Synthesis of a Mesoporous MCM-41 Material with High Levels of Tetrahedral Aluminium

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A crystalline mesoporous member of the MCM-41 family has been synthesised with a Si : Al ratio as low as 8.5 : 1, without observing octahedral aluminium.

Recently a new family of mesoporous molecular sieves designated as MCM-41 was discovered in the laboratories of the Mobil Oil Company.[1–3] The MCM-41 materials possess a regular array of uniform, unidimensional mesopores, which can be systematically varied in size from around 16 to 100 Å. They bridge the gap between microporous (zeolites) and macroporous materials (*e.g.* amorphous aluminosilicates). These characteristics together with their high surface areas (up to 1000 m^2 g^{-1}) and their distinct adsorption properties (pore condensation without hysteresis)[4,5] open up new potential applications. However, for this material to be useful for catalytic applications, it is essential to incorporate metal ions, *e.g.* trivalent aluminium, into the siliceous framework. Until now the incorporation of tetrahedral aluminium into the framework has been limited to a Si : Al of 14 : 1 though details of the synthesis were not presented.[6] The lowest Si : Al reported (without the presence of extra framework octahedral aluminium) while stating the synthesis procedure was 29 : 1.[7]

We report here on the synthesis of a mesoporous MCM-41 material with the lowest published Si : Al ratio of 8.5 : 1 without any observable octahedral aluminium present.

The synthesis mixture was prepared using precipitated silica (Ketjensil 500, PQ Corporation), sodium aluminate (54% Al_2O_3, 41% Na_2O, Riedel de Hahn), NMe_4OH solution (20%, Riedel de Hahn) and tetradecyltrimethylammonium bromide ($C_{14}H_{29}Me_3NBr$, 99%, Aldrich). Additionally a tetramethylammonium silicate solution (TMA : Si mol ratio of 1 : 1, containing 10 wt% Si) was prepared by combining tetramethylammonium hydroxide pentahydrate (100 g, 97%, Jansen) with colloidal silica (114.7 g, Ludox LS, 30% SiO_2, DuPont) and distilled water (164 g), and aged for two days.

A gel with the following molar chemical composition was prepared: 26 SiO_2, Al_2O_3, 2.11 $C_{14}H_{29}Me_3NBr$, 9.47 NMe_4OH, 1.4 NaO_2, 478 H_2O.

The synthesis procedure was as follows: sodium aluminate (2.1 g) was added slowly (10 min) to a solution containing $C_{14}H_{29}Me_3NBr$ (8 g) dissolved in distilled water (50 g), which was aged for 12 h. Aged tetramethylammonium silicate solution (50 g) and Ketjensil (12.5 g) were added while stirring with an ultrastirrer. After 10 min tetramethylammonium hydroxide solution (10 g) was added, and the gel was homogenised for 10 min. The resultant gel was loaded into a stoppered Teflon bottle and heated without stirring for 24 h at 100 °C. After cooling to room temp. the resulting solid product was recovered by filtration, washed extensively with distilled water, and dried in air at ambient temperature. Part of the material was calcined at 540 °C for 1 h in a flow of N_2, followed by 6 h in air.

The powder X-ray diffraction of the resultant calcined material presented in Fig. 1 corresponds to those reported for MCM-41 materials.[3] The surface area was determined as 982 m^2 g^{-1} by a full adsorption/desorption nitrogen isotherm using BET analysis. In accordance to Franke *et al.*[4] and Branton *et al.*[5] a step of the nitrogen isotherm, characteristic for MCM-41 materials, representing the filling of the pores, can be observed. The ^{27}Al solid state MAS NMR spectra were recorded at 78.157 MHz (room temp.) on a VARIAN VXR 300 S WB spectrometer. This was equipped with a Jakobson probe using a 7 mm zirconia rotor (MAS spinning speed: 6 kHz) with a pulse length of $\pi/5$ [90° pulse ($\pi/2$) = 5 μs]. Varying the pulse length ($\pi/12$, $\pi/20$) showed no qualitative effect on the spectra recorded. As reference a 1 mol dm^{-3} $Al(NO_3)_3$ ($\delta = 0$) was used. The as-synthesised sample was not thermally treated in any way (drying at room temp.) and the calcined material was kept in absence of humidity before recording the ^{27}Al MAS spectra. The bulk chemical composition was determined by microprobe analysis using a Cameca microbeam instrument. The Si : Al bulk ratio of the as-synthesised and calcined material were found to be 8.5 : 1.

The ^{27}Al MAS NMR analysis of the as-synthesised material (Fig. 2) suggests that all the aluminium observed in the sample

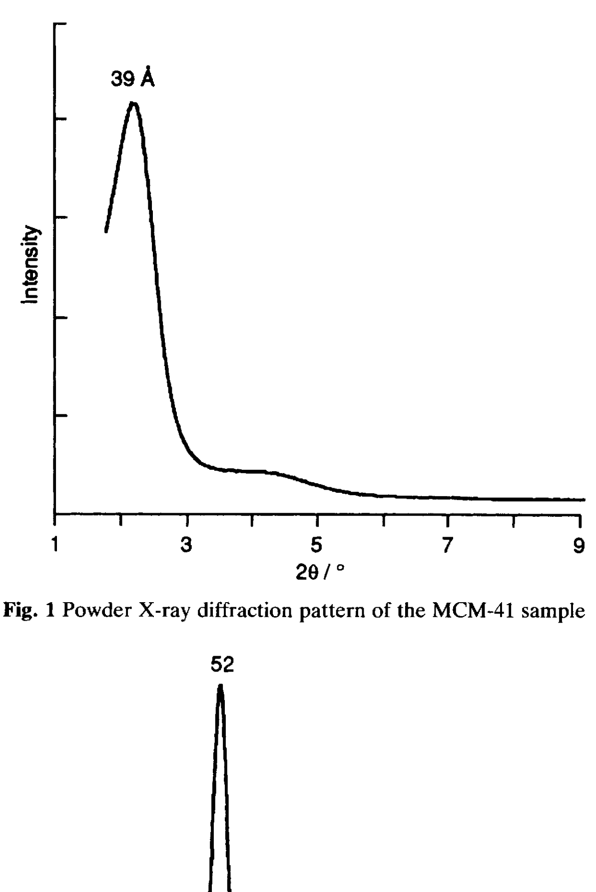

Fig. 1 Powder X-ray diffraction pattern of the MCM-41 sample

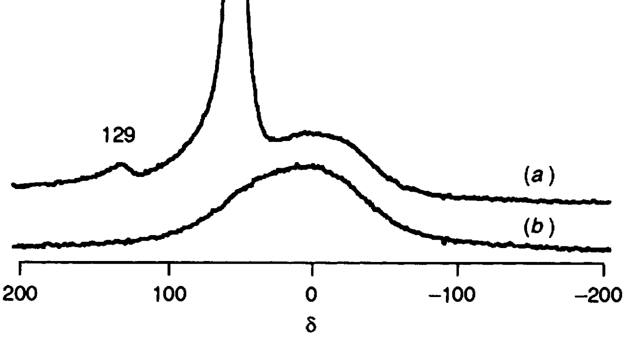

Fig. 2 ^{27}Al MAS NMR spectra of the as-synthesised MCM-41 sample (*a*) and of the background from the MAS probe (*b*)

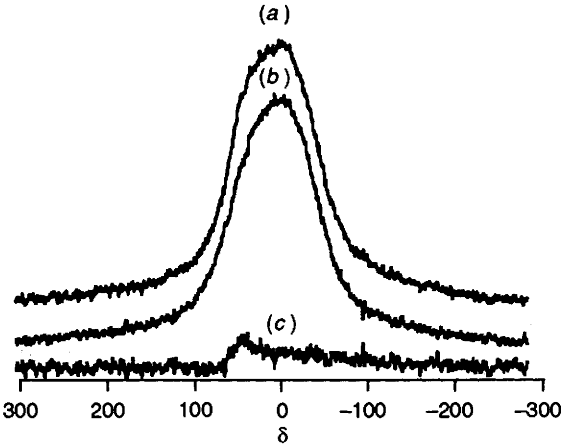

Fig. 3 ^{27}Al MAS NMR spectra of the calcined MCM-41 sample (*a*), the background from the MAS probe (*b*) and of background subtracted calcined sample (*c*)

is tetrahedrally coordinated, represented by the sharp peak at δ52. The broad peak centred at δ0 is due to background aluminium in the MAS probe itself and the peak around δ129 represents a spinning sideband. Subtraction of the background showed the absence of octahedrally coordinated aluminium, normally represented by a sharp peak with a chemical shift at δ *ca.* 0. Octahedrally coordinated aluminium was clearly observed in MCM-41 materials obtained by synthesis procedures different from the one described above.[8]

Upon calcination at 540 °C for 1 h in N_2 followed by 6 h in air, the sharp ^{27}Al MAS NMR tetrahedral aluminium peak (δ52) disappeared [Fig. 3(*a*)]. At the same time there was no evidence of the appearance of a peak due to octahedrally coordinated aluminium. The background subtracted ^{27}Al-MAS NMR spectra of the calcined sample [Fig. 3(*c*)], suggests that the aluminium present in the calcined sample can no longer be observed by ^{27}Al MAS NMR under the conditions of the experiment. This indicates the transformation of the original tetrahedrally coordinated aluminium into aluminium in a lower symmetry environment. In accordance with this, Kolodziejski *et al.*[6] and Chen *et al.*[7] observed for their MCM-41 material a transformation upon calcination of the originally tetrahedrally coordinated aluminium (as-synthesised sample) into aluminium in highly disordered environments.

Considering the large unidimensional pores of the MCM-41 material, alternative ways of template removal such as liquid extraction methods instead of calcination[8,9] may be feasible, allowing the removal of the template of the as-synthesised MCM-41 material with less perturbation of the aluminium environment. However, studies of different template extraction conditions[8] applied to MCM-41 materials currently show difficulties in removing the template associated with the aluminium present.

In conclusion, the first member of the MCM-41 family with a silica to (tetrahedral) aluminium ratio as low as 8.5 : 1 has been synthesised. Removal of the template by calcination leads to a transformation of the tetrahedrally coordinated aluminium to disordered aluminium which could not be observed by ^{27}Al MAS NMR under the conditions of the experiment.

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