

MESOPOROUS FUNCTIONALIZED ACID CATALYSTS AND THEIR USE AS ENVIRONMENTALLY FRIENDLY CATALYSTS IN ESTERIFICATION OF GLYCEROLS FOR MONOGLYCERIDE PRODUCTION

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ABSTRACT

Monoglycerides are valuable compounds with wide applications as emulsifiers in food, pharmaceutical and cosmetic industries. They can be produced by esterification of glycerols with fatty acids. Traditional homogeneous catalysts are usually used in the reaction for commercial scale productions. The processes utilizing homogeneous catalysts possess some drawbacks due to environmental aspect, such as corrosiveness, hazards of waste catalysts, etc. Because of simplicity in catalysts removal and minimization of the amount of waste formed, the utilization of heterogeneous or solid acid catalysts, as an alternative for this process, is an emerging topic on the aspect of the green-chemical processes. However, diffusion limitation of liquids within porous solids dictates that the use of mesoporous materials with pore diameter ranging from 20^oA to 100^oA is expected to be successful in liquid-phase reactions. The discovery of a family of ordered mesoporous silicas opens up new possibilities for preparing heterogeneous catalysts for liquid phase reactions. This review highlights on recent developments in the synthesis of mesoporous functionalized acid catalysts, for esterification of glycerols by fatty acids to produce monoglycerides.

Keywords: Monoglycerides; Esterification; Glycerol; Mesoporous Functionalized Acid Catalysts

INTRODUCTION

Monoglycerides are valuable compounds that are used as emulsifiers in food, pharmaceutical and cosmetic industries. Monoglycerides are composed of a hydrophilic head and hydrophobic tail. This composition gives them detergency characteristics. They increase permeability of skin and thus make drug absorptions easy [1].

Currently, the commercial scale production of monoglyceride is through direct esterification of glycerols with fatty acids [Fig. 1] that generally relies on traditional homogeneous catalysts using strong mineral acids, such as sulfuric acid and phosphoric acid [1, 2, 3]. However, this technology possesses severe drawbacks, such as the generation

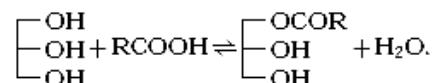


Figure 1: Direct Esterification of Glycerols and Fatty Acid [1]

of large amount of by products, high energy demand and environmental aspects. Techniques for the purification of monoglycerides e.g., distillation are limited to food applications as such process steps are expensive [4]. The replacement of homogeneous catalysts by heterogeneous

catalysts can offer advantages in process design and may improve yield and selectivity to the desired product by designing specific solid catalysts for the particular process [5]. There are several intrinsic advantages offered by heterogeneous catalysts over their homogeneous counterparts i.e., ease of product separation and catalysts reuse; bifunctional phenomena involving reactant activation/spillover between support and active phases; and process advantages through reactor operation in continuous flow versus batch configuration. Therefore, the development of new processes based on more selective solid acid catalysts has a great economical interest [6].

Acidic resins have been used as solid acid catalysts in this application [7]. 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 ($>150^{\circ}\text{C}$), causing them to be unfavorable for the esterification reactions. Attempts to use zeolites have also been made for monoglyceride production [8, 9]. Zeolite may exhibit a high monoglyceride selectivity, but the activity and consequently monoglyceride yield are low [10]. This is due to the small pore diameter of around $<8^{\circ}\text{A}$, which makes them unsuitable for liquid phase reactions and reactions involving bulky molecules like monoglycerides [11].

The discovery of the M41S family of mesoporous molecular sieves [12] offering pore sizes in the range from 20°A to 100°A opens up new possibilities for liquid-phase reactions using solid catalysts. This basic structural chemical feature of the mesoporous materials would allow processing of large molecules and the eventual accommodation of intermediate transition states which are too bulky to exist within the cavities and voids of zeolites [13]. This article focuses on recent developments in the synthesis of mesoporous functionalized acid catalysts used in esterification of glycerols and fatty acids for monoglyceride production.

SYNTHESIS OF MESOPOROUS MOLECULAR SIEVES (MMSs)

In catalytic application, there are three kinds of relevant materials of mesoporous molecular sieves (MMSs) obtained by using different synthetic procedures [14]. The first type is the so-called M41S family of silica and aluminosilicates introduced by the Mobil group [15] which consists of hexagonal MCM-41, cubic MCM-48 and lamellar MCM-50 phases. The preparation of M41S materials is based on charge matching between ionic surfactants and ionic inorganic reagents. The original preparation of the materials involves direct co-condensation of a cationic surfactant (S^+) and anionic species (I^-) to produce assembled ion pairs (S^+I^-). Depending on the synthesis conditions, and principally the surfactant/ SiO_2 ratio, different phases could be obtained, like the hexagonal phase MCM-41, the cubic one MCM-48 as well as the lamellar compound MCM-50, as shown in Fig. 2. In 1994, Stucky and co-worker extended this mechanism including the charge reversal situation i.e., an anionic template (S^-) was used to direct the self-assembly of cationic inorganic species (I^+) through S^-I^+ ion pairs. The next mechanisms involved counterion (X^- or M^+) mediated assemblies of surfactants and inorganic species of similar charge. These counterion-mediated mechanisms produces assembled solution species of the type $\text{S}^+\text{X}^-\text{I}^+$ (where $\text{X}^- = \text{Cl}^-$ or Br^-) or $\text{S}^-\text{M}^+\text{I}^+$ (where $\text{M}^+ = \text{Na}^+$ or K^+), respectively. The ionic surfactant or template is recovered by ion-exchange in cation donor solutions [16].



Figure 2: Structures of Mesoporous M41S Family:
a. MCM-41 (2D hexagonal, space group $p6mm$); b. MCM-48 (cubic, space group $Ia3-d$);
c. MCM-50 (lamellar, space group $p2$) [27]

The second group of mesoporous materials was introduced by Pinnavaia and co-workers who created MMSs using two neutral routes based on hydrogen bonding and self assembly between neutral primary amine micelles (S^0) and neutral or inorganic precursors (I^0) [17-25]. This mechanism produces neutral $S^0 I^0$ templating route. MMS's produced by this technique are hexagonal mesoporous silica (HMS and MSU). These materials are less ordered than MMS's produced with ionic surfactants. One of the most important advantages of HMS compared with MCM-41 is that the organic phase can be totally removed from as-synthesized samples by solvent extraction.

Finally, a new synthesis route involving amphiphilic di- and tri-block copolymers as the organic structure directing agents was introduced by Stucky and co-workers [26]. These materials, exemplified by SBA-15, have long range order, large monodispersed mesopores (up to 50 nm) and thicker walls (typically between 3 and 9 nm) which make them more thermally and hydrothermally stable than previous materials. The surfactant separation from the composite, either by calcination or solvent extraction, is easier than in the case of ionic surfactants.

Interactions between the inorganic species and the head group of the surfactant with consideration of the possible synthetic pathway in acidic, basic, or neutral media, are depicted in Fig.3 [27]. Based on the template used for synthesis and the interaction of inorganic species and organic surfactant molecule, the mesoporous molecular sieves might be grouped as listed in Table 1 [28].

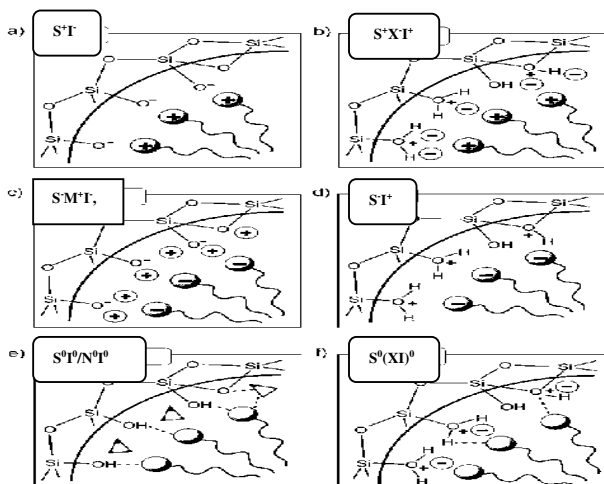


Figure 3: Interactions Between the Inorganic Species and the Head group of the Surfactant with Consideration of the Possible Synthetic Pathway in Acidic, Basic, or Neutral Media. Electrostatic: S^+T , S^+XI^+ , S^+M^+T , S^+T^+ ; through Hydrogen Bonds: S^0I^0/N^0I^0 , $S^0(XI)^0$, [27]

Table 1: Possible Pathways for the Synthesis of Mesoporous Molecular Sieves [28]

Template conditions	Interaction	Synthesis	Example	
Ionic surfactant	Direct interaction (Ionic)	I^+S^+AAAA	Basic	MCM-41, MCM-48, MCM-50
	Intermediated interaction (Ionic)	I^+S^+AAAA	Neutral-basic	FSM-16 (Aluminum, iron, lead oxides, etc.)
		$I^+X^+S^+AA$	Acidic	AMS
Non-ionic surfactant	(Non-ionic)	I^+S^0AAAA	Basic	SBA-1, SBA-2, SBA-3, HMS, TLCT (Aluminum, zinc oxides etc)
		I^+S^0AAAA	Acidic	HMS
Co-polymer (Ligand assisted)	(Co-valent bonding)	I^+N^0AAAA	Acidic	MSU, SBA-15, TLCT
Nanocasting	-	-	-	Nb-TMS, Ta-TMS CMK-n

MESOPOROUS FUNCTIONALIZED ACID CATALYSTS

The incorporation of active sites in the silica walls or deposition of active species on the inner surface of the mesoporous materials was more frequently applied to convert the MMS's into a mesoporous functionalized acid catalyst. First attempts were focused on incorporation of Al atoms tetrahedrally coordinated within the framework through hydrothermal methods analogous to those used in the preparation of zeolites. The trivalent cations, Al^{3+} , substitute for silicon in the walls of the mesoporous silica, the framework possesses negative charges. This negative charge is balanced by a metal cation or a proton that constitutes a Lewis- or a Bronsted-acid site, respectively. The Si MAS NMR results indicated the amorphous nature of the pore walls [29]. Since the O–Al–O angle is less flexible than the O–Si–O angle, the mesoporous silicas of Al-MCM-41 are commonly less well ordered on the mesoscale and show a broader pore size distribution than their pure silica analogues. Therefore, their catalytic properties are closer to a mildly acidic amorphous silica-alumina than to a strongly acidic zeolite, which limit their potential catalytic applications [29]. Recently, considerable efforts have been undertaken to incorporate organic components within an inorganic silica framework to tune the acid strength and control the hydrophobic microenvironment of the sulfonic-acid sites and subsequent improvements of the catalytic performance. There are three fundamental principles for the preparation of organically modified or functionalized silica phases [27]. They are post synthetic functionalization of silicas, the direct methods of co-condensation and periodic mesoporous organosilicas (PMOs).

Post synthetic Functionalization of Silicas

Grafting. Grafting refers to the modification of a pre-fabricated mesoporous support by attachment of functional molecules to the surface of the mesopores, usually after surfactant removal (Fig. 3) [42]. Mesoporous silicates possess surface silanol (Si-OH) groups that act as convenient anchoring points for organic functionalization. Surface modification with organic groups is most commonly carried out by silylation. Typically, silylation is accomplished by one of the following procedures:

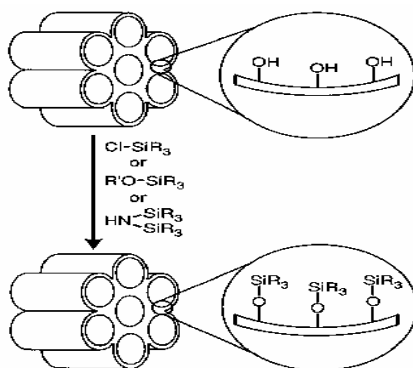
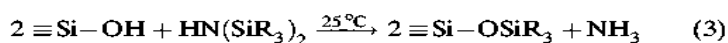
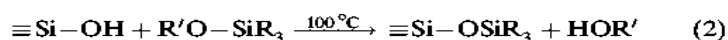
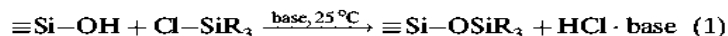


Figure 3: Functionalization of Mesoporous Silicates by Grafting [42]

Coating. Coating refers to formation a monolayer on the pore surface by utilizing just enough water in the process. More continuous coats of organosilanes may be obtained, leading to a high concentration of organics in the product (Fig. 4). This technique is different from the grafting processes in which the organosilanes typically are added under dry conditions to avoid hydrolysis and condensation away from the pore walls [1, 42].

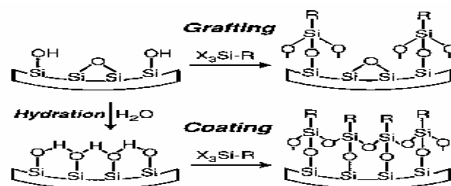


Figure 4: Comparison of Coating and Grafting Processes [42]

Under the synthetic conditions used, the advantage of post synthetic method is that the mesostructure of the starting silica phase is usually retained, whereas the lining of the walls is accompanied by a reduction in the porosity of the hybrid material [27].

Co-Condensation method (Direct Synthesis). The co-condensation method (direct synthesis) involves the preparation of mesostructured silica phases by the co-condensation of tetraalkoxysilanes [(RO)₄Si (TEOS or TMOS)] with terminal trialkoxyorganosilanes of the type (R'O)₃SiR in the presence of structure-directing agents that bring about materials with organic residues anchored covalently to the pore walls (Fig. 5). By using structure-directing agents known from the synthesis of pure mesoporous silica phases (e.g., MCM or SBA silica phases), organically modified silicas can be prepared in such a way that the organic functionalities present into the pores.

The organic units are generally more homogeneously distributed than in materials synthesized with the post synthesis process. However, the cocondensation method also has a number of disadvantages. In general, the degree of mesoscopic order of the products decreases with increasing concentration of (R'O)₃SiR in the reaction mixture, which ultimately leads to totally disordered products. Moreover, an increase in loading of the incorporated organic groups can lead to a reduction in the pore diameter, pore volume, and specific surface areas. A further, purely methodological disadvantage that is associated with

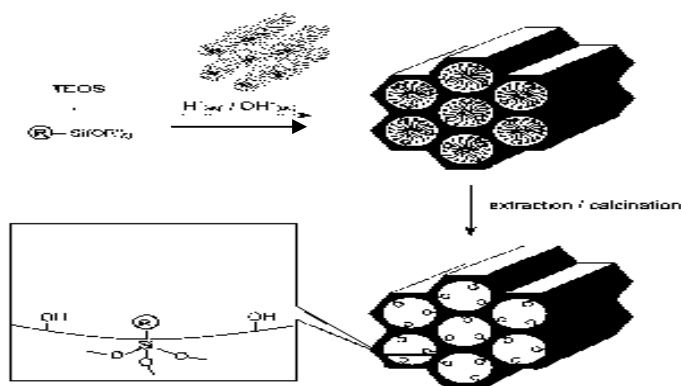


Figure 5: Co-condensation Method (direct synthesis) for the Organic Modification of Mesoporous Pure Silica Phases. R=organic functionalgroup [27]

the co-condensation method is that care must be taken not to destroy the organic functionality during removal of the surfactant, which is why commonly only extractive methods can be used, and calcinations is not suitable in most cases.

Preparation of Periodic Mesoporous Organosilicas (PMOs). In contrast to the organically functionalized silica phases, which are obtained by post synthesis or direct synthesis, the organic units in periodic mesoporous organosilicas (PMOs) are incorporated in the three-dimensional network structure of the silica matrix through two covalent bonds and thus distributed homogeneously in the pore walls.

The transfer of the concept of the structure-directed synthesis of pure silica mesophases by surfactants to the bissilylated organosilica precursors described above allows the construction of a new class of mesostructured organic– inorganic hybrid materials— (PMOs)—in which the organic bridges are integral components of the silica network (Fig. 6). PMOs are characterized by a periodically organized pore system and a very narrow pore radius distribution. The first PMO was synthesized in 1999 by three research groups working independently [30, 31, 32].

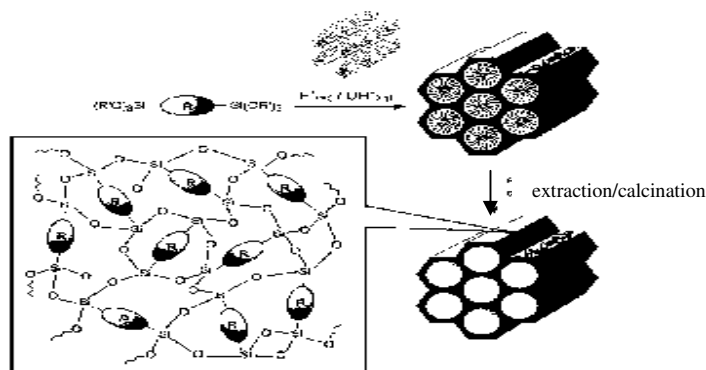


Figure 6: General Synthetic Pathway to PMOs that are Constructed from Bissilylated Organic bridging units. R=organic bridge [27]

RECENT APPLICATION OF MESOPOROUS FUNCTIONALIZED ACID CATALYSTS IN ESTERIFICATION OF GLYCEROL BY FATTY ACIDS FOR MONOGLYCERIDE PRODUCTION

Bossaert et al., (1999) investigated the synthesis of monoglycerides via direct esterification of glycerols with lauric acid over propylsulfonic- acid MCM-41 and HMS materials prepared by means of different strategies of synthesis, i.e.: co-condensation and post synthesis methods. In co-condensation method, the alkylthiol molecules are introduced in the synthesis gels, and the hybrid materials are obtained directly. The template was eliminated by solvent extraction. It was reported that this synthesis method permits to incorporate higher content of 3-Mercaptopropyl TriMethoxy Silane (MPTMS). Moreover, the post synthesis methods comprised the silylation calcined MCM support with MPTMS in dry toluene and the coating of a partially hydrated support with an MPTMS layer (Fig.7).

They reported that the most active solid catalyst among the propylsulfonic acid-functionalized mesoporous materials was a coated silica gel-SO₃H. The HMS-SO₃H synthesized by the co-condensation method was the second most active, while the silylated MCM-41-SO₃H and coated MCM-41-SO₃H were the least active. They also observed that

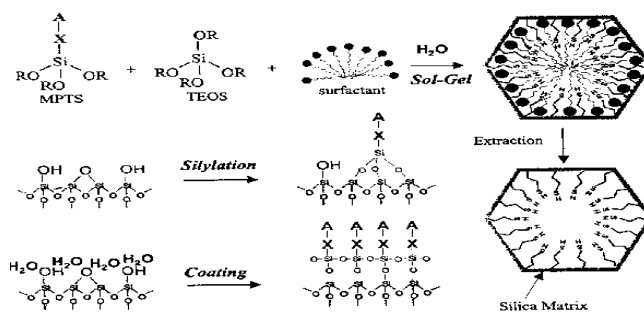


Figure 7: Mercaptopropyl Encapsulation into Mesoporous Materials by Direct Synthesis or Post-Synthesis Methods [43]

propylsulfonic acid-functionalized mesoporous silica catalysts were slightly better than Amberlyst-15 resins but significantly more active than H-USY, a commercial zeolite-type acidic catalyst. These mesoporous silica catalysts gave a maximum acid conversion of 80% with selectivity to the monoglycerides of 52% after 10.2 h of reaction, while Amberlysts-15 gave a maximum acid conversion of about 75% with the selectivity of about 44% after 11.5 h of reaction. Then the H-USY showed a maximum acid conversion and the selectivity of about 55% and 36% respectively, after 23.5 h of reaction. The H-USY had both a surface area and a number of acidic sites that were higher than those of the acid-functionalized mesoporous silica, which implied that the esterification reaction catalyzed by the zeolite catalyst was likely diffusion limited.

Diaz et al., (2001) have extensively observed the same esterification reaction over optimized propylsulfonic-modified mesoporous materials by direct synthesis [33,34]. They reported that the selectivity toward monoglycerides in the esterification of glycerols with fatty acids was improved by propyl- SO_3H -MCM-41 materials synthesized using mixtures of cationic surfactants as compared with standard materials due to the better pore arrangement of these catalysts [33]. Moreover, the same research group examined the catalytic activity of propylsulfonic-modified MCM-41 materials synthesized using mixtures of cationic and neutral surfactants in the esterification of glycerol with lauric acid [34]. The catalyst showed an acid conversion of 90% with selectivity to the monoglycerides of 75% after 24 h of reaction. On the contrary, the propyl- SO_3H MCM-41 synthesized in the absence of amine gave selectivity as low as 40% with an acid conversion of 96%. Both works clearly explained that a wise mixture of surfactants provides sulfonic-acid-bearing MCM-41 catalysts with clear improved catalytic properties for the esterification reaction as compared with the conventional single-surfactant synthesis process.

By reason of the relatively bulky molecules involved in the esterification process, Diaz et al., (2001) examined direct synthesis of SBA-15 and SBA12 mesostructured materials, with a larger pore size than MCM-type materials, functionalized with propylthiol moieties for this esterification [35,36]. The catalysts exhibited a maximum acid conversion of 80% and the selectivity of 20% after 8 h of reaction. Moreover, the catalytic results showed that the turnover number (TON) for MCM-41 materials is higher than those materials. For SO_3HSBA -15, the low TON value was attributed to the presence of sulfonic groups located in structural micropores of the silica walls. In this case, the esterification reaction would be extremely hindered as it occurs when using zeolites, influencing on the overall TON. Low activity in SO_3HSBA -12, even lower than that observed in SBA-15 material, was related to the small size of the windows that interconnect the large cavities. This result was consistent with the severe pore blocking of the structure as a consequence of the high population of stacking faults detected in this material [37, 38]. Besides, the pore size of SBA-15 and SBA-12 seems to be too large for significant shape-selectivity effects in the esterification reactions.

In order to increase the efficiency of the oxidation of thiol to sulfonic acid, Diaz et al., (2003) studied direct synthesis of different MCM-41 materials functionalised with 3-mercaptopropyl(methyl)dimethoxy silane (MPMDS) in presence of the amino acid leucine, used as co-structuring agent. The $[\text{CH}_3, \text{SO}_3\text{H}]$ -MCM-41 catalysts, containing different amounts of $[\text{CH}_3, \text{SO}_3]$, obtained upon oxidation of the thiol precursors have been tested in the esterification of glycerol with lauric and oleic acids. The turnover number (TON) of these catalysts containing both functional groups attached to the same Si atom is higher than that of the conventional samples containing methyl and sulfonic groups on independent Si atoms. The catalyst with the highest TON value is the most selective to monoglycerides. In this case, the catalyst showed a maximum acid conversion of 85% with corresponding selectivity to the monoglycerides of 59% after 8 h of reaction.

With the aim of improving both activity and selectivity, furthermore, Diaz et al., (2005) reported the new one-step hydrothermal syntheses of MCM-41 materials bearing materials which contain two functionalities, vinyl and methyl moieties, as well as a new material, chloromethyl-MCM-41. The corresponding sulfonated forms HSO_3 -ethyl-MCM-41, HSO_3 -ethyl/methyl-MCM-41 and HSO_3 -methyl-MCM-41 were tested in the same reaction of esterification. The catalysts gave a maximum acid conversion and the selectivity of 97% and 55% respectively, after 8 h reaction. In addition, the hydrophilic character of the surface of the catalyst pores decreased when methyl groups are incorporated in addition to the active functional groups. This effect of the higher hydrophobic character of the catalysts containing methyl moieties was also noted in the selectivity to the monoglycerides, at the same acid conversion, which was higher for the catalysts with the methyl groups.

In 2002, Mohino et al., [41] studied the synthesis and characterisation of phenyl and combined methyl/phenyl functionalised MCM-41 materials using by co-condensation method and the sulfonation procedure, using chlorosulfonic acid in liquid phase or SO_3 , to obtain the corresponding SO_3H -phenyl-MCM-41 catalysts. The catalysts were also tested in esterification of glycerols with lauric and oleic acids. The most active catalysts were combined methyl/phenyl functionalised MCM-41 materials with sulfonation procedure using the chlorosulfonic acid ($\text{SO}_3\text{-Ph-(Me)-MCM-41}$). These catalysts gave a maximum acid conversion of 98% with selectivity to the monoglycerides of 35% after 24 h of reaction.

CONCLUSION

Until recently several researchers had shown that mesoporous materials of MCM-41, SBA-15 and SBA-12 had good catalytic properties compared with other solid acid catalysts in the direct esterification of glycerols by fatty acids for monoglyceride production. The mesoporous materials of MCM-41 were functionalized with organic sulfonic group by post synthesis and direct synthesis, while those of SBA-15 and SBA-12 were functionalized with organic sulfonic group by direct synthesis. Further insights into reaction mechanisms catalyzed by mesoporous materials would further bolster the ability to design functionalized mesoporous materials with the goal of enhancing reaction rates and selectivity to the desired products. The application of functionalized mesoporous catalysts has the possibility for simplifying reaction systems, reducing production costs, and eliminating environmental hazards posed by wastes generated in homogeneous catalyzed reactions. As synthesis techniques and the characterization of functionalized mesoporous catalyst are grown-up, one would expect more applications of these nanostructured materials for the direct esterification.

REFERENCES

- [1] Bossaert, W.D., Vos, D.E.D., Rhijn, W.M.V., Bullen, J., Grobet, P.J., and Jacobs, P.A., Mesoporous Sulfonic Acids as Selective Heterogeneous Catalysts for the Synthesis of Monoglycerides, *Journal of Catalysis*, Vol.182, 1999, pp.156–164.

- [2] Corma, A. and Kumar, D., Possibilities of Mesoporous Materials in Catalysis, *Studies in Surface Science and Catalysis*, Vol. 117, 1998, pp.201 – 222.
- [3] Formo, M.W., Ester Reactions of Fatty Materials, *The Journal of American Oil Chemists Society*, Vol. 31,1958, pp.548 559
- [4] Nakamura, R., Komura,K., and Sugi, Y., The esterification of Glycerine with Lauric Acid Catalysts by Multi-valent Metal Salts. Selective Formation of Mono- and Dilaurins. *Catalysis Communication*, 2007.
- [5] Corma, A., Hamid, S.B.A., Iborra, S., and Velty., Lewis and Bronsted Basic Active Sites on solid catalysts and their role in the synthesis of monoglycerides, *Journal of Catalysts* ,Vol. 234, 2005,pp. 340-347.
- [6] Bancquart, S., Vanhove, C., Pouilloux, Y., and Barrault, J., Glycerol Transesterification with Methyl Stearate Over Solid Basic Catalysts. Relationship Between Activity and Basicity. *Applied Catalysis A* , Vol. 218, 2001, pp.1-11.
- [7] Pouilloux , Y., Abro, S., Vanhove, C., Barrault, J. , Reaction of glycerol with fatty acids in the presence of ion-exchange resins Preparation of monoglycerides *Journal of Molecular Catalysis A: Chemical* Vol.149, 1999, pp.243–254.
- [8] Sanchez, N., Martinez, M., and Aracil, J., Selective Esterification of Glycerine to 1-Glycerol Monooleate. 1. Kinetic Modeling, *Ind. Eng. Chem. Res.* Vol.36,1997, pp.1524-1528
- [9] Aracil, J., Martinez, M., Sanchez, N., and Corma, A., Formation of a jojoba oil analog by esterification of oleic acid using zeolites as catalyst, *Zeolites* ,Vol.12,1992, pp.233-236
- [10] Heykants, E., Verrelst, W. H., Parton, R. F., and Jacobs, P. A., Progress in Zeolite and Microporous Materials, *Stud. Surf. Sci. Catal.*, Vol. 105, 1996, pp. 1277
- [11] Wilson, K. and Clark, J.H. , Solid acids and their use as environmentally friendly catalysts in organic synthesis, *Pure Appl. Chem.*, Vol. 72, No. 7, 2000, pp. 1313–1319.
- [12] Beck, J. S., Vartuli, J. C., Roth, W. J., Leonowicz, M. E., Kresge, C. T., Schmitt, K. D., Chu, C. T-W., Olson, D.H., Sheppard, E.W., McCullen, S.B., Higgins, J.B., and Schlenkert, J.L., A New Family of Mesoporous Molecular Sieves Prepared with Liquid Crystal Templates, *J. Am. Chem. Soc.* Vol. 114, 1992, pp.10834-10843.
- [13] Perez-Pariente, J., Diaz, I., Mohino, F., and Satre, E., Selective synthesis of monoglycerides by using functionalised mesoporous catalysts, *Applied Catalysts A*, Vol.254, 2003, pp.173- 188.
- [14] On, D.T., Giscard, D.D., Danumah, C., Kaliaguine, S., Perspectives in catalytic applications of mesostructured materials, *Applied Catalysis A: General*, Vol.253, 2003, pp. 545–602
- [15] Stucky, G. D. , Monnier, A., Schüth, F., Huo, Q., Margolese, D., Kumar, D., Krishnamurty, M., Petroff, P., Firouzi, A., Janicke, M., Chmelka, B.F., Molecular and Atomic Arrays in Nano- and Mesoporous Materials Synthesis, *Molecular Crystal and Liquid Crystal Volume* 240, 1994 , pp. 187 - 200
- [16] Whitehurst, D.D. (Titusville, NJ), Method to recover organic templates from freshly synthesized molecular sieves, *U. S. Patent* No. 5,143,879 , 1992
- [17] Tanev, P.T., Chibwe, M., Pinnavaia, T.J, Titanium-containing mesoporous molecular sieves for catalytic oxidation of aromatic compounds, *Nature* , Vol.368, 1994, pp. 321-323.
- [18] Tanev, P.T., Pinnavaia, T.J., A Neutral Templating Route to Mesoporous Molecular Sieves, *Science*, Vol. 267, 1995, pp.865- 867.
- [19] Bagshaw, S.A., Prouzet, E., Pinnavaia, T.J., Templating of Mesoporous Molecular Sieves by Nonionic Polyethylene Oxide Surfactants, *Science*, Vol. 269, 1995, pp.1242 – 1244.

- [20] [20] Zhang, W., Pauly, T.R., Pinnavaia, T.J., Tailoring the Framework and Textural Mesopores of HMS Molecular Sieves through an Electrically Neutral ($S^{\circ}I^{\circ}$) Assembly Pathway *Chem. Mater.* Vol. 9, 1997, pp.2491 – 1498.
- [21] Zhang, W., Froeba, M., Wang, J., Tanev, P.T., Wong, J., Pinnavaia, T.J., Mesoporous Titanosilicate Molecular Sieves Prepared at Ambient Temperature by Electrostatic (S+I, S+X-I+) and Neutral ($S^{\circ}I^{\circ}$) Assembly Pathways: A Comparison of Physical Properties and Catalytic Activity for Peroxide Oxidations, *J. Am. Chem. Soc.* Vol.118, 1996, pp. 9164-9171
- [22] Zhang, W., Wang, J., Tanev, P.T., Pinnavaia, T.J., Catalytic hydroxylation of benzene over transition-metal substituted hexagonal mesoporous silicas, *J. Chem. Soc., Chem. Commun.*, 1996 pp. 979 - 980
- [23] Bagshaw, S.A., Pinnavaia, T.J., Mesoporous Alumina Molecular Sieves, *Angew. Chem. Int. Ed. Eng.*, Vol. 35, 1996, pp. 1102 - 1105.
- [24] Prouzet, E., Pinnavaia, T.J., Assembly of Mesoporous Molecular Sieves Containing Wormhole Motifs by a Nonionic Surfactant Pathway: Control of Pore Size by Synthesis Temperature, *Angew. Chem. Int. Ed.* Vol. 36, 1997, pp. 516 – 518.
- [25] Pinnavaia, T.J., Zhang, W., Catalytic properties of mesoporous molecular sieves prepared by neutral surfactant assembly, *Stud. Surf. Sci. Catal.* Vol. 117, 1998, pp. 23 - 36.
- [26] Zhao, D., Feng, J., Huo, Q., Melosh, N., Fredrickson, G.H., Chmelka, B.F., Stucky, G.D., Triblock Copolymer Syntheses of Mesoporous Silica with Periodic 50 to 300 Angstrom Pores, *Science*, Vol. 279, 1998, pp.548 - 552
- [27] Hoffmann, F., Cornelius, M., Morell, J., and Froba, M., Silica-Based Mesoporous Organic-Inorganic Hybrid Materials, *Angew. Chem. Int. Ed.*, Vol. 45, 2006, pp.3216 – 3251
- [28] Taguchi, A., Schuth, F., Ordered Mesoporous Materials in Catalysis, *Microporous and Mesoporous Materials*, Vol. 77, 2005, pp. 1–45.
- [29] Corma, A., From Microporous to Mesoporous Molecular Sieve Materials and Their Use in Catalysis, *Chem. Rev.*, Vol. 97, 1997, pp. 2373-2419
- [30] Inagaki, S., Guan, S., Fukushima, Y., Ohsuna, T., Terasaki, O., Novel Mesoporous Materials with a Uniform Distribution of Organic Groups and Inorganic Oxide in Their Frameworks *J. Am. Chem. Soc.* Vol.121, 1999, pp. 9611 – 9614.
- [31] Melde, B. J., Holland, B. T., Blanford, C. F., Stein, A., Mesoporous Sieves with Unified Hybrid Inorganic/Organic Frameworks, *Chem. Mater.*, Vol. 11, 1999, pp. 3302 – 3308.
- [32] Asefa, T., MacLachlan, M. J., Coombs, N., Ozin, G.A., Periodic mesoporous Organosilicas with Organic Groups Inside the Channel Walls, *Nature*, Vol. 402, 1999, pp. 867 – 871.
- [33] Diaz, I., Mohino, F., Pe´rez-Pariente, J., Satre, E., Synthesis, characterization and catalytic activity of MCM-41-type mesoporous silicas functionalized with sulfonic acid *Appl. Catal., A:Gen.* Vo. 205, 2001, pp.19-30
- [34] Diaz, I.; Ma´rquez-Alvarez, C.; Mohino, F.; Pe´rez-Pariente, J.; Satre E. A novel synthesis route of well ordered, sulfur-bearing MCM-41 catalysts involving mixtures of neutral and cationic surfactants, *Microporous Mesoporous Mater.* 2001, Vol. 44-45, pp.295-302
- [35] Diaz, I., Mohino, F., Pe´rez-Pariente, J., Satre, E., Wright, P. A., Zhou, W. A direct synthesis route to the mesoporous silicate SBA-2 bearing thiol groups *Stud. Surf. Sci. Catal.*, Vol. 135, 2001, pp.252
- [36] Diaz, I., Mohino, F., Satre, E., Pe´rez-Pariente, J., Synthesis and Catalytic Properties of SO_3H -mesoporous materials from Gels Containin g non-ionic Surfactants *Stud. Surf. Sci. Catal.* Vol.135,2001, pp. 1383-1390

- [37] Hou, Q., Leon, R., Petroff, P. M., Stucky, G. D., Mesostructure Design with Gemini Surfactants: Supercage Formation in a Three-Dimensional Hexagonal Array *Science*, Vol. 268, 1995, 1324 - 1327
- [38] Zhou, W., Hunter, H. M. A., Wright, P. A., Ge, Q., Thomas, J. M., Imaging the Pore Structure and Polytropic Intergrowths in Mesoporous Silica. *J. Phys. Chem. B*, Vol. 102, 1998, pp. 6933-6936
- [39] Diaz, I., Mohino, F., Pérez-Pariente, J., Sastre, E., Synthesis of MCM-41 Materials Functionalised with Dialkylsilane groups and Their Catalytic Activity in the Esterification of Glycerol with Fatty acids, *Applied Catalysis A: General* Vol. 242, 2003, pp. 161–169.
- [40] Diaz, I., Mohino, F., Blasco, T., Sastre, E., Perez-Pariente, J., Influence of the alkyl chain length of HSO₃-R-MCM-41 on the esterification of glycerol with fatty, *Microporous and Mesoporous Materials* Vol.80, 2005, pp.33–42
- [41] Mohino, F., Diaz, I., Perez-Pariente, J. and Sastre, E., Synthesis, characterisation and catalytic activity of SO₃H- phenyl-MCM-41 Materials, *Studies in Surface Science and Catalysis*, Vol.142, 2002, pp.1275 – 1282
- [42] Stein, A., Melde, B.J., and Schroden, R. C., Hybrid Inorganic-Organic Mesoporous Silicates- Nanoscopic Reactors Coming of Age, *Adv. Mater.* Vol. 12, 2000, pp. 1403 – 1419
- [43] Van Rhijn, W.M., Vos, D.E., Bossaert, W.D., Bullen, J., Vouters, B., Grobert, P., Jacobs, P.A., Sulfonic acid bearing mesoporous materials as catalysts in furan and polyol derivatization, *Stud. Surf. Sci. Catal.*, Vol.117, 1998, pp.183 - 190