

Direct syntheses of ordered SBA-15 mesoporous materials containing arenesulfonic acid groups

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SBA-15 mesoporous silica has been functionalized with arenesulfonic acid groups by means of a one-step simple synthesis approach involving co-condensation of tetraethoxysilane (TEOS) and 2-(4-chlorosulfonylphenyl)ethyltrimethoxysilane (CSPTMS) in the presence of a poly(alkylene oxide) block copolymer (Pluronic 123) under acid silica-based catalysis. The resultant materials show hexagonal mesoscopic order and pores sizes up to 60 Å, with acid exchange capacities of *ca.* 1.3 mequiv. H⁺ per g SiO₂ and surface areas up to 600 m² g⁻¹. The sulfonic groups anchored to the silica surface of the pore walls are thermally stable to temperatures up to 380 °C and resistant to leaching in organic and aqueous solutions under mild conditions. ³¹P MAS NMR measurements of chemically adsorbed triethylphosphine oxide and the catalytic properties confirm the presence of Brønsted acid centers in these mesoporous materials containing arenesulfonic acid groups that are stronger than those found in propanesulfonic-modified SBA-15 and Al-MCM-41.

1 Introduction

The organic tailoring of the internal surface of mesoporous materials has recently received great attention in terms of the application of such materials in the fields of catalysis, sensing and adsorption. This organic mesoporous functionalization has been widely achieved by the grafting of functional groups.¹ Recently, direct synthesis involving co-condensation of siloxane and organosiloxane species in the presence of different templating surfactants has been shown to be a promising alternative to the grafting procedures.^{2–13} The covalent attachment of sulfonic acid groups to the surface of silica,¹⁴ microporous¹⁵ and mesoporous MCM and HMS molecular sieves^{16–24} has been proposed and successfully tested in several acid-catalysed reactions.^{14–23} Silylation and direct synthesis procedures have been used for the preparation of these sulfonic functionalized silica-based materials. The active sulfonic group is obtained post-synthetically by the oxidation of propanethiol groups previously anchored to the surface^{14,17–23} or by sulfonation reactions.^{14,15,24} These treatments lead to a loss of mesoscopic order and, in general, to damage of the textural properties and an incomplete oxidation of the thiol groups accompanied by a loss of sulfur species.

Recently,¹³ we have devised an one-step direct synthesis procedure to create periodic ordered alkanesulfonic-functionalized mesostructures with pores sizes up to 60 Å and high acid exchange capacities (1 to 2 mequiv. H⁺ per g SiO₂) using poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) block copolymer species (Pluronic 123) as the templating surfactant^{25,26} and acid catalysis.²⁷ This new procedure involves an one-step synthetic strategy based on the co-condensation of tetraethoxysilane (TEOS) and 3-mercaptopropyltrimethoxysilane (MPTMS), in the presence of Pluronic 123 species and H₂O₂ in HCl aqueous solutions. This prompted us to report in this paper the results that we have obtained by the same route on the preparation and the physicochemical and catalytic properties of periodic hybrid mesoporous materials containing arenesulfonic groups. The synthetic strategy involves the co-condensation of TEOS and

2-(4-chlorosulfonylphenyl)ethyltrimethoxysilane (CSPTMS) using Pluronic 123 as a template in the presence or absence of an oxidant medium under acidic conditions. The hydrolysis of the chlorosulfonyl groups (–SO₂Cl) to the corresponding sulfonic acid groups is achieved under the conditions of acidic condensation.

Heterogeneously catalysed chemical reactions are dramatically influenced by the strength and number of acid sites as well as the morphology of the support (surface area, pore size, *etc.*). The application of acid zeolites for the production of fine chemicals is currently an active area of research,^{28,29} however an important drawback is the range of available pore sizes (< 10 Å). The synthesis of Al-MCM-41 mesoporous materials with pore sizes up to 100 Å constituted a remarkable breakthrough in this field. Although Al-MCM-41 is applicable in principle to reactions involving large reactants and products, there are numerous examples showing the limitation of the acid strength of its sites.³⁰ In this context, mesoporous materials containing sulfonic groups, which combine a relatively high acid strength with a large surface area and reactant accessibility, are promising acid catalysts.

Likewise, the feasibility of tuning the acid strength of the sulfonic groups by close attachment of different functionalities might increase their potential catalytic applications. In this regard, a recent publication demonstrates how the attachment of perfluorosulfonic acid [Si(CH₂)₃(CF₂)₂(O)(CF₂)₂SO₃H] to a silica surface generates a solid with an acid strength comparable to that shown by perfluorinated sulfonic acid resins.³¹ The presence of the fluorine atoms increases significantly the acid strength of the sulfonic group. However, the complexity of the preparation of the organosilane precursor [(OH)₃Si(CH₂)₃(CF₂)₂(O)(CF₂)₂SO₃⁻M⁺] makes this material not really cost-effective as compared with the use of MPTMS. Herein we show that the presence of a phenyl group close to the sulfonic group significantly increases the acid strength in comparison to other environments such as those with methyl groups, and hence an enhancement of catalytic activity in acid-catalysed reactions is easily observed.

2 Experimental

2.1 Sample preparation

Propanethiol mesoporous silica materials. These materials were synthesised as follows: 4 g of Pluronic 123 (Aldrich) were dissolved with stirring in 125 g of 1.9 M HCl at room temperature. The solution was heated to 40 °C before addition of TEOS (Aldrich). A TEOS prehydrolysis time of 45 min was used prior to the addition of the thiol precursor [MPTMS (Gelest)] to the mixture. The molar composition of the mixture for 4 g of copolymer was 0.0369 TEOS:0.0041 MPTMS:0.24 HCl:6.67 H₂O. The resultant solution was stirred for 20 h at 40 °C, after which time 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-synthesised material by washing with ethanol under reflux for 24 h (1.5 g of as-synthesised material per 400 mL of ethanol).

The propanesulfonic-functionalized mesoporous silica sample. This sample was synthesised as described above for the propanethiol mesostructural solid. Following TEOS prehydrolysis, MPTMS and an 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 mixture for 4 g of copolymer was: 0.0369 TEOS:0.0041 MPTMS:0.0369 H₂O₂:0.24 HCl: ~6.67 H₂O.

Arenesulfonic-functionalized mesoporous silica samples. These samples were synthesised as described above for the functionalized mesostructural solid. Following TEOS prehydrolysis, CSPTMS (Gelest) was added 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. Two different materials were prepared in the presence and absence of hydrogen peroxide during the condensation. The molar composition of the different mixtures for 4 g of copolymer was: 0.0369 TEOS:0.0041 CSPTMS:Z H₂O₂:0.24 HCl: ~6.67 H₂O with Z = 0 and 0.0123, respectively.

Other acid solids. Amberlyst-15 was supplied by Aldrich. Al-MCM-41 with Si/Al molar ratios of 30 was prepared following a sol-gel approach recently described in literature.³²

2.2 Sample characterisation

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°.

Nitrogen adsorption and desorption isotherms at 77 K were measured using a Micromeritics ASAP 2000 system. The data were analysed using the Broekoff-de Boer (BdB) model.³³ 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 thermoanalyser STA 409 was used for simultaneous thermal analysis combining thermogravimetry (TGA) and differential thermoanalysis (DTA) at a heating rate of 10 °C min⁻¹ in air. The ion-exchange capacities of the sulfonic mesoporous materials were determined using aqueous solutions of sodium chloride (NaCl, 2 M), tetramethylammonium chloride (TMACl, 0.05 M) and tetraethylammonium fluoride (TEAF, 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 resultant suspension

was allowed to equilibrate and was then titrated potentiometrically by dropwise addition of 0.01 M NaOH (aq). The sulfur content was determined by ICP-atomic emission spectroscopy.

Transmission electron microscopy (TEM) microphotographs were obtained on a JEOL JEM-200 FX electron microscope operating at 200 kV. 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; and 200 scans. ²⁹Si 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; and 5000 scans. The spectra were referenced to tetramethylsilane.

The acidic properties of the solid were monitored by reference to the ³¹P NMR chemical shift of triethylphosphine oxide (TEPO) chemically adsorbed on the sulfonic-functionalized mesoporous silica. In a typical measurement, 0.015 g of TEPO were 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 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 a 85 wt% phosphoric acid external standard.

2.3 Catalytic and stability tests

Catalytic tests of the Fries rearrangement of phenyl acetate were carried out in a stirred batch reactor equipped with a temperature controller and pressure gauge at 150 °C for 5 hours under autogenous pressure and using phenol as solvent. The reactant, the solvent and the catalyst were transferred into the teflon-lined reactor and the system was heated up to 150 °C (phenyl acetate/acid site molar ratio = 7.5; phenol/phenyl acetate mass ratio = 60; and mass of phenol = 30 g.). After reaction an aliquot of product was dissolved in dichloromethane and analysed by gas chromatography (VARIAN CP-3380) on a capillary column HP-5 30 m \times 0.25 mm.

Stability tests were carried out as follows: 0.3 g of sulfonic-modified material was suspended in 30 ml of water or toluene and magnetically stirred for different times and temperatures. After treatment the solid product was filtered, washed with ethanol several times and air-dried overnight. The decrease in acid capacity has been used as a direct measurement of the leaching of sulfonic groups to the solution.

3 Results and discussion

3.1 Physicochemical properties of the arenesulfonic-modified mesoporous materials

Table 1 summarises the preparation conditions as well as the physicochemical and textural properties of the different organically modified SBA-15 materials. For comparison, a propanethiol- (sample S-1; Table 1) and propanesulfonic-modified SBA-15 (sample S-2; Table 1) have been also included. According to results published elsewhere,¹³ in which the presence of hydrogen peroxide profoundly influenced the physical and chemical properties of the sulfonic acid-functionalized mesoporous materials, the hybrid arenesulfonic ordered materials described in this work have been synthesised in the absence and presence of an oxidant medium (samples S-3 and S-4, respectively; Table 1).

Small-angle X-ray powder diffraction for all of the samples

Table 1 Physicochemical and textural properties of extracted materials

Sample	Organosilane	Type	Molar composition ^a		XRD		Textural properties		
			X	Z	d_{100}^b	Wall thickness ^c	$D_p^d/\text{Å}$	$S_{\text{BET}}/m^2\text{ g}^{-1}$	$V_p^e/cm^3\text{ g}^{-1}$
S-1	MPTMS	M-Alk-SH	0.0369	0	97.1	57.1	55	866	0.95
S-2	MPTMS	M-Alk-SO ₃ H	0.0369	0.0369	102.4	45.2	73	820	1.40
S-3	CSPTMS	M-Ar-SO ₃ H	0.0369	0	106.8	60.3	63	629	0.72
S-4	CSPTMS	M-Ar-SO ₃ H	0.0369	0.0123	107.8	61.5	63	646	0.78

^a4 g of copolymer: X TEOS:(0.041 - X) organosilane: Z H₂O₂:0.24 HCl: ~6.67 H₂O. ^b d (100) spacing. ^cCalculated by a_0 - pore size ($a_0 = 2 d(100)/\sqrt{3}$). ^dPore size from adsorption branch applying the Broekoff-de Boer (BdB) model. ^eThe pore volume was taken at $P/P_0 = 0.985$ single point.

(XRD, Fig. 1) gave signals corresponding to hexagonally-ordered silica SBA-15 mesophases^{25,26} with the unit cell parameters (d_{100}) shown in Table 1. The XRD peaks of the arenesulfonic-modified SBA-15 were significantly lower in intensity compared with samples 1 and 2 and displayed a complete absence of long-order reflections. This feature can be explained in terms of the presence of a larger organic molecule, which could partially disturb the assembly of the mesophase, although a higher contrast matching effect arising from the higher size of the organic moiety should not be ruled out. In these particular cases (samples S-3 and S-4) the presence of H₂O₂ does not seem to have an influence on the mesoscopic order of the final materials, as was noted in the synthesis of propanesulfonic SBA-15 materials under analogous synthetic conditions.¹³

Quantitative determinations of the functional groups after template extraction were performed by thermogravimetric analysis in air (Fig. 2). The TGA/DTA analysis of arenesulfonic-modified SBA-15 materials shows two desorption peaks centred at *ca.* 490 and 586 °C arising from the organic group [Fig. 2(a)]. Such thermal stability is not displayed by the polystyrene based sulfonic resins [Amberlyst-15; Fig. 2(b)], which show a decomposition peak starting from 260 °C and with the much more pronounced loss at 360 °C. The quantification of the desorption peaks demonstrated a high degree of organic incorporation for arenesulfonic-modified samples, similar to that obtained for samples 1 and 2 (*ca.* 90%; Table 2).

The acid capacity of the sulfonic-modified materials was measured by means of acid-base titration using different

ion-exchange agents; the results are shown in Table 2. An acid capacity of *ca.* 1.3 mmol H⁺ per g of SiO₂ for both of the arenesulfonic-modified SBA-15 materials is observed when sodium chloride is used as exchange agent. This result clearly reveals that the transformation of chlorosulfonyl moieties into sulfonic groups is just mediated by acid-catalysed hydrolysis. Recently, several reports have demonstrated that the structure of SBA-15 consists not only of large uniform and ordered channels but also of complementary micropores located on the silica wall and providing connectivity between them.³⁴⁻³⁷ In order to check the localisation of the arenesulfonic groups, additional acid-base titration experiments were carried out using larger exchange cations such as TMA⁺ and TEA⁺. The results demonstrate a similar acid capacity to that measured using Na⁺ cations, which is a strong indication that the arenesulfonic groups are located on the surface of mesopore walls and are not embedded within the microporous structure of the silica walls. Moreover, the close agreement between the ion-exchange capacities and organic loading determined by

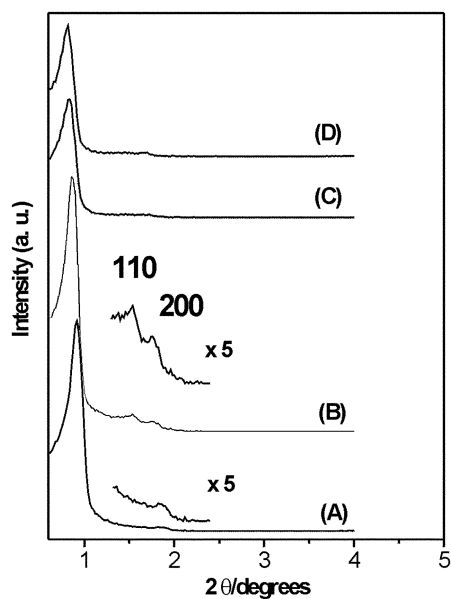


Fig. 1 XRD spectra of organic functionalized SBA-15 samples after extraction. (A) Alk-SH SBA-15; (B) Alk-SO₃H SBA-15; (C) Ar-SO₃H SBA-15 synthesised in the absence of hydrogen peroxide; (D) Ar-SO₃H SBA-15 synthesised in the presence of hydrogen peroxide.

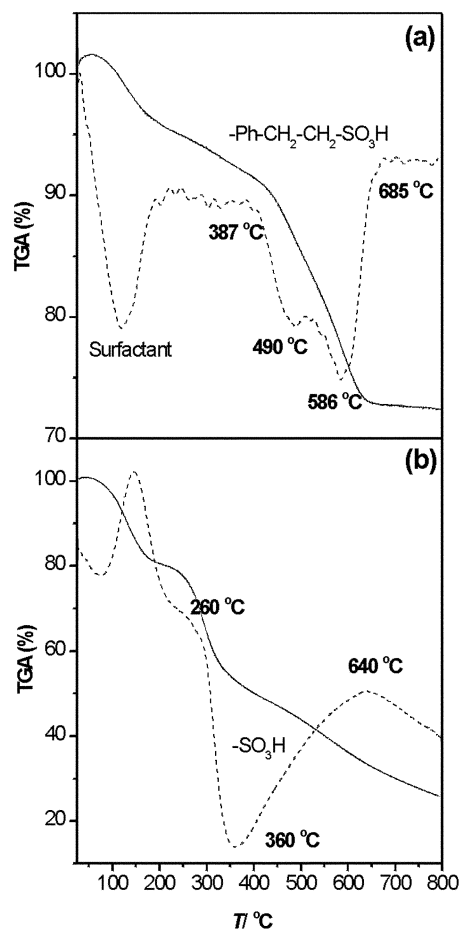


Fig. 2 TGA and DTA measurements. (a) Arenesulfonic functionalized mesoporous silica, S-4 sample in Table 1. (b) Sulfonic resin, Amberlyst-15.

Table 2 Organic incorporation and acid capacity of the organically modified SBA-15 materials

Sample	Acid capacity titration ^a			Organic content TGA/DTA ^b	Sulfur content ICP ^c	Incorporation (%) ^d
	Na ⁺	TMA ⁺	TEA ⁺			
S-1	—	—	—	1.50	1.47	90
S-2	1.26	1.22	1.23	1.36	1.26	82
S-3	1.35	1.39	1.42	1.47	1.40	88
S-4	1.34	1.34	1.33	1.45	1.33	87

^ammol of H⁺ per g SiO₂. ^bmmol of organic per g SiO₂. ^cmmol of S per g SiO₂. ^dIncorporation of the organic moiety after synthesis based on thermogravimetric analysis (theoretical value: 1.67 mmol of organic per g SiO₂).

TGA and inductively coupled plasma (ICP) is clear evidence that most of the arenosulfonic groups effectively incorporated in the silica network are located *on the pore wall* and are accessible and useful for adsorption and catalytic reaction processes. Likewise, the acid capacity is analogous to that obtained for propanesulfonic-modified materials.

Solid-state ²⁹Si MAS-NMR confirmed the presence of organo-functionalized moieties as part of the silica wall structure for all of the organically modified SBA-15 materials (Fig. 3). Distinct resonances can be clearly observed for the siloxane [Qⁿ = Si(OSi)_n(OH)_{4-n}, n = 2–4; Q³ at –100 ppm; Q⁴ at –110 ppm] and organosiloxane [T^m = RSi(OSi)_m(OH)_{3-m}, m = 1–3; T³ at –65 ppm; T² at –57 ppm] units. All the samples show a similar relative integrated intensity of the organosiloxane (T^m) and siloxane (Qⁿ) NMR signals (T^m/Qⁿ) of close to 0.1 in fair agreement with those theoretically expected on the basis of the composition of the initial mixture. The ²⁹Si NMR measurements correlate well with the TG analysis. An important point is the enhancement of the cross-linking of siloxane species in the presence of H₂O₂ as evidenced by the increase in the Q⁴/Q³ ratio for samples (C) and (E) in Fig. 3. Likewise, this effect seems to be more apparent for the organosiloxane species when CSPTMS is used as the precursor. The T^m signals show a narrower feature in the presence of H₂O₂ [sample (E); Fig. 3] as compared to that obtained in the absence of the oxidant [sample (D), Fig. 3], where isolated species (T¹) could be present.

The results of the analysis of the adsorption–desorption isotherms measured for the extracted arenosulfonic SBA-15

samples are summarised in Table 1. Arenosulfonic-modified SBA-15 samples show a type IV isotherm, characteristic of mesoporous solids³⁸ (Fig. 4; inset) with a significant increase of the pore size in comparison to sample 1 at the same organic content. As would be expected, the incorporation of larger groups (arenosulfonic) should diminish the pore sizes to a greater extent than would smaller groups such as propanethiol. The *in situ* formation of sulfonic groups induces significant changes of the hexagonal cell parameter as well as an enlargement of the pore size, as described elsewhere using MPTMS as precursor.¹³ The use of non-ionic poly(alkylene oxide) block copolymers as surfactants allows the synthesis of arenosulfonic functionalized mesoporous materials with pore sizes up to 63 Å with relatively high surface areas. From the *d*(100) spacing and the mean pore size determined by N₂ adsorption, the estimated mean thickness of the pore walls of the arenosulfonic SBA-15 is substantially thicker (wall thickness of ca. 60 Å) than that of the walls of sulfonic functionalized MCM-41 and HMS, made with low molecular weight surfactants.^{16–23} The increase in the thickness of the walls of the hybrid mesoporous materials leads to structures that are more stable to collapse induced by thermal or hydrothermal treatments. The TEM images shown in Fig. 5 confirm the high mesoscopic order of the arenosulfonic materials synthesised in this work. These materials exhibit a hexagonal array of uniform channels with the typical honeycomb appearance of SBA-15 materials.^{25,26}

The organic nature of the ordered arenosulfonic SBA-15 material has been investigated by ¹³C CP MAS NMR (Fig. 6). The extracted SBA-15 material shows evidence of peaks from residual block copolymer species, which are also observed in the organically modified materials. The arenosulfonic functionalized SBA-15 shows two peaks at 15.6 and 28.8 ppm

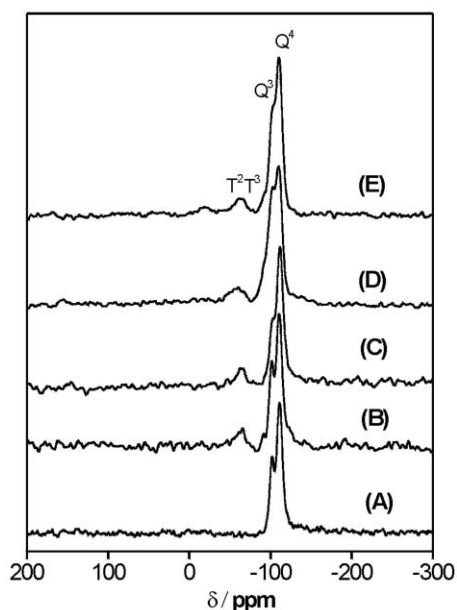


Fig. 3 ²⁹Si NMR spectra of functionalized SBA-15 samples after extraction. (A) Pure silica SBA-15. (B) Alk-SH SBA-15. (C) Alk-SO₃H SBA-15. (D) Ar-SO₃H SBA-15 synthesised in the absence of hydrogen peroxide. (E) Ar-SO₃H SBA-15 synthesised in the presence of hydrogen peroxide.

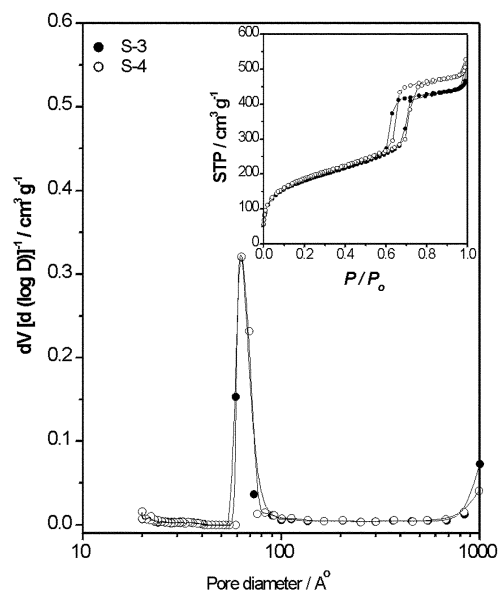


Fig. 4 N₂ adsorption–desorption isotherms and pore size distributions of arenosulfonic-modified SBA-15 materials.

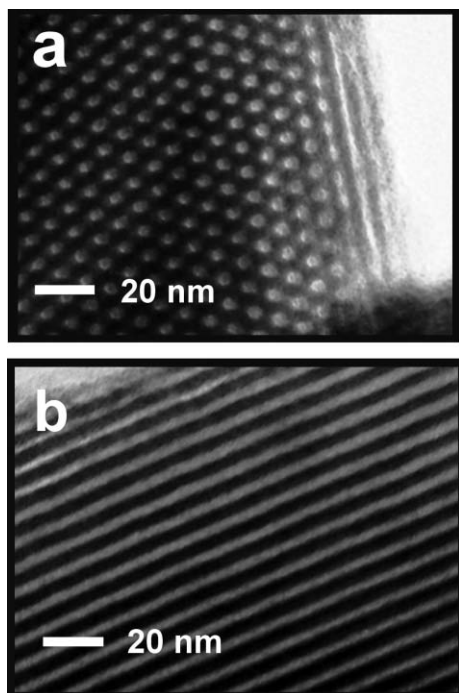


Fig. 5 TEM images (a) in the direction of the pore axis and (b) in the direction perpendicular to the pore axis of an extracted arenosulfonic-modified SBA-15 material (S-3 sample; Table 1).

corresponding to the methylene C² and C³ carbons and also signals at 148.8, 135.5 and 128.1 ppm from the aromatic carbons.

The solid-acidity of the arenosulfonic mesostructured materials has been characterised by means of ³¹P NMR of chemisorbed triethylphosphine oxide and compared with other acid solids (Fig. 7). Increasing values of δ indicate increasing

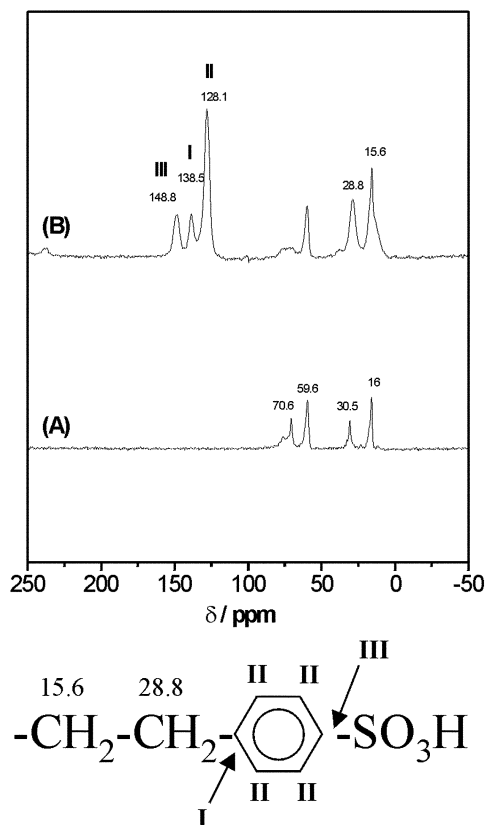


Fig. 6 CP MAS ¹³C NMR spectra. (A) Extracted pure silica SBA-15. (B) Arenosulfonic functionalized SBA-15, S-3 sample in Table 1.

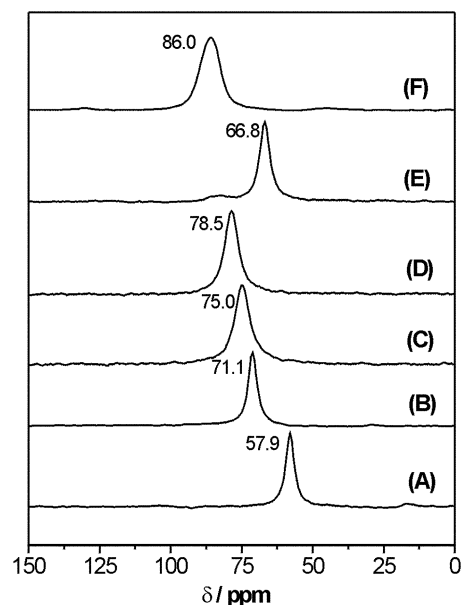


Fig. 7 ³¹P NMR of chemisorbed TEPO over different materials. (A) Extracted pure silica SBA-15. (B) Alkanesulfonic SBA-15; sample S-2 in Table 1. (C) Arenosulfonic SBA-15; sample S-3 in Table 1. (D) Arenosulfonic SBA-15; sample S-4 in Table 1. (E) Al-MCM-41; Si/Al = 30. (F) Amberlyst-15.

acid strength.^{39,40} Pure silica extracted SBA-15 displays a signal centred at 57.9 ppm that corresponds to weak Lewis-acid centres^{39,40} arising from the presence of silanol groups. The alkanesulfonic-modified SBA-15 mesoporous material (S-2 sample; Table 1) has a peak centred at 71.1 ppm, demonstrating the presence of strong Brønsted acid centres. The arenosulfonic SBA-15 material synthesised in the absence of H₂O₂ displays a ³¹P shift displaced to higher values indicating an increase of the Brønsted acidity. The presence of an electron-withdrawing substituent adjacent to the sulfonic groups, such as a phenyl group, disperses the negative charge, stabilising the anion, and thus increasing the acid strength. Moreover, when the synthesis of the arenosulfonic SBA-15 materials is carried out in the presence of an oxidant, the ³¹P NMR shift is displaced to even higher values. The acid strength exhibited by these materials is comparable to that found for silica gel treated with sulfuric acid followed by mild drying.³⁹ The possibility of tuning the acid strength of the sulfonic groups by the attachment of different adjacent functionalities is readily apparent in this work.

Finally, we have compared the acid strength of these sulfonic-modified SBA-15 mesoporous materials with two conventional acid catalysts: Al-MCM-41 (Si/Al = 30) and a sulfonic resin (Amberlyst-15; 4.8 mequiv. g⁻¹). Al-MCM-41 displays a signal centred at 66 ppm, showing a medium acid strength in agreement with the results of the adsorption-desorption of pyridine and NH₃ carried out on this material.⁴¹ All of the sulfonic-modified SBA-15 materials described in this work presented a higher acid strength than the Al-MCM-41 sample. The arenosulfonic-modified materials synthesised in this work show a comparable acid strength to the Amberlyst-15.

In summary, the arenosulfonic mesostructural materials produced by the direct synthesis method have large uniform pore sizes, high surface areas, and good mesoscopic order. Moreover, the acid centres of these materials display an excellent thermal stability and relatively high acid strength.

3.2 Catalytic properties of the arenosulfonic-modified mesoporous materials

One of the aims of the present work is to provide a comparison between the catalytic activity of propanesulfonic-modified

SBA-15 and conventional acid solids (Amberlyst-15 and Al-MCM-41) with that of the arenesulfonic-modified SBA-15 materials in order to confirm the relatively high acid strength deduced from the ^{31}P NMR results. We have chosen as a test reaction the Fries rearrangement of phenyl acetate to yield *p*- and *o*-hydroxyacetophenones. The selective Fries rearrangement of esters derived from aromatic alcohols is an interesting reaction for the production of industrial pharmaceuticals, dyes and agrochemicals.

The catalytic results of the Fries rearrangement of phenyl acetate in the liquid phase over different acid catalysts using phenol as the solvent are depicted in Fig. 8. First, a blank reaction was performed in the presence of pure silica extracted SBA-15 free of acid centres. The results show a negligible substrate conversion and hence thermal catalysis must be ruled out. The beneficial influence of a phenyl ring close to the sulfonic group (rather than methyl groups) is clearly manifested by the significant enhancement of the catalytic activity for the arenesulfonic-modified materials (S-4 vs. S-2). In comparison to the results of the homogeneously catalysed reaction using methanesulfonic acid as the catalyst, the sulfonic-modified SBA-15 materials show "shape selectivity" imposed by the structure of the solid, since an enhancement of the *para*:*ortho* molar ratio can be readily observed. It is interesting to note that the catalytic activity for Al-MCM-41 is significant lower than that measured for the arenesulfonic-modified material. In all the experiments, the substrate to acid sites molar ratio was kept constant, and therefore the higher conversion of arenesulfonic-modified materials with respect to Al-MCM-41 and propanesulfonic-modified SBA-15 is likely to be ascribed to the higher acid strength of the sites present in this material. Furthermore, the catalytic activity of these materials has been compared with commercial sulfonic resins (Amberlyst-15). Although the arenesulfonic-modified material showed a slightly lower activity, their high surface area, large uniform pore sizes and the high thermal stability of sulfonic groups provide processing latitude not present in Amberlyst-15, which has been reported to be unstable above 90 °C.⁴² A final interesting observation is related to the fair agreement between the acid strength measured by ^{31}P NMR and the catalytic activity.

Another important factor in the catalytic performance of these arenesulfonic-modified materials is their stability towards the leaching of the sulfonic groups during reaction. To test the stability of the material against leaching, sample S-3 was treated in aqueous and organic solutions under different times and temperatures. Fig. 9 shows the acid capacity measured by acid–base titration of the sample after the different treatments.

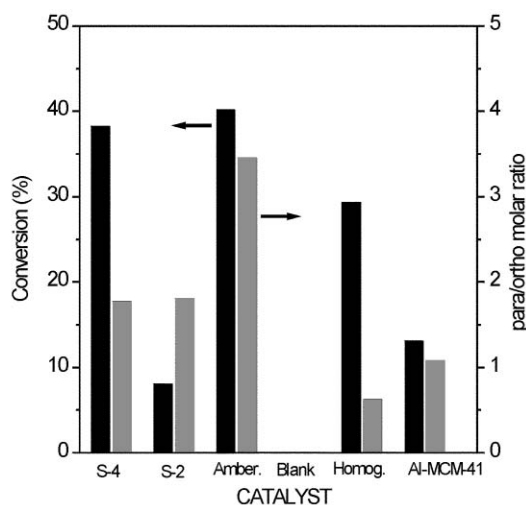


Fig. 8 Catalytic results of the Fries rearrangement of phenyl acetate over different acid catalytic systems.

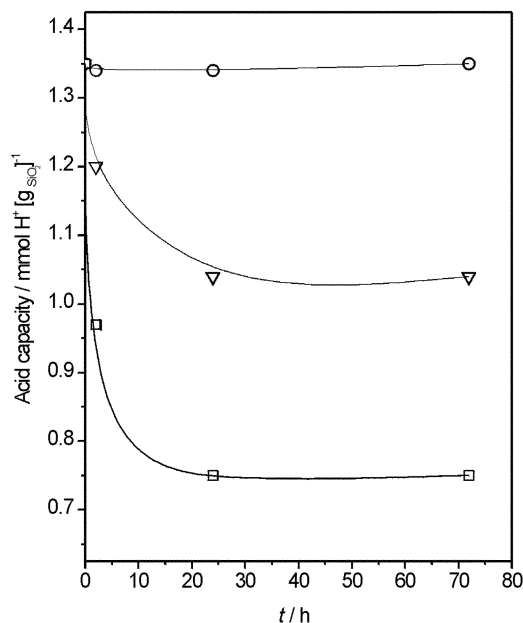


Fig. 9 Stability of the arenesulfonic groups towards leaching in aqueous and organic media. (○) Toluene under reflux; (▽) water at room temperature; (□) boiling water.

The plot clearly shows that the rate of leaching in an aqueous medium at 100 °C is significantly higher than that of the same substrate in toluene under reflux. After 24 h of treatment, the material had lost about 50% of its initial acid capacity in an aqueous medium at 100 °C, whereas when toluene was used as the solvent, the material remained unaffected by the treatment. It should be also noted that the major fraction of the overall loss occurred during the early stages of the treatment in agreement with the observations of other authors studying organically bonded silica.⁴³ Extension of the treatment to up to 72 h did not change the acid capacity of the material from that achieved after 24 h. The results suggest that the sulfonic groups anchored to the silica surface of the pore walls display different hydrolytic stability. Likewise, a lowering of the temperature leads to a remarkable enhancement of the hydrolytic stability of the sulfonic groups.

4 Conclusions

The direct synthesis procedure allows the effective anchoring of arenesulfonic groups on the pore surface of SBA-15 meso-structural materials. The resultant materials had large uniform pore sizes with high surface areas, good mesoscopic order and thick walls leading to hydrothermally stable materials. The acid centres display excellent thermal resistance and significant stability towards leaching in aqueous and organic media. By the selection of a liquid-phase reaction catalysed by acid sites of relative high strength, the benefits of arenesulfonic-modified SBA-15 with respect to propanesulfonic-modified SBA-15 and Al-MCM-41 are readily demonstrated. These preliminary catalytic results illustrate the potential of the sulfonic-modified SBA-15 for catalytic applications in the production of fine chemicals.

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