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1. INTRODUCTION

The heterogenisation of catalytic homogeneous systems is currently considered as a priority research field. Serious research efforts are addressed to the development of heterogeneous solid acid catalyst in order to avoid the use of traditional homogeneous acid catalytic systems (H_2SO_4 , HF, $AlCl_3$, BF_3 ,...) which present serious drawbacks including hazards in handling, corrosiveness, production of toxic waste and difficulties in separation. Zeolites have been widely used in acid catalysed processes¹ but unfortunately their limited pore size (< 8 Å) hinders the access of bulky substrates. In this context novel silica-based ordered mesoporous materials such as MCM-41 and SBA-15 are being widely used as inorganic supports of acid active species². Sulfonic-acid functionalised mesoporous silica³⁻⁴, which are solid Brönsted acid, have been recently synthesised and successfully used in different acid-catalysed reactions, including esterifications and condensations⁵⁻⁶. These sulfonic-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. The thiol groups can be treated postsynthetically to yield sulfonic groups by sequential oxidation with H_2O_2 , acidification, and finally washing. These postsynthetical treatments had led to a loss of mesoscopic order and, in general, damage of the textural properties of the materials and loss of sulphur. Recently a direct synthesis method has been developed to create periodic ordered sulfonic-functionalized mesostructures using block copolymer species (Pluronic 123) as the templating surfactant⁷. 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 H_2O_2 in HCl aqueous solutions. This approach allows the in-situ oxidation of thiol groups and consequent acid exchange of the formed sulfonic groups. This strategy is simpler and utilises less time and less material than the post-oxidative methods without the disadvantages described above.

Since steric constraints imposed by the pore size of the acid solid influence the reaction pathway resulting in “shape-selective catalysis”, in this contribution we have modified the synthesis conditions in order to tailor the pore size of these sulfonic modified mesoporous materials using this novel method. Likewise, this one-step procedure has been generalised for the synthesis of sulfonic-functionalised mesoporous silica using non-ionic surfactants other than Pluronic 123.

2. EXPERIMENTAL SECTION

2.1 Sample Preparation.

Sulfonic modified mesoporous materials using P₁₂₃ as polymeric template. Materials were synthesised as follows: Pluronic 123 (Aldrich) was dissolved with stirring in 125 g of 1.9 M HCl at room temperature. The solution was heated up to 40°C before adding TEOS (Aldrich). Prior to the addition of the thiol precursor (MPTMS, Aldrich) and the oxidising agent (aqueous solution of H₂O₂, 30 wt. %, Merck), a prehydrolysis time was fixed. The resulting mixture was stirred at 40°C for 20 h and aged at 100°C for additional 24 h under static conditions. The molar composition of the mixture was: 0.0368TEOS: 0.0041MPTMS: 0.0368H₂O₂: 0.24HCl:~6.67H₂O. After synthesis, the solid product was recovered by filtration and air-dried overnight. The template was removed from the as-synthesised material by washing with ethanol under reflux for 24 h (2 g of as-synthesised material per 200 ml of ethanol).

Sulfonic modified mesoporous materials using non-ionic surfactants other than P₁₂₃. Other non-ionic surfactants were used (PL64, EO₁₃PO₃₀EO₁₃; Brij56, C₁₆EO₁₀; Brij76, C₁₈EO₁₀, all of them supplied from Aldrich). The molar composition of the mixture was similar to that used for the Pluronic 123. However, the dissolving conditions were changed in order to obtain a clear micellar solution before adding the silicon source: Brij56 was stirred for 30min at 50°C; Brij76 was stirred 3 h at 50°C and the PL64 was dissolved almost instantaneously at room temperature.

Tailoring of the pore size. Different experimental conditions were tested with the purpose of modifying the pore size of the sulfonic modified materials including: different TEOS hydrolysis times, TEOS/surfactant molar ratios and ageing conditions. Additionally, swelling agents such as TMB (1,3,5-trimethylbenzene) and n-decane have also been added to the mixture in different concentrations.

2.2 Sample Characterization.

Nitrogen adsorption and desorption isotherms at 77 K were measured using a Micromeritics TRISTAR 3000 system. The data were analysed using the BJH model and the pore volume (V_p) was taken at P/P₀= 0.989 single point. X-ray powder diffraction (XRD) data were acquired on a PHILIPS X'PERT diffractometer using Cu K α radiation. The data were collected from 0.6 to 4° (2θ) with a resolution of 0.02°. Ion-exchange capacities of the sulfonic mesoporous materials were determined using aqueous solutions of sodium chloride (NaCl, 2M) as exchange agent. In a typical experiment, 0.05g of solid was added to 10g of aqueous solution containing the salt. The resulting suspension was allowed to equilibrate and thereafter titrated potentiometrically by dropwise addition of 0.01 M NaOH (aq). Sulphur content was determined by means of Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES) analysis collected in a VARIAN VISTA apparatus. Transmission electron microscopy (TEM) microphotographs were carried out on a JEOL 2000 electron microscope operating at 200 kV.

3. RESULTS AND DISCUSSION

3.1 Sulfonic-Functionalised Mesoporous Silica Using Pluronic 123.

Tables 1-4 summarise the preparation conditions as well as the physicochemical and textural properties of the sulfonic modified mesoporous materials using Pluronic 123 as surfactant. Thickness of the silica walls was calculated by a_o – pore size ($a_o = 2d_{100}\sqrt{3}$). Acid capacity and sulphur content are defined per g of dried sample. Firstly, it is important to note that most of the samples synthesised show a close agreement between the ion-exchange capacities measured by acid titration and sulphur loading determined by ICP-AES independently of the synthesis conditions. This is a clear evidence that most of the sulfonic groups are located *on the pore wall* and are accessible and useful for adsorption and catalytic reaction processes. The influence of the different synthesis conditions on the pore size was as follows:

Influence of swelling agent TMB and n-decane have been used to increase the pore diameter of the sulfonic modified mesoporous material. The swelling effect of the n-decane is slightly higher than that observed using TMB. In contrast with the results reported by other authors⁸ for silica based mesoporous materials the presence of cosolvent organic molecules expands slightly the pore size. The in-situ formation of sulfonic moieties apparently produces hydrophilic/hydrophobic interfacial conditions that do not promote expanding of the hydrophobic core of the PEO-PPO-PEO copolymer blocks in presence of swelling agents. Moreover, the presence of TMB seems to have a negligible influence on the thickness of mesoporous walls, whereas the increase of n-decane yields significant lowering of the wall thickness.

Table 1. Influence of swelling agent on the physicochemical and textural properties.

Sample	Parameter	Textural properties					Acidity mmol H ⁺ /g	S content mmol S/g
		d ₁₀₀ (Å)	D _p (Å)	S _{BET} (m ² /g)	V _p (cm ³ /g)	Wall Thickness (Å)		
1	0	97	82	666	1.23	30	1.16	1.20
2	0.25	108	91	663	1.20	33	1.13	1.08
3	0.5	107	89	708	1.27	35	1.17	1.12
4	1	109	90	621	1.01	36	1.23	1.08
5	0.5*	100	95	691	0.64	21	1.02	1.02
6	0.05*	95	95	726	1.27	15	1.07	1.16

The parameter is the swelling agent/surfactant mass ratio.* indicates that the swelling agent is n-decane, otherwise is TMB. The synthesis hydrolysis conditions were 40°C for 20 h and the ageing conditions were 100°C for 24 h. The TEOS/surfactant molar ratio was 55.

Influence of ageing conditions. Enlargement of the hydrothermal treatment promotes higher pore sizes for the sulfonic modified materials. Alternatively, increasing of temperature leads to an increase of unit cell size and the pore diameter, but the wall thickness decreases with the temperature. Likewise, sulfonic modified mesoporous materials after hydrothermal treatment at 170 °C for 24 h become slightly amorphous showing a poorly ordered XRD patterns.

Table 2. Influence of ageing conditions on the physicochemical and textural properties.

Sample	Parameter	Textural properties					Acidity mmol H ⁺ /g	S content mmol S/g
		d ₁₀₀	D _p	S _{BET}	V _p	Wall		

		(Å)	(Å)	(m ² /g)	(cm ³ /g)	Thickness (Å)		
7	24/ 80	90	70	772	0.96	34	1.05	0.97
8	72/ 80	88	81	836	1.26	21	1.10	1.03
9	24/ 60	79	37	484	0.43	54	1.07	1.04
10	24/ 170	101	110	441	1.35	7	0.84	0.78

The parameter indicates ageing conditions: time in hours / temperature in °C. The hydrolysis conditions were 40°C for 20 h and the TEOS/surfactant molar ratio was 55. No swelling agent was used.

Influence of TEOS/surfactant molar ratio. The increase of TEOS species promotes more silica condensation and a decrease of pore size with and enlargement of wall thickness.

Table 3. Influence of TEOS/surfactant ratio on the physicochemical and textural properties.

Sample	Parameter	Textural properties						Acidity mmol H ⁺ /g	S content mmol S/g
		d ₁₀₀ (Å)	D _p (Å)	S _{BET} (m ² /g)	V _p (cm ³ /g)	Wall Thickness (Å)			
11	90	94	68	719	0.87	40	1.13	1.03	
12	120	96	54	647	0.63	57	0.92	0.98	

The parameter is TEOS/surfactant molar ratio. The synthesis hydrolysis conditions were 40°C for 20 h and the ageing conditions were 100°C for 24 h. No swelling agent was used.

Influence of hydrolysis time. XRD and adsorption results demonstrate that the mesostructure of the triblock copolymer-silica complex is formed within 2 h. However, this time is low for the complete condensation of sulphur species as evidenced by the low acidity and sulphur content of this sample (Table 4; sample 13). However, after four hours of hydrolysis the sulphur species are almost completely incorporated into the mesoscopic structure.

Table 4. Influence of hydrolysis time on the physicochemical and textural properties.

Sample	Parameter	Textural properties						Acidity mmol H ⁺ /g	S content mmol S/g
		d ₁₀₀ (Å)	D _p (Å)	S _{BET} (m ² /g)	V _p (cm ³ /g)	Wall Thickness (Å)			
13	2	92	71	764	1.04	35	0.42	0.72	
14	4	95	83	742	1.31	27	1.20	1.13	
15	10	96	77	745	1.16	34	1.13	1.09	

The parameter is the hydrolysis time in hours. The TEOS/surfactant molar ratio was 55 and the ageing conditions were 100°C for 24 h. No swelling agent was used.

Figure 1 (A) and (B) depicts the nitrogen adsorption/desorption isotherms and pore size distributions of samples synthesised using Pluronic 123 as polymeric template under different conditions. Under the particular conditions checked in this work, we have expanded the pore size of this sulfonic modified materials from 40 to 100 Å obtaining relative high surface areas (600-750 m²/g; Tables 1-4). The combination of high surface areas and the presence of accessible Brønsted acid sites provide these materials with good potential catalytic properties.

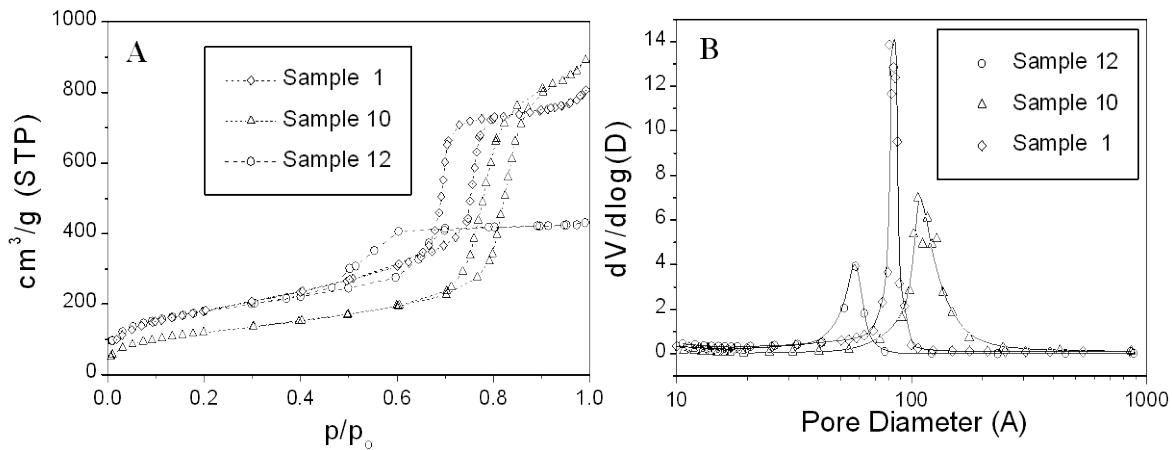


Figure 1. (A) N₂ adsorption/desorption isotherms and (B) Pore size distributions of sulfonic-functionalised mesoporous silica using Pluronic 123.

Figure 2 shows TEM images of two samples synthesised under different conditions (Samples 1, Table 1; and Sample 11, Table 3). These images confirm the mesoscopic order of the materials where it is evident the hexagonal array of uniform channels with the typical honeycomb appearance of SBA-15 materials⁸.

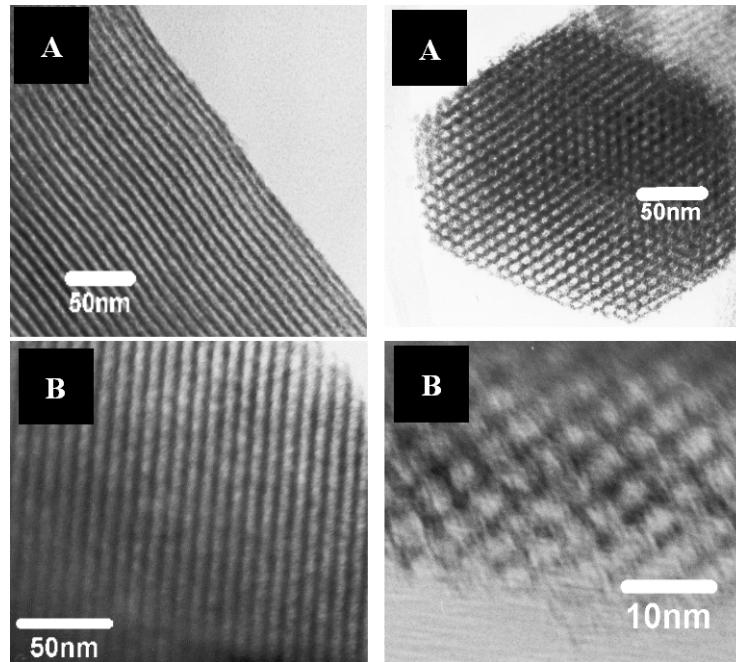


Figure 2. Transmission Electron Microscopy images for samples 1 (A) and 11 (B), in the direction parallel to the pore axis and in the direction perpendicular to the pore axis.

3.2 Sulfonic-Functionalised Mesoporous Silica using non-ionic templates other than P₁₂₃.

Table 5 summarises the preparation conditions as well as the physicochemical and textural properties of the sulfonic modified mesoporous materials prepared with Brij56, Brij76 and PL64 as surfactants.

Table 5. Physicochemical and textural properties of sulfonic modified materials prepared using Pluronic PL64, Brij56 and Brij76 as surfactants

Sample	Synthesis conditions				Textural properties				Acidity ^d mmol H ⁺ /g	S content ^e mmol S/g
	Ageing t (h)	T (°C)	TEOS/ Surf.	TMB ^a / Surf.	d (\AA)	D _p ^b (\AA)	S _{BET} m ² /g	V _p cm ³ /g		
Pluronic L64 (EO₁₃/PO₃₀/EO₁₃)										
16	24	100	27	0	74	48	725	0.68	33	0.43
Brij 56 (C₁₆EO₁₀)										
17	24	100	6	0	57	34	763	0.83	31	0.93
Brij 76 (C₁₈EO₁₀)										
18	0	-	7	0	53	30	718	0.51	31	1.06
19	24	80	7	0	56	38	710	0.87	27	1.15
20	24	100	7	0	60	38	678	0.81	31	1.23
21	24	100	7	0.5	60	38	713	0.85	31	1.16
22	24	100	7	1.0	58	47	745	1.11	20	1.17
23	24	100	12	0	58	37	764	0.83	31	0.92
24	24	100	20	0	60	34	779	0.76	35	1.04

^a TMB/Surfactant mass ratio. ^b Calculated from the adsorption branch. ^c Calculated by $a_o - \text{pore size}$ ($a_o = 2d_{100}\sqrt{3}$). ^d Acidity obtained from ion exchange and titration data and defined per g of dried sample. ^e Sulphur content obtained from ICP-AES measurements and defined per g of dried sample. Hydrolysis conditions were 40 °C during 20 hours for sample 18 (PL64) and 50 °C during 20 hours for the other samples (Brij 56 and 76)

Pluronic L64 as surfactant. Figure 3 (A) depicts the pore size distribution whereas Figure 3 (B) illustrates the XRD pattern corresponding to the sulfonic modified material after surfactant removal and its comparison with sample 1 synthesised in presence of Pluronic 123. As expected, a lower molecular-weight block copolymer gives a smaller pore system. Nevertheless, a clear broad distribution of pore sizes is evidenced which reveals a low ordered material. This lack of mesoscopic ordering is also evidenced from XRD diffractogram where a unique peak is observed with complete absence of high ordering reflections typical of materials synthesised using Pluronic 123. The incorporation of the sulphur species is lower to that obtained using Pluronic 123 and more important the acid capacity disagrees with this content evidencing limited accessibility of sulfonic sites which might be occluded within the walls.

Oligomeric alkyl-ethylene oxide surfactants: Brij 56 and 76. All the synthesis conditions tested using Brij56 or Brij76 as surfactants yielded similar organic degree incorporation than that achieved using Pluronic 123. Likewise, these materials show a close agreement between sulphur content and acid capacity indicating the high accessibility of the acid groups. Figure 4 (A) shows the pore size distribution whereas Figure 4 (B) shows X-ray pattern corresponding to sample 17, and its comparison with sample 1 synthesised in presence of Pluronic 123. This organically modified material displays a well-defined pore size distribution with a mean pore size of 34 Å, which is significantly lower than the pore size obtained using Pluronic 123. This is consistent with the size of the hydrophobic block of the template: the smaller the hydrophobic block, the lower the size of the micelle core and the lower the resultant pore size. X-ray pattern of this sample prepared with Brij56 evidenced a clear signal at $2\theta = 1.51$ and two weak long ordering reflections confirming the good mesoscopic ordering of the material.

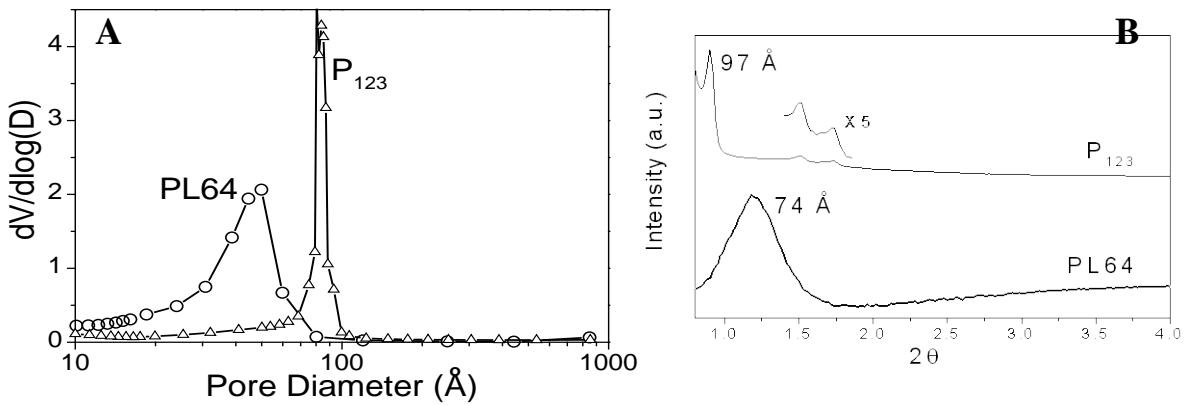


Figure 3. (A) Pore size distribution and (B) X-ray diffraction pattern of sulfonic-functionalised mesoporous silica using Pluronic L64.

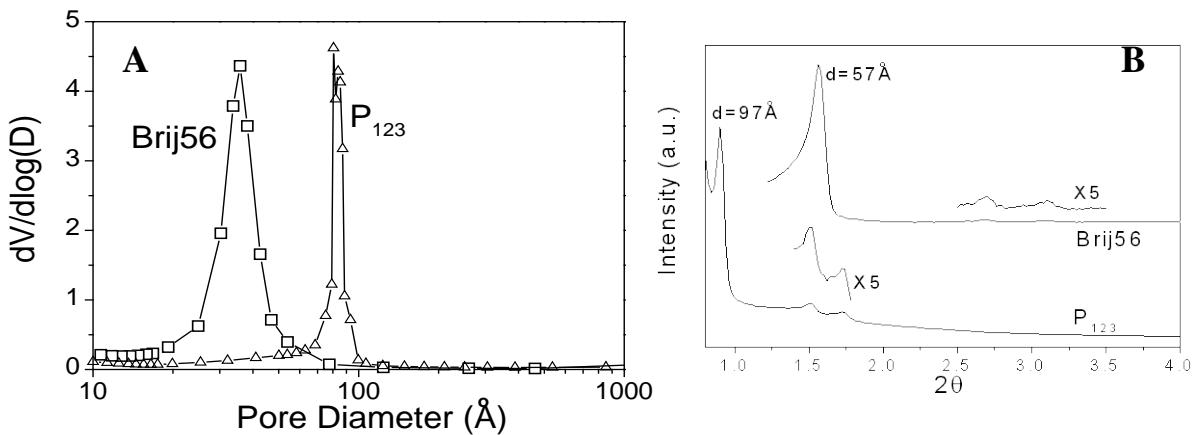


Figure 4. (A) Pore size distribution and (B) X-ray diffraction pattern of sulfonic-functionalised mesoporous silica using Brij56.

The pore size of the sulfonic modified materials synthesised with Brij 76 has been modified using analogous strategies of synthesis than those described before for Pluronic 123. The enlargement of ageing time as well as an increase of temperature yielded an increase of pore size. However, the effect was less pronounced than that monitored using Pluronic 123 as surfactant. Likewise, the addition of a swelling agent such as TMB, leads to a moderate increase of the mean pore size up to 47 Å for a TMB/surfactant mass ratio of 1. The increase of TEOS/surfactant ratio promoted more silica condensation and a decrease of pore size with and enlargement of wall thickness. Figure 5 (A) shows the tailoring of the pore size of these materials under different synthetic conditions. These materials display well-defined pore-size distributions with mean pore sizes ranging from 30 to 47 Å and high surface areas ($600\text{-}800\text{ m}^2/\text{g}$). Finally, the good mesoscopic ordering of these materials is evidenced in the XRD diffractograms depicted in Figure 5 (B) and confirmed by the TEM images showed in Fig. 6.

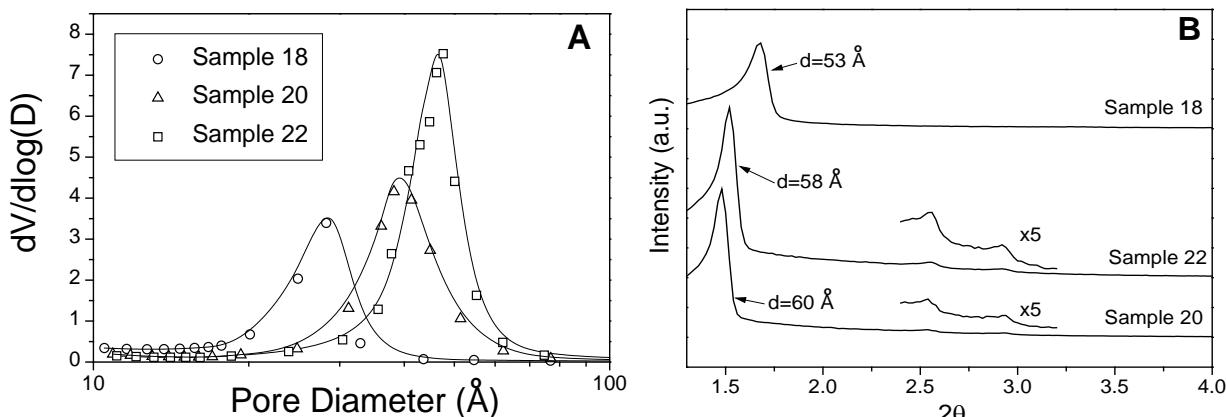


Figure 5. (A) Pore size distributions and (B) X-ray diffraction patterns of sulfonic-functionalised mesoporous silica using Brij76.

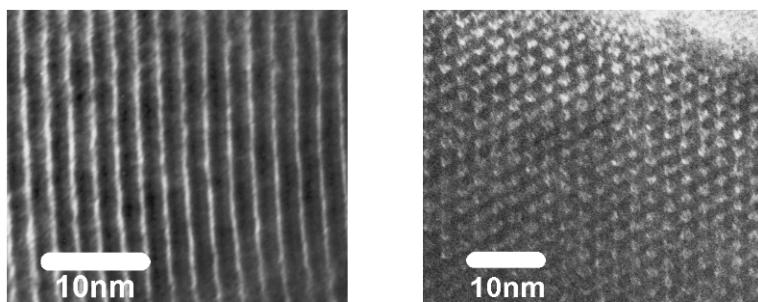


Figure 6. Transmission Electron Microscopy images for sample 22, in the direction parallel to the pore axis and in the direction perpendicular to the pore axis.

4. CONCLUSIONS

An one-step procedure has been generalised for the synthesis of sulfonic-functionalised mesoporous silica using non-ionic surfactants other than Pluronic 123. Pore size of sulfonic modified mesoporous materials prepared using non-ionic templates has been tailored using a judicious choice of TEOS/surfactant molar ratio, prehydrolysis time, duration and temperature of ageing process and the use of swelling agents. Under the particular conditions tested in this work, the pore size of the resultant sulfonic modified mesoporous material were tailored from 30 Å to 110 Å which provides them with an enlargement of the catalytic potential applications.

5. REFERENCES

1. A. Corma. *Chem. Rev.* 95 (1995) 559.
2. K. Wilson and J.H. Clark. *Pure Appl. Chem.* 72 (2000) 1313.
3. W.M. Van Rhijn et al. *J. Chem. Soc., Chem. Commun.* (1998) 317.
4. M. H. Lim et al. *Chem. Mater.* 10 (1998) 467.
5. C.E. Fowler et al. *J. Chem. Soc., Chem. Commun.* (1998) 1825.
6. M.H. Lim et al. *Chem. Mater.* 11 (1999) 3285
7. D.Margolese et al., *Chem. Mater.* 12 (2000) 2448.
8. D. Zhao et al. *J. Am. Chem. Soc.* 120 (1998) 6024.