Direct preparation of organically modified MCM-type materials. Preparation and characterisation of aminopropyl–MCM and 2-cyanoethyl–MCM

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Very stable organically modified MCMs are prepared by a simple one-step procedure from readily available starting materials.

The discovery of the MCM series of mesoporous materials has opened up the way to zeolitic materials of controlled meso-porosity.[1] Such materials are promising as catalysts in their own right[2] and should also prove to be of use as catalyst supports,[3] leading to potential improvements in reaction selectivity in the conversion of medium-size molecules due to their well defined and tightly controlled pore size distribution. The initial method of preparation of the MCMs involved high temperature calcination (typically 550–650 °C) to remove the ionic template. Such a requirement precludes this method from the preparation of MCM-type materials containing organic functional groups. Recently, Tanev and Pinnavaia published details of non-ionic routes to the MCMs, in which an amine[4] or a poly(alkylene oxide)[5] was used as a template. Such templates can be removed by extraction with hot solvents such as ethanol, and avoid the necessity of calcination. We now wish to report the first example of an organically modified MCM material of

potential use in catalysis, prepared using the non-ionic amine template route.[4] Aminopropyl-modified silicas (AMPSi) have been prepared and used as basic catalysts,[6] and as precursors for surface bound groups of interest in a number of applications.[7] One drawback of these materials is the lack of controlled mesoporosity of the support silica. A second problem is the low specificity of such derivatisation techniques and the associated modest stability of at least some of the bound groups. Sol–gel variants have been synthesised which display enhanced stability,[8] but initial results suggest that they have unfavourable porosity characteristics.[9]
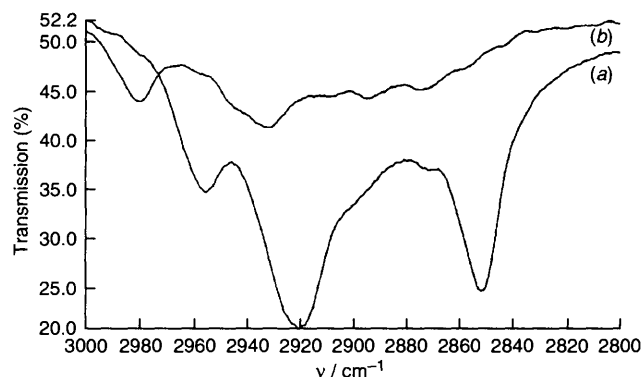
Fig. 1 DRIFT IR spectra of the C–H stretching region of **1a** (*a*) before and (*b*) after removal of dodecylamine template. The spectra were run using an environmental DRIFT accessory at 130 °C and 20 Torr.
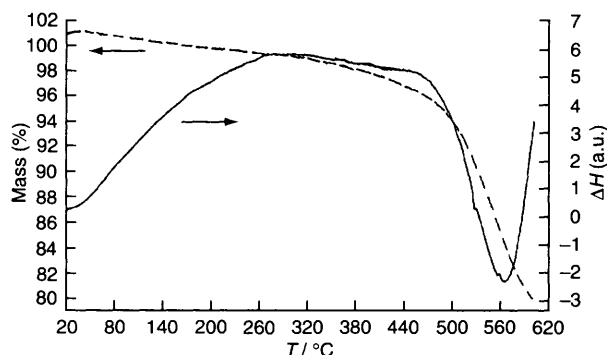
Fig. 2 Simultaneous thermal analysis of **2**; TG (- - -) and DTA (———).
The trace was recorded at 20 °C min⁻¹ under an atmosphere of flowing nitrogen.
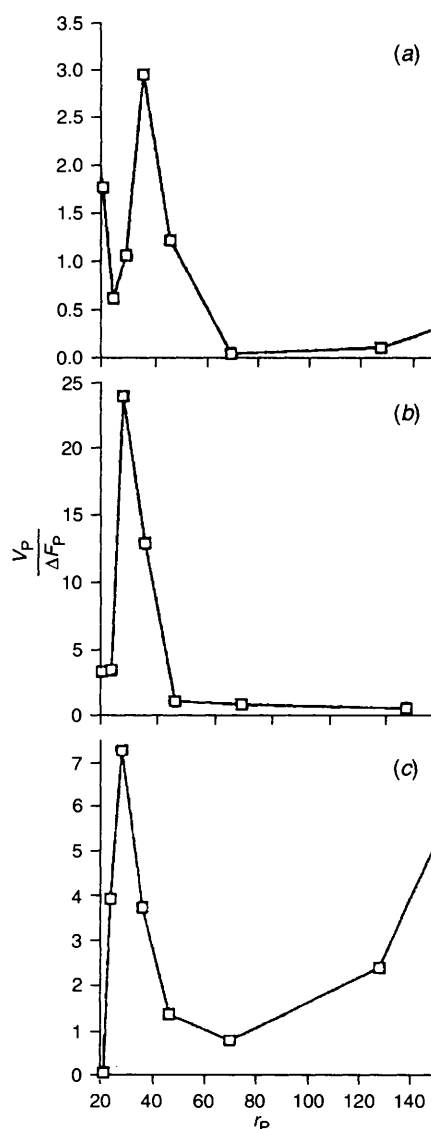
Fig. 3 Pore size distributions for **1a** (*a*), **b** (*b*) and for **2** (*c*). Porosity measurements were carried out using dinitrogen as adsorbate.

A typical preparation of an aminopropyl-modified MCM is as follows. Tetraethoxysilane (TEOS, 18.75 g, 0.09 mol) and trimethoxy(3-aminopropyl)silane (AMPS, 1.79 g, 0.01 mol) were added, separately, to a stirred mixture of ethanol (41 g), distilled water (53 g) and n-dodecylamine (5.09 g) at room temp. After 10–15 min the turbid solution became milky, and stirring was continued for 18 h, yielding a thick white suspension. This was filtered and n-dodecylamine removed by heating the solid ($ca.$ 10 g) at reflux in absolute ethanol (100 ml) for 3 h. This extraction was repeated three times. Analysis of the filtrate showed that only dodecylamine was removed, and that removal was complete after three cycles. After the final filtration, the product was dried at 120 °C and atmospheric pressure to yield a fine white solid **1a**. Similarly prepared were **1b** (containing 10 mol% AMPS) and **2** [10 mol% 2-cyanoethyl-(trimethoxy)silane]. In all cases the total amount of silane was 0.1 mol.

IR spectroscopy of the products was carried out using an environmental DRIFT chamber at 130 °C (5 mmHg vacuum), and was compared to the crude product before extraction of template. Comparison of the C–H stretching region clearly shows the loss of template amine (Fig. 1). Material containing dodecylamine shows a C–H stretching pattern distinctly different from the final product. The final products display the expected IR bands for CH_2, and $N-H_{def}$ (1590 cm^{-1}) and $C{\equiv}N_{str}$ (2254 cm^{-1}, sharp) respectively.

Simultaneous thermal analysis (thermal analysis coupled with differential thermal analysis, STA) of **1a** indicates loss of residual solvent with a maximum at $T = 80$ °C, followed by a minor mass loss ($ca.$ 1%) centred at 300 °C, and a major mass loss (>8%) centred at 575 °C (Fig. 2). Thermal desorption/mass spectrometry indicates that the latter two events are due to loss of aminopropyl groups from the material. Both these losses are at temperatures characteristic of chemisorbed material, the second being indicative of very stably bound material. Indeed, IR analysis of material obtained from an initial STA run terminating at 600 °C clearly shows aminopropyl groups intact on the surface. The STA of **1b** and **2** are similar to that of **1a**, with the exception of the minor event at $ca.$ 300 °C. For the latter two compounds, the only significant event occurs at $T > 500$ °C and is due to loss of the organic groups. The STA trace for **2** is shown in Fig. 2. Such thermal stability is not displayed by the conventional aminopropyl-modified silicas, which have a much more pronounced loss at 250–350 °C.

Pore size distributions and specific surface areas were also determined using the BET isotherm with dinitrogen as ad-

sorbate. The pore size distributions of the materials are shown in Fig. 3, and the pore size distribution maxima along with specific surface area measurements are summarised in Table 1. As can be seen, each of the materials has a tightly controlled pore size distribution in the mesoporous range, and typical of those seen for MCMs. The aminopropyl substituted compounds **1a, b** have specific surface areas which are relatively low for MCM materials, whereas the cyanoethyl compound has a particularly high value of 1358 m^2 g^{-1}. The reasons for this large variance in specific surface areas are not yet clear, but may be related to the hydrogen-bonding ability of the amino groups in **1**, which may interact with the template amine groups, a mode of action which is unlikely to be available to the cyanoethylsilane. Alternatively, the presence of primary amines is known to catalyse the condensation of silane,[8] and it may be that the extra amines present in **1** increase the extent of polymerisation around the micellar template, leading to thicker walls and thus lower specific surface area.

In conclusion, the first examples of organically modified mesoporous silicates with narrow pore size distributions have been prepared by a direct and simple route. These materials display remarkable thermal stability, as evidenced by thermal analysis, as well as high solvolytic stability (refluxing ethanol fails to remove any of the bound groups). Further extension of this work, including applications in catalysis and mechanistic studies, is currently under way.

Footnote

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References

1 J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T.-W. Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B. Higgins and J. L. Schlenker, *J. Am. Chem. Soc.*, 1992, **114**, 10834; C. T. Kresge, M. E. Leonowicz, W. K. J. Roth, J. C. Vartuli and J. S. Beck, *Nature*, 1992, **359**, 710.
2 E. Armengol, M. L. Cano, A. Corma, H. Garcia and M. T. Navarro, *J. Chem. Soc., Chem. Commun.*, 1955, 519; A. Corma, V. Fornes, H. Garcia, M. A. Miranda and M. J. Sabatier, *J. Am. Chem. Soc.*, 1994, **116**, 9767; K. R. Kloetstra and H. van Bekkum, *J. Chem. Res.*, 1995, 26.
3 U. Junges, W. Jacobs, I. Voigt-Martin, B. Krutzsch and F. Schueth, *J. Chem. Soc., Chem. Commun.*, 1995, 2283.
4 P. T. Tanev and T. J. Pinnavaia, *Science*, 1995, **269**, 865.
5 S. A. Bagshaw, E. Prouzet and T. J. Pinnavaia, *Science*, 1995, **269**, 1242.
6 E. Angeletti, C. Canepa, G. Martinetti and P. Venturello, *J. Chem. Soc., Perkin Trans. 2*, 1989, 105.
7 K. K. Unger, N. Becker and P. Roumeliotis, *J. Chromatogr.*, 1976, **125**, 115.
8 I. S. Khatib and R. V. Parish, *J. Organomet. Chem.*, 1989, **369**, 9.
9 D. J. Macquarrie and A. Lambert, unpublished work.

Table 1 Pore size determination and specific surface area measurements

Compound	Pore size distribution maximum/nm	Specific surface area/m^2 g^{-1}
1a	3.9	597
1b	3.0	649
2	2.9	1358