

Direct Syntheses of Ordered SBA-15 Mesoporous Silica Containing Sulfonic Acid Groups

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A simple procedure has been developed for the syntheses of functionalized mesoporous materials with sulfonic groups involving the co-condensation of tetraethoxysilane and mercaptopropyltrimethoxysilane in the presence of block copolymers and hydrogen peroxide under acidic conditions. The modified SBA-15 materials show hexagonal mesoscopic order and pore sizes up to 60 Å, with acid exchange capacities ranging from 1 to 2 mequiv of H⁺/g of SiO₂, surface areas up to 800 m²/g, and excellent thermal and hydrothermal stabilities. The formation of the sulfonic groups during co-condensation of the silica species coincides with enhanced mesoscopic ordering and changes in the adsorption properties of the final materials. ³¹P MAS NMR measurements of chemically adsorbed triethylphosphine oxide confirm the presence of Brønsted acid centers that are stronger than those found in Al-MCM-41. Finally, this procedure has been generalized to prepare functionalized mesoporous solids containing sulfonic groups and other organic moieties.

1. Introduction

Organically functionalized mesoporous materials have generated a great deal of interest in their application in the field of catalysis, sensing, and adsorption due to their high surface areas and large ordered pores ranging from 20 to 300 Å^{1–5} with narrow size distributions. Several routes are described in the literature for modifying interior pore surfaces in mesoporous solids.^{6–11}

Grafting of functional organosilanes by using surface hydroxyl groups as anchor points has been widely used.⁶ The catalytically active groups can be present in the silane, which are attached to the pore walls, or they can be introduced by subsequent postsynthesis reactions. A similar route involves the direct reaction of surface hydroxyl groups with functional complexes containing reactive ligands.^{6a} Recently, a new synthetic approach has been developed for the preparation of hybrid inorganic–organic mesoporous materials based on the co-condensation of siloxane and organosiloxane precursors in the presence of different templating surfactant solutions.^{7–11} Under basic conditions and using cetyltrimethylammonium bromide (CTAB), a wide range of functional groups have been incorporated through direct syntheses, including thiol, amine, epoxide, imadizole, chromophore, phenyl, and alkylorganosilane moieties.⁸ Although the authors demonstrated the synthesis of well-ordered organically modified MCM-41 materials, in some instances, the functionalized mesoporous materials tended to become mesostructurally disordered upon removal of the surfactant through acid leaching.^{8a,b,g} As an alternative, the synthesis of inorganic–organic hybrid mesoporous materials in the presence of CTAB and silica under acidic conditions¹² has resulted in more stable materials after removal of the surfactant species through acid-solvent extraction.^{8g,9} Several authors have

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(1) Yanagisawa, T.; Shimizu, T.; Kuroda, K.; Kato C. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 988.

(2) Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature* **1992**, *359*, 710.

(3) Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowicz, M. E.; Kresge, C. T.; Schmitt, K. D.; Chu, C. T. W.; Olson, D. H.; Sheppard, E. W. *J. Am. Chem. Soc.* **1992**, *114*, 10834.

(4) Zhao, D.; Huo, Q.; Feng, J.; Chmelka, B. F.; Stucky, G. D. *J. Am. Chem. Soc.* **1998**, *120*, 6024.

(5) Zhao, D.; Feng, J.; Huo, Q.; Melosh, N.; Fredrickson, G. H.; Chmelka, B. F.; Stucky, G. D. *Science* **1998**, *279*, 548.

(6) (a) Moller, K.; Bein, T. *Chem. Mater.* **1998**, *10*, 2950. (b) Clark, J. H.; Macquarrie, D. J. *J. Chem. Soc., Chem. Commun.* **1998**, 853. (c) Fryxell, G. E.; Liu, J.; Hauser, T. A.; Nie, Z.; Ferris, K. F.; Mattigod, S.; Meiling, G.; Hallen, R. T. *Chem. Mater.* **1999**, *11*, 2148. (d) Brunel, D. *Microporous Mesoporous Mater.* **1999**, *27*, 329.

(7) Huo, Q.; Margolese, D. I.; Stucky, G. D. *Chem. Mater.* **1996**, *8*, 1147.

(8) (a) Burkett, S. L.; Sim, S. D.; Mann, S. *J. Chem. Soc., Chem. Commun.* **1996**, 1367. (b) Fowler, C. E.; Burkett, S. L.; Mann, S. *J. Chem. Soc., Chem. Commun.* **1997**, 1769. (c) Lim, M. H.; Blanford, C. F.; Stein, A. *J. Am. Chem. Soc.* **1997**, *119*, 4090. (d) Bamnolung, C. M.; Slade, R. C. T.; Williams, R. T. *J. Mater. Chem.* **1998**, *8*, 569. (e) Van Rhijn, W. M.; De Vos, D. E.; Sels, B. F.; Bossaert, W. D.; Jacobs, P. A. *J. Chem. Soc., Chem. Commun.* **1998**, 317. (f) Lim, M. H.; Blanford, C. F.; Stein, A. *Chem. Mater.* **1998**, *10*, 467. (g) Fowler, C. E.; Lebeau, B.; Mann, S. *J. Chem. Soc., Chem. Commun.* **1998**, 1825. (h) Lim, M. H.; Stein, A. *Chem. Mater.* **1999**, *11*, 3285.

(9) Babonneau, F.; Leite, L.; Fontlupt, S. *J. Mater. Chem.* **1999**, *9*, 175.

(10) (a) Macquarrie, D. J. *J. Chem. Soc., Chem. Commun.* **1996**, 1961. (b) Macquarrie, D. J.; Jackson, D. B. *J. Chem. Soc., Chem. Commun.* **1997**, 1781. (c) Brown, J.; Mercier, L.; Pinnavaia, T. J. *J. Chem. Soc., Chem. Commun.* **1999**, 69. (d) Mercier, L.; Pinnavaia, T. J. *Chem. Mater.* **2000**, *12*, 188.

(11) Richer, R.; Mercier, L. *J. Chem. Soc., Chem. Commun.* **1998**, 1175.

(12) Huo, Q.; Margolese, D. I.; Ciesla, U.; Feng, P.; Gier, T. E.; Sieger, P.; Leon, R.; Petroff, P. M.; Schüth, F.; Stucky, G. D. *Nature* **1994**, *368*, 317.

also used the neutral S^oT^o assembly pathway for the preparation of functionalized HMS molecular sieves in the presence of amine surfactants.^{8e,10} Likewise, Richer and Mercier¹¹ have reported the synthesis of organically functionalized charge-neutral mesoporous silica using nonionic alkylpolyethyleneoxides as structure-directing agents (MSU). In both cases, the use of a self-assembly strategy without strong electrostatic interactions between the inorganic and surfactant species allows the nondestructive removal of the surfactant by simple solvent extraction.

There has been considerable interest in the development of heterogeneous solid acid catalysts to avoid the use of traditional homogeneous acid catalytic systems (H₂SO₄, HF, AlCl₃, BF₃, ...) which present serious drawbacks including hazards in handling, corrosiveness, production of toxic waste, and difficulties in separation. In this context, aluminum-substituted base-synthesized mesoporous silica (Al-MCM-41) has been tested in acid catalysis, though this material displays weak acidity in comparison to conventional acid zeolites, such as ultrastable zeolite Y or H-ZSM-5.¹³ As an alternative, the covalent attachment of alkylsulfonic acid groups to the surface of MCM and HMS molecular sieves has been proposed by several authors^{8e,f} and successfully tested in several acid-catalyzed reactions, including esterifications and condensations.^{8e,f,14} These alkylsulfonic-functionalized mesoporous materials can be prepared either via silylation of preformed mesoporous silica or via co-condensation of the primary building blocks using 3-mercaptopropyltrimethoxysilane (MPTMS) as the key precursor. Postsynthetically, the thiol groups can be treated to yield sulfonic groups by sequential oxidation with H₂O₂, acidification, and finally washing. Materials made in this way have yielded XRD patterns with lower scattering intensities that indicate relatively poor long-range order in comparison to the initial material containing the thiol groups.^{8e,f} In addition, decreases in the surface area and pore volume were observed after oxidation of such postsynthetically treated materials, which have used low molecular weight amphiphilic surfactants to establish their mesostructural order. Consequently, the resulting functionalized materials showed pore sizes less than 20 Å and, in some cases, type I nitrogen adsorption isotherms corresponding to nanoporous materials.

We have improved the direct synthesis method to create periodic ordered sulfonic-functionalized mesostructures with pores sizes up to 60 Å and high acid exchange capacities (1–2 mequiv of H⁺/g of SiO₂) using poly(ethyleneoxide)–poly(propyleneoxide)–poly(ethyleneoxide) block copolymer species (Pluronic 123) as the templating surfactant^{4,5} and acid catalysis.^{7,12} This new procedure involves a one-step synthetic strategy based on the co-condensation of tetraethoxysilane (TEOS) and MPTMS, in the presence of Pluronic 123 species and H₂O₂ in HCl aqueous solutions. This approach allows the in situ oxidation of thiol groups and resulting acid exchange of the sulfonic groups formed.

The acid-synthesized sulfonic-functionalized products reported here have large uniform pore sizes, high surface areas, good mesoscopic order, high thermal and

hydrothermal stabilities, and relatively high acid strengths, all of which are appealing properties for prospective catalytic applications. To the best of our knowledge, the work reported here is the first one-step synthesis of functionalized mesoporous silica in the presence of block copolymers and one of the few under acidic conditions. We have also found that this procedure is suitable for the simultaneous incorporation of sulfonic groups along with other organic moieties. For example, sulfonic acid mesoporous surfaces have been prepared mixed with benzyl and methyl groups. These mixed functionalities should have interesting effects on the adsorption and diffusion of reactants and products in the interior mesopores and ultimately on controlling the surface reactivity of these materials.

2. Experimental Section

2.1. Sample Preparation. Propyl–thiol mesoporous silica materials were synthesized as follows: 4 g of Pluronic 123 (Aldrich) was dissolved with stirring in 125 g of 1.9 M HCl at room temperature. The solution was heated to 40 °C before adding TEOS (Aldrich). Different TEOS prehydrolysis times were used prior to the addition of the thiol precursor (MPTMS (Gelest)) to the mixture ranging from 0 to 180 min. The molar composition of each mixture for 4 g of copolymer was XTEOS:(0.041 – X)MPTMS:0.24HCl:6.67H₂O, where X = 0.041 (0%), 0.0402 (2%), 0.0389 (5%), 0.0369 (10%), 0.0349 (15%), and 0.0328 (20%). The numbers in parentheses indicate the percentages of silicon atoms in the initial mixture as MPTMS. The resultant solution was stirred for 20 h at 40 °C, after which the mixture was aged at 100 °C for 24 h under static conditions. The solid product was recovered by filtration and air-dried at room-temperature overnight. The template was removed from the as-synthesized material by washing with ethanol under reflux for 24 h (1.5 g of as-synthesized material per 400 mL of ethanol).

Following solvent extraction of the block copolymer surfactant species, conversion to a sulfonic acid-derivatized mesoporous solid was accomplished as follows. Mesoporous silica with immobilized mercaptopropyl groups was oxidized with H₂O₂, following methods slightly modified from those described in the literature,^{8e,15} to produce sulfonic moieties on the interior silica surfaces. Typically, 0.3 g of extracted material was suspended in 10 g of aqueous 30 wt % H₂O₂. This suspension was stirred at room temperature in an Ar atmosphere for different lengths of time. Dilute H₂O₂ in methanol was also used as an oxidant solution.¹⁴ After the oxidation treatment, the resulting solution was filtered and washed separately with water and ethanol. The wet material was suspended (1 wt %) in 1 M H₂SO₄ solution for 2 h. Finally, the material was washed several times with water and ethanol and dried at 333 K under vacuum overnight.

One-step sulfonic-functionalized mesoporous silica samples were synthesized as described for the propylthiol mesostructured solid above. Following TEOS prehydrolysis, the MPTMS and the aqueous solution of H₂O₂ (30 wt %) were added at once and the resulting mixture was stirred at 40 °C for 20 h and aged at 100 °C for an additional 24 h under static conditions. The solid product was recovered and extracted as previously described.

The molar composition of the different mixtures for 4 g of copolymer was XTEOS:(0.041 – X)MPTMS:ZH₂O:0.24HCl:≈6.67H₂O, where X = 0.0369 (10%) and Z = 0.0123, 0.0369, or 0.0738. An additional sample with higher loading of sulfonic groups was prepared where X = 0.0328 (20%) and Z = 0.0738.

Mesoporous materials containing sulfonic groups with other organic moieties were synthesized in a manner

(13) Corma, A. *Chem. Rev.* **1997**, *97*, 2373.

(14) Bossaert, W. D.; De Vos, D. E.; Van Rhijn, W. M.; Bullen, J.; Grobet, P. J.; Jacobs, P. A. *J. Catal.* **1999**, *182*, 156.

similar to the sulfonic mesoporous materials described above. The time allowed for TEOS prehydrolysis was fixed at 180 min, after which the MPTMS, the second organotrialkoxysilane [(RO)₃-Si-R' with R' = benzyl and methyl, respectively; Gelest], and an aqueous solution of H₂O₂ (30 wt %) were added at once. The resulting mixture was stirred at 40 °C for 20 h and aged at 100 °C for 24 h under static conditions. The solid product was recovered, as described above.

The molar composition of the different mixtures for 4 g of copolymer was 0.0349TEOS:0.0041MPTMS:0.0021(RO)₃-Si-R':0.0369H₂O₂:0.24HCl:≈6.67H₂O.

Other Acid Solids. H-USY zeolite was supplied by W. R. Grace (Si/Al molar ratio = 3.5), and Amberlyst-15 was supplied by Aldrich. Al-MCM-41 samples with Si/Al molar ratios of 14 and 30, were prepared following a sol-gel approach recently described in the literature.¹⁶

2.2. Sample Characterization. X-ray powder diffraction (XRD) data were acquired on a SCINTAG PADX diffractometer using Cu K α radiation. The data were collected from 0.6 to 4° (2 θ) with a resolution of 0.02°. Photoacoustic infrared spectra were collected with a Nicolet 850 IR spectrometer and a photoacoustic cell, MTEC model 300. For each sample, 128 scans were added to achieve acceptable signal-to-noise levels.

Nitrogen adsorption and desorption isotherms at 77 K were measured using a Micromeritics ASAP 2000 system. The data were analyzed using the Broekhoff-de Boer (BdB) model.¹⁷ Both adsorption and desorption branches were used to calculate the pore size distribution. Good agreement between both values was found for all of the samples. The pore volume was taken at the $P/P_0 = 0.989$ single point.

A Netzsch thermoanalyzer STA 409 was used for simultaneous thermal analysis combining thermogravimetry (TGA) and differential thermoanalysis (DTA) at a heating rate of 10 °C/min in air.

Ion-exchange capacities of the sulfonic mesoporous materials were determined using aqueous solutions of sodium chloride (NaCl, 2 M) and tetramethylammonium chloride (TMACl, 0.05 M) as exchange agents. In a typical experiment, 0.05 g of solid was added to 10 g of aqueous solution containing the corresponding salts. The resulting suspension was allowed to equilibrate and thereafter titrated potentiometrically by dropwise addition of 0.01 M NaOH (aq).

Transmission electron microscopy (TEM) microphotographs were carried out on a JEOL 2000 electron microscope operating at 200 kV. Morphology and size of the particles were determined by scanning electron microscopy (SEM) with a JEOL 6300-F microscope.

Solid-state ²⁹Si NMR experiments were performed on a GE-300 spectrometer operating at a frequency of 59.70 MHz with the following conditions: magic-angle spinning at 5 kHz; $\pi/2$ pulse, 7 μ s; a repetition delay of 600 s; 200 scans. ¹H NMR measurements were made on the same spectrometer operating at 300.55 MHz with the following conditions: magic-angle spinning at 5 kHz; $\pi/2$ pulse, 6.5 μ s; a repetition delay of 15 s; 32 scans. The ²⁹Si and ¹H MAS spectra were referenced to tetramethylsilane.

Solid-state CP MAS ¹³C NMR measurements were recorded on a CMX-180 Chemagnetics spectrometer operating at a ¹³C frequency of 45.297 MHz and ¹H frequency of 180.129 MHz with the following conditions: magic angle spinning at 5 kHz; $\pi/2$ pulse, 7 μ s; a CP contact time of 2 ms; high power proton decoupling during detection; a repetition delay of 1.25 s; 50 000 scans. The spectra were referenced to tetramethylsilane.

Solid acid properties were assessed by monitoring the ³¹P NMR chemical shift of triethylphosphineoxide (TEPO) chemically adsorbed on the sulfonic-functionalized mesoporous silica. In a typical measurement, 0.015 g of TEPO was dissolved in 5 mL of anhydrous pentane, and this solution was mixed with 0.15 g of solid acid and allowed to equilibrate under stirring for 25 min before drying at 50 °C under vacuum. ³¹P NMR

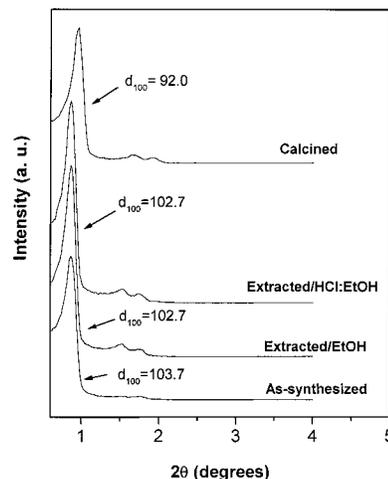


Figure 1. X-ray diffraction patterns obtained from conventional as-synthesized SBA-15 after different surfactant removal procedures.

measurements were performed on a GE-300 spectrometer operating at a frequency of 121.65 MHz under the following conditions: magic angle spinning at 5 kHz; $\pi/2$ pulse, 5 μ s; 32 scans; 30 s repetition delay. The spectra were referenced to an 85 wt % phosphoric acid external standard.

3. Results and Discussion

3.1. Thiol-Functionalized Mesoporous Silica Prepared Using Pluronic 123. Compared to alkaline syntheses of M41S materials prepared using low-molecular-weight cationic surfactants, preparations of mesoporous silica under acidic conditions in the presence of a poly(alkyleneoxide) block copolymers yield materials with significantly enhanced hydrothermal stabilities.^{4,5}

Mesoporous silica containing thiol groups was synthesized as described in the Experimental Section. A key step in the synthetic procedure is the extraction of the block copolymer surfactant species, which motivated a detailed study of the efficiency and extent of surfactant removal using conventional as-synthesized SBA-15.⁵ Photoacoustic IR spectra demonstrated that washing the material with ethanol under reflux resulted in almost complete extraction of the surfactant, as evidenced by the disappearances of the strong template C-H vibrations at 2970 and 2873 cm⁻¹, as well as those of the C-O-C vibrations at 1375 and 1456 cm⁻¹. The residual peaks accounted for 6 wt % as measured by TGA. For comparison, a method developed by Chen et al.¹⁸ and adapted for the removal of surfactant in MCM-41,^{8c,19} using acidified ethanol under reflux (1.5 g of as-made SBA-15 was refluxed for 24 h in 210 g of 1.5 wt % HCl/2.5 wt % water/ethanol mixture), was employed. From the TGA analysis (loss of 6 wt %) and IR data, this acid leaching did not improve the removal of the surfactant and is unnecessary for SBA-15, unlike base-synthesized MCM-41, where an acid wash is required for low-temperature surfactant removal.¹⁹ The mesoscopic order of the samples is completely retained on extraction with ethanol, as shown in the X-ray patterns of Figure 1.

During the syntheses, different amounts of TEOS were replaced by MPTMS in increasing relative molar

(15) Badley, R. D.; Ford, W. T. *J. Org. Chem.* **1989**, *54*, 5437.

(16) Aguado, J.; Serrano, D. P.; Escola, J. M. *Microporous Mesoporous Mater.* **2000**, *34*, 43.

(17) Broekhoff, J. C. P.; de Boer, J. H. *J. Catal.* **1967**, *9*, 8.

(18) Chen, C. Y.; Li, H. X.; Davis, M. E. *Microporous Mater.* **1993**, *2*, 17.

(19) Moller, K.; Bein, T.; Fischer, R. X. *Chem. Mater.* **1999**, *11*, 665.

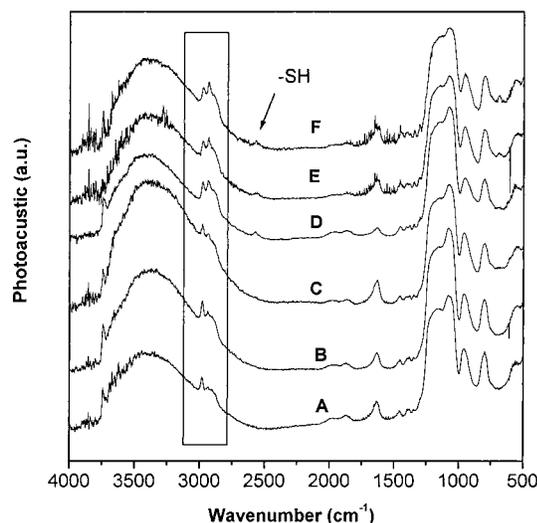


Figure 2. Photoacoustic infrared spectra of extracted functionalized SBA-15 synthesized with different molar ratios of MPTMS/(MPTMS + TEOS) in the initial mixture: (A) 0, (B) 0.02, (C) 0.05, (D) 0.10, (E) 0.15, and (F) 0.20.

ratios MPTMS/(MPTMS + TEOS) from 0.02 to 0.20. We have studied the influence of MPTMS, as a function of its concentration in the initial mixture, on the final properties of the functionalized mesoporous materials. Evidence for the presence of the mercaptopropyl groups on the interior mesopore surfaces of functionalized SBA-15 is clearly observed in the IR spectra of Figure 2. It can be seen that the strong vibration at 2900 cm^{-1} corresponding to C–H stretch vibrations (of the propyl chains) increases as the MPTMS/(MPTMS + TEOS) molar ratio in the initial mixture is increased. In addition, for the samples synthesized with higher concentrations of MPTMS, the weak vibration corresponding to the –SH group (2580 cm^{-1}) is readily observed.

Figure 3a shows X-ray diffraction patterns of samples prepared with different concentrations of MPTMS in the initial mixture, after ethanol washing. For the samples synthesized with MPTMS/(MPTMS + TEOS) molar ratios below 0.10, an XRD pattern typical of hexagonal SBA-15 is obtained. However, a gradual decrease of the d_{100} spacing is observed for samples synthesized with higher concentrations of MPTMS, the intensities of the peaks decrease, and the higher order (110) and (200) reflections have diminished in intensities (disappearing entirely for the sample prepared with a molar ratio MPTMS/(MPTMS + TEOS) of 0.10). Moreover, for the sample with a molar MPTMS ratio of 0.2 in the initial mixture, an amorphous material was obtained, as established by both TEM and X-ray measurements. These results are in agreement with those reported by other authors for syntheses of organosilica mesophases with MCM-41,^{8b} HMS,^{8b} and MSU-type¹¹ architectures using MPTMS as the organosilane. Because the presence of an elevated concentration (above MPTMS/(TEOS + MPTMS) molar ratio of 0.05) of mercaptopropyl groups during the co-condensation apparently perturbs the formation and self-assembly of surfactant aggregates, the TEOS was allowed to prehydrolyze for specified times (45–360 min) before the addition of MPTMS.

Mesoporous silicas functionalized with thiol groups were prepared from reaction mixtures containing molar

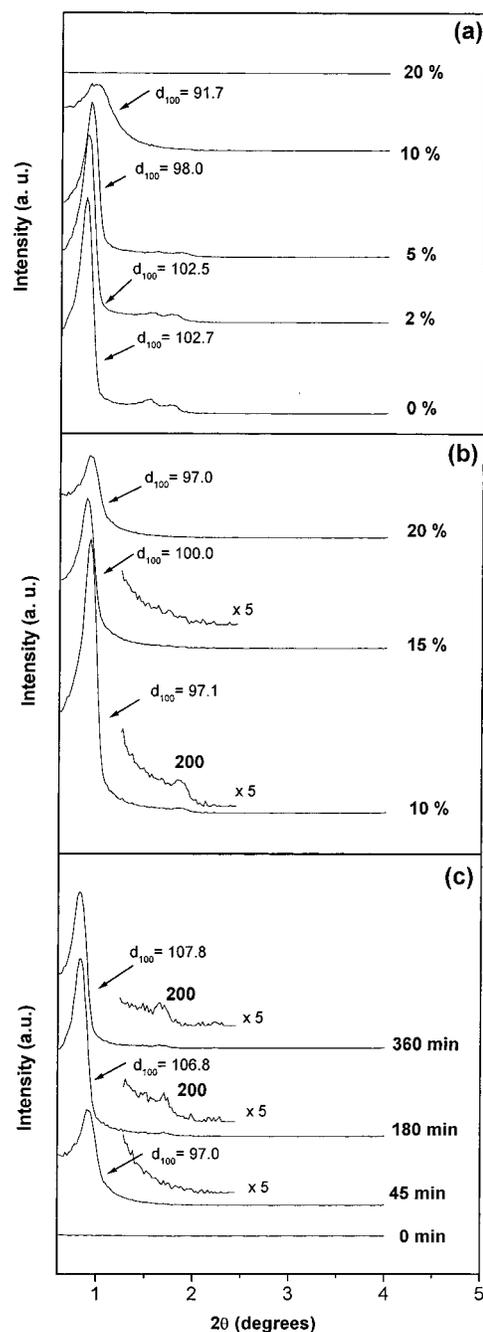


Figure 3. XRD patterns of extracted functionalized SBA-15 (a) with different molar ratios of MPTMS/(MPTMS + TEOS) in the initial mixture; (b) with different molar ratios of MPTMS/(MPTMS + TEOS) in the initial mixture and a TEOS prehydrolysis time of 45 min; (c) with MPTMS/(MPTMS + TEOS) = 0.2 in the initial mixture and different TEOS prehydrolysis times.

ratios MPTMS/(MPTMS + TEOS) of 0.1, 0.15, and 0.20 and using a TEOS prehydrolysis step of 45 min. Allowing the TEOS to prehydrolyze yields materials with improved mesoscopic order: from the XRD patterns shown in Figure 3b, the intensities of the (100) reflections are substantially higher, in comparison to the patterns in Figure 3a for the same MPTMS contents. For instance, the sample prepared with TEOS prehydrolysis and a MPTMS/(MPTMS + TEOS) molar ratio of 0.1 in the initial mixture yielded a small (200) peak and a (100) reflection with a factor of 3 higher intensity compared to the product obtained without prehydrolysis.

Table 1. Physicochemical Properties of Extracted Mesoporous Silicas Containing Thiol or Sulfonic Acid Moieties

sample	type	synthesis conditions			postsynthesis oxidation		d_{100}^d (Å)	type ^e isotherm	D_p^f (Å)	S_{BET} (m ² /g)	V_p (cm ³ /g)	wall ^g thickness
		TEOS prehydr ^a (min)	MPTMS ^b	H ₂ O ₂ ^c	oxidant	time (h)						
1	M-SH	45	0.1	0		5	97.1	IV	55	866	0.95	57.1
2	M-SH	180	0.2	0		24	106.8	IV	55	502	0.60	68.3
3	M-SO ₃ H	45	0.1	0	H ₂ O ₂ /H ₂ O	48	91.7	nm ^h	49	690	0.67	60.4
4	M-SO ₃ H	45	0.1	0	H ₂ O ₂ /H ₂ O	24	94.7	IV	47	582	0.53	51.0
5	M-SO ₃ H	45	0.1	0	H ₂ O ₂ /H ₂ O		84.7	IV	52	871	0.90	58.2
6	M-SO ₃ H	45	0.1	0	H ₂ O ₂ /MeOH		95.5	IV	69	645	1.00	46.7
7	M-SO ₃ H	45	0.1	3			100.2	IV	73	820	1.36	45.2
8	M-SO ₃ H	45	0.1	9			102.4	IV	72	732	1.25	49.6
9	M-SO ₃ H	45	0.1	18			105.3	IV	67	672	0.91	64.4
10	M-SO ₃ H	180	0.2	9			113.8	IV				

^a TEOS prehydrolysis. ^b MPTMS:(MPTMS + TEOS) molar ratio in the initial mixture. ^c H₂O₂:MPTMS molar ratio in the initial mixture. ^d $d(100)$ spacing. ^e According to the IUPAC classification. ^f Calculated from the adsorption branch. ^g Calculated by $a_0 - \text{pore size}$ ($a_0 = 2d(100)/\sqrt{3}$). ^h Not measured.

Likewise, the XRD patterns in Figure 3c show that, for the samples synthesized with an initial MPTMS molar ratio of 0.20, longer TEOS prehydrolysis times yield products with increased mesoscopic order. These data indicate that, in the presence of TEOS, low organosilane concentrations are required to form ordered mesophase materials, apparently because of comparable solubilities of the respective PEO-PPO block copolymer moieties in organosilanes, which act as cosolvents that prevent nanophase separation.

Quantitative determinations of the functional group contents of the mesoporous silicas after extraction of the block copolymer species were performed with thermogravimetric analysis (TGA) and differential scanning calorimetry (DTA) in air. The TGA and DTA analyses of these samples show a first peak due to the desorption of water (centered at 100 °C). This is followed by a second peak at 340 °C, corresponding to the loss of mercaptopropyl groups accompanied by a slight shoulder centered at 250 °C, which corresponds to the loss of the remaining surfactant species, about 6 wt % (see Figure 6a). Under these conditions, the sample containing a MPTMS molar ratio of 0.1 in the initial mixture (sample 1, Table 1) desorbed about 1.5 mmol of organic species/g of SiO₂; a loss of 1.66 mmol of organic/g of SiO₂ is expected, based on component concentrations used in the synthesis. For the sample with an initial MPTMS molar ratio of 0.2 (sample 2, Table 1), a weight loss of 2.9 mmol of organic/g of SiO₂ was measured (expected: 3.32 mmol of organic/g of SiO₂). Both values indicate a high degree of organotrialkoxysilane incorporation (around 90%). This value is similar to those reported by other authors in the presence of different ionic structure-directing agents, such as CTAB,^{8(b)} and neutral surfactants, such as *n*-octylamine,^{10c} and alkylpoly-(ethylene oxide)s.¹¹ The extent of organotrialkoxysilane incorporation into the mesostructured materials can also be monitored by means of ²⁹Si NMR. Distinct resonances can be observed for the siloxane [$Q^n = \text{Si}(\text{OSi})_n(\text{OH})_{4-n}$, $n = 2-4$; Q^4 at -111 ppm and Q^3 at -101 ppm] and organosiloxane [$T^m = \text{RSi}(\text{OSi})_m(\text{OH})_{3-m}$, $m = 1-3$; T^3 at -65 ppm and T^2 at -57 ppm] species. The data for the extracted materials shown in Figure 4 indicate that an increase of MPTMS concentration in the initial mixture yields increasing amounts of organo-functionalized moieties in the silica wall structures (a gradual increase in the intensities of T^m signals is readily observed). The relative integrated

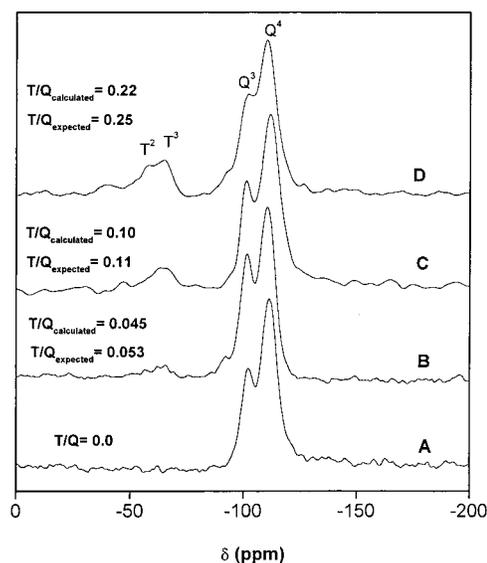


Figure 4. ²⁹Si NMR spectra of extracted functionalized SBA-15 synthesized with different molar ratios of MPTMS/(MPTMS + TEOS) in the initial mixture: (A) 0; (B) 0.05; (C) 0.1, TEOS prehydrolysis 45 min; and (D) 0.2, TEOS prehydrolysis 180 min. The measured relative integrated intensity (T^m/Q^n) of the organosiloxane (T^m) and siloxane (Q^n) NMR signals is depicted for each spectrum and compared to that expected from the composition of the initial mixture.

intensities of the siloxane (Q^n) and organosiloxane (T^m) NMR signals (T^m/Q^n) allow the quantitative assessment of the incorporation degree of the organic moiety. Thus, the good agreement among the measured ratios and those expected based on the composition of the initial mixture (Figure 4) indicates high yields of organic incorporation according to the results of TG analyses.

Nitrogen adsorption isotherms were used to study the changes induced in the textural properties of these materials after inclusion of mercaptopropyl groups. From the results shown in Table 1, it can be seen that the thiol-functionalized materials (samples 1 and 2) appear to have constrictions in the mesopore channels as compared to the calcined SBA-15 synthesized in an analogous way, though without the organic groups, for which a mean pore size of 80 Å was measured.^{4,5} The differences are attributed to the distribution of mercaptopropyl group moieties on the interior mesopore surfaces, which reduce the mean pore diameter. From the $d(100)$ spacing and the mean pore size determined by N₂ adsorption, the estimated mean thickness of the pore

walls of the hexagonal organic-functionalized SBA-15 is substantially thicker (wall thickness ca. 60 Å) than the walls of mercapto-functionalized MCM-41,^{8b} HMS,^{10c} and MSU¹¹ materials.

3.2. Preparation of Sulfonic Mesoporous Silica.

3.2.1. Postsynthesis Oxidation. Oxidation of mercaptopropyl groups to sulfonic moieties under mild conditions using H₂O₂ has been demonstrated for groups bound to silica¹⁵ or anchored to the pore walls of alkaline-synthesized MCM-41 or neutral-synthesized HMS mesoporous solids.^{8e,14} Using this method, we prepared sulfonic-functionalized mesoporous silica by oxidation of thiol-containing SBA-15. Figure 5a shows X-ray patterns of different samples oxidized for different reaction times at room temperature. Prolonged oxidation treatment results in samples that yield XRD (100) reflections with continually decreasing intensities, indicating progressively lower degrees of mesoscopic order.

Analyses of N₂ adsorption–desorption isotherms obtained from the sulfonic-functionalized mesoporous silicas produced by postsynthesis oxidation of thiol-containing precursor materials are summarized in Table 1 (samples 4 and 5). The data indicate that postsynthesis oxidation induces significant changes in the adsorption properties of the final material: the BET surface areas decrease gradually from 866 to 582 m²/g and the pore volumes from 0.95 to 0.53 cm³/g with the time of treatment, in agreement with results reported by other authors for post-oxidized mercapto-containing mesoporous materials.^{8e,8f}

The concentrations of sulfonic groups in the modified SBA-15 silicas were measured by acid–base titration and the results summarized in Table 2. Titration analyses show an increase in the acid capacity of the final products with an increase in the oxidation time. Postsynthesis oxidation, using H₂O₂ diluted in methanol (sample 6), yielded a product with better mesoscopic order, based on the XRD pattern shown in Figure 5a (top). Less significant changes in the adsorption properties of this sample were observed, though the extent of oxidation was reduced. The TGA and DTA analyses for these samples show a peak centered at 350 °C, which is a clear indication of the presence of unreacted thiol groups. This peak is followed of a second peak at 460 °C, corresponding to the decomposition of the alkylsulfonic groups.

3.2.2. Direct Synthesis Approach. The preparation of sulfonic mesoporous silica through oxidation of mesoscopically ordered solids containing mercaptopropyl groups presents serious drawbacks, such as the presence of unreacted thiol groups and the loss of mesoscopic order. We have improved the method to create well-ordered sulfonic-functionalized mesoporous silicas through co-condensation of MPTMS and TEOS in the presence of H₂O₂ and Pluronic 123 under acidic conditions.

Three samples were prepared from mixtures containing MPTMS/(TEOS + MPTMS) molar ratio of 0.10 and H₂O₂/MPTMS = 3, 9, or 18. In the preparation of these samples, a TEOS prehydrolysis time of 45 min was chosen. The amounts of sulfonic groups after synthesis in the extracted materials were measured by means of acid–base titration, TGA, and DTA measurements. The TGA and DTA analyses of these samples in Figure 6b show no evidence of the thiol decomposition peak

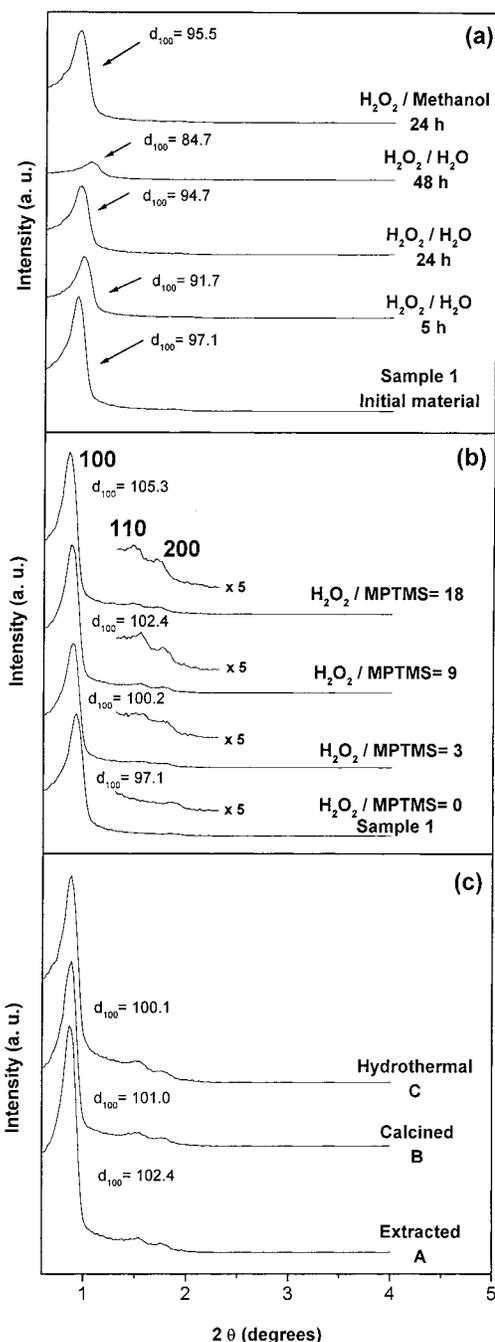


Figure 5. (a) XRD patterns of mercapto-modified samples after oxidation treatment in Ar atmosphere at different times and oxidant mixtures. (b) XRD patterns of different extracted functionalized mesoporous silicas synthesized in the presence of different H₂O₂/MPTMS molar ratios and using a MPTMS/(MPTMS + TEOS) molar ratio of 0.1 in the initial mixture. (c) XRD patterns of sulfonic-functionalized mesoporous silica after different treatments: (A) extraction with ethanol, sample 8 in Table 1; (B) as-made sample 8 after calcination in air, sample 11 in Table 2; (C) sample 8 after treatment in boiling water for 24 h.

centered at 350 °C, though an intense peak is observed at 450 °C, indicating the presence of alkyl–sulfonic acid groups. From the results shown in Table 2 (samples 7, 8, and 9), it can be seen that an acid capacity around 1.3 mmol of H⁺/g of SiO₂ is found for all the samples using both ion-exchange agents, independent of the amount of H₂O₂ in the initial mixture. Stoichiometric amounts of oxidant are adequate to obtain complete

Table 2. Acid Capacities of Sulfonic Mesoporous Materials^a

postsynthesis oxidation treatment				direct synthesis					
sample	titration (NaCl)	calcd content ^b	extent of oxidn (%)	sample	titration		TGA	calcd content ^c	incorporn (%)
					NaCl	TMACl			
3	0.49	1.50	33	7	1.28	1.26	1.37	1.67	79
4	0.82	1.50	55	8	1.26	1.22	1.36	1.67	78
5	1.16	1.50	77	9	1.36	1.31	1.39	1.67	82
6	0.38	1.50	25	10	2.24	2.18	2.12	3.33	66
				11 ^d	1.19		1.13	1.67	69

^a All the acid capacities defined as mmol of H⁺ per g of SiO₂. ^b Expected acid capacity at 100% of conversion of thiol groups. ^c Expected acid capacity at 100% of incorporation of MPTMS. ^d All the samples were extracted with ethanol under reflux for 24 h except sample 11 obtained by calcination of as-synthesized sample 8 at 300 °C for 1 h under air atmosphere with a heating rate of 1.5 °C/min.

conversion of the thiol groups during the co-condensation, in comparison to other postsynthesis oxidation methods described in the literature, which used excess oxidant.¹⁵ Moreover, the agreement between the ion-exchange capacities measured using sodium and a larger cation such as tetramethylammonium as exchange ions, as well as with the organic loading determined by TGA, is clear evidence that the sulfonic groups incorporated in the silica network are principally located on the mesopore surfaces, where they are accessible for adsorption and catalytic reaction processes. Table 2 summarizes the percent incorporation of the organosilane species. The incorporation of organic groups is slightly lower than that found in absence of H₂O₂, but independent of the amount of oxidant used during the co-condensation. Rhijn et al., using an initial mixture with a MPTMS/(TEOS + MPTMS) mole ratio of 0.10, though under basic/neutral conditions and using postsynthesis oxidation with H₂O₂ found a similar concentration of sulfonic groups (1 mequiv of H⁺/g of sulfonic material).^{8e}

The total consumption of thiol groups has also been confirmed by means of cross-polarization (CP) magic-angle spinning (MAS) ¹³C NMR and photoacoustic FT-IR spectroscopies. Figure 7a shows CP MAS ¹³C NMR spectra of different extracted samples: (A) conventional SBA-15, (B) thiol-functionalized SBA-15 (sample 1, Table 1), and (C) sulfonic-functionalized SBA-15 (sample 8, Table 1). The extracted SBA-15 shows evidence of peaks from residual block copolymer species, which are also observed in the other materials. Comparing spectra A and B, it can be seen that the thiol-functionalized material presents two intense additional signals with NMR shifts of 27.9 ppm (C¹ and C² carbons, adjacent to the -SH functionality) and 11.4 ppm (C³ carbon), confirming the presence of mercaptopropyl groups anchored to the pore walls. Additionally, the material prepared using H₂O₂ during the co-condensation shows distinct C¹, C², and C³ carbon peaks at 54.0, 18.2, and 11.4 ppm, respectively, without any evidence of the thiol resonance (27.9 ppm). Comparison of the FT-IR spectra of thiol-functionalized SBA-15 and sulfonic-functionalized SBA-15 show the disappearance of the S-H stretching band at 2580 cm⁻¹, accompanied by the appearance of a wide band from 3300 to 2500 cm⁻¹ that corresponds to the O-H bond of the sulfonic group. It can be concluded that this method avoids leaving residual unreacted thiol groups and/or the presence of other sulfur compounds arising from incomplete oxidation, which have been reported by Rhijn et al.^{8e} using postoxidation methods on mercapto-functionalized base-synthesized MCM-41 and neutral-synthesized HMS.

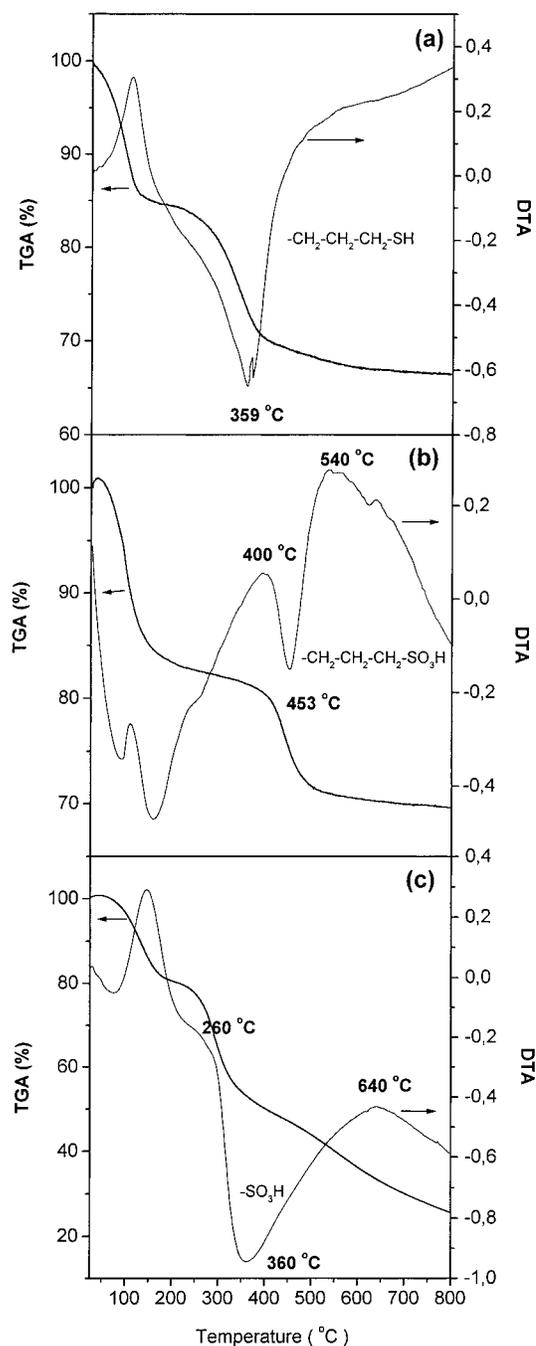


Figure 6. TGA and DTA measurements of different samples. (a) Thiol-functionalized mesoporous silica, sample 1 in Table 1. (b) Sulfonic-functionalized mesoporous silica obtained through the direct-synthesis approach, sample 8 in Table 1. (c) Sulfonic resin, Amberlyst-15.

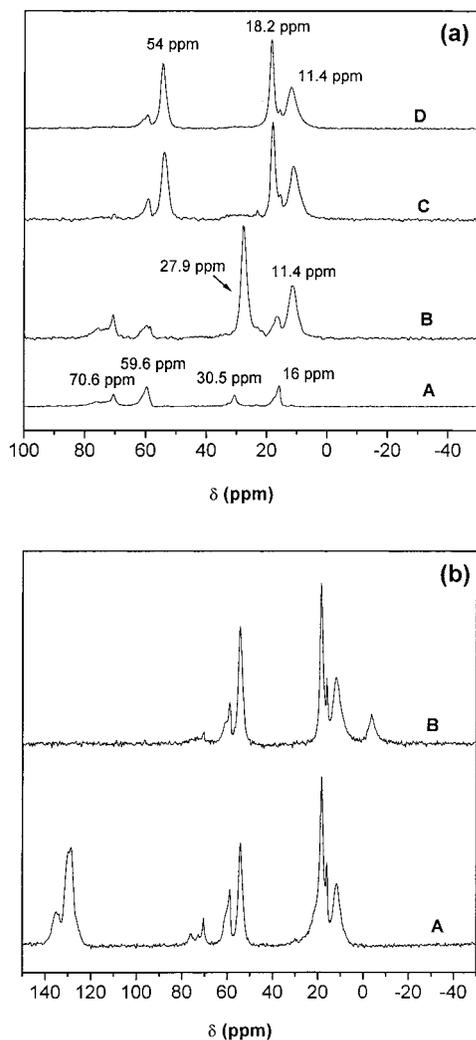


Figure 7. (a) CP MAS ^{13}C NMR spectra of different extracted SBA-15 mesoporous silicas: (A) conventional SBA-15; (B) thiol-functionalized SBA-15, sample 1 in Table 1; (C) sulfonic-functionalized SBA-15 obtained through the direct-synthesis approach, sample 8 in Table 1; (D) sulfonic-functionalized SBA-15 obtained through the direct-synthesis approach, sample 10 in Table 1 (b) CP MAS ^{13}C NMR spectra of bifunctionalized sulfonic mesoporous materials after extraction: (A) benzyl-sulfonic functionalized SBA-15; (B) methylsulfonic functionalized SBA-15.

Figure 5b shows the powder X-ray patterns of the extracted sulfonic-functionalized mesoporous silica products that are obtained using different concentrations of H_2O_2 in the initial mixture (samples 7, 8, and 9, Table 1) and the corresponding thiol-containing silica synthesized from analogous initial mixtures, but in the absence of oxidant (sample 1, Table 1). The sulfonic products show (110) and (200) reflections that indicate greater mesoscopic ordering than the corresponding material prepared in absence of oxidant during the co-condensation. The presence of the oxidant not only influences the mesoscopic organization, but also the unit cell parameter, as evidenced by the changes in the d_{100} spacings, which increase with the concentration of H_2O_2 .

Analyses of N_2 adsorption-desorption isotherms measured for the sulfonic-functionalized mesoporous silicas made by the direct synthesis procedure (samples 7, 8, and 9) are summarized in Table 1. The adsorption results indicate a significant increase in the mean

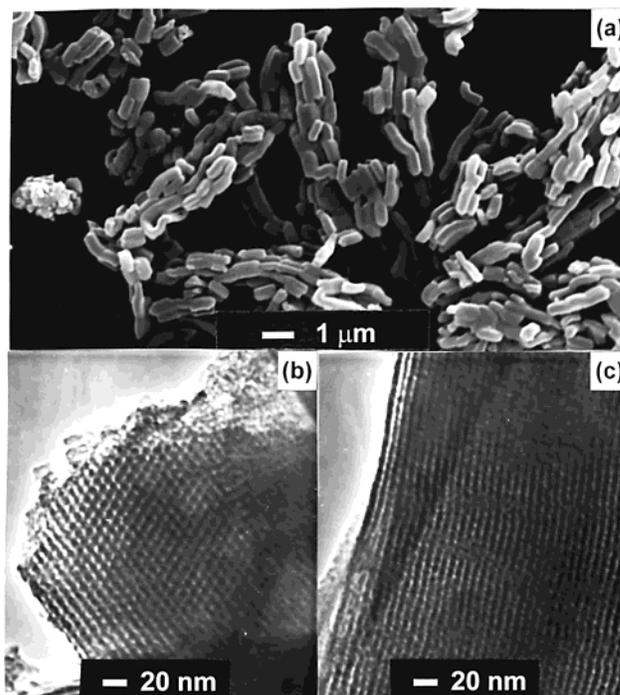


Figure 8. (a) SEM image and TEM images (b) in the direction of the pore axis and (c) in the direction perpendicular to the pore axis of an extracted sulfonic modified SBA-15 material (sample 9, Table 1).

uniform pore size and pore volume for materials prepared by co-condensing TEOS and MPTMS in the presence of H_2O_2 , compared to the sample synthesized in absence of oxidant (sample 1, Table 1) or prepared by postsynthesis oxidation (samples 4, 5, and 6). Such larger pore sizes and pore volumes correlate with higher relative concentrations of $\text{H}_2\text{O}_2/\text{MPTMS}$ in the reaction mixture.

The SEM image (Figure 8a) reveals that the extracted sulfonic-modified SBA-15 material consists of many ropelike domains with a uniform size around $1\ \mu\text{m}$, which are aggregated into wheatlike macrostructures similar to those found for conventional SBA-15.⁵ TEM images (Figure 8, parts b and c) show the hexagonal array of uniform channels with the typical honeycomb appearance of SBA-15 materials.⁵

The thermal and hydrothermal stabilities of these materials have been examined in a variety of ways: calcination in air, comparative TG analysis with a commercial sulfonic resin (Amberlyst-15), and treatment in boiling water. An as-synthesized sample (sample 8; Table 1) was calcined in air at $300\ ^\circ\text{C}$ for 1 h with a heating rate of $1.5\ ^\circ\text{C}/\text{min}$, the resulting material denoted as sample 11 (Table 2). From the results shown in Table 2 (sample 11), it is clear that most of the alkylsulfonic groups remain after thermal treatment at $300\ ^\circ\text{C}$, with the acid capacity being similar to that of the extracted sulfonic SBA-15 synthesized under similar conditions (sample 8). These results reflect the high thermal stability of the Si-alkylsulfonic bond in an oxidative environment. Moreover, it can be seen from the TGA measurements of a polystyrene-based sulfonic acid resin (Amberlyst-15) shown in Figure 6c, that the sulfonic groups present in the mesoporous silica show a much higher thermal stability than those found in the conventional acid catalyst. For the resin catalyst, a

decomposition peak is observed starting at 260 °C and continuing to 640 °C. Evaluation of this peak yielded a sulfonic concentration of 4.9 mequiv/g of resin (consistent with the reported commercial value of 4.8 mequiv/g.). The agreement between both values confirms that this peak can be attributed to the desorption/decomposition of the sulfonic group, although slight decomposition of the polymeric resin cannot be completely ruled out. Additionally, the X-ray diffraction pattern of the calcined material (sample 11) depicted in Figure 5c shows (100), (110), and (200) reflections, indicating that this material retains a high degree of mesoscopic ordering without significant contraction of the hexagonal cell parameter. Finally, the TGA analyses of this sample showed a residual surfactant content around 6 wt %, similar to that found for the extracted materials, indicating that this removal procedure is a good alternative to solvent extraction.

Hydrothermal stability is an important issue in many potential applications of these porous materials.^{20,21} While MCM-41 has been reported to have a high thermal stability in air,^{22,23} it shows low hydrothermal stability in water or aqueous solutions.²¹ Zhao et al.^{4,5} have demonstrated that mesoporous SBA-15 silica prepared using block copolymer surfactants under acid synthesis conditions exhibit enhanced long-range order and no observable decomposition after 48 h or more in water at 100 °C. Also, it is well-known that MCM-41 materials will degrade over the course of months when stored under ambient conditions,²⁴ due to the hydrolysis of siloxane bonds. Hydrothermal stability tests were carried out for one of these extracted sulfonic-functionalized mesoporous silicas (sample 8). As shown in Figure 5c, the XRD patterns (A and C) of this sample before and after hydrothermal treatment in boiling water for 24 h, both reveal clear (100), (110), and (200) reflections, indicating that the structure is hydrothermally stable.

We have applied the direct-synthesis approach to the preparation of mesoporous silicas with a higher concentrations of sulfonic groups starting from mixtures with a MPTMS/(MPTMS + TEOS) molar ratio of 0.20 and H₂O₂/MPTMS molar ratio of 9 (sample 10, Table 1). As shown in Table 2, the acid capacity of this sample is higher, as measured by acid–base titration and TGA. However, a significant decrease in the percent incorporation of MPTMS is found, compared to that observed when lower MPTMS contents are used in the initial synthesis mixture (samples 7, 8, and 9). TGA/DTA and CP MAS ¹³C NMR (Figure 7D) confirm the total absence of thiol groups in this sulfonic-functionalized mesoporous silica. Moreover, good agreement is found between the concentrations of sulfonic groups measured by acid–base titration using both salts and that calculated from the decomposition peak (400–540 °C) of the TGA data. These results indicate that this procedure allows the incorporation of high concentrations of sulfonic groups up to 2 mequiv of H⁺/g of SiO₂ and, importantly, that

they are accessible on the mesopore surfaces. Rhijn et al.^{8e} reported a sulfonic loading of 1.5 mequiv/g of base-synthesized MCM-41, following oxidation of an extracted thiol-containing precursor product synthesized from a mixture with a MPTMS/(MPTMS+TEOS) molar ratio of 0.20 (2.4 mequiv/g of material expected after oxidation). The authors attributed the difference to the presence of byproducts arising from an incomplete oxidation, such as disulfides detected by ¹³C NMR. Lim et al.^{8f} have reported recently an ordered mesoporous MCM-41 material containing 4.7 mmol of S/g of SiO₂ (4.8 expected from the initial mixture composition). However, after treatment with HNO₃, its proton exchange capacity was relatively low: 1.76 mequiv/g of material (2.98 expected). The ¹³C NMR spectrum showed only the presence of sulfonic groups and no signal indicating the presence of thiol groups. These results indicate that a significant fraction of the sulfonic groups may not be accessible in the MCM-41 material.

X-ray patterns of the sulfonic-functionalized SBA-15 silica showed a higher mesoscopic order than the corresponding thiol-containing precursor material (sample 2, Table 1) with a significant change of the hexagonal cell parameter (Table 1). Large increases are observed in the pore size (from 55 to 67 Å), pore volume (from 0.6 to 0.9 cm³/g), and surface area (from 502 to 672 m²/g). These values are higher than those reported (pore sizes <20 Å and BET surface areas around 500 m²/g) for MCM-41 and HMS sulfonic mesoporous materials containing a similar concentration of acid moieties.^{8e,8f}

One of the more interesting consequences of the production of in situ sulfonic groups is the observed enhancement of the long-range order found in the mesoporous products. The formation of sulfonic moieties apparently produces solvent and hydrophilic/hydrophobic interfacial conditions that promote nanophase separation of the PEO–PPO–PEO copolymer blocks and thus increased mesoscopic ordering. Sulfonic mesoporous materials made by postsynthesis oxidation methods typically exhibit lower long range order showing only (100) peaks in their respective X-ray diffraction patterns. The direct-synthesis procedure described here typically yields sulfonic-functionalized SBA-15 silica that display (100), (110), and (200) reflections in their X-ray diffraction patterns, similar to conventional SBA-15 by Zhao et al.⁵

Solid acidity is often characterized by measuring spectral line shifts of chemically adsorbed probe species using techniques, such as IR,²⁵ UV,²⁶ and NMR.²⁷ Recently, Osegovic et al.^{28,29} have demonstrated that the isotropic ³¹P NMR chemical shift (δ) of triethylphosphineoxide (TEPO) is a good probe of the relative acidities of solid acids; larger ³¹P chemical shifts were shown to be correlated with increasing acid strengths. Figure 9a shows ³¹P NMR spectrum of TEPO adsorbed on different extracted materials: (A) conventional SBA-15, (B) SBA-15 treated with H₂O₂ at room temperature, and (C and D) different alkylsulfonic SBA-15 mesoporous materials. Spectrum A for conventional extracted SBA-

(20) Ryoo, R.; Kim, J. M.; Ko, C. H.; Shin, C. H. *J. Phys. Chem.* **1996**, *100*, 17718.

(21) Ryoo, R.; Jun, S. *J. Phys. Chem. B* **1997**, *101*, 317.

(22) Chen, C. Y.; Burkett, S. L.; Li, H. X.; Davis, M. E. *Microporous Mater.* **1993**, *2*, 22.

(23) Chen, C. Y.; Li, H. X.; Davis, M. E. *Microporous Mater.* **1993**, *2*, 17.

(24) Zhao, X. S.; Audsley, F.; Lu, G. Q. *J. Phys. Chem. B* **1998**, *102*, 1413.

(25) Bazetti, T.; Selli, E.; Moscotti, D.; Forni, L. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 1401.

(26) Yamanaka, T.; Tanabe, K. *J. Phys. Chem.* **1975**, *79*, 2409.

(27) Sheng, T.; Gay, I. D. *J. Catal.* **1994**, *145*, 10.

(28) Osegovic, J. P.; Drago, R. S. *J. Catal.* **1999**, *182*, 1.

(29) Osegovic, J. P.; Drago, R. S. *J. Phys. Chem. B* **2000**, *104*, 147.

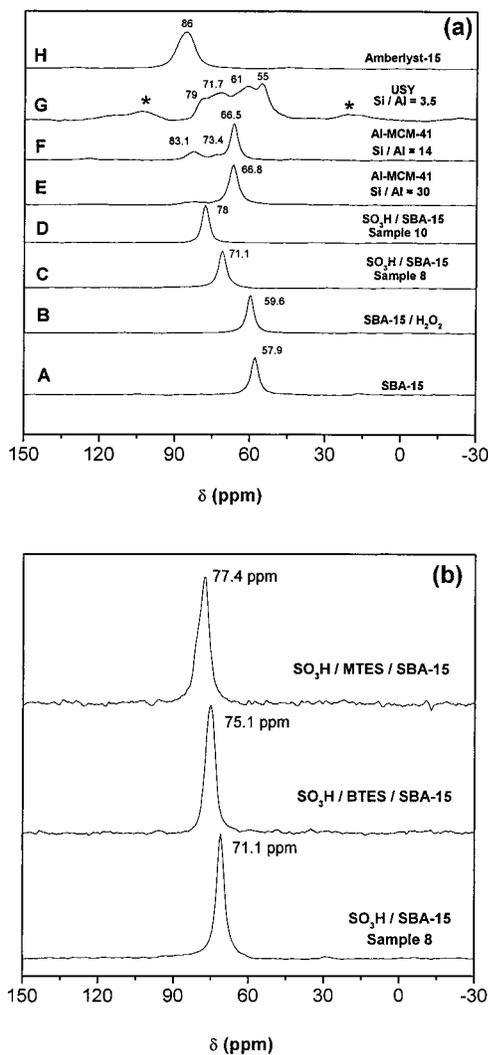


Figure 9. ^{31}P NMR spectra of TEPO chemically adsorbed (a) on conventional extracted SBA-15 (A), conventional extracted SBA-15 after treatment with aqueous H_2O_2 (30 wt %) at room temperature for 5 h (B), sulfonic-functionalized SBA-15 (C and D) and different conventional acid solids (E–H) and (b) on benzyl- and methylsulfonic-functionalized SBA-15 mesoporous materials.

15 shows a ^{31}P peak centered at 57.9 ppm that corresponds to TEPO adsorbed on weak Lewis-acid centers²⁸ arising from the presence of silanol groups. When SBA-15 is treated with H_2O_2 , the ^{31}P chemical shift increases to 59.6 ppm (spectrum B); this indicates a slight increase in silanol group acidity, in accordance with results published by other authors for amorphous silica.³⁰ The mesoporous silica materials containing alkylsulfonic groups (sample 8 and 10, Table 1) show ^{31}P NMR peaks centered at 71.1 and 78 ppm, respectively (spectra C and D), indicating the presence of strong Brønsted acid sites.²⁸ The difference in the ^{31}P chemical shift found for these modified SBA-15 materials containing different loading of sulfonic groups could be influenced by aggregation effects as well as additional van der Waals interactions.²⁹ In addition, the ^1H NMR spectra of these samples (not shown) confirm these results, showing strong signals around 6 ppm (assigned to sulfonic acid),

which are absent for the conventional SBA-15 material. The ^1H NMR and ^{31}P NMR results indicate the relatively high acid strengths of the acid sites in the sulfonic-functionalized mesoporous silicas.

By analyzing the respective ^{31}P NMR spectra, the relative acid strengths of these sulfonic-functionalized SBA-15 mesoporous silicas can be compared with other acid catalysts: Al-MCM-41 with different aluminum contents (Si/Al = 30 and Si/Al = 14); an H-USY zeolite; and a sulfonic resin (Amberlyst-15). Figure 9a shows ^{31}P NMR spectra acquired from these samples and from sulfonic-modified SBA-15 mesoporous silica (sample 8 and 10, Table 1). In mesoporous Al-MCM-41, most of the acid centers show a signal at 66 ppm, with strong acid sites showing relatively weak intensities at 73 and 83 ppm. These results are in agreement with separate measurements of pyridine and NH_3 adsorption–desorption on this material showing the presence of Brønsted and Lewis acidities and the concentration of Brønsted acid sites increasing with the aluminum content of the sample.³¹ The ^{31}P NMR spectra of the SBA-15 mesoporous silicas functionalized with alkylsulfonic groups show a single intense peak over 70 ppm, indicating a higher acid strength than the Al-MCM-41 samples. This is an important improvement, as until now acid-catalysis using mesoporous materials has been limited to the use of Al-MCM-41 as catalysts in processes involving cracking of large molecules,^{32,33} hydroisomerization, and olefin oligomerization using modified Al-MCM-41 with different dispersed noble metals.¹³ However, the use of aluminosilicate MCM-41 in the preparation of fine chemicals has been limited.¹³ In addition, USY zeolite shows numerous broad and overlapping ^{31}P NMR signals that indicate weaker and more heterogeneous acidity than the sulfonic-modified SBA-15. The sulfonic SBA-15 mesoporous silica materials, with stronger and more uniform acid sites, appear to be good candidates for catalysis applications, where large pores, hydrothermal stability, and stronger acidity are required. Finally, these sulfonic-functionalized SBA-15 materials were compared with a sulfonic resin (Amberlyst-15) used in important acid-catalyzed reactions, such as alcohol and alcohol/olefin etherifications, esterification, and alkylations. Though the sulfonic SBA-15 materials show a lower acid strength, their high surface areas, large uniform pore sizes, and high thermal stability of sulfonic groups provide several advantages over the Amberlyst-15 catalyst, which has been reported to be unstable above temperatures of 90 °C.³⁴

3.2.3. Sulfonic Mesoporous Materials Containing Other Organic Moieties. Two important factors that can influence the selectivity of heterogeneously catalyzed chemical reactions are the pore size and the interior pore surface properties of the catalyst. These properties can have large effects on the internal mass transfer of reactant, product, and intermediate species within the internal pore spaces. The pore sizes of SBA-15 materials can be adjusted by controlling the block

(31) Corma, A.; Fornes, V.; Navarro, M. T.; Perez-Pariente, J. *J. Catal.* **1994**, *148*, 569.

(32) Aguado, J.; Serrano, D. P.; Romero, M. D.; Escola, J. M. *J. Chem. Soc., Chem. Commun.* **1996**, 275.

(33) Corma, A.; Grande, M. S.; Gonzalez-Alfaro, V.; Orchilles, A. *V. J. Catal.* **1996**, *159*, 375.

(34) Takesono, T.; Fujiwara, Y. *US 4 182 913* **1980**.

(30) Chronister, C. W.; Drago, R. S. *J. Am. Chem. Soc.* **1993**, *115*, 4793.

copolymer species and hydrophobic components present during material synthesis.⁵ The direct-synthesis approach described here additionally permits multiple surface functionalities to be incorporated into the SBA-15 mesopore channels, thereby allowing direct modification of material pore surface properties. Recently, Tatsumi et al.³⁵ have reported the direct synthesis of organically modified Ti-MCM-41 catalysts which are more hydrophobic than the parent one and present good performance in the epoxidation reactions.

The preparation of sulfonic-modified SBA-15 mesoporous silicas containing an additional organic group involves the co-condensation TEOS, MPTMS, and a second organosilane in the presence of H₂O₂ and Pluronic 123 under acidic conditions. For the purposes of demonstration, two different functionalities were chosen, one with polar character (benzyltriethoxysilane, BTES) and one with nonpolar character (methyltethoxysilane, MTES). To the best of our knowledge, only one work has been previously published regarding the synthesis of mesoporous materials containing two types of organic functionalities: phenyl and another organosilane (allyl, amine, and thiol),³⁶ in that case, MCM-41 and MCM-48-type materials were prepared under basic conditions, though the latter was shown to be unstable after surfactant extraction.

Two SBA-15-type silica materials were synthesized starting from acidic Pluronic 123 mixtures with a MPTMS/(MPTMS + TEOS + (RO)₃-Si-R') and (RO)₃-Si-R'/(MPTMS + TEOS + (RO)₃-Si-R') molar ratios of 0.1 and 0.05, respectively, and a H₂O₂/MPTMS molar ratio of 9. Acid-base titration of the extracted materials after synthesis measured concentrations of 1.3 mequiv of H⁺/g of SiO₂ for both samples, similar to that found for the sample prepared in absence of the additional organosilane.

XRD patterns acquired for both bifunctionalized samples after removal of surfactant are shown in Figure 10a and indicate ordered hexagonal mesostructures. Analyses of the nitrogen adsorption/desorption isotherms yielded BET surface areas of approximately 700 m²/g and pore volumes of 1 cm³/g. Also, both samples showed type IV isotherms (Figure 10b), with clear hysteresis loops associated with capillary condensation in the mesopores and with regular pore sizes larger than 60 Å.

The incorporation of the two functional groups of both materials has been confirmed in both materials by means of CP MAS ¹³C NMR, as shown in Figure 7b. The ¹³C NMR spectrum for the bifunctionalized material containing sulfonic and benzyl groups (A) shows three clear signals at 11.6, 18.8, and 54.6 ppm corresponding to the alkylsulfonic group. In addition, there are two broad signals at 128 and 135 ppm arising from the phenyl group. Analogously, the methyl group attached to the benzene ring can be seen as a shoulder of the signal centered at 18.8 ppm. Other peaks visible in the range 70–80 ppm are attributed to the remaining surfactant. The ¹³C NMR spectrum (B) of the sample containing methyl groups shows signals corresponding to the alkylsulfonic group and a signal centered at -3.5

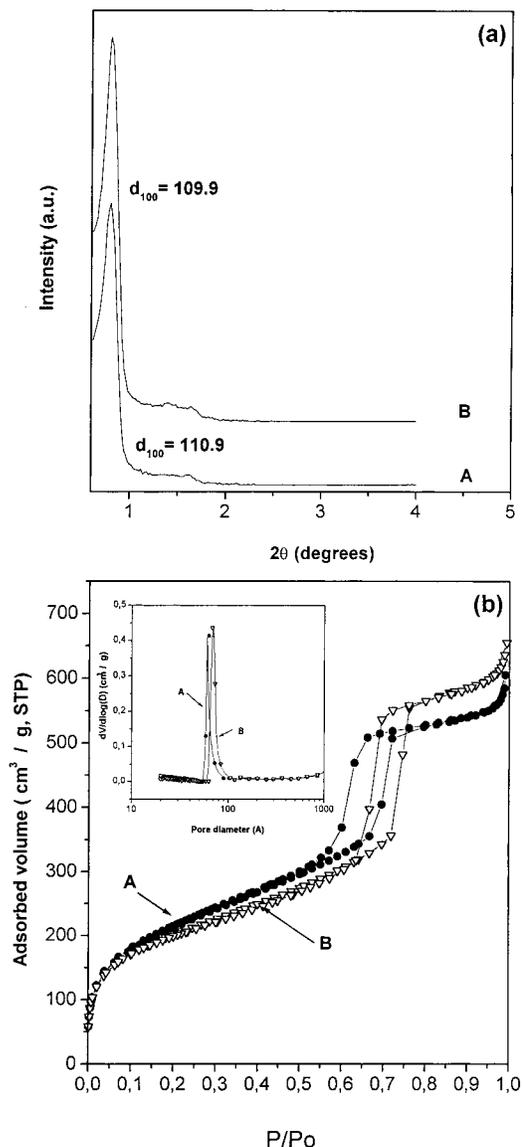


Figure 10. (a) XRD patterns of benzyl- and methylsulfonic-functionalized SBA-15 mesoporous materials after solvent extraction of the surfactant species. (b) N₂ adsorption/desorption isotherms and pore size distributions: (A) benzylsulfonic SBA-15 (●); (B) methylsulfonic SBA-15 (∇).

ppm corresponding to the methyl functionality. No thiol groups are present in the ¹³C NMR spectra, indicating their complete conversion to sulfonic groups.

To examine whether the presences of the second functional groups influence the strengths of the sulfonic acid centers, ³¹P MAS NMR measurements were performed on these bifunctionalized materials containing adsorbed TEPO probe species. As shown in Figure 9b, the presence of the second functionalities yields single, somewhat broader, ³¹P NMR peaks in each spectrum with larger chemical shifts than found for a similar mono-functionalized material containing the same loading of sulfonic groups, but without additional organic moieties (sample 8, Table 1). Possible explanations for these observations are (1) that both functionalities are uniformly distributed and in sufficiently close proximity to interact producing changes in the ³¹P NMR chemical shift or (2) that segregation of the sulfonic and organic groups leads to zones with higher concentrations of sulfonic groups.

(35) Bhaumik, A.; Tatsumi, T. *J. Catal.* **2000**, *189*, 31.

(36) Hall, S. R.; Fowler, C. E.; Lebeau, B.; Mann, S. *J. Chem. Soc., Chem. Commun.* **1999**, 201.

4. Conclusions

The in situ oxidation of the mercapto functionality with H_2O_2 profoundly influences the physical and chemical properties of the sulfonic acid-functionalized mesoporous material relative to that made by post oxidation techniques. The one step synthesis using acid catalysis in the presence of Pluronic 123 produces SBA-15 modified materials with greater oxidation efficiency (100% vs 25–77%), with larger more uniform pores, with higher surface areas, and with good long-range order in contrast to post oxidative methods. Moreover, this outcome is achieved under milder and simpler synthetic conditions utilizing less time and less material. The net result is a sulfonic mesoporous silica with acid capacities several times greater than those achieved with post oxidative methods and with thermal stabili-

ties to 450 °C in air. Likewise, the advantages and differences between SBA-15 acid synthesis and M41-S synthesis in terms of easier surfactant removal, structure and wall properties are clearly evidenced and desirable.

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