Synthesis of acidic aluminosilicate mesoporous molecular sieves using primary amines

Robert Mokaya and William Jones

Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, UK CB2 1EW

Mesoporous molecular sieves are generated using primary amine surfactants as the template in the assembly of aluminosilicate inorganic species; aluminium incorporation is accompanied by charge-balancing protonated amine molecules.

The recent synthesis of a family of silica based mesoporous molecular-sieve materials (designated M14S)[1,2] has attracted considerable interest because of the potential of these materials for use as solid-acid catalysts. There have been several reports describing the synthesis of these materials and it is now recognised that there are a variety of routes by which they may be prepared.[3–5] The catalytic properties of mesoporous molecular sieves rely on the presence of active (*e.g.* acidic) sites in their framework. In the case of MCM-41 active sites are generated by the incorporation of heteroatoms (*e.g.* Al, Ti). In particular, Brønsted-acid sites are introduced by isomorphous substitution of Al for Si which is achieved by hydrothermal synthesis in which charged quaternary ammonium micelles are used as the template for charged aluminosilicate inorganic precursors.[6–10] The resulting (calcined) template free material (which contains charge-balancing inorganic cations) is ammonium exchanged and recalcined to generate protons which give rise to Brønsted-acid sites in the form of 'bridging' SiOHAl hydroxy groups.[10] Tanev *et al.* have recently reported the synthesis of (neutral framework) mesoporous materials *via* a route which involves self-assembly between neutral primary amines and *neutral* inorganic framework precursor.[4,5] Here we report on a synthesis route to aluminosilicate mesoporous molecular sieves (Al-MMS) which, in contrast to previously reported routes,[1–10] is based on primary amine surfactants acting as the template for *charged* aluminosilicate inorganic precursors. Unlike the report in ref. 5 where only tetravalent heteroatoms are incorporated, the procedure described here allows charge balancing during the incorporation of trivalent aluminium. Furthermore, in contrast to the synthesis of protonic MCM-41, Brønsted-acid sites are generated by simply calcining the as-synthesised material thereby precluding the need for ammonium exchange and calcination, which is known to result in the undesirable loss of framework Al.[8,9] Our findings indicate that Si and Al are incorporated into the resulting Al-MMS solid framework in proportions dependent on the gel (stoichiometric) Si : Al ratio and that during calcination of the as-synthesised material, the templating amine surfactant decomposes to generate charge-balancing protons (Brønsted-acid sites).

The aluminosilicate materials (designated Al-MMSX, where X is the Si : Al ratio used in the synthesis gel) were prepared as follows; mixtures of aluminium isopropoxide [$Al(OPr^i)_3$, in 35 ml isopropyl alcohol] and 0.2 mol tetraethylorthosilicate (TEOS in 80 ml ethanol) at (Si : Al) molar ratios in the range 40–5 : 1 were heated with vigorous stirring at 70 °C for 4 h and added to 0.05 mol dodecylamine (in a mixture of 80 ml water and 120 ml ethanol at room temp.). The pH of the reaction mixture was close to 9.5. For purely siliceous material (designated MMS), TEOS (0.2 mol) was added to 0.05 mol dodecylamine. In each case the resulting gel mixture was allowed to react at room temperature for 20 h following which the solid product was obtained by filtration, air dried at room temperature and finally calcined in air at 650 °C for 4 h.

Elemental compositions determined using X-ray fluorescence (XRF), are given in Table 1. The Si : Al molar ratios of the aluminosilicate samples are in close agreement with the composition of the gel mixtures indicating that Si and Al are incorporated into the solid framework in equal proportions. Further evidence of the incorporation of Al was provided by ^{27}Al MAS NMR analysis. The spectra of the as-synthesised materials showed a sharp resonance from four-coordinate Al at δ 53.0 confirming that the Al in the gel mixture was incorporated into the framework.[8,9] For samples with high aluminium content (Al-MMS5 and Al-MMS10), an additional broad low-intensity peak at δ 0 was observed indicating that a small amount of Al in this samples is extra-framework. Upon calcination the amount of extra-framework Al increased indicating that in the course of calcination some Al is removed from the framework. Similar observations are reported for aluminosilicate MCM-41.[8,9] The powder XRD patterns obtained for the samples are similar to those observed by Pinnavaia and coworkers,[4,5] *i.e.*, a single (100) peak (which becomes sharper and more intense upon calcination) corresponding to a *d*-spacing of 35 Å for MMS and between 29 and 34 Å for Al-MMS samples. Materials exhibiting such single-peak XRD patterns have been previously reported and are known to possess short-range hexagonal symmetry.[4,5,11]

Table 1 also gives the textural properties obtained on a Micromeritics ASAP 2400 Sorptometer using standard volumetric techniques. Before measurement each sample was oven dried at 200 °C and evacuated overnight at 200 °C. The average pore size was obtained by BJH analysis of N_2 sorption data. The surface area obtained for the Al-MMS materials decreases with increasing aluminium incorporation but is generally comparable to that previously reported for MCM-41 type materials.[1–5] We did not observe any hysteresis in the mesopore filling region of the isotherms of the Al-MMS samples which is an indication that these materials possess pores in the lower mesopore range. Hysteresis at high partial pressure (p/p_0 = 0.8), which is indicative of textural mesoporosity or macroporosity, was only observed for the purely siliceous (MMS) sample and the high-aluminium containing Al-MMS5 sample.

Information concerning the mechanism of synthesis of the Al-MMS materials has been obtained. Fig. 1 shows the TGA and DTG curves obtained for the as-synthesised samples. The

Table 1 Elemental composition and textural properties of the purely siliceous (MMS) and aluminosilicate (Al-MMS) samples

	Si : Al ratio				
Sample	XRF	TGA	BET surface area/m^2 g^{-1}	Pore volume/ cm^3 g^{-1}	Pore size/Å
MMS			1240	1.68	28.0
Al-MMS40	45.6	47.0	1200	0.65	25.0
Al-MMS20	23.7	25.0	1195	0.52	20.0
Al-MMS10	13.8	12.8	967	0.49	19.8
Al-MMS5	6.8	6.5	737	0.49	20.5

curves were obtained using a Polymer Laboratories TGA 1500 with a heating rate of 20 °C min^{-1} under a nitrogen flow of 25 ml min^{-1}. The mass loss centred at 60 °C is attributed to the release of adsorbed water and/or ethanol and that centred at 250 °C due to amine desorption. The Al-MMS samples show a further mass loss centred at 450 °C which increases with increasing aluminium incorporation and develops at the expense of the mass loss centred at 250 °C. We propose that for samples in which aluminium is incorporated the (templating) amine is present in two forms; (*i*) neutral, 'low'-temperature amine similar to that present in the purely siliceous material which is desorbed and decomposed between 100 and 300 °C and (*ii*) protonated 'high'-temperature amine which is removed between 300 and 500 °C.

To verify our proposal, we subjected the purely siliceous sample (MMS) and one aluminosilicate sample (Al-MMS5) to an extraction process: 1.5 g of sample in 150 ml ethanol, stirred at 65 °C for 1 h followed by filtration. Following three extractions all amine in MMS is removed and the TGA curve of the extracted sample indicates only two mass losses; (*i*) the loss of water/ethanol (centred at 60 °C) and (*ii*) a hitherto absent mass loss centred at 570 °C probably associated with the dehydroxylation of the surface. Total mass loss for the extracted MMS sample was 12% compared to 53% for the as-synthesised material. Only one extraction was required to remove the 'low'-temperature amine from sample Al-MMS5. The amount of 'high'-temperature amine was not affected and remained the same after three extractions indicating that it could not be removed by simple filtration. We suggest that as more isormorphously substituted Al is incorporated into the solid framework increasing amounts of electrostatically bound amine are required to balance the framework charge. Indeed, the Si : Al ratios computed from the mass loss between 300 and 500 °C are comparable to those obtained from XRF analysis (see Table 1). Furthermore the presence of protonated amine in the as-synthesised Al-MMS samples was confirmed by IR spectroscopy; the intensity of the spectral band associated with protonated amine (at 1510 cm^{-1}) was observed to increase as the amount of aluminium incorporated increased. This band was not observed for the as-synthesised MMS sample. The TGA and IR studies clearly indicate that, for the purely siliceous material, neutral amines are responsible for the assembly of neutral inorganic species,[4,5] similar to that of Pinnavaia and coworkers.[4,5] However, unlike the cases reported in ref. 4 and 5 where only tetravalent ions are incorporated (*e.g.* Ti^{4+}) the amine procedure described above allows charge balancing during the incorporation of trivalent aluminium. The full mechanism by which the aluminosilicate samples are formed is not clear, although our results suggest that the addition of the aluminosilicate inorganic precursor influences the electrostatic nature of the templating species and mediates the ordering of the amine surfactant molecules. An important observation concerning the materials we have reported here is that they possess significantly higher Brønsted acidity and display enhanced catalytic activity. This is described in the following paper.[12]

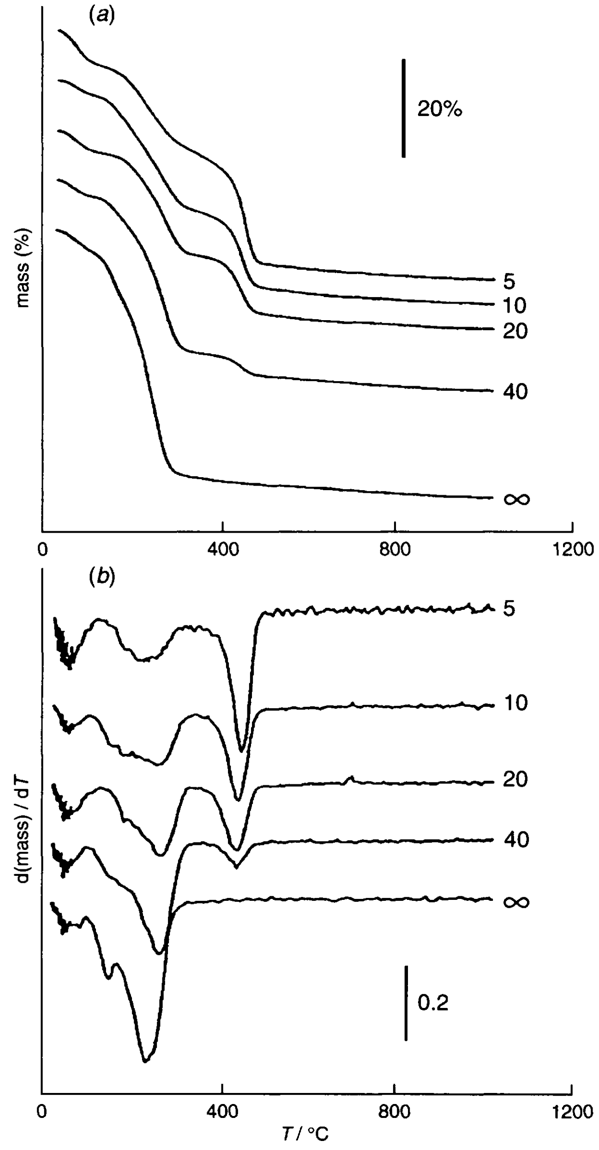

Fig 1 Thermogravimetric analysis (*a*) and differential thermogravimetric analysis (*b*) curves obtained for the as-synthesised purely siliceous material (Si : Al = ∞) and aluminosilicate (Al-MMS) samples prepared at the Si : Al ratios indicated

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