Room-temperature Formation of Molecular Sieve MCM-41

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A pure silica mesomorphous analogue of MCM-41, synthesised at ambient temperatures, shows similar characteristics to materials heated during preparation.

We report here small-angle X-ray scattering and gas adsorption measurements showing the ambient temperature formation of a pure silica molecular sieve closely related to MCM-41. Previously, the formation of a templated aluminosilicate MCM-41 at 25 °C in an alkaline preparation was reported briefly by Stucky *et al.*,[1] who noted a lack of hydrothermal, thermal and mechanical stability for this compound compared to that obtained from a heated preparation. We have found, however, considerable retention of structure in molecular sieves prepared using a version of the procedure published by Beck *et al.*[2] The stability of these compounds is probably due to the condensation reactions which occur during ageing. Previous work does not allude to the time between the creation of the reaction mixture and sample removal. Formation of a hexagonal mesoporous pure silica product, templated around a primary ammonium ion, dodecylamine, in an acidic preparation at room temperature was also reported by Tanev *et al.*,[3] and the material was stable to calcination but no characterisation of the surface properties was done.

A solution of sodium silicate (Aldrich, *ca.* 14% NaOH, *ca.* 27% SiO_2) was diluted with Millipore filtered water and slightly acidified. This was stirred for 10 min. A solution of cetyltrimethylammonium bromide (CTAB, Fluka, 98%) in water was heated to 80 °C for 45 min and added to the first solution. This mixture was stirred for 30 min before further water was added and the resulting synthesis gel stirred for another 5 min. From this point the synthesis gel was sealed and left to age with aliquots being removed at 3, 7, 11 and 16 days. These samples were filtered, washed with hot water and dried in a desiccator before being calcined under air at 350 °C.

Small-angle X-ray scattering (SAXS) patterns were taken for the wet synthesis gel at times between 1 and 395 h after the initial mixing to discover any ageing phenomena. SAXS patterns were also taken for each dried and calcined sample. Nitrogen adsorption isotherms at 77 K were determined for the calcined samples using a Satorius microbalance and the results compared with data from a preparation similar in all respects to that described above, except that the starting mixture had been heated in an autoclave at 100 °C for varying amounts of time.

The SAXS measurements on the wet synthesis gel show that the major diffraction peak, at a Bragg *d*-spacing of 42 Å which is characteristic of MCM-41, appeared in the earliest pattern recorded (1 h after the last mixing of the preparation) and persisted at the same *d*-spacing and with almost the same intensity at room temperature for the whole of the period covered by the experiment. This major diffraction peak arises from the hexagonal-templated surfactant–silica precursor which results in MCM-41 in the standard preparation. The result suggests that this structure is formed almost immediately upon the preparation of the synthesis gel and no further structural changes occur on ageing. Peaks at 26 and 13 Å were assigned to the lamellar crystalline form of CTAB which is present in the synthesis gel in excess. No lamellar silica–surfactant phase was identified at any point in the synthesis gel, unlike that observed by Monnier *et al.*[4] However, the lamellar phase in that case was observed at times between 1 and 20 min after the preparation of the synthesis gel, whereas these measurements were taken on time scales of hours.

Table 1 Diffraction and surface area data on unheated samples

Elapsed time at 25 °C/days	Wet spacing/Å	Dry spacing/Å	Calcined spacing/Å	Surface area/m² g⁻¹
3	41.8 ± 0.3	40.0	32.1	1030
7	41.9	41.0	33.0	1150
11	42.3	41.5	32.9	1210
16	42.7	40.9	34.5	1200

The stability of the structure to washing and drying was followed by the SAXS measurements on the resultant powders. This procedure produced a lattice contraction of approximately 2 ± 1 Å (see Table 1). The variation in the degree of contraction observed may be due to different degrees of dehydration caused by slightly different drying times, but it is obvious that the removal of water from the hexagonal network causes a

Table 2 Diffraction data on samples heated during preparation

Heating time at 100 °C/days	Wet spacing/Å	Dry spacing/Å	Calcined spacing/Å
Uncooked	44.2 ± 0.3	38.1	
2	42.7	38.9	30.5
3	43.0	39.9	33.8
6	42.8	38.8	32.5

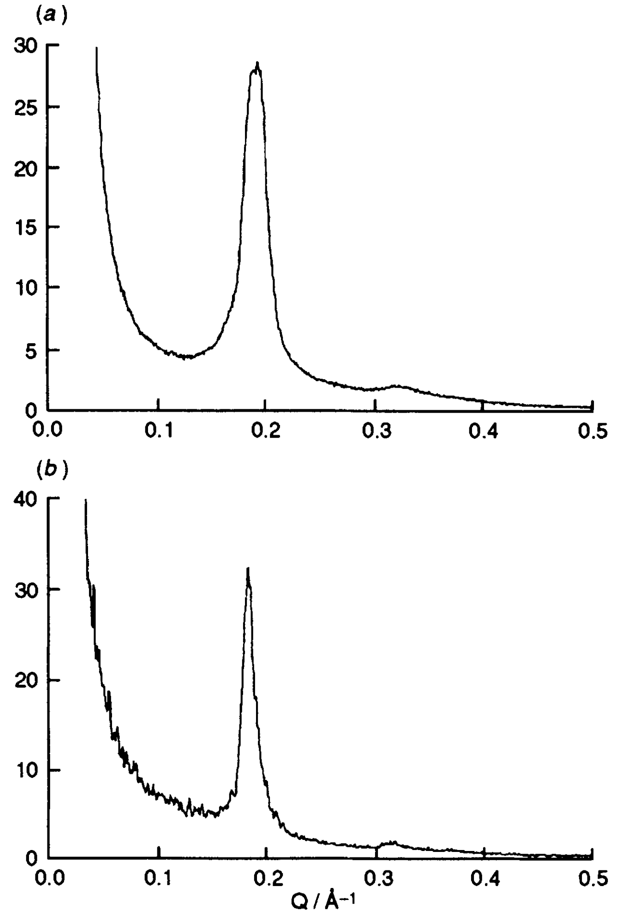

Fig. 1 SAXS Data on (*a*) calcined material taken from the unheated preparation after 7 days ageing time and (*b*) calcined material taken from the heated preparation after 3 days at 100 °C

shrinkage and this has been noted elsewhere.[5] That this contraction occurs without significant loss of diffraction intensity indicates an interesting flexibility of the silica walls of the composite. [A similar contraction is noted when material which has been heated during synthesis is washed and dried (see Table 2).] Although no effect of ageing was noticed on the wet gel diffraction peaks, the intensities of the 40 Å diffraction peaks from the dried materials were nearly 5 times larger for the samples aged for longer than 3 d, although there was no significant change in the peak width. This suggests that the longer aged samples had higher degrees of condensation of the silica walls and so were more stable to this treatment.

Calcination caused further shrinkage of the hexagonal lattice, by 8 ± 1 Å for the unheated materials (Table 1), but the more aged materials shrink less, which again suggests a higher degree of condensation for the silica species in the walls. By comparison, the materials formed in the heated preparation suffered a shrinkage of 7 ± 1 Å as a result of calcination (Table 2) and thus may be even more condensed before calcination. The amount of shrinkage is very similar, and it can be concluded that the product from room-temperature synthesis and that made by heating have similar degrees of condensation.

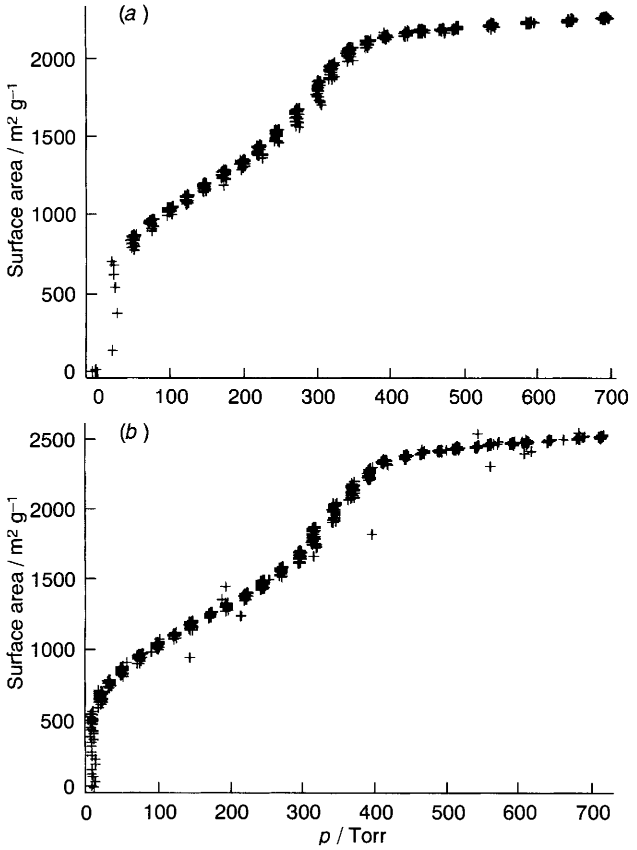

Fig. 2 Nitrogen adsorption isotherms for (*a*) calcined material taken from the unheated preparation after 7 days ageing time and (*b*) calcined material taken from the heated preparation after 3 days at 100 °C

The diffraction peaks seen in the SAXS from the unheated preparations are broader upon calcination and have less high-angle structure than those for heated preparations (Fig. 1). A rough analysis of crystallite size using the Scherrer equation[6] showed that the coherence length in the particles went from *ca.* 1400 Å in the washed and dried material to *ca.* 500 Å in the calcined materials, which suggests that there is partial destruction of the hexagonally close-packed tubes by the escape of water and combustion products from the CTAB during the calcination process.

We do not exclude some condensation of the silanol groups to form siloxane bonds during calcination at 350 °C. Chen *et al.*[5] have carried out ^{29}Si NMR on similar systems and report an increase in the number of Q4 sites over Q3 and Q2 sites upon calcination, showing that further reactions have occurred. The fact that calcination appears to have a much smaller affect on the materials which were heated in the gel phase suggests a supplementary role for the calcination in that case.

Nitrogen adsorption isotherms were run on each of the calcined samples from the unheated preparation and on the standard products for comparison, and Fig 2 compares examples. The unheated materials showed reversible isotherms with the characteristic type IV shape associated with MCM-41.[7] The BET surface areas were calculated by fitting the straight part of the $p/x(p - p_0)$ *vs.* p/p_0 curve (where p is the pressure of nitrogen, and x is the number of grams of adsorbed nitrogen per gram of solid). The resulting surface areas ranged from 1030 m^2 g^{-1} to 1210 m^2 g^{-1}, and show a rough correspondence with ageing time up to 11 d. These surface areas are within the range expected for this mesoporous material and correspond with those measured for materials from the standard alkali heated preparation (typically 1100 m^2 g^{-1}).

The room-temperature synthesised pure silica mesoporous material thus appears to be as stable as materials formed from heated preparations, and to retain its structure upon calcination.

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