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Michael A. Jackson
United States Department of Agriculture

Isa K. Mbaraka
Iowa State University

Brent H. Shanks
Iowa State University, bshanks@iastate.edu

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Keywords

Solid acid catalysts, Novozym 435, Methyl oleate, Supercritical carbon dioxide

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Esterification of oleic acid in supercritical carbon dioxide catalyzed by functionalized mesoporous silica and an immobilized lipase

Michael A. Jackson^{a,*}, Isa K. Mbaraka^b, Brent H. Shanks^b

^a *New Crops Research Unit, USDA/ARS/NCAUR, 1815 North University Street, Peoria, IL 61604, United States*

^b *The Department of Chemical and Biological Engineering, Iowa State University, Ames, IA 50011, United States*

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Abstract

Organosulfonic acid-functionalized mesoporous silicas were tested for catalytic performance in the esterification of oleic acid with methanol in flowing supercritical carbon dioxide. The energy of activation of the sulfonic acid catalysts was found to be about 42 kJ/mol and was shown to be independent of pore size. The catalytic activity of the functionalized silicas was compared to a standard acidic resin, Amberlyst 15, and to an immobilized lipase, Novozym 435. The most active catalyst was Novozym 435.

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1. Introduction

The esterification of fatty acids and transesterification of triglycerides with methanol are two fundamental reactions in oil chemistry. These reactions (also called alcoholysis) are catalyzed either by alkaline or acid catalysts or by lipases. Alkaline catalysis is the preferred approach since this gives high yields at moderate temperatures and short reaction times [1], whereas acid catalysis requires longer times and higher temperatures [2]. The advantages of alkaline catalysis may appear obvious but a serious shortcoming lies in the fact that these catalysts tend to undergo saponification with free fatty acids forming soaps. Both the soaps and catalyst, either alkaline or acid, need to be neutralized and washed from the product mixture. Lipases are the hydrolytic enzymes that catalyze the reversible cleavage of triglycerides to free fatty acids and glycerol. These ubiquitous enzymes have found numerous commercial uses in the food, pharmaceutical, and detergent industries. The stability and activity of these enzymes in non-aqueous media have long been recognized [3]. Under low-water conditions, the reversible reaction is favored and esters are synthesized. Researchers have exploited this property for the

synthesis of esters valuable to the flavors and fragrances trade, modified triglycerides for specialty diets, and mono- and diglycerides commonly used as emulsifiers in spreads and sauces.

Regardless of catalyst used, the targeted methyl esters are valuable due to their higher volatility compared to the parent acid and are the basis for fatty acid analysis for triglyceride characterization and, on production-scale, are used in skin care products, pharmaceutical formulations, lubricants, and are the main component of the renewable transportation fuel, biodiesel.

Current methods for the production of methyl esters for use in biodiesel involve the use of sodium hydroxide or methoxide to catalyze the conversion [4]. While the transesterification is 99% complete in as little as 1 h, the successful use of alkaline catalysts requires that the free fatty acid content of the feedstock be <0.5% to prevent the formation of soaps. This requirement is easily met by using high quality feedstock such as soybean or rapeseed oil. However, tallow and waste restaurant frying oil, a promising and inexpensive supply, oftentimes have higher free fatty acid levels [5]. One approach to solving this problem is to perform a pretreatment step in the presence of an acid catalyst, such as sulfuric acid [6], thereby forming alkyl esters from the free fatty acids prior to the transesterification step. Using a homogenous catalyst such as sulfuric acid necessitates an additional step to neutralize and or

* Corresponding author. Tel.: +1 309 681 6255; fax: +1 309 681 6524.

E-mail address: jacksonmic@ncaur.usda.gov (M.A. Jackson).

remove the acid and also causes corrosion of the equipment. The use of a solid acid catalyst would bypass this step in that the catalyst could be retained in a separate, continuous flow reactor. Biodiesel synthesis using acid catalysts has been recently reviewed [7].

An alternative approach to preparing biodiesel is the transesterification of triglycerides using methanol and ethanol near their critical points [8–10]. Madras and coworkers measured activation energies of the transesterification sunflower oil in near-critical methanol and ethanol and compared these to transesterification by Novozym 435 in supercritical carbon dioxide. They found high conversions of 80–100% in alcohol but only 30% when the enzyme was the catalyst.

The pursuit of solid acid catalysts has focused on mesoporous silica substrates [11]. Ordered silica catalysts have received much attention since the development of the mesoporous materials by researchers at Mobil Oil [12]. These materials, designated M41S, were synthesized around large, ordered, surfactant micelles. Removal of the surfactant, followed by calcination, gave a product that contained pores of tunable dimensions in a narrow size range. Subsequent developments around this theme gave silica and aluminosilicas such as HMS [13] and SBA-15 [14]. It was then shown that hybrid silicas containing organic moieties effectively functionalized the surface [15,16]. The combination of a wide range of possible functionalities and control of pore size distribution has offered promise for catalyst design.

Supercritical carbon dioxide is well known for its compatibility with lipases [17–22,27]. It is also regarded as a green solvent [23] owing to its low toxicity, non-flammability, and its environmentally benign character. Other advantageous properties of supercritical carbon dioxide include its tunable density, high diffusivity, and manageable critical point of 31 °C and 8.3 MPa. It is these properties that allow us to make a direct comparison under identical reaction conditions of the catalytic activity of two classes of heterogeneous catalysts: acid-functionalized mesoporous silicas and an immobilized enzyme. To our knowledge, this has not been done previously. In this paper, we present kinetics data for the methanolysis of oleic acid in a flow system using supercritical carbon dioxide as solvent and acid-functionalized mesoporous silicas and an immobilized lipase as catalysts.

2. Experimental

2.1. Synthesis of organosulfonic acid-functionalized mesoporous silicas

Organosulfonic acid-functionalized mesoporous silicas were synthesized according to the procedures described previously [24–26]. Tetraethoxysilane (TEOS) (98%, Aldrich) was used as the silica precursor, (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. The relative hydrophobicity of the solid acid catalyst was modified with propyltrimethoxysilane (PrTMS)

(98%, Aldrich), which was introduced via the co-condensation synthesis technique. Pluronic P123 (BASF Co., USA), which is a triblock copolymer of polyethylene oxide–polypropylene oxide–polyethylene oxide with the molecular structure PEO₂₀–PPO₇₀–PEO₂₀ (MW = 5800), was used as purchased to tailor the textural properties of the mesoporous materials. Mesoporous silica material functionalized with propylsulfonic or arenesulfonic acid groups were denoted as SBA-15-PrSO₃H and SBA-15-ArSO₃H, respectively. Mesoporous silica materials functionalized with both propylsulfonic acid and propyl groups was abbreviated as SBA-15-PrSO₃H-Pr. The catalytic performance of the synthesized solid acid catalysts in the methanol esterification reaction of oleic acid was compared to Novozym 435 (Novozyme, Franklinton, NC).

2.2. Characterization

The textural properties of the organosulfonic acid-functionalized mesoporous silicas, before and after the esterification reactions, were measured using the BET procedure. Nitrogen adsorption–desorption isotherms were taken at –196 °C using a Micromeritics ASAP 2020 system. The pore volume/pore size distributions and surface area of the samples were calculated using the BET and BJH methods, respectively. Prior to taking measurements, all samples were degassed at 100 °C for 5 h. The organic material present in the fresh and used mesoporous acid catalysts was quantified by elemental analysis performed on a Perkin-Elmer Series II 2400 CHNS analyzer. The ion capacities of the sulfonic acid groups were determined by acid–base titration.

NMR spectra were acquired on a Bruker 300 Avance Spectrometer operating at a 7.0 T magnetic field. Samples were loaded into a 7 mm zirconia rotor and were spun at 3.2 kHz. Proton decoupled ²⁹Si MAS NMR spectra were collected over 400 ppm using a 600 s repetition delay.

2.3. Catalytic tests

Alcoholysis reactions were carried out in a system depicted schematically in Fig. 1. Carbon dioxide (Linde, 20 ppm H₂O) was introduced into the system after first passing over a bed of activated alumina then brought up to 48.3 MPa by means of air driven booster pump (Haskel Milton Roy, Burbank, CA). Oleic acid (93% Cognis, Inc., stabilized with 200 ppm BHT) and methanol (Fisher Inc.) were pumped into the carbon dioxide stream by means of syringe pumps (Teledyne Isco, Lincoln, NE). Oleic acid flow was set at either 100 or 200 μL/min depending on the activity of the catalyst being examined. Alcohol was added at a 10-fold molar excess over oleic acid. Carbon dioxide flow was set at about 1.7 L/min with a micrometering valve and measured by means of a dry test meter. Control of the CO₂ flow is difficult with each change in temperature requiring adjustment of the micrometering valve. Actual flow rate ranged from 1.3 to 2.1 L/min. Despite this range, data were good enough to make kinetics measurements. At 70 °C and 48.3 MPa the density of CO₂ is 0.901 g/mL which gives a fluid flow through the system of 3.7 mL/min with

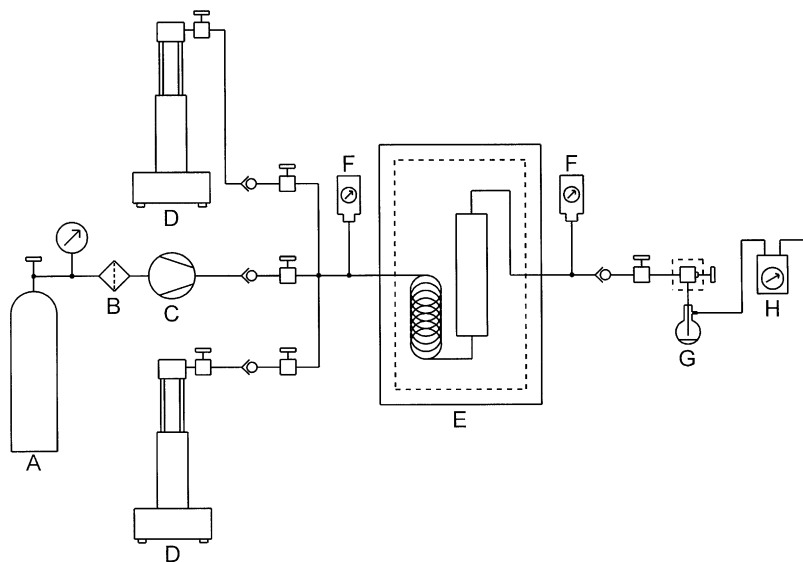


Fig. 1. Schematic of the system used for the esterification reactions. (A) CO₂ supply; (B) alumina filter bed; (C) booster pump; (D) syringe pumps containing reagents; (E) heated zone containing catalyst bed; (F) pressure transducers; (G) receiver under a heated micrometering valve; (H) dry test meter.

expanded gas flow at 1.7 L/min. With oleic acid added at 100 μ L/min, the oleic acid passed through the system at 0.17 mol/L. The silica catalysts were retained in a 5 mL extraction vessel (Thar Technology, Pittsburgh, PA) capped with 1 μ m frits. The Novozym 435 was contained in a 6 cm length of 4.7 mm i.d. stainless steel tubing plugged with glass wool. The different reactors were used due to the small volume of enzyme needed to keep conversion levels at an appropriately low level. Flow through the reactor was from the bottom to the top. The reactor was allowed to equilibrate for 30 min following each temperature change. Product was collected in a flask upon depressurization. In order to ensure that all of the product was being collected and was therefore representative, product was collected in a tared flask over a recorded period of time. This mass had to correspond to the known mass of oil and alcohol being pumped into the system. Also, the rate at which oleic acid was added was low enough that it remained within the range of its solubility in condensed CO₂ [25].

Products were analyzed by supercritical fluid chromatography using a Lee Scientific Series 600 SFC/GC (Dionex, Inc., Salt Lake City, UT) with a Selerity Technologies (Salt Lake City, UT) SB-phenyl-50 column (10 m \times 50 μ m i.d. \times 0.5 μ m film thickness). Under an operating temperature of 110 $^{\circ}$ C, the imposed pressure gradient was 100 atm for 5 min followed by

an increase of 4 atm/min to 164 atm. Samples were injected using a Valco (Valco, Inc., Houston, TX) injection loop with a volume of 200 nL. Analytes were detected by a flame ionization detector operating at 350 $^{\circ}$ C. Conversion was determined by the ratio of the ester peak to the acid peak. Retention times were determined using known sample of oleic acid and methyl oleate (Aldrich).

3. Results and discussion

The textural and chemical properties of the modified mesoporous silicas for the current work are summarized in Table 1. The large BET surface areas of the synthesized organic–inorganic hybrid materials were consistent with mesoporous silicas reported in the literature [29,30]. The N₂ adsorption–desorption isotherms of the synthesized organosulfonic acid-functionalized mesoporous catalysts had Type IV hysteresis loops, which are consistent with mesoporous materials tailored by non-ionic surfactant and functionalized with organic moieties [24,26]. Neither mono-functionalization nor bi-functionalization of the mesoporous silica materials had significant effect on the surface area of the resulting solid acid catalyst, implying that the organic species co-condensation with the inorganic precursor had no consequence on the final structure.

Table 1
Textural and chemical properties of fresh catalyst

Catalysts	Textural properties			Chemical properties		
	S_{BET} (m ² /g)	MPD (\AA)	V_p (cm ³ /g)	C/S (mol/mol)	S (mmol/g)	H ⁺ (meq/g)
SBA-15-PrSO ₃ H	740	55	0.98	4.59	1.77	1.05
SBA-15-ArSO ₃ H	680	65	1.02	16.3	0.63	0.72
SBA-15-PrSO ₃ H-Pr	920	48	1.02	9.1	0.89	0.91
HMS-SO ₃ H	830	20	0.4	3.85	2.36	0.56
SBA-15	800	58	1.17	–	–	–

The median pore diameter (MPD) of the acid-functionalized mesoporous materials, which was determined by the BJH method on the adsorption branch of the N_2 adsorption–desorption isotherm, was in the range reported in the literature. Material functionalized with arenesulfonic acid groups had larger MPD than propylsulfonic acid-functionalized mesoporous material while the bi-functionalized sample (SBA-15- $PrSO_3H$ -Pr) had the smallest pore diameter of 48 Å. The pore size distributions of the synthesized samples (not shown) were narrow and unimodal and were not affected by the organic species incorporated into the mesostructure. The pore volumes of the functionalized mesoporous silica materials were comparable, as seen in Table 1, and there was no apparent correlation to either the BET surface area or the pore diameter.

The relative carbon/sulfur ratio and the sulfur content of the functionalized mesoporous silica materials, as determined by elemental analysis, are summarized in Table 1. The sulfur content of propylsulfonic acid-functionalized samples gave good agreement with the molar ratios of the precursor used to synthesize the materials, demonstrating high incorporation yield of the MPTMS. The sulfur equivalence of arenesulfonic acid-modified mesoporous catalyst was slightly lower than expected, which may have been due to the presence of impurities in the precursor. The carbon/sulfur ratio of the mesoporous silica material modified with propylsulfonic acid was slightly higher than the theoretical value expected for the propylthiol group, suggesting that probably unhydrolyzed methoxy and/or ethoxy groups from the parent precursors were still present in the synthesized catalyst [26,31]. The C/S ratio of arenesulfonic acid-functionalized silica was twice the expected ratio, suggesting that there was relative high retention of carbonaceous material in the final sample. The C/S ratio of SBA-15- $PrSO_3H$ -Pr was higher than SBA-15- $PrSO_3H$, which is consistent with the incorporation of the hydrophobic propyl groups onto the mesostructure of the synthesized catalyst.

As seen in Table 1, the ion capacity of the sulfonic acid in the synthesized catalysts, as determined quantitatively by acid–base titration, was consistent with the sulfur content measured for the SBA-15- $ArSO_3H$ and SBA-15- $PrSO_3H$ -Pr samples, suggesting that the in situ oxidation of the sulfur compounds to sulfonic acid species was successful. The ion capacity of SBA-15- $PrSO_3H$ sample was 40% less than its sulfur content suggesting that not all of the sulfur was converted to the sulfonic acid groups [32]. The comparable equivalence of sulfur content and the number of sulfonic acid in SBA-15- $PrSO_3H$ -Pr signified that the introduction of the propyl group into the mesostructure had insignificant effect on the resulting ion capacity of the final sample.

Reaction conditions were chosen such that the concentration of oleic acid did not exceed its solubility in CO_2 at 48 MPa in the temperature range of 50–120 °C [28]. This prevents complications caused by precipitation of oleic acid and formation of a liquid phase in the reactor. Oleic acid was pumped into the system at a rate that limited conversion to less than 15%. Thus, for the kinetic analysis, the system was deemed to be operating as a differential reactor.

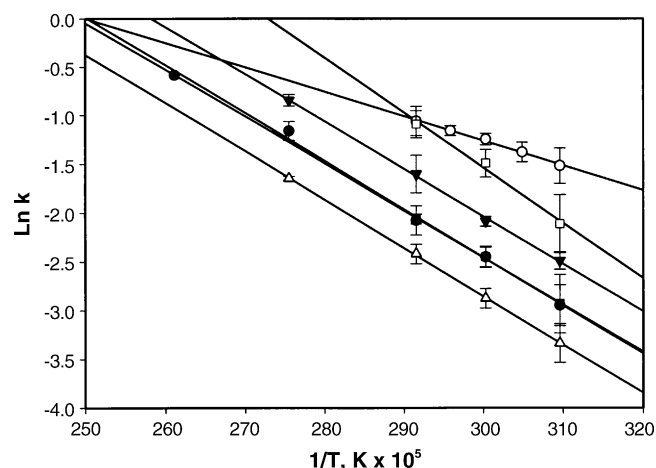


Fig. 2. Arrhenius plots for the methanolysis of oleic acid as catalyzed by SBA-15- $ArSO_3H$ (●), Novozym 435 (○), SBA-15- $PrSO_3H$ (▼), HMS- SO_3H (△), SBA-15- $PrSO_3H$ -Pr (□), and Amberlyst 15 (■). Reaction conditions as described in the text.

The Arrhenius plot used to determine E_a for the functionalized silicas and Novozym 435 are shown in Fig. 2. Table 2 contains the kinetics data extracted from the Arrhenius plots for each of the catalysts. In a previous paper, Mbaraka et al. [25], showed that the E_a values for the methanolysis of palmitic acid in methanol decreased with increasing pore size of the modified silica catalyst used. This was attributed to the importance of activated diffusion. However, we find that in flowing supercritical carbon dioxide E_a values of all of the sulfonic acid catalysts are about 42 kJ/mol and that pore size was irrelevant as demonstrated by comparison of the E_a values for SBA-15- $PrSO_3H$ and HMS- SO_3H . Even the membranous, reticular Amberlyst 15, which should have easily accessible acid groups, had an activation energy of 40 kJ/mol. This suggests that the high diffusivity achievable in supercritical CO_2 overcomes the limitation of internal diffusion [33].

Turnover number (TON) defined as molecules of product formed per active site measured in the fresh catalyst per second, varied within the inorganic catalysts by an order of magnitude but also appears unrelated to pore size and showed no relation to activation energy. The two better TONs were found for SBA-15- $ArSO_3H$ and SBA-15- $PrSO_3H$ -Pr. These differ from the other two silicas in separate ways. The former has the aromatic sulfonic acid group which is more acidic than the aliphatic acids and this could increase its catalytic activity. The latter has propyl groups within the silica pores, which increase the

Table 2
Kinetics parameters for the methanolysis of oleic acid

Catalyst	Apparent E_a (kJ/mol)	Turnover number (molecules/s)
Amberlyst 15	40 ± 2	2.1 × 10 ⁻⁴
SBA-15- $PrSO_3H$	41 ± 1	1.2 × 10 ⁻³
SBA-15- $ArSO_3H$	40 ± 1	2.4 × 10 ⁻³
SBA-15- $PrSO_3H$ -Pr	47 ± 5	2.9 × 10 ⁻³
HMS- SO_3H	41 ± 1	3.0 × 10 ⁻⁴
Novozym 435	21 ± 1	13

Table 3
Textural and chemical properties of used catalyst

Catalysts	Textural properties			Chemical properties		
	S_{BET} (m ² /g)	MPD (Å)	V_p (cm ³ /g)	C/S (mol/mol)	S (mmol/g)	H ⁺ (meq/g)
SBA-15-PrSO ₃ H	160	48	0.23	11.86	1.23	1.31
SBA-15-ArSO ₃ H	520	63	0.85	17.15	0.65	0.69
SBA-15-PrSO ₃ H-Pr	130	48	0.2	42.59	0.62	0.63
HMS-SO ₃ H	175	24	0.09	9.26	1.90	0.43
SBA-15	460	64	0.85	–	–	–

hydrophobicity of the pores. This more hydrophobic layer could serve to increase the availability of oleic acid by making it more soluble in this layer nearest the acid groups. All of the modified silicas had a greater TON than did Amberlyst 15. Also included in Table 2 are the E_a and TON for the immobilized lipase Novozym 435. The TON was determined based on molecular weight of the enzyme (33 kDa) and the catalyst containing 10 wt% protein. It is clear that the enzyme is by far the most active catalyst by weight that we examined. The activation energy is the lowest and the TON is more than 6000 times greater than the best modified silica. This advantage of the enzyme is considerably reduced by the bulk densities of the two classes of catalyst. SBA-15-PrSO₃H has a bulk density of 270 mg/mL whereas Novozym 435 has bulk density of 400 mg/mL or about 1.5 times greater. This means that in terms of filling a reactor of fixed volume, a greater mass, and therefore a greater number of active sites, of inorganic catalyst could be added compared to enzyme active sites. In fact, if a turnover number per volume is calculated, the enzyme is found to be only 46 times as active as SBA-15-PrSO₃H.

Liu et al. [34] have recently shown that water effectively inhibits ester formation between acetic acid and methanol when sulfuric acid is used as catalyst. By studying initial water addition in a batch reactor, they were able to show that the loss in acid strength of the catalytic protons due to water solvation reduced the concentration of protonated carboxylic acid and, therefore, ester formation. In our flowing system, we see no such deactivating effect of water since water is removed from the catalyst bed by the flowing carbon dioxide. As mentioned

above, the arenesulfonic acid, being a stronger acid than the propylsulfonic analogue, also had greater activity as an esterification catalyst. If water generated by the condensation of oleic acid and methanol were to inhibit the reaction, we would have seen a leveling of activity when comparing these two catalysts.

To determine the stability of the synthesized organosulfonic acid-functionalized mesoporous silica in the methanol esterification of oleic acid, the textural and chemical properties of the used catalysts were determined and are summarized in Table 3. All the organo-modified mesoporous silicas showed significant structure loss after exposure to the reaction conditions in supercritical carbon dioxide. Among the organosulfonic acid-functionalized mesoporous materials, SBA-15-ArSO₃H showed the least change in textural properties, where BET surface area, pore volume, and MPD decreased by 24, 17, and 3%, respectively. All of the propylsulfonic acid-functionalized samples had worse structure stability under the reaction conditions, with significant changes in the textural properties.

As seen in Table 3, the relative sulfur/carbon ratio and the sulfur content of the used catalysts showed that there was an accumulation of carbonaceous material on the functionalized mesoporous catalysts. The amount of carbonaceous material appeared to depend on the type of organic moieties incorporated into the mesoporous silica, since the carbon content of the synthesized samples increased in the order of SBA-15-ArSO₃H > SBA-15-PrSO₃H > SBA-15-PrSO₃H-Pr. The significant increase in carbon could partly explain the loss

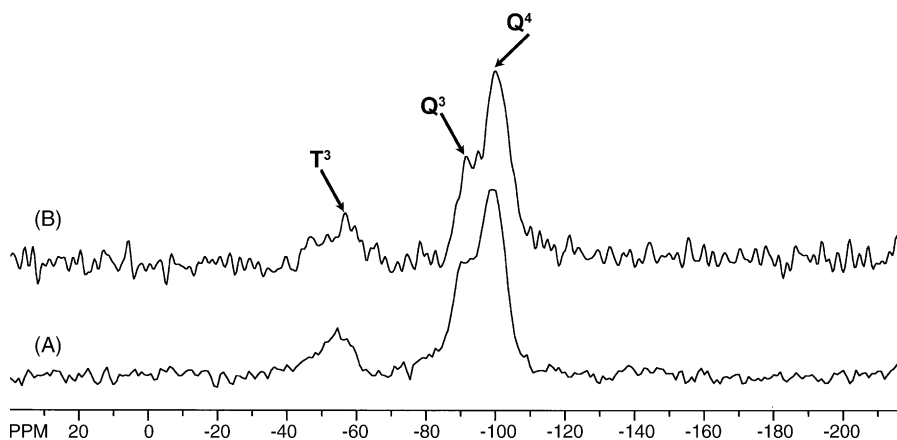


Fig. 3. ²⁹Si NMR spectra of: (A) fresh and (B) used SBA-15-PrSO₃H.

of catalytic activity as well as poor textural properties of the used catalysts. The used propylsulfonic acid-functionalized samples showed substantial loss of sulfur content (>30%) unlike the arenesulfonic acid-modified sample, which was not significantly affected by the methanolysis reaction. Loss of sulfur on used propylsulfonic acid-functionalized mesoporous silica samples led to decrease in the ion capacity of the catalysts, as seen in the table, except for SBA-15-PrSO₃H, which unexpectedly increased by 25%. It is noteworthy that the significant loss of sulfur in the used organosulfonic acid-modified mesoporous catalysts inevitably led to poor catalytic performance of the recycled catalysts. For example, SBA-15-PrSO₃H lost 23% of its activity after 8 h on line at 80 °C as conversion fell from 13 to 10% but did not lose further activity for the next 13 h.

The ²⁹Si NMR spectra of fresh and used SBA-15-PrSO₃H are shown in Fig. 3. Assignment of the peaks is as follows: –105 ppm, Q⁴ Si ((SiO)₄Si); –95 ppm, Q³ Si ((SiO)₃SiOH); –60 ppm, T³ Si ((SiO)₃SiR) [35]. The ratio of Q⁴ + Q³ to T³ remained 5.5 indicating that the organic functional groups on the silica were not lost during reaction.

4. Conclusions

Sulfonic acid-functionalized mesoporous silicas have been shown to have higher catalytic activity toward the methanolysis of oleic acid in supercritical carbon dioxide than commercially available Amberlyst 15. Using supercritical carbon dioxide as solvent had a leveling effect on the silica catalysts by overcoming the diffusion limitation encountered in methanolic solution thereby making pore size irrelevant in the determination of activation energy. However, acid strength still had an effect on turnover number with the more acidic aromatic acid having the greater activity by this measure. Also, increasing the hydrophobicity of the catalyst surface also increased turnover number. Thus, improvement in acid catalysts can still be realized by design. In direct comparison and under identical reaction conditions, the catalysts described here were much less active than the immobilized lipase, Novozym 435. Furthermore, the lack of stability and durability of the silicas shows that these catalysts need to be improved upon before they can perform near the levels of a biocatalyst.

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