Design of catalytic domains within organosulfonic acid-functionalized mesoporous silica

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ABSTRACT

Organic-inorganic hybrid mesoporous silicas were synthesized via nonionic supramolecular assembly using the co-condensation synthesis technique with the intention of understanding the catalytic domain as well as developing strategies to control the catalytic functionalities at the molecular level. Esterification of free fatty acids in natural oils and fats was used to probe the catalytic activity of the synthesized acid-modified mesoporous catalysts. Application of solid acid catalysts in such reaction systems can possibly simplify the manufacturing process, reducing production costs, as well as eliminate environmental hazards posed by toxic wastes generated in homogeneous catalyzed reactions.

The catalytic performance of the functionalized mesoporous silicas was significantly influenced by the median pore diameter of the catalyst, which was tuned using different surfactants. Incorporation of hydrophobic groups into the organic-inorganic acid catalyst enhanced the catalytic conversion of the fatty acids, although the catalytic performance of the resulting catalyst strongly depended on the incorporation technique as well as the size of the hydrophobic organic groups. Decreasing the spatial positioning of the sulfonic acid groups on the pore surface of mesostructured material increased the acid strength of the resulting acid catalyst. This study demonstrated that the catalytic properties of the functionalized mesoporous catalyst were complex and reaction kinetics studies alone could overlook other important factors, such as solution effects, site collaboration, and hydrophobicity of the catalytic domain, that could affect the ultimate performance of the acid solid catalyst. The work demonstrates the potential of intentionally designing the catalytic environment of the organic-inorganic hybrid mesoporous materials at the molecular level.

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CHAPTER 1

General Introduction and Literature Review

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1.1. Introduction

Catalysts have been used for many years to increase reaction rates as well as selectivity of desired products, especially in the petrochemical industries. However, biological feedstocks, which can be processed into a variety of biobased products owing to the presence of multiple reactive groups, present a difficult challenge for these conventional catalysts. For instance, biocatalysts are exceptionally selective catalysts that can interact with specific biological molecules to transform them into desired products with little byproduct formation. Unfortunately, biocatalysts typically impart high production costs due to low reaction rates, short cell life spans, inhibitor intolerance, difficulties in product separation, and expensive sterile equipment requirements. These attributes adversely affect 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 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 substitution of homogeneous catalysts with solid catalysts in many reactions used for large-scale chemical production. While heterogeneous catalysts have many positive features, the application of solid catalysts in liquid-phase reactions involving biological-based molecules has been limited due to poor reactant/catalyst contacting, caused by either pore diffusion limitation or low active site availability for catalytic reaction. For example, the application of zeolite-type catalysts (pores <15 Å) to liquid-phase reactions of biological feedstocks has been of little success because such reactions are generally pore diffusion controlled. In addition, biological feedstocks, which have multiple reactive functional groups, require molecularly well-defined reaction domains to minimize the formation of byproducts.

Inadequate performance of solid catalysts in liquid-phase reactions has led to extensive research to increase the average pore size of catalytic materials while maintaining high surface area. The discovery of mesoporous materials by Mobil Research and Development Corporation in 1992 has sparked interest among researchers due to the potential application of these materials as solid catalyst supports, particularly for liquid-phase reaction systems [1-3]. New 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 section 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. Then the application of these functionalized mesoporous silica materials to the catalytic conversion of natural oils and fats in various esterification reaction systems is given.

1.2.   Advanced Nanostructured 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 employed where 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 an opportunity to construct a structure of desired dimensions and functionality. This synthesis approach overcomes a key drawback in synthetic zeolite-type catalysts whose pore sizes are constrained to the microporous range, which limits its 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 increase in pore size. These physical properties are highly advantageous for solid catalysts because it allows the reactants to access the large

internal surfaces where 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, which have been reviewed [8-11]. The sophisticated framework of the mesostructure materials originate from cooperative assembly of an inorganic precursor with an organic structure-directing template, as illustrated systematically in Figure 1-1. The organic templates, which are typically surfactants, comprise both a hydrophilic domain and a distinct hydrophobic domain. The surfactant molecules form ordered complex structures in aqueous solution, as shown in Figure 1-1(a), by either (i) self-assembly or (ii) cooperative-assembly coordinated in some manner by interacting with the inorganic precursor. The fundamental characteristic of surfactants to form micelles in solutions makes them excellent templates. The introduction of supramolecular assemblies (micellar aggregates) as templating agents paved the way for the synthesis of mesoporous metal oxide materials that differ significantly from the single molecular species employed in the synthesis of zeolite-type catalysts. The addition of the inorganic precursor into 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 that gives rise to a supramolecular structure, as shown in Figure 1-1(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 a mesoporous materials that have worm-like 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 by calcining at high temperatures. Due to the nature of the templates used, the as-synthesized mesoporous materials have narrow pore size distributions as well as long channels, as shown in Figure 1-1(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. There are several examples of mesoporous materials with different pore sizes reported in the literature, owing to the precise tuning of the pores by selecting the appropriate surfactants with desired carbon chain length [1,12-14]. This synthesis strategy can be 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 having the aforementioned textural properties makes the material an excellent catalyst support. 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 1-2. Several methods of incorporating organic functional groups onto the mesoporous silica surface 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 applied for incorporating organotrialkoxysilanes into the mesoporous silica are grafting and direct co-condensation. The grafting technique is a post-synthesis modification performed on a preformed mesoporous material by reacting organic groups with the surface hydroxyl (silanols) groups, usually after removal of surfactant [11]. High concentrations of silanol groups are found on the external and internal surface area of 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. Organotrialkoxysilanes are highly susceptible to hydrolysis, so mesoporous materials are normally evacuated at high temperature to eliminate moisture prior to silylation. Such a pretreatment will decrease the number of surface silanols, leading to an anhydrous silica with isolated free ($\equiv$Si-OH) and geminal ($=$Si-(OH)$_2$) silanols. This creates a silica surface that is not readily functionalized [11]. To improve the surface silylation, it is necessary to selectivity hydrate the mesoporous silica material with only sufficient moisture to form a monolayer of silanols on the surface [16]. Organotrialkoxysilane could then be coated on the monolayer to attain an even distribution of the functional groups. However, this method is not widely practiced since the presence of any excess moisture leads to uncontrolled polymerization of organotrialkoxysilanes, causing pore blockage. Mesoporous materials functionalized via post-synthesis grafting typically have higher concentrations of the grafted functional group on the external surface area due to the high reactivity of the organotrialkoxysilanes [17,18]. This nonuniform distribution of functional groups is not optimal and can result in reduced catalytic activity and selectivity to the desired products due

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 direct co-condensation method require fewer synthesis steps, 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 post-synthesis techniques have better control of textural properties than materials synthesized by direct co-condensation procedure since the incorporation of the organic group during synthesis can influence the resulting structure. Whichever method is employed to incorporate the organic functional groups, the modification of the mesoporous silica at the nano-scale 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.

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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 catalytic active compound is mixed with the mesoporous powder material to form a slurry, which is then calcined to generate the active metal compound. 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 to introduce organic functional groups.

1.3. Application of Nanostructured Materials in Esterification Reactions

Mesoporous materials are versatile supports that could 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, this review will focus on esterification reactions of oils and fats that are catalyzed with these materials. Ultimately, the use of these types of heterogeneous catalysts in such reactions could be highly advantageous for improving conversion efficiencies and economics.

The conversion of vegetable oils and animal fats into specialty and commodity products holds promise as a means for replacing some crude oil-based products. Natural oils

have a number of attractive features over conventional crude oil, as they are renewable, biodegradable, and nontoxic. However, the conversion of natural oils into non-edible products has been limited due to their inability to compete effectively with mature petrochemicals as result of high raw material and production costs. To improve the economic aspect of these processes, the selection of raw materials, 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 appropriate reaction conditions and catalysts are used.

Acid-catalyzed esterification reactions of fatty acids and alcohols to produce fatty acid 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 of fatty acids due to 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 because not only are they more thermostable, but they also possess excellent tunable textural properties. Therefore, incorporation of organosulfonic

acid groups onto the mesoporous silica material, as shown in Figure 1-3, could generate a more effective solid catalyst. Functionalization of mesoporous silica materials with propylsulfonic acid ($-SO_3H$) groups, as shown in Figure 1-3(a), yields good catalytic activity in acid-catalyzed reactions [18,24-26]. The organosulfonic acid anchored on mesoporous silica acts as a simple Brønsted acid that can readily donate the protons needed to catalyze esterification reaction, thereby creating the possibility of replacing homogeneous catalysts (e.g. H_2SO_4) in such reactions.

Esterification of glycerol with fatty acids to produce monoglycerides is an important reaction system because the fatty acid monoesters of glycerol are surface-active agents that find wide applications in the food and pharmaceutical industries owing to their emulsifying capabilities and biocompatibility [27]. Although the esterification of glycerol with fatty acid can lead to formation of mono-, di- or even triglycerides, as shown in Figure 1-4, only the chemical properties of monoglycerides are suitable as emulsifying agents, and so there is a need to minimize the formation of di- and triglycerides. Sulfonic acid-functionalized mesoporous silica esterifies fatty acid with glycerol to produce monoglycerides at selectivities higher than is seen with homogeneous acids [28]. Diaz *et al.* [29-32] have studied extensively the application of propylsulfonic acid-functionalized mesoporous silica catalysts in the esterification of fatty acids, e.g., lauric and oleic acids, with glycerol to give monoglycerides. They investigated different mesoporous silica structures (e.g. MCM-41, SBA-2) in which all of the propylsulfonic acid-functionalized mesoporous silica catalysts have 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 were found for materials synthesized with dodecyltrimethylammonium bromide ($C_{12}TAB$)

than those tailored with hexadecyltrimethylammonium bromide (C_{16}TAB). All of the synthesized mesoporous materials had uniform and narrow pore size distributions, which was important for selectivity of the desired product. Thermo gravimetric analysis (TGA) of the propylsulfonic acid-functionalized mesoporous silica suggested that the organic functional groups had high thermal stability (>400 °C). The esterification of fatty acids with glycerol was performed at 120 °C for 6 h, yielding 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 propylsulfonic acid-functionalized mesoporous silica catalyst was attributed to a combination of strong acidic sites located insides the mesopores as well as to the narrow pore size distributions that curbed the formation of secondary bulky products (e.g. di- and triglycerides). The catalytic activity of the propylsulfonic acid-functionalized mesoporous silica catalyst was compared to 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 fatty acid monoesters. Despite the high catalytic activity for pTSA, the lack of specificity to the desired compound made it a poor catalyst for this esterification reaction.

Diaz et al. [28] also studied the performance of MCM-41 catalysts functionalized with both alkyl groups (methyl or propyl) and propylsulfonic acid groups on the esterification of fatty acid with glycerol. They found that the esterification reaction rate was improved with an increase in alkyl group loading, which suggested that water had been excluded from the nano-environment within the pore as shown in Figure 1-5. The methylated propylsulfonic acid-functionalized MCM-41 catalyst had a three-fold increase in catalytic activity relative to the non-methylated organosulfonic acid-functionalized

mesoporous silica material. The methylated catalyst was also more selective to the monoester than propyl-functionalized material even though the degree of hydrophobicity was similar.

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 [33,34]. 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.

Bossaert and co-workers [35] evaluated the catalytic activity of MCM-41-SO$_3$H with that of commercially available acidic solid catalysts in the esterification of lauric acid with glycerol. They examined several techniques to incorporate the propylsulfonic acid group onto mesoporous silica. They reported that the most active solid catalyst among the propylsulfonic acid-functionalized mesoporous materials was a coated silica gel-SO$_3$H. HMS-SO$_3$H synthesized by the co-condensation method was the second most active, while silylated MCM-41-SO$_3$H and coated MCM-41-SO$_3$H 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. H-USY had both higher surface area and more acidic sites than acid-functionalized mesoporous silica, which implied that esterification catalyzed by zeolite

catalyst was likely diffusion-limited. The different catalytic performance of propylsulfonic acid-functionalized mesoporous silica materials demonstrated that the technique employed to incorporate the functional groups significantly affects the performance of the final solid catalyst.

Esterification of fatty acids 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.* [24] reported the esterification of lauric acid with D-sorbitol over MCM-41-SO$_3$H catalysts to produce monolaurylisosorbide, which is a detergent component. D-sorbitol and lauric acid are immiscible, so the reaction mixture forms a three-phase system with the solid catalyst, which leads to mass transfer limitation. 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$_3$H catalyst, high selectivity of the desired product was achieved although the yield was low due to 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.

Melero *et al.* [36] incorporated arenesulfonic acid groups onto SBA-15, as shown in Figure 1-3(b), to enhance the acid strength of the sulfonic acid group. The phenyl-linked spacer, which has higher electron affinity than the propyl-linked spacer, stabilizes the sulfonate anion formed after removal of the proton readily by distributing the charge to the aromatic ring, thus increasing its acid strength. To demonstrate the effect of the phenyl-

linked sulfonic acid, they evaluated the catalytic activity of SBA-15 functionalized with arenesulfonic and propylsulfonic acid groups in the Fried rearrangement reaction of phenyl acetate. The significant enhancement of the catalytic activity for the arenesulfonic acid-functionalized mesoporous material as compared to that of propylsulfonic acid-functionalized mesoporous silica demonstrated the beneficial influence of the phenyl-ring located adjacent to the sulfonic acid group on the acid strength of the catalyst.

In a similar attempt to enhance the acid strength of the organic acid groups tethered on the mesoporous silica, Alvaro *et al.* [37,38] functionalized MCM-41 with highly electron-negative perfluoroalkylsulfonic acid group, as shown in Figure 1-3(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 while the turnover frequency increased by an order of magnitude when compared to that of a commercial Nafion-silica composite catalyst.

In addition to supporting organic acids, mesoporous silica materials can also be used to support inorganic acids that can catalyze esterification reactions. Verhoef *et al.* [39] 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 can catalyze esterification reactions [40-42].

1.4. Motivations

It is evident from the numerous studies that organosulfonic acid-functionalized mesoporous silica material can catalyze esterification. Although extensive work has been done in this area, it has been limited to demonstrating the catalytic capabilities of the acid functional groups incorporated on the mesoporous silica materials in such reaction systems. As a result, little has been reported in the literature on understanding and controlling the catalytic domains of functionalized mesoporous catalysts, in addition to developing strategies of designing reaction environment on the molecular level in order to increase the reaction rates as well as the selectivity of the desired products. Accordingly, the focus of this work is to develop strategies to understand and control the catalytic domain of organosulfonic acid-functionalized mesoporous materials. The esterification of free fatty acids in triglyceride mixtures was chosen as a probe to study the reaction kinetics of acid-modified mesoporous

silicas, given that there is significant interest for the conversion of natural oils and fats into biobased chemicals.

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 transesterification [43]. These cheap feedstocks have high levels of free fatty acids (FFA), which saponify the alkali catalyst used in transesterification, causing depletion of catalyst through 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 by esterifying the FFA with a short-chain alcohol to no more than 0.5 wt% [44]. In such an attempt, synthesis and application of an organosulfonic acid-functionalized mesoporous silica catalyst in the methanol esterification of fatty acid in a soybean oil mixture will be discussed in Chapter 2. Means of increasing the conversion of fatty acid through alternative synthesis strategies will also be presented.

The esterification of fatty acids 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. Therefore, a synthesis strategy that creates an environment in which water is excluded from the mesopores could enhance the catalytic conversion of the fatty acids. A method for potentially accomplishing such an objective will be discussed in Chapter 3.

Understanding the acidity of organosulfonic acid-functionalized mesoporous silica catalysts is important in order to improve the overall catalytic performance of these materials.

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Discussed in Chapter 4 are factors that affect the acid strength of sulfonic acid groups as well as strategies to incorporate the organosulfonic acid groups into SBA-15 mesostructure with the intention of increasing the acid strength of the final solid catalyst.

The catalytic performance of organosulfonic acid-functionalized mesoporous materials in the esterification of free fatty acid in a real feedstock, such as beef tallow, as a pretreatment step in the production of biodiesel was also investigated. Use of solid catalyst in the pretreatment step could significantly simplify biodiesel manufacturing process by eliminating the neutralization step prior to alkali-catalyzed transesterification of triglycerides, as shown in Figure 1-6. Discussed in Chapter 5 is the catalytic performance of a propylsulfonic acid-functionalized mesoporous silica catalyst in the esterification of fatty acid in beef tallow, as well as strategies to improve the overall reaction conversion. Finally, the general conclusions of this project and future plans will be presented in the last chapter.

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Figure Captions:

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

Figure 1-2. Schematic representation of a mesoporous material functionalized with organic groups on the external and internal surfaces.

Figure 1-3. Organosulfonic acid moieties functionalized on mesoporous silicas; (a) propylsulfonic groups, (b) arenesulfonic groups, (c) perfluoroalkylsulfonic groups.

Figure 1-4. Esterification of glycerol and fatty acid to form monoglycerides, which could lead to formation of diglycerides and triglycerides as byproducts.

Figure 1-5. Schematic of mesoporous silica functionalized with organosulfonic acid and hydrophobic groups for fatty acid esterification with alcohol.

Figure 1-6. Schematic presentation of production of alkyl esters from triglycerides with high free fatty acid content.
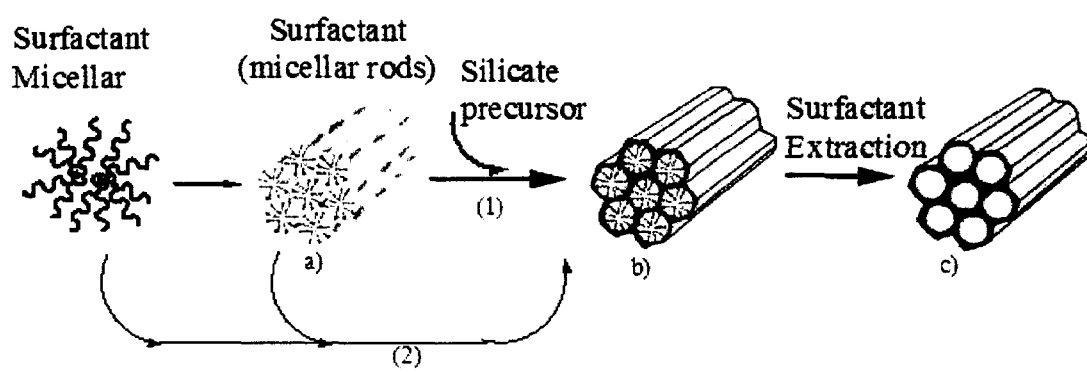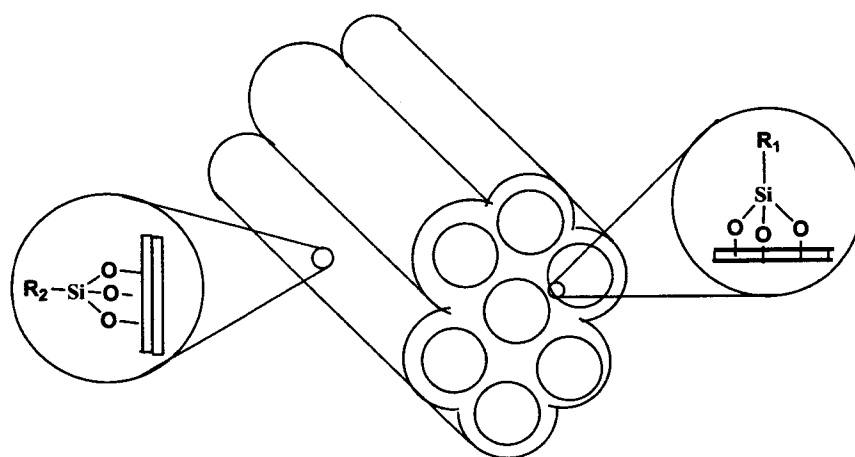
Figure 1-1.

Figure 1-2.

(a)   (b)   (c)
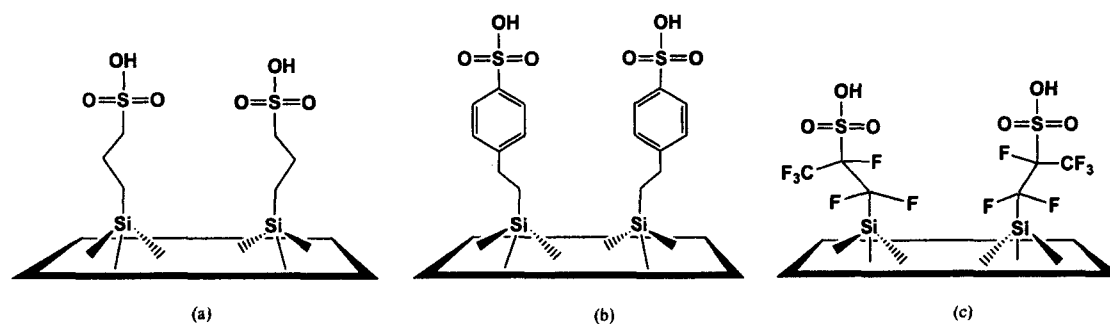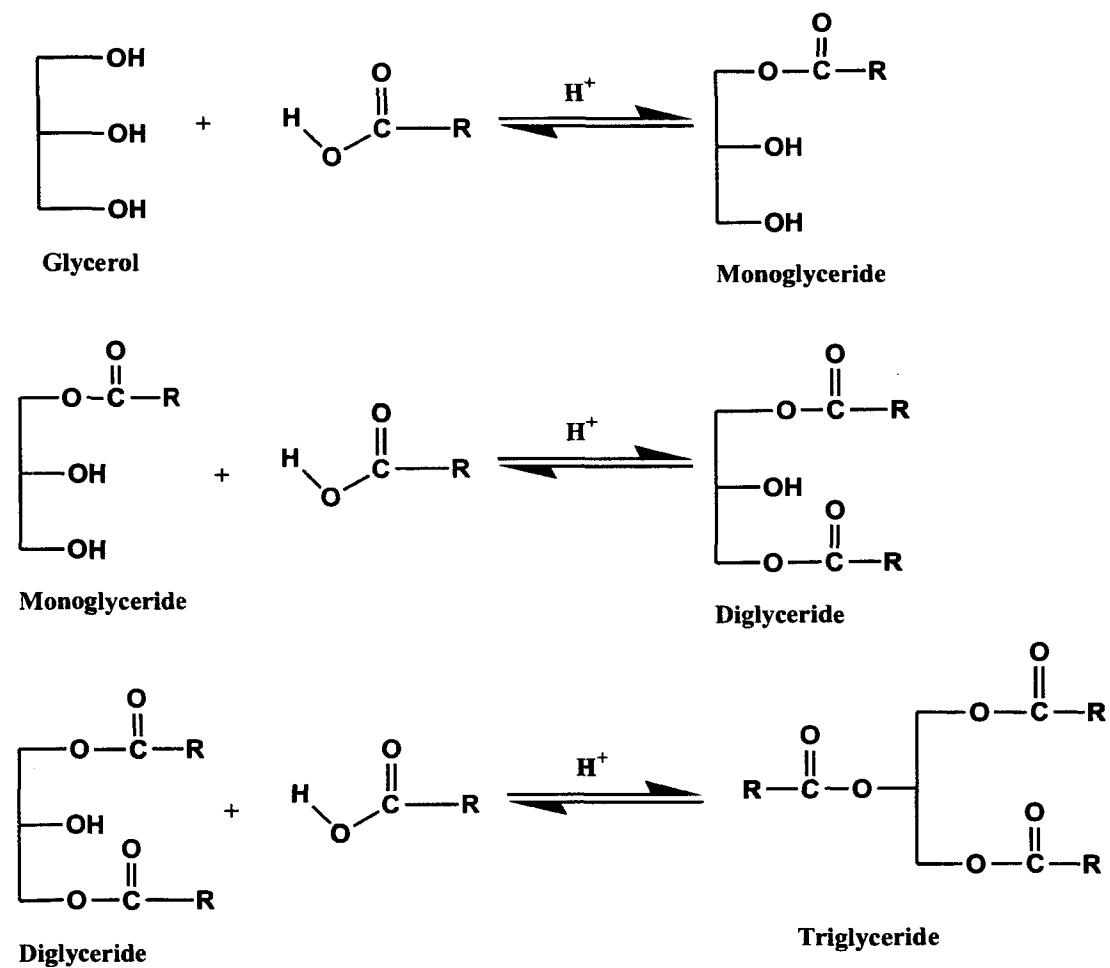
Figure 1-3.

Figure 1-4.
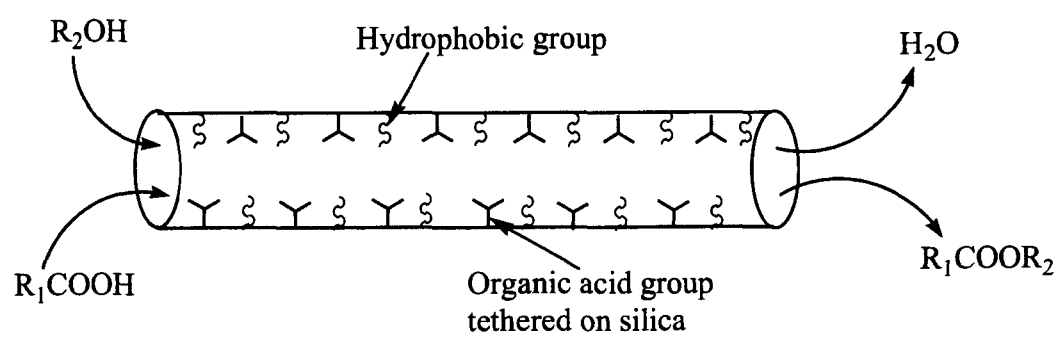
Figure 1-5.
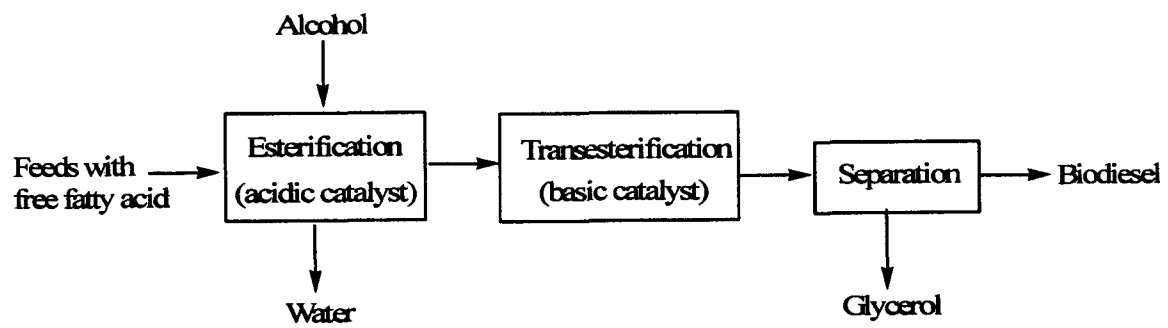
Figure 1-6.

CHAPTER 2

Organosulfonic Acid-Functionalized Mesoporous Silicas

for the Esterification of Fatty Acid

A paper published in *The Journal of Catalysis*[1]

2.1. Introduction

The transesterification of vegetable oils with short-chain alcohols (e.g. methanol and ethanol) to form alkyl esters has shown potential application as an intermediate for value-added products (e.g. fatty alcohols) and biodiesel fuel [1-5]. The production of biodiesel has received extensive interest as a result of its desirable renewable, biodegradable, and nontoxic properties [2,6]. However, it is currently not cost competitive with conventional diesel fuel due to high raw material and production costs. To improve the economic outlook of biodiesel and alkyl esters in general, the feedstock selection becomes critical. In particular, oil feeds containing high free fatty acid content, such as found in beef tallow or yellow grease, are significantly less expensive than vegetable oils, such as soybean or rapeseed oil [3,7]. These high free fatty acid feeds present significant processing problems in standard biodiesel manufacture since the free fatty acid is saponified by the homogeneous alkali catalyst used to transesterify triglycerides, leading to a loss of catalyst as well as increased purification costs [8].

One approach for improving the processing of high free fatty acid oils is to first esterify the free fatty acids to alkyl esters in the presence of an acidic catalyst. The pretreated

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oils in which the free fatty acid content is lowered to no more than 0.5 wt% can then be processed under standard transesterification reaction conditions [9]. This pretreatment step has been successfully demonstrated using sulfuric acid [10]. Unfortunately, use of the homogeneous sulfuric acid catalyst adds neutralization and separation steps as well as the esterification reaction to the process. Therefore, it would be desirable to perform the esterification pretreatment step with a heterogeneous acidic catalyst, which would significantly simplify the pretreatment process.

Due to a combination of extremely high surface areas and flexible pore sizes, surfactant-templated mesostructured materials have been studied extensively. The physical and chemical properties of these mesoporous materials can be modified by incorporating functionalized organic groups, either by grafting on the preformed mesopore surface or by co-condensation during synthesis [11-13]. Organic-inorganic hybrid mesoporous silicas functionalized with sulfonic acid groups have shown successful results for acid-catalyzed reactions [14-16]. The direct co-condensation synthesis technique, in which the mesostructure and functional group are simultaneously introduced, appears to be a desirable route for incorporating functional groups because it increases the concentration of the sulfonic groups in the mesoporous silica relative to grafting [15,17]. One approach demonstrated previously involves one-step synthesis based on the simultaneous hydrolysis and condensation of tetraethoxysilane (TEOS) with (3-mercaptopropyl)trimethoxysilane (MPTMS) in the presence of template surfactant using *in situ* oxidation of the thiol groups with H_2O_2. Melero *et al.* [18] has shown that the acid strength of the sulfonic groups in the mesoporous materials can be adjusted by choice of the organosulfonic precursor. For example, incorporation of a more electron-withdrawing group (e.g. phenyl group) with the

sulfonic group will significantly increase the acidic strength of the resulting mesoporous material. Due to their large pore diameters, these acid-functionalized mesoporous silicas provide improved accessibility to large reactants such as fatty acids and its esters [16].

Herein is described the synthesis and utilization of silica mesoporous materials modified with sulfonic groups for the pretreatment esterification of high free fatty acid oils. The results for the catalytic performance of the mesoporous materials are also compared to commercial acidic catalysts.

2.2. Experimental

The mesoporous materials were synthesized following the procedures of Boessaert *et al.* [16] and Melero *et al.* [18] with only slight modification. Tetraethoxysilane (TEOS, 98%, Aldrich) was used as the silica source. The mesoporous silicas were modified using (3-mercaptopropyl)trimethoxysilane (MPTMS, 85%, Fluka) without further treatment. The surfactants, n-dodecylamine (Aldrich), Pluronic L64 and Pluronic P123 (BASF Co., USA), were used as purchased to tailor the textural properties of the mesoporous materials. Mesoporous silica synthesized using the amine surfactant was denoted as HMS, while those synthesized with the tri-block copolymers were abbreviated SBA-15 [12].

2.2.1. HMS-SO$_3$H

A molar composition of 0.08 TEOS, 0.02 MPTMS, 0.0275 n-dodecylamine, 0.89 EtOH and 2.94 H$_2$O was used to synthesize HMS-SO$_3$H. The amine was dissolved in an

alcohol-water mixture prior to addition of the TEOS-MPTMS mixture. The mixture was aged for 24 h at room temperature under continuous stirring. The resulting solid product was filtered and air-dried. The template was extracted by refluxing in boiling EtOH for 24 h. The thiol groups were oxidized with H_2O_2 (2.04 g/g solid) in a methanol-water mixture. The suspension was stirred at room temperature for 24 h followed by washing with EtOH and H_2O. The wet cake was acidified in 0.1 M H_2SO_4 for an additional 4 h before being washed thoroughly with H_2O. The product was finally dried at 120 °C.

2.2.2. SBA-15-SO₃H

SBA-15-SO₃H was prepared by dissolving 4 g of Pluronic (P123 or L64) in 125 g of 1.9 M HCl at room temperature under stirring with subsequent heating to 40 °C before adding TEOS. Approximately 45 min was allowed for prehydrolysis of TEOS prior to addition of the MPTMS-H_2O_2 solution. The resulting mixture with a molar composition of 0.0369 TEOS, 0.0041 MPTMS, and 0.0369 H_2O_2 was stirred for 24 h at 40 °C and thereafter aged for 24 h at 100 °C under static condition. The product was collected and subjected to the same extraction method as previously described.

2.2.3. SBA-15-ph-SO₃H

SBA-15-ph-SO₃H mesoporous silica functionalized with benzenesulfonic acid groups was synthesized by dissolving Pluronic P123 (4 g) in 125 ml of 1.9 M HCl at room temperature while stirring. After complete dissolution, the solution was heated to 35 °C.

TEOS (8.76 g) was added dropwise to the solution at a constant temperature of 35 °C. After a TEOS prehydrolysis of 45 min, 2.66 mL of 2-(4-chloro-sulfonylphenyl)ethyltrimethoxysilane (CSPTMS) solution in methylene chloride (50%, Gelest) was added dropwise (to prevent phase separation). The resulting mixture was stirred for 20 h at 35 °C followed by aging at 95 °C for another 24 h. The molar composition of the mixture for 4 g of copolymer was 7.4 TEOS:1 CSPTMS:48 HCl: 1466 H_2O. The solid was isolated via filtration, washed extensively with methanol, and dried in air. The surfactant template was removed by suspending the solid material in ethanol and refluxing for 48 h. The sulfonyl chloride groups underwent hydrolysis in the acidic medium of the reaction.

2.2.4. Characterization

The textural properties of the mesoporous materials were measured using the BET procedure. Nitrogen adsorption-desorption isotherms were taken at -196 °C using a Micromeritics ASAP 2000 system. The ion capacities of the sulfonic acid groups in the functionalized mesoporous silica were quantified using 2 M $NaCl_{(aq)}$ as the ion-exchange agent. Approximately 0.05 g of the sample was added to 15 ml of the salt solution and allowed to equilibrate. Thereafter it was titrated by dropwise addition of 0.01 M $NaOH_{(aq)}$ [15].

2.2.5. Catalytic tests

The reagents used for the catalytic test included palmitic acid (PA, ≥95%, Sigma), refined soybean oil (SBO, Wesson) and methanol (MeOH, ≥99.9%, Fisher Scientific). A model high free fatty acid oil feed was simulated using 15% wt PA in SBO. The oil mixture was charged into the 100 ml reaction vessel with MeOH at a ratio of 1:20 w/w (PA: MeOH). The esterification reactions were performed in a stainless steel high-pressure batch reactor, Series 4565 Bench Top Mini Reactor (Parr Instrument Co., USA), fitted with mechanical stirrer and sample outlet. The reaction vessel was held at constant temperature with the aid of the heating mantle and integrated water-cooling system. Catalysts were screened using different loadings (5-20% w/w of the PA). The range of reaction temperature studied was 85 to 120 °C. Samples were drawn at hour intervals and their acid values were determined using AOCS method Cd 3a-63.

Shown in Figure 2-1 are the respective organosulfonic acid functional groups used in the study. The catalytic activities of the functionalized mesoporous silicas were compared with several commercial catalysts. These included homogeneous catalysts (sulfuric acid and p-toluenesulfonic acid, pTSA) from Fisher Scientific and heterogeneous catalysts, Nafion NR50 (SA = 0.02 m^2/g, H^+ capacity = 0.8 meq/g, Alfa Aesar Co., USA) and Amberlyst-15wet (SA = 45 m^2/g, Dp = 250 Å, H^+ capacity = 4.7 meq/g, Rohm and Haas Co., USA). All experiments were performed at least twice to evaluate reproducibility.

2.3. Results and discussion

The textural properties of the functionalized mesoporous silicas synthesized for the current work are summarized in Table 2-1, where the suffix designates the surfactant used. The N_2 adsorption-desorption isotherms of the synthesized samples had the hysteresis behavior associated with mesoporous materials [11,14,19,20]. The shape of the hysteresis loop indicated that the mesopores were disordered, which is a characteristic of mesoporous silica synthesized using nonionic surfactants as templates.

As seen in the table, the median pore diameter (MPD) of the mesoporous materials as determined by the BJH method was dependent on the surfactant template used, which is consistent with previous reports, and can be attributed to the size of the micelle structure formed during synthesis [11,21-23]. For the propylsulfonic acid-functionalized samples, HMS-SO_3H-C12 had the smallest MPD of 21 Å. The HMS material was formed from the cooperative self-assembly of the neutral primary amine, n-dodecylamine (C_{12}), with the neutral silica precursor. This procedure yielded mesoporous materials with worm-like pore structure and large wall thickness [19]. The pore diameter of the HMS material strongly depends on the length of the aliphatic carbon chain of the surfactant. The SBA-15 materials were synthesized using Pluronic L64 and P123, which are tri-block copolymers of polyethylene oxide-polypropylene oxide-polyethylene oxide, with molecular structure of EO_{13}-PO_{30}-EO_{13} and EO_{20}-PO_{70}-EO_{20}, respectively [11,20,24]. The SBA-15-SO_3H-P123 sample gave the largest MPD among the propylsulfonic acid-functionalized silicas. The larger MPD from the use of Pluronic P123 can be attributed to the lower EO:PO ratio of Pluronic P123 relative to Pluronic L64, 0.29 and 0.43, respectively. The decreased EO:PO

ratio, which is the result of an increase in the molecular weight of the propylene oxide in the copolymer, increased the hydrophobicity of the resulting micelles. This increased their size, leading to an enlarged MPD in the resulting mesoporous material [11].

The BET surface area of the samples was in the range reported in the literature for these types of mesoporous materials, which validates that the solvent extraction of the surfactant was successful. No clear relation between the surface areas of the functionalized mesoporous silica and the surfactant template was observed. Due to differences in preparation conditions, it was difficult to compare directly the surface area results with those reported in the literature.

The pore size distributions for the propylsulfonic acid-functionalized silicas as calculated from the BJH method are shown in Figure 2-2. The unimodal pore diameter distribution was consistent with that reported for organo-modified mesoporous silicas synthesized with nonionic surfactants. The pore volume followed the same trend with surfactant as was observed for the MPD. There was no apparent correlation between the pore volume and the BET surface area.

The number of sulfonic acid groups in the mesoporous silica, which were determined quantitatively using acid-base titration, are given in Table 2-1. It is noteworthy that the acid capacity of the materials increased with increasing MPD. This result was unexpected given that equal concentrations of the MPTMS and the oxidation reagent were used in the synthesis of all the samples. This difference indicates that all of the sulfur must not reside in the sulfonic acid groups. It is possible that the oxidation process that converts the thiol in the MPTMS precursor to the sulfonic acid group may also be oxidizing some of the adjacent thiol groups to disulfides, which would not be reactive [25].

The reaction performance of the functionalized mesoporous silicas was evaluated for the esterification of free fatty acids in a fatty acid/triglyceride mixture. A mixture of 15 wt% palmitic acid in soybean oil was used as the model high free fatty acid feed. This free fatty acid content is consistent with the value expected for a typical yellow grease. The transesterification of vegetable oil, which is performed with a homogeneous alkali catalyst such as sodium hydroxide or sodium methoxide, prefers a feedstock with <0.5 wt% free fatty acid due to saponification of the free fatty acid with the alkali catalyst. Transesterification of oil feeds with higher concentrations of free fatty acid leads to low yields and high production cost due to the depletion of the catalyst and subsequent formation of soap, which increases purification costs [9]. Pretreatment of a high free fatty acid oil via acid catalyzed esterification of the free fatty acid would provide a means for producing a feedstock that could be used in a standard transesterification reaction system. Therefore, the performance objective of the acid catalyst with the model feed was to decrease the palmitic acid content to less than <0.5 wt%. The esterification reaction was performed in excess methanol to favor the forward reaction, since the esterification of fatty acids with alcohol is extremely reversible [26].

To provide a comparison basis for the functionalized mesoporous silicas, the esterification reaction was also performed with H_2SO_4 and two commercial acidic resins, Amberlyst-15 and Nafion. Shown in Figure 2-3 are the results for reaction studies performed at 85 °C with a methanol to palmitic acid ratio of 20:1 by weight. The figure gives the palmitic acid concentration by weight as a function of reaction time. A catalyst concentration of 10 wt% was used for all of the catalysts except H_2SO_4, which was used at only 5 wt% concentration. In addition to the experimental data, trend lines are given in the

figure. The trend lines were determined by fitting the experimental data to a pseudo first order reaction model with respect to the palmitic acid concentration, given that the methanol was in excess and the soybean oil was not significantly reacting. The model assumption is validated by the reasonable fit between the trend lines and experimental data. As can be seen from the figure, the H_2SO_4 homogeneous catalyst was the most active with a conversion of more than 90% in less than 1.5 h. The high activity of H_2SO_4 was consistent with results reported in the literature, where as low as 5 wt% loading of the catalyst was reported to be sufficient to esterify free fatty acids to levels of less than 0.5 wt% [27]. The kinetic model fit the H_2SO_4 data least well, which may be attributed to reaction inhibition due to the presence of water at high palmitic acid conversion.

Among the functionalized mesoporous silicas, SBA-15-SO$_3$H-P123 gave the highest catalytic activity and HMS-SO$_3$H-C12 gave the least, with palmitic acid conversions of 85% and 55%, respectively, after 3 h. The higher activity with SBA-15-SO$_3$H-P123 was consistent with the material having the largest number of active sites (1.44 meq/g sample) as well as the largest pore diameter (35 Å). This observation was consistent with that reported by Bossaert et al. [16] for the esterification of gylcerol with lauric acid using propylsulfonic acid-functionalized mesoporous silica catalysts.

As seen in Figure 2-3, Amberlyst-15 despite its high exchange capacity gave the least catalytic activity with a conversion of 40%, while the Nafion was intermediate relative to the mesoporous silica catalysts with a conversion of 70%. Amberlyst-15 is known to be an active catalyst in a number of esterification reactions and Nafion contains highly acidic sites; however, their low activity suggests that either their catalytic sites are not accessible or under the given reaction conditions they are not sufficiently reactive.

Since the superiority of the H_2SO_4 catalyst in the reaction may be attributable to external mass transfer limitation with the solid catalysts, the esterification reaction was performed at a range of agitation speeds. Shown in Figure 2-4 are the results for the SBA-15-SO_3H-P123 catalyst, which was the most active solid catalyst. No significant differences in conversion rates were observed between the three stirring rates, demonstrating that at the higher stirring rates that were used in the current study no significant external mass transfer limitations were experienced.

Determining the cause of the higher activity for the SBA-15-SO_3H-P123 catalyst requires understanding of the relative importance of its higher active site concentration and its larger MPD, since both of these attributes could be contributing to the improved performance. To better understand these features, the reaction was performed at a range of temperatures from 85 to 120 °C. These data were then used to calculate apparent activation energies for the catalysts. The apparent activation energies were calculated assuming a pseudo first order reaction with respect to the palmitic acid as discussed previously. The linear regressions fit for the resulting values (R^2>0.95) confirmed that the assumed first order kinetics were reasonable.

The calculated rate constants and apparent activation energies are summarized in Table 2-2 for the synthesized mesoporous silica catalysts as well as the Nafion. A temperature increase of 15 – 20 °C caused a 2-3 times increase in the rate constants, which is as expected for activated reactions. The apparent activation energy of the mesoporous catalysts decreased in the order of HMS-SO_3H-C12 > SBA-15-SO_3H-L64 > SBA-15-SO_3H-P123. It is significant to note that the apparent activation energy decreased with increasing MPD. If internal diffusion was not significantly limiting the catalyst, the apparent activation

energies for these catalysts should be the same since the identical propylsulfonic acid-functional group was the active site present in all of the catalysts. The importance of the propylsulfonic acid groups in the conversion reaction was validated by testing a mesoporous silica that contained a low level of grafted propylsulfonic acid groups (0.02 meq/g). This catalyst was nearly inactive for the esterification reaction, indicating that the silica has no significant esterification activity.

A likely cause of the decreased apparent activation energy with increase in MPD is the importance of activated diffusion. The impact of activated diffusion on reaction kinetics has been amply demonstrated with zeolitic catalysts in which the activation energy of diffusion is strongly dependent on temperature and follows an Arrhenius relationship. In these systems, activation energies of up to 84 kJ/mol have been reported for activated diffusion [28]. If the esterification reaction was limited by activated diffusion for the HMS-SO_3H-C12 catalyst, subsequent increase in MPD as realized with the SBA-15 catalysts would lead to decreasing reaction limitation by activated diffusion. Therefore, the results in the current study appear to support the importance of activated diffusion in the esterification of palmitic acid with mesoporous materials having a MPD at least within the range of 22-35 Å.

In addition to the accessibility of the acidic sites, a potentially important characteristic is the strength of the acid site. A more acidic catalyst was synthesized by introducing a phenyl group within the organosulfonic acid (Figure 2-1b). The phenyl group, which is more electronegative than the aliphatic carbon chain, would be expected to increase the acid strength of the sulfonic acid group within the catalyst [18]. To diminish the possible effect of activated diffusion, arenesulfonic acid-functionalized mesoporous silica was synthesized

using Pluronic P123, which would be expected to yield a larger MPD than from the other surfactants used in the study. The sample, which is denoted SBA-15-ph-SO_3H-P123, had the textural properties and number of active site as given in Table 2-1. Despite the use of a common surfactant template, this material had a larger MPD and pore volume than the SBA-15-SO_3H-P123 material.

Shown in Figure 2-5 is the catalytic activity of SBA-15-ph-SO_3H-P123 for the esterification of palmitic acid relative to SBA-15-SO_3H-P123 as well as the homogeneous catalysts, H_2SO_4 and p-toluenesulfonic acid (pTSA). SBA-15-ph-SO_3H-P123 had significantly higher activity than SBA-15-SO_3H-P123 despite its lower number of acidic sites. In addition, it had higher the esterification activity than free pTSA. While the overall conversion achieved using SBA-15-ph-SO_3H-P123 was similar to H_2SO_4, the initial reactivity of the solid catalyst was higher than for H_2SO_4. As discussed previously, the fit of the pseudo first order kinetic model to the H_2SO_4 data was inferior to the heterogeneous catalysts, which was attributed to reaction inhibition from water at the high conversion level. This effect was more pronounced in the reactions with free pTSA and SBA-15-ph-SO_3H-P123, since both of these catalyst systems were very reactive. As such, the pseudo first order reaction trend lines are not included in Figure 2-5. Esterification of free fatty acids with methanol releases water that is known to limit the extent of the esterification reaction. Therefore, the low level of palmitic acid conversion after 60 min for the homogeneous catalysts and SBA-15-ph-SO_3H-P123 is likely due to the presence of water.

Comparison of the reaction performance of catalysts relative to a mass-based loading of the catalysts has limitations when catalysts with different numbers of active sites are considered. An apparent reactivity can be defined as the average turnover rate per total

number of active sites. Since internal diffusion is significant in mesoporous catalysts, the apparent reactivity can only represent an average turnover number that is convoluted with diffusion effects. For the current catalysts the number of active sites was defined by the H^+ equivalents in the catalyst. Using this definition, the apparent reactivities for the catalysts at 85 °C are given in Table 2-2. As can be seen from the table, SBA-15-ph-SO$_3$H-P123 gave significantly higher apparent reactivity than any of the other catalysts, while the apparent reactivities for all of the propylsulfonic acid-functionalized silicas as well as the Nafion were comparable. The high apparent reactivity for SBA-15-ph-SO$_3$H-P123 supports the conclusion that increasing the acidity of the sulfonic acid group enhances the reactivity of the material in the esterification reaction.

2.4. Conclusions

Organosulfonic acid-functionalized mesoporous silicas have higher reactivities than commercially available solid acid esterification catalysts for the conversion of fatty acids to methyl esters. Tailoring the textural properties of the catalyst structure and tuning the acidity of the active site can enhance the performance of the mesoporous materials. By choice of surfactant template, the pore diameter can be systematically increased to decrease internal mass transfer resistance. Due to the narrow pore size distribution of mesoporous materials, the pore size effect on internal mass transfer could be definitively determined. Increasing the acidity of the organosulfonic acid group improved significantly the activity of the mesoporous catalyst for the fatty acid esterification reaction. Proper choice of the organosulfonic acid group produced a functionalized mesoporous silica with activity at least

comparable to H_2SO_4. This work demonstrates the potential of organic-inorganic mesoporous materials for rational design of heterogeneous catalysts.

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Table 2-1. Textural properties of the functionalized mesoporous silicas.

Catalyst	Surfactant	S_{BET} ($m^2 g^{-1}$)	V_p ($cm^3 g^{-1}$)	MPD (Å)	H^+ meq/g sample
		Textural Properties			
HMS-SO$_3$H-C12	n-dodecylamine	550	0.30	22	0.60
SBA-15-SO$_3$H -L64	Pluronic L64	820	0.58	27	0.84
SBA-15-SO$_3$H -P123	Pluronic P123	735	0.67	35	1.44
SBA-15-ph-SO$_3$H -P123	Pluronic P123	540	0.71	50	0.92

Table 2-2. Comparison of the kinetic performance of the functionalized mesoporous silica catalysts.

Catalysts	Rate Constant (min^{-1})			Apparent Activation Energy (kJ/mol)	Apparent Reactivity (min^{-1})
	85 °C	100 °C	120 °C		85 °C
Nafion	6.6×10^{-3}	1.3×10^{-2}		60 ± 9	0.16
HMS-SO$_3$H-C12	2.6×10^{-3}	9.0×10^{-3}	2.4×10^{-2}	75 ± 10	0.14
SBA-15-SO$_3$H-L64	5.4×10^{-3}	1.3×10^{-2}	2.8×10^{-2}	55 ± 5	0.16
SBA-15-SO$_3$H-P123	7.5×10^{-3}	1.5×10^{-2}	3.4×10^{-2}	40 ± 1	0.11
SBA-15-phSO$_3$H-P123	1.7×10^{-2}				0.68

Figure Captions:

Figure 2-1. Organosulfonic acid functional groups incorporated into the mesoporous silicas;

a) propylsulfonic groups, b) arenesulfonic groups.

Figure 2-2. Pore size distribution curves for the mesoporous materials (×: HMS-SH-C12, ◊:

SBA-15-SH-L64, •: SBA-15-SH-P123).

Figure 2-3. Catalytic results for the esterification of palmitic acid in soybean oil with

methanol (85 °C; PA:MeOH = 1:20, catalyst: 10% Amberlyst 15-wet (□: Exp.,

model, 10% HMS-SO$_3$H-C12 (■: Exp., model), 10% SBA-15-SO$_3$H-

L64 (♦: Exp., model), 10% Nafion (Δ: Exp.,

········ model), 10% SBA-15-SO$_3$H-P123 (o: Exp., ── ── model), 5%

H$_2$SO$_4$ (◊: Exp., ──── model).

Figure 2-4. Effect of external mass transfer (■:200 rpm, •:350 rpm, □:500 rpm) on the

esterification of palmitic acid in soybean oil (85 °C; PA:MeOH = 1:20, catalyst:

10% SBA-15-SO$_3$H-P123).

Figure 2-5. Esterification of palmitic acid in soybean oil with methanol (85 °C; PA:MeOH =

1:20, catalyst: □:5% H$_2$SO$_4$, o:10% pTSA, ■:10% SBA-15-SO$_3$H-P123, •:10%
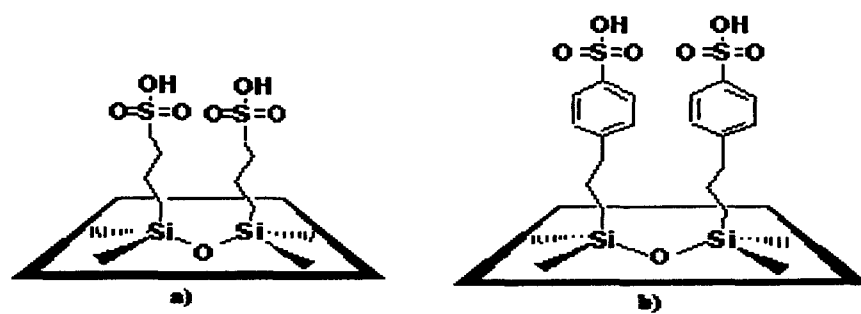
SBA-15-ph- SO$_3$H -P123).

Figure 2-1.
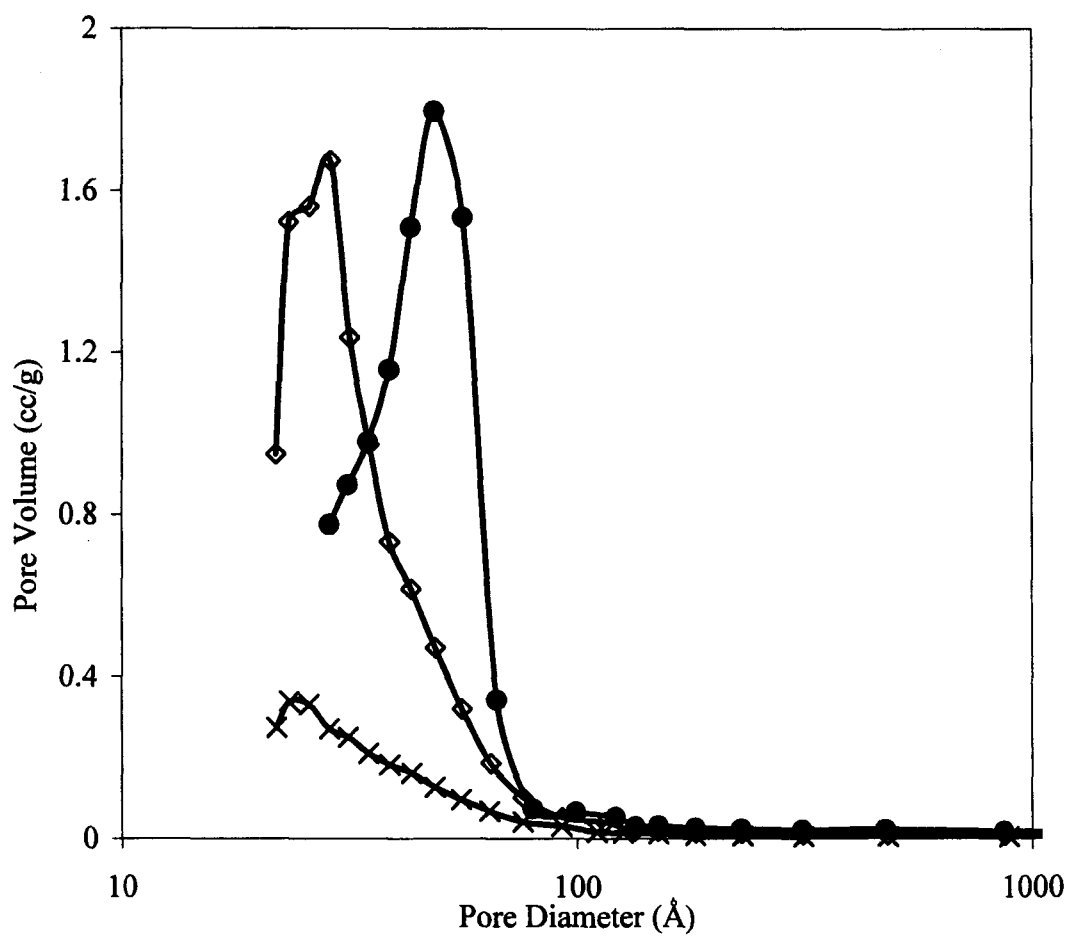
Figure 2-2.
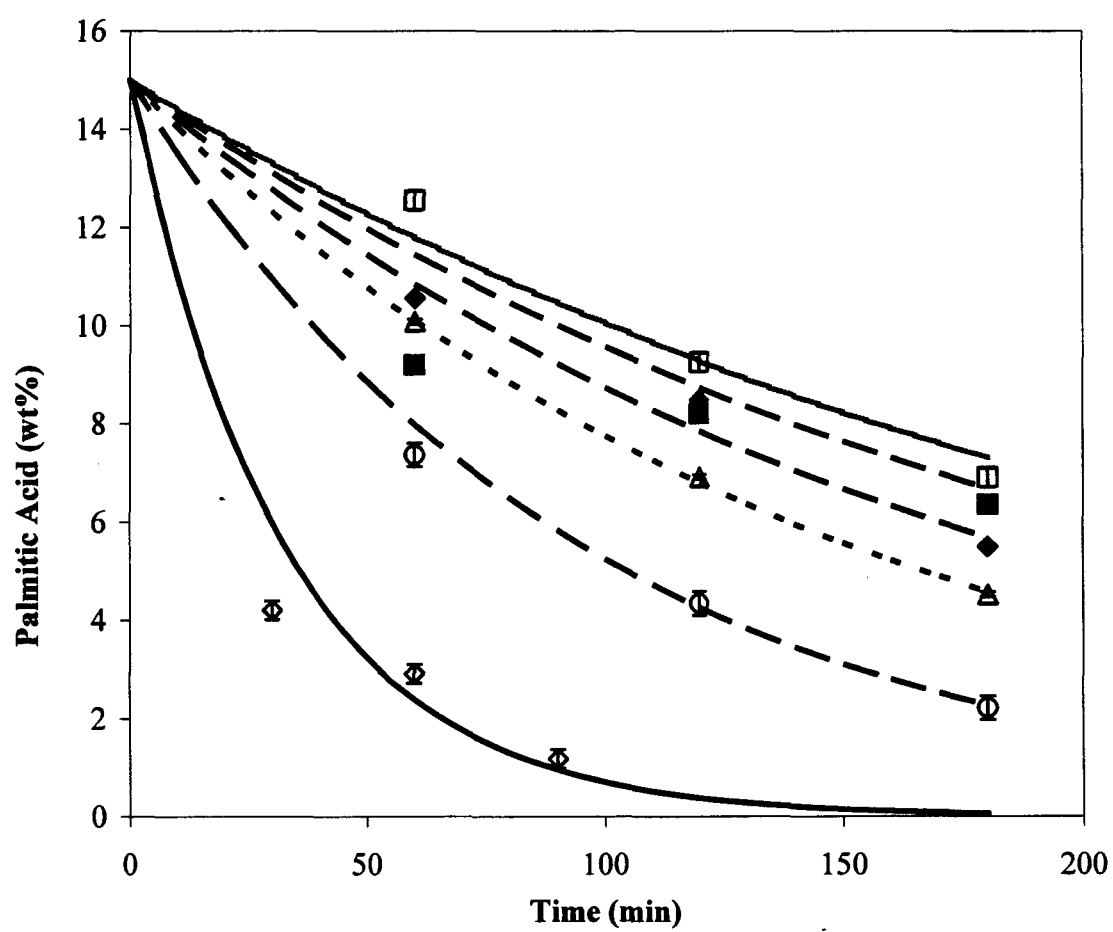
Figure 2-3.
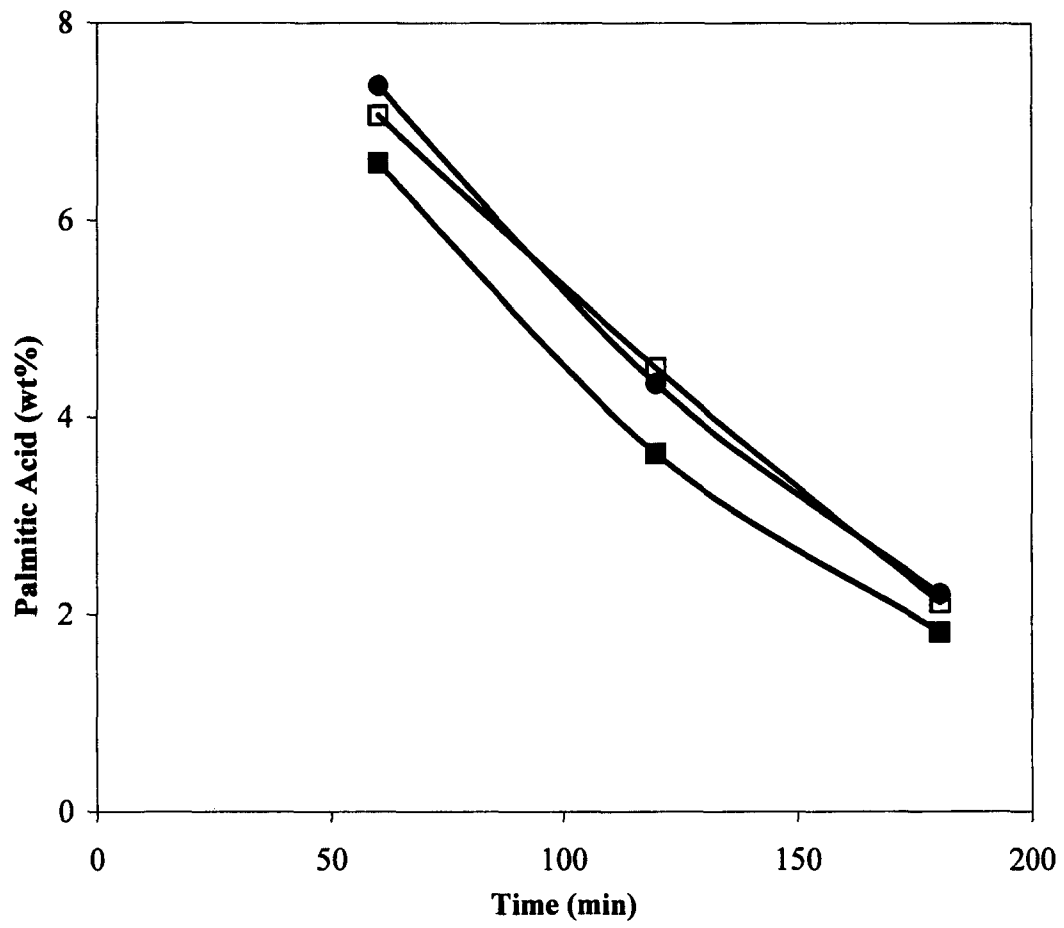
Figure 2-4.
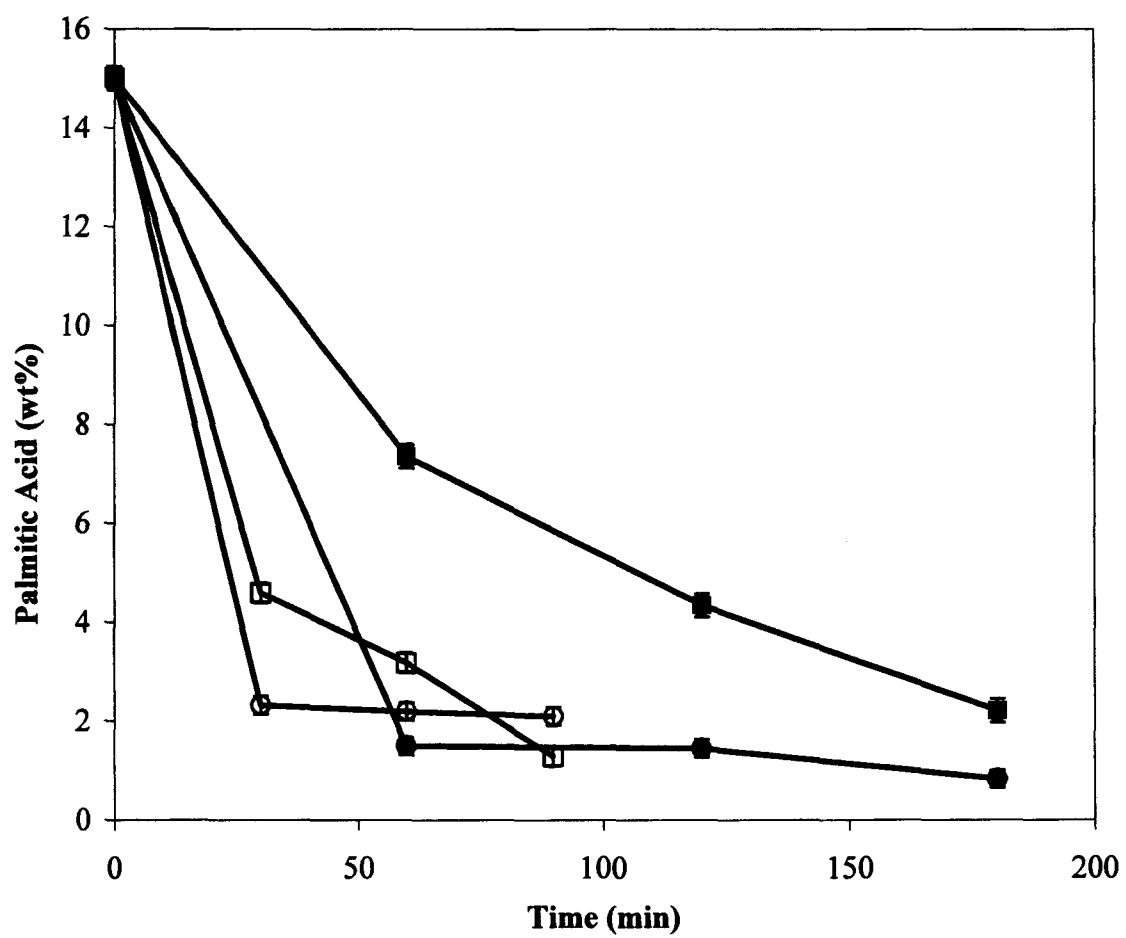
Figure 2-5.

CHAPTER 3

Design of Multi-Functionalized Mesoporous Silicas

for Esterification of Fatty Acid

A paper published in *The Journal of Catalysis*[1]

3.1. Introduction

Organic-inorganic hybrid silicas synthesized by supramolecular assembly have received increasing attention due to their high surface area and flexible pore sizes as well as their potential for controlling catalytic functionalities at the molecular level [1-4]. Utilization of these mesostructured materials can be tailored by incorporating specific organo-functionalized groups onto the surface of the inorganic framework, which will modify the physical and chemical properties of the metal oxide supports at the nano-scale to the desired application requirements, e.g. separation, chemical sensing, adsorption, and catalysts. In solid acid catalysis, zeolites are widely used, but they are limited to pores in the microporous range (<15 Å) that are not accessible by large reactants. Incorporation of organosulfonic acid groups into mesoporous materials to create a solid acid catalyst has been explored as a means to increase the pore size range available for heterogeneous acidic catalysts [5-7]. In addition to flexibility to larger pore diameter, the performance of organosulfonic acid-functionalized mesoporous silica can be improved by selectively excluding unwanted molecules that can inhibit the reactants from the proximity of the active sites [8-10]. This

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attribute is particularly important in processing biobased reactants, which commonly have

impurities that require pretreatment prior to catalytic chemical conversion [11].

One such application is the esterification of free fatty acids with acidic catalysts as a

pretreatment step in the production of biodiesel [12-14]. The production of biodiesel has

received extensive interest as a result of its desirable renewable, biodegradable, and nontoxic

properties [15-17]. Generally, biodiesel is produced via the transesterification of vegetable

oils with short-chain alcohols (e.g. methanol) to form alkyl esters that have similar properties

as fossil-derived diesel [18,19]. However, biodiesel is currently not cost competitive with

conventional diesel fuel due to its high raw material and production costs. To improve

biodiesel economics, feedstock selection becomes critical. The conventional biodiesel feeds,

vegetable oils, are more expensive than oil feeds containing high free fatty acid content, such

as found in beef tallow or yellow grease. Unfortunately, utilization of these high free fatty

acid feeds in traditional biodiesel production processes leads to depletion of the catalysts as

well as increased purification costs since the free fatty acid is saponified by the homogeneous

alkaline catalyst, producing excess soap [20].

The free fatty acid processing problem can be circumvented by first esterifying the

free fatty acid to alkyl esters in the presence of an acidic catalyst. The pretreated oils in

which the free fatty acid content is lowered to no more than 0.5 wt% can then be processed

under standard transesterification reaction conditions [12]. Koono *et al.* [21] successfully

demonstrated the pretreatment step using sulfuric acid; however, the use of a homogeneous

acidic catalyst adds neutralization and separation steps to the process. It would be

advantageous to use a heterogeneous acidic catalyst in the esterification pretreatment step,

since it would significantly simplify biodiesel production as well as lower the manufacturing cost.

Mbaraka *et al.* [22] investigated the use of organic-inorganic hybrid mesoporous silica mono-functionalized with propylsulfonic acid and arenesulfonic acid groups in the esterification of a model feed containing 15 wt% free fatty acid. They observed high esterification conversion for both catalysts, but the arenesulfonic acid catalyst was more active, with a conversion above 90% within 60 min. As noted in the work, the reversible esterification reaction appeared to be inhibited by water once the conversion was above 85%. It was concluded that the release of water from the esterification of the free fatty acids limited the extent of the reaction. This effect may have been exacerbated by the hydrophilicity of the reaction environment within the pores of the silica-based catalyst.

An approach to improve the performance of organosulfonic acid-functionalized mesoporous silicas for the esterification of free fatty acid is to create a reaction environment that will continuously remove water from the mesopores. A method for potentially accomplishing this goal would be the introduction of hydrophobic groups into the mesopores of the organosulfonic acid-functionalized mesoporous silica framework. The hydrophobic organic groups (e.g. allyl and phenyl) would be expected to decrease the amount of water adsorbed into the mesoporous silica [10,23]. These organic groups could be integrated into the mesostructured materials either by grafting onto the preformed mesoporous surface or by direct co-condensation during synthesis [23-25].

Herein is described the synthesis and characterization of multi-functionalized mesoporous silica materials, which contain both organosulfonic acid and hydrophobic

organic groups. These materials were subsequently utilized as catalysts in the esterification reaction of high free fatty acid oils as pretreatment steps in the production of biodiesel.

3.2.   Experimental

Organosulfonic acid-functionalized mesoporous silicas were synthesized according to the method described previously [5,22,25]. These mesoporous silicas were further modified with hydrophobic organic groups to obtain the multi-functionalized mesostructured materials. Tetraethoxysilane (TEOS, 98%, Aldrich) was used as the silica precursor while (3-mercaptopropyl)trimethoxysilane (MPTMS, 85%, Acros) was used without further purification as the organosulfonic acid source. Pluronic P123 (BASF Co., USA), which is a tri-block copolymer of polyethylene oxide-polypropylene oxide-polyethylene oxide with molecular structure of PEO_{20}-PPO_{70}-PEO_{20}, was used as purchased to tailor the textural properties of the mesoporous materials. The organosulfonic acid-functionalized mesoporous silica was further modified with methyltrimethoxysilane (MeTMS, 95%), ethyltrimethoxysilane (EtTMS, 97%), or phenyltrimethoxysilane (PhTMS, 97%) purchased from Aldrich via either a one-step synthesis or by a post-synthesis grafting procedure. The organosulfonic acid-functionalized mesoporous material was denoted as SBA-15-SO_3H while the multi-functionalized mesostructured silica was symbolized by a prefix or suffix to the parent name (SBA-15-SO_3H), indicating either a post-synthesis grafting or a one-step synthesis procedure, respectively.

3.2.1. One-step synthesis procedure

In a typical one-step synthesis, 4 g of Pluronic P123 was dissolved in 125 ml of 1.9 M HCl at room temperature under stirring with subsequent heating to 40 °C before adding TEOS. The TEOS was prehydrolyzed for approximately 45 min before addition of MPTMS, H_2O_2, and a hydrophobic organic precursor. The resulting mixture with a molar composition of 0.0369 TEOS, 0.0041 MPTMS, 0.0369 H_2O_2, and 0.0041 hydrophobic organic group was agitated for 24 h at 40 °C and thereafter aged for 24 h at 100 °C under static conditions. The resulting solid material was filtered and air-dried. The template was extracted by suspending the solid product in EtOH and refluxing for 24 h. To ensure complete removal of the surfactant, fresh EtOH was introduced after 12 h. The final product was air-dried, then stored in a desiccator.

3.2.2. Post-synthesis grafting procedure

SBA-15-SO_3H was synthesized as described in the one-step co-condensation procedure with the exclusion of the hydrophobic organic group precursor. The product was collected and subjected to the same template extraction method as discussed above. Prior to incorporation of the hydrophobic organic groups, the solid samples were evacuated overnight at 125 °C. The dried solid (~3 g) was suspended in a mixture of the hydrophobic organosilane (0.004 moles) in 300 ml toluene and refluxed for 4 h. The product was collected and air-dried overnight, then washed in a Soxhlet extractor with CH_2Cl_2/Et_2O for 24 h. The final product was air-dried, then stored in a desiccator.

3.2.3. Characterization

The textural properties of the multi-functionalized mesoporous silica were measured from nitrogen adsorption-desorption isotherms at -196 °C using a Micromeritics ASAP 2000 system. The surface area and pore size distribution were calculated from the BET and BJH method, respectively. Prior to measurement, all samples were degassed at 100 °C for 6 h. Powder X-ray diffraction (XRD) analysis of the synthesized samples was performed on a Scintag XDS 2000 diffractometer with a Cu Kα radiation source. Analysis of the organic material present in the solids was determined by elemental analysis performed on a Perkin-Elmer Series II 2400 CHNS-analyzer. The organic composition of the modified mesoporous materials was determined by thermogravimetric analysis (TGA) and differential thermoanalysis (DTA) with on a Perkin-Elmer TGA7 instrument, heating from 50 to 600 °C at a rate of 10 °C/min under air flow. The ion-exchange capacities of the multi-functionalized mesoporous silica were determined by acid-base titration.

The multi-functionalized mesoporous silica were tested for catalytic activity using similar conditions as those described previously [22]. The reagents used for the esterification reaction included palmitic acid ($\geq$ 95%, Sigma), refined soybean oil (SBO, Wesson) and methanol (MeOH, $\geq$ 99.9%, Fisher Scientific). The esterification reactions were performed under nitrogen in a stainless steel high-pressure batch reactor, Eze-Seal (Autoclave Engineers Co., USA), fitted with mechanical stirrer and sample outlet. The reaction mixture used in the study was a 15:85 weight ratio of palmitic acid to SBO and a palmitic acid to MeOH weight ratio of 1:20. The catalyst loading was equivalent to 10 wt% of the palmitic acid and the

range of reaction temperature studied was 85 to 120 °C. The reaction mixture was continuously stirred at a rate of 350 rpm.

3.3.   Results and discussion

The textural properties of the multi-functionalized organic-inorganic hybrid mesoporous silicas synthesized for the current work are summarized in Table 3-1. The large BET surface areas of the synthesized multi-functionalized mesoporous silicas were consistent with previous reports [24-26], validating the efficacy of the approach used to extract the surfactant template. The N_2 adsorption-desorption isotherms of the synthesized samples had Type IV hysteresis loops with sharp adsorption and desorption curves as seen in Figure 3-1, which are consistent with mesoporous materials tailored by nonionic templates [26,27]. The mono-functionalized mesoporous silica (SBA-15-SO$_3$H), which was the reference catalyst, was synthesized without incorporating a hydrophobic organic group. The post-synthesis grafting of the hydrophobic organic groups (denoted by the prefix) was performed on a SBA-15-SO$_3$H synthesis batch that was subsequently divided into four samples. Addition of the hydrophobic group to the reference organic-inorganic hybrid mesoporous silica by the grafting technique had no significant effect on the resulting surface area, but the size of the hysteresis loop and pore volume decreased, which implied a possible accumulation of the grafted organic species around the pore openings. The same trend was not observed for samples synthesized by the one-step co-condensation technique. The differences in surface area and pore volume between the reference catalyst and co-condensed multi-functionalized catalysts were insignificant with the exception of the material multi-functionalized with

organosulfonic acid and phenyl (SBA-15-SO$_3$H-Ph), which had a statistically significant decrease in pore volume compared to the other co-condensed samples. Moreover, the N$_2$ adsorption-desorption isotherm of SBA-15-SO$_3$H-Ph (not shown) resembled Type I with a narrow hysteresis loop, suggesting that the pores were not the long cylindrical shape reported for mesoporous materials tailored by nonionic surfactants [23,28]. These features could indicate that the phenyl groups affected the final structure of the mesoporous silica.

The median pore diameters (MPD) of the multi-functionalized organic-inorganic mesoporous silicas synthesized by the post-synthesis grafting procedure and one-step condensation technique were calculated using the BJH method on the adsorption branch of the N$_2$ adsorption-desorption isotherm and are summarized in Table 3-1. The pore size distribution of the synthesized samples (not shown) was unimodal for both synthesis techniques. The grafting of the hydrophobic organic groups onto the mesostructure of the reference sample had no significant effect on the pore size distribution; however, the pore volume of the functionalized material decreased. The pore diameter distribution of the Ph/SBA-15-SO$_3$H was shifted slightly towards smaller pore diameter when compared to other grafted samples. This difference may indicate that the presence of phenyl groups may have partially blocked the pore openings. In contrast, the hydrophobic organic group incorporated into the mesoporous silica during the one-step co-condensation method seemed to change the pore size distribution relative to the reference catalyst. Therefore, incorporation of the hydrophobic organic groups during the synthesis of the mesoporous silica framework did appear to affect the structure formation of the final mesoporous material.

Replicate syntheses were performed on several of the materials to validate the reproducibility of the textural properties. The catalysts made in replicate are displayed in the table with the number of replicates in parentheses following the name. The standard deviations for their textural properties are tabulated in the table and were found to be less than 10%.

The influence of hydrophobic organic groups on the mesostructure properties of the organosulfonic acid-functionalized mesoporous silica was studied with XRD. All the samples showed an intense single peak in the range of 1.6 to 2 degree with the exception of the SBA-15-SO$_3$H-Ph catalyst, which showed a high degree of disorder. The XRD pattern for materials grafted with hydrophobic groups showed that the anchoring of organosilanes on the mesostructure framework had insignificant consequence on the structure of the final mesoporous catalyst. The same trend was observed for materials synthesized by co-condensation technique; however, the material was increasingly disordered as the molecular size of the organosilane group increased.

The relative carbon/sulfur ratio as well as the sulfur content present in the multi-functionalized mesoporous samples as determined by elemental analysis is summarized in Table 3-1. The equivalence of the sulfur composition in the different samples suggested that the incorporation of hydrophobic groups by either the grafting method or the co-condensation technique had an insignificant effect on the resulting sulfur content. The mass balance performed on sulfur from the synthesis solution to dry solid (0.95 S mmol/g) was consistent with the elemental analysis, demonstrating a high incorporation yield of the organosulfonic acid precursor. The C/S molar ratio in the reference sample was higher than that expected for only propylsulfonic acid groups. This likely implies that unhydrolyzed methoxy and/or

ethoxy groups from the parent MPTMS and TEOS were still present in the synthesized catalyst or that unreacted silanols reacted with ethanol during solvent extraction [24,29]. The C/S ratio was a function of the hydrophobic group incorporated into the mesoporous silica, with the ratio increasing as the carbon number of the hydrophobic group increased. The proportionality of the C/S ratio to the carbon number suggested that organosilane addition into the mesoporous silica was not dependent on either the incorporation method or the type of hydrophobic group.

The thermal decomposition of organo-functional groups in the reference sample and mesoporous catalyst functionalized with ethyl and organosulfonic acid (SBA-15-SO$_3$H-Et), which was synthesized by the co-condensation method, is shown in Figure 3-2. The TGA and DTA analysis of SBA-15-SO$_3$H-Et shows weight losses peaks centered at 80 °C, 280 °C, and 460 °C. The first weight loss was assigned to desorption of water and the last weight loss, which was also observed in the reference sample, was due to organosulfonic acid decomposition as reported in the literature [24,25,30]. The weight loss at 280 °C was observed only in the multi-functionalized samples. TGA analysis of an as-synthesized SBA-15 sample without the incorporation of any functional groups gave two weight losses at 80 °C and 190 °C, which were due to water desorption and surfactant decomposition [26]. Propylthiol decomposition has been shown to occur at 350 °C (29,30). No weight loss was observed at 350 °C for any of the functionalized materials, suggesting that the thiol precursor was converted.

The textural properties of the reference sample (SBA-15-SO$_3$H) before and after the TGA analysis were determined using N$_2$ adsorption-desorption. Following the TGA analysis, the organic functional group was no longer present in the mesoporous material. As

shown in Figure 3-1, no significant change was observed before and after the thermal removal of an organic functional group. Therefore, the presence of the organic group in the reference material did not alter the N_2 adsorption-desorption results.

The number of sulfonic acid groups in the catalysts as determined by acid-base titration is given in Table 3-1. The concentration of sulfonic acid groups for the materials synthesized by the one-step co-condensation technique and the post-synthesis grafting method were in the range of $0.92 - 1.43$ H^+ meq/g sample. The number of acidic sites in the multi-functionalized mesoporous silicas was consistent with that in the reference catalyst and was similar to previous reports [22,30]. Therefore, the incorporation of the hydrophobic groups had no significant effect on the concentration of acidic sites in the multi-functionalized samples. The acid-base titration yielded concentrations of sulfonic acid that were about 20% higher than that determined by elemental analysis. This discrepancy could be due to the high ionic strength of the salt solution used in the titration, which would affect the solution pH.

The reaction performance of the catalysts was evaluated by the esterification of a fatty acid in a fatty acid/triglyceride mixture. The results represent an extension of our previous study on the application of organosulfonic acid-functionalized mesoporous silica in the esterification of fatty acids [22]. In that study, we postulated that the production of byproduct water in the esterification of palmitic acid with methanol inhibited the esterification reaction. To validate this postulate, the esterification performance of the SBA-15-SO_3H catalyst was compared between a reaction mixture doped with 3800 ppm (by weight) water and one free of water. Under the reaction conditions used in the present study, the transesterification of triglycerides would be minuscule using an acidic heterogeneous

catalyst [14,31]. Shown in Figure 3-3 is the palmitic acid weight concentration as a function of reaction time for the water-free and water-doped reactions. The detrimental effect of water on the performance of the organosulfonic acid catalyst was conspicuous, as shown by the decreased palmitic conversion in the water-doped reaction system. The negative effect of water has also been reported for esterification reactions catalyzed by homogeneous acidic catalysts where as little as 0.1 wt% water concentration inhibited the reaction [14,32]. Aafaqi et $al.$ [33] have calculated the equilibrium constant for the esterification of palmitic acid with isopropanol from both experimental and thermodynamic data and found that it was 2–10 for a temperature range of 100–170 °C, which demonstrated the reversibility of fatty acid esterification with alcohol. To favor the forward reaction, the esterification of palmitic acid was performed in excess methanol in the current work. The equilibrium effect would be exacerbated by the mesoporous silica catalysts due to the hydrophilicity of the pore interiors, which would lead to an enriched water concentration within the pore. The intention of designing the multi-functionalized mesoporous silica was to modify the reaction environment adjacent to the propylsulfonic acid catalytic sites inside the mesopores such that the water would be excluded. A proposed schematic of the desired system is shown in Figure 3-4. Incorporation of the hydrophobic organic groups into the organosulfonic acid-functionalized mesoporous silica would selectively create an unsuitable environment for water, leading to its exclusion from the active site. Accordingly, the objective of functionalizing the organosulfonic acid mesoporous silica with the inert hydrophobic organic groups was to study the effectiveness of the catalyst in eliminating water from the proximity of the active sites while esterifying palmitic acid.

To investigate the effect of incorporation technique on the performance of the catalysts, the hydrophobic organic groups were introduced through either post-synthesis grafting or co-condensation. The results from the esterification reactions catalyzed by the mesoporous silica modified by the two incorporation techniques are shown in Figure 3-5. The unmodified SBA-15-SO₃H gave the highest catalytic activity, with palmitic acid conversions of 88% after 3 h of reaction. In contrast, Et/SBA-15-SO₃H and Ph/SBA-15-SO₃H gave the lowest activity, with only 70% conversion after 3 h. These results indicate that the post-synthesis grafting of the hydrophobic groups actually led to a decrease in catalyst performance relative to the reference catalyst. No significant difference between the catalytic performances for each different allyl group on the multi-functionalized mesoporous silica was observed despite the differences in their degree of hydrophobicity.

When the same experiments were performed with mesoporous silica multi-functionalized via the co-condensation technique, the results were substantially different, as can be seen in Figure 3-5. The co-condensed samples exhibited similar overall conversion (~ 84%) after 3 h of reaction as unmodified SBA-15-SO₃H. However, the co-condensed catalysts gave higher initial catalytic activity, as can be seen after 60 min, where SBA-15-SO₃H-Ph was the most active and SBA-15-SO₃H was the least with 61% and 47% palmitic acid conversion, respectively. It is noteworthy that SBA-15-SO₃H-Ph achieved higher activity despite its apparent inferior textural properties relative to SBA-15-SO₃H. The reaction results demonstrated that the hydrophobic organic groups did appear to influence the catalytic activity of the hybrid catalysts in the esterification of palmitic acid. Diaz *et al.* reported similar results for the esterification of glycerol with lauric acid or oleic acid to monoglycerides as catalyzed by multi-functionalized MCM-41 [8].

The results for the grafted and co-condensed catalysts demonstrate that the method of incorporating the inert hydrophobic organosilanes into the mesoporous silica gave dramatically different performance in the esterification of palmitic acid. Shown in Figure 3-6 are possible schematics of the catalyst particles resulting from the two incorporation methods. Post-synthesis grafting would likely incorporate the allyl silanes through reaction with surface silanol groups. Due to mass transfer, silanol groups on the outside of the mesoporous particles and at the pore mouth would preferentially react first, creating a hydrophobic exterior of the particle. In contrast, co-condensation would place the organosilanes within the pores, leaving the exterior of the particles hydrophilic. The difference in external particle functionalization for the two incorporation methods was validated by placing the multi-functionalized particles in water. The co-condensed material was able to be slurried with water but the post-synthesis grafted particles could not be slurried with water unless methanol was added. This observation suggested that the external surface of the grafted samples was highly hydrophobic, thereby preventing water from accessing the pores.

To further probe the catalytic behavior of the mesoporous silica functionalized via the one-step co-condensation and the post-synthesis grafting techniques, the esterification reaction was performed in a reaction mixture doped with 3800 ppm water. Shown in Figure 3-7 are the reaction results for both mono-functionalized (SBA-15-SO$_3$H) and multi-functionalized mesoporous silica catalysts in the presence of added water. Under these conditions, all of the multi-functionalized mesoporous silicas exhibited higher catalytic activity than the reference catalyst, with conversions of above 80% after 3 h compared to only 75% conversion with the reference catalyst. The results demonstrated the presence of

the inert hydrophobic organic groups in the materials allowed the catalysts to sustain higher reaction rates presumably by selectively preventing water from inhibiting the reaction. Unlike SBA-15-SO3H, which was significantly less active in the presence of water doped at 3800 ppm, the activity of the co-condensed catalysts was only slightly lower for the water-doped reaction than reaction with no added water. This result further supports the assertion that creating a hydrophobic environment within the pores served to exclude water from the active sites. Unexpectedly, the activity of the grafted samples with the water-doped reaction system actually improved relative to the reaction system free of water. The improvement in activity with water doping for the grafted system was such that the grafted catalysts now outperformed the reference SBA-15-SO3H catalyst.

Determining the cause of the performance enhancement of the grafted samples in the presence of excess water requires understanding the relative importance of the location of the hydrophobic organic groups and their relationship with the reactants, since both of these attributes could contribute to the improved performance. To better understand these features, reactions with 3800 ppm water-doped mixtures were performed at temperatures from 85 to 120 °C. These data were then used to calculate apparent activation energies for the catalysts, assuming a pseudo-first-order reaction with respect to palmitic acid, as discussed previously [22]. The calculated rate constants and apparent activation energies are summarized in Table 3-2 for the mono-functionalized and multi-functionalized mesoporous silica catalysts. A 15-20 °C temperature increase approximately doubled the rate constants in all the catalysts except Ph/SBA-15-SO3H. The range of activation energies for the mono-functionalized and multi-functionalized mesoporous silica catalysts were consistent with the range reported for propylsulfonic acid SBA-15 materials tailored with Pluronic P123 [22]. Similar activation

energy for the esterification reaction of palmitic acid with alcohol has been reported [33]. The low activation energy of Ph/SBA-15-SO3H was possibly due to external mass transfer limitation resulting from a strong interaction between the phenyl group and the reactants around the pore mouth.

Dixit *et al.* [34] studied the solution behavior of alcohols under strict anhydrous conditions and in the presence of low water levels. They observed with anhydrous methanol that the hydroxyl groups of adjacent methanol molecules interact with each other through hydrogen bonding leading to oligomeric-type chains, which behave as hydrophobic compounds due to their conformation. These hydrogen bonding-derived chains were completely broken upon the addition of only ppm levels of water. A similar phenomenon may be playing a role in the esterification reaction system. The esterification reaction mixture consists mainly of amphiphilic reactants (palmitic acid and methanol) and soybean oil, which in analogy to the methanol study could form long hydrophobic chains. The bulky chains of palmitic acid could then limit the accessibility of the catalytic active sites due to blockage of the mesopores. To minimize the external mass transfer limitations of the reactants with the catalysts, the hydrophobic chains of the reactants would need to be eliminated. One approach for breaking the chains would be to introduce a strong polar compound into the reaction mixture, which would then interact with the hydroxyl groups of the amphiphilic compounds. The presence of water molecules in the reaction mixture or the existence of silanols on the external surface area of the mesoporous catalysts could disrupt the solution chains. The higher performance of the catalysts synthesized via the one-step co-condensation technique in the esterification reaction of palmitic acid without addition of excess water may suggest that the external surface area was sufficiently hydrophilic due to

the presence of surface hydroxyl groups. As a result, the esterification reaction occurred within the mesopores where the reactants were catalyzed by the organosulfonic acid and the water produced was excluded from the catalytic site by the hydrophobic organic groups. However, the post-synthesis grafting method had the opposite effect on the mesoporous catalysts, i.e. high concentrations of the hydrophobic organic groups could be found on the external surface area while the organosulfonic acid was in the interior of the mesopores. Consequently, in the water-free reaction system the reactant chains were maintained, resulting in poor diffusion of reactants into the mesopores and thus low conversions of palmitic acid. As demonstrated in Figure 3-7, the addition of water into the reaction mixture with the grafted catalyst gave higher reaction rates than in the absence of water that may be attributed to improved accessibility of the reactive sites through disruption of the solution chains.

To determine the effect of water concentration on the esterification of palmitic acid with methanol as catalyzed by Et/SBA-15-SO$_3$H, the reaction system was doped with different amounts of water, with the reaction results shown in Figure 3-8. As seen in the figure, doping with 1200 ppm water gave the highest conversion of 74% after 2 h followed by doping with 3800 ppm water with conversion of 62% after 2 h. The least active was the system in which no water was introduced prior to reaction, which only achieved a conversion of 52% after 2 h. The results were consistent with water inhibiting the esterification reaction, as demonstrated by the loss in activity when water doping was increased from 1200 to 3800 ppm. However, the presence of a small concentration of water in the reaction mixture enhanced the performance of the catalysts, which was consistent with the speculated chain formation mechanism discussed above. It is interesting to note that the activity of the grafted

catalyst diminished significantly by 12% upon the change of water doping from 1200 to 3800 ppm, while the performance of the co-condensed catalyst functionalized with ethyl group only decreased slightly by less than 1% upon increasing the water doping from 0 to 3800 ppm. These results were further indirect conformation that the co-condensed catalysts led to hydrophobic environments within the pores while the grafted catalysts still had significant hydrophilicity within the pores.

The proposed solution effects due to hydrogen bonding would be expected to be less pronounced at higher temperatures, so a final set of experiments was performed at 120 °C using 25 wt% palmitic acid in soybean oil. The results for these experiments are shown in Figure 3-9. All of the multi-functionalized catalysts, with the exception of Ph/SBA-15-SO$_3$H, were more active than the mono-functionalized acid catalysts, achieving palmitic acid conversion of above 99% after 2 h. The high catalytic activity of the Et/SBA-15-SO$_3$H is consistent with the assumption that at high reaction temperature, the hydrophobic chains are eliminated due to the absence of hydrogen bonding. The low catalytic performance of the Ph/SBA-15-SO$_3$H catalyst in the esterification reaction is consistent with the apparent activation energy results given in Table 3-2. The higher temperature results confirm that the addition of the hydrophobic organic groups into the structure of the mesoporous silica modifies the catalytic environment so that water produced from the reaction is excluded, enabling higher catalytic conversions.

3.4. Conclusions

Mesoporous silica multi-functionalized with both organosulfonic acid and hydrophobic organic groups were effective in esterifying free fatty acid while excluding water, which is an undesired reaction product, from the proximity of the active sites. Both post-synthesis grafting and one-step co-condensation techniques were used to introduce the hydrophobic organic groups, with the techniques preferably modifying the external and internal surface area, respectively. The technique of incorporating the hydrophobic organic group into the mesoporous silica as well as the knowledge of the reaction mixture were important in enhancing the performance of the catalysts. This work demonstrates the potential of utilizing organic-inorganic hybrid mesoporous materials for rational design of heterogeneous catalysts at the molecular scale.

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Table 3-1. Textural and chemical properties of the multifunctionalized mesoporous silica materials.

Catalysts	Textural Properties			Chemical Properties		
	S_{BET} ($m^2\,g^{-1}$)	MPD (Å)	V_P ($cm^3\,g^{-1}$)	C/S (mol/mol)	S (mmol/g)	H^+ (meq g^{-1})
SBA-15-SO$_3$H (2)	740 ± 40	52 ± 3	0.95 ± 0	5.80	1.00	1.17 ± 0.07
Me/SBA-15-SO$_3$H	600	54	0.81	6.58	0.82	1.43
Et/SBA-15-SO$_3$H	630	53	0.82	7.98	0.95	1.20
Ph/SBA-15-SO$_3$H (2)	520 ± 60	58 ± 1	0.76 ± 0.07	14.07	0.94	0.92 ± 0.04
SBA-15-SO$_3$H-Me	810	45	0.91	6.35	0.92	1.30
SBA-15-SO$_3$H-Et (4)	770 ± 20	47 ± 4	0.90 ± 0.07	7.97	0.96	1.18 ± 0.10
SBA-15-SO$_3$H-Ph	630	34	0.54	12.69	0.98	1.18

Table 3-2. Comparison of the kinetic performance of the multifunctionalized mesoporous silica catalysts.

Catalysts	Rate constant (min^{-1})			Apparent activation energy (kJ/mol)
	85 °C	100 °C	120 °C	
SBA-15-SO$_3$H	1.0×10^{-2}	1.8×10^{-2}	2.6×10^{-2}	30 ± 14
SBA-15-SO$_3$H-Et	1.2×10^{-2}	2.1×10^{-2}	3.7×10^{-2}	40 ± 2
SBA-15-SO$_3$H-Ph	6.4×10^{-3}	1.1×10^{-2}	2.2×10^{-2}	40 ± 1
Et/SBA-15-SO$_3$H	8.4×10^{-3}	1.6×10^{-2}	2.4×10^{-2}	35 ± 1
Ph/SBA-15-SO$_3$H	1.5×10^{-2}	1.9×10^{-2}	1.9×10^{-2}	10 ± 1

Figure Captions

Figure 3-1. N_2 adsorption-desorption isotherms of the multi-functionalized mesoporous materials synthesized by the post-synthesis grafting and co-condensation procedures (▲: SBA-15-SO$_3$H; ♦: SBA-15-SO$_3$H-Et; ●: Et/SBA-15-SO$_3$H; -- ▲---: SBA-15-SO$_3$H after TGA analysis).

Figure 3-2. TGA and DTA analysis of the functionalized mesoporous silica (Δ: SBA-15-SO$_3$H; ○: SBA-15-SO$_3$H-Et)

Figure 3-3. Effect of water on the esterification of palmitic acid in soybean oil with methanol (85 °C; PA:MeOH = 1:20; Catalyst: 10 wt% SBA-15-SO$_3$H; ♦: 3800 ppm water; ■: 0 ppm water).

Figure 3-4. Schematic of desired water exclusion process with a multi-functionalized mesoporous silica in the esterification of fatty acid with methanol.

Figure 3-5. Catalytic results for the esterification reaction as catalyzed by the grafted and co-condensed multi-functionalized silica (85 °C; PA:MeOH = 1:20; ♦: SBA-15-SO$_3$H; ▲: Me/SBA-15-SO$_3$H; ●: Et/SBA-15-SO$_3$H; ■: Ph/SBA-15-SO$_3$H; Δ: SBA-15-SO$_3$H-Me; ○: SBA-15-SO$_3$H-Et; □: SBA-15-SO$_3$H-Ph).

Figure 3-6. Schematic comparison of the apparent functionality locations for (a) post-synthesis grafting and (b) one-step co-condensation (∿ : hydrophobic groups, ↑: propylsulfonic acid sites).

Figure 3-7. Catalytic activity of the multi-functionalized silicas resulting from doping 3800 ppm water into the reaction (85 °C; PA:MeOH = 1:20; ♦: SBA-15-SO$_3$H; ▲:

SBA-15-SO₃H-Et; □: SBA-15-SO₃H-Ph; ●: Et/SBA-15-SO₃H; ■: Ph/SBA-15-SO₃H).

Figure 3-8. Effect of water doping on the catalytic activity of Et/SBA-15-SO$_3$H (85 ^{o}C; PA:MeOH = 1:20; ▲: 0 ppm; ■: 1200 ppm; ♦: 3800 ppm).

Figure 3-9. Catalytic results for the esterification of 25 wt% palmitic acid in soybean oil catalyzed by the multi-functionalized silicas   (120 ^{o}C; PA:MeOH = 1:20; ♦: SBA-15-SO$_3$H; ●: SBA-15-SO$_3$H-Et; ■: SBA-15-SO$_3$H-Ph; ▲: Et/SBA-15-SO$_3$H; □: Ph/SBA-15-SO$_3$H).
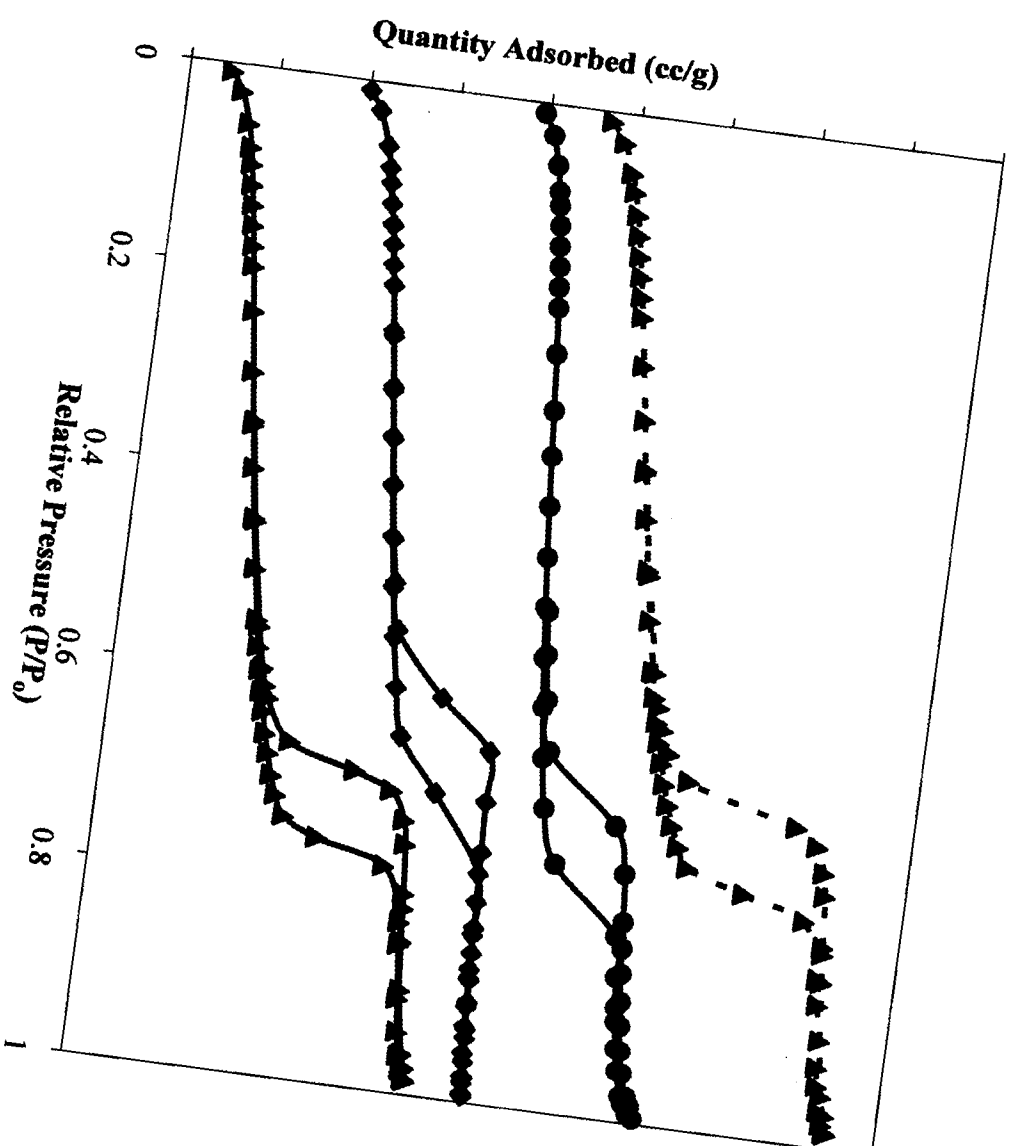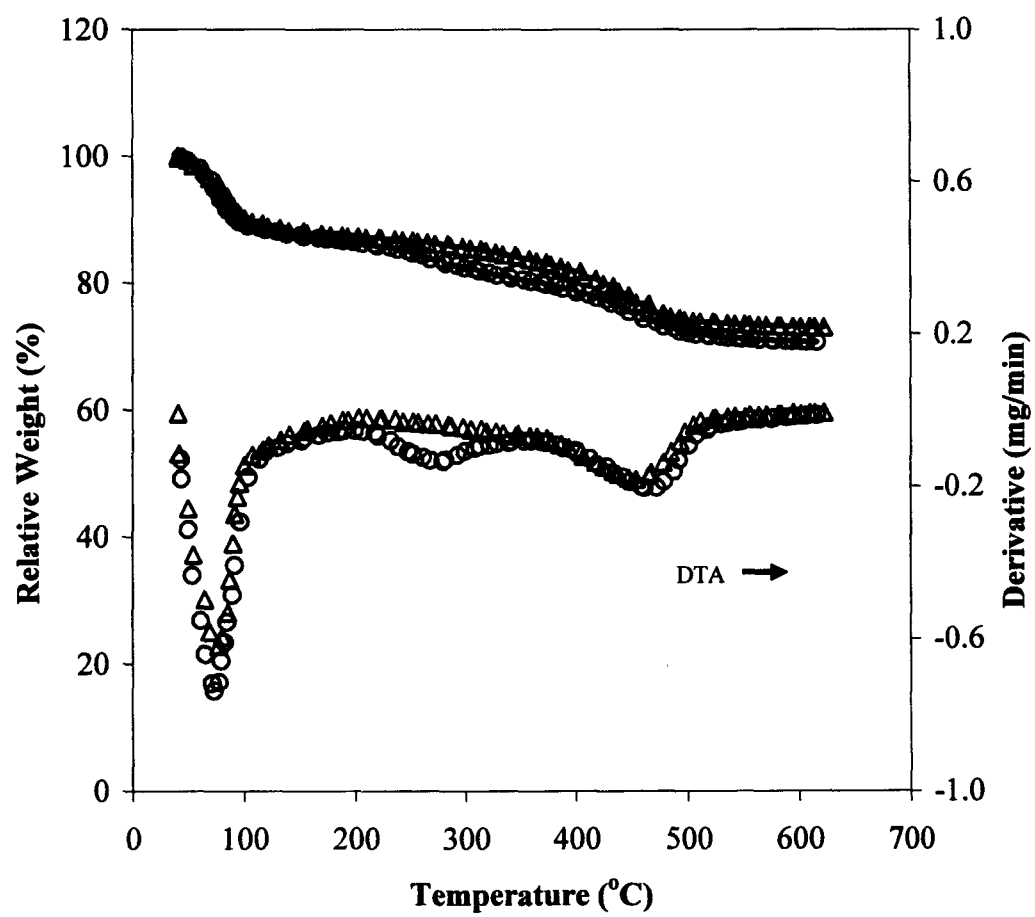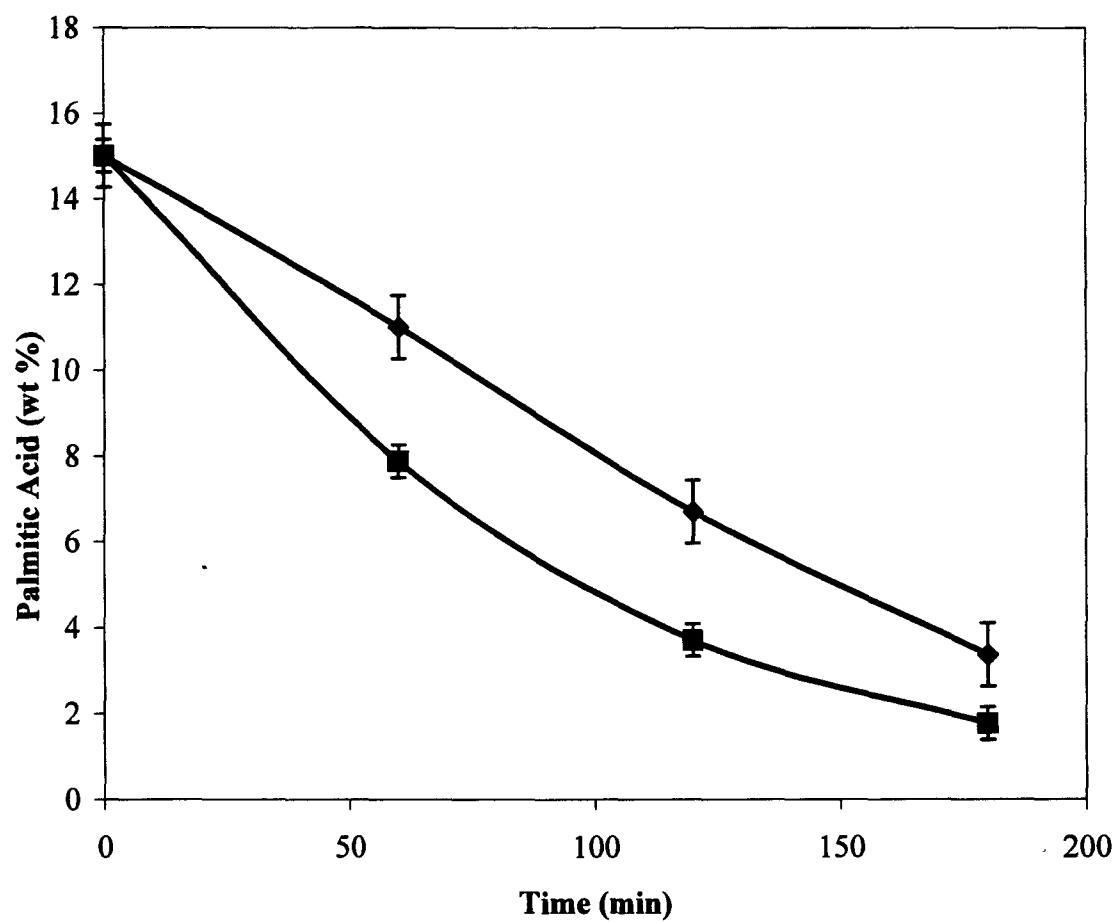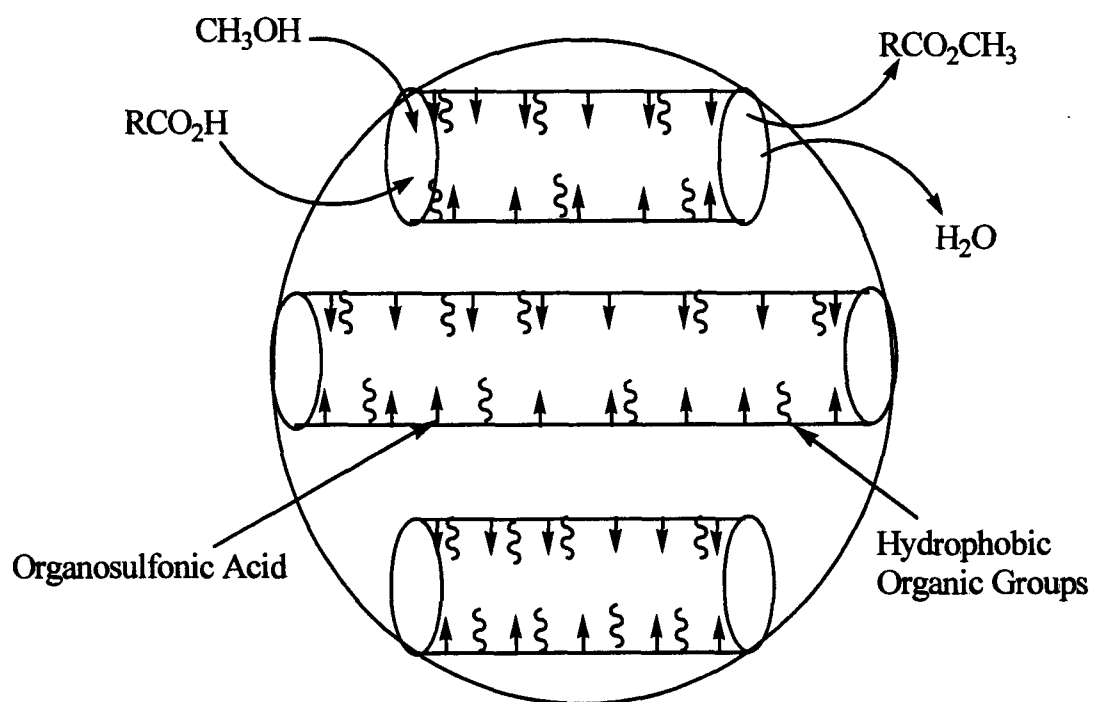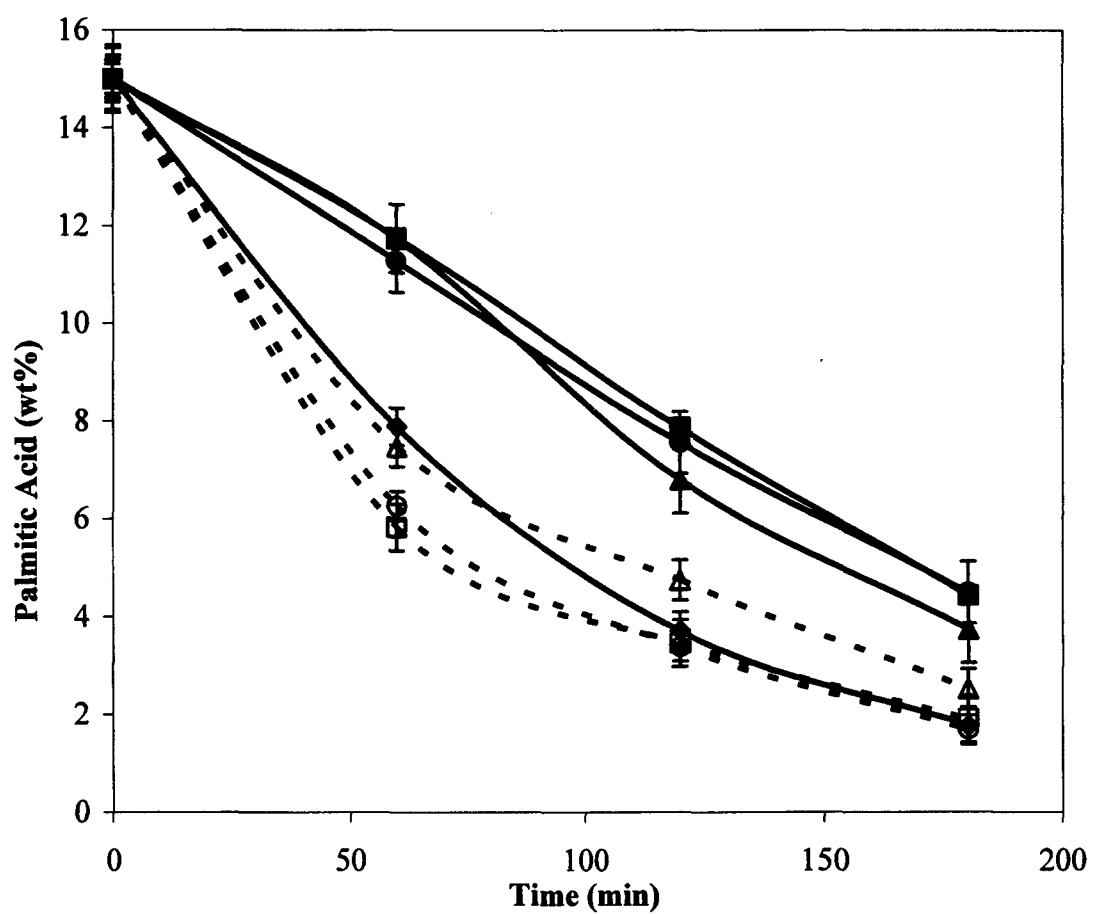
Figure 3-1.

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Figure 3-2.

Figure 3-3.

Figure 3-4.

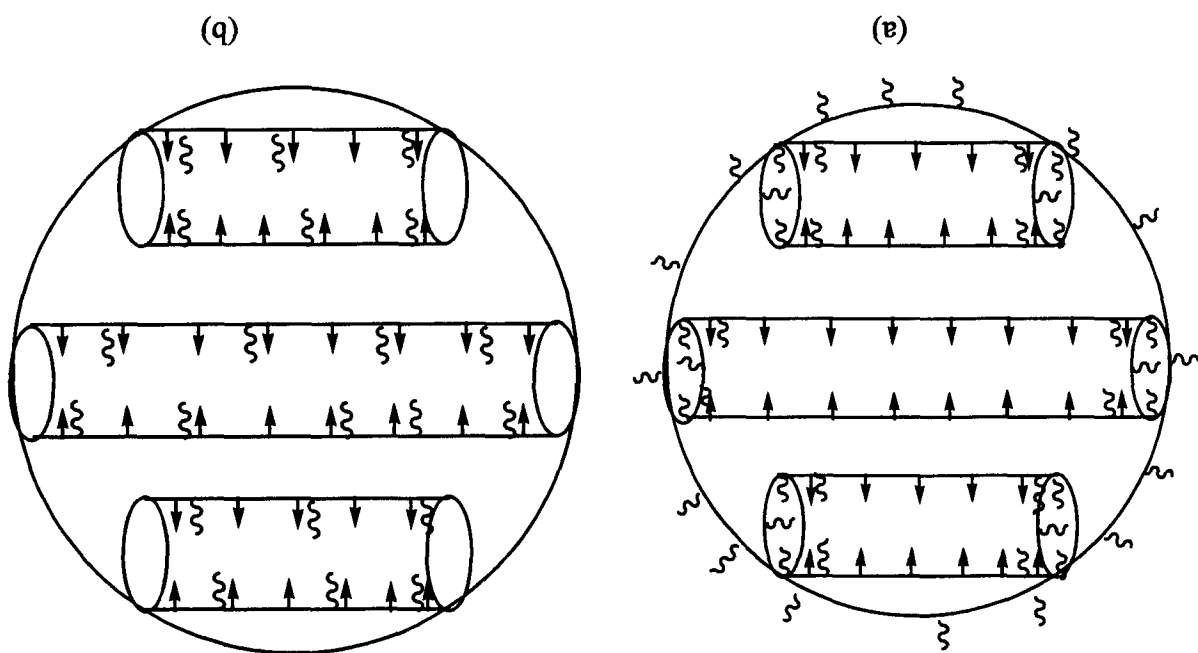Figure 3-5.

Figure 3-6.

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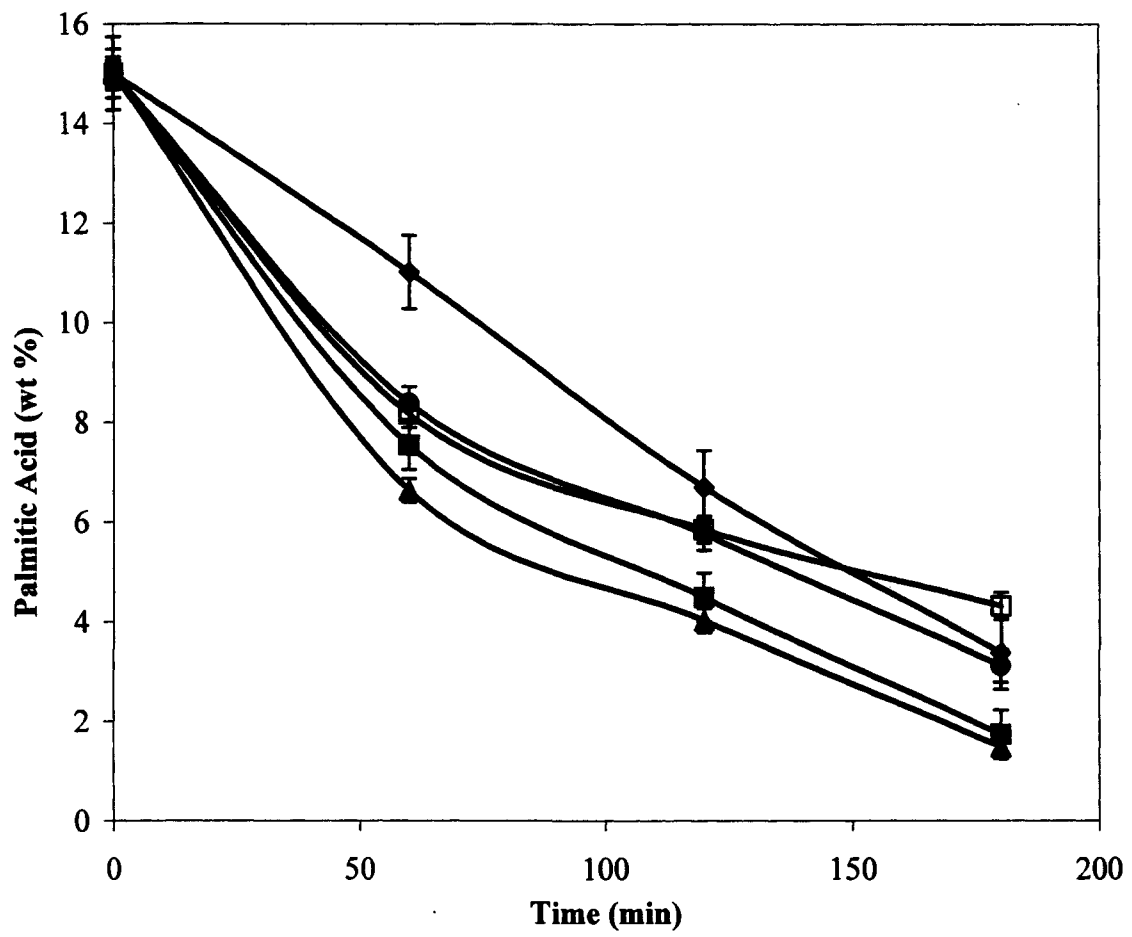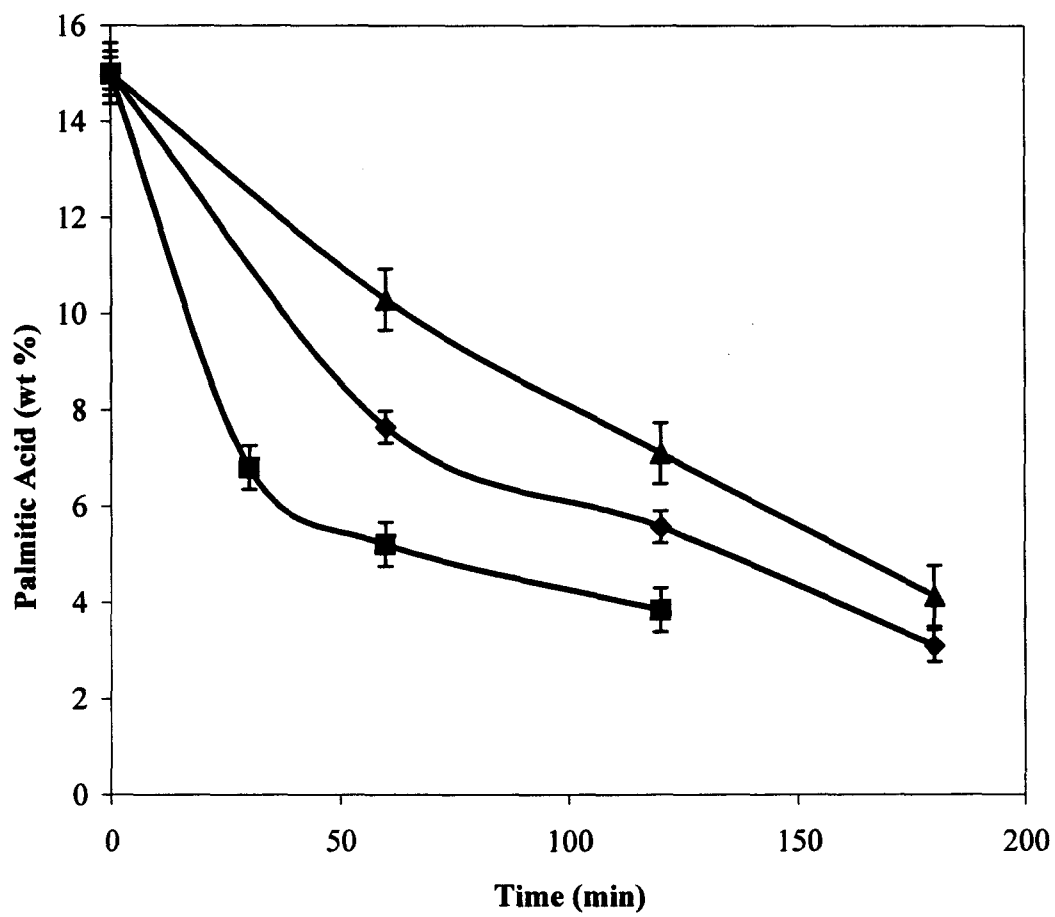Figure 3-7.

Figure 3-8.
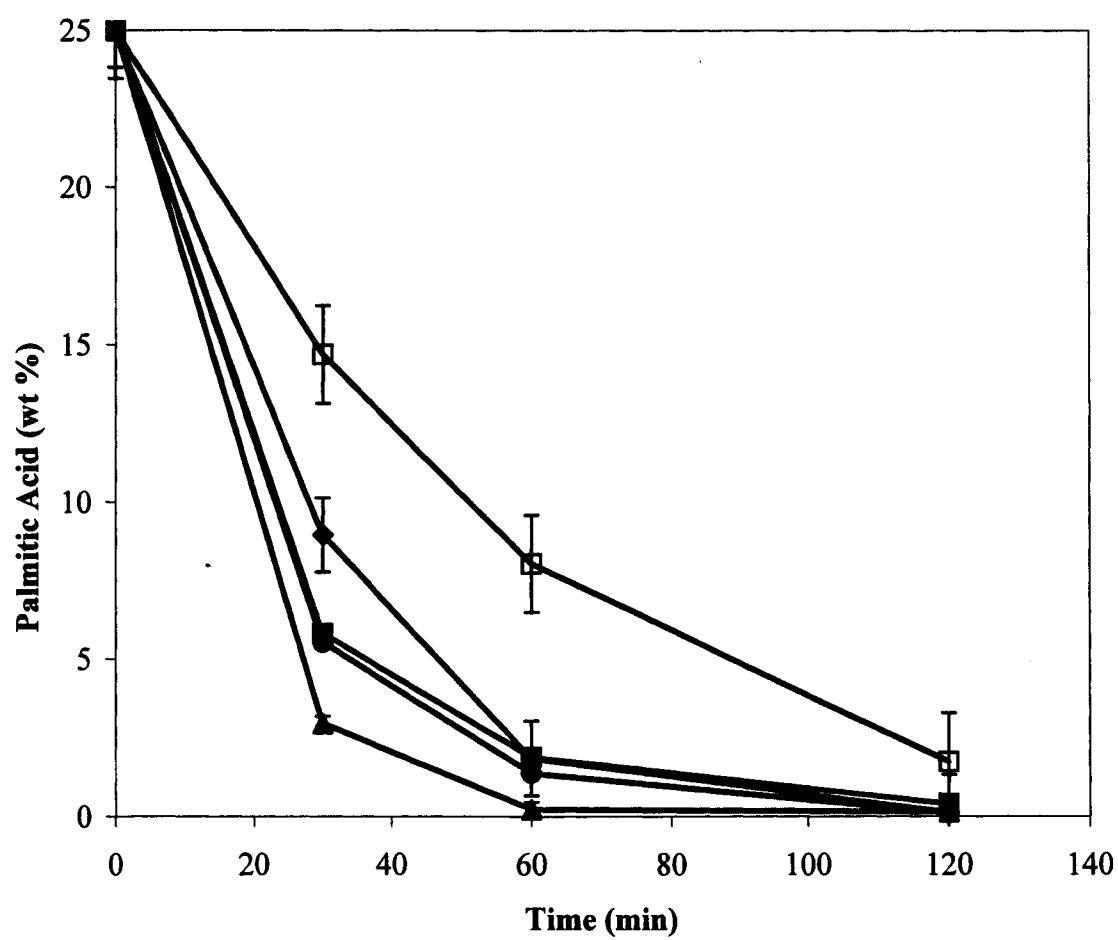
Figure 3-9.

CHAPTER 4

Acid Strength Variation Due to Spatial Location of Propylsulfonic

Acid Groups on Mesoporous Silica

A paper to be submitted to *The Journal of the American Chemical Society*

4.1. Introduction

Supramolecular-templated mesoporous materials, with their combination of high surface area, flexible pore sizes, and well-defined mesostructure, are attractive for designing catalysts and catalytic supports for improved product selectivity and yield [1-3]. These mesostructured materials can be tailored for catalytic applications by incorporating specific organo-functionalized groups onto the surface of the inorganic framework, which would modify the physical and chemical properties of the metal oxide support at the nanoscale to the desired application. For example, solid acid mesoporous catalysts have been formed by incorporating propylsulfonic acid groups into the mesopores by either grafting on the preformed mesostructure [4-7] or direct co-condensation during synthesis [8-12]. These organic-inorganic hybrids have demonstrated interesting catalytic properties [13-17], and as such understanding and controlling the properties of the acidic functional groups is important to optimal catalytic performance. Factors including solvent interaction, location of acidic sites, and proximity of the tethered acidic functional groups influence the catalytic activity of organosulfonic acid-functionalized mesoporous silica catalysts [18-20].

Herein is described the surface positioning of tethered propylsulfonic acid groups on SBA-15 mesostructured material as incorporated by the co-condensation synthesis technique, with the subsequent determination of the resulting acid strength for the catalytic material. The goal of this work is to demonstrate the importance of surface positioning of sulfonic acid groups functionalized on mesoporous silica materials on acid strength and catalytic performance of the resulting acidic solid catalyst.

4.2.   Experimental and Results

4.2.1. Synthesis of the Propylsulfonic Acid-Functionalized Mesoporous Silica (SBA-15-PrSO₃H)

Propylsulfonic acid-functionalized mesoporous silica materials were synthesized as described previously [21,22] with only slight modifications. In a typical synthesis of SBA-15-PrSO₃H, Pluronic P123 (8 g, 1.5 mmol) was dissolved in 250 ml of 1.9 M HCl solution at room temperature under stirring with subsequent heating to 40 °C before adding tetraethoxysilane (TEOS) (16.5 ml, 73.66 mmol). Approximately 45 min was allowed for prehydrolysis of TEOS prior to addition of x moles of (3-mercaptopropyl)trimethoxysilane (MTPMS) and y moles of H_2O_2 (where $x = 2.5 - 10$ mole ratio percent relative to the TEOS and $y = 3.5$ times the moles of MPTMS). The resulting mixture was agitated for 24 h at 40 °C and thereafter aged for 24 h at 100 °C under static conditions. The resulting solids were collected by filtration and then air-dried. The template was extracted by suspending the

white solid product in ethanol and refluxing for 24 h. To ensure complete removal of the surfactant, fresh ethanol was introduced after 12 h.

4.2.2. Synthesis of the Arenesulfonic Acid-Functionalized Mesoporous Silica (SBA-15-ArSO₃H)

SBA-15-ArSO₃H mesoporous silicas functionalized with arenesulfonic acid groups were synthesized as described elsewhere [21,22]. Following TEOS prehydrolysis, 2-(4-chlorosulfonylphenyl)ethyltrimethoxysilane (CSPTMS) was added and the resulting mixtures with molar composition of 0.0737 TEOS and x CSPTMS (where x = 2.5 – 10 mole ratio percent relative to the TEOS) were stirred for 24 h at 40 °C and thereafter aged for 24 h at 100 °C under static conditions. The solid product was recovered and the template was extracted as previously described.

4.2.3. Synthesis of Spatially Prearranged Propylsulfonic Acid-Functionalized Mesoporous Silica (SBA-15-PrSO₃H-Prox)

Mesoporous silica material modified with prearranged propylsulfonic acid groups was synthesized as described by Dufaud and Davis [19] with slight modifications. Dipropyl disulfide, a precursor for the spatially prearrangement of propylsulfonic acid groups, was synthesized by reacting 2,2'-dipyridyl disulfide (o,o'-Aldrithiol) (2 g, 9.08 mmol) dissolved in 20 ml dichloromethane with MTPMS (4.45 g, 22.6 mmol) at room temperature for 4 days under protection from light. The yellow solution was concentrated by rotary vaporization of

the solvent. Dry petroleum ether was subsequently added to the solution to precipitate pyridine-2-thione, then dipropyl disulfide was extracted by filtration and vaporization of the solvent. The precursor was further dried in a vacuum oven for 4 h and afterward stored in airtight vial.

SBA-15-PrSO$_3$H-Prox mesoporous silica, which was functionalized with prearranged propylsulfonic acid, was synthesized as previously described using the co-condensation technique. Following prehydrolysis of TEOS (16.5 ml, 73.66 mmol) in acidic solution (1.9 M HCl) with Pluronic P123 surfactant, x moles of dipropyl disulfide (where $x = 1.25 - 5$ mole ratio percent relative to the TEOS) was added to the synthesis mixture. The resulting synthesis mixture was treated as described previously for the propylsulfonic acid-functionalized materials. The resulting solid product was denoted SBA-15-PrSS.

The generation of adjacent propylsulfonic acid groups on the mesoporous silica was achieved by cleaving and oxidizing the disulfide bonds of the tethered moieties with tris(2-carboxyethyl)-phosphine (TCEP) and H$_2$O$_2$, respectively. In a typical synthesis procedure, TCEP (4:1 molar ratio of TCEP to disulfide) was dissolved in 100 ml of 1.9 M HCl solution. The SBA-15-PrSS sample was subsequently suspended in the solution and agitated for 1 h at 40 °C. Afterward H$_2$O$_2$ (20:1 molar ratio of H$_2$O$_2$ to disulfide) was added and the mixture was continuously stirred for 24 h at 40 °C. The solid product was then filtered and thoroughly washed with ethanol. Scheme 4-1 shows the reaction pathway for the synthesis of spatially arranged propylsulfonic acid groups on the SBA-15 mesostructure.

4.2.4. Characterization

The textural properties of the acid-functionalized mesoporous silicas were measured using the BET procedure. Nitrogen adsorption-desorption isotherms were taken at -196 °C using a Micromeritics ASAP 2020 system. The surface area and pore volume/pore size distribution were calculated by the BET and BJH methods, respectively. All samples were degassed at 100 °C for 5 h prior to taking measurements. The organic content of the synthesized mesoporous materials was quantified by elemental analysis performed on a Perkin-Elmer Series II 2400 CHNS analyzer. The ion capacities of the acid-functionalized mesoporous silica were determined by acid-base titration. The textural and chemical properties of the synthesized organosulfonic acid-functionalized mesoporous silica materials are shown in Table 4-1. The organic composition and thermal stability of the solids were evaluated by thermogravimetric analysis (TGA) and differential thermoanalysis (DTA) with a Perkin-Elmer TGA7 instrument, with heating from 50 to 600 °C at a rate of 10 °C/min under airflow. Shown in Figure 4-1 is the DTA for organosulfonic acid-functionalized mesoporous silica materials. The relative *pKa* values of the sulfonic acid functional groups in the mesoporous silica were estimated by means of a Gran Plot. In a typical experiment, a sample with approximately 0.05 mmol acid sites was suspended in 100 ml of 1.5 mM NaCl in methanol. The resulting mixture was titrated potentiometrically by drop-wise addition of 2 mM NaOH in methanol.

4.2.5. Catalytic testing

The functionalized mesoporous silica materials were tested for catalytic activity under similar conditions as previously described [18,22]. The reagents used for the esterification reaction included palmitic acid (PA), refined soybean oil (SBO), and methanol (MeOH). The esterification reaction was performed under a nitrogen blanket in a high-pressure stainless-steel batch reactor (Eze-Seal, Autoclave Engineers Co., USA) fitted with a mechanical stirrer and a sample outlet. The oil mixture with PA/SBO weight ratio of 15:85 and PA/MeOH weight ratio of 1:20 was charged into the 100 ml reaction vessel. The catalyst loading with approximately 0.05 mmol acid sites per gram of PA and a reaction temperature of 85 °C was used. The reaction mixture was continuously stirred at a rate of 350 rpm. Samples were drawn at 10 min intervals and their acid values were determined using AOCS method Cd 3a-63 to determine the extent of palmitic acid conversion. Results shown in Figure 4-2 are for the acid-functionalized mesoporous silica samples, which had an MPTMS/TEOS molar ratio of 5%.

4.3. Discussion

Mesoporous silica materials functionalized with either propylsulfonic or arenesulfonic acid groups were synthesized as described elsewhere [21,22] and were denoted as SBA-15-PrSO$_3$H and SBA-15-ArSO$_3$H, respectively. The molar ratio of organosulfonic acid precursor to silica precursor was varied between 2.5 and 10%. Prior to co-condensation synthesis of the spatially organized propylsulfonic acid-functionalized mesoporous silica

material, the organic precursor was molecularly synthesized as described previously [19]. The disulfide bond of the tethered dipropyl disulfide moieties on the SBA-15 mesostructure was cleaved and oxidized in acidic medium with tris(2-carboxyethyl)-phosphine (TCEP) and H_2O_2 to generate propylsulfonic acid pairs. The resulting material was denoted SBA-15-PrSO$_3$H-Prox, where the suffix *Prox* designates intentional proximity of the functional groups.

The averaged textural properties of the synthesized organic-inorganic hybrid materials are summarized in Table 4-2. The incorporation of organosulfonic acid groups via co-condensation technique did not significantly affect the textural properties of the resulting materials relative to the unfunctionalized material. Incorporation of dipropyl disulfide moieties into the SBA-15 mesostructure and subsequent cleavage and oxidation of the disulfide bond to generate propylsulfonic acid pairs had no effect on the final structure of the material. The material functionalized with arenesulfonic acid groups had a larger median pore diameter (MPD) than propylsulfonic acid-modified mesoporous silica, which suggested that the hydrolysis and co-condensation of the hydrophobic benzenesulfonic acid and silica precursors around the surfactant micelles enlarged the micelles, leading to the larger mesopores.

The incorporation of the dipropyl disulfide organic groups into the SBA-15 mesostructure and subsequent conversion to propylsulfonic acid pairs was confirmed by differential thermoanalysis (DTA) as shown in Figure 4-3. Desorption of physisorbed water was observed below 110 °C for both the SBA-15-PrSS and SBA-15-PrSO$_3$H samples. SBA-15-PrSS showed a peak centered at 330 °C, which completely disappeared after reaction with TCEP and H_2O_2. The new peak centered at 460 °C, which was also observed in the SBA-15-

PrSO$_3$H samples (Figure 4-1) and assigned previously to propylsulfonic acid groups [12], demonstrated that the cleavage and oxidation of the disulfide bond was successfully accomplished. Figure 4-4a shows the sulfur content of the modified mesoporous silicas as determined by elemental analysis versus the molar ratio of the precursors used in the synthesis reaction. There was quantitative agreement between the molar ratios of the precursors used to synthesize the materials and the sulfur content of the final product, demonstrating a high incorporation yield of the organosulfonic acid precursor. The ion capacity of the acid-functionalized mesoporous materials as determined by acid-base titration was consistent with the sulfur content of the final product (Figure 4-4b), confirming that the *in situ* oxidation of the propylthiol moieties was also successful.

Many researchers have employed reaction kinetics as a tool to investigate the acid strength of organosulfonic acid-functionalized mesoporous materials, which can be deceiving since the apparent acid strength of the solid catalyst determined by the reaction models will depend on complex and subtle factors such as reaction medium, location of the acid groups, ion capacity, and accessibility of the acid sites. As a result, it is important to quantify the acid strength of the acid-functionalized materials independently. Potentiometric titration with the Gran Plot technique was used to determine the relative *pKa* values of the synthesized acid-functionalized mesoporous silica samples in dilute methanol solution (ionic strength = 1.8×10^{-3} M). Methanol was selected as the solvent for the study because it is a differentiating solvent for the type of acidic groups used in the current study. Shown in Figure 4-5 are the calculated *pKa* values versus the molar ratio of synthesis precursors. To eliminate the effect of the sulfonic acid group concentration on the measured acid strength value, 0.05 mmol acid sites per sample was used in all potentiometric titrations. As shown in

the figure, the relative pKa values of the samples indicated that the acid strength of SBA-15-PrSO$_3$H-Prox was higher than SBA-15-PrSO$_3$H and comparable to SBA-15-ArSO$_3$H. The lower pKa values for SBA-15-PrSO$_3$H-Prox were consistent with enhancement of the acid strength of the sulfonic acid groups through a cooperative effect due to the proximity of acidic groups [19]. The relative pKa values for each catalyst type decreased as the number of sulfonic acid groups increased, which indicates that the mutual interaction between the acid sites increased for increasing surface concentration, leading to a higher overall acid strength of the solid catalyst. It is noteworthy that the relative pKa values of the SBA-15-PrSO$_3$H sample set decreased faster than SBA-15-PrSO$_3$H-Prox samples as the concentration of sulfonic acid was increased. This result suggests that the co-condensation technique incorporated the propylsulfonic acid groups randomly across the pore surface since the acidic sites only interacted when the sulfonic acid concentration on the surface was increased. The lower pKa values for the arenesulfonic acid-functionalized mesoporous silica samples was consistent with the introduction of a phenyl group in the tether, which is more electronegative than the aliphatic carbon chain, leading to an organosulfonic acid with increased acid strength [21].

The catalytic activity of the organosulfonic acid-functionalized mesoporous silica materials was investigated in the methanol esterification of palmitic acid using the procedure discussed previously [22]. The order of catalytic reactivity, as estimated by turnover frequency, for the functionalized mesoporous silica samples, which had an MPTMS/TEOS molar ratio of 5%, was SBA-15-ArSO$_3$H (1.08 min^{-1}) > SBA-15-PrSO$_3$H-Prox (0.85 min^{-1}) > SBA-15-PrSO$_3$H (0.68 min^{-1}). The difference between the catalytic performance and acid strength of the organosulfonic acid-functionalized mesoporous silica materials suggest that

additional factors beyond acid strength can affect the ultimate performance of the acid solid catalyst.

4.4. Conclusions

In summary, this work demonstrated that incorporation of propylsulfonic acid groups via the co-condensation technique will result in randomly tethered sulfonic acid groups that must be at a higher surface concentration to achieve a cooperative effect between acid sites. However, incorporation of spatially organized sulfonic acid groups enhanced acid site collaboration even at low surface concentrations, which resulted in higher acid strength. The esterification results confirmed that kinetic studies alone can underestimate or exaggerate the relative acid strength of a solid acid catalyst. In addition, the potential of designing the catalytic environments of propylsulfonic acid-functionalized mesoporous silica material to enhance the acid strength of the final solid catalyst was demonstrated.

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Table 4-1. Physical and chemical properties of the organosulfonic acid-functionalized mesoporous silica samples

Catalysts	MPTMS/TEOS molar ratio (%)	Textural Properties			Chemical Properties		
		S_{BET} (m²/g)	MPD (Å)	V_p (cm³/g)	C/S (mol/mol)	S (mmol/g)	H^+ (mmol/g)
SBA-15-PrSO₃H	2.5	780	59	1.12	18.8	0.29	0.35
	5.0	650 ± 70	56 ± 1	0.91 ± 0.07	17.6 ± 2.3	0.54 ± 0.10	0.54 ± 0.03
	7.5	700 ± 50	57 ± 4	0.99 ± 0.01	8.3 ± 1.1	0.73 ± 0.03	0.72 ± 0.01
	10	740 ± 60	55 ± 1	0.98 ± 0.01	5.3 ± 0.0	1.00 ± 0.05	0.98 ± 0.03
SBA-15-ArSO₃H	2.5	680	67	1.10	40.6	0.19	0.27
	5.0	680	68	1.07	26.2	0.38	0.46
	7.5	720	69	1.13	19.3	0.54	0.67
	10	680	65	1.02	16.3	0.63	0.71
SBA-15-PrSS	2.5	770	57	1.05	24.0	0.31	
	5.0	730	53	0.95	16.0	0.51	
	7.5	680	57	0.90	13.2	0.66	
	10	740	44	0.72	8.8	1.31	
SBA-15-PrSO₃H-Prox	2.5	760	60	1.08	19.7	0.23	0.28
	5	790	57	1.04	9.4	0.48	0.43
	7.5	650	56	0.88	10.4	0.65	0.46
	10	680	44	0.66	5.7	1.06	1.04

Table 4-2. The textural properties of the synthesized organic-inorganic hybrid mesoporous materials

Sample Description	Textural Properties [a]		
	S_{BET} (m^2/g)	MPD (Å)	V_p (cm^3/g)
SBA-15-PrSO₃H	710 ± 50	58 ± 2	1.01 ± 0.07
SBA-15-ArSO₃H	690 ± 20	67 ± 2	1.08 ± 0.05
SBA-15-PrSS	730 ± 40	53 ± 6	0.91 ± 0.14
SBA-15-PrSO₃H-Prox	720 ± 70	54 ± 7	0.92 ± 0.19

[a] The textural properties of each sample are an average of four samples with different MPTMS/TEOS molar ratios. See Table 4-1 for detailed results.

Scheme Captions

Scheme 4-1. Schematic representation of dipropyl disulfide synthesis, incorporation into

SBA-15 mesostructured material and subsequent cleavage and oxidation to

form the spatially arranged sulfonic acid groups.
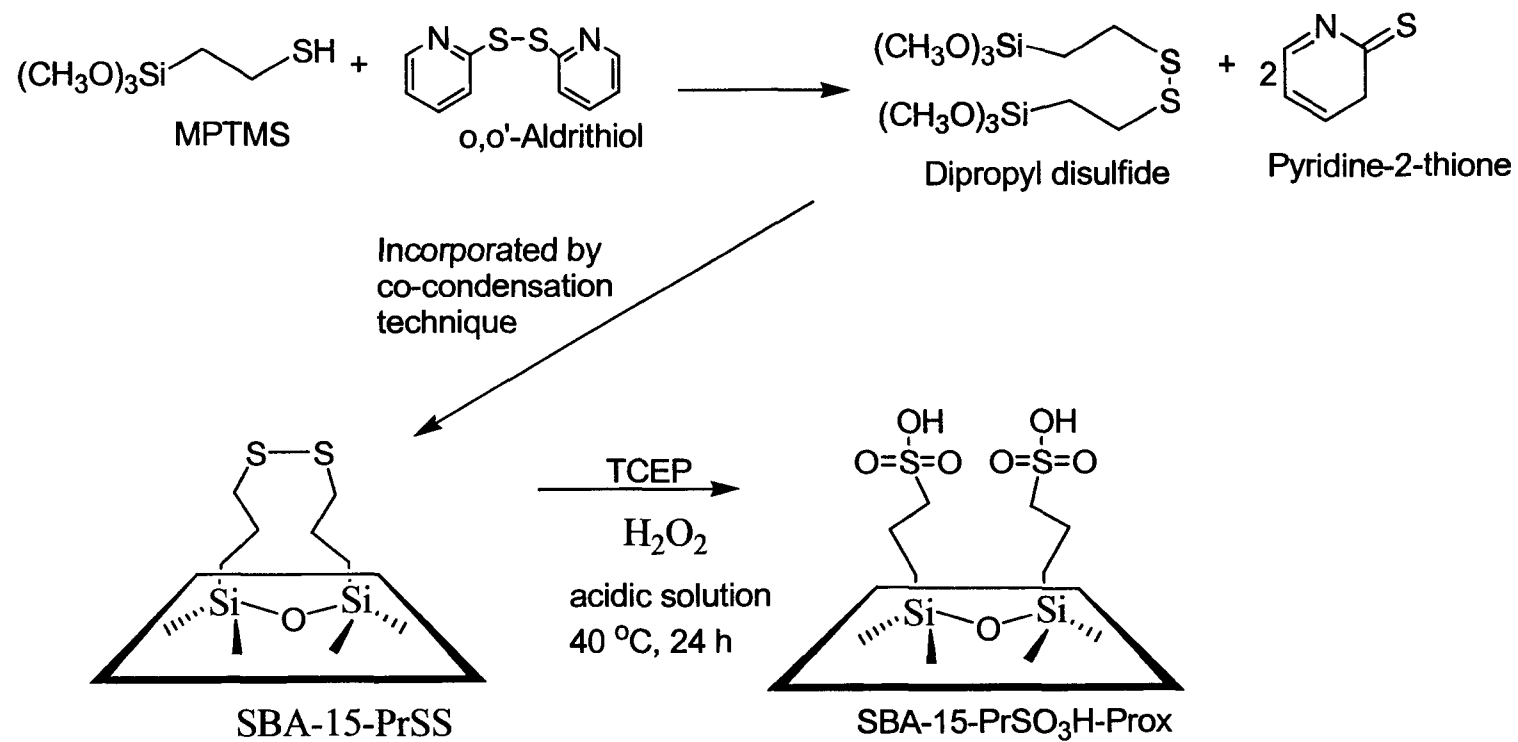
Figure Captions

Figure 4-1. Differential thermoanalysis of organosulfonic acid-functionalized mesoporous

silica materials.

Figure 4-2. Catalytic performance of the organosulfonic acid-functionalized mesoporous

silica catalysts in the methanol esterification of palmitic acid in a soybean oil

mixture.

Figure 4-3. Differential thermoanalysis (DTA) of organosulfonic acid-functionalized

materials (○: SBA-15-PrSS; □: SBA-15-PrSO3H-Prox)

Figure 4-4. Chemical properties of sulfonic acid-functionalized materials as determined by

(a) CHNS elemental analysis, (b) acid-base titration (♦: SBA-15-PrSO3H; ■:

SBA-15-ArSO3H; ▲: SBA-15-PrSO3H-Prox)

Figure 4-5. Acid strength of acid-functionalized materials as determined by potentiometric

titration in dilute methanol solution (♦: SBA-15-PrSO3H; ■: SBA-15-ArSO3H;
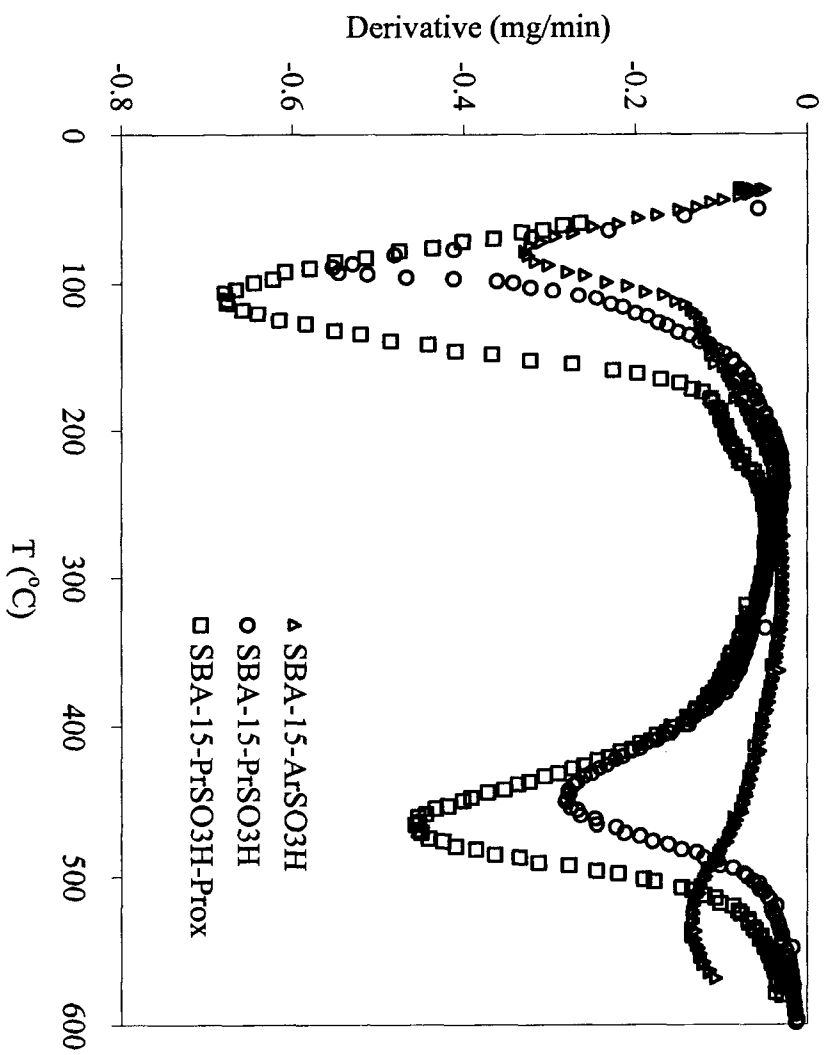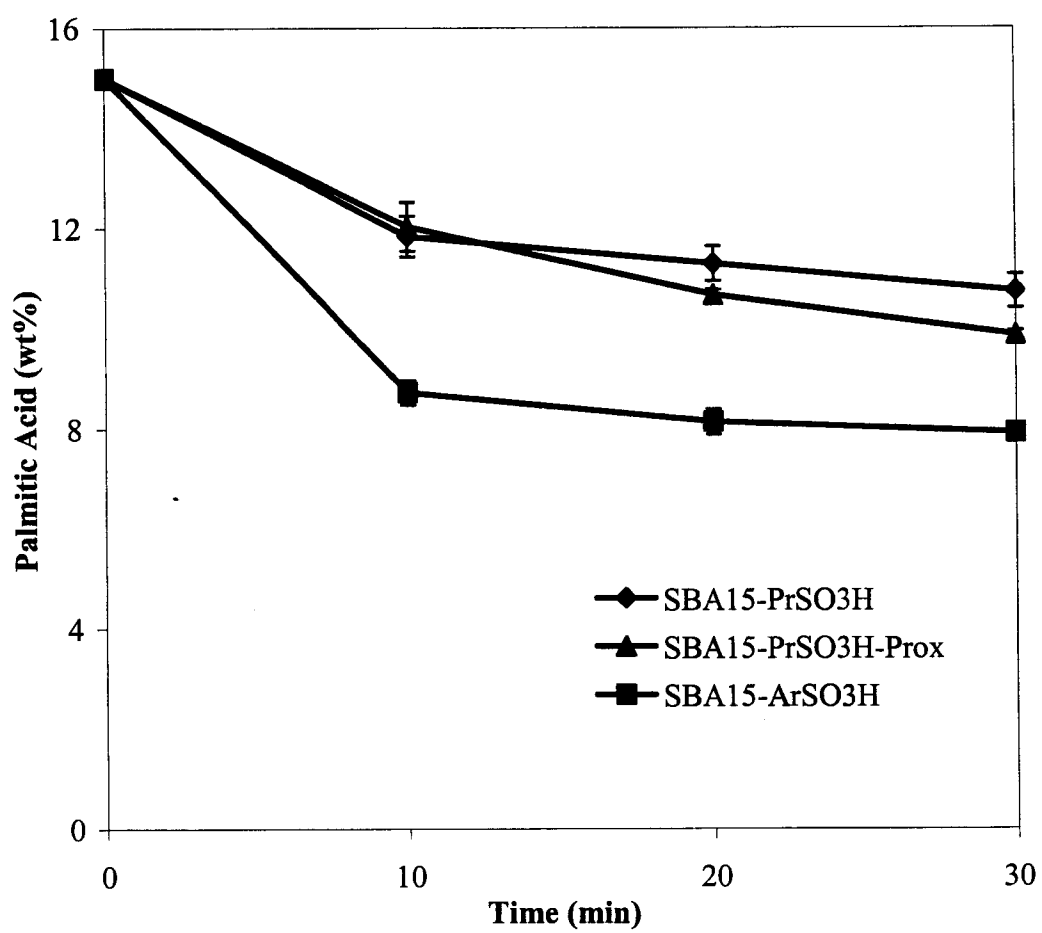
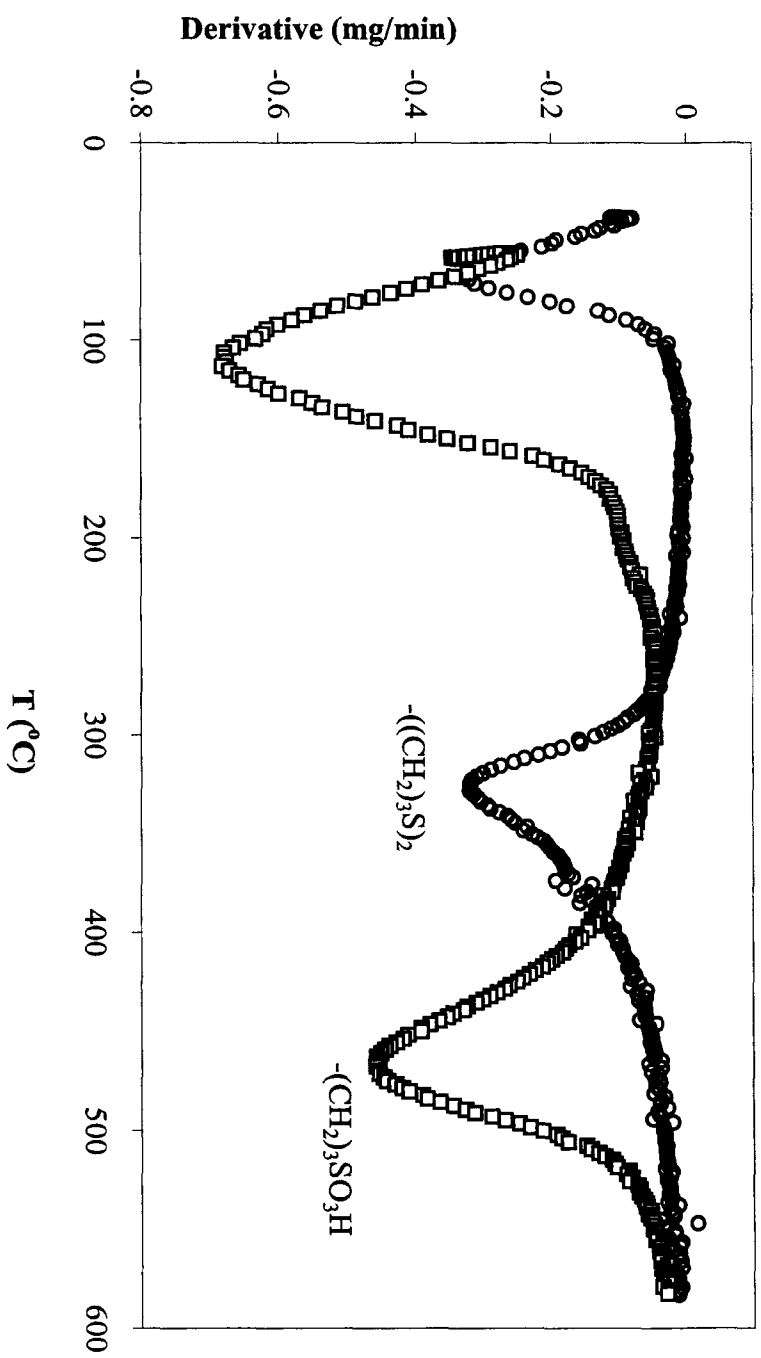▲: SBA-15-PrSO3H-Prox).

Scheme 4-1.

Figure 4-1.

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Figure 4-2.

Figure 4-3.

-((CH$_2$)$_3$S)$_2$

-(CH$_2$)$_3$SO$_3$H

Figure 4-4.

(a)
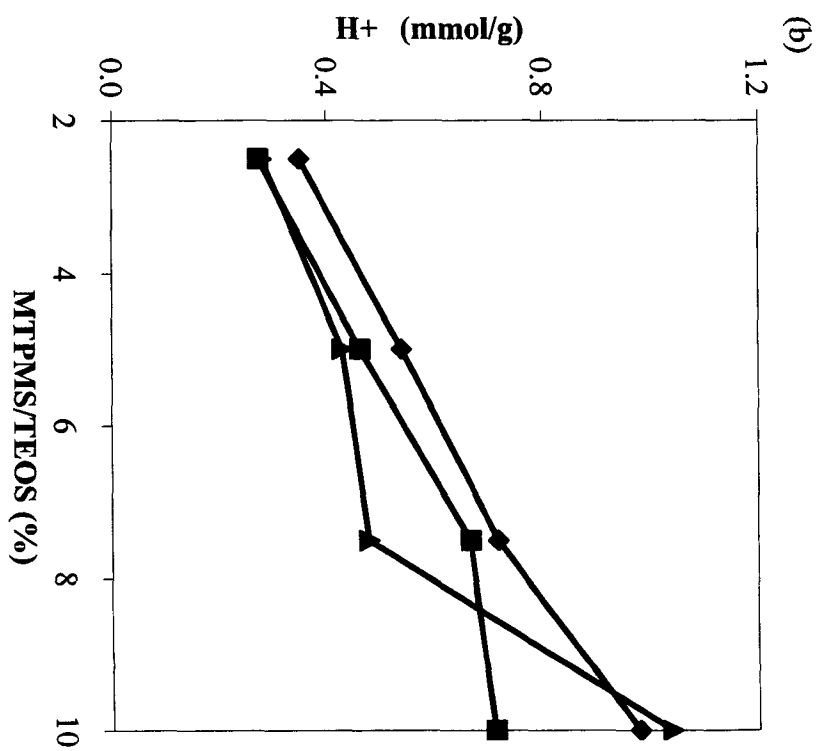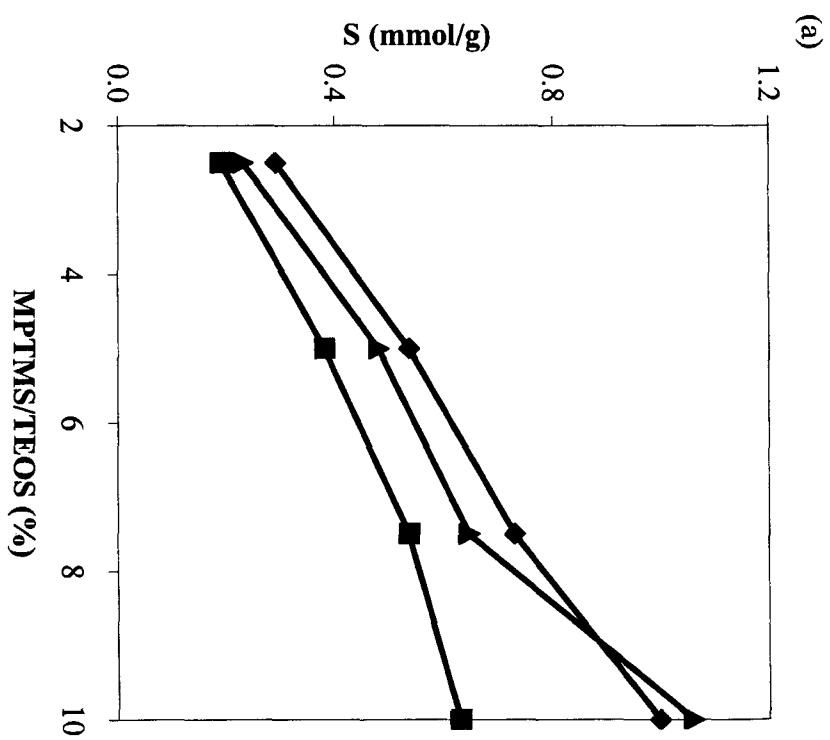
S (mmol/g)

MPTMS/TEOS (%)

(b)

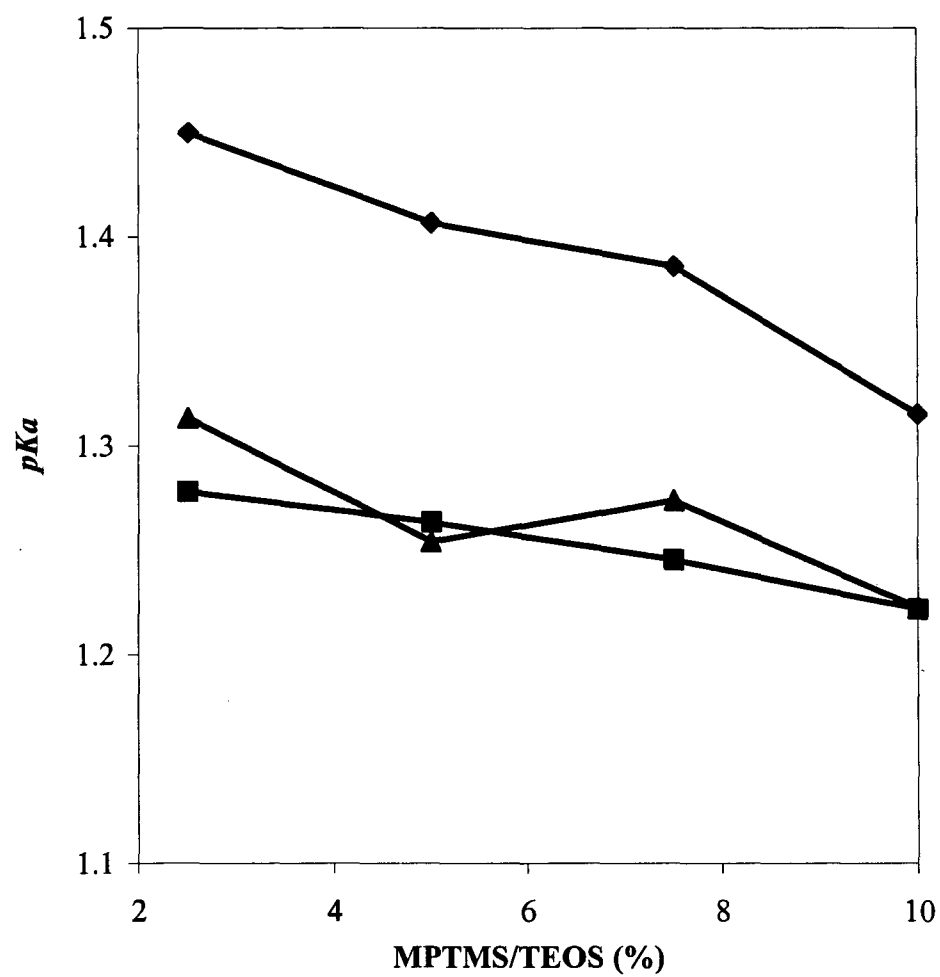H+ (mmol/g)

MTPMS/TEOS (%)

Figure 4-5.

CHAPTER 5

Acidic Mesoporous Silica for the Catalytic Conversion

of Free Fatty Acids in Beef Tallow

A paper to be submitted to *Industrial & Engineering Chemistry Research*

5.1   Introduction

The transesterification of vegetable oils with short-chain alcohols (e.g. methanol) in the presence of an alkaline catalyst to form alkyl esters has shown potential application as an intermediate for value-added chemicals as well as alternative transportation fuel (biodiesel) [1-6]. However, the production of alkyl esters has been limited due to inability to compete effectively with mature petrochemicals because of high raw and production cost. To improve the economic outlook of alkyl esters in general, the selection of raw materials, reaction conditions, and the use of efficient catalysts become critical. The availability of significantly less expensive oil feeds such as beef tallow or yellow grease provides an alternative feedstock to vegetable oils [7-10]. Unfortunately, these oil feeds have high free fatty acid (FFA) content, which is not compatible with the homogeneous catalyst used in the transesterification reaction given, that the FFA will saponify the alkaline catalyst, causing depletion of catalyst through formation of soap as well as subsequent difficulties in product separation. For these feedstocks to be processed in a standard transesterification process, the FFA content should be lowered to no more than 0.5 wt% [11], which could be achieved by first esterifying the FFA in the presence of acidic catalyst. Such a pretreatment process has

been successfully demonstrated using sulfuric acid; however, the use of homogeneous catalyst adds neutralization as well as separation steps to the process [12]. Consequently, it would be desirable to use heterogeneous acidic catalyst to esterify the FFAs to simplify the pretreatment process.

Inorganic mesoporous silica materials are emerging to be of significant interest, particularly in catalysis applications, owing to a combination of large surface area, flexible pore sizes, and the ability to control the catalytic functionalities at the molecular level [13-16]. The physical and chemical properties of these surfactant-templated mesostructured materials can be modified by incorporating functionalized organic groups, either by grafting on the preformed mesopore surface or by one-step co-condensation during synthesis [17-20]. Several studies have shown that incorporation of alkylsulfonic acid groups into the mesoporous silicas framework would generate acidic solid catalysts that could catalyze esterification [20-24]. We recently demonstrated an application of alkylsulfonic acid-functionalized mesoporous silicas in the esterification of a model feed containing 15 wt% palmitic acid in refined soybean oil [25]. The composition of the model feed was comparable to that of natural oil with high FFA content. The organosulfonic acid-functionalized mesoporous catalysts exhibited high catalytic performance in the methanol esterification of palmitic acid.

It is noteworthy that, although the amount of palmitic acid used in the model feed was equivalent to the quantity of FFA found in beef tallow or yellow grease, the assorted distribution of fatty acid composition in animal fats could affect the catalytic performance of the solid acidic catalyst. Animal fats typically have high concentrations of saturated fatty acids (e.g. palmitic and stearic acids) and low concentrations of polyunsaturated fatty acids

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(e.g. linoleic and linolenic acids) as compared to that of vegetable oils, which is expected to have minimum effect on the catalytic performance of the solid catalyst. To further reduce the raw material and production costs in the manufacture of alkyl esters for fuel consumption (biodiesel), it would be prudent to use unrefined beef tallow as produced from meat packinghouses. However, such feedstocks have nitrogenous materials (e.g. proteinaceous matter and phosphatides), which could affect the catalytic performance of the acid-modified mesoporous silica catalyst. Therefore, esterification of FFA, such as found in unrefined beef tallow, would give a meaningful catalytic demonstration of the organosulfonic acid-functionalized mesoporous silicas in the pretreatment of natural oil feeds with high FFA concentrations of for biodiesel production.

Herein the utilization of propylsulfonic acid-functionalized mesoporous silica catalyst in the pretreatment esterification of FFA in unrefined beef tallow is described. The results for the catalytic performance of the acid-functionalized mesoporous silicas are compared to commercial acidic catalysts.

5.2. Experimental

Floatation beef tallow grade (Tyson Foods Inc., USA) with approximately 7 wt% FFA concentration, as measured according to AOCS method Ca 3a-63, was used in this study. Anhydrous methanol (MeOH) was obtained from Fisher Scientific Inc. Activated charcoal (Acros) and TriSyl 300 (Grace Davison Co., USA) were used to pretreat the floatation beef tallow. Propylsulfonic acid-functionalized mesoporous silica (SBA-15-SO₃H) was synthesized according to the procedure described elsewhere [25]. Tetraethoxysilane

(TEOS) (98%, Aldrich) and (3-mercaptopropyl)-trimethoxysilane (MPTMS) (85%, Acros) were used as purchased for silica matrix and propylsulfonic acid precursors, respectively. MPTMS was oxidized *in situ* with H_2O_2 to convert the thiol species into propylsulfonic acid moieties. Hydrophobicity of the acidic catalyst was modified by incorporating propyltrimethoxysilane (PrTMS) (98%, Aldrich) into the mesostructure of the mesoporous silica during the co-condensation as described previously [26]. The mesoporous silica material modified with both the hydrophobic and acid functional groups was denoted as SBA-15-SO$_3$H-Pr. Pluronic P123 (BASF Co., USA), a triblock copolymer of polyethylene oxide-polypropylene oxide-polyethylene oxide with a molecular structure of PEO_{20}-PPO_{70}-PEO_{20}, was used as a template to tailor the textural properties of the mesoporous silica catalyst. Once the mesostructure of the silica materials was formed, the template was extracted from the mesopores by refluxing the solid in boiling ethanol for 24 h.

5.2.1. Catalyst Characterization

The textural properties of the acid-modified mesoporous material were determined by nitrogen adsorption-desorption isotherms measured at -196 °C with a Micromeritics ASAP 2020 system. The surface area and pore size distribution were calculated by the BET and BJH methods, respectively. Prior to taking measurements, all samples were degassed at 100 °C for 5 h. The ion-exchange capacities of the propylsulfonic acid-functionalized mesoporous silica materials were determined using an acid-base titration technique. The organic content of the synthesized material was determined by elemental analysis performed on a Perkin-Elmer Series II 2400 CHNS analyzer. The organic composition of the organic-

inorganic hybrid mesoporous silica was determined by thermogravimetric analysis (TGA) and differential thermoanalysis (DTA) performed on a Perkin-Elmer TGA7, with heating from 50 to 600 °C at a rate of 10 °C/min under airflow.

5.2.2. Catalytic Testing

The catalytic activity of the synthesized propylsulfonic acid-functionalized mesoporous silica catalyst was tested in the methanol esterification of FFA present in floatation beef tallow. The reaction was performed under similar conditions as described previously [25,26]. The esterification reactions were performed under nitrogen in a 100 ml high-pressure stainless-steel batch reactor (Eze-Seal, Autoclave Engineers Co., USA) fitted with a mechanical stirrer and a sample outlet. The reaction mixture was maintained at a constant temperature with the aid of heating mantle and integrated water-cooling system. The floatation beef tallow was charged into the reaction vessel with methanol at a ratio of 1:20 w/w (FFA:MeOH). The reaction conditions used in this study included a catalyst loading equivalent to 10 wt% of FFA, reaction temperature of 120 °C, and mixing rate of 350 rpm. Samples were drawn at preset time intervals and their acid values were determined using the AOCS method. The catalytic performance of the synthesized mesoporous catalyst was compared to sulfuric acid (Fisher Scientific) and Nafion NR50 (SA = 0.02 m^2/g, H^+ capacity = 0.8 meq/g, Alfa Aesar Co., USA) catalysts.

5.2.3. Beef Tallow Purification

To understand the effect of impurities present in beef tallow on the catalytic performance of the propylsulfonic acid-functionalized mesoporous silica catalysts, the flotation beef tallow was purified with industrial purification agents, such as activated charcoal or activated clay, prior to the esterification reaction. In the first batch, activated charcoal equivalent to 20 wt% of beef tallow was charged into the oil and heated to 80 °C for 1 h under continuous stirring. Prior to the purification step, the activated charcoal was evacuated overnight at 200 °C. The purified oil was filtered using Whatman filter paper No. 41. In the second batch, the floatation beef tallow was purified with TriSyl 300 silica powder according to the procedure described by Verhe [27]. In a typical purification procedure, TriSyl 300 silica powder and water equivalent to 0.3 and 0.5 wt% of beef tallow were added into the oil and heated to 80 °C for 30 min while mixing vigorously. The oil was filtered as described previously then subsequently dried at 95 °C in vacuum oven for 2 h.

5.3.   Results and discussion

The textural properties of the synthesized modified mesoporous silica are summarized in Table 5-1. The large BET surface area was consistent with reported surface areas of organosulfonic acid-functionalized mesoporous materials synthesized using nonionic surfactants as templates [28]. In the previous study, it was shown that the catalytic performance of the organosulfonic acid-functionalized mesoporous silica catalyst in the methanol esterification reaction of palmitic acid in soybean oil mixture was dependent on the

size of the median pore diameter (MPD) [25]. Since the composition of FFA in beef tallow is typically long chains of saturated and monounsaturated fatty acid, it is necessary to design a mesoporous catalyst with large pore mouths in order to minimize pore diffusion of the reactants. Consequently, Pluronic P123, which Zhao *et al.* [29] have shown to generate large mesopores, was used to tailor the textural property of the acid-functionalized mesoporous silica with the intention of enlarging the pore size of the catalyst. As seen in the table, the MPD of the synthesized organic-inorganic hybrid material, which was determined by the BJH method, was in the range reported for mesoporous silica synthesized with Pluronic P123 [26,29]. Co-condensation of hydrophobic and acid functional groups into the mesostructure of the silica matrix seemed to insignificantly affect the BET surface area, pore volume, and MPD of the final solid material.

Shown in Figure 5-1 is the nitrogen adsorption-desorption isotherm of the synthesized propylsulfonic acid-functionalized mesoporous (SBA-15-SO_3H) catalyst measured at -196 °C. The isotherm shows a hysteresis loop with sharp adsorption and desorption curves, which is a typical characteristic of mesoporous materials tailored with nonionic surfactant [29,30]. The pore-size distribution for the synthesized organic-inorganic hybrid mesoporous material was calculated with the BJH method on the adsorption branch of the nitrogen adsorption-desorption isotherm and is shown in Figure 5-1 insert. The unimodal pore-size distribution of the SBA-15-SO_3H was consistent with that reported for mesoporous silica templated with nonionic surfactant. Similar physical characteristics of mono-functionalized mesoporous material were observed in the synthesized bi-functionalized catalyst.

The relative carbon/sulfur molar ratio and the sulfur content of the synthesized mesoporous catalysts, as determined by elemental analysis, are summarized in Table 5-1.

The C/S molar ratio was greater than that expected for propylsulfonic acid (C/S = 3), indicating the presence of extra carbon from either unhydrolyzed precursor groups or chemisorbed ethanol [26]. The mass balance performed on sulfur from synthesis solution to dry solid (0.92 S mmol/g dry sample) agreed well with the sulfur content determined by elemental analysis, signifying high incorporation yield of the propylsulfonic acid precursor into the silica matrix. The similarity of the sulfur composition between the mono- and bi-functionalized mesoporous silica implied that incorporation of propyl group insignificantly affected the resulting sulfur content of the catalysts. The C/S molar ratio of the SBA-15-SO$_3$H-Pr was higher than the SBA-15-SO$_3$H, as expected given that the incorporation of the propyl group in the bi-functionalized mesostructured material would double the carbon content since the molar ratio of the propyl/propylthiol precursors was unity. The ionic capacity of the acid-modified mesoporous silica materials as determined by acid-base titration is given in Table 5-1. The number of sulfonic acid groups in both the mono- and bi-functionalized mesoporous silica materials was consistent with that of the sulfur content as determined by elemental analysis, implying that the oxidation of the tethered thiol group to generate propylsulfonic acid moieties on the mesoporous silica surface was effective. Addition of hydrophobic group to propylsulfonic acid-functionalized mesoporous silica material had no effect on the concentration of the acidic sites of the resulting solid catalyst.

The thermal decomposition of the propylsulfonic acid-modified mesoporous silica catalyst is shown in Figure 5-2. The TGA and DTA analysis of SBA-15-SO$_3$H show weight losses centered at 80 and 460 °C. The first and second weight losses were assigned to water desorption and organic decomposition of the organosulfonic acid group, as reported in the literature [23,31,32]. The thermal decomposition of SBA-15-SO$_3$H-Pr sample showed

similar peaks to that of mono-functionalized mesoporous silica, implying that probably both the propyl and propylsulfonic acid groups decomposed at approximately the same temperature. Decomposition of the propylthiol group, which Diaz *et al.* [23] has reported to occur around 350 °C, was not observed on either the mono- or bi-functionalized mesoporous silica catalysts, demonstrating that the thiol precursor was converted to propylsulfonic acid moieties. This observation further substantiates the results of sulfur content and the number of sulfonic acid groups in the synthesized mesoporous silica materials, as determined by elemental analysis and acid-base titration, respectively.

The objective of this study was to lower the FFA content in floatation beef tallow to no more than 0.5 wt% by esterifying the FFA in the presence of acidic catalyst, so that the unreacted triglycerides can be processed in a standard transesterification reaction system. Besides the esterification of FFA in floatation beef tallow, evaluation of the long-term catalytic performance of the catalysts is important to minimize the production cost of biodiesel. Prior to conducting experimental tests with floatation beef tallow, we investigated the recyclability of propylsulfonic acid-functionalized mesoporous silica catalyst in the methanol esterification of a model feed, composed of 15 wt% palmitic acid and 85 wt% refined soybean oil, under similar reaction conditions as described previously. The catalytic performance of the recycled catalyst in esterifying palmitic acid was similar to that of fresh catalyst, achieving a conversion of 95 wt% after 2 h, which demonstrated that propylsulfonic acid-functionalized mesoporous silica catalyst could catalyze multi-cycles without significant loss of catalytic activity. Therefore, esterification reaction of FFA in floatation beef tallow was expected to give better insight on the catalytic performance of the synthesized solid acid catalyst in pretreating unrefined oil feeds for biodiesel production. The pretreatment step

was performed in excess methanol to favor the forward reaction, given that the esterification reaction of FFA with alcohol is reversible [33]. To provide a comparison for the synthesized catalyst, the esterification was also performed with sulfuric acid and Nafion NR50. A catalyst loading equivalent to 10 wt% of FFA was used for all reactions studied.

Shown in Figure 5-3 are the results for reaction studies performed at 120 °C with a methanol to FFA ratio of 20:1 by weight. The figure gives the weight percentage conversion of FFA in floatation beef tallow as a function of reaction time. Since this study is an extension of previous work on applying organosulfonic acid-functionalized mesoporous silica in esterifying palmitic acid in soybean oil mixture, the reaction parameters, such as reaction temperature, reaction time, and stirring rate, were determined according to the conclusions of those studies [25,26]. As shown in the figure, both the propylsulfonic acid-functionalized mesoporous catalyst (Figure 5-3(a)) and Nafion NR50 (Figure 5-3(b)) gave high catalytic performance in the methanol esterification of FFA in floatation beef tallow, achieving a conversion of 94 and 96 wt% after 2 h, respectively. The catalytic activity of the SBA-15-SO$_3$H was consistent with previous studies, which demonstrated that propylsulfonic acid-modified mesostructured silica material could catalyze the esterification of fatty acids in beef tallow [20-23,25]. The high catalytic performance of both solid catalysts in esterifying FFA in floatation beef tallow could be attributed to robust acidic sites that were readily accessible. The initial catalytic activity of SBA-15-SO$_3$H was higher than that of Nafion NR50, as can be seen after 30 min, attaining FFA conversions of 93 and 87 wt%, respectively. This observation suggested that the high initial catalytic activity of the propylsulfonic acid-modified mesoporous material was due to accessibility of acidic sites on the large internal surface area, given that the number of sulfonic acid groups was comparable

for the two solid catalysts. Nafion NR50 catalysts have low surface areas ($SA = 0.02$ m^2/g) and greatly depend on the swelling of their polymer matrices, unlike mesoporous silicas that have rigid mesostructures, resulting in poor accessibility of the highly acidic sites [34]. Sulfuric acid was the most active catalyst, attaining a FFA conversion of 96 wt% after 30 min (result not shown), was consistent with results reported in previous studies where loadings as low as 5 wt% were sufficient to esterify FFA completely [25,35]. The superior performance of sulfuric acid in FFA esterification was attributed to lack of mass transfer limitation, which is mostly encountered in solid catalysts. Unfortunately, the long-term catalytic performance of sulfuric acid could not be measured because the homogeneous catalyst forms uniform mixtures with the reactants, making it difficult to separate the catalyst from the product mixture.

Contrary to sulfuric acid, propylsulfonic acid-functionalized mesoporous silica and Nafion NR50 are solid catalysts that can easily be recovered from the reaction mixture by filtration. The recovered catalysts were rinsed with ethanol and then air-dried prior to being recycled for esterifying the FFA in floatation beef tallow. The catalytic performance of the catalysts recycled up to three times is shown in Figure 5-3. In the second cycle, Nafion NR50 showed a higher performance than SBA-15-SO$_3$H after 2 h, attaining FFA conversions of 94 and 68%, respectively. It is noteworthy that SBA-15-SO$_3$H exhibited a robust initial catalytic activity in the second cycle, attaining a conversion of 60 wt% after 30 min, despite a low overall catalytic performance (Figure 5-3). The reused acid-modified mesoporous silica and Nafion NR50 resin lost about 30% and 15% of its catalytic performance after the first cycle, respectively. The detrimental loss of catalytic activity was also observed in the third cycle, where the acidic mesoporous catalyst and Nafion NR50 had lost two-third and half of

their catalytic performances, respectively. It is evident that the loss of the catalytic activity did not vary greatly with the catalyst type, although the adverse effect was more apparent on the synthesized acidic mesoporous catalyst than on Nafion NR50. One possibility for reduced catalytic performance of the recycled catalyst was deposition of organic matter in the mesopores, which could result in poor accessibility of the acidic sites. However, after refluxing the synthesized acid-modified mesoporous silica in ethanol for 24 h to extract any trapped materials in the mesopores, there was no improvement in the esterification. This observation implied that either the sulfonic acid groups were leached or the acidic sites were poisoned.

To investigate the cause of poor performance of the reused acidic mesoporous catalyst in FFA esterification, the chemical and textural properties of the spent SBA-15-SO_3H catalyst were evaluated after refluxing in ethanol, and the results are summarized in Table 5-1. The relative C/S molar ratio doubled while the sulfur content decreased by 10%, which demonstrated that there was accumulation of carbon in the mesoporous silica material. This could indirectly affect the sulfur composition of the spent acidic solid catalyst, because elemental analysis determines the organic composition of a material based on the relative weight percentage. As a result, the low sulfur content of the spent catalyst does not imply that the sulfonic acid moieties were leached during the reaction. This observation was corroborated with the results of the number of sulfonic acid groups (Table 5-1). The ionic capacity of the sulfonic acid groups of the spent catalyst dropped by 33% even though only 10% of the sulfur content was lost, which implied that some of the acidic sites were inaccessible due to accumulation of carbonaceous materials. Thermal decomposition of organic materials in the spent catalyst was analyzed by TGA and DTA. The spent

mesoporous silica catalyst showed three peaks centered at 80, 300, and 460 °C, as shown in Figure 5-2. The first and third peaks were similar to that of a fresh catalyst, signifying the presence of physisorbed water and propylsulfonic acid moieties, respectively. The peak centered at 300 °C, which was also observed when beef tallow was decomposed (not shown), was assigned to the decomposition of carbonaceous material associated with beef tallow deposited inside the mesopores of the synthesized mesoporous sample. The accumulation of carbon inside the spent catalyst was further confirmed by nitrogen adsorption-desorption analysis (Figure 5-1). The adsorption-desorption isotherm of the spent catalyst had a similar profile as that of fresh catalyst except that less nitrogen was adsorbed. This observation illustrated that the methanol esterification of FFA in floatation beef tallow had an insignificant affect on the mesostructure of the synthesized propylsulfonic acid-functionalized mesoporous silica catalyst. However, the accumulation of carbonaceous materials associated with beef tallow inside the mesopores led to blockage of pores, as seen in the pore-size distribution graph (Figure 5-1 insert) as well as the decrease in surface area of the spent catalyst (Table 5-1).

Hitherto the only evidence that seems to significantly affect the catalytic performance of the synthesized acidic catalyst in FFA esterification in floatation beef tallow is the accumulation of carbon inside the mesopores. However, it should be noted that when palmitic acid in the model feed was esterified with methanol, loss of catalytic performance of the propylsulfonic acid-functionalized mesoporous catalyst was not observed after multiple cycles. Therefore, the deteriorating catalytic performance of the solid acid catalyst in FFA esterification would suggest that impurities in floatation beef tallow were poisoning the acidic sites.

Molten floatation beef tallow had dark brown color with a pungent odor, which indicated that the oil had impurities [36]. These impurities could interact with the acidic sites of the catalysts, rendering them inactive for further catalytic reactions. One approach to understand the effect of the impurities in beef tallow in the methanol esterification of FFA was to investigate the catalytic performance of the acid-modified mesoporous catalyst with purified beef tallow oil. The impurities in beef tallow can be extracted using adsorbents such as activated charcoal or clay, which are typically used in industries to extract coloring and polar compounds from natural oils. In this study, activated charcoal and TriSyl 300 silica powder were used to purify floatation beef tallow prior to esterifying FFA with methanol. After adsorbents filtration, beef tallow that was purified with activated charcoal was light yellow and almost odorless, while oil purified with TriSyl 300 was yellowish with a mild odor. Overall, these observations suggested that the impurities in the floatation beef tallow were reduced. The FFA content in both activated charcoal and TriSyl 300 purified beef tallow was approximately 7 wt%, which implied that the purification insignificantly affected the beef tallow's FFA content.

To probe the effect of the purification step on the catalytic performance of the acidic solid catalyst, SBA-15-SO$_3$H was used to catalyze FFA esterification in refined oil. Figure 5-4 shows a comparison of catalytic performance of SBA-15-SO$_3$H catalyst in FFA esterification in floatation beef tallow purified with (a) activated charcoal, and (b) TriSyl 300 silica powder. The purification of floatation beef tallow significantly affected the catalytic performance of the synthesized solid catalyst. In the first cycle, acid-functionalized mesoporous silica material performed typically with both activated charcoal and TriSyl 300 pretreated floatation beef tallow, attaining conversions of 86 and 91 wt% after 2 h,

respectively. However, the catalytic performance of reused SBA-15-SO₃H depended on the adsorbent used in the purification. For beef tallow purified with TriSyl 300 powder, reused SBA-15-SO₃H catalyst showed performed better in esterifying FFA, attaining similar conversions to that of fresh catalyst (Figure 5-4(b)) where FFA was reduced by 91 and 88 wt % in the second and third cycles, respectively. In contrast, reused solid catalyst performed relative less with beef tallow purified with activated charcoal, although the final conversion of 76 wt% was modestly better than that of unpurified oil. These results suggested that TriSyl 300 powder, unlike activated charcoal, eliminated impurities that inhibited the catalytic performance of the acid-functionalized mesoporous catalyst. Since these impurities were extracted with TriSyl 300 rather than hydrophobic activated charcoal, it indirectly suggest that the impurities in the beef tallow were polar compounds [37]. This would appear to explain the poisoning of the acidic sites of the synthesized catalyst, given that both the impurities and the organosulfonic acid groups are polar compounds.

An approach for improving the catalytic performance of organosulfonic acid group without requiring feedstock purification in biodiesel production is to modify the physical properties of the acid-functionalized mesoporous silica catalyst such that the impurities will not interact with the active sites. A method to potentially achieve this objective is to introduce hydrophobic groups (e.g. alkyl groups) into the mesopores of the propylsulfonic acid-functionalized mesoporous framework. The hydrophobic groups in the bi-functionalized mesoporous silica catalyst would be expected to prevent the polar impurities from interacting with the sulfonic acid groups. To accomplish this goal, the hydrophobic groups must be tethered adjacent to the sulfonic acid groups, located inside the mesopores. It was recently reported that mesoporous silica materials synthesized by co-condensation would

incorporate the bi-functional groups inside the mesoporous channels [26]. As a result, the same synthesis technique was used to integrate both the sulfonic acid and propyl groups into the silica mesostructure. The textural and chemical properties of the bi-functionalized mesoporous silica material were described previously.

The catalytic performance of the bi-functionalized mesoporous silica catalyst was evaluated in the methanol esterification of FFA in either unpurified or purified floatation beef tallow. In this study, TriSyl 300 silica powder was used to purify the beef tallow. The catalytic performance of the recycled bi-functionalized mesoporous catalyst improved significantly for both the purified and unpurified floatation beef tallow feeds, as shown in Figure 5-5. The SBA-15-SO_3H-Pr catalyst attained FFA conversions of 92 and 84 wt% in untreated beef tallow in the first and second cycles, respectively (Figure 5-5(a)). The catalytic performance of the reused SBA-15-SO_3H-Pr in FFA esterification in unpurified beef tallow was superior to that of SBA-15-SO_3H when reused in oil purified with activated charcoal. This result demonstrated that the introduction of the hydrophobic groups into the acid-modified solid catalyst inhibited the poisoning of the acidic sites. It is noteworthy that there was an insignificant drop in the catalytic performance of SBA-15-SO_3H-Pr in FFA esterification in oil purified with TriSyl 300, where the FFA conversion reached 92 and 91 wt% in the first and second cycles respectively (Figure 5-5(b)). More importantly, the initial catalytic activity of the reused catalyst was comparable to that of fresh catalyst. This result demonstrates that the introduction of the hydrophobic groups did not affect the performance of the sulfonic acid groups.

5.4. Conclusions

Propylsulfonic acid-functionalized mesoporous silica catalyst demonstrated high catalytic activity in the methanol esterification of FFA in floatation beef tallow. The synthesized acid-functionalized mesoporous silica showed a robust initial catalytic activity as compared to Nafion NR50. The catalytic performance of the recycled acidic mesoporous catalyst was negatively affected by the presence of polar impurities in floatation beef tallow. The performance of the acid-functionalized catalyst was significantly improved when the floatation beef tallow was treated with TriSyl 300 silica powder prior to the esterification. An acidic mesoporous catalyst integrated with a hydrophobic group showed enhanced catalytic performance in FFA esterification in untreated floatation beef tallow. This work demonstrates that mesoporous silicas are versatile materials that can be molecularly designed into acidic catalysts for the conversion of biorenewable feedstocks with minimum feedstock preparation.

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Table 5-1. Textural and chemical properties of the synthesized propylsulfonic acid-functionalized mesoporous silica catalyst before and after the esterification reaction of FFA in floatation beef tallow.

Catalyst	Catalyst Status	Textural Properties			Chemical Properties		
		S_{BET} $(m^2\,g^{-1})$	MPD (Å)	V_p $(cm^3\,g^{-1})$	C/S (mol/mol)	S (mmol/g)	H^+ (meq/g)
SBA-15-SO$_3$H	Fresh	780	51	0.98	5.35	0.96	1.00
SBA-15-SO$_3$H	Spent	500	57	0.72	11.21	0.86	0.67
SBA-15-SO$_3$H-Pr	Fresh	920	48	1.02	9.10	0.89	0.91

Figure Captions

Figure 5-1. Nitrogen adsorption-desorption isotherms of the propylsulfonic acid-

functionalized mesoporous silica (SBA-15-SO$_3$H) catalyst before and after FFA

esterification in floatation beef tallow. (●: fresh catalyst; ▲: spent catalyst)

Figure 5-2. TGA and DTA analysis of fresh and recycled SBA-15-SO$_3$H catalyst (◊: fresh

catalyst; Δ: spent catalyst).

Figure 5-3. Catalytic results for FFA esterification in floatation beef tallow with methanol

catalyzed by (a) SBA-15-SO$_3$H and (b) Nafion NR50 (120 °C; FFA:MeOH =

1:20; catalyst condition, ♦: 1st cycle; ■: 2nd cycle; ▲: 3rd cycle).

Figure 5-4. Reaction results for the methanol esterification of FFA in floatation beef tallow

purified with (a) activated charcoal (b) TriSyl 300 (120 °C; Catalyst = SBA-15-

SO$_3$H; FFA:MeOH = 1:20; catalyst condition, ♦: 1st cycle; ■: 2nd cycle; ▲: 3rd

cycle).

Figure 5-5. Catalytic performance of SBA-15-SO$_3$H-Pr in the methanol esterification of FFA

in floatation beef tallow (a) no purification (b) oil purified with Trysil 300 (120

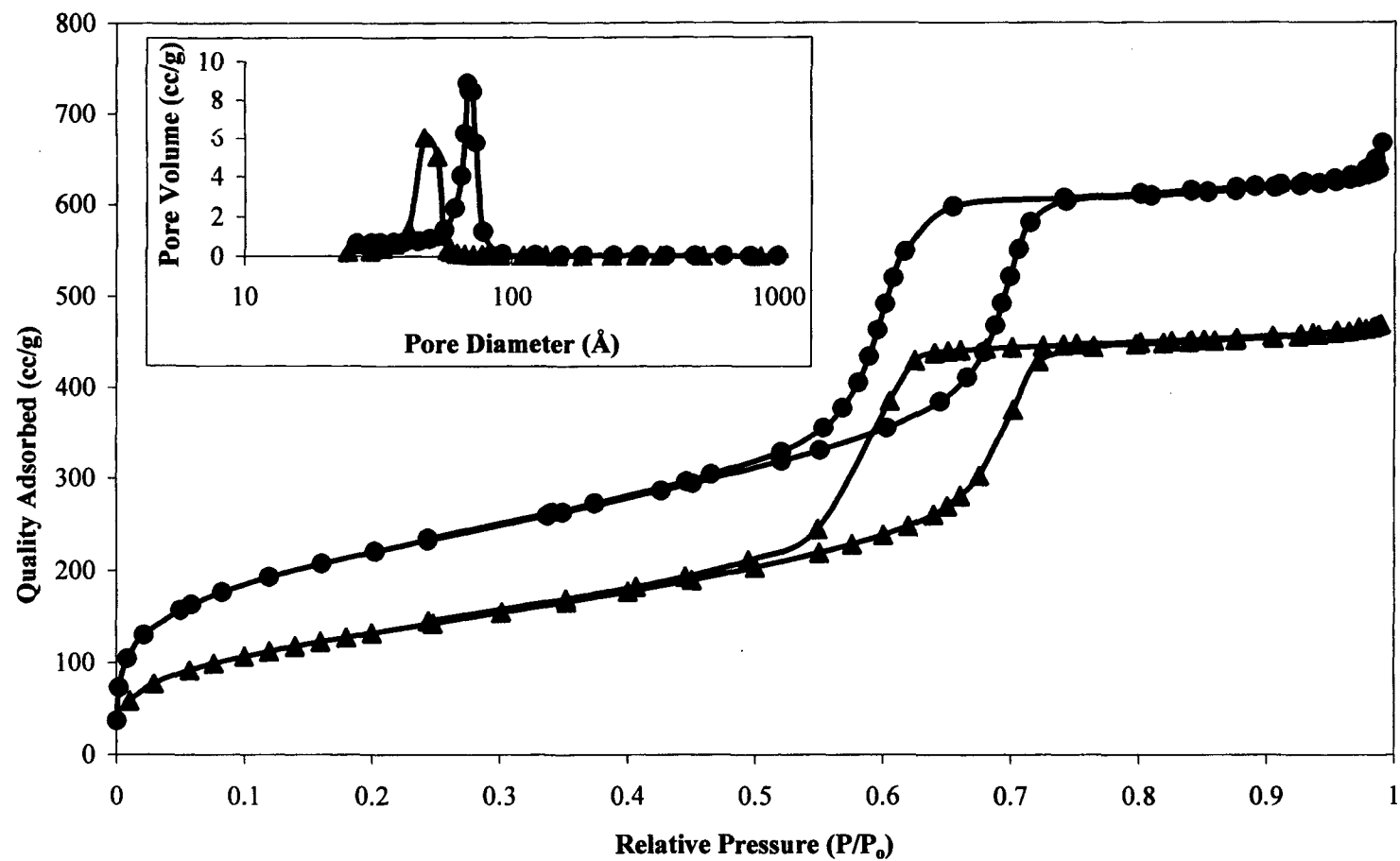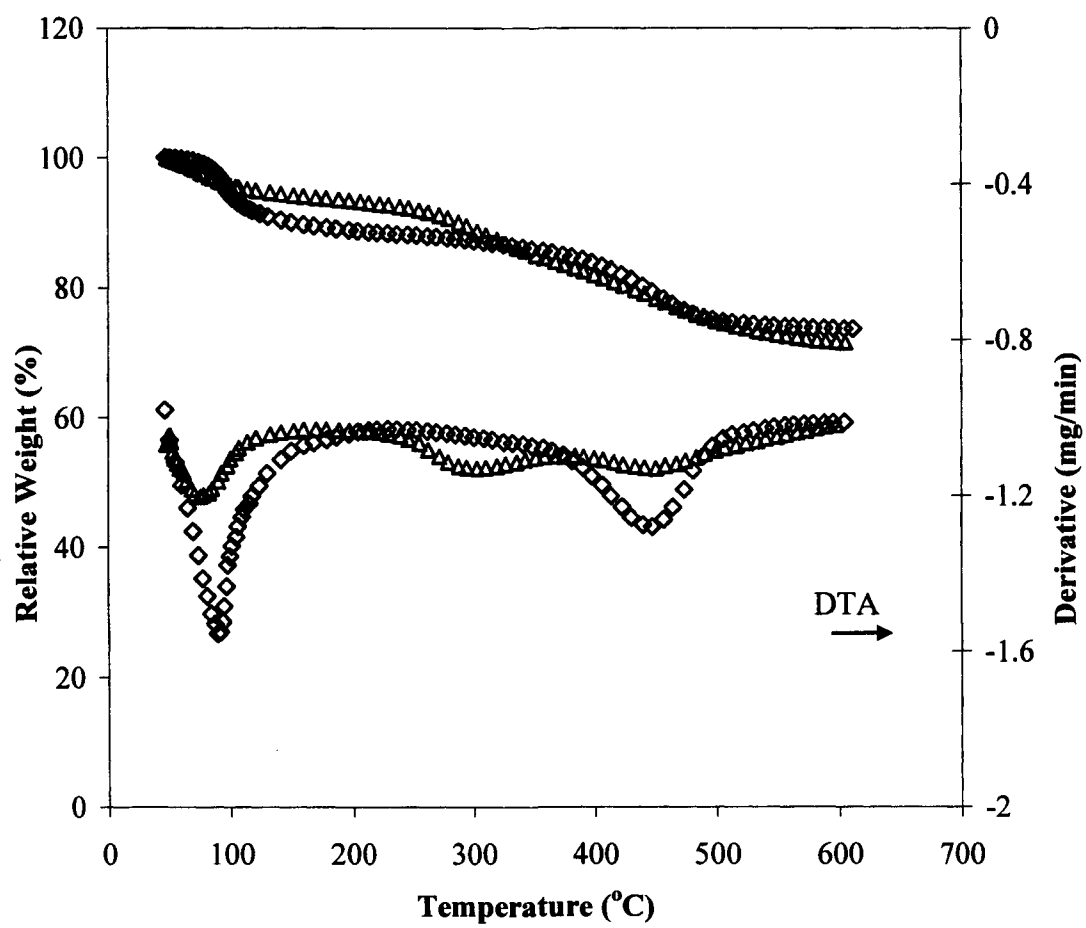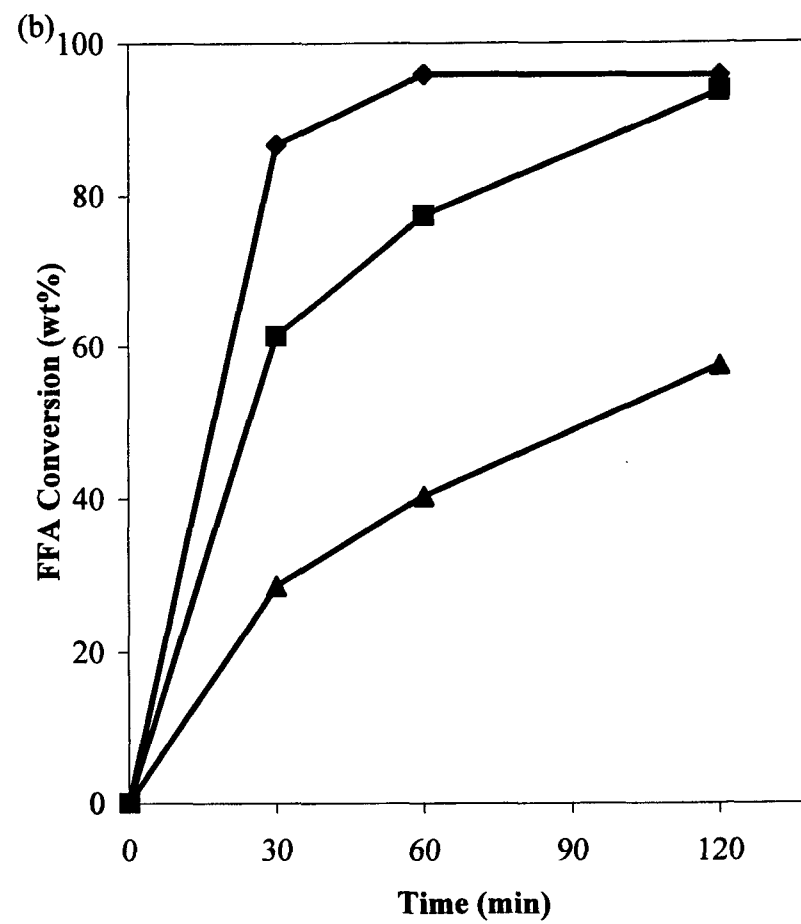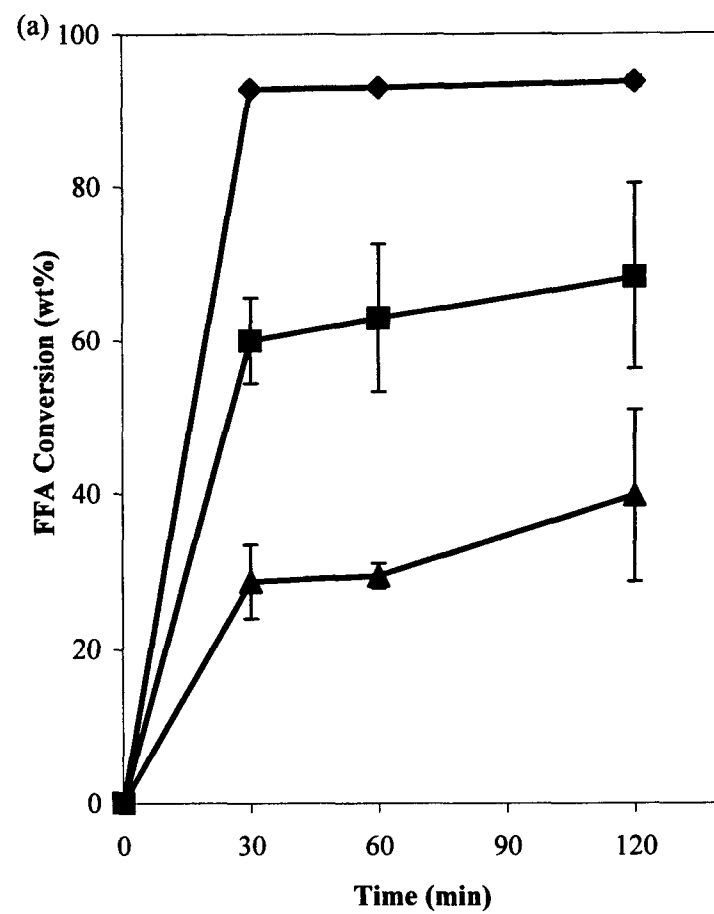°C; FFA:MeOH = 1:20; catalyst condition, ♦: 1st cycle; ■: 2nd cycle)
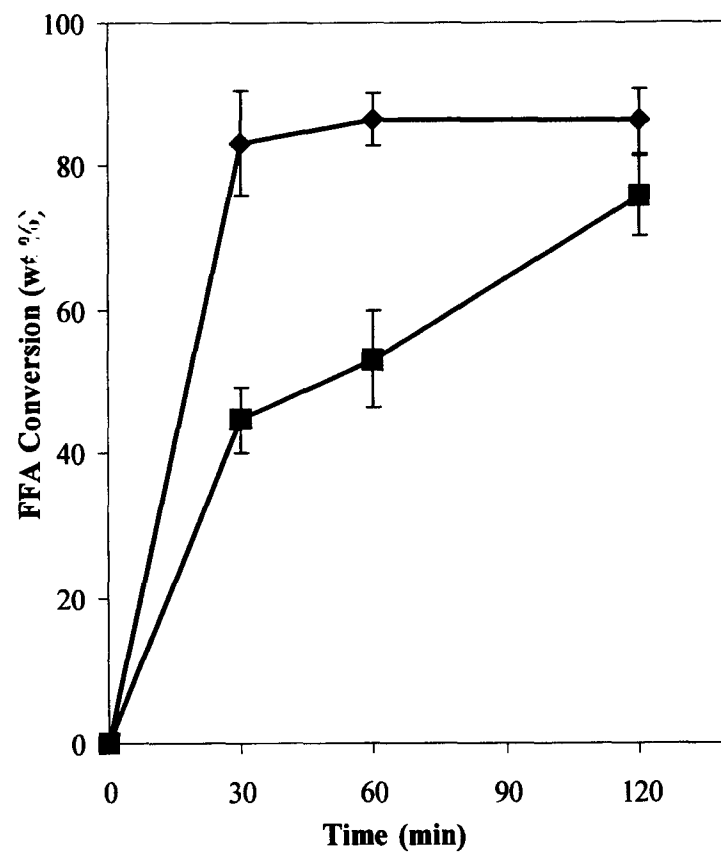
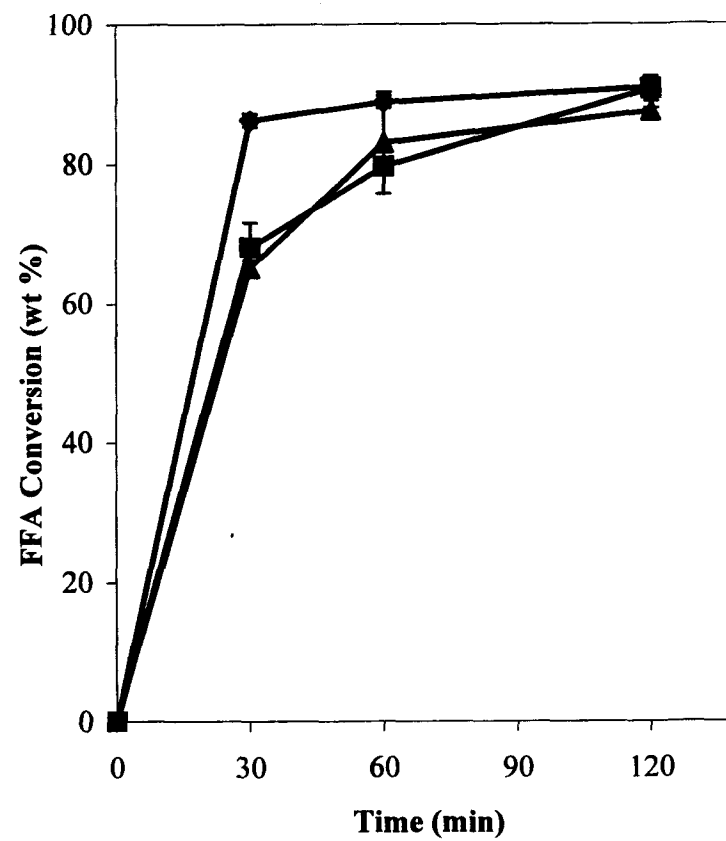Figure 5-1.

Figure 5-2.

Figure 5-3.
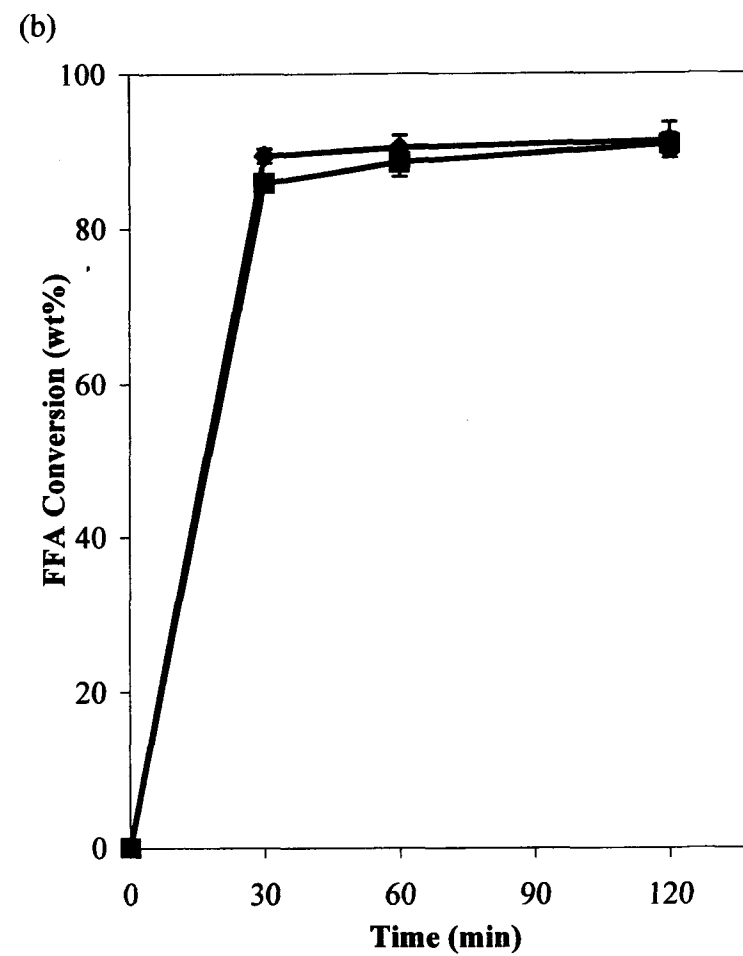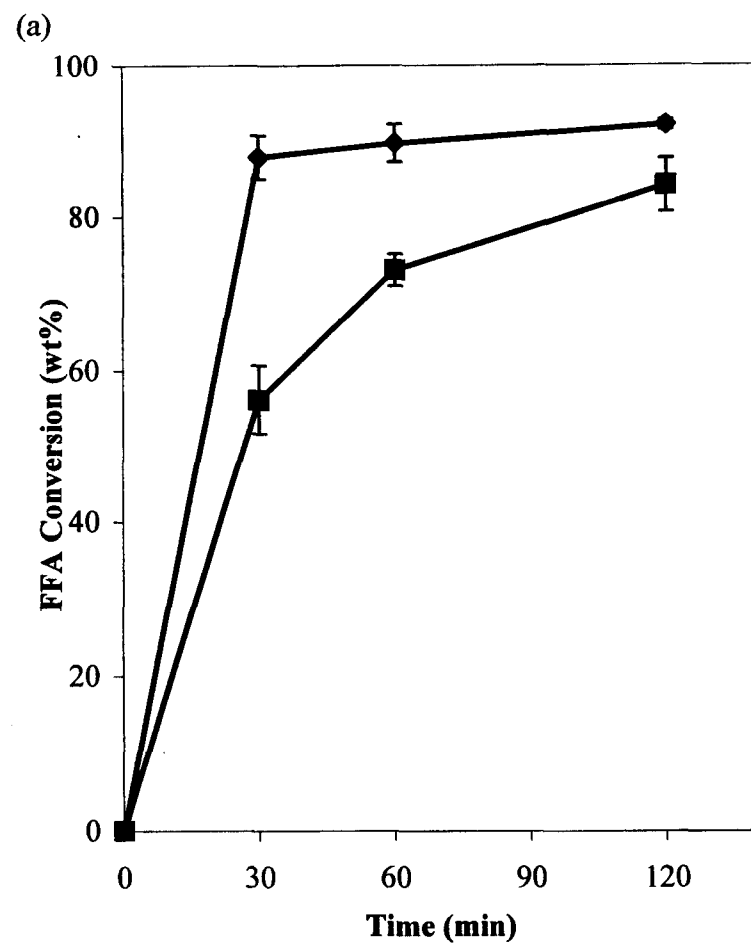
(a)

(b)

Figure 5-4

Figure 5-5.

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CHAPTER 6

General Conclusions and Future Work

6.1. General Conclusions

The focus of this work was to design the catalytic domain of organosulfonic acid-functionalized mesoporous silica materials to understand and control the reaction environment at a molecular level. Physical and chemical characterization as well as the kinetic studies of the synthesized acid-modified mesoporous silica materials demonstrated that these materials could catalyze liquid-phase reaction systems. The esterification of free fatty acids in triglyceride mixtures was chosen as a probe to study the reaction kinetics of the acidic mesoporous silicas, given that there is significant interest for the conversion of natural oils and fats into biobased chemicals. Application of solid acidic catalysts in such reaction systems could simplify the manufacturing process, reducing production costs, and eliminating environmental hazards posed by wastes generated in homogeneous catalyzed reactions.

Organic-inorganic hybrid mesoporous materials were synthesized via the nonionic supramolecular assembly using co-condensation. The resulting acidic mesoporous materials were more reactive than commercially available solid acid esterification catalysts for converting fatty acids to methyl esters. As demonstrated in a multi-cycle study for esterifying fatty acids in floatation beef tallow, the structural and chemical properties of the

propylsulfonic acid-functionalized mesoporous catalyst were stable under the reaction conditions.

By choice of surfactant template, the pore diameter was systematically increased to decrease internal mass transfer resistance, which could be determined owing to uniform narrow pore-size distribution of the mesoporous materials. Such tuning of the textural properties of the mesoporous silica enhanced the catalytic performance of the catalyst. Modification of the physical and chemical properties of the organosulfonic acid-functionalized mesoporous silica by introducing hydrophobic organic groups enhanced the catalytic performance of the solid acid catalyst while excluding polar compounds (e.g. water and impurities in beef tallow) from the active sites. The catalytic performance of multifunctionalized mesoporous silicas in the methanol esterification of palmitic acid in soybean oil mixture was strongly dependent on the method of incorporating hydrophobic groups and the size of the hydrophobic organic group. Modifying the acid strength of the organosulfonic acid group significantly improved the catalytic activity of the mesoporous catalyst for the fatty acid esterification reaction. A decrease in spatial positioning of the sulfonic acid groups on the pore surface of mesostructured material increased the acid strength of the resulting acid catalyst.

Although the polar impurities in the floatation beef tallow inhibited the catalytic performance of the acidic mesoporous catalyst in esterifying fatty acids, strategically designing the catalytic domain at the molecular level averted further inhibition of sulfonic acid sites. The study demonstrated that understanding the catalytic properties of the tethered organosulfonic acids on mesoporous silica materials was complex, and that reaction kinetics

studies alone could overlook other important factors (e.g. site collaboration, solution effects, hydrophobicity) in characterizing the catalytic activity of the sulfonic acid sites.

6.2. Future Work

Clearly, organosulfonic acid-functionalized mesoporous catalysts are potential solid acid catalysts to convert fatty acids. Multi-functionalization of the mesoporous silica with organosulfonic acid and hydrophobic groups can control the reaction domain in the mesopores. Insights on the surface coverage of organosulfonic acid-functionalized mesoporous silica materials, as discussed in Chapter 4, demonstrated that mutual interactions of the tethered organosulfonic acid moieties resulted in increase of acid strength of the resulting solid catalyst. Although these modified materials were synthesized via co-condensation, characterizing organosulfonic acid-functionalized mesoporous materials synthesized by post-synthesis grafting could provide important information on the location of the acidic sites. Lim and Stein [1] compared the techniques of incorporating organic functional groups on mesoporous silica material and concluded that functional groups introduced via post-synthesis grafting were preferably located on the external surface area and around the mesopore mouth. Chapter 3 showed that incorporation of hydrophobic groups via either co-condensation or post-synthesis grafting on the propylsulfonic acid-functionalized mesoporous materials gave different catalytic performances in fatty acid esterification. This further demonstrated that there are significant differences between the two popular techniques of incorporating organic functional groups on mesoporous catalysts. Therefore, it would be necessary to compare the acid strength of sulfonic acid groups

incorporated into mesoporous silica materials by co-condensation and grafting by determining the pKa values in conjunction with kinetic studies to understand the influence of the synthesis procedure on the resulting catalytic performance of the solid acid catalyst.

Chapter 3 and 5 showed that introduction of hydrophobic groups enhanced the catalytic performance of propylsulfonic acid-functionalized mesoporous silicas by preventing the polar compounds from interacting with the sulfonic acid groups. Although such incorporation of hydrophobic groups gave improved overall catalytic performance by the multifunctionalized mesoporous materials, little is known of their location on the surface of the mesostructured material. Probing the location of the hydrophobic groups relative to the sulfonic acid moieties could infer the mechanism of preventing the acidic sites from interacting with the polar compounds as well as the influence of the hydrophobic groups on the acid strength of the resulting solid acid catalyst. The location of the functional groups on the mesoporous silica materials could be investigated using a probe molecule in combination with the pKa method, NMR, and kinetic studies. Such knowledge of the positioning of the functional groups on the surface of mesostructured materials could lead to a better molecular design of functionalized mesoporous silicas to improve the catalytic performance of the resulting solid catalysts.

The discovery of advanced material synthesis strategies has created new opportunities in tailoring catalyst properties specifically for the conversion challenges encountered in liquid-phase reaction systems. Although numerous studies have shown that these mesoporous materials have good catalytic properties in liquid-phase reaction systems, studies on the solution effect (also known as the solvent effect) on the catalytic performance of the functionalized mesoporous catalysts have been scantily reported in the literature. Koujout's

group [2,3] have shown that the enthalpies of neutralization of supported sulfonic acid groups varies when measured in different solvents. Such differences in neutralization enthalpies indicate that solvents have distinctly differential potentials of the acid strength of the sulfonic acid groups. As a result, it is important to investigate which solvents can increase the acid strength of organosulfonic acid moieties to increase the catalytic performance of acidic mesoporous catalysts. Potentiometric titration of the tethered sulfonic acid groups in different solvents could determine the influence of the solution effect on *pKa* values. In addition to understanding the solution effect, basic knowledge of solvent interaction with reactants and products could result into liquid-phase reaction systems that have enhanced reaction rates as well as selectivity of the desired products.

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APPENDIX

Oxidative Cleavage of Unsaturated Fatty Acids

A.1. Introduction

Oxidative cleavage of unsaturated fatty acids derived from soybean oil holds the potential to produce valuable chemicals for use in polymer production. Products such as azelaic and suberic acid that are derived from oxidation cleavage of oleic and linoleic acid respectively, could be used to replace fossil-fuel derived adipic acid, a large volume chemical used in the production of Nylon. The ability to achieve this conversion has been demonstrated [1-4], however, the process is expensive and impractical at a significant commercial size due to the required use of ozone as the oxidant. The objective of this work is to demonstrate a conversion process for converting unsaturated fatty acids derived from soybean oil to these valuable oxidation products using highly efficient solid catalysts, which are based on recent advancements in the synthesis of nanostructured inorganic materials.

A.2. Experiments

Amine-functionalized mesoporous silicas were synthesized according to the method described previously [5,6]. Tetraethoxysilane (TEOS, 98%, Aldrich) was used as the silica precursor while 3-aminopropyltrimethoxysilane (APTMS, 95%, Acros) was used without further purification as the amine source. Pluronic P123 (BASF Co., USA), which is a tri-

block copolymer of polyethylene oxide-polypropylene oxide-polyethylene oxide with molecular structure of PEO_{20}-PPO_{70}-PEO_{20}, was used as purchased to tailor the textural properties of the mesoporous materials. The amine-functionalized mesoporous silica was impregnated with ruthenium (II) complex (3,7,8,12,13,17,18-Octaethyl-21H,23H-porphine ruthenium (II) carbonyl) purchased from Aldrich via a post-synthesis grafting procedure. The modified mesoporous material was denoted as SBA-15-NH_2-Ru.

A.2.1. Synthesis of SBA-15-NH₂

In a typical one-step synthesis, 8 g of Pluronic P123 was dissolved in 250 ml of 1.9 M HCl at room temperature under stirring with subsequent heating to 40 °C before adding TEOS. The TEOS was prehydrolyzed for approximately 45 min before addition of APTMS. The resulting mixture with a molar composition of 0.0736 TEOS and 0.0074 APTMS was agitated for 24 h at 40 °C and thereafter aged for 24 h at 100 °C under static conditions. The resulting solid material was filtered and air-dried. The template was extracted by suspending the solid product in EtOH and refluxing for 24 h. To ensure complete removal of the surfactant, fresh EtOH was introduced after 12 h. The final product was air-dried, then stored in a desiccator.

A.2.2. Impregnation of SBA-15-NH₂ with Ru-complex

Prior to impregnation of SBA-15-NH_2 with the Ru-complex, the amine-functionalized mesoporous silica was evacuated overnight at 90 °C. The dried sample (~4 g) was then

suspended in 100 ml CH_2Cl_2 for 15 min before adding the Ru-complex. The solution was stirred at room temperature for 4 h. The solvent was rotary vaporized then the solid product was dried in vacuum oven overnight at 50 °C.

A.2.3. Characterization

The textural properties of the functionalized mesoporous silicas were measured from nitrogen adsorption-desorption isotherms at -196 °C using a Micromeritics ASAP 2000 system. The surface area and pore size distribution were calculated from the BET and BJH method, respectively. Prior to measurement, all samples were degassed at 100 °C for 6 h.

A.2.4. Catalytic testing

The reagents used for the catalytic test included oleic acid ($\geq$80%, Fisher), peracetic acid solution (32 wt% in dilute acetic acid, Aldrich), and hexane (reagent grade, Fisher). The reagents were charged into a 100 ml reaction vessel at molar ratio of 10:10:1 for peracetic acid, hexane, and oleic acid, respectively. The oxidation cleavage was performed under nitrogen in a stainless steel high-pressure batch reactor, Eze-Seal (Autoclave Engineers Co., USA), fitted with mechanical stirrer and sample outlet. The reaction vessel was held at constant temperature with the aid of the heating mantle and integrated water-cooling system. The catalyst loading was equivalent of 10 wt% of the oleic acid. The range of reaction temperature studied was 55 to 75 °C under continuously stirring at a rate of 500 rpm.

A.2.5. GC Analysis

Samples were collected every 20 min then analyzed with GC method. Prior to injecting the sample into GC, the fatty acids were methylated using BF_3-methanol. Water generated from the methylation was scavenged with dimethoxypropane (DMP). The resulting mixture was separated by adding water and hexane. The hexane phase was then analyzed for the products.

The GC was fitted with auto-sampler and DB-5HT column (30 m x 0.25 mm x 0.1 μm) and the samples were analyzed with FID detector. The injector port and FID were set to 300 and 350 °C, respectively. 1 μL sample from the hexane phase was injected into the column, which was heated at a rate of 4 °C/min from 70 to 220 °C.

A.3. Results

The textural properties of the modified mesoporous silica materials are summarized in Table A-1. The large BET surface area of the synthesized amino-functionalized were consistent with previous reports. Incorporation of ruthenium (II) complex had insignificant effect on the surface area of the resulting catalyst. As seen in the table, the median pore diameter (MPD) of the synthesized catalyst as determined by the BJH method on the adsorption branch of the N_2 adsorption-desorption isotherm was similar for both amino-functionalized and ruthenium impregnated amino-functionalized mesoporous silica. These results suggested that incorporation of ruthenium complex had no significant effect on the pore size of the resulting catalyst. The pore size distribution of the synthesized samples (not

shown) was unimodal for both amino-functionalized and ruthenium impregnated mesoporous silica, which implied that the introducing ruthenium complex into the amino-functionalized mesostructured material had negligible effect on the pore size.

The catalytic performance of the synthesized catalyst was evaluated in the oxidative cleavage of oleic acid. The oxidative cleavage of oleic acid will result into dibasic acid (azelaic acid or nonanedioc acid) and monobasic acid (pelargonic acid or nonanioc acid), which are intermediate chemicals for industrial applications such as lubricants, plasticizers and polymers [7]. To provide a comparison basis for the synthesized SBA-15-NH$_2$-Ru catalyst, the oxidation cleavage reaction was also performed with RuCl$_3$ and without catalyst. The formation of the desired products was determined with GC-MS, which showed that azelaic and pelargonic acids were formed, in addition to other products. It should be noted that the oxidative cleavage reaction was very exothermic and it was difficult to control the temperature in the initial stages of the reaction. Shown in Table A-2 are the results for the reaction studies performed between 55 and 75 °C after 2 h. The table gives moles percentage of the azelaic and pelargonic acid while the conversion oleic acid was not included. The results show that the synthesized SBA-15-NH$_2$-Ru catalyst was active for the oxidative cleavage of oleic acid. The yield of azelaic acid was lower than pelargonic acid at different temperatures studied despite the fact that they should be equivalent. This observation suggested that probably azelaic acid was further converted into other byproducts. The yield of the mono- and dibasic acids increased with increase in temperature when the oxidative cleavage of oleic acid was catalyzed with RuCl$_3$.

A.4. Conclusions

This was a preliminary study to investigate the feasibility of introducing ruthenium complex into mesoporous silica and then test the catalytic activity of the catalyst in the oxidative cleavage of oleic acid. However, to improve the catalytic performance of such catalyst, better understanding of the catalyst and reaction system need to be developed, which was not the scope of this study. Nonetheless, the initial results indicate that this is a promising catalytic system for oxidation reactions. This work demonstrated that ruthenium (II) complex impregnated on mesoporous silica could catalyze the oxidative cleavage of unsaturated fatty acid.

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Table A-1. Textural properties of functionalized mesoporous silica materials.

Sample	SA (m^2/g)	MPD (Å)	Vol (cm^3/g)
SBA15-NH$_2$	640	54	0.86
SBA15-NH$_2$-Ru	590	56	0.82

Table A-2. Yields of pelargonic and azelaic acid at different reaction temperatures.

T (°C)	Catalysts	Pelargonic Acid mol%	Azelaic Acid mol%
55	SBA-15-NH$_2$-Ru	15	4.5
	RuCl$_3$	3.5	0
65	SBA-15-NH$_2$-Ru	40	16
	No Catalyst	18	13
75	SBA-15-NH$_2$-Ru	24	35
	RuCl$_3$	45	25