconium propoxide and ammonium sulfate for the zirconia source. In the synthesis, the surfactant (P123) was dissolved in H<sub>2</sub>O; HCl solution, tetraethoxyorthosilicate (TEOS), zirconium propoxide and ammonium sulfate were mixed and stirred for 20 h at 40°C and further aged at 100°C for 24 h. The products were then filtered, dried and calcined at 650°C. The incorporation of zirconium (IV) into the mesoporous framework was confirmed by UV-visible spectra and TEM analyses. Moreover, other research groups have incorporated sulfated zirconia into MCM-41, MCM-48 and SBA-15 either by post-synthesis impregnation or by direct synthesis methods. All of these procedures were reported to result in solid acid catalysts with high catalytic activities (Sun et al. 2002, Landau et al. 2003, Degirmenci et al. 2007, Fuxiang et al. 2007, Ghedini et al. 2008, Du et al. 2009, Garg et al. 2009).

 $ZrOCl_2$  has been reported to be an efficient zirconia source to produce solid acid catalyst for the esterification of long chain carboxylic acids and alcohols. It also successfully enhanced the catalytic activity of MCM-41, FSM and SBA-15 through post-synthesis impregnation method of zirconia (Mantri et al. 2005a,b). Zirconium cation cluster  $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$  was suggested as the catalytic active species. It was suggested that the deposition of ZrOCl<sub>2</sub> onto the mesoporous silica, especially MCM-41, produced a material with good catalytic activity because the cation cluster was highly dispersed over the mesoporous silica.

Furthermore, Krishnan et al. (2008) examined a new  $NH_3/water$  vapor-induced internal hydrolysis (VIH) method for coating of zirconia on the pore walls of SBA-15 (Figure 8). The method included the hydrolysis of pre-dispersed precursor [i.e.  $ZrO(NO_3)_2$ ] inside the pores



**Figure 8**: Vapor-induced internal hydrolysis (VIH) method in coating of zirconia onto the pore walls of SBA-15 (Krishnan et al. 2008); copyright permission obtained from Institute of Industrial Science, The University of Tokyo Komaba 4-6-1, Meguro, Tokyo, Japan.

of SBA-15 in the presence of NH<sub>2</sub>/water vapor under autogenously generated pressure. They claimed that by using this method, the product (i.e. zirconium hydroxide) tended to be dispersed inside the pores more evenly and hence the procedure resulted in a composite material with a uniform coating of zirconia on the pore walls after calcination. The zirconia-coated SBA-15 samples prepared by VIH showed improved acidity, and the prevalent surface oxygen species in them was significantly reduced at a lower temperature than that for conventionally prepared zirconia (Schüth et al. 2001, Landau et al. 2005). The zirconia-coated materials prepared by this method also showed less pore blocking even at 60 wt.% loading. The syntheses of solid acid catalysts through the incorporation of zirconia into mesoporous silica as reported by some researchers are summarized in Table 5.

Table 5:	Various	zirconia-based	acid	catalysts	supporte	d by	y mesoporous	silicas.
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Mesoporous silica	Modification agent	Synthesis method	References
SBA-15	Zirconium nitrate, H <sub>2</sub> SO	Impregnation, sulfation	Hua et al. 2001
SBA-15	Zirconium propoxide, ammonium sulfate	Direct synthesis	Chen et al. 2007
SBA-15, MCM-41 & MCM-48	Zr(SO <sub>4</sub> ) <sub>2</sub>	Impregnation	Ghedini et al. 2008
MCM-41	ZrOCI,.8H,O, NH,OH	Hydrolysis, sulfation	Sun et al. 2002
MCM-41	H <sub>2</sub> SO <sup>2</sup>	Hydrothermal method	Xu et al. 2008
SBA-15	Zr(SO)	Direct synthesis, sulfation	Fuxiang et al. 2007
SBA-15	Zr(NO,),.3H,O, H,SO,	Impregnation, chemical solution	Landau et al. 2003
SBA-15	ZrOCl, 8H, 0, H, SO, , urea	Decomposition (CSD), sulfation	Du et al. 2009
SBA-15	ZrOCl, 8H, 0, H, SO, , urea	Direct synthesis, sulfation	Garg et al. 2009
SBA-15	ZrOCl,.8H,0	Post-synthesis hydrolysis, sulfation	Mantri et al. 2005a,b
SBA-15	ZrO(NO <sub>2</sub> ),2H <sub>2</sub> O	Impregnation	Krishnan et al. 2008
SBA-15 (SZSBA-15)	Sulfated zirconia	Post-synthesis homogeneous urea hydrolysis method	Abdullah et al. 2016

#### 5 Mesoporous silica functionalized with organo sulfonic acid groups

Catalysts based on organo sulfonic acid-functionalized mesoporous silicas usually have very high surface areas and more tunable pore diameters as compared to zeolites. In the literature, there are two strategies to synthesize the acid modified mesoporous silica, i.e. one-step-preparation strategy and two-step-preparation strategy. The conventionally used method is the two-step strategy, while further advancement in the synthesis method resulted in the elimination of some unnecessary steps. The synthesis of the organo-sulfonic acid-functionalized mesoporous catalysts using these strategies is schematically depicted in Table 6.

#### 5.1 Two-step-preparation strategy

The first step of this strategy is carried out by anchoring organosilane (usually 3-mercaptopropyltrialkoxylane, MPTMS) to create solid mercaptan followed by the second step, which is the oxidation of the solid mercaptan using hydrogen peroxide to sulfonic acid. The whole reactions are schematically represented by Figure 9. If the organosilane used is phenyltriethoxysilane (PTES), the second step of the strategy is to achieve the sulfonation of phenyl groups to arenesulfonic acid (Lim et al. 1998, Zhao et al. 2008).

The anchoring of the organosilane can be performed by direct synthesis (Zhao et al. 2008) or post-synthesis route (Das et al. 2004, Shimizu et al. 2005, Reddy et al. 2007). Direct synthesis route usually involves co-condensation of the organosilane with TEOS or TMOS in the presence of structure directing agents that cause materials with covalently anchored organic moieties to the pore walls (Lim et al. 1998). The post-synthesis route involves the modification of the mesoporous silica, usually after the surfactant removal (Stein et al. 2000). The post-synthesis route includes grafting and coating methods.

In the post-synthesis grafting method, modification of the mesoporous silica is carried out by silylation of the organosilane with silanol on the structure of the mesoporous surface. The silylation is accomplished by the following reaction:

$$\equiv Si - OH + R'O - SiR_3 \xrightarrow{100^{\circ}C} \equiv Si - OSiR_3 + HOR'$$

The post-synthesis coating method refers to formation of monolayer on the pore surface by utilizing a certain amount of water in the process. More continuous coats of organosilanes may be obtained, leading to high concentration of organics in the product (Reddy et al. 2007). This technique is different from grafting process (Figure 10) in which organosilanes are typically added under dry conditions in order to avoid the occurrence of hydrolysis and condensation (Stein et al. 2000).

MCM-41 and HMS functionalized with 3-mercaptopropyl-trimethoxysilane (MPTMS) by two-step preparation strategy have been studied by Saikia et al. (2006). The first step was thiol incorporation using different routes, i.e. post-synthesis grafting, post-synthesis coating and direct synthesis, while the second step was post-oxidation of thiol to the sulfonic acid. Thiol incorporations were observed using IR  $v_{CH}$  and thermogravimetric analysis (TGA), and it showed that all synthesis routes resulted in mesoporous

 Table 6:
 Mesophase silicas and functional molecules for the synthesis of mesoporous organo sulfonic acid-functionalized catalysts using single-step or two-step methods.

Preparation strategy	Mesophase silica	Functional molecule	Anchoring method	References
Two steps	SBA-15	MPTMS	Post-syn. grafting	Reddy et al. 2007
	MCM-41, MCM-48	MPTMS	Post-syn. grafting	Das et al. 2004
	FSM-16	MPTMS	Post-syn. grafting	Shimizu et al. 2005
	SBA-15	MPTMS	Direct syn.	Saikia et al. 2006
	HMS	MPTMS	Direct syn.	Mbaraka et al. 2003
	MCM-41, HMS, SBA-15	MPTMS, PTMS	Direct syn., post-syn., coating	Rác et al. 2006
One step	SBA-15,	MPTMS, CSPTMS	Direct syn.	Mbaraka et al. 2003
	SBA-15	CSPTMS	Direct syn., post-syn.	Mbaraka and Shanks 2005
	SBA-15	CSPTMS	Direct syn.	Van Grieken et al. 2006
	SBA-15	MPTMS	Direct syn.	Zheng et al. 2005
	SBA-15	MPTMS, CSPTMS	Direct syn.	Melero et al. 2007
	SBA-15	MPTMS	Direct syn.	Caetano et al. 2009
	SBA-15	MPTMS	Direct syn.	Habib et al. 2007
	SBA-15	MPTMS	Direct syn.	Zhao et al. 2008



**Figure 9:** A two-step preparation strategy for the preparation of organo sulfonic acid covalently anchored to mesoporous silica (Ziarani et al. 2015); copyright permission obtained from School of Chemistry, College of Science, Tehran University.



**Figure 10:** Two possible post-synthesis methods for the formation of alkoxysilane layer on the silica surface.

materials functionalized with  $-(CH_2)_3$ -SH groups. It was also found that the concentration of covalently linked  $-(CH_2)_3$ -SH in the material functionalized by post-synthesis coating method was higher than that one by post-synthesis grafting method. Once oxidized with  $H_2O_2$ , a material with sulfonic acid group with residual disulfide contaminations was proven to be obtained based on nuclear magnetic resonance (NMR) spectra results of the material. Moreover, Stein et al. (2000) also reported a two-steppreparation strategy to synthesize thiol-functionalized porous MCM-41 using tetramethyl orthosilicate (TMOS) as the silicon source instead of TEOS in basic medium with cethyltrimethylammonium bromide (CTAB) as a cationic surfactant. Higher structural order was shown by X-ray diffraction (XRD) and transmission electron microscopy (TEM) results using TMOS because of its faster hydrolysis rate. However, after the second step, i.e. the oxidation of the solid mercaptan, <sup>13</sup>C MAS NMR also detected residual disulfide species that resulted from incomplete oxidation of thiol moieties during the oxidation reaction.

Furthermore, Mbaraka et al. (2003) developed a simple and effective procedure for the incorporation of sulfonic groups on mesoporous silica. It was performed through controlled oxidation of thiol-functionalized surface, which quantitatively converted into sulfonic acid groups. They observed that the extent of oxidation of the thiol precursor was moderate at ambient temperature and much more effective at 333 K. The chemical structure of the functionalization agent was found to influence the kinetics and the extent of oxidation of thiol groups. The mesoporous acid catalysts prepared using this grafting-oxidation methodology showed strong acid sites (Cano-Serrano et al. 2003).

Boveri et al. (2005) optimized the preparation method of SO<sub>3</sub>H-MCM-41 solid materials. They carried out a systematic study of the acid extraction of the surfactant from the MCM-41 mesoporous materials. Besides, effect on the grafting capacity of propylthiol functional groups on the acid catalysts was also studied. The increase in the sulfur loading was detected in the sample treated using optimized extraction conditions. The authors also noticed a large difference in the number of most accessible silanols groups after the calcination process. In post-synthesis grafting procedures, surface concentration of organic groups is governed by the number of reactive silanol groups as well as by diffusion restrictions. Hence, it is usually required to utilize a good excess of organic silane and anhydrous conditions to avoid the occurrence of homo-condensation reactions (Cano-Serrano et al. 2003).

#### 5.2 One-step preparation strategy

One-step preparation of organosulfonic acid catalyst offers simplicity and rapid completion of the catalyst preparation procedure as only one preparation step is involved. It usually involves co-condensation of organosilane such as MPTMS and 2-(4-chlorosulfonylphenyl)ethyltrimethoxysilane (CSPTMS) and TEOS in the presence of a structure directing agent and  $H_2O_2$  in HCl aqueous solutions. The reaction is schematically shown in Figure 11. This approach allows *in situ* oxidation of the thiol groups and acid exchange of the resultant sulfonic-acid groups.

Alkyl sulfonic acid-modified SBA-15 prepared using one-step preparation strategy based on the co-condensation of 3-mercaptopropyltrimethoxysilane (MPTMS)



**Figure 11:** One-step synthesis strategy of sulfonic acid-functionalized silica based on co-condensation of TEOS and MPTMS in the presence of H<sub>2</sub>O<sub>2</sub> in HCl aqueous solution.

and TEOS in the presence of Pluronic 123 species and the  $H_2O_2$  solutions has been performed (Margolese et al. 2000). SBA-15-modified materials had greater oxidation efficiency (100% vs. 25–77% in the two-step preparation strategy) with larger (up to 70 Å) and more uniform pores. It also had higher surface areas (700–800 m<sup>2</sup>/g) and good long-range order in contrast to that one obtained through a two-step strategy. The net result was a sulfonic-mesostructured material with acid capacities several times greater than that achieved with the two-step strategy with a thermal stability of up to 450°C in air. This route was also investigated by another research group using the same organosilane (MPTMS), and similar level of success was reported (Mohino et al. 2002).

Later, Van Grieken et al. (2002) expanded the *in situ* oxidation procedure for the preparation of sulfonic-modified hexagonal mesostructured materials using nonionic surfactants other than Pluronic 123. Materials with high mesoscopic ordering were obtained in contradiction to those results previously reported by means of the two-step preparation strategy. Several researchers used the same route for the preparation of ordered SBA-15 materials containing arenesulfonic acid groups (Van Rhijn et al. 1998, Díaz et al. 2000a, Das et al. 2001, Hoffmann et al. 2006), as schematically represented in Figure 12. The synthesis



**Figure 12:** Alkyl sulfonic acid-modified SBA-15 prepared using one-step preparation strategy based on the co-condensation of 3-mercaptopropyltrimethoxysilane (MPTMS) and TEOS.

strategy involved co-condensation of TEOS and CSPTMS using Pluronic 123 as the templating agent under acidic condition. Hydrolysis of chlorosulfonyl groups (-SO<sub>2</sub>Cl) to corresponding sulfonic acid groups was achieved under acidic condensation conditions.

## 6 Mesoporous silica functionalized with perfluorosulfonic acid groups

Nafion, a polymeric perfluoroalanesulfonic acid, is an extremely acidic and stable solid catalyst for a number of organic reactions (Olah et al. 1986). Nafion contains terminal sulfonic acid groups attached to a perfluoropolymeric backbone (Harmer et al. 1998). The presence of electron-withdrawing F atoms in the structure significantly increases the acid strength of the terminal sulfonic acid groups, which becomes comparable to that of pure sulfuric acid (Olah et al. 1986). However, the catalytic activity of Nafion is far-off from optimal due to small surface area of the perfluoroalkanesulfonic sites. In order to improve the catalytic activity, de-polymerized Nafion was supported on high surface area silicas by Harmer et al. (1996). These nanocomposite materials had large surface areas  $(150-500 \text{ m}^2/\text{g})$  and contained small (<100 nm) Nafion particles captured in their porous silica frameworks. However, the materials suffered from limited availability of the acid groups due to the insufficient dispersion of the resin within the silica pores (Harmer et al. 1998).

Alvaro et al. (2005) reported for the first time that MCM-41 and SBA-15 could be functionalized with perfluoroalkyl sulfonic-acid groups, which is analogous to Nafion by post-synthesis grafting of 1,2,2-trifluoro-2-hydroxy-1trifluoromethylethane sulfonic acid sultone (as precursor) on the silica surface (Figure 13). This synthesis strategy allows the preparation of hybrid organic-inorganic mesoporous silica catalysts functionalized with perfluorosulfonic-acid groups in a single-step process using a method that was similar to the method first reported by Harmer et al. (1996). The reaction would occur on the precursor with surface silanol groups by this mechanism, opening up the sulfanyl ring and forming a covalent bond between the silica framework and the perfluoroalkyl chain with terminal sulfonic acid functional groups, as confirmed by 19F MAS NMR experiments. Hybrid materials with high acid capacities of up to 0.5 mmol per gram of the material were obtained. The attachment process of active species retained the mesoscopic ordering and



**Figure 13:** Preparation of Nafion-MCM-4 by functionalization through post-synthesis grafting of 1,2,2-trifluoro-2-hydroxy-1-trifluoromethylethane sulfonic acid sultone on the silica surface.

textural properties of the parent MCM-41 and SBA-15 materials. The simplicity of this method could be seen from a single-step perfluoro sulfonic acid anchoring process and this fact that the formation of the sulfonic group would be achieved without oxidation step after the anchoring.

Martínez et al. (2008) functionalized SBA-15 with perfluoro sulfonic acid groups by a simple post-synthetic impregnation procedure using 5 wt.% Nafion in an alcoholic solution precursor. The acid capacity of Nafion/ SBA-15 would be increased up to 0.14 mmol/g. This was an evidence for the successful incorporation of the organic perfluorosulfonated resin over highly accessible reaction location and not merely the entrapment within the micropore system of the SBA-15.

#### 6.1 Dispersing HPA on mesoporous silica

Heteropoly acids (HPA),  $H_{8,x}XM_{12}O_{40}$ , where X is the central atom (Si<sup>4+</sup>, P<sup>5+</sup>, etc.), x is its oxidation state and M the metal ion (Mo<sup>6+</sup>, W<sup>6+</sup>), are widely used as acid catalysts due to their very strong Brønsted acidity. They are hydrogen forms of heteropolyanion produced by the condensation of more than two types of oxoanion (Misono 2001). The possible types of heteropolyanion are Keggin-type polyanion, Dowson-type polyanion and disubstituted polyanion.

Among a wide variety of heteropolyanions (HPANs), Keggin series are of greatest importance for catalysis. They include quite rigid HPANs, in which the original molecular formula is  $XM_{12}O_{40x-8}$ . Keggin HPANs have three types of outer oxygen atoms as potential protonation centers. They include terminal oxygen (M=O) and two types of bridging oxygen, i.e. edge-sharing and corner-sharing M-O-M. The detail structure of HPAs has been discussed elsewhere (Kozhevnikov 1987, Kozhevnikov et al. 1994).

 $\rm H_{3}PW_{12}O_{40}$  (PW) is the strongest HPA in the Keggin series. It is totally deprotonated in aqueous solution and partially deprotonated in polar organic solvents (Kozhevnikov 1987). In solid HPA, proton takes part in the formation of HPA crystal structure by connecting the neighboring HPANs. In this case, the more accessible terminal oxygen can be easily protonated (Brown et al. 1977). Thus, bulk proton sites in crystalline hexahydrate H<sub>2</sub>PW<sub>12</sub>O<sub>40</sub>·6H<sub>2</sub>O are demonstrated as a diaquahydrogen ions  $(H_{c}O_{2}^{+})$ , which links four neighboring HPANs by forming hydrogen bonds with the terminal W=O oxygen as indicated by single-crystal X-ray and neutron diffraction data (Brown et al. 1977). Furthermore, by comparing chemical shift values for the solid-state and solution <sup>17</sup>O NMR spectra, Kozhevnikov et al. (1995) investigated that in dehydrated solid HPAs, the predominant protonation sites are the terminal W=O oxygen. The structure of proton sites in dehydrated HPAs can be represented as shown in Figure 14. Such acid sites dominate in "pseudo-liquid phase" conversions of polar molecules, and they are discussed in great detail elsewhere (Misono 1987, Kozhevnikov 1995). Both surface proton sites may be localized on the terminal W=O oxygen and the edge-bridging W-O-W oxygen on the surface of HPANs. The latter can play a particularly important role in supported HPA catalysts (Brown et al. 1977).

Although solid HPA catalysts have very strong Brønsted acidity, they are non-porous materials with surface areas below 10 m<sup>2</sup>/g and only few acid sites are present on the external surface when nonpolar molecules like hydrocarbons are reacted with them. In order to address this problem down,  $H_3PW_{12}O_{40}$  (PW) has been supported on neutral substances such as SiO<sub>2</sub> either by direct synthesis or by post-synthesis method (Lefebvre 1992, Blasco et al. 1998, Izumi et al. 1999, Cardoso et al. 2004, Farhadi et al. 2006, Said et al. 2007, Caetano et al. 2008, Cánepa et al. 2008, Mohammadpoor-Baltork et al. 2008). Based on <sup>31</sup>P NMR study on a series of PW/SiO<sub>2</sub> catalysts, acidity



**Figure 14:** Proton site in a solid heteropoly acid forming a "pseudoliquid phase" of polar molecules: (A)  $H_3PW_{12}O_{40}$  hexahydrate and (B) dehydrated  $H_3PW_{12}O_{40}$ .

was found to increase with increasing HPA loading from 13 to 87 wt.%, and it was assigned to the bulk crystalline PW and the "interacting" form ( $\equiv$ Si-OH<sub>2</sub>)<sup>+</sup>(H<sub>2</sub>PW<sub>12</sub>O<sub>40</sub>)<sup>-</sup> (Mbaraka and Shanks 2005). The interacting species may be formed by proton transfer according to the following reaction:

$$H_{3}PW_{12}O_{40} + \equiv Si - OH \rightarrow (\equiv Si - OH_{2})^{+}(H_{2}PW_{12}O_{40})^{-}$$

The relative amount of the interacting form of acid sites increased as HPA loading decreased. This observation was consistent with the reported result of Caetano et al. (2008). They prepared heteropoly acids immobilized on silica by direct synthesis method. The FTIR spectrum of the PW/SiO<sub>2</sub> showed stretching modes of oxygen atom bond to tungsten and phosphorous (W=O, P-O) and W-O-W edge. Although several researchers observed that silica-included PW showed high activity and stability (Izumi et al. 1999, Cardoso et al. 2004), there are some pieces of evidence on the leaching of active PW from the silica support when the supported catalysts (PW/SiO<sub>2</sub>) were used for catalytic reactions (Cardoso et al. 2004). The H<sub>3</sub>PW<sub>13</sub>O<sub>40</sub> heteropoly acid immobilized on the other inert supports such as activated clay, kenyaite and mesoporous molecular sieve (HMS) was also investigated (Marme et al. 1998). It was found that the HPA supported on HMS was the most active because of high dispersion of the HPA on the mesoporous silica.

HPA supported on mesoporous silica has been developed using other types of mesostructured materials such as MCM-41, SBA-15 and FSM (Mbaraka et al. 2003). The acidity of heteropoly acid PW supported on MCM-41 prepared through impregnation has been investigated using MAS NMR and FTIR (Ghanbari-Siahkali et al. 2000). It was found that the highly acidic PW protons interacted with the host hydroxyls to form protonated hydroxyls. The resulting PW anion interacting with local non-protonated hydroxyls is as shown in Figure 15.



**Figure 15:** Interaction of PW with the silanol groups (Si-OH) within the pores of MCM-41 materials with acidic PW protons interacting with host hydroxyl groups to form protonated hydroxyls.

The interaction between PW anion and local hydroxyl and its dispersion were directly responsible in enhancing the acidity of the system. This interaction might be recognized as the interaction between a stronger Brønsted acid with a weaker Brønsted acid in the solid phase. Moreover, PW introduced into SBA-15 by direct synthesis was compared with that produced by impregnation method (Yang et al. 2005a). The direct synthesis involved dissolving P123, TEOS, HCl and HPA under stirring at 313 K for 24 h in a water bath, and the product was dried and subsequently calcined. In the impregnation method, the dispersion of HPA on SBA-15 was carried out by dissolving calcined SBA-15 in HPA solution under stirring for 4 h, and then the product was dried overnight and finally calcined. It was found that the amount of acid sites of the fresh impregnated catalyst was higher than that of the directly synthesized catalyst. However, the directly synthesized catalyst was more stable in acidic condition and had better structural regularity. On the other hand, the catalyst, MCM-48 impregnated with PW, showed high activity even after several cycles of use (Sakthivel et al. 2008). The impregnation method was also successfully used by the other research groups to disperse HPA into SBA-15, MCM-41 and FSM-16 (Kamalakar et al. 2006, Kumar et al. 2006, Revathi et al. 2008).

#### 7 Discussion and suggestion

Recent applications of acid-functionalized mesoporous catalyst in esterification of fatty acid with glycerol to produce monoglyceride are given in Table 7. Díaz et al. (2001a,b) extensively studied the esterification of various fatty acids (lauric acid and oleic acid) with glycerol over optimized propylsulfonic-modified MCM-41 prepared by direct synthesis route. They reported that the selectivity to monoglyceride was improved by using propyl-SO<sub>2</sub>H-MCM-41 catalyst synthesized using tetramethylammonium hydroxide (TMOH) instead of sodium hydroxide. A mixture of two surfactants with different chain lengths, i.e. hexadecyltrimethylammonium bromide (C16 TAB) and dodecyltrimethylammonium bromide (C<sub>12</sub>TAB), led to better pore arrangement in the material as indicated by narrower d<sub>(100)</sub> reflections in the XRD pattern (Díaz et al. 2001c,d). This indicates that the surfactant with the shortest chain  $-(C_{12})$  would occupy the area in front of the thiol group but no interaction occurred between them. While the longest chain interacted with the wall Si-Ogroups, bromine anion would occupy the spaces in the cationic heads of the surfactant for charge balance. The

Mesoporous silica	Functional molecule, modification agent	Synthesis method	Time (h)	Temperature (°C)	Conv (%)	Select./ yield (%)	References
MCM-41	MPTMS	Post-synthesis (grafting)	24	112	85	53	Bossaert et al. 1999
MCM-41	MPTMS	Post-synthesis (coating)	24	112	75	47	Bossaert et al. 1999
HMS	MPTMS	Direct synthesis	10.2	112	80	52	Bossaert et al. 1999
MCM-41	MPTMS,(TMOH), (C <sub>16</sub> TAB),(C <sub>12</sub> TAB)	Direct synthesis	24	100	80	60	Díaz et al. 2001b
MCM-41	MPTMS,(TMOH), (C <sub>16</sub> TAB), (C <sub>12</sub> A)	Direct synthesis	24	100	90	75	Díaz et al. 2001a
MCM-41	MPMTS, MTMS	Direct synthesis	24	100	95	63	Zwierzykowski, 1998
SBA-15	MPTMS	Direct synthesis	4	135	40	65	Díaz et al. 2001a
SBA-12	MPTMS	Direct synthesis	7	135	40	65	Díaz et al. 2001b
MCM-41	MPMDS	Direct synthesis	8	100	85	59	Díaz et al. 2003
MCM-41	VTES, MTES	Direct synthesis	8	100	97	55	Díaz et al. 2005
MCM-41	PTES, MTES	Direct synthesis	24	120	95	35	Mohino et al. 2002

Table 7:	Esterification of fatty	v acid with glycerol to	produce monoglyceride in the r	presence of acid-functionalized meso	porous catalysts.
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replacement of dodecyltrimethylammonium bromide  $(C_{12}TAB)$  with an amine like n-dodecylamine  $(C_{12} A)$  was also studied (Díaz et al. 2001a,b). It was found that an interaction between thiol group and amine polar head took place as confirmed by the infrared spectroscopy. The XRD pattern of the material prepared using  $(C_{12} A)$  showed higher intensity of  $d_{(100)}$  reflections than that obtained using  $(C_{12}TAB)$ .

This indicated that amine group from the surfactants had stronger influence to significantly increase the surface area and pore volume. However, despite higher acid contents, the activity of the catalysts synthesized using amine as the surfactant was lower than that obtained using amine-free gels, as given in Table 8. The lower activity of the amine-derived catalysts was attributed to the greater affinity for water as compared to that in amine-free sample (Pérez-Pariente et al. 2003).

In order to improve both activity and selectivity to monoglyceride, MCM-41 materials containing both alkyl and sulfonic groups with increased hydrophobicity have been synthesized (Da Silva-Machado et al. 2000a, Díaz et al. 2000a). Sulfonic acid-functionalized MCM-41 containing higher methyl group showed a reduction in the amount of water adsorbed, indicating that the hydrophobic character of the surface increased with the content of methyl groups. In the esterification of glycerol with lauric acid for 24 h, a lauric acid conversion of 95% with 63% monolaurin yield could be achieved using this functionalized MCM-41 catalyst.

The incorporation of phenyl and combined methyl/ phenyl groups in MCM-41 had been carried out by direct synthesis method. The materials were further sulfonated using two different sulfonation procedures, i.e. treatment with chlorosulfonic acid and treatment with SO<sub>2</sub> vapor (Mohino et al. 2002). It was found that both sulfonation procedures eliminated some the organic contents of the catalysts, especially the phenyl-incorporated catalysts. The use of SO<sub>3</sub> vapor created slightly higher acid content in the sulfonated material, while the treatment with chlorosulfonic acid diminished the content of non-sulfonated phenyl groups on the catalysts surface. Although the phenyl sulfonic acid MCM-41 could achieve high oleic acid conversion (95%), the monoolein selectivity in the esterification of glycerol with oleic acid for 24 h reaction at 120°C was rather low (35%) (Mohino et al. 2002).

MCM-41 materials had also been functionalized via direct synthesis with 3-mercaptopropyl(methyl)dimethoxysilane (MPMDS) in the presence of leucine amino acid used as the co-structure directing agent (Díaz et al. 2003). The efficiency of the oxidation of thiol to sulfonic acid group was found to be significantly enhanced by the presence of leucine. In addition, both activity and

Table 8: Performance of MCM-41SO<sub>3</sub>H catalyst via selective esterification of lauric acid with glycerol to produce monolaurin.

Catalyst	Surfactant	H+ (meq)	Conversion (%)	Monolaurin selectivity (%)	References
MCM-41SO <sub>3</sub> H	(C <sub>16</sub> TAB), (C <sub>12</sub> TAB)	1.33	80	60	Pérez-Pariente et al. 2003
MCM-41SO <sub>3</sub> H	(C <sub>16</sub> TAB)	1.37	96	40	Pérez-Pariente et al. 2003
MCM-41SO <sub>3</sub> H	(C <sub>16</sub> TAB), (C <sub>12</sub> A)	3.16	90	75	Pérez-Pariente et al. 2003

monoglyceride selectivity were found to show a significant increase. Díaz et al. (2005) also reported a new onestep hydrothermal synthesis of MCM-41 material, which contained two functionalities, i.e. vinyl and methyl moieties, as well as a new material, chloromethyl-MCM-41. The hydrophilic character of the surface of the catalyst pores decreased when methyl groups were incorporated in addition to the active functional groups. The higher hydrophobic character of the catalysts containing methyl moieties also led to higher selectivity to the monoglycerides at the same acid conversion.

In order to accommodate bulky reactant molecules in the esterification process of glycerol with fatty acid, Díaz et al. (2001a,b) examined direct synthesis of SBA-15 and SBA-12 mesostructured materials. These materials, which had relatively larger pore size than MCM-type materials, were then functionalized with MPTMS before being used in the esterification process. The catalytic results showed that the turnover number (TON) for MCM-41-based material was higher than that of functionalized SBA-15. For SO<sub>2</sub>HSBA-15, the low TON value was attributed to the presence of sulfonic groups located in structural micropores of the silica walls. Low catalytic activity of SO<sub>2</sub>HSBA-12 was attributed to the small size of the windows that interconnect the large cavities. This observation was found to be consistent with the severe pore blockage of the structure as a consequence of the high population of stacking faults as detected in this material (Huo et al. 1995, Zhou et al. 1998). Based on Table 9, most supported catalysts were active in the range of 380-440 K of reaction temperature, 2-16 wt.% of catalyst loading, 3:1-10:1 of glycerol/lauric acid molar ratio and 3-13 h of reaction time.

We previously reported esterification of lauric acid with glycerol using two different catalysts, i.e. SBA-15 functionalized with propyl sulfonic acid (HSO<sub>2</sub>SBA-15) and SBA-15 functionalized with sulfated zirconia (SZSBA-15) (Hermida et al. 2011). HSO<sub>2</sub>(1)SBA-15 and SZSBA-15 were prepared through post-synthesis (grafting) route. It was found that HSO<sub>2</sub>(1)SBA-15 catalyst achieved higher lauric acid conversion and monoglyceride selectivity under the same reaction conditions (Hermida et al. 2010), as shown in Table 7. This was due to the higher mesopore surface area and the amount of available acid sites of HSO<sub>2</sub>SBA-15 compared with those of SZSBA-15. Although the average pore size of HSO<sub>2</sub>SBA-15 (67 Å) was a bit smaller than that of SZSBA-15 (71 Å), the pore structure of HSO<sub>2</sub>SBA-15 catalyst was adequate for lauric acid (with dimensions from 1.8 Å to 17 Å) to react with glycerol to selectively produce monoglyceride. Furthermore, effects of preparation conditions of HSO<sub>2</sub>(1)SBA-15 catalysts on the catalytic activity were studied using a factorial design coupled with response surface analysis (Hermida et al. 2012). Parameters of the preparation conditions studied were the amount of MPTMS and reflux time. It was found that the MPTMS amount was the most critical factor in the catalyst preparations to eventually affect the catalytic activity. The increase in the catalytic activity of SBA-15-SO<sub>3</sub>H catalysts was attributed to an increase in the mesopore area and the amount of propyl sulfonic acid groups successfully grafted on the surface of the catalysts.

Some points have been proposed regarding thermal stability and reusability of acid-functionalized mesoporous catalysts. The thermal stability of the catalyst under the operating conditions is very important for successful industrial application. The thermal stability of propyl sulfonic acid-functionalized SBA-15 was studied using thermal gravimetric analysis (TGA) by heating the catalyst from 31°C to 800°C with a heating rate of 10°C/ min and air flow rate of 25 ml/min (Hermida et al. 2012). It was found from the TGA result that the thermal gravimetric profile of the catalyst had notable two steps of weight loss. The first weight loss from 31 to 80°C was ascribed to water removal, while the second weight loss at temperatures from 300 to 650°C was mainly due to the decomposition of the propyl sulfonic acid in the catalyst. There was no change in the weight of the catalyst at 160°C. This observation was comparable with that reported in the literatures (Margolese et al. 2000, Yang et al. 2005b) indicating that the catalyst should be stable for the esterification of lauric acid with glycerol, which is usually carried out at around 160°C.

Reusability of catalyst has to be considered in order to get an efficient and cost-effective catalyst. A number of reusability studies of acid-functionalized mesoporous catalyst have been carried out (Zhiqing and Wei 2008, Kureshy et al. 2009). Reusability studies of tungsten functionalized HMS catalyst (WOx/W-HMS) and propyl sulfonic acid-functionalized SBA-15 catalyst (HSO<sub>2</sub>SBA-15) for selective oxidation of cyclopentene to glutaraldehyde and for the synthesis of chromenes from chromanols have been reported (Zhiqing and Wei 2008, Kureshy et al. 2009). WO<sub>v</sub>/W-HMS catalyst was found to be fairly reusable for up to five times without significant decreases in conversion and product selectivity in the oxidation of cyclopentene to glutaraldehyde at 35°C for 16 h (Zhiqing and Wei 2008). Meanwhile, HSO<sub>2</sub>SBA-15 could be reused for up to ten times in the synthesis of chromenes from chromanols under reflux condition in toluene (Kureshy et al. 2009). The reusability study of HSO<sub>2</sub>SBA-15 catalyst for esterification of lauric acid and glycerol has also been

No.	Catalyst	Catalyst preparation method	Properties	Explanation	Conversion (%)	Yield (%)	References
-	Sulfated zirconia SBA-15 (SZSBA-15)	Post-synthesis homogeneous urea hydrolysis method	T=433 K; 16 wt.% catalyst loading; 4:1 glycerol/lauric acid molar ratio; 6 h	Super acidic catalyst Larger mesopore surface area Lower micropore area High zirconia content Regular pore size and ordered pore arrangement Excellent hydrothermal stability	94.9	79.1	Abdullah et al. 2016
7	Aluminum and zirconium on mesoporous MMS-H (AlZrMMS-H)	Post-hydrothermal synthesis method	T= 423K; AlZrMMS-H (100–50), parenthesis denote Si/Zr ratio; 18 h; CO <sub>2</sub> pressure= 10 MPa	Reaction was carried out in CO <sub>2</sub> (SCC) medium Improved catalytic performance due to high diffusivities of reactants, products and coke-precursors; reduction in coke formation Better removal of water formed on the acid catalyst	6	44.6	Sakthivel et al. 2007
ς	Sulfated pillared clay (AP-S)	Clay treated with concentrated fuming sulfuric acid	T=393K; 5 wt.% catalyst loading; 8:1 glycerol/ octanoic acid molar ratio; 5 h	The catalyst was more selective towards dicaprylin Selectivity over monocaprylin was only observed in the first 3 h of reaction Stable and reusable up to 4 cycles of reaction with no severe loss of catalytic activity Catalyst was more selective towards di- and tricaprylin (over 84% selectivity) signifying that the reaction occurred on the catalyst surface, which had no stearic hindrance that could prevent the production of di- and tricaprylin	62	27	Dal Bosco et al. 2016
4	Molybdophosphoric acid (MPA) functionalized hybrid SBA-15 (MPA/SBAH-15)	Post-synthesis method Thermal degradation of MPA species in the lattice of SBAH-15	T=383K; 1:6 glycerol/acetic acid molar ratio; 3 h	Research was focused on producing di- and triacetyl glycerol Stable and reusable up to 4 cycles of reaction with no severe loss of catalytic activity Potential catalyst for monoglyceride production	100	14	Khayoon and Hameed 2012
2	Propyl sulfonic acid- functionalized SBA-15 (HSO3SBA-15)	Post synthetic functionalization method	T=433K; 5 wt.% catalyst loading; 4:1 glycerol/lauric acid molar ratio; 7 h	Activation energy (42 kJ/mol) is considerably low compared to previously reported works Reusable up to 4 cycles without severe loss of activity	93.7	67.5	Hermida et al. 2011
6	Organosulfonic acid functionalized SBA-15	Post-synthetic functionalization method	T= 433K; 1:1 glycerol/lauric acid molar ratio; 6 h	Increase in selectivity to monolaurin due to increased mesopore surface area of the catalyst as well as the amount of acid sites Better catalytic performance than the sulfated zirconia- functionalized SBA-15	94	65.8	Hermida et al. 2010
~	Propyl sulfonic acid- modified SBA-15 (SBA-15SO3H)	Post-functionalization synthesis method	T=433K; 4:1 glycerol/lauric acid molar ratio; 6 h	Evaluated different MPTMS amounts and reflux time in the catalyst preparation Increased catalyst efficiency due to successful grafting of propyl sulfonic acid on the catalyst surface Optimum reflux time and amount of MPTMS were 20 h and 1 ml/g SBA-15, respectively	95	66.7	Hermida et al. 2012

Table 9: Catalyst preparation methods and properties of silica supported catalysts in esterification of fatty acid with glycerol to produce monoglyceride.

No.	Catalyst	Catalyst preparation method	Properties	Explanation	Conversion (%)	Yield (%)	References
ø	12-Thungstophosphoric acid SBA-15 (HPW/SBA-15)	Direct synthesis method	T=433K; 20 wt.% catalyst loading; 4:1 glycerol/lauric acid molar ratio; 6 h	Better thermal stability Ordered mesoporosity; catalyst had shape selectivity effect which helped suppress the formation of by-products	70	50	Hoo and Abdullah 2014
6	12-thungstophosphoric acid SBA-15 (HPW/SBA-15)	Post-synthesis method	T= 433K; 40 wt.% catalyst loading; 4:1 glycerol/lauric acid molar ratio; 6 h	The reaction was governed by the combination of two models; nucleophilic substitution mechanism and Langmuir-Hinshelwood kinetics model	NA	NA	Hoo and Abdullah 2015
10	Silicotungstic acid nanoparticles on ionic liquid (STA-IL)	Sol gel synthesis method	T= 373K; 7 wt.% catalyst loading; 6:1 glycerol/oleic acid molar ratio; 8 h	Narrow structure and cylindrical pore type Selectivity towards glycerol monooleate increased due to the addition of supported IL which produced synergistic effect Good recyclability potential; could be recycled up to two times without severe loss of activity	96.4	92.2	Isahak et al. 2014
11	Sulfated mesoporous KIL-2 silica (SO 42-/ZrKIL-2)	Post impregnation synthesis method	T = 373K; 1:10 glycerol/acetic acid molar ratio; 2 h T = 373K; 12 wt.% catalyst loading; 1:10 glycerol/acetic acid molar ratio; 2 h	Activity increase with increasing ZrO <sub>2</sub> content due to increased amount of available acid sites Stable catalyst for consecutive cycles without severe loss in activity but the selectivity was shifted to di- and triacetyl glycerol The study was focused on the production of di- and triacetyl glycerol and best conditions led to complete conversion with 97.2% selectivity towards di- and triacetyl glycerol	91.1	58	Popova et al. 2014
12	SBA-15 supported silicotungstic acid (STA/ SBA-15)	Direct hydrothermal synthesis method	T = 393K; 1 g catalyst loading; 3:3:1 glycerol:ethanol:lauric acid molar ratio; 3 h T = 393K; 1 g catalyst loading; 3:3:1 glycerol:ethanol:lauric acid molar ratio; 3 h	The catalyst had shape selectivity effect towards monoglyceride formation at lower temperatures. At elevated temperatures, there was competitive adsorption between the reactant molecules and water, which was produced as a side product of this reaction. The catalyst was reusable up to 6 cycles of reaction	09<	>95	Simsek et al. 2016
13	12-Thungstophosphoric acid anchored to MCM-48	Post impregnation synthesis method	T=373K; 1:6 glycerol:acetic acid molar ratio; 6 h	The study was focused towards producing di- and triacetyl glycerol rather than monoacetyl glycerol At 2 h of reaction, the yield of monoacetyl glycerol obtained was reasonably high Reusable up to four cycles of reaction without severe loss in the conversion and selectivity High turnover frequency (TON)	67	40.9	Singh and Patel 2014
14	SBA-15 supported sulfated zirconia	Surfactant-templating method	T= 443K; 2 wt.% catalyst loading; 4:1 glycerol:palmitic acid molar ratio; 3 h	Increasing temperature and catalyst loading increased the palmitic acid conversion and monopalmitin yield. However, the yield could not reach more than 50% due to the pore characteristics. The catalyst basically did permit the diffusion of bulkier molecules. Reusable for up to four cycles without significant loss in catalytic activity	86	43	Yusoff and Abdullah 2016

Table 9 (continued)

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reported (Hermida et al. 2011). They reported that, after the first esterification run, the catalyst was filtered and washed with toluene and then dried at 100°C. Then, the catalyst was reused for the subsequent esterification runs under the same reaction conditions. HSO<sub>3</sub>SBA-15 catalyst was found to be reusable for up to five times without significant loss of activity.

#### 8 Conclusions

In this review paper, recently reported results concerning the preparation of acid-functionalized mesoporous catalysts, their characteristics as well as their recent applications in the esterification of fatty acid with glycerol to produce monoglycerides are discussed. Mesoporous molecular sieves (MMSs) such as MCM-41, SBA-15, HMS etc. can be functionalized with aluminum, zirconium, organosulfonic acid, perfluoro sulfonic acid and heteropoly acid either through direct synthesis or through post-synthesis techniques. Microporous catalysts and acid-functionalized mesoporous catalysts have been investigated in order to demonstrate their capability, and process behaviors have been elucidated. Their good activity is attributed to a fast diffusion and accessibility of fatty acid to the internal pore structure of the mesoporous catalysts to react with glycerol to produce monoglyceride. The esterification reaction should occur in the internal pores of the catalyst where most of the active acidic sites are available. Meanwhile, the pore sizes of microporous catalysts are generally smaller than the molecular dimension of fatty acid. As such, esterification can only occur on the external surface of the catalysts leading to the formation of undesired bulkier molecules including diglycerides and triglycerides. Functionalized mesoporous solid acid catalysts with propyl sulfonic groups often demonstrate good activity, stability and reusability for this process. The successful application of functionalized solid acid mesoporous catalysts provides the opportunity to simplify the reaction system. This will bring about significant reductions in the production costs and eliminates environmental hazards post by wastes that are commonly generated by homogeneous catalytic reactions.

#### Nomenclature

Å	angstrom
BET	Brunauer-Emmett-Teller
C <sub>FA</sub>	fatty acid concentration
FTIR	Fourier transform infrared

C <sub>G</sub>	glycerol concentration
HPA	heteropoly acids
HRTEM	high resolution transmission electron microscope
A <sub>AL</sub> 2	mechanism of esterification reaction through alcohol
A <sub>AC</sub> 2	mechanism of esterification reaction through carboxylic
	acid
MPMDS	mercaptopropyl(methyl)dimethoxysilane
MPTMS	mercaptopropyltrialkoxylane
NMR	nuclear magnetic resonance
PTES	phenyltriethoxysilane
SEM	scanning electron microscope
TEOS	tetraethoxyorthosilicate
TGA	thermogravimetric analysis
TEM	transmission electron microscopy
TMA	trimethyl aluminium
C <sub>12</sub> TAB	trimethylammonium bromides
TLCT	true liquid-crystal template mechanism
WDD	X7 1100 /

XRD X-ray diffractometer

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