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Acid strength variation due to spatial location of organosulfonic acid groups on mesoporous silica

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Abstract

Evaluation of acid strength was used to investigate the location of organosulfonic acid groups within mesoporous silica materials. Mesoporous silica functionalized with either propylsulfonic or arenesulfonic acid groups at different surface concentrations were synthesized via the co-condensation technique, and their resulting acid strength was determined in a methanol solution using potentiometric titration with the Gran Plot technique. A decrease in spatial distance between the sulfonic acid groups on the pore surface of the mesostructured materials was found to increase the acid strength of the resulting solid acid catalyst as result of acid site cooperativity. Comparison of these results with the catalytic performance of the organosulfonic acid-functionalized mesoporous silica materials in the methanol esterification of palmitic acid suggested that the reaction performance of these materials is not simply related to the effects induced by spatial location of the acidic sites on the acid solid catalyst. The results demonstrate the potential of intentionally designing the catalytic environments of the organic–inorganic hybrid mesoporous materials at the molecular level.

Keywords: Organic–inorganic hybrid catalysts; Propylsulfonic acid; Arenesulfonic acid; Spatial location; pK_a values; Acid strength

1. Introduction

Supramolecular assembled mesoporous materials with their combination of high surface area, flexible pore sizes, and well-defined mesostructure are attractive for designing catalysts and catalytic supports with potential for improved product selectivity and yield [1–3]. These mesostructured materials can be tailored at nanoscale to meet desired application requirements through the incorporation of specific organic functional groups onto the surface of the inorganic framework, which modify the physical and chemical properties of the metal oxide support. 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 hybrid materials have demonstrated interesting catalytic properties [13–18]; however, the literature contains little comprehensive and systematic information about the characteristics of the reaction environment within these catalytic materials. Such an understanding with the concomitant ability to control the catalytic domain of the acidic functional groups is of importance for optimizing catalytic performance.

One approach to understanding the catalytic domain of the organic functional groups is by spatially imbedding single organic active sites within bulk amorphous silica via a molecular imprint technique [19–21]. This synthesis technique has the advantage of creating isolated reaction domains within the amorphous silica that could enhance the catalytic activity of the resulting solid catalyst owing to shape selectivity of the reactive cavities. However, catalytic conversions of large molecules, as encountered mostly in liquid-phase reaction systems, could be hindered due to mass transfer limitations. To reduce diffusion effects on the catalytic performance of the solid material, it would be useful to incorporate the organic moieties on a support with large surface area and flexible pore sizes, such as mesoporous silica materials. Dufaud and Davis [22] recently

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demonstrated a technique for coupling organosulfonic acid precursors, which, after grafting onto mesoporous silica material, could be decoupled and oxidized to form pairs of acidic moieties. Incorporating such organic species into mesoporous silica material could enhance the acid strength of the resulting solid acid catalyst due to the intermolecular interaction of the acidic sites. Unfortunately, incorporating organic moieties on mesoporous silica material via a grafting technique commonly leads to nonuniform distribution of the functional groups, with higher concentration on the external surface area of the particle and around the pore openings instead of on the internal surface area [23,24]. Therefore, it would be desirable to incorporate the coupled organosulfonic acid precursors via a co-condensation technique.

Although synthesis of organosulfonic acid-functionalized mesoporous silica materials via a co-condensation method has been studied extensively, to the best of our knowledge there is no evidence in the literature demonstrating the surface distribution of the organosulfonic acid groups within the mesopores. A potential technique of understanding the surface distribution of the acidic functional moieties is to determine their acid strength. The acid strength of an organic acid tethered on a substrate is influenced by the nature of acid group (e.g., $–SO_3H > –COOH$), the electronic properties of the organic backbone, the surface concentration of the acid moieties, and the solvent used [25–30]. Kinetic studies have been the technique of choice in determining the acid strength of organosulfonic acid-functionalized mesoporous materials, but it is difficult to infer the spatial location of the acid sites due to the effect of physical (e.g., pore diffusion) and chemical (e.g., hydrophobicity, site interaction) properties of the support as well as solvent on the catalytic performance of the acidic functional groups [22,24,27,31]. A more direct approach for potentially determining the acid strength, and thus the surface distribution of the organosulfonic acid moieties, while circumventing the aforementioned difficulties is to measure the $\mathrm{p}K_\mathrm{a}$ value of the organic–inorganic material. The $\mathrm{p}K_\mathrm{a}$ values in conjunction with the surface concentration of the acidic functional group could give insight into the surface distribution of the acidic sites. For any functionalized organic acid, an increase in the proximity of the acidic moieties will result in increased acid strength due to a site cooperation effect through formation of hydrogen bonds between adjacent acid pairs, which stabilizes the anion formed after deprotonation of the acid group [25,30].

Herein we report the spatial location of tethered propylsulfonic acid groups on SBA-15 mesostructured material as incorporated via the co-condensation synthesis technique, with the subsequent determination of the resulting acid strength of the catalytic material by a potentiometric titration technique. We compare the results with those for mesoporous silica materials functionalized with arenesulfonic acid groups. We also compare the acid strength of the synthesized organosulfonic acid-functionalized mesoporous silica samples as determined by potentiometric titration method with the catalytic performance of the solid acid catalysts in the esterification reaction of free fatty acid oils as a pretreatment step in the production of alkyl esters.

2. Experimental

Organosulfonic acid-functionalized mesoporous silicas were synthesized as described previously [26,27] with only slight modifications. Tetraethoxysilane (TEOS) (98%, Aldrich) was used as the silica precursor, and (3-mercaptopropyl)trimethoxysilane (MPTMS) (85%, Acros) and 2-(4-chlorosulfonylphenyl)-ethyltrimethoxysilane (CSPTMS) solution in dichloromethane (50%, Gelest) were used without further purification as the organosulfonic acid source. Pluronic P123 (BASF), a triblock copolymer of polyethylene oxide–polypropylene oxide–polyethylene oxide with the molecular structure $PEO_{20}–PPO_{70}–PEO_{20}$ ($M_\mathrm{w} = 5800$), was used as purchased to tailor the textural properties of the mesoporous materials. Mesoporous silica material functionalized with either propylsulfonic or arenesulfonic acid groups was denoted as SBA-15-$PrSO_3H$ and SBA-15-$ArSO_3H$, respectively.

2.1. Synthesis of the propylsulfonic acid-functionalized mesoporous silica (SBA-15-$PrSO_3H$)

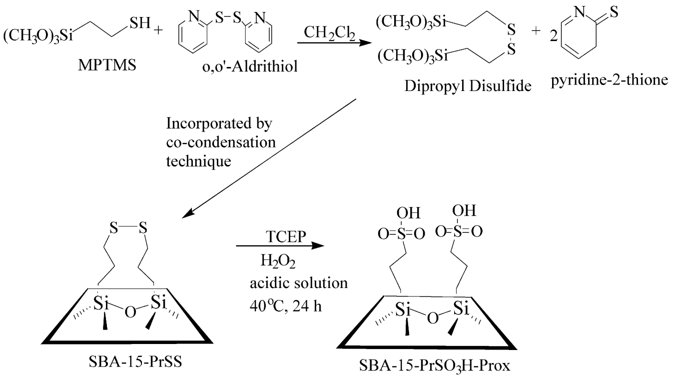
In a typical synthesis of propylsulfonic acid-functionalized mesoporous silica, Pluronic P123 (8 g, 1.4 mmol) was dissolved in 250 ml of 1.9 M HCl solution at room temperature under stirring with subsequent heating to 40 °C before adding TEOS (16.5 ml, 73.66 mmol). Approximately 45 min was allowed for prehydrolysis of TEOS before the addition of x mol of MTPMS and y mol of H_2O_2 (where $x = 2.5$–10% of the TEOS molar quantity and $y = 3.5$ times the MPTMS molar quantity). The resulting mixture was agitated for 24 h at 40 °C and then aged for 24 h at 100 °C under static conditions. The resulting solids were collected by filtration and air-dried. The template was extracted by suspending the white solid product in 10% v/v HCl in ethanol and refluxing for 24 h. To ensure complete removal of the surfactant, fresh ethanol was introduced after 12 h.

2.2. Synthesis of the arenesulfonic acid-functionalized mesoporous silica (SBA-15-$ArSO_3H$)

After TEOS prehydrolysis, CSPTMS was added, and the resulting mixtures with molar composition of 0.0737 TEOS and xCSPTMS (where $x = 2.5$–10% of the TEOS molar quantity) were stirred for 24 h at 40 °C and then aged for 24 h at 100 °C under static conditions. The solid product was recovered and the template extracted as described previously.

2.3. Synthesis of spatially prearranged propylsulfonic acid-functionalized mesoporous silica (SBA–15–$PrSO_3H$–Prox)

Mesoporous silica material modified with prearranged propylsulfonic acid groups was synthesized as described by Dufaud and Davis [22] with modifications. Scheme 1 shows the reaction pathway for the synthesis of spatially arranged propylsulfonic acid groups on the SBA-15 mesostructure. Bis(trimethoxysilyl)propyl disulfide, a precursor for the spatially prearrangement of propylsulfonic acid groups, was synthesized by reacting 2,2′-dipyridyl disulfide (o,o'-Aldrithiol)



Scheme 1. Schematic representation of bis(trimethoxysilyl)propyl disulfide synthesis, incorporation into SBA-15 mesostructured material, and subsequent cleavage and oxidation to form the spatially arranged propylsulfonic acid groups.

(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, after which bis(trimethoxysilyl)propyl disulfide was extracted by filtration and vaporization of the solvent. The precursor was further dried in a vacuum oven for 4 h and then stored in airtight vial.

SBA-15-PrSO3H-Prox mesoporous silica (where the suffix Prox designates the intentional proximity of the functional groups) was synthesized as described previously using the co-condensation technique. After prehydrolysis of TEOS (16.5 ml, 73.66 mmol) in 250 ml of acidic solution (1.9 M HCl) with Pluronic P123 (8 g, 1.4 mmol) surfactant, x mol of bis(trimethoxysilyl)propyl disulfide (where $x = 1.25$–5% of the TEOS molar quantity) 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 as SBA-15-PrSS.

Generation of adjacent propylsulfonic acid groups on the mesoporous silica was achieved by cleaving and oxidizing the disulfide bonds of the tethered bis(trimethoxysilyl)propyl disulfide moieties with tris(2-carboxyethyl)-phosphine (TCEP) and H_2O_2, respectively. In a typical oxidative cleavage procedure, TCEP (TCEP-to-disulfide molar ratio of 4:1) was dissolved in 100 ml of 1.9 M HCl solution. Then SBA-15-PrSS sample was suspended in the solution and agitated for 1 h at 40 °C. Afterward, H_2O_2 (H_2O_2-to-disulfide bonds molar ratio of 20:1) 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.

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 before measurement. 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 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. The relative pK_a 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 meq of acid sites was suspended in 100 ml of 1.5 mM NaCl in methanol. This dilute solution was used to ensure that the activity coefficient for the solution was unity. The resulting mixture was titrated potentiometrically by dropwise addition of 2 mM NaOH in methanol.

2.5. Catalytic testing

The functionalized mesoporous silica materials were tested for catalytic activity as described previously [24,27]. The reagents used for the esterification reaction included palmitic acid, refined soybean oil, and methanol. The esterification reaction was performed under a nitrogen blanket in a high-pressure stainless steel batch reactor (Eze-Seal; Autoclave Engineers) fitted with a mechanical stirrer and a sample outlet. The oil mixture with a palmitic acid/soybean oil weight ratio of 15:85 and a palmitic acid/methanol 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 palmitic acid 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.

3. Results and discussion

The N_2 adsorption–desorption isotherms of the synthesized propylsulfonic acid-functionalized mesoporous silica materials, shown in Fig. 1, had type IV hysteresis loops, consistent with mesoporous materials tailored by nonionic surfactant [32–34]. As shown in the figure, the shape of the hysteresis loop appeared to be affected by the molar ratio of MPTMS/TEOS, indicating that formation of a regular inorganic mesostructure began to break down at greater incorporation of the organic species [12,23,35]. As a result, only samples with a molar ratio of organosulfonic acid precursor/TEOS equivalent to or less than 10% were considered for further studies.

The textural properties of the synthesized organic–inorganic hybrid materials are summarized in Table 1. As shown in the table, the median pore diameter (MPD) of the organosulfonic acid-functionalized mesoporous materials, as determined by the BJH method on the adsorption branch of the N_2 adsorption–desorption isotherm, was not proportional to the concentration of the organosulfonic acid precursors. The lack of direct correlation between the molar ratios of organic–inorganic precursors and MPD implied that the range of concentration studied had an insignificant affect on pore structure. The large BET surface areas of the synthesized organic–inorganic hybrid mesoporous silicas was in the range reported in the literature, implying that incorporation of organosulfonic acid groups, at least in the studied range, via the co-condensation technique had an insignificant affect on the pore structure and surface area of the resulting materials as compared with an unfunctionalized silica material [12,33]. Incorporation of the bis(trimethoxysilyl)propyl 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, as demonstrated by the MPD and surface area given in Table 1. The retention of the SBA-15 mesostructure was further confirmed by the N_2 adsorption–desorption isotherm shown in Fig. 2, in which the adsorption and desorption curves of both SBA-15-PrSS-5% and SBA-15-PrSO3H-Prox-5% samples (shifted upward) appear identical. The MPD of the material functionalized with arenesulfonic acid was approximately 10 Å larger than that of the propylsulfonic acid-modified mesoporous silica, suggesting that the cooperative assembly and co-condensation of the hydrophobic benzenesulfonic acid and silica precursors around the surfactant micelles resulted in an enlargement of the micelles, leading to the larger mesopores [32]. The pore size distribution and pore volume of the synthesized organosulfonic acid-functionalized mesoporous materials was consistent with that reported in the literature.

The thermal decomposition of the organo-functional groups incorporated into mesoporous silica material, as determined by differential thermoanalysis (DTA), is shown in Fig. 3. The DTA method allows for the determination of different organic species present in the functionalized mesoporous materials by measuring the rate of decomposition of the organic compounds (weight loss) as a function of heating temperature. Desorption

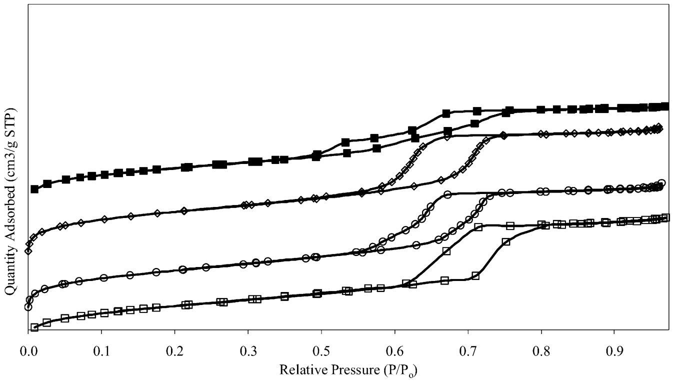


Fig. 1. N_2 adsorption–desorption isotherms of the propylsulfonic acid-functionalized mesoporous silica materials. (□) SBA-15-$PrSO_3H$-5%; (○) SBA-15-$PrSO_3H$-7.5%; (◇) SBA-15-$PrSO_3H$-10%; (■) SBA-15-$PrSO_3H$-20%.

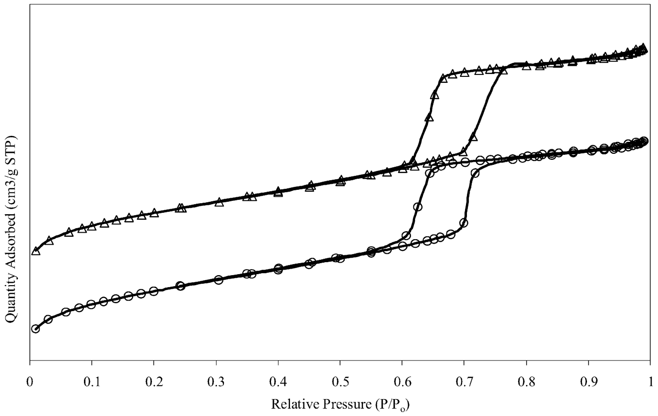


Fig. 2. N_2 adsorption–desorption isotherms of mesoporous silica materials functionalized with bis(trimethoxysilyl)propyl disulfide and propylsulfonic acid pairs. (○) SBA-15-PrSS-5%; (△) SBA-15-$PrSO_3H$-Prox-5%.

Table 1
Textural and chemical properties of the organosulfonic acid-functionalized mesoporous silica samples

Catalysts	Molar ratio (%)[a]	Textural properties			Chemical properties		
		S_{BET} (m^2/g)	MPD (Å)	V_p (cm^3/g)	C/S (mol/mol)	S (mmol/g)	H^+ (mmol/g)
SBA-15-$PrSO_3H$	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-$ArSO_3H$	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	1.25	770	57	1.05	24.0	0.31	
	2.5	730	53	0.95	16.0	0.51	
	3.75	680	57	0.90	13.2	0.66	
	5.0	740	44	0.72	8.8	1.31	
SBA-15-$PrSO_3H$-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

[a] Molar ratio of organic acid precursor to TEOS.

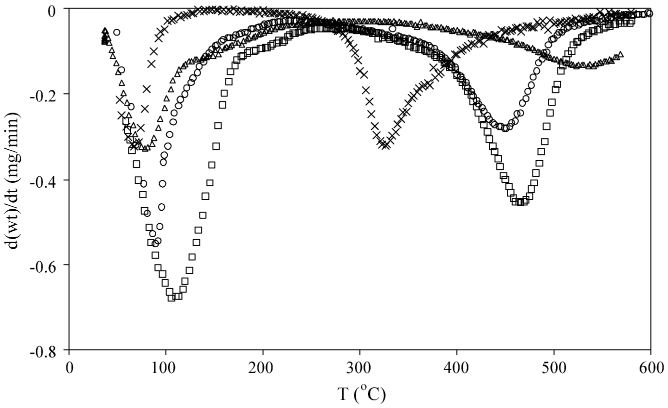


Fig. 3. Differential thermoanalysis (DTA) of the functionalized mesoporous silica materials. (△) SBA-15-ArSO$_3$H; (○) SBA-15-PrSO$_3$H; (□) SBA-15-PrSO$_3$H-Prox; (×) SBA-15-PrSS.

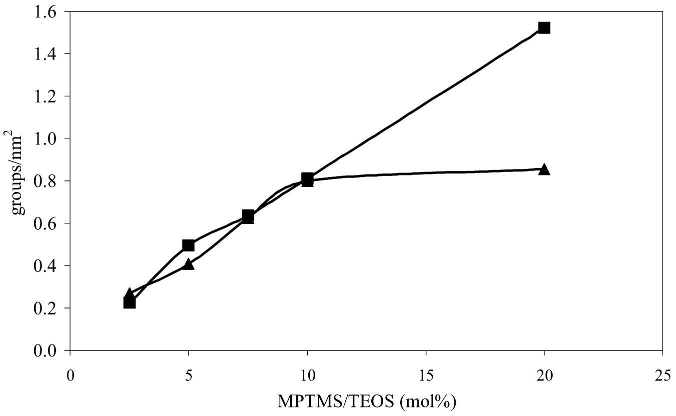


Fig. 4. Surface density of organic species incorporated onto the mesoporous silica material computed based on (▲) ion capacity; (■) sulfur content.

of physisorbed water was observed below 110 °C in all the synthesized organofunctionalized mesoporous silica samples. The DTA analysis of SBA-15-PrSO$_3$H samples showed a second weight loss peak centered at 460 °C, which was previously assigned to propylsulfonic acid groups [8,12], demonstrating successful in situ oxidation of propylthiol precursor to generate propylsulfonic acid species. The weight loss derivative of SBA-15-PrSS showed a peak centered at 330 °C, probably due to decomposition of the disulfide moieties, because it disappeared after the tethered disulfide moieties were reacted with TCEP and H_2O_2. The new peak centered at 460 °C appeared in SBA-15-PrSO$_3$H-Prox samples, which was also observed in the SBA-15-PrSO$_3$H samples, demonstrated successful cleavage and oxidation of the disulfide bond to generate propylsulfonic acid pairs. The absence of a peak centered at 350 °C, which was previously assigned to the thiol group [36], validated the procedure used to convert propylthiol and bis(trimethoxysilyl)propyl disulfide species into propylsulfonic acid groups. The decomposition of arenesulfonic acid groups was observed at 540 °C [37], implying that arenesulfonic acid-functionalized mesoporous materials have higher thermal stability than the propylsulfonic acid-modified SBA-15 mesostructured samples.

The relative carbon/sulfur molar ratio and the sulfur content of the modified mesoporous silica, as determined by elemental analysis, are summarized in Table 1. The results show 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 sulfur content of the arenesulfonic acid-functionalized mesoporous materials was slightly lower than expected, possibly due to the presence of an impurity in the precursor. The C/S molar ratio was unexpectedly dependent on the concentration of organosulfonic acid precursor, suggesting a higher retention of residual surfactant when lower concentrations of organic species were incorporated into the mesoporous silica. The retention of the surfactant was further substantiated by DTA analysis of the samples showing the intensity of a third peak centered at 220 °C, which is reportedly associated with decomposition of the tri-block copolymer [38], increasing with decreasing molar ratio of the synthesis precursors. This observation suggests a strong interaction between the tri-block copolymer and the mesoporous silica surface at low surface concentrations of the tethered organic species such that solvent extraction technique was inadequate to completely extract the residual surfactant.

As shown in Table 1, the ion capacity of the propylsulfonic acid-functionalized mesoporous materials, as determined by acid–base titration, was consistent with the sulfur content of the final product, confirming successful in situ oxidation of the propylthiol moieties. The number of sulfonic acid groups for the materials synthesized via the proximity technique was in good agreement with the sulfur equivalence, demonstrating successful simultaneous cleavage, and oxidation of the disulfide bonds to generate propylsulfonic acid groups. The comparable equivalence of sulfur content and sulfonic acid groups of both propylsulfonic and arenesulfonic acid groups indicate that the co-condensation synthesis technique incorporates the organic species onto the mesopore surface and not within the silica mesostructure. Moreover, the comparable results of sulfur content and ion capacity of the synthesized organosulfonic acid-functionalized mesoporous materials demonstrates that the presence of residual surfactant had insignificant effect on the accessibility of the sulfonic acid groups.

Fig. 4 shows the surface density of the organic species incorporated onto the mesoporous silica material, which was computed independently from the sulfur content and ion capacity of the sulfonic acid according to procedures described by Liu et al. [39]. The figure gives the number of groups per area as a function of molar ratio of organic precursor in the synthesis of SBA-15-PrSO$_3$H samples. The results show good agreement between sulfur and sulfonic acid species for samples with molar ratios of organic–inorganic precursor of up to 10 mol%, implying that the organosulfonic acid moieties were located on the mesopore surface. The calculated amount of sulfonic acid groups of the SBA-15-PrSO$_3$H-10% sample was equivalent to 27% of the surface silanols present in mesoporous silica-type material, which previously has been reported to be approximately 3.0 groups/nm^2 for MCM-41, a relatively similar material [39–41]. As the molar ratio of the organosulfonic acid precursor was increased (>10 mol%), the sulfur content per area increased linearly but the surface concentration of sulfonic acid groups leveled off, implying that excess propylthiol was integrated into the support's mesostructure, thus resulting in poor textural properties, as shown in the N_2 adsorption–desorption isothermal in Fig. 1. These results further confirm that incorporating high concentrations of organic moieties via the co-condensation technique is limited.

Replicate syntheses were performed on the propylsulfonic acid-functionalized mesoporous materials to validate the reproducibility of the synthesis procedure. As shown in Table 1, the textural and chemical properties of the synthesized propylsulfonic acid-modified mesoporous silica materials were highly reproducible, with low standard deviations ($<10\%$).

Many researchers have used reaction kinetics as a tool to investigate the catalytic activity of organosulfonic acid-functionalized mesoporous materials. However, this technique can be deceiving for determining the acid strength of a site, because the apparent acid strength of the solid catalyst determined by reaction models will also depend on additional factors, such as the reaction medium, location of the acid groups, ion capacity, and accessibility of the acid sites. As a result, it is important to be able to quantify the acid strength of the functionalized materials independently. Potentiometric titration with the Gran Plot technique was used in the current study to determine the relative pK_a values of the synthesized acid-functionalized mesoporous silica samples in methanol. Methanol was selected as the solvent for probing the acid strength of the organosulfonic moieties because it is a better differentiating solvent than water for the type of highly acidic groups used in the current study. In addition, methanol is a reagent and solvent of interest in the esterification of free fatty acid, thus providing a direct comparison of the acid strength of the organosulfonic acid-functionalized mesoporous materials as determined by the potentiometric titration method and reaction kinetics. The potentiometric titration was performed on samples with an ion capacity equivalent to only 0.05 meq, to minimize nonideal solution effects.

The acid strength of the organic acid group tethered to the substrate is dictated by the nature of the acid group (e.g., $-SO_3H > -COOH$), the electronic properties of the backbone, and the surface concentration of the acid moieties [25–28]. Along with these factors, the dissociation constant of organic acids is highly dependent on the physical and chemical properties of the solvent selected [25,30,42]. For instance, Brønsted acid sites that have higher acid strength than hydronium ions will protonate water to form hydrated protons and consequently level the acid strength of the sites [43–46]. Koujout and coworkers recently demonstrated that silica with attached sulfonic acid groups have higher acid strength than hydrated protons by determining the heat of neutralization in different solvents [29,47]. In the current study, propylsulfonic and arenesulfonic acid-functionalized mesoporous silica materials gave comparable relative pK_a values when water was used as the solvent, yet arenesulfonic acid has a higher acid strength than propylsulfonic acid due to the presence of the more electronegative phenyl group adjacent to sulfonic acid [22,26]. As such, water is a poor differentiating solvent for tethered sulfonic acid groups, owing to the leveling effect.

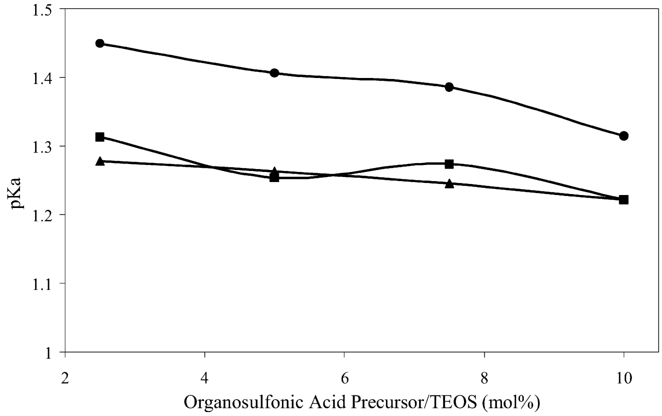


Fig. 5. Relative pK_a values of the synthesized solid acid catalysts. (●) SBA-15-$PrSO_3H$; (▲) SBA-15-$ArSO_3H$; (■) SBA-15-$PrSO_3H$-Prox.

Fig. 5 shows the pK_a values as determined in methanol versus the molar ratio of synthesis precursors. As shown, the relative pK_a values of the synthesized samples in methanol were lower than those determined in water. In addition, a significant difference was found in the relative pK_a values between propylsulfonic and arenesulfonic acid-functionalized mesoporous silica materials with comparable ion capacity (e.g., pK_a values of 1.40 for SBA-15-$PrSO_3H$-5% and 1.26 for SBA-15-$ArSO_3H$-5%). The lower pK_a values for the arenesulfonic acid-functionalized samples were consistent with the phenyl group's ability to better stabilize the sulfonate ion compared with the aliphatic carbon chain of propylsulfonic acid groups after deprotonation.

As shown in the figure, the relative pK_a of the samples indicated that the acid strength of SBA-15-$PrSO_3H$-Prox was higher than that of SBA-15-$PrSO_3H$ and similar to that of SBA-15-$ArSO_3H$. The lower pK_a values for SBA-15-$PrSO_3H$-Prox were consistent with the enhanced acid strength of the sulfonic acid groups through a cooperative effect due to the proximity of acidic groups [25,30]. Although Dufaud and Davis have demonstrated the introduction of sulfonic acid pairs into mesoporous silica materials via grafting technique, this is the first time that the co-condensation synthesis technique has been used to incorporate the propylsulfonic acid pairs on a mesopore surface with the intention of controlling site cooperation. This synthesis procedure has the advantage of increasing the acid strength through mutual interaction of the tethered propylsulfonic acid species without necessarily increasing the surface concentration of the organic moieties.

Although many researchers have postulated from reaction kinetics and adsorption data that organic–inorganic hybrid mesoporous materials, which are synthesized via the co-condensation technique, have uniform distributions of organic moieties inside the mesopore surface, determination of the pK_a values provides a more direct technique of understanding the surface distributions of the tethered sulfonic acid groups. For example, as seen in Fig. 5, the relative pK_a values for each catalyst type decreased as the number of sulfonic acid groups increased, indicating that the mutual interaction between the acid sites increased for increasing surface concentration due to the formation of hydrogen bonds between adjacent acid sites, leading to a higher overall acid strength of the solid catalyst. It is noteworthy that the relative pK_a values for the SBA-15-PrSO$_3$H sample set decreased faster than the SBA-15-PrSO$_3$H-Prox samples as the surface concentration of sulfonic acid was increased, and, if extrapolated to higher surface concentration, would appear to intersect with the SBA-15-PrSO$_3$H-Prox samples at an approximate 25% molar ratio of MPTMS/TEOS or about 60% of the surface silanols. This result suggests that the co-condensation technique incorporated the propylsulfonic acid groups randomly across the pore surface, because the acidic sites interacted only when the sulfonic acid concentration on the surface was increased, which is consistent with previous reports. The decreasing pK_a values of the SBA-15-PrSO$_3$H-Prox with increasing surface concentration of the sulfonic acid pairs also signified that the bis(trimethoxysilyl)propyl disulfide moieties were randomly distributed on the mesopore surface. The same trend was observed for the arenesulfonic acid-functionalized mesoporous silica catalysts even though the change in the pK_a values was smaller than that of SBA-15-PrSO$_3$H samples.

To determine the catalytic effect of functionalizing the mesoporous silica materials with propylsulfonic acid moieties in proximity, the performance of the synthesized solid acid materials was compared in the methanol esterification of palmitic acid in a mixture with soybean oil as discussed previously [27]. The model high-free fatty acid feed was 15 wt% palmitic acid. This free fatty acid content is consistent with the value expected for a typical yellow grease or beef tallow, which are inexpensive sources of triglycerides that can be used in the production of alkyl esters. Unfortunately, a high fatty acid content in such oil feeds poses significant processing problems in the transesterification reaction due to saponification of the alkali catalyst and subsequent formation of soap, resulting in low yields and increased purification costs [48]. Pretreating such oil feeds via acid-catalyzed esterification of the free fatty acid would provide a means of producing a feedstock that could be used in a standard transesterification reaction system.

To investigate the effect of acid strength on the catalytic performance of the organosulfonic acid-functionalized mesoporous silica, the synthesized samples were used to catalyze the esterification reaction. The catalysts used were those synthesized with a precursor molar ratio of 5%, giving an equivalent ion capacity of 0.05 meq acidic sites per gram of palmitic acid. Fig. 6 shows the results of reaction studies performed at 85 °C with a methanol-to-palmitic acid weight ratio of 20:1. The figure gives the palmitic acid concentration by weight as a function of time. The order of catalytic activity was SBA-15-ArSO$_3$H > SBA-15-PrSO$_3$H-Prox > SBA-15-PrSO$_3$H, with palmitic acid conversions of 47, 34, and 28%, respectively, after 30 min. The higher activity of SBA-15-ArSO$_3$H compared with that of SBA-15-PrSO$_3$H was consistent with the material having the lowest relative pK_a value, confirming that the methanol esterification of palmitic acid was dependent on the acid strength of the solid acid catalyst [27]. Whereas the SBA-15-PrSO$_3$H-Prox sample had a similar relative pK_a value to that of SBA-15-ArSO$_3$H, it unexpectedly gave a lower palmitic acid conversion.

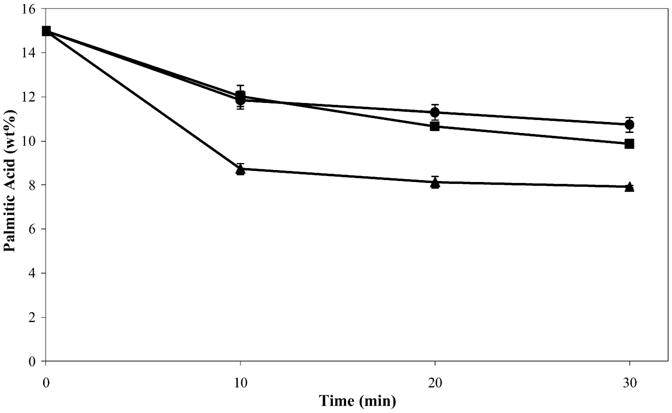


Fig. 6. Catalytic performance of the organosulfonic acid-functionalized mesoporous silica catalysts in the methanol esterification of palmitic acid. (●) SBA-15-PrSO$_3$H; (▲) SBA-15-ArSO$_3$H; (■) SBA-15-PrSO$_3$H-Prox.

The rate constant of the esterification reaction was determined using a pseudo-first-order reaction model with respect to palmitic acid concentration given that the methanol was in excess and the soybean oil was insignificantly reactive at these reaction conditions. For the organosulfonic acid-functionalized mesoporous silica materials studied, the rate constant was determined to be 1.05×10^{-2} min^{-1} for SBA-15-PrSO$_3$H, 1.38×10^{-2} min^{-1} for SBA-15-PrSO$_3$H-Prox, and 1.99×10^{-2} min^{-1} for SBA-15-ArSO$_3$H. These rate constants were slightly higher than we had previously reported [27], by magnitudes of 1.4 and 1.2 for mesoporous materials functionalized with propylsulfonic and arenesulfonic acid groups, respectively. The increase in rate constants can be attributed to increased MPD of the functionalized mesoporous materials, because the catalytic esterification of palmitic acid with methanol using mesoporous silica catalysts was shown to be pore diffusion-limited. Indeed, the reaction rate constant of SBA-15-PrSO$_3$H was equivalent to a sample with similar MPD [24].

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. A possible explanation for the discrepancy between the acid strength and catalytic activity for the mesoporous silica materials functionalized with propylsulfonic acid in proximity could be a decreased cooperation effect between the acid pairs due to weakened hydrogen bonds at elevated reaction temperature. This supposition was validated by measuring the pK_a of the synthesized solid acid catalysts at different temperatures, which gave increased pK_a values with increasing titration temperature. Consequently, the potentiometric titration method performed at ambient temperature was more sensitive to the surface distribution of organic moieties in the mesopores of the synthesized solid acid catalysts than the kinetics studies.

4. Conclusion

Incorporating propylsulfonic acid groups via the co-condensation technique resulted in tethered sulfonic acid groups that were not sufficiently close to each other to interact. As such, a higher surface concentration was required to achieve a cooperative effect between acid moieties. However, incorporation of spatially organized sulfonic acid groups enhanced acid site collaboration even at low surface concentrations, resulting in higher acid strength. The esterification results confirmed that by themselves, kinetic studies 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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