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Organosulfonic acid-functionalized mesoporous silicas for the esterification of fatty acid

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Abstract

Organosulfonic acid-functionalized mesoporous silicas were synthesized in a one-step approach of co-condensing inorganic–organic reagents in the presence of different surfactant templates with in situ oxidation of the thiol groups to the sulfonic acid groups. The resulting materials were tested for their catalytic performance in the esterification of fatty acid with methanol to produce methyl esters. The performance of the functionalized mesoporous materials demonstrated a strong dependence on the median pore diameter of the catalyst as well as the acidic strength of the organosulfonic acid group. The activity of the organosulfonic acid-functionalized silicas in the esterification was compared to that of standard acidic resins. The results indicate the potential of rational catalysis design using organic–inorganic mesoporous materials.

Keywords: Acid-functionalized mesoporous silicas; Organic–inorganic acidic catalysts; Fatty acid esterification; Methyl esters

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 [1,7]. 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 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-

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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 has been shown that 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. have shown that the acid strength of the sulfonic groups in the mesoporous materials can be adjusted by choice of the organosulfonic precursor [18]. 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 their esters [16].

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

2. Experimental

The mesoporous materials were synthesized following the procedures of Bossaert et al. [16] and Melero et al. [18] with only slight modification. Tetraethoxysilane (98%, Aldrich) was used as the silica source. The mesoporous silicas were modified using (3-mercaptopropyl)trimethoxysilane (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].

2.1. HMS–SO_3H

A molar composition of 0.08 TEOS, 0.02 MPTMS, 0.0275 *n*-dodecylamine, 0.89 EtOH, and 2.94 H_2O was used to synthesize HMS–SO_3H. 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 393 K.

2.2. SBA-15–SO_3H

SBA-15–SO_3H 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 conditions. The product was collected and subjected to the same extraction method as previously described.

2.3. SBA-15–ph-SO_3H

SBA-15–ph-SO_3H 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-chlorosulfonylphenyl)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 following 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 media of the reaction.

2.4. Characterization

The textural properties of the mesoporous materials were measured using the BET procedure. Nitrogen adsorption–desorption isotherms were taken at 77 K 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].

2.5. Catalytic tests

The reagents used for the catalytic test included palmitic acid (PA, $\geqslant$ 95%, Sigma), refined soybean oil (SBO, Wesson), and methanol (MeOH, $\geqslant$ 99.9%, Fisher Scientific).

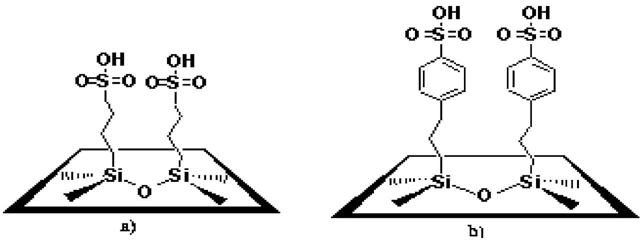

Fig. 1. Organosulfonic acid functional groups incorporated into the mesoporous silicas; (a) propylsulfonic groups, (b) arenesulfonic groups.

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 hourly intervals and their acid values were determined using the AOCS method Cd 3a-63.

Shown in Fig. 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.

3. Results and discussion

The textural properties of the functionalized mesoporous silicas synthesized for the current work are summarized in Table 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 22 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 a result of an increase in the molecular weight of the propylene oxide in the copolymer, increased the hydrophobicity of the resulting micelles. The increase in hydrophobicity of the micelles 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 Fig. 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.

Table 1
Textural properties of the functionalized mesoporous silicas

Catalyst	Surfactant	Textural properties			H^+ meq/g
		S_{BET} ($m^2\,g^{-1}$)	V_p ($cm^3\,g^{-1}$)	MPD (Å)	sample
HMS–SO_3H–C12	*n*-Dodecylamine	550	0.30	22	0.60
SBA-15–SO_3H–L64	Pluronic L64	820	0.58	27	0.84
SBA-15–SO_3H–P123	Pluronic P123	735	0.67	35	1.44
SBA-15–ph-SO_3H–P123	Pluronic P123	540	0.71	50	0.92

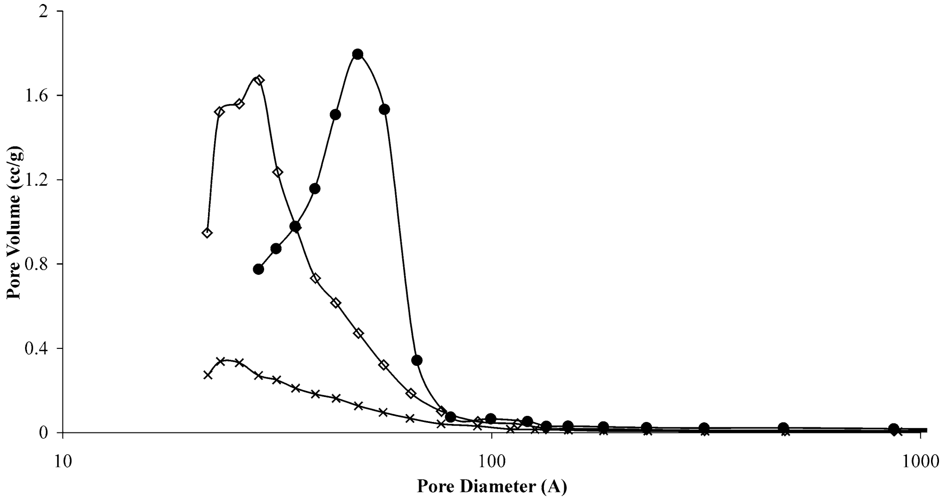

Fig. 2. Pore-size distribution curves for the mesoporous materials (×, HMS–SH–C12; ◇, SBA-15–SH–L64; ●, SBA-15–SH–P123).

The number of sulfonic acid groups in the mesoporous silica, which were determined quantitatively using acid-base titration, are given in Table 1. It is noteworthy that the acid capacity of the materials was found to increase 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 this 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 Fig. 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 the 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_3H–P123 gave the highest catalytic activity and HMS–SO_3H–C12 gave the least, with palmitic acid conversions of 85 and 55%, respectively, after 3 h. The higher activity with SBA-15–SO_3H–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. for the esterification of gylcerol with lauric acid using propylsulfonic acid-functionalized mesoporous silica catalysts [16].

As seen in Fig. 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-

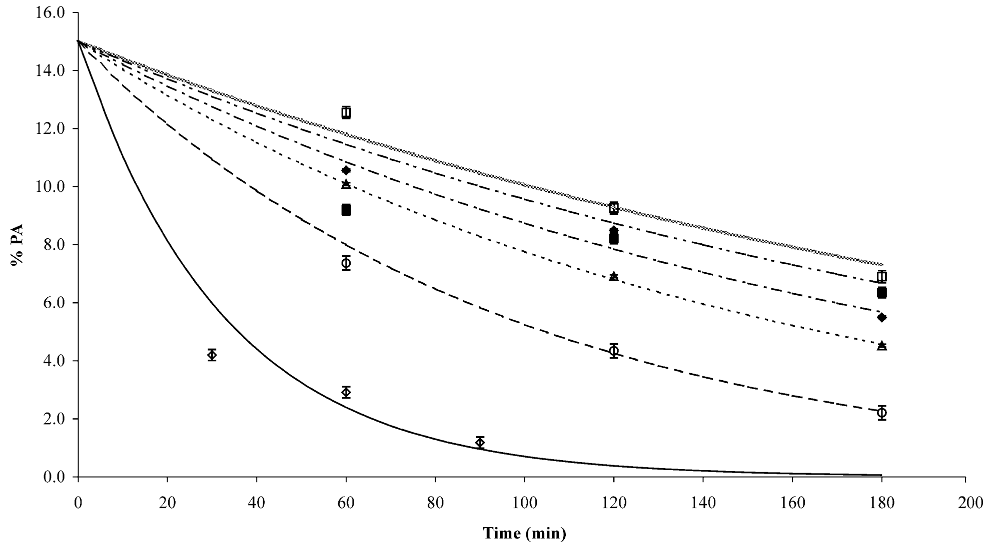

Fig. 3. Catalytic results for the esterification of palmitic acid in soybean oil with methanol (85 °C; PA:MeOH = 1:20; catalyst, 10% Amberlyst 15-wet (□, Exp., ▨▨▨ model), 10% HMS–SO_3H–C12 (■, Exp., –··– model), 10% SBA-15–SO_3H–L64 (◆, Exp., –·– model), 10% Nafion (△, Exp., ···· model), 10% SBA-15–SO_3H–P123 (○, Exp., – – model), 5% H_2SO_4 (◇, Exp., — model)).

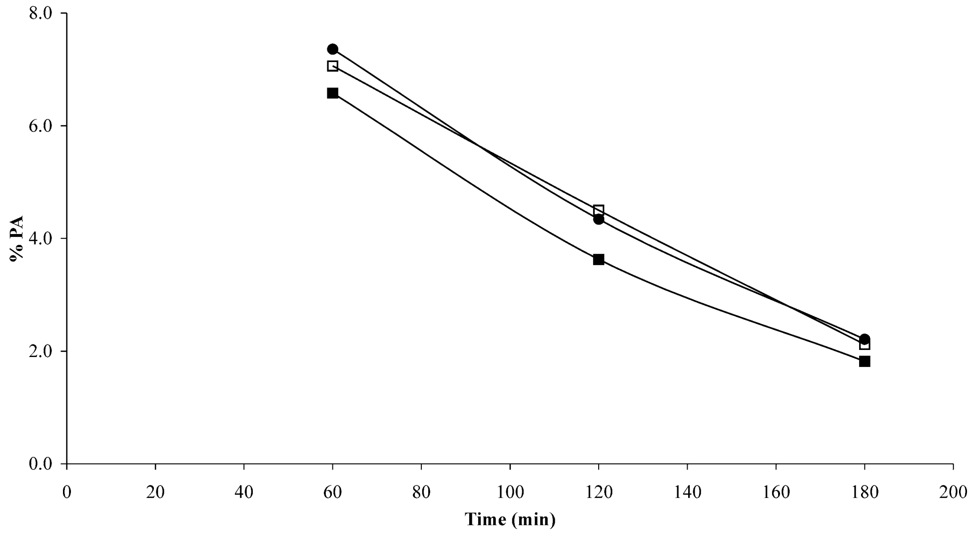

Fig. 4. Effect of external mass transfer (■, 200 rpm; ●, 350 rpm; □, 500 rpm) on the esterification of palmitic acid in soybean oil (85 °C; PA:MeOH = 1:20, catalyst: 10% SBA-15–SO_3H–P123).

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 either that their catalytic sites are not accessible or that 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 Fig. 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 for the synthesized meso-

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

Catalyst	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_3H–C12	2.6×10^{-3}	9.0×10^{-3}	2.4×10^{-2}	75 ± 10	0.14
SBA-15–SO_3H–L64	5.4×10^{-3}	1.3×10^{-2}	2.8×10^{-2}	55 ± 5	0.16
SBA-15–SO_3H–P123	7.5×10^{-3}	1.5×10^{-2}	3.4×10^{-2}	40 ± 1	0.11
SBA-15–ph-SO_3H–P123	1.7×10^{-2}				0.68

porous 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 was found to decrease with increasing MPD. If internal diffusion were 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 (Fig. 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 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 Fig. 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. 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 outperformed the esterification activity of the 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 Fig. 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 number 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 has been demonstrated to be significant in the 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. As can be seen from the table, SBA-15–ph-SO_3H–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_3H–P123 supports the conclusion that increasing the acidity of the sulfonic acid

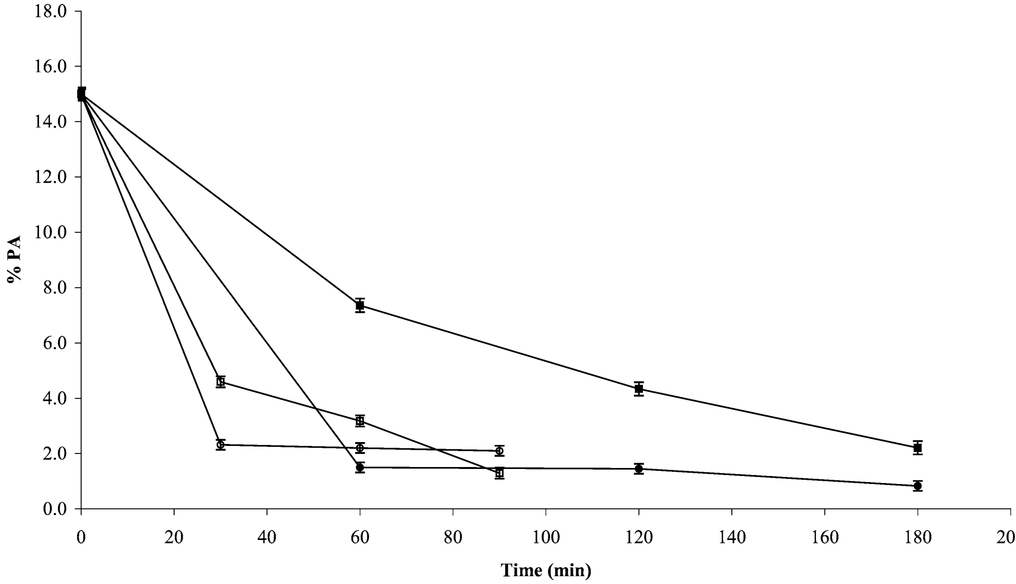

Fig. 5. Esterification of palmitic acid in soybean oil with methanol (85 °C; PA:MeOH = 1:20, catalyst: □, 5% H_2SO_4; ○, 10% pTSA; ■, 10% SBA-15–SO_3H–P123; ●, 10% SBA-15–ph-SO_3H–P123).

group enhances the reactivity of the material in the esterification reaction.

4. Conclusions

Organosulfonic acid-functionalized mesoporous silicas have been demonstrated to have higher reactivity 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 the mesoporous materials, the pore-size effect on internal mass transfer could be definitively determined. Increasing the acidity of organosulfonic acid group was found to improve significantly that 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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