ChemComm

# Synthesis of microporous surfactant-templated aluminosilicates

**David P. Serrano,*[a] José Aguado,[a] José M. Escola[a] and Eduardo Garagorri[b]**

[a] *Department of Experimental Sciences and Engineering, ESCET, Rey Juan Carlos University, c/Tulipán s/n 28933, Móstoles, Madrid, Spain. E-mail: dserrano@escet.urjc.es*
[b] *Department of Chemical Engineering, Complutense University, Av. Complutense s/n, 28040 Madrid, Spain.*

***Received (in Cambridge, UK) 31st July 2000, Accepted 7th September 2000***
***First published as an Advance Article on the web 2nd October 2000***

**Microporous aluminosilicates have been synthesized in the presence of organic surfactants according to a procedure based on a two-step sol–gel process at room temperature; varying the surfactant chain length and/or the Si/Al ratio, materials with pore diameters adjustable in the range 1.0–2.5 nm have been obtained; the Al atoms in the as-synthesized samples present tetrahedral coordination, even for materials with high Al content (Si/Al = 6).**

The M41S family of surfactant-templated mesoporous silicates and aluminosilicates was discovered and characterized in 1992 by Mobil Oil researchers.[1] The presence of Al atoms incorporated into the walls and large pores provide these materials with interesting properties for the catalytic conversion of bulky molecules.[2–4] In past years, a number of studies have been published aimed to the synthesis of mesoporous materials with increasing pore size by incorporation of swelling agents to the synthesis medium or by using block copolymer surfactants.[5–8] Accordingly, micelle-templated silicates and aluminosilicates have been prepared with uniform pore sizes in the range 2–10 nm.[9–13] However, less attention has been devoted to the synthesis of surfactant-templated materials with pore diameters below 2.0 nm. This is an interesting goal as it would contribute to fill the pore size gap existing between microporous zeolitic materials ($D_p < 1$ nm) and surfactant-templated mesoporous solids ($D_p > 2$ nm). Moreover, materials with uniform pore size in the range 1.0–2.0 nm are expected to exhibit interesting shape-selectivity properties in the conversion of large substrates.

Several papers have recently appeared with the aim of obtaining surfactant templated materials with small pore diameters. Thus, a novel method for tailoring the pore opening size of MCM-41 materials has been reported,[14] although based on a complex post-synthesis treatment with three steps. A completely different approach has been developed by Bagshaw and Haymann,[15] which has led to silicates with pore sizes in the range 1.4–2.0 nm through the use of a new family of ω-hydroxy-bolaform surfactants. However, at present it is not clear whether this last alternative would also allow microporous aluminosilicates to be synthesized.

In a recent work,[16] we have reported a new method for the preparation of Al-containing micelle-templated silica (Al-MTS) based on a sol–gel process at room temperature. We have found that when increasing the aluminium content, materials with pore sizes in the range 1.5–2.0 nm are obtained. In the present work we show that this method is also useful for the synthesis of Al-MTS solids with pore sizes that can be tailored in the range 1.0–2.0 nm through the variation of both surfactant alkyl chain length and Al content.

The materials were synthesized at room temperature according to the following procedure. The silica and aluminium sources (tetraethyl orthosilicate, TEOS, and aluminium isopropoxide, IPA) were first hydrolyzed under acidic conditions (aqueous HCl), the starting Si/Al ratio being varied within the range 5–30. The surfactant was added and the mixture obtained was stirred and kept under acidic conditions for 1 h (TEOS/Surf. molar ratio = 0.3). Both cetyltrimethylammonium chloride (CTMACl) and dodecyltrimethylammonium bromide (DTMABr) were employed as surfactants. In a second step, condensation reactions were promoted by dropwise addition of 2 wt% aqueous $NH_3$ until the gel point is reached. The solid material so obtained was filtered off, washed with deionized water and dried at 110 °C overnight. Finally, it was calcined in $N_2$ flow at a heating rate of 1 °C $min^{-1}$ up to 550 °C and then kept in air flow at this temperature for 5 h.

Table 1 summarizes the physicochemical properties of different Al-MTS materials prepared. Although in general the samples obtained show Al contents lower than those of the synthesis mixture, a close correspondence is observed among them, even for the synthesis with the lowest Si/Al ratios. TG analysis of the as-synthesized samples show the presence of the surfactant molecules occluded in the pores with weight losses in the range 40–55 wt%, confirming that they can be regarded as micelle-templated materials. Fig. 1 illustrates the XRD spectra of samples prepared with surfactants of different chain length, a sharp diffraction peak at low angle being observed, which is

**Table 1** Synthesis conditions and physicochemical properties of the synthesized materials

| | | | $N_2$ adsorption isotherm (77 K) | | |
|---|---|---|---|---|---|
| Surfactant | Si/Al (medium) | Si/Al (product) | Pore volume[a]/ $cm^3\ g^{-1}$ | BET surface area[b]/$m^2\ g^{-1}$ | Surfactant content[c] (wt%) |
| CTMACl | 30 | 45.2 | 0.93 | 1180 | 55 |
| CTMACl | 20 | 31.5 | 0.66 | 1020 | 52 |
| CTMACl | 10 | 18.9 | 0.56 | 910 | 50 |
| CTMACl | 5 | 8.3 | 0.45 | 790 | 43 |
| DTMABr | 20 | 42.4 | 0.47 | 960 | 46 |
| DTMABr | 15 | 18.9 | 0.40 | 840 | 42 |
| DTMABr | 8 | 10.4 | 0.39 | 820 | 35 |
| DTMABr | 5 | 6.3 | 0.32 | 770 | 40 |

[a] Measured at $p/p_o = 0.9$. [b] Measured within the range $p/p_o = 0.01$–$0.125$. [c] Determined from the TGA weight loss in the range 150–450 °C.

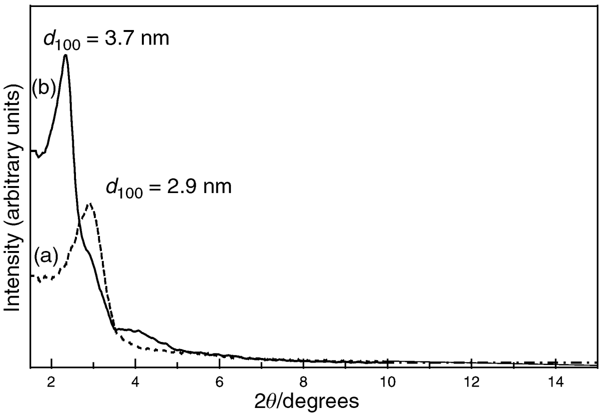

**Fig. 1** XRD spectra of calcined samples: (a) DTMABr, Si/Al = 6.3 and (b) CTMACl, Si/Al = 45.2.

DOI: 10.1039/b006186g

**This journal is © The Royal Society of Chemistry 2000**

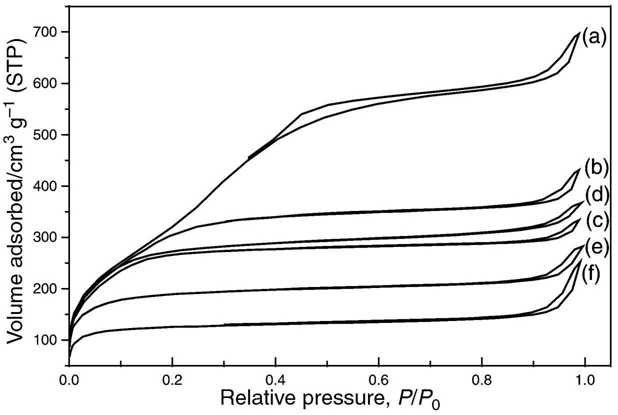

**Fig. 2** $N_2$ adsorption–desorption isotherms: (a) CTMACl, Si/Al = 45.2; (b) CTMACl, Si/Al = 31.5; (c) CTMACl, Si/Al = 8.3; (d) DTMABr, Si/Al = 42.4; (e) DTMABr, Si/Al = 18.9; (f) DTMABr, Si/Al = 6.3.

characteristic of M41S amorphous structured materials. The *d*-spacings of the calcined samples prepared with DTMABr are higher than those obtained with CTMACl, which shows that a lower chain length of the surfactant leads to a reduction in the unit cell size.

Fig. 2 compares the $N_2$ adsorption–desorption isotherms at 77 K of a number of samples synthesized varying both the surfactant and the starting Si/Al ratio. A type IV isotherm is obtained for the sample prepared using CTMACl and Si/Al = 45.2, which is typical of a mesoporous material. This sample shows a pore diameter of 2.5 nm, calculated by the BJH method. However, increasing the Al content and/or reducing the alkyl chain length of the surfactant leads to type I isotherms, typical of microporous solids, which is accompanied by a decrease in both surface area and pore volume. Fig. 3 shows the variation in the pore size of these samples *vs.* the Al content. For both surfactants, the pore diameter is progressively reduced as the Al content is increased, showing that the presence of aluminium species during the synthesis process strongly affects the ionic surfactant-templated mechanism. For the samples prepared using CTMACl, the lowest pore diameter obtained is 1.5 nm, clearly within the micropore region. Interestingly, this limit can be reduced using DTMABr as surfactant, which leads to the synthesis of materials with pore sizes in the range 1.0–1.7 nm.

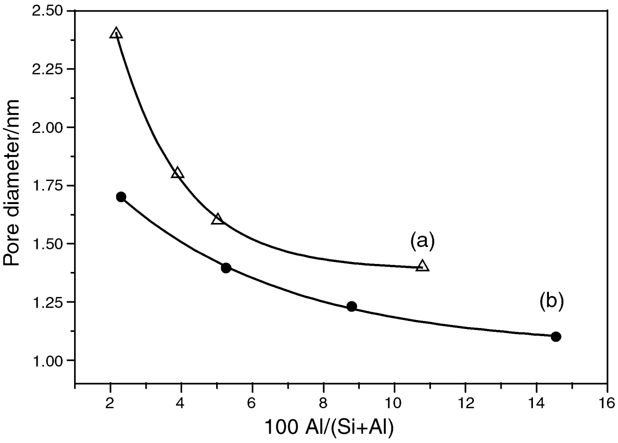

**Fig. 3** Relationship between the pore diameter and the aluminium content of the samples: (a) CTMACl (pore diameters calculated according to the BJH method) and (b) DTMABr (pore diameters calculated according to the Saito–Foley method).

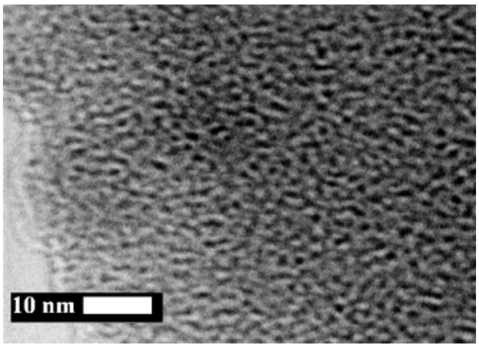

**Fig. 4** TEM micrograph of the sample with Si/Al = 6.3 synthesized using DTMABr as surfactant.

These results are further confirmed by TEM micrographs of the samples (see Fig. 4). The pore diameters measured in these micrographs agree well with those derived from the $N_2$ adsorption measurements. Moreover, from XRD spacings and pore diameters, a large wall thickness (1.5–2.0 nm) is obtained. This result may be also important in terms of the stability of these materials.

In order to study the Al environment in the samples, $^{27}Al$ MAS NMR spectra were measured, which show that in the as-synthesized materials all the Al atoms present tetrahedral coordination. This result indicates that even for samples with high aluminium content (Si/Al = 6), most of the Al species are effectively incorporated into the pore walls.

In summary, it can be concluded that using this new synthesis method, and through a suitable combination of surfactant chain length and Al content, Al-MTS materials with pore size adjustable in the range 1.0 - 2.5 nm can be prepared.

This work was funded by the Spanish Comisión Interministerial de Ciencia y Tecnología (CICYT), project number AMB-97/0530, and by Comunidad de Madrid, Strategic Group Project.

## Notes and references

1 C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, *Nature*, 1992, **359**, 710.
2 A. Corma, A. Martínez, V. Martínez.Soria and J. B. Montón, *J. Catal.*, 1995, **153**, 25.
3 J. Aguado, J. L. Sotelo, D. P. Serrano, J. A. Calles and J. M. Escola, *Energy Fuels*, 1997, **11**, 1225.
4 D. P. Serrano, J. Aguado, J. L. Sotelo, R. Van Grieken, J. M. Escola and J. M. Menéndez, *Stud. Surf. Sci. Catal.*, 1998, **117**, 437.
5 I. Díaz, J. Pérez Pariente and E. Sastre, *Stud. Surf. Sci. Catal.*, 1999, **125**, 53.
6 M. Janicke, D. Kumar, G. D. Stucky and B. F. Chmelka, *Stud. Surf. Sci. Catal.*, 1994, **84**, 243.
7 S. A. Bagshaw, E. Prouzet and T. J. Pinnavaia, *Science*, 1995, **269**, 1242.
8 Y. Yue, A. Gedeón, J. Bonardet, N. Melosh, J. D'Espinose and J. Fraissard, *Chem. Commun.*, 1999, 1967.
9 C. Y. Chen, H. X. Li and M. E. Davis, *Microporous Mater.*, 1993, **2**, 17.
10 Z. Luan, C. Cheng, W. Zhou and J. Klinowski, *J. Phys. Chem.*, 1993, **99**, 1018.
11 K. R. Kloetstra, H. W. Zandbergen and H. Van Bekkum, *Catal. Lett.*, 1995, **33**, 157.
12 R. Mokaya and W. Jones, *Chem. Commun.*, 1996, 981.
13 P. T. Tareu and T. J. Pinnavaia, *Science*, 1996, **271**, 1267.
14 X. S. Zhao, G. Q. Lu and X. Hu, *Chem. Commun.*, 1999, 1391.
15 S. A. Bagshaw and A. R. Hayman, *Chem. Commun.*, 2000, 533.
16 J. Aguado, D. P. Serrano and J. M. Escola, *Microporous Mesoporous Mater.*, 2000, **34**, 43.