Improved Stability of MCM-41 through Textural Control

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Control of silicoaluminate activity during synthesis of MCM-41 leads to thicker pore walls, and hence to improved thermal and hydrothermal stabilities.

Mobil's recently developed proprietary material MCM-41 is formed by the aggregation of silicate units and surfactant micelles under mild hydrothermal conditions.[1] It features cylindrical mesopores of uniform diameter[2] limited by a honeycomb of amorphous silica–alumina.[3] The availability of mesoporous solids of uniform diameter extends the concept of molecular sieves beyond the zeolite scale, and fulfils a long-standing expectation of the catalysis and adsorption communities.[4,5]

MCM-41 is the collective name for a family of solids with a pore size between 16 and 100 Å. Poor thermal and hydrothermal stabilities are the limiting factors in the potential application of these materials to several types of hydrocarbon processing procedures[6] and adsorption processes requiring heavy-duty regeneration. The relevance of thermal stability has been evident since the earliest disclosure of the material.[7] The first reported MCM-41 featured a silica–alumina wall thickness, t, of *ca* ≈ 5 Å at the thinnest point; this corresponds to only two silica monolayers. Such a thin curtain can be easily pierced by local hydrolysis of the Si–O–Al bonds, and by dealumination caused by the thermal treatment needed to clean the pores of the organic compounds used during synthesis. The existence of a small hole between the parallel pores creates a highly unstable situation according to the laws of sintering.[8]

This phenomenon probably accounts for the lower than expected pore volume (0.79 $\text{cm}^3\ \text{g}^{-1}$) observed for the original material. An infinite array of close-packed cylindrical pores is expected to feature a pore volume, ε, see eqn. (1),

$$\varepsilon = [S/(A - S)]V_{Si}\ (\text{cm}^3\ \text{g}^{-1}) \qquad (1)$$

where $S = \pi\, d^2/4$ is the section of a pore of diameter d, $A = a^2 \sin 60\,°$ is the area of the hexagonal unit cell normal to the pore axis, and $V_{Si} = 2.20$ is the volume mass of amorphous silica.[9] This calculation, applied to an MCM-41 featuring an intact structure with $d = 40$ Å and $a = 45$ Å,[7] gives a pore volume of 1.14 $\text{cm}^3\ \text{g}^{-1}$. To improve the hydrothermal stability of MCM-41, Mobil researchers developed a post-synthesis treatment involving lining agents[6] such as the alkoxides of Si, Al or Ti. Our approach to stiffening the pore walls has been instead based on modification of the synthesis conditions. The most probable model for the formation of MCM-41 materials implies aggregation of silica-coated micelles.[10] We have assumed that by modifying the activity of the silicoaluminate units in solution we can control the thickness of the silicate coating of the surfactant micelles, and hence, the thickness of the walls separating the pores of the final solid.

This effect is clearly observed in the products of a series of syntheses based on hydrogels in the following composition range: 2.8–5.6 hexadecyltetramethylammonium bromide (CTMAB), 7.5–1.5 Na_2O–Al_2O_3, 15 SiO_2, 300–1200 H_2O. All gels were prepared by blending and stirring commercial reagents [CTMAB, precipitated silica (Rhône Poulenc Zeosil 175 MP), $NaAlO_4$ and NaOH] in aqueous solution, followed by heating at 120 °C for 24 h in static autoclaves. The solid phase formed was separated from the mother solution by filtering, washed to pH 8 and dried overnight at 80 °C.

The product of each synthesis featured the characteristic fingerprints of MCM-41: the principal X-ray diffraction line appearing in the range 40–60 Å, further lines confirming hexagonal packing, a typical thermogravimetry (TG) pattern[3] and a nitrogen adsorption–desorption isotherm with a sharp, reversible step at $P/P_0 = 0.35$.[2] Nitrogen sorption isotherms recorded following calcination at 550 °C under a flow of air indicate that the diameter of the uniform mesopores always lies in the range 36–39 Å; this agrees with the results obtained by applying the Kelvin law[2] or the Horvath–Kavazoe method.[11] The lattice parameter, a, of the calcined samples varied from 40 to 55 Å depending on the conditions of synthesis. As Fig. 1 shows, the pore wall thickness, $t = a - d$, varied from 4 to 16 Å. As the pore diameter was almost constant, variation in the pore spacing (*i.e.* wall thickness) accounts completely for the increase in the lattice parameter.

Alkalinity is the synthetic parameter that most influenced wall thickness. The pore spacing increased as the $OH^- : SiO_2$ ratio in the synthesis gel decreased; this suggests that a thicker silica–alumina coating is deposited on the surfactant micelles

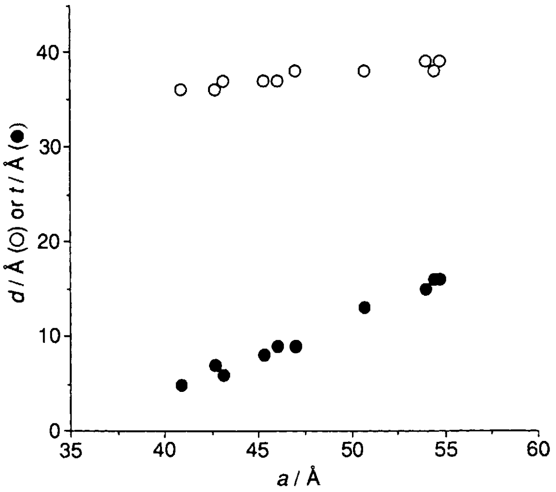

Fig. 1 Mesopore diameter (○) and wall thickness (●) of MCM-41 materials as functions of the lattice parameter, a

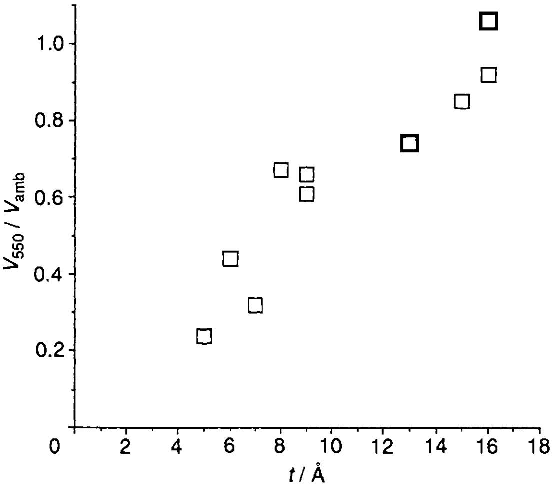

Fig. 2 Ratio between the volumes of uniform-sized mesopores following calcination at 550 °C under an air flow (V_{550}) and in the as-synthesised MCM-41 (V_{Amb}) as a function of wall thickness, t

when the silicate solubility decreases. Other parameters affecting the concentration of silicate units in solution exerted some influence on wall thickness. Moderate increases of the lattice parameter could be obtained by increasing the $H_2O:SiO_2$ ratio of the gel or by ageing the colloidal silica in alkaline solution prior to gel preparation.

The effect of wall thickness on the stability of MCM-41 can be observed by comparing the pore volume after a given thermal treatment with an initial value calculated from eqn. (1). For all samples, evaluation of the mesopore volume of the as-synthesised solid through eqn. (1) closely fits the value obtained by TG by measuring the mass ratio between the organic compounds and silica–alumina. The presence of water vapour, generated by the oxidation of the organic compounds, makes calcination at 550 °C under flowing air a reliable test of the hydrothermal stability of these materials. Fig. 2 represents the ratio between the volume left in the uniform-sized mesopores after such an hydrothermal treatment and the initial mesopore volume. The control of the thickness of the walls, which bound the pores, appears to be an efficient tool to preserve the mesopore volume.

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