

THERMAL METHODS IN THE SYNTHESIS OF NEW ORDERED MESOPOROUS ADSORBENTS

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Abstract

The synthesis of new ordered mesoporous adsorbents, specifically of the MCM-41 type, involves a step of thermal elimination of the template (a surfactant) where CRTA is shown to provide a 'soft chemistry' route. Once the mesoporous (i.e. 2 to 50 nm pore width) material is obtained, the pore size is determined by thermoporometry, a convenient application for low temperature DSC. Finally, the hydrophobic – hydrophilic properties of the pore walls are explored by immersion microcalorimetry in water

Keywords: adsorbents, CRTA, immersion microcalorimetry, MCM-41, thermoporometry

Introduction

New ordered mesoporous materials

It was only in 1992 that Mobil scientists disclosed the synthesis of a new family of adsorbents [1, 2] with well ordered, regular pores in the size range just above that of zeolites, where such well-defined porous materials are especially interesting as reference materials for testing and developing methods of characterization like 'thermoporometry', which is dealt with further in this paper.

The best known member of this mesoporous family is MCM-41 (Mobil Catalytic Material, number 41) which has a silicate or aluminosilicate framework around a hexagonal tubular array of non-intersecting, open pores. The pore width can be easily selected, today, between 1.2 and 10 nm. This is done by appropriate selection of the experimental conditions, specifically the alkyl chain length of the surfactant which is used as a template, as illustrated in Fig. 1. The general idea, as originally given by Kresge *et al.* [1] is indeed that a silicate framework is thought to precipitate around tubular micelles of the surfactant, supposedly already arranged in a hexagonal array. A more detailed study of the formation of the 'mesophase' (the central, intermediate product in Fig. 1) was carried out by Stucky, Schüth *et al.* [3]. The role of thermal analysis is in the last step, i.e. that of the elimination of the template in order to leave an open porous structure. Although other routes have been used (conven-

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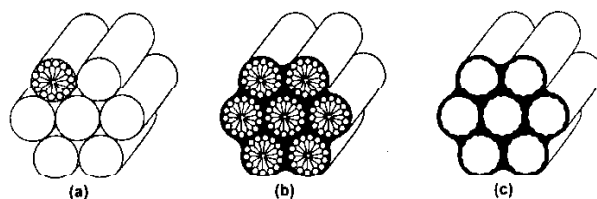


Fig. 1 MCM-41 formation by the liquid crystal templating mechanism first proposed by Kresge *et al.* [11]. (From (4a))

tional or supercritical solvent extraction) thermal extraction is indeed the most common. The problems raised are mainly those of the preservation of the high degree of ordering (in spite of the over-pressures due to the thermolysis of the surfactant and of the temperatures needed) and of the recovery of the surfactant in its initial, non-pyrolysed, form (both for economical and environmental reasons). This is why we tried to apply Controlled Rate Thermal Analysis which can provide a 'soft' heat treatment. We then decided to determine the pore-size by another thermal method which is worth being more widely used, thermoporometry. Finally, we found it useful to follow the changes in hydrophobicity by using a sensitive and quantitative technique, i.e. immersion microcalorimetry in water.

Results and discussion

Thermolysis of the mesophase

In Fig. 2 we report the thermal analysis recordings obtained, under various experimental conditions, on heating an MCM-41 mesophase obtained with cetyltrimethyl-ammonium-bromide as the template ($\text{CH}_3(\text{CH}_2)_{15}\text{N}((\text{CH}_3)_3\text{Br})$, commonly known as 'CTAB'.

Two recordings were obtained by conventional TG at atmospheric pressure: reducing the heating rate (from 10 to 1 K min^{-1}) and passing from static air to an air flux of course shifts the curve towards lower temperatures. The third recording, obtained by Controlled Rate EGA under low pressure (i.e. close to 2.5 mbar) with one of our standard set-ups [5] is still at lower temperatures, which is expected both from the lower pressure and from the control of the rate of reaction at a low value: the whole experiment takes place, at a controlled rate, over 13 h, whereas, in the slowest TG experiment, most of the degradation takes place under 300°C, i.e. in less than 5 h. Carrying out the same CRTA experiment with association of a gas analyser [6] proved to be interesting, especially in comparison with the behaviour of the pure, crystalline, CTAB surfactant. As recently shown [7], the surfactant from the mesophase is eliminated at a lower temperature than from the pure, crystalline state. The pyrolysis is also different: for similar CR-EGA conditions, the pure surfactant mainly releases head groups (between 200 and 250°C) and then alkyl chains, whereas the surfactant from the mesophase is first vaporized (from 100 to 175°C, which shows a lower stability, or a higher vapour pressure, of the surfactant located

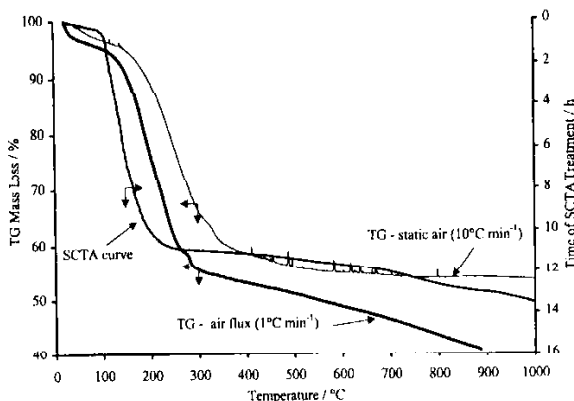


Fig. 2 Thermal Analysis (by conventional TG and by Controlled Rate EGA) of an MCM-41 mesophase containing 'CTAB'

in the pores than that in its crystalline form) and then successively releases mainly head groups (between 175 and 300°C) and then also short alkyl chains. These results show a possibility of partial recovery of the surfactant (under 175°C in our CR-EGA conditions, in the absence of air). It is probably the slow diffusion of CTAB in the long tubular pores of MCM-41 which limits this recovery. This ought to be checked by lowering further the rate of reaction in the CR-EGA experiment (Fig. 2), without lowering the controlled pressure so as not to change the regime of diffusion.

Pore-size characterization

For this type of material, the pore-size characterization can be carried out in several ways:

a – by the analysis of the full nitrogen adsorption-desorption isotherm at 77 K, by making use of the Kelvin equation

b – by the simple use of the Gurvich rule (pore volume=volume of adsorbate at saturation, calculated in a liquid state with same density as 3-D liquid) and of the BET method (to determine the internal surface area of the pores) and by assuming that all pores are cylindrical and of same diameter (or 'width'), $r=2V/A$

c – by XRD, drawing benefit from the periodicity of the array of pores (but, here the *a priori* unknown thickness of the pore walls must be subtracted from the XRD results)

d – by thermoporometry, i.e. from the freezing-point depression of any liquid confined in a mesoporous structure. The thermodynamic basis of this analysis was well developed by Quinson *et al.* [8]. It relies on the relationship between the curvature of the liquid/solid interface in the pore (during freezing), the corresponding pressure drop through the interface and the resulting change in the freezing temperature. Complications may arise (i) from the persistence of an unfrozen adsorbed layer on the pore walls, (ii) from the fact that the freezing can start from the walls of the

pores, from their mouth or from any other germination point, and (iii) from the possible dissolution of adsorbed species by the 'pure' liquid medium. On the other hand this method is easy to apply and makes use of simple DSC equipment fitted with a low-temperature device allowing operation in the -100 to $+20^{\circ}\text{C}$ temperature range.

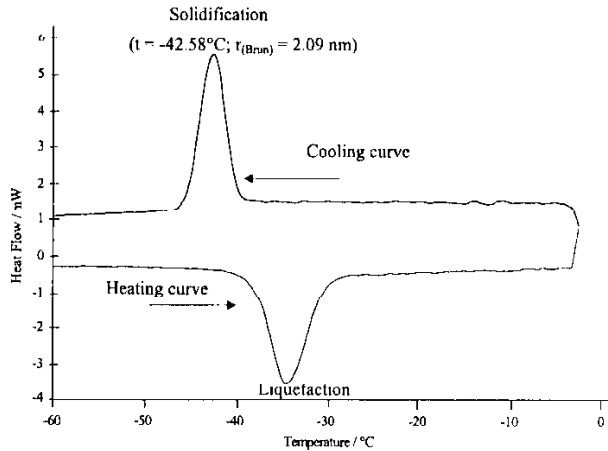


Fig. 3 Typical recording for a thermoporometry experiment on our MCM-41 sample

Other interesting features are the assessment of the internal diameter of the pores (not only the mouth diameter) and that of a shape factor (by comparison of the position of the freezing to melting points). Figure 3 reports a typical DSC recording obtained with a Setaram DSC-92 for a thermoporometry experiment with water on our

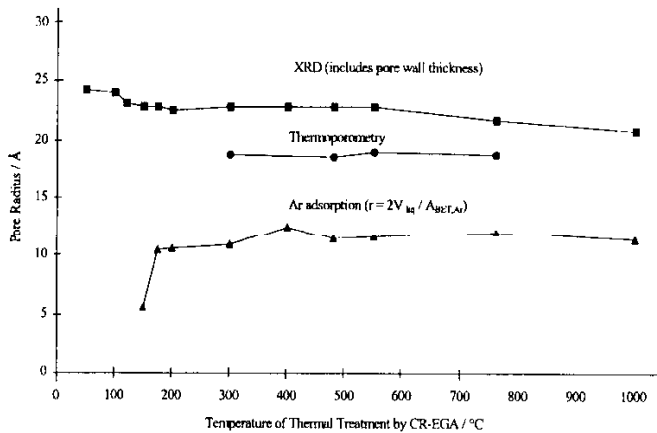


Fig. 4 Assessment of pore radius of our MCM-41 sample by three different methods (see text)

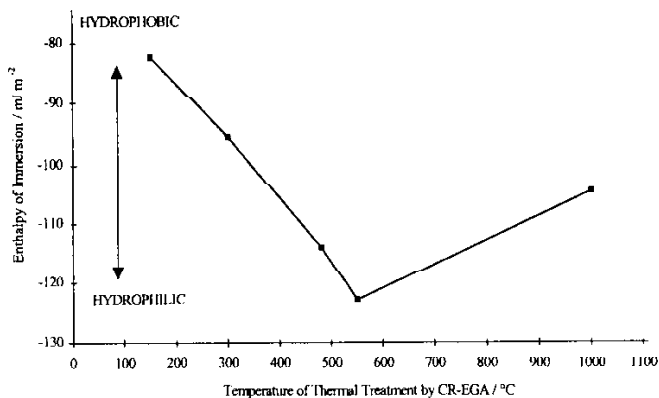


Fig. 5 Immersion microcalorimetry in H₂O of the MCM-41 mesophase treated by Controlled Rate EGA

MCM 41 sample: the freezing temperature depression, which amounts to ca. 43 K corresponds to a pore width of 4.2 nm (using Quinson and Brun's treatment).

Figure 4 reports the comparison between the results obtained by the three last methods mentioned. The broader size obtained from XRD is due, as already mentioned, to the pore wall thickness, whereas the difference between the thermoporometry (middle curve) and the Gurvich-BET method (bottom curve) may be due to the fact that thermoporometry, like the Barrett, Joyner and Halenda analysis of gas adsorption-desorption isotherms, relies on the assumption that macroscopic laws of thermodynamics still apply at molecular size level. Nevertheless, all three methods show a relatively constant pore-size, indicating that, in spite of a 4-fold increase in BET (N₂) specific surface between 150 and 760°C, the fraction of pores accessible to N₂, Ar or H₂O are always fully void and are not narrowed by any residual adsorption of the thermolysis products from the template.

Hydrophobicity of the pore walls

Since, during its thermal treatment the mesophase progressively loses its amphiphile organic component, we thought it worthwhile to follow the hydrophobicity of the pore walls by immersion microcalorimetry in water. The technique used is described precisely elsewhere [4-6]. The enthalpies of immersion per m² (BET, N₂) are reported in Fig. 5. The interpretation of this curve with a clear minimum (actually a maximum in the absolute value of enthalpy of immersion) is relatively straightforward: as the template is removed, the proportion of alkyl chain interacting with water is reduced, whereas heating above 550°C now removes the surface hydroxyls from the silica surface which is becoming less hydrophilic.

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The authors acknowledge support received from the European Community within the scope of the MESOP network (TMR programme 95-98 contract no. ERB FM RX CT 960084). They also specially thank members of the team at Frankfurt University (Prof. F. Schüth, Dr M. Linden and Dr J. Blanchard) for kindly carrying out the XRD measurements.

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