REVIEW

Conversion of Oils and Fats Using Advanced Mesoporous Heterogeneous Catalysts

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ABSTRACT: Natural oils and fats are emerging as a biobased alternative feedstock to conventional crude oil in the production of chemicals and transportation fuel. However, many of these biobased chemicals are not currently cost competitive with petrochemicals because of high raw material and production costs. To improve the economic outlook of the biobased chemicals, the use of suitable catalysts becomes imperative. Recently, the discovery of advanced material synthesis strategies such as supramolecular-assembled mesoporous materials has created new opportunities in tailoring catalyst properties specifically for the conversion challenges encountered with oils and fats. These nanostructured materials have a combination of extremely high surface areas and flexible pore sizes that makes them attractive for catalysis applications. This article reviews the application of this new class of advanced materials for the conversion of oils and fats to biobased chemicals.

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KEY WORDS: Esterification, etherification, functionalized mesoporous silicas, lipids, transesterification.

The conversion of vegetable oils and animal fats into specialty and commodity products holds promise as a means of replacing some crude oil-based products. Natural oils have a number of attractive features over conventional crude oil, such as that they are renewable, are biodegradable, and have nontoxic properties. However, the conversion of natural oils into nonedible products has been limited because of the inability to compete effectively with mature petrochemical industries as the result of high raw material and production costs. To improve the economic aspect of these processes, the selection of raw materials and reaction conditions and the use of efficient catalysts becomes critical.

Natural oils and fats can be used for the production of a variety of biobased products because they have multiple reactive groups that can be converted into desired products when the appropriate reaction conditions and catalysts are used. Biocatalysts exemplify exceptionally selective catalysts that interact with specific oil molecules to transform them into the desired product with little by-product formation. Unfortunately, biocatalysts typically impart a high production cost because of their low reaction rates, short cell life spans, inhibitor intolerance, difficulties in product separation, and expensive sterile equipment requirements. These attributes adversely affect the production of biobased chemicals, especially for manufacturing large-volume chemicals such as transportation fuel. Specially designed inorganic and organic homogeneous and heterogeneous catalysts have the potential to overcome many of the obstacles that hinder the catalytic performance of biocatalysts. Homogeneous catalysts are robust and ideal for liquid-phase reactions since they form uniform mixtures with the reactants, resulting in minimum mass transfer limitations and high reaction rates. Although homogeneous catalysts have preferred reaction characteristics in many liquid-phase reactions, they are also associated with difficulties in recovering the catalysts, disposal of potentially toxic wastes, and separation of the desired products. These unfavorable attributes have led to the substitution of homogeneous catalysts with solid catalysts in many reactions used for large-scale chemical production. Although heterogeneous catalysts have many positive features, the application of solid catalysts in liquid-phase reactions involving biologically based molecules has been limited because of poor reactant/catalyst contacting from either pore diffusion limitations or low active site availability for the catalytic reaction. For example, the application of zeolite-type catalysts (pores <15 Å) to liquid-phase reactions of biological feedstocks would be expected to have limited success because such reactions will likely be pore diffusion controlled. In addition, biological feedstocks, which have multiple reactive functional groups, will likely require molecularly well-defined reaction domains to minimize the formation of by-products.

The inadequate performance of solid catalysts in liquid-phase reactions has led to extensive research to increase the pore size of catalytic materials while maintaining high surface area. The discovery of mesoporous materials in 1992 by Mobil Research and Development Corporation, which allowed tunable pore sizes from 2 to 30 nm, has sparked interest among researchers owing to the potential application of these materials as solid catalyst supports, particularly for liquid-phase reaction systems (1–3). Recent advances in developing these materials will allow researchers to design and customize solid catalyst materials that could meet the unique specifications of reactants and products based on oils and fats. As such, mesoporous materials hold promise for increasing both the selectivity and yield of desirable products.

This review paper will focus on the application of organic–inorganic hybrid mesoporous silica materials as heterogeneous catalysts for the conversion of biorenewable feedstocks. The first part of the review is a brief description of the synthesis and functionalization of mesoporous silica materials. The application of these functionalized mesoporous silica materials to the catalytic

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*To whom correspondence should be addressed at 2119 Sweeney Hall, Ames, IA 50011. E-mail: bshanks@iastate.edu conversion of natural oils and fats in various reaction systems is then given.

ADVANCED MESOPOROUS CATALYTIC MATERIALS

The initial discovery of a novel molecular sieve family (M41S) has provided scaffolds with unprecedented control of textural features that can be exploited for heterogeneous catalysts in liquid-phase reactions (1–3). This breakthrough in material engineering has introduced a novel route for synthesizing metal oxides, particularly silica and aluminosilicate mesoporous materials that have a combination of extremely high surface areas and well-defined pores with uniform sizes. The novelty of these mesoporous materials lies in the synthesis technique used, in which the design of complex inorganic structures is guided by rational synthetic pathways (4–7). More notably, the new synthesis route offers the capability of adjusting the pore sizes of these materials on the nanoscale by selecting the appropriate building blocks, which presents the opportunity for constructing a structure of desired dimensions and functionality. This synthesis approach overcomes a key drawback to synthetic zeolite-type catalysts whose pore sizes are constrained to the microporous range, which limits their application to reactions of smaller molecules. The large mesopores increase the possibility of utilizing these mesoporous materials in liquid-phase reaction systems, given that the effect of diffusion diminishes with an increase in the size of the pores. These physical properties are highly advantageous for solid catalysts because they allow the reactants to access the large internal surfaces where a high concentrations of active sites can be incorporated, thereby enhancing the catalytic activity.

The ability to manipulate the framework of mesoporous materials has been of interest to many researchers, leading to a variety of synthesis strategies that have been reviewed (8–11). The sophisticated framework of the mesostructure materials originates from cooperative assembly of an inorganic precursor with an organic structure-directing template, as illustrated systematically in Figure 1. The organic templates are typically surfactants comprising both a hydrophilic domain and a distinct hydrophobic domain. The surfactant molecules form ordered complex structures in aqueous solution, as shown in Figure 1(a), either (i) by self-assembly or (ii) by cooperative-assembly coordinated in some manner by interacting with the inorganic precursor. The fundamental behavior of surfactants to form micelles in solutions makes them excellent templates. The addition of the inorganic precursor to a solution with surfactant templates under appropriate conditions initiates a cascade of cooperative-assembly arrangements between the inorganic and organic species, with concomitant hydrolysis of the inorganic species that gives rise to a supramolecular structure, as shown in Figure 1(b). The interaction between the inorganic precursor and the surfactant micelles is created *via* forces that include electrostatic, Van der Waals, and hydrogen bonding. These interactions subsequently determine the textural characteristics of the final material. Materials synthesized using an ionic surfactant generally have hexagonal structures and are commonly abbreviated as MCM (1,2). Neutral and nonionic surfactants give rise to mesoporous materials that have wormlike channels and are usually abbreviated as HMS and SBA, respectively (6,12–14). The template in the mesopores of the as-synthesized mesoporous material is removed by either refluxing in a suitable solvent or calcining at high temperatures. Because of the nature of the templates used, the as-synthesized mesoporous materials have a narrow pore size distribution as well as long channels, as shown in Figure 1(c). An important benefit of utilizing surfactants as templating agents is the capability of adjusting the pore size of the mesoporous materials, which is directly proportional to the size of micelles formed in solution. Several examples of mesoporous materials with different pore sizes are reported in the literature owing to the precise tuning of the pores by selecting the appropriate surfactants with the desired carbon chain length (1,12–14). This synthesis strategy has been used to produce a broad range of metal oxides, but silica remains the most extensively used (10).

The physical and chemical properties of these mesoporous materials can be manipulated by incorporating suitable organic or inorganic functional groups into the mesoporous silica matrix, which has been described in great detail in the literature (9,11,15). The functionalization process introduces distinct functionality to the material, e.g., adsorption or catalytic properties, through changes in the physical and/or chemical properties of the mesoporous material. The ability to functionalize mesoporous materials with different catalytically active groups as well as with the aforementioned textural properties allows the materials to be excellent catalyst supports. The functional groups can be incorporated onto the large internal surface area and/or the external surface area of the mesostructured material, as shown in Figure 2. There are several

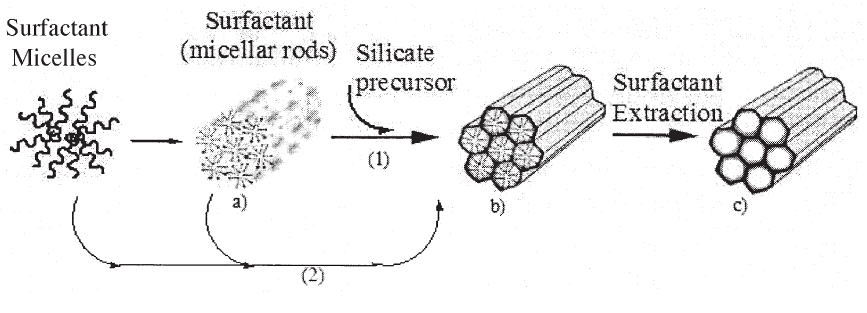

FIG. 1. Schematic representation of the synthetic route for mesoporous material formation through supramolecular assembly.

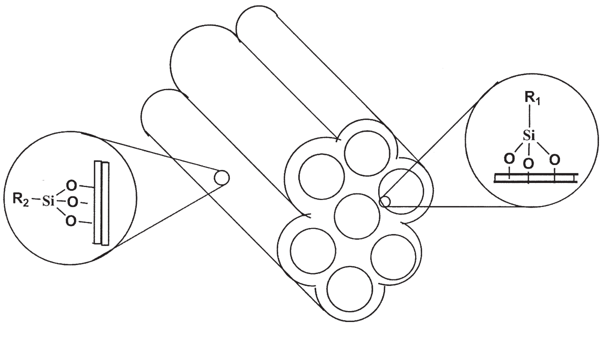

FIG. 2. Schematic representation of a mesoporous material functionalized with organic groups on the external and internal surfaces.

methods of incorporating organic functional groups onto the mesoporous silica surface that will be described.

Organotrialkoxysilanes are frequently used to incorporate organic functional groups, which include alkyl halides, amines, alkenes, or thiols, onto the mesostructure. The two techniques most often applied for incorporating organotrialkoxysilanes into the mesoporous silica are grafting and direct co-condensation. The grafting technique is a postsynthesis modification performed on a preformed mesoporous material by reacting organic groups with the surface hydroxyl (silanol) groups, usually after removal of the surfactant (11). High concentrations of silanol groups are found on the external and internal surface areas of the mesoporous silica materials, and these silanol groups act as anchoring sites for organic moieties since the surface hydroxyls react readily with the silane's alkoxy groups by silylation. The postsynthesis grafting technique typically leads to higher concentrations of the grafted functional group on the external surface area because of the high reactivity of the organotrialkoxysilanes (16–18). This nonuniform distribution of functional groups is not optimal and can result in reduced catalytic activity and selectivity to the desired products owing to nonuse of the large internal surface area as well as forfeiture of the pore discrimination capabilities.

In contrast to the grafting method, direct co-condensation (also called "one-pot" synthesis) refers to the synthesis technique whereby all the components of the desired final organic–inorganic hybrid mesoporous material (e.g., silica precursor, surfactant, and functional groups precursors) are simultaneously introduced (19). The basis for the direct co-condensation technique is that the organic functional groups are hydrophobic, so they will intrude into the surfactant micelles. Accordingly, after solvent extraction of the surfactant, the interior pore surface of the mesoporous channels will be decorated with the organic moieties.

The two organic functional group incorporation techniques have both advantages and disadvantages. Mesoporous silicas synthesized *via* the direct co-condensation method require fewer synthesis steps and fewer reagents, and would seem to have a more uniform distribution of the organic moieties than the grafting method. However, incorporation of organic groups during the synthesis of the mesoporous structure can affect the textural properties of the resulting material, particularly when high loadings of the organic group are introduced. Mesoporous materials modified *via* postsynthesis techniques have better control of textural properties than do materials synthesized by the direct co-condensation procedure since the incorporation of the organic group during synthesis can influence the resulting structure. Whichever method is used to incorporate the organic functional groups, the modification of the mesoporous silica at the nanoscale creates many opportunities for designing nano-reaction environments that may be tailored to convert a specific biorenewable feedstock to a desired product at high conversion and selectivity.

Besides functionalization of the mesoporous materials with catalytic organic groups, incorporation of inorganic compounds into mesoporous metal oxides has also been studied in great detail, as reviewed by Ying *et al.* (9). The inorganic compounds are commonly incorporated into the mesoporous materials by the incipient wetness impregnation technique. In this method, a salt of the catalytically active compound is mixed with the mesoporous powder material to form a slurry, which is then calcined to generate the active metal compound. The tethering of organometallic complexes to organic spacers incorporated in the mesoporous material surface is another popular technique of introducing inorganic compounds (9,11). The organic spacers are incorporated into the mesoporous materials according to the above-mentioned synthesis techniques for the introduction of organic functional groups.

APPLICATION OF MESOPOROUS CATALYTIC MATERIALS

Mesoporous materials are versatile supports that can host a variety of catalytically active functional groups. Depending on the functional group, a modified mesoporous material can then find diverse catalytic applications. Functionalized mesoporous silica catalysts have been reported in the literature for quite a number of different applications; however, we will focus on the reactions of oils and fats that are catalyzed with these materials. Ultimately, the utilization of these types of heterogeneous catalysts in such reactions could be highly advantageous for improving conversion efficiencies and economics.

Esterification reactions. Acid-catalyzed esterification reactions of FA and alcohols to produce FA esters have been known for many years, yet there is still an intensive search for newer catalysts with better performance than is possible with traditional catalysts (20). Homogeneous acidic catalysts have predominantly been used in catalyzing the esterification reaction, but the high costs associated with product purification as well as reactor vessel metallurgy have led to the desire to use heterogeneous acidic catalysts. Acidic resins such as Nafion and Amberlyst are used as solid acid catalysts for the esterification reaction of FA because of their strong acidic sites (21–23). The catalytic active sites on these resins are organosulfonic acid groups that are attached to the polymer backbone. Although these resins have good catalytic activity, they are highly susceptible to swelling in organic solvents and will be unstable at elevated reaction temperatures (>150°C), causing them to be unfavorable for many esterification reactions. Inorganic mesoporous materials are emerging as a promising alternative catalytic support, not only because they overcome the thermal stability issue associated with polymeric support, but also because they possess excellent tunable textural properties. Therefore, incorporation of organosulfonic acid groups onto the mesoporous silica

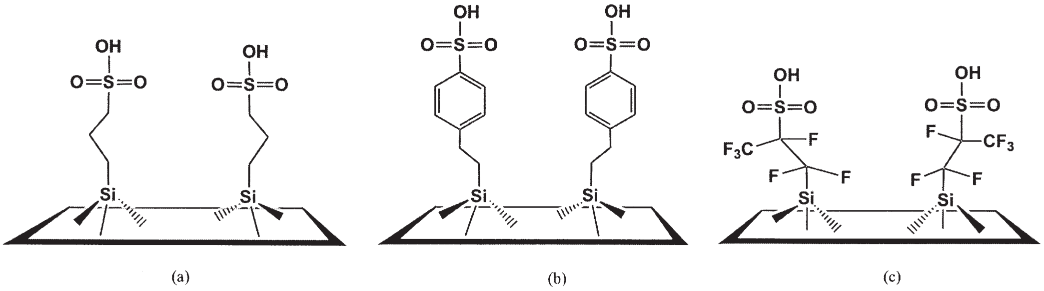

FIG. 3. Organosulfonic acid moieties functionalized on mesoporous silicas: (a) propylsulfonic groups, (b) arenesulfonic groups, (c) perfluoroalkylsulfonic groups.

material, as shown in Figure 3, could generate a more effective solid catalyst. The organosulfonic acid anchored on mesoporous silica acts as a simple Brønsted acid that readily donates the protons needed to catalyze the esterification reaction, thereby creating the possibility of replacing homogeneous catalysts (e.g., H_2SO_4) in such reactions.

The esterification of glycerol with FA to produce MG is an important reaction system because the FA monoesters of glycerol are surface-active agents that find wide applications in the food and pharmaceutical industries owing to their emulsifying capabilities and biocompatibility (24). Although the esterification reaction of glycerol with FA can lead to the formation of MG, DG, or even TG, as shown in Figure 4, only the chemical properties of MG are suitable as emulsifying agents, and so there is a need to minimize the formation of DG and TG. Mesoporous silica materials functionalized with propylsulfonic acid ($–SO_3H$) groups, as shown in Figure 3(a), have been reported to have good catalytic activity in acid-catalyzed reactions (18,25–27). Diaz *et al.* (28–32) have extensively studied the application of propylsulfonic acid-functionalized mesoporous silica catalysts in the esterification of FA, e.g., lauric and oleic acid, with glycerol to give MG. They investigated different mesoporous silica structures (e.g., MCM-41, SBA-2) in which all of the propylsulfonic acid-functionalized mesoporous silica catalysts had high surface areas (>500 m^2/g) and pore diameters in the range of 10–16 Å depending on the surfactant used in the synthesis procedure. For example, smaller-diameter mesopores

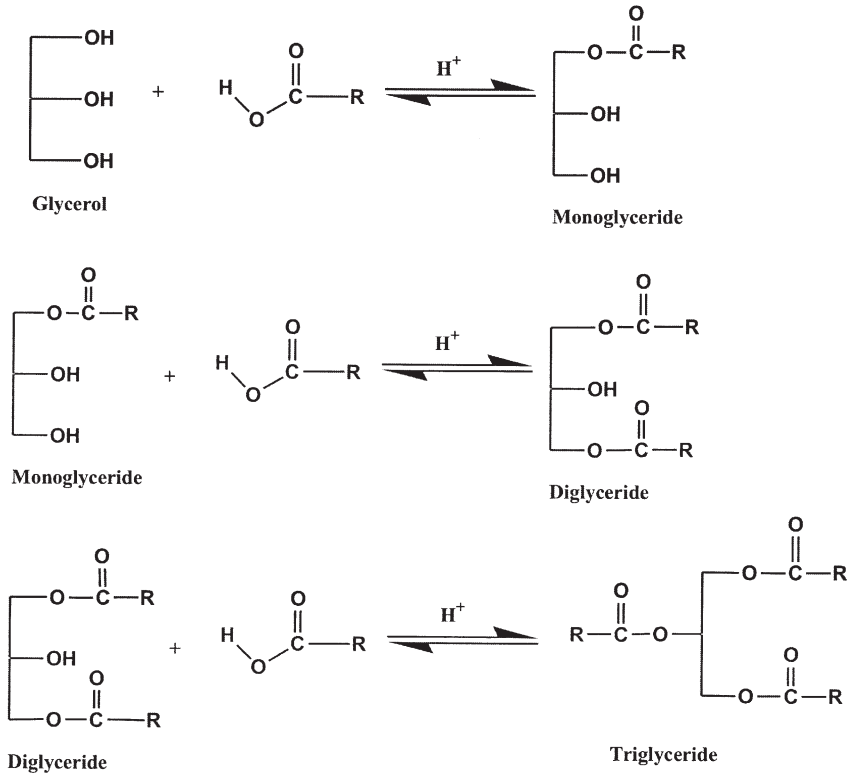

FIG. 4. Esterification reaction of glycerol and FA to form MG, which could lead to the formation of DG and TG as by-products.

were found for materials synthesized with dodecyltrimethylammonium bromide (C_{12}TAB) than for those tailored with hexadecyltrimethylammonium bromide (C_{16}TAB). All of the synthesized mesoporous materials showed a uniform and narrow pore size distribution, which was important for selectivity to the desired product. Thermal gravimetric analysis of the propylsulfonic acid-functionalized mesoporous silica suggested that the organic functional groups had high thermal stability (>400°C). The esterification reaction of FA with glycerol was performed at 120°C for 6 h, and the results showed high conversion of oleic acid as well as high selectivity to glycerol monoesters when using MCM-41-SO_3H catalysts. The good catalytic performance of the propylsulfonic acid-functionalized mesoporous silica catalyst was attributed to a combination of strong acidic sites located inside the mesopores as well as a narrow pore size distribution that curbed the formation of secondary bulky products (e.g., DG and TG). The catalytic activity of the propylsulfonic acid-functionalized mesoporous silica catalyst was compared with that of *p*-toluenesulfonic acid (pTSA), a highly acidic homogeneous catalyst, in the esterification reaction. The pTSA had a high catalytic activity, attaining 100% conversion in less than 6 h at 120°C, but it had poor selectivity for the FA monoesters. Despite the high catalytic activity of pTSA, the lack of specificity to the desired compound made it a poor catalyst for this esterification reaction.

Diaz *et al.* (32) also studied the performance of MCM-41 catalysts functionalized with both alkyl groups (methyl or propyl) and propylsulfonic acid groups on the esterification of FA with glycerol. They found that the methylated propylsulfonic acid-functionalized MCM-41 catalyst had a threefold increase in catalytic activity relative to the nonmethylated organosulfonic acid-functionalized mesoporous silica material, which suggested that water was excluded from the nano-environment within the pore. The methylated catalyst was also more selective to the monoester than was the propyl-functionalized material, even though the degree of hydrophobicity was reported to be similar.

Bossaert *et al*. (33) evaluated the catalytic activity of MCM-41-SO_3H with that of commercially available acidic solid catalysts in the esterification reaction of lauric acid with glycerol. They examined several incorporation techniques for the propylsulfonic acid group onto the mesoporous silica. They reported that the most active solid catalyst among the propylsulfonic acid-functionalized mesoporous materials was a coated silica gel-SO_3H. The HMS-SO_3H synthesized by the co-condensation method was the second most active, whereas the silylated MCM-41-SO_3H and coated MCM-41-SO_3H were the least active. They also observed that 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. The H-USY had both a higher surface area and a higher number of acidic sites than did the acid-functionalized mesoporous silica, which implied that the esterification reaction catalyzed by the zeolite catalyst was likely diffusion limited. The different catalytic performance of the propylsulfonic acid-functionalized mesoporous silica materials demonstrated that the technique used to incorporate the functional groups significantly affected the performance of the final solid catalyst.

The esterification of FA with polyhydroxyl compounds (e.g., glucose) has a number of possible applications, yet the multiple hydroxyl groups that can react on the carbohydrate molecule present an interesting regiospecificity challenge. Van Rhijin *et al.* (25) reported the esterification of lauric acid with D-sorbitol over MCM-41-SO_3H catalysts to produce monolaurylisosorbide, which is a detergent component. D-Sorbitol and lauric acid are immiscible, so the reaction mixture formed a three-phase system with the solid catalyst, which led to mass transfer limitations. The authors reported that when the esterification reaction was catalyzed with an acidic hydrophilic zeolite, there was no formation of products. However, when the same reaction was catalyzed with a slightly hydrophobic MCM-41-SO_3H catalyst, high selectivity of the desired product was achieved, although the yield was low because of the immiscibility of the reactants. These results demonstrated that the modification of the mesoporous silica material with organosulfonic acid altered the hydrophobicity as well as the chemical properties of the resulting solid such that it could catalyze the immiscible reaction mixture.

Alkyl esters such as those used in biodiesel are primarily produced from refined vegetable oils since feedstocks such as beef tallow and yellow grease, which are significantly cheaper, are not compatible with the homogeneous catalyst used in the transesterification reaction (34). These cheap feedstocks have high levels of FFA, which saponify the alkali catalyst used in the transesterification reaction, causing depletion of the catalyst through the formation of soap as well as subsequent difficulties in product separation. For these feedstocks to be processed in a standard transesterification reaction system, the FFA content should be reduced to no more than 0.5 wt% (35). One approach for reducing the FFA content in such feedstocks is to first esterify the FFA to alkyl esters in the presence of an acidic catalyst. Although this pretreatment step has been successfully demonstrated with sulfuric acid, the use of a homogeneous acidic catalyst adds neutralization as well as separation steps to the process (36). Therefore, it would be desirable to use heterogeneous acidic catalysts to esterify the FFA to simplify the pretreatment process.

We synthesized propylsulfonic acid-functionalized mesoporous silica catalysts and demonstrated that better catalytic performance can be achieved in the esterification reaction of FFA than with commercial acidic resins (37). By designing propylsulfonic acid-functionalized mesoporous silica catalysts with different pore sizes (22–35 Å), we were able to demonstrate that the rate of esterification of palmitic acid with methanol could be controlled by modifying the diffusional properties of the mesoporous catalyst. Besides controlling the pore sizes, we also showed that the type of organosulfonic acid group tethered on the mesoporous silica material could significantly affect the catalytic activity of the synthesized solid catalyst. Melero *et al.* (38) incorporated arenesulfonic acid groups onto SBA-15, as shown in Figure 3(b), to enhance the acid strength of the sulfonic acid group by increasing the electron affinity of the spacer. To demonstrate the effect of the phenyl-linked sulfonic acid, we evaluated the catalytic activity of SBA-15 functionalized with arenesulfonic acid (SBA-15-ph-SO_3H), propylsulfonic acid (SBA-15-SO_3H), and the homogeneous catalysts H_2SO_4 and pTSA in the esterification of palmitic acid with methanol in a soybean oil mixture (37). The results showed that SBA-15-ph-SO_3H had significantly higher catalytic activity than did SBA-15-SO_3H and even exhibited performance comparable to that of the homogeneous acidic catalysts.

In a similar attempt to enhance the acid strength of the organic acid groups tethered on the mesoporous silica, Alvaro *et al.* (39,40) functionalized MCM-41 with a highly electron-negative perfluoroalkylsulfonic acid groups, as shown in Figure 3(c). Perfluoroalkylsulfonic acid groups are also found in Nafion, which is a strong acidic catalyst, but the low surface area of the polymeric material severely limits the number of readily accessible acidic sites. It was anticipated that functionalizing the mesoporous silica material with the perfluoroalkylsulfonic acid groups would create an opportunity to disperse Nafion-type acidic sites on a large surface-area support, thereby improving the catalytic performance of the material. The catalytic activity of the mesoporous silica functionalized with perfluoroalkylsulfonic acid was investigated in the esterification of C_8 to C_{12} aliphatic acids with alcohols such as ethanol and dodecanol, and high conversions were obtained. The authors noted that the catalytic activity of the perfluorosulfonic acid-functionalized mesoporous silica was doubled whereas the turnover frequency increased by an order of magnitude when compared with that of a commercial Nafion-silica composite catalyst.

The esterification of FA with short-chain alcohols is a reversible reaction, with the formation of the alkyl ester favored in excess alcohol. However, the rate of the esterification reaction using a mesoporous catalyst is dictated by the local concentration of the chemical species within the pores of the catalyst and not the concentrations in the bulk. We found that the esterification reaction rate for palmitic acid when catalyzed with the arenesulfonic acid-functionalized mesoporous silica catalyst was decreased as higher conversions were obtained (37). The reaction rate decrease was attributed to the accumulation of water within the silica mesopores since the presence of silanol groups makes the pore hydrophilic. Therefore, a synthesis strategy that creates an environment in which water is excluded from the mesopores could enhance the catalytic conversion of the FA. The method used to accomplish this goal was to introduce hydrophobic groups into the mesopores of the organosulfonic acid-functionalized mesoporous silica catalyst, as shown by the schematic in Figure 5. The incorporation of hydrophobic organic groups (e.g., allyl and phenyl) into mesoporous silica materials has been shown to decrease the amount of water adsorbed (41,42). We evaluated two methods of integrating hydrophobic (methyl, ethyl, and phenyl) groups into propylsulfonic acid-functionalized mesoporous silica either through grafting on the preformed surface of the propylsulfonic acid-functionalized hybrid material or by co-condensation of the propylsulfonic acid and silica precursors in a “one-pot” synthesis. The multifunctionalized materials were subsequently evaluated for their catalytic performance in the esterification of palmitic acid with methanol (17). After extraction of the surfactant, the resulting materials had large surface areas (>600 m^2/g) and pore sizes (>45 Å), implying that the incorporation of the organic groups on the mesoporous silica material had an insignificant effect on the textural properties. All the mesoporous silica catalysts that were synthesized by the co-condensation technique showed significantly higher catalytic performance than did grafted catalysts, which demonstrated that the method of incorporating the hydrophobic groups affected the catalytic properties of the synthesized catalysts. The low catalytic activity for propylsulfonic acid-functionalized catalysts with grafted hydrophobic groups suggested that the esterification reaction was mass transfer limited, with a high percentage of the alkyl groups located on the external surface and around the pore mouth of the mesopores. In contrast, hybrid mesoporous silica catalysts synthesized by the co-condensation technique incorporated both the propylsulfonic acid and alkyl groups into the mesopores, resulting in an effective system for esterifying the FA as well as for eliminating water from the nano-reactor. It was noted that incorporation of large hydrophobic molecules (e.g., phenyl group) into the mesoporous silica by the co-condensation technique produced a more poorly defined mesostructure in the materials.

Besides incorporating hydrophobic groups onto the mesoporous silica scaffold by either the co-condensation or grafting technique, the hydrophobicity of the silica scaffold can also be adjusted by synthesizing hybrid mesoporous organosilicas having bridging organic groups (e.g., ethane, benzene) as an integral component of the silicon oxide framework (43,44). Organic acid groups could then be integrated onto the organosilica mesostructure by either the grafting method or the co-condensation technique to generate a solid acid catalyst. This approach creates a unique surface structure with an alternating arrangement of hydrophobic groups and acidic sites, which could enhance the catalytic performance of the organic acid-functionalized mesoporous silica catalysts in the esterification reaction.

In addition to supporting organic acids, mesoporous silica ma-

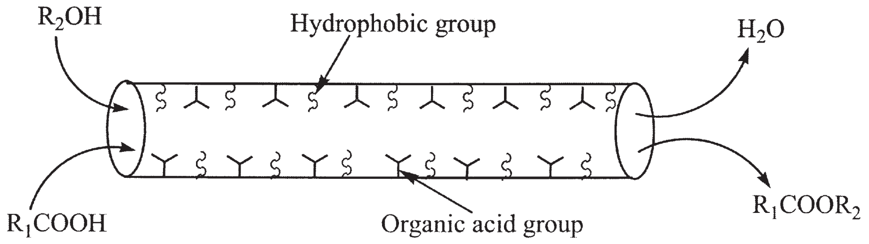

FIG. 5. Schematic of mesoporous silica functionalized with organosulfonic acid and hydrophobic groups for FA esterification with alcohol.

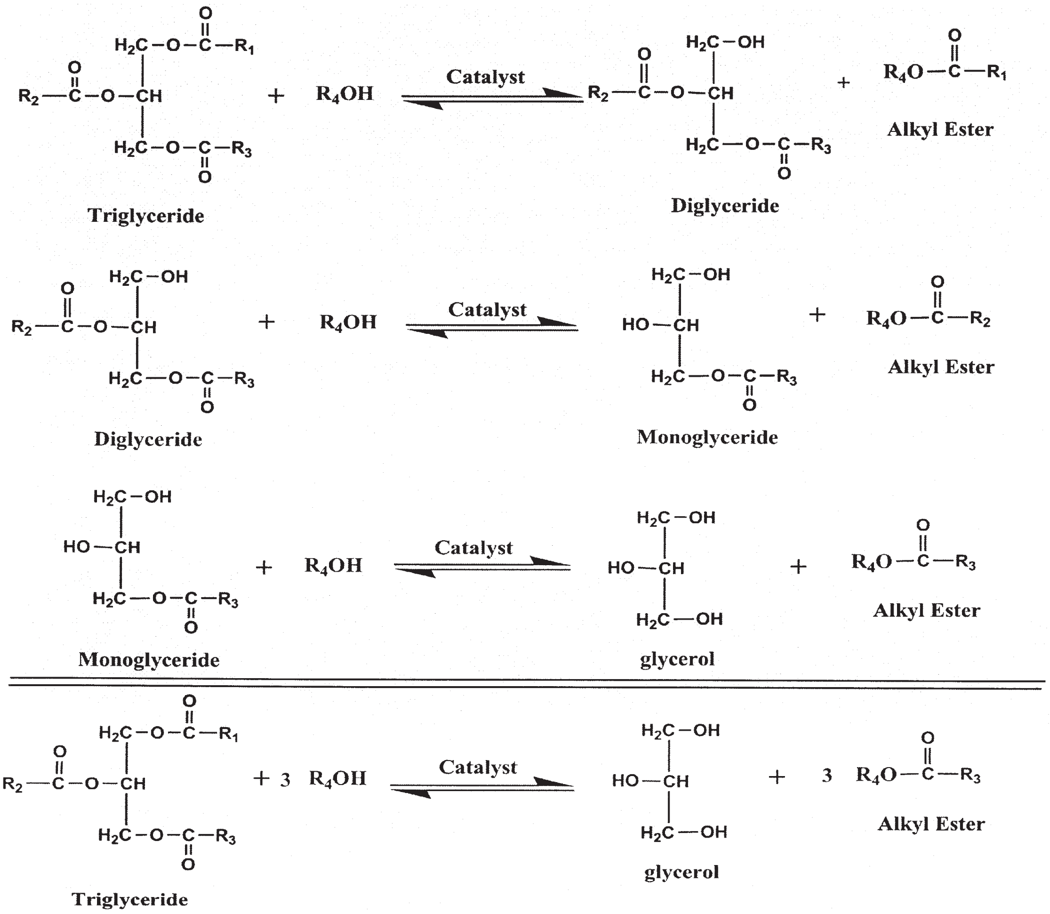

FIG. 6. Stepwise reaction mechanism for TG transesterification with alcohol, producing alkyl esters and glycerol.

terials can also be used to support inorganic acids that can catalyze esterification reactions. Verhoef *et al.* (45) impregnated MCM-41 with heteropoly acid (HPA), having a molecular structure of $H_3PW_{12}O_{40}$, and tested its catalytic activity in the liquid-phase esterification of 1-propanol with hexanoic acid at reflux temperature. The authors reported that the catalytic activity of HPA impregnated on MCM-41 material was higher than for pure HPA. The enhancement in catalytic performance of the catalyst was attributed to the high dispersion of HPA on the large surface area of the mesoporous material, which led to increased contact time between the reactants and active sites since pure HPA is only slightly soluble in the reaction mixture. Other elements such as tin, titanium, and aluminum have also been impregnated into the mesostructure of mesoporous silica materials to generate both Brønsted and Lewis acid sites, which has the potential of catalyzing esterification reactions (46–48).

Transesterification reactions. The transesterification of natural oils and fats with short-chain alcohols (e.g., methanol and ethanol) to produce FA alkyl esters has been shown to lower the viscosity of the starting oil and to decrease carbon deposition in the engine as well as to reduce air pollution while maintaining the desirable energy content, flash point, and biodegradability properties (49–55). To this end, the objective of transesterifying natural oils and fats with short-chain alcohols is to produce alkyl esters that will readily meet the requirements of traditional diesel but with more benefit to the environment and the rural economy (34).

The transesterification of TG with alcohol is a stepwise reversible acid- or base-catalyzed reaction that sequentially converts TG to DG and then to MG and finally to glycerol with the liberation of three moles of alkyl esters (Fig. 6) (56–58). Basic catalysts are the catalysts of choice in the transesterification reaction of TG with alcohol because they exhibit significantly higher catalytic activity than do acidic catalysts (51,59). The first step in the alkali-catalyzed transesterification reactions is the formation of an alkoxide nucleophile, which then attacks the carbonyl carbon of the FA. This species then rearranges to release the methyl ester from the glycerol backbone, as illustrated in Figure 7(a). The alkoxide ion formed on the glycerol backbone is immediately protonated to form a hydroxyl, thereby regenerating the catalyst. In contrast, the first step in the acid-catalyzed transesterification reaction is the protonation of oxygen on the carbonyl carbon of the FA, as depicted in Figure 7(b). The protonation of the oxygen increases the positive charge on the carbonyl carbon, making it susceptible to nucleophilic attack from an alcohol. The key difference between the two reaction mechanisms is the strength of the nucleophilic attack on the carbonyl carbon of the FA. The nucleophile generated in the basic-catalyzed reaction (alkoxide ion) is significantly stronger than the alcohol nucleophile such that the formation of the FAME is significantly faster.

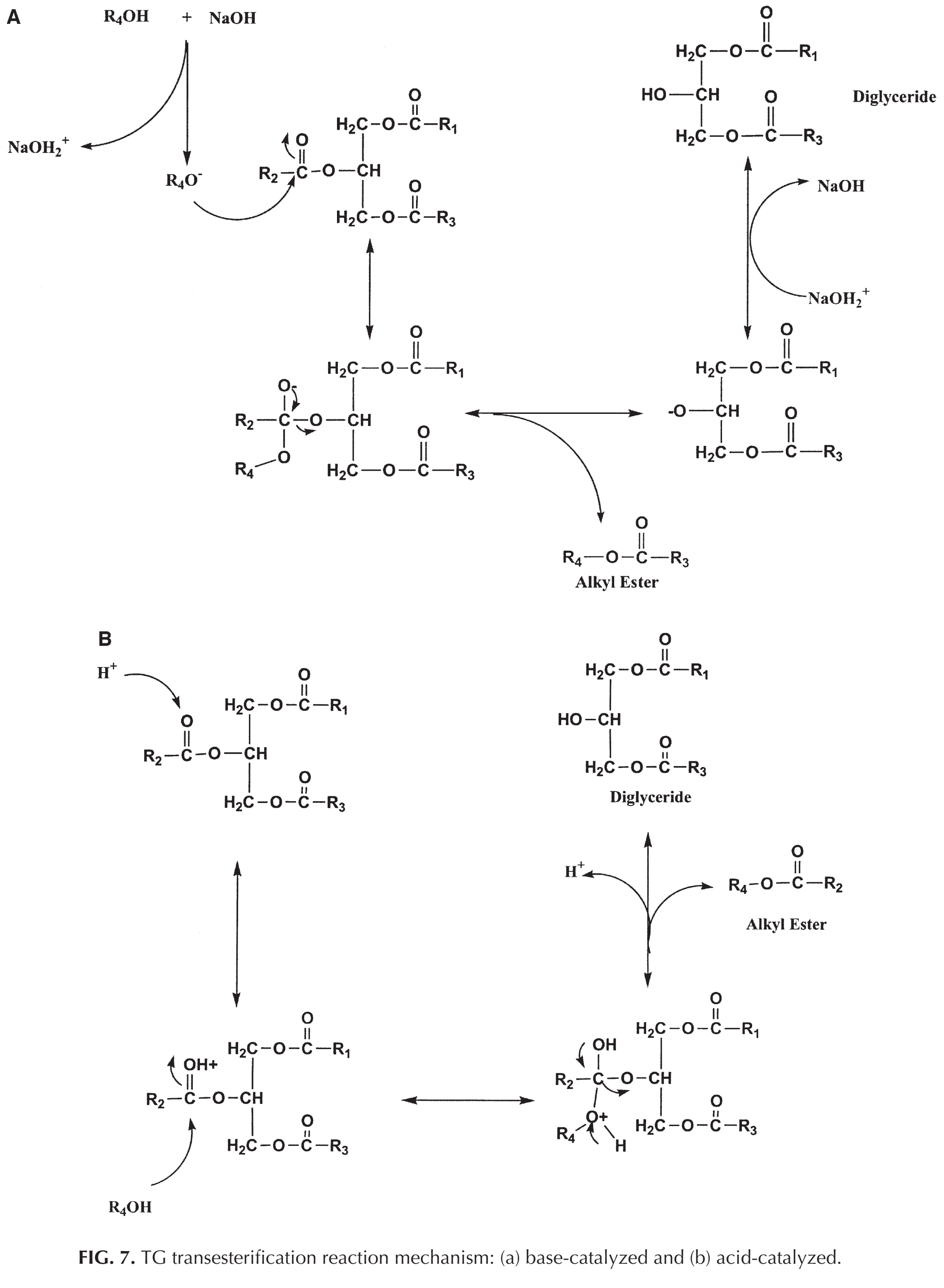

FIG. 7. TG transesterification reaction mechanism: (a) base-catalyzed and (b) acid-catalyzed.

Homogeneous alkali catalysts (e.g., NaOH, KOH) have primarily been used for the transesterification of TG (59–62). However, as the demand for alkyl esters (e.g., biodiesel) increases, there is interest in improving the production process. Utilization of a heterogeneous catalyst in the transesterification reaction could lead to improved reactor designs as well as streamlined separation following the reactor. A strategy for developing such a solid TG transesterification catalyst is to incorporate known basic moieties onto a support that has a large surface area to ensure high dispersion of the catalytic active sites. Mesoporous silicas are ideal candidates for such immobilization because of their large surface area and tunable pore sizing. In addition, these mesoporous materials can be functionalized with the basic moieties through different methods.

Common organic bases are bicylic amidines and bicylic guanidines, which are effective homogeneous basic catalysts (63). Incorporation of these organic bases onto a stable structure with a high surface area can produce a heterogeneous basic catalyst that could catalyze the transesterification reactions (64). Gelbard and Vielfaure-Joly (65) investigated the catalytic activity of alkyl-

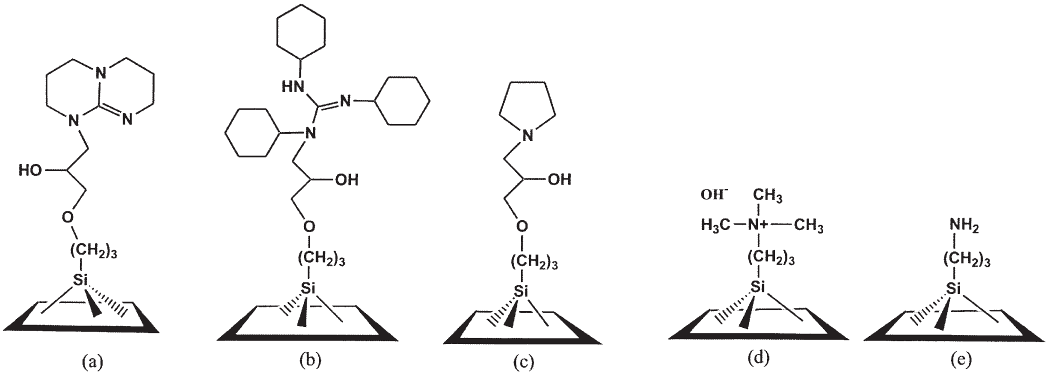

FIG. 8. Structures of organic bases functionalized on mesoporous silicas: (a) 1,5,7-triazabicyclodec-5-ene (TBD), (b) 1,2,3-tricyclohexylguanidine (TCG), (c) pyrrolidine, (d) propyl-*N,N,N*-trimethylammonium hydroxide, (e) propylamine.

guanidines supported on polystyrene and their homogeneous analogs in the transesterification reaction of vegetable oils with methanol. They reported more than 90% yield of methyl esters within 15 min when the reaction was catalyzed by either free or immobilized guanidines. These results indicated that the guanidines preserved their catalytic activity even when immobilized. Owing to the low surface area, poor thermal stability, and limited swelling in organic solvents, the application of immobilized guanidines on a polystyrene support has limitations. Mesoporous silica could be a substitute for the polystyrene support because of its high surface area and hydrothermal stability. The alkyl spacer used in tethering the guanidines on the polymeric support was altered such that it covalently bonded with silanols on the silica surface (66). Shown schematically in Figure 8 are examples of some organic basic moieties that have been incorporated onto mesoporous silica supports through bonding to surface silanols by either a 3-glycidyloxy propyl or propyl spacer to generate a solid base catalyst (65–69).

Sercheli *et al.* (70) successfully immobilized alkylguanidines (1,5,7-triazabicyclodec-5-ene and 1,2,3-tricyclohexylguanidine) onto polystyrene, MCM-41, and zeolite Y. They tested the catalytic performance of the immobilized alkylguanidines in the transesterification of soybean oil with methanol and compared the results to that of homogeneous alkylguanidines. The alkylguanidines supported on the polystyrene gave the best catalytic results among the heterogeneous catalysts, although they were slightly lower in activity than the homogeneous catalysts. The difference in catalytic activities for alkylguanidines supported on polystyrene and those unsupported was attributed to the hydrophobicity of the polymer backbone and reduction of symmetry of the alkylguanidine cations. Alkylguanidines supported on MCM-41 showed low initial catalytic conversion of TG but were significantly improved when the reaction time was extended. The authors suggested that the low initial catalytic activity of alkylguanidines supported on MCM-41 was due to pore diffusion, given that TG are relative large molecules and could not access the internal surface area easily. It is worth noting that with the present knowledge of engineering the textural properties of mesoporous silica materials, the low catalytic performance attributed to mass transfer limitations could be significantly reduced by synthesizing supports with larger pore diameters. Alkylguanidines encapsulated into zeolite Y cages were the least active among the heterogeneous catalysts, which implies that the encapsulated active sites were inaccessible to the reactant.

Although basic organic groups are strong base catalysts that can maintain their catalytic activity upon being immobilized onto mesoporous silica supports, inorganic basic compounds such as alkaline earth oxides and alkali metal oxides are also potentially suitable for the transesterification reaction. Their incorporation into mesoporous silica material would generate solid base catalysts (71). However, immobilization of alkaline metals (e.g., sodium and potassium) on large surface area supports has been difficult because of their high reactivity and solubility in the reaction medium. Cesium, a less reactive element in the alkaline group, has been of particular interest as a base catalyst when incorporated onto mesoporous silica because of its hydrothermal stability and decreased solubility characteristics. Corma *et al.* (72) successfully incorporated cesium into mesoporous silica by fully exchanging the MCM-41 with a cesium chloride solution. They conducted an investigation on the catalytic activity of MCM-41-Cs in the transesterification of TG with glycerol to produce MG and compared the results to hydrotalcites, magnesium oxide, and sepiolite impregnated with cesium. MCM-41-Cs had the lowest catalytic activity among the basic solid catalysts, with a total conversion of TG and selectivity of MG of less than 50%. The poor performance was attributed to the low capability of MCM-41-Cs to extract a proton from glycerol. Despite the poor catalytic activity of MCM-41-Cs, the study demonstrated that alkaline elements could also be supported on mesoporous silica and had the potential for catalyzing the transesterification reaction. In a similar attempt, Jaenicke *et al.* (67) incorporated potassium oxide, barium oxide, and a mixture of potassium oxide and lanthanum oxide on an MCM-41 mesoporous material. Although these metal oxides are somewhat weak bases, they can tolerate high reaction temperatures, in contrast to organic basic catalysts, and as a result achieve high conversions in a shorter reaction time. Furthermore, these catalysts are easily regenerated by calcination at high temperatures.

Other applications of nanostructured mesoporous silica for conversion of oils and fats. Apart from the esterification and transesterification of natural oils and fats with alcohols or polyols, oils and fats are feedstocks that could also be modified through other reaction mechanisms to produce a variety of products. For instance, the nucleophilic addition of FA to glycidol to produce MG, as shown in Figure 9, is an interesting reaction system because epoxides are very reactive and stereospecific, which will enhance the selectivity and yield of α-MG when the reaction is carried out at mild reaction conditions (73). The nucleophilic addition of FA to glycidol can be catalyzed by organic base catalysts such as amines or ammonium salts. Owing to difficulties associated with product purification, the use of homogeneous catalysts will further increase complications to the production process.

The immobilization of the amine groups on mesoporous silica, as shown in Figure 8, has been reported to yield an active basic catalyst that catalyzes the nucleophilic addition of FA to glycidol (68,74). Such immobilization of alkyl amino groups on the mesoporous silica could be performed either by grafting on the preformed surface or by the one-pot synthesis technique. Lin *et al.* (75) immobilized different organic basic moieties on mesoporous silica; they reported that the catalysts showed good activity in the nucleophilic addition reaction of glycidol to lauric acid, although more glycidol was consumed when fresh catalyst was used owing to polymerization of the epoxide ring with residual silanol groups on the mesoporous silica surface. The glycidation reaction in the presence of surface silanols led to a low yield of monolaurin in the first run, although the yield increased significantly in subsequent runs. In principal, the glycidation reaction on the mesoporous silica surface can be minimized by converting the silanol groups into inert moieties (e.g., grafting alkyl groups) to inhibit the acid-catalyzed electrophilic attack on the epoxide ring. For example, Brunel's group (68,73) blocked the silanol groups by grafting hexamethyldisilazane on an amino-functionalized mesoporous silica, after which glycidol was reacted with lauric acid. The authors reported that the conversion of glycidol to monolaurin increased appreciably in the first run, in contrast to when the reaction was catalyzed with unmodified amino-functionalized mesoporous silica. The results demonstrated that the acidic silanol groups on mesoporous silica could be made passive so as to the inhibit the polymerization reaction.

As the demand for and production of biodiesel increases, the value for the by-product glycerol will fall dramatically unless new glycerol utilization approaches are developed. The polymerization of glycerol to produce di- and triglycerol has potential as an ingredient for new cosmetics, surfactants, lubricants, and solvents (76). Clacens *et al.* (77) studied the catalytic activity of silica or aluminosilica mesoporous materials impregnated with different elements, e.g., lithium, cesium, lanthanum, sodium, and magnesium, on the polymerization of glycerol. They reported that the choice of element incorporated into the framework of the mesoporous materials modified the resulting performance of the catalyst. The polymerization of glycerol using a lanthanum-impregnated mesoporous silica was the most active but the least selective solid catalyst, whereas the material impregnated with magnesium was less active but more selective. However, both the lanthanum- and magnesium-impregnated catalysts favored the dehydration of glycerol, forming acrolein. Cesium impregnated onto mesoporous silica gave the best catalytic activity as well as significant selectivity toward di- and triglycerols.

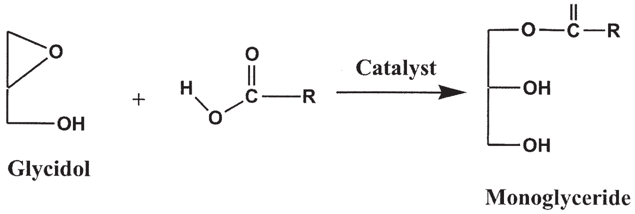

FIG. 9. Addition of a FA to glycidol to produce α-MG.

Epoxidation of unsaturated FA has been of interest since epoxidized FA and their derivatives have many possible industrial applications, including as lubricant additives and plasticizer components that have the potential to replace the hazardous reagents that are currently used. The epoxidation of unsaturated alcohols with an oxidant over a titanium-based mesoporous silica catalyst has been demonstrated successfully (78). Guidotti *et al.* (79) expanded the investigation of unsaturated alcohol epoxidation to unsaturated FAME using titanium impregnated on mesoporous silica (MCM-41-Ti) as the catalyst and *tert*-butylhydroperoxide as the oxidant. They reported high selectivity (>95%) and conversion in less than 24 h when the reaction was performed at 90°C. Moreover, the investigators did not observe the formation of the organic acidic compounds that are usually formed when the traditional peracid epoxidation method is used. They observed that the reaction rate of methyl elaidate epoxidation was twice that of methyl oleate, which was attributed to the configuration of the unsaturated FA, since the double bonds of oleic acid and elaidic acid that are positioned between C_9 and C_{10} have *cis* and *trans* configurations, respectively. As a result, methyl oleate is kinked at the C_9–C_{10} position, which leads to a pore diffusion limitation, whereas methyl elaidate is a straight chain, which could readily access the active sites inside the mesopores. Interestingly, the epoxidation reaction was stereospecific given that *cis*-epoxy-stearate and *trans*-epoxy-stearate were the only products observed when methyl oleate and methyl elaidate, respectively, were used as feedstocks.

Raney nickel catalysts are commonly used commercially for the hydrogenation of unsaturated vegetable oils. The hydrogenation of vegetable oils is usually done to convert PUFA such as linoleic (C18:2) and linolenic (C18:3) acids to monounsaturated oleic acid (C18:1) with the purpose of slightly hardening the oil as well as stabilizing the oil from oxidation reactions. However, the hydrogenation process produces a mixture of *cis* (desired) and *trans* (undesired) monounsaturated TG, given that nickel is not a stereospecific catalyst. One possible approach for introducing stereospecificity to the hydrogenation catalyst is to use a solid support with a uniform pore size distribution such as mesoporous silica. In such an attempt to demonstrate the stereospecificity of the mesoporous silica support, Plourde *et al.* (80) reported the hydrogenation of sunflower oil over palladium impregnated onto SBA-15 and MCM-41. They investigated the effect of pore size on the catalytic performance of the supported palladium mesoporous materials in the hydrogenation reaction. They found that palladium supported on SBA-15, the material with the largest pore size, had the highest catalytic activity compared with either palladium supported on MCM-41 or a nickel-based catalyst. In addition, the palladium-impregnated SBA-15 exhibited higher selectivity toward the desired oleic acid than did either palladium impregnated on MCM-41 or the nickel-based catalyst.

Bhatia's group (81–84) has reported the catalytic cracking of vegetable oil over mesoporous materials to produce sulfur-free hydrocarbon fuel. They showed that MCM-41-type catalysts gave better conversion and selectivity toward C^{5+} olefins than did traditional zeolite-type catalysts, which was attributed to their larger pore size. These olefin products could then be processed by either alkylation or etherification to produce high-octane gasoline. By applying different synthesis techniques and changing the Si/Al ratio, the authors concluded that the catalytic cracking of palm oil depends strongly on the catalyst's acidity and structure. The product stream had a mixture of gasoline, kerosene, and diesel fractions with a composition of approximately 25, 10, and 25 wt%, respectively (83). The formation of coke and water was less than 10 wt% of the product stream for the mesoporous catalysts. By using a microporous/mesoporous composite catalyst, the authors reported that the pyrrolysis of the FA and selectivity to the gasoline fraction was significantly enhanced while the formation of coke was minimized to less than 3 wt% (84).

CONCLUSION AND FUTURE OPPORTUNITIES

The discovery of surfactant-templated mesoporous materials more than a decade ago and their continued development have created a class of materials with unparalleled potential for tailoring textural properties at the mesoscale. Numerous studies have shown that these mesoporous materials have good catalytic properties as well as the capability of supporting highly dispersed organic and inorganic active catalytic moieties. However, until recently few researchers have studied the potential of these materials in converting natural oils and fats into biobased chemicals. These more recent studies have shown that surfactant-templated mesostructured materials offer many advantages over traditional solid catalysts in the conversion of lipid feedstocks because of their combination of high surface areas, flexible large pore sizes, and high thermal stability as well as their potential for controlling the catalytic domains at the molecular scale. The application of functionalized mesoporous catalysts has the possibility of simplifying reaction systems, reducing production costs, and eliminating environmental hazards posed by wastes generated in homogeneous catalyzed reactions. 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. As synthesis techniques and the characterization of functionalized mesoporous catalyst mature, one would expect more catalytic applications of these nanostructured materials in the conversion of biorenewable feedstocks, especially oils and fats, into biobased chemicals.

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