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# A novel highly acidic sulfonic functionalized SBA-1 cubic mesoporous catalyst and its application in the esterification of palmitic acid

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Propylsulfonic acid functionalized cubic mesoporous silica was fabricated through in situ oxidization of mercaptopropyl groups with $H_2O_2$ during co-condensation of tetraethyl orthosilicate and 3-mercaptopropyl trimethoxysilane under strong acidic conditions. The materials obtained with 5–20 mol % loadings of sulfonic acid groups had surface areas of up to 1300 $m^2/g$ and pore sizes of ca. 2.5 nm. The catalytic activity of this material was investigated: tests were performed on the esterification of palmitic acid being a model compound in the process of biodiesel production. Methyl ester yield on this new nanoporous catalyst is very remarkable during a mild liquid phase reaction.

Keywords: *cubic mesoporous silica; SBA-1; esterification; biodiesel; palmitic acid*

## 1. Introduction

The discovery of an ordered M41S family of mesoporous materials has stimulated extensive research in the field of their potential use as catalysts, adsorbents, and templates for the syntheses of nanostructures [1, 2]. To further explore possible applications of these materials, much effort was devoted to syntheses of organically hybrid well defined pore structures, highly accessible functional groups, and controlled surface reactivity [3, 4]. Grafting of functional organosilanes by using surface hydroxyl groups as anchor points has been widely used [5, 6].

It is generally accepted that a cubic mesostructure is more advantageous for catalytic applications than a hexagonal one, since three dimensional pore arrangements of cubic mesostructures are more resistant to pore blocking and allow faster diffusion of reactants. Therefore, organo-functionalized mesoporous silicas with cubic mesostruc-

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tures would be more desirable than those with hexagonal mesostructures such as MCM-41. For the first time, Huo et al. [7–9] reported a successful synthesis of SBA-1 (cubic *Pm*3*n*) through the S+XI route, where S, X, and I correspond to surfactant, halide, and inorganic species, respectively. In this approach, acidic conditions were imposed, and a surfactant having a large head group, namely cetyltriethylammonium bromide (CTEABr) was used. However, so far only a few functionalized SBA-1 mesoporous materials have been reported. Indeed, it has a direct relation to poor structural stability of SBA-1 under hydrothermal conditions. On the other hand, the addition of organosilanes during the direct synthesis of organo-functionalized SBA-1 mesoporous materials in strongly acidic conditions is much more favourable [10].

Sulfonic-functionalized mesoporous materials received exceptional attention because of their numerous practical applications in heterogeneous acid catalysis, toxic mercury ion trapping, biomolecule immobilization, and as a support material for metallic nanoparticles [11]. Acid catalysts increase reaction rates of esterification and trans-esterification processes. Fatty acid methyl esters are products of trans-esterification of vegetable oils and fats with methanol in the presence of acid or basic catalysts. These products are so-called biodiesels. A worldwide interest in biofuels being an alternative to diesel fuel is growing, especially in environmentally conscious countries.

Many researchers made attempts to synthesize vegetable oil based derivatives with properties and performance similar to those of petroleum based diesel fuel. Biodiesel (monoalkyl esters) is one such alternative fuel, which is obtained by the trans-esterification of triglyceride oil with monohydric alcohols. It has been reported that biodiesel obtained from canola and soybean oil is a very good substitute for diesel fuel [12]. Despite its environmental benefits, the high cost of biodiesel production is the major obstacle to its commercialization. Trans-esterification of waste cooking oil is an effective way to reduce the cost of raw materials and to solve the problem of waste oil disposal. Unlike virgin oils, waste oils contain high quantities of free fatty acids (FFA) and water. Free fatty acid and water can limit the effectiveness of alkali-catalyzed processes. Also free fatty acids react with alkali catalysts and produce soaps and water. Therefore, saponification not only consumes the catalyst, but the resulting soaps can also cause the formation of emulsions. Both the aforementioned problems make the production of biodiesel more expensive. For this reason, acid catalysts, especially heterogeneous catalysts, attracted much more attention in regard to esterification reactions and biodiesel production.

This joint study is focused on synthesizing a novel organoacid functionalized mesoporous catalyst with remarkable hydrothermal stability, in order to catalyze the esterification of palmitic acid.

## 2. Experimental

*Template preparation*. The surfactant cetyltriethylammonium bromide (CTEAB) was fabricated by mixing of 1-bromohexadecane (98%, Merck) and triethylamine

(99%, Merck) in absolute ethanol under reflux conditions for 24 h. The ethanol was then removed with a rotary evaporator until a white, viscous paste was obtained. The resulting gel is recrystallised by a minimum addition of chloroform, and then ethyl acetate, until the whole solid precipitates [13].

*Sulfonic acid-functionalized SBA-1 preparation*. Sulfonic acid-functionalized mesoporous silica materials were fabricated by one-pot co-condensation of tetraethoxysilane (TEOS) and MPTMS in the presence of CTEAB under acidic conditions, along with a direct reaction with $H_2O_2$ at room temperature. The final molar composition of the initial gel was as follows: TEOS: *y* MPTMS: 0.2 CTEAB: (30–40) HCl: 700 $H_2O$:( 0–2) $H_2O_2$.

In a typical procedure, 8 g of TEOS was first placed in an opening beaker with 12.5 $cm^3$ of 12 M HCl and 100 $cm^3$ of water, and was subsequently hydrolyzed at room temperature under stirring for an appropriate duration. Then, 1.5 g of CTEAB was added to a prehydrolyzed mixture and the stirring was continued. The mixture became a slightly viscous solution; appropriate quantities of MPTMS and aqueous solution of $H_2O_2$ (30 wt. %) were slowly added to the solution. Stirring of the mixture was maintained at a constant temperature for 3 h. The solution was then transferred to a Teflon lined autoclave for about 1 h at 100 °C, and finally the solid was filtered, washed and dried at 100 °C overnight. The MPTMS/$H_2O_2$ molar ratio was 1/10, and the MPTMS/(TEOS + MPTMS) ratio varied from 0 to 0.20. The resultant samples are referred to as SBA-1-$SO_3H$-*x*-*T*, where *T* stands for the "prehydrolysis time of TEOS in minutes" and *x* is the MPTMS/(TEOS + MPTMS) molar percentage.

For example, SBA-1-$SO_3H$-10-30 represents the sample prepared with TEOS prehydrolysis for 30 min and such that MPTMS/(TEOS + MPTMS) = 10 mol %. For comparison, samples were also prepared without TEOS prehydrolysis. They are labelled as SBA-1-$SO_3H$-*x*-0. Another sample containing 10 mol % of MPTMS was prepared with TEOS prehydrolysis in the absence of $H_2O_2$ and is denoted SBA-1-SH-10-*T*. The thiol groups in SBA-1-SH-10-*T* were post-oxidized to sulfonic acid groups with a 15-fold excess of aqueous solution of $H_2O_2$ (30 wt. %) at room temperature for 4 h. The solids were then acidified with aqueous solution of 2M HCl, followed by filtration, washing with water and ethanol, and finally drying at 100 °C. The post-oxidized sample was defined as SBA-1-$SO_3H$-10-*P*. A hexagonal MCM-41 sample was synthesized as described in literature [2]. It was functionalized and post-oxidized in the same way, and was named as MCM-41-$SO_3H$-10-P.

*Template extraction*. Resultant samples were extracted in a soxhlet extraction apparatus, with ethanol as the extraction solvent, in order to remove templates. FTIR was used to monitor the removal of templates. All characterizations and catalytic tests confirmed the samples were template-free.

*Catalyst characterization*. $N_2$ sorption isotherms were recorded using a Belsorp-18 (Bel Japan Inc.,) at liquid nitrogen temperature. Before taking the measurements, the samples were degassed at 150 °C for 4 h. The specific surface areas were evaluated using the Brunauer–Emmett–Teller (BET) method in the $p/p_0$ range of 0.05–0.3. Pore size distribution curves were calculated from the adsorption branch of the isotherms and by the Barrett–Joyner–Halenda (BJH) method. The pore volume was taken at the $p/p_0$= 0.990 point. X-ray powder diffraction (XRD) patterns were obtained on a Philips X'Pert diffractometer using $CuK_\alpha$ radiation (1.5418 Å).

Thermogravimetric (TG) analyses were carried out on a Shimadzu DTG 60 thermogravimetric analyzer with the heating rate of 10 °C/min in the air flow of 50 $cm^3$/min. Fourier transform infrared (FTIR) spectra were taken on a Bruker Equinox 55 spectrometer, with the resolution of 2 $cm^{-1}$, using the KBr method. The content of sulfonic acid centres in the materials was determined by ion-exchange with sodium cations followed by acid titration [11]. Aqueous solutions of sodium chloride (NaCl, 2M), were used as the exchange agents. In a typical experiment, 0.20 g of solid, treated at 150 °C for 5 h, was added to 20 $cm^3$ of aqueous solution containing the corresponding salt. The resultant suspension was equilibrated for 4 h, then filtered and washed with a small amount of water. Finally, the filtrate was titrated potentiometrically by dropwise addition of aqueous solution of 0.01 M NaOH.

*Catalytic reactions*. The catalysts were heat treated at 200 °C for 6 h in order to remove adsorbed water in the materials. Then, esterification of palmitic acid with methanol was carried out in a two-necked flask of 50 $cm^3$ with a reflux condenser placed in a hot plate with a magnetic stirrer. In a typical experiment, 0.02 mol of palmitic acid and 0.2 mol of methanol were mixed under vigorous stirring and heated to 50 °C. Then 0.1 g of the treated catalyst was added into the reaction mixture. Reaction rates were determined during the reaction intervals. Quantitative analysis was based on the methyl ester products and the corresponding standard methyl palmitate (from Supelco).

In all cases, the liquid products were extracted from the reaction mixture at appropriate reaction intervals with a filtering syringe, and analyzed using an Agilent 5890 gas chromatograph (GC) equipped with a 30 m × 0.53 mm HP-5 capillary column and an FID detector.

## 3. Results and discussion

Powder X-ray diffraction analyses were performed on all the MPTMS-functionalized materials. The X-ray diffraction patterns of functionalized SBA-1 samples contain (200), (210), and (211) reflections belonging to the space group *pm*3*n*. Such patterns are characteristic of materials having ordered cubic arrays of a cage-like channel structure (Fig. 1).

The $N_2$ adsorption–desorption isotherms of the sulfonic acid-functionalized materials are illustrated in Fig. 2. The samples prepared with prehydrolysis of TEOS exhibit characteristic isotherms of type IV with apparent hysteresis loops, which are typical of mesoporous materials, according to the IUPAC classification. Pore diameter increases with the prehydrolysis time in the initial gel.

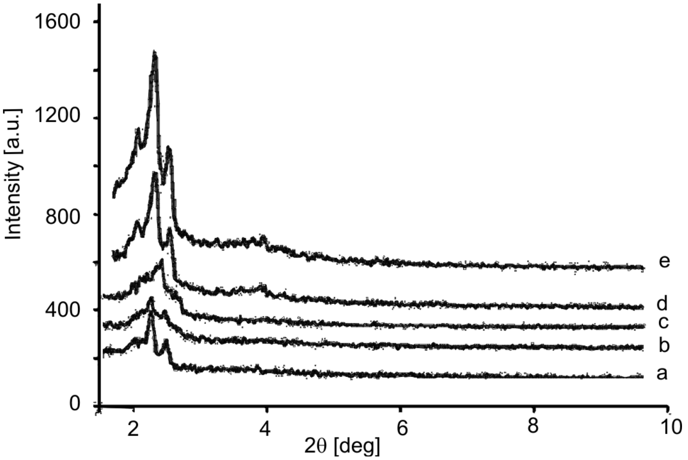

Fig. 1. XRD patterns of template extracted of: a) SBA-1-$SO_3H$-10-0, b) SBA-1-$SO_3H$-15-0, c) SBA-1-$SO_3H$-20-0, d) SBA-1-$SO_3H$-10-30, e) SBA-1-$SO_3H$-10-60

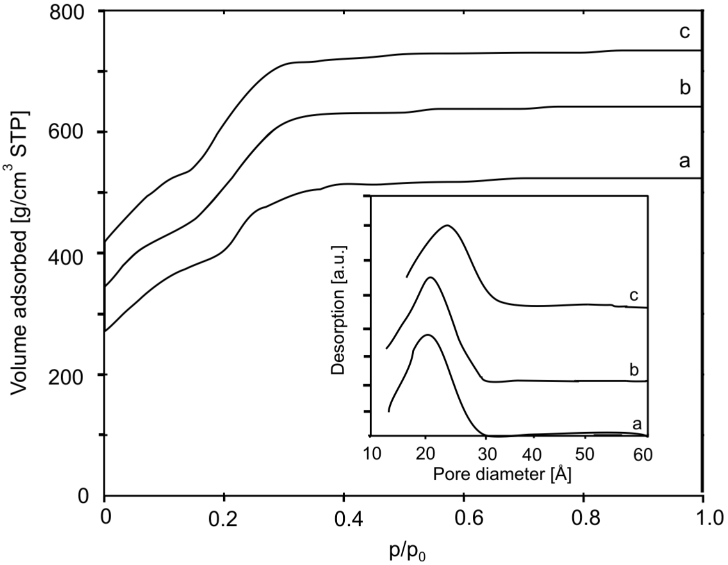

Fig. 2. $N_2$ adsorption isotherms of: a) SBA-1-$SO_3H$-10-0, b) SBA-1-$SO_3H$-10-30 and c) SBA-1-$SO_3H$-10-60

Basic physicochemical and textural data on the functionalized materials are shown in Table 1. All the samples prepared by co-condensation of TEOS and MPTMS show high surface areas and the BJH pore sizes (Dp) are around 2.1–2.5 nm. The surface area and the pore volume decrease as the MPTMS content is increased from 5 to 20 mol % in the synthesis mixture. Conversely, the samples prepared without TEOS prehydrolysis exhibit lower surface areas, smaller pore volumes, and smaller average pore sizes than their counterparts synthesized with TEOS prehydrolysis.

Table 1. Textural properties of silica materials

| Sample | $(A_{BET})^a$ [m$^2$/g] | $(V_p)^b$ [cm$^3$/g] | $(D_p)^c$ [nm] |
|---|---|---|---|
| SBA-1-$SO_3H$-10-30 | 1140 | 1.06 | 2.2 |
| SBA-1-$SO_3H$-10-60 | 1170 | 0.97 | 2.3 |
| SBA-1-$SO_3H$-10-180 | 1290 | 1.14 | 2.5 |
| SBA-1-$SO_3H$-10-0 | 1050 | 0.95 | 2.1 |
| SBA-1-$SO_3H$-10-PO | 1018 | 0.98 | 2.1 |
| SBA-1-$SO_3H$-5-0 | 1103 | 0.99 | 2.1 |
| SBA-1-$SO_3H$-15-0 | 1037 | 0.85 | 2.1 |

[a] BET surface area.
[b] Total pore volume.
[c] BJH pore size.

The sulfur contents in the MPTMS-functionalized materials was analyzed by TG and elemental analyses (EA), and the results are given in Table 2. It can be seen that MPTMS in the initial mixture was mostly incorporated into the silica materials. The acid capacities of the materials fabricated in the presence of $H_2O_2$ increased with the MPTMS content in the initial mixture. The numerical values for the acid capacity are very close to those obtained from EA or TG analyses, and constitute further confirmation that complete oxidation of the thiol groups had occurred. By contrast, the SBA-1 -$SO_3H$-10-P sample obtained by post-oxidation shows lower values for acid capacity than those obtained from EA or TG analyses: this is attributed to the incomplete oxidation of thiol groups.

Table 2. Sulfur contents and acid capacities
of functionalized SBA-1 materials with MPTMS

| Sample | Sulphur content [mmol/g] | | | Acid capacity [mmol/g] |
|---|---|---|---|---|
| | Calculated by EA by TG | | | NaCl |
| SBA-1-$SO_3H$-10-30 | 1.4 | 1.28 | 1.30 | 1.2 |
| SBA-1-$SO_3H$-10-60 | 1.4 | 1.32 | 1.30 | 1.21 |
| SBA-1-$SO_3H$-10-180 | 1.4 | 1.32 | 1.33 | 1.25 |
| SBA-1-$SO_3H$-10-0 | 1.4 | 1.20 | 1.13 | 1.10 |
| SBA-1-$SO_3H$-10-PO | 1.4 | 1.10 | 1.11 | 0.91 |
| SBA-1-$SO_3H$-5-0 | 0.75 | 0.77 | 0.58 | 0.68 |
| SBA-1-$SO_3H$-15-0 | 1.9 | 1.5 | 1.45 | 1.3 |

Esterification of palmitic acid with methanol was used to test the catalytic activities of a propylsulfonic acid functionalized catalyst in liquid phase reactions. The activities in the reactions were expressed by ester production.

The catalytic performance of the SBA-1-$SO_3H$-10-60 catalyst in esterification at 50 °C, expressed as a function of the reaction time, is shown in Fig. 3. The methyl ester content increases very rapidly and almost linearly with the reaction time in the first 150 min. Then, the reaction rate slows down as the reaction time prolongs. After 4 h, a conversion of around 85% had been obtained.

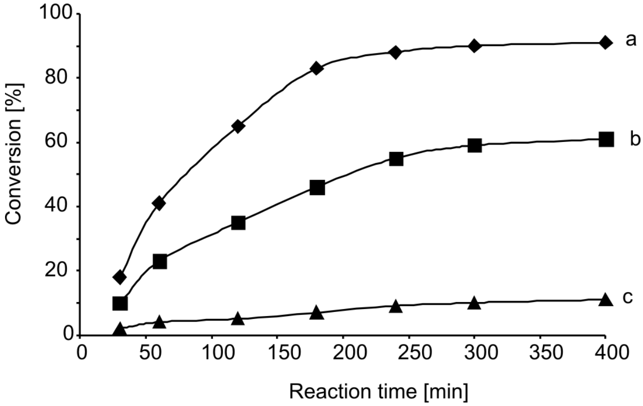

Fig. 3. Time dependence of degree of conversion of palmitic acid at 50 °C over sulfonic acid functionalized silica SBA-1 (a), MCM-41-$SO_3H$-10-P (b) and pure silica (c)

Esterification in a homogeneous system without solid catalysts or over pure silica was inefficient. Even after 4 h, the conversion did not exceed 10%. The catalytic activity of hexagonal MCM-41-$SO_3H$-10-P catalyst is lower than that of the acidified cubic SBA-1 (Fig. 3).

## 4. Conclusions

Novel functionalized cubic SBA-1 silica materials with different loadings of propylsulfonic acid groups were prepared by a simple co-condensation of TEOS and MPTMS under acidic conditions at room temperature. Samples prepared with TEOS prehydrolysis showed higher surface areas and larger pore volumes than those prepared without TEOS prehydrolysis. Thiol groups could be completely in situ oxidized into sulfonic acid groups in the procedure of synthesis, when $H_2O_2$ was also added to the mixture.

Esterification of palmitic acid with methanol was used to investigate the catalytic activity. This reaction opens up a new synthesis route which facilitates the use of inexpensive waste oils, having high free fatty acid contents, for the production of biofuels in mild conditions. Furthermore, the yield is high in comparison with conventional base catalysts.

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