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Fast and easy preparation of 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 prepared 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 around 2.5 nm. Next, the catalytic activity of this material was investigated in esterification of palmitic acid as a compound model in the process of biodiesel production. Methyl ester production by this new nanoporous catalyst shows a very remarkable yield 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, due to the potential use of these materials as prospective catalysts, adsorbents, and templates for the syntheses of nanostructures [1, 2]. To further explore possible applications of these materials, much research work has been devoted to the synthesis 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].

Generally speaking, it is 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, organofunctionalized mesoporous silicas with cubic

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mesostructures 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 $S^+X^-I^+$ 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. So far, only a few functionalized SBA-1 mesoporous materials have been reported due to their poor structural stability under hydrothermal conditions. On the other hand, addition of organosilanes in strongly acidic conditions during the direct synthesis of organofunctionalized SBA-1 mesoporous materials is gives better results [10].

Sulfonic functionalized mesoporous materials have received exceptional attention because of their many practical applications, such as heterogeneous acid catalysis, toxic mercury ion trapping, biomolecule immobilization, and as a support material for metallic nanoparticles [11]. Acid catalysts increase the 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 an acid or basic catalyst. These products are defined as biodiesels. There is a growing worldwide interest in biofuels as an alternative to diesel fuels, especially in environmentally conscious countries.

Many researchers tried to develop vegetable oil-based derivatives that have 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, a high cost of biodiesel production is the major obstacle to its commercialization. The transesterification 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 an alkali catalyst 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 biodiesels more expensive. For this reason, acid catalysts, especially heterogeneous catalysts, have attracted much more attention in regard to esterification reactions and biodiesel production.

This joint study focuses 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. Cetyltriethylammonium bromide (CTEAB) was prepared by mixing 1-bromohexadecane (98%, Merck) and triethylamine (99%, Merck) in absolute ethanol under reflux conditions for 24 h. The ethanol is then removed with a rotary evaporator until a white, viscous paste is 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 prepared 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 a 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 was varied from 0 to 0.20, or 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 15fold 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]. The resultant MCM-41 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 measured 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 applying 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_α 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 an 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, 2 M) 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 a 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 three reflections, which correspond to the (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 (illustrated in Fig. 1).

N_2 adsorption-desorption isotherms of the sulfonic acid functionalized materials are shown in Fig. 2. The samples prepared with prehydrolysis of TEOS exhibit characteristic type IV isotherms 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.

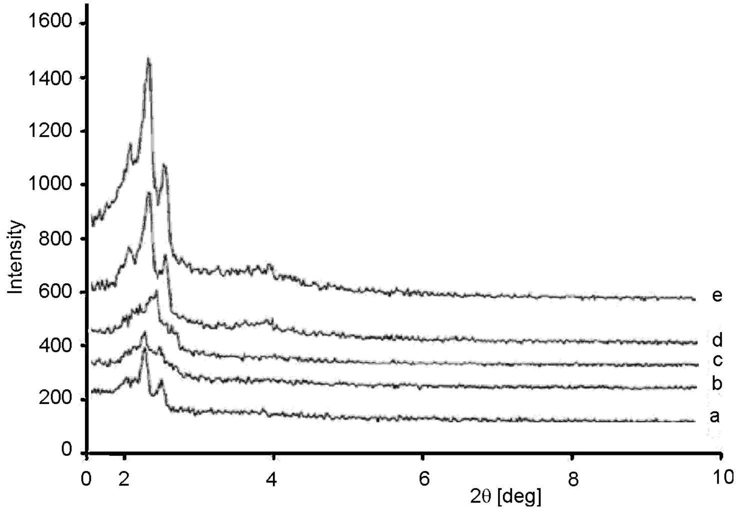

Fig. 1. XRD patterns of template extracted of: a) SBA-1-SO_3H-10-0, b) SBA-1-SO_3H-15-0, c) SBA-1-SO_3H-20-0, d) SBA-1-SO_3H-10-30, e) SBA-1-SO_3H-10-60

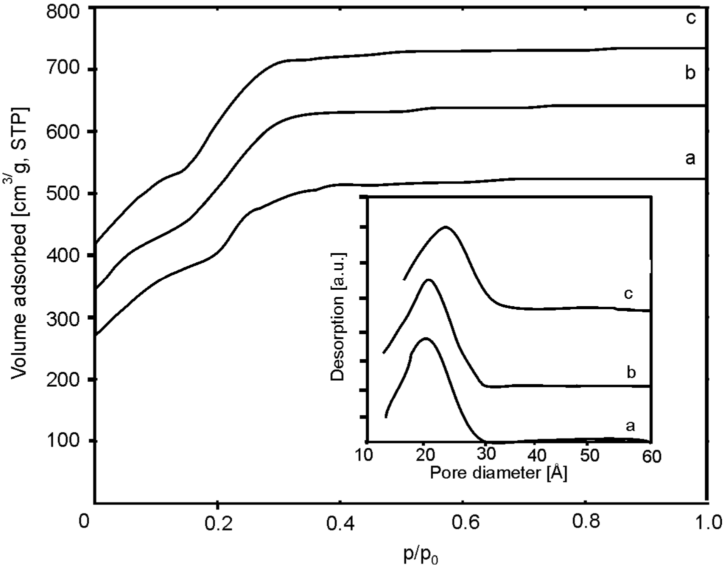

Fig. 2. N_2 adsorption isotherms of: a) SBA-1-SO_3H-10-0, b) SBA-1-SO_3H-10-30 and c) SBA-1-SO_3H-10-60

Basic physicochemical and textural properties of the functionalized materials are presented in Table 1. A_{BET} is the BET surface area, V_p – total pore volume and D_p

– the BJH pore size All samples prepared by co-condensation of TEOS and MPTMS show high surface areas and the BJH pore sizes 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}[1] $[\mathrm{m^2/g}]$	V_p[2] $[\mathrm{cm^3/g}]$	D_p[3] [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

The sulfur content 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 prepared 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 which is further confirmation that complete oxidation of 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 incomplete oxidation of the thiol groups.

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

Sample	S content [mmol/g]			Acid capacity [mmol/g]
	Calc	by EA	by TG	
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 propylsulfonic acid functionalized catalyst in liquid phase reactions expressed by ester yield. The catalytic performance of the SBA-1-SO_3H-10-60 catalyst during 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% is obtained.

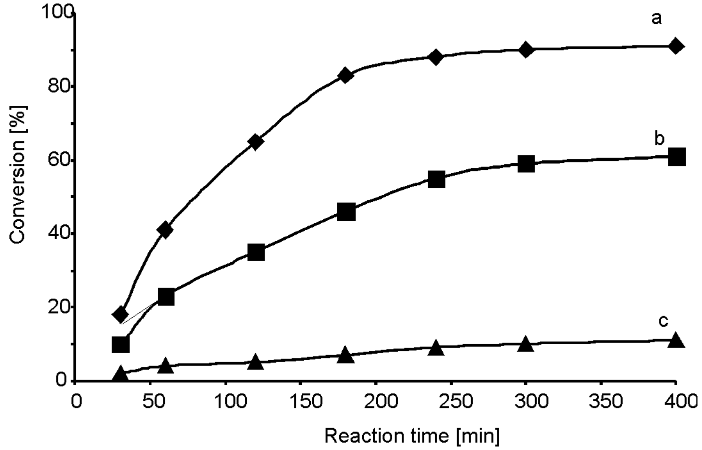

Fig. 3. Catalytic esterification of palmitic acid with methanol in function of reaction time at 50 °C over sulfonic acid-functionalized silica SBA-1 (a), in comparison to the results over MCM-41-SO_3H-10-P (b) and pure silica (c)

Figure 3 also shows that esterification in a homogeneous system without solid catalysts or over pure silica was very weak. Even after 4 h, conversion was lower than 10%. The catalytic activity of MCM-41-SO_3H-10-P is also shown in Fig. 3. As one can see, the acidified cubic SBA-1 catalyst delivers better activity in comparison with hexagonal MCM-41.

4. Conclusions

Novel functionalized cubic SBA-1 silica materials with various loadings of propylsulfonic acid groups were fabricated 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 pore volumes than those prepared without TEOS prehydrolysis. Thiol groups could be completely in situ oxidized into sulfonic acid groups in the synthesis procedure, when H_2O_2 was also added in the synthesis mixture.

Esterification of palmitic acid with methanol was used to confirm and quantify catalytic activity. This catalytic reaction opens up a new synthesis route which facilitates 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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