Towards the Loewenstein limit (Si/Al = 1) in thermally stable mesoporous aluminosilicates

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The use of complexing agents to generate polynuclear precursor species containing both Al and Si allows the synthesis of thermally stable mesoporous aluminosilicates including solely tetrahedrally coordinated aluminium, in which the Si/Al ratio can be modulated down to a minimum Si/Al value of 1.06(4).

A great part of fine chemicals production is dependent on high surface Al–Si mixed oxides or zeolites which act as catalysts or serve as catalyst supports.[1–3] After the discovery of silica-based MCM-41 mesoporous derivatives,[4] a key scientific objective has been the attainment of increasing content of tetrahedral Al in the framework of materials of this type to achieve higher Brønsted acidity and thus improved catalytic activity. Different direct surfactant-assisted synthetic procedures related to that of MCM-41[5–8] or, alternatively, post-synthesis reactions[9] have been explored with this aim. Indeed, the use as principal reagent of $Al_4Si_4(OH)_8O_{12}^{4-}$ cube-like molecular polyanions (*i.e.* by incorporating the optimal Si/Al = 1 molar ratio into the precursor) led to a mesostructured material with high Al content.[5] Unfortunately, surfactant removal led to a collapse of the pore system together with partial conversion of tetrahedral Al centers into octahedral ones. In general, the best results have been obtained by reproducing the MCM-41 synthesis in the presence of an Al source. As far as we know, stable mesoporous solids prepared through surfactant-assisted procedures having the largest contents of tetrahedral Al are those reported by Luan *et al.*[6] (Si/Al = 2.5) and Borarde and Clearfield[7] (Si/Al = 2), who used $Al_2(SO_4)_3$ and $NaAlO_2$, respectively. This notwithstanding, as stated by Hamdan *et al.*,[8] the outcome of direct synthesis of Al containing MCM-41 depends strongly on the nature of the Al source used, which often leads to irreproducible results.

We report here a new direct and reproducible procedure that provides thermally stable mesoporous aluminosilicate molecular sieves in which the Al content in the framework can be modulated down to a minimum Si/Al value of 1.06(4), very close to the ideal molar ratio of 1 (compatible with the presence of mainly tetrahedrally coordinated Al centers).[10]

Aluminium rich mesoporous materials of the MCM-41 type have been synthesized using CTABr as surfactant in TEAH₃–water (CTABr = cetyltrimethylammonium bromide, $TEAH_3$ = triethanolamine). A typical preparation leading to the Si/Al

= 1.06 mesoporous aluminosilicate can be described as follows: a mixture of TEOS (7.2 mL, 0.033 mol) and Al(OBuˢ)₃ (8.4 mL, 0.033 mol) was added to a solution containing TEAH₃ (30 mL, 0.226 mol) and 1.32 g (0.03 mol) of NaOH in 2 mL of water, and heated at 190 °C for 10 min [TEOS = tetraethylorthosilicate, Al(OBuˢ)₃ = aluminium *sec*-butoxide]. The resulting solution was cooled to 50 °C, and CTABr (6.5 g, 0.018 mol) in 180 mL of water was added while stirring. The mixture was allowed to age for 5 days at room temperature, resulting in the formation of a white solid. This was then filtered off washed with ethanol and air dried. To obtain the final mesoporous material, the as-synthesized solid, which is mesostructured, was calcined at 500 °C for 5 h under air to eliminate the surfactant. Table 1 summarises the main synthesis variables and physical data corresponding to some selected samples. All the samples were analyzed and characterized by electron probe microanalysis (EPMA), (Philips SEM-515 instrument), XRD techniques (Seifert 3000TT diffractometer using Cu-Kα radiation), TEM (Philips CM10 microscope), ²⁹Si and ²⁷Al MAS NMR (Varian Unity-300 spectrometer), and N₂ adsorption–desorption isotherms (Micromeritics ASAP2010 analyzer). Moreover, fast atom bombardment (FAB) analysis of the precursor solutions was been performed to gain insight into the role of TEAH₃.

EPMA analysis shows that all the samples are chemically homogeneous with a regular distribution of aluminium and silicon atoms throughout the inorganic walls. Hence, the solids can be considered as monophasic products. The Si/Al molar ratio in the final material is very close to that present in the mother-liquor, indicating that there is no preferential incorporation of aluminium or silicon into the final net.

XRD pattern resolution of mesoporous materials is poorer than for purely siliceous MCM-41 solids. This fact indicates a degree of loss of the typical hexagonal order observed for MCM-41 solids. Hence, the pore packing motif can be better described as disordered hexagonal, as confirmed by TEM micrographs (Fig. 1).

Previous ²⁷Al NMR results indicate that Al containing MCM-41 solids may include octahedrally coordinated aluminium atoms, with a degree of controversy about their extra- or intra-framework nature. Thus, on the basis on 2-D NMR data, Janicke *et al.*[11] have recently concluded that both four- and six-coordinate Al centers can coexist in the inorganic walls. In any case, it seems clear that Al atoms in octahedral environments do

Table 1 Selected synthetic and physical data for some mesoporous aluminosilicates samples

Sample	Si/Al (Precursor)	Si/Al[a] (Solid)	δ^b	d_{100}/Å	a^c/Å	Pore size/Å	Pore wall thickness/Å	Surface area/ m² g⁻¹
1	∞	∞	−113.3	37.5	43.3	25.6	17.7	1118
2	14.0	8.17(3)	−105.0	38.5	44.5	25.0	19.5	985
3	5.0	4.51(6)	−97.8	38.5	44.5	21.5	23.0	832
4	1.0	1.06(4)	−87.9	41.8	48.3	20.0	28.3	430

[a] Values averaged from EPMA of *ca.* 40 different particles, (statistical esds in parenthesis). [b] ²⁹Si MAS NMR chemical shifts. [c] Calculated cell parameter values assuming an MCM-41 type hexagonal cell.
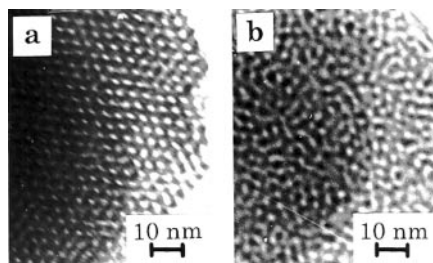
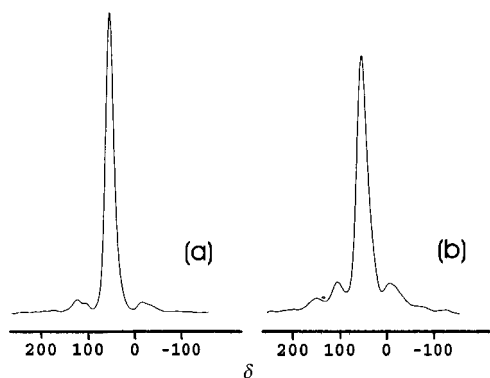**Fig. 1** TEM micrographs of (a) sample 1 (Si/Al = ∞) and (b) sample 4 [Si/Al = 1.06(4)].

Fig. 2 ^{27}Al MAS NMR spectra of sample 4 [Si/Al = 1.06(4)]. (a) mesostructured; (b) mesoporous. Small signals at either side of the main one are due to the spinning of the sample (side bands).
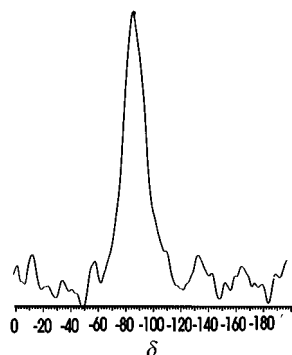

Fig. 3 ^{29}Si MAS NMR spectrum of mesoporous sample 4 [Si/Al = 1.06(4)].

not contribute to the Brønsted acidity. The ^{27}Al MAS NMR spectra of all mesostructured or mesoporous materials reported here show essentially only one resonance signal at δ ca. 55 (Fig. 2), which is characteristic of tetrahedral Al. The small signals at either side of the main signal are due to the spinning of the sample (side bands) as they move equally when changing the spinning frequency. A remarkable fact is that neither dealumination nor conversion from tetrahedral into octahedral aluminium occurs as a consequence of surfactant removal. ^{29}Si MAS NMR spectra for all samples show a very strong and broad signal whose center shifts from δ −113 for pure siliceous MCM-41 materials to δ −87.9 for sample 4 (Fig. 3) (see Table 1). In this last case, the displacement of the signal is in accordance with the resonance of Q^4 (4Al) and Q^3 (3Al) Si environments. The broadness of the signal may be a consequence of resonances of other minor Si environments such as Q^4 (3Al) and other Q^3 sites, similarly to results reported in ref. 5. Thus, both ^{27}Al and ^{29}Si MAS NMR results are in good accordance with the Si/Al = 1.06 molar ratio calculated from EPMA analysis.

All samples show one well defined step in their N$_2$ adsorption isotherms. According to previous observations, incorporation of Al leads to significant decreases in BET surface area and pore size (Table 1). Despite this, the high surface area, porosity and thermal stability characteristic of the parent mesoporous silicas, are retained even for the highest Al content [Si/Al = 1.06(4)]. An estimation of the pore wall dimensions can be made from XRD and porosity data. As shown in Table 1, the pore wall thickness increases (17.7–28.3 Å) with Al content and probably leads to the materials' high thermal stability.

A preliminary mass-spectral analysis (FAB) carried out on TEOS–Al(OBu^s)$_3$–TEAH$_3$ mixtures, prior to surfactant addition, indicates the presence of entities of different nuclearity in which triethanolamine must displace the initial alkoxide anions from the metallic coordination spheres and give rise to more hydrolysis stable complexes when water is added [TEAH$_{3−n}$-(TEASi)$_n$ (n = 1–3); Al(TEA)]. Although MS FAB analysis cannot differentiate between Si and Al in polynuclear species, taking into account the similar affinity of both Si and Al towards coordination of TEA,[12] mixed molecular precursor species can be envisaged, *e.g.* Si$_{3−n}$Al$_n$ (TEA)$_{4−n}$(TEAH)$_n$ (n = 1,2) This fact indicates that Al and Si are essentially mixed to a nearly atomic level in the precursor solution, and explains the high chemical homogeneity observed both in the mesostructured and in the final mesoporous solids.

In summary, this work demonstrates that it is possible to increase, in a continuous way, the Al content in MCM-41-like mesoporous materials up to virtually a 1/1 Si/Al molar ratio, the maximum possible for an aluminosilicate without formation of Al–O–Al links. Taking into account the ready formation of stable monomeric and polynuclear species, the role played by triethanolamine can be viewed as a 'hydrolysis retarding agent' for both Si and Al. This allows a balance between the hydrolysis and condensation reactions affecting the inorganic species and the self-assembling processes between the resulting inorganic fragments and the organic surfactant. Moreover, by leading to an intimate mixture of Al and Si in the mother-liquor, the presence of triethanolamine favours chemical homogeneity and hence the thermal stability of the resulting materials. In this context, complexing agents such as triethanolamine appear invaluable and highly promising tools for the preparation of new mesoporous materials.

Note added at proof: During the revision of this work a paper describing low silica Al-MCM-41 materials has appeared (M. T. Janicke *et al., Chem. Mater.*, 1999, **11**, 1342)

Notes and references

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