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Polymer mesofibres

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A novel process is described for synthesizing high aspect ratio, controlled diameter mesoscale poly(phenolformaldehyde) fibres using the well defined channels of mesoporous silica as a mold and their extraction with the structure intact.

Ever since the discovery of the MCM-41S family of mesoporous materials by Kresge *et al.*,[1] a great deal of interest has been generated in the study of various aspects of these materials including varying pore sizes through a variety of techniques,[2] tuning the framework composition,[3] and employing the internal channels for probing reactions in restricted dimensions.[4]

Here we present a route to the formation of a polymer mold of the channel structure of the hexagonal phase of MCM-41 mesoporous silica. The technique involves creating a replica by polymerizing formaldehyde and phenol inside the channels. This replica, through the novel idea of etching the host around it, is then able to be characterized *ex situ* by various physical methods. High resolution transmission electron microscopy (HRTEM) in particular allows the study of the structure and morphology of the resultant polymer fibres after extraction. It should be noted that in the past there has also been some debate over the actual access of different sized molecular adsorbates into the mesoporous silica. Channel restriction or blockage was envisaged in certain cases. Also, it was debatable whether the reactions were occurring inside the mesoporous structure or instead on the external surface of the particle. The technique presented here helps to clarify these issues and provides a way of directly visualizing the length of the channels within mesoporous silica materials.

Mesoporous silica was synthesized according to the literature procedure[5] followed by calcination at 540 °C over 12 h. The final surface area, pore size, and pore volume were determined to be 969.2 $m^2 g^{-1}$, 38.7 Å, and 1.40 ml g^{-1}, respectively. In order to fill the pores with the phenolic resin, solid phenol was added to a flask containing the MCM-41 template and incubated at 65 °C under reduced pressure overnight. The amount of phenol incorporated was determined [1.57 g (g MCM-41)$^{-1}$] by the pore volume of the dehydrated MCM-41 material. Excess solid paraformaldehyde [1.27 g (g MCM-41)$^{-1}$] was heated to 120 °C in order to liberate monomeric formaldehyde, which was transferred as a vapour to the phenol/MCM-41 composite. To initiate polymerization, anhydrous HCl vapor produced from a mixture of NaCl and H_2SO_4 was allowed to enter the reaction chamber. The resulting polymer/porous silica composite was cured in argon at 125 °C for 3 h and then at 500 °C for 12 h in order to induce cross-linking. A subsequent second loading of the monomer was performed to ensure complete filling of the channels. The samples were then shaken in 48% hydrofluoric acid overnight and filtered to leave the organic replica materials. Ashing analysis of the products consistently gave compositions with $<2\%$ residual silicate. Characterization of the samples was accomplished using powder X-ray diffraction (PXRD), adsorption studies, elemental analysis, ^{13}C CP MAS NMR, FTIR spectroscopy and HRTEM.

PXRD analysis of the silica/polymer composite (before etching) displayed a pattern at low 2θ values that is characteristic of the hexagonal form of mesoporous silica. The low electron contrast of the carbon-based polymer compared to that of the silica host had little effect on the intensity of the PXRD pattern of the composite relative to the empty host. At a 2θ value of *ca.* 25°, a broad peak was observed suggesting the presence of disordered polymer in a glassy silica host matrix. Moreover, this peak was retained for the sample obtained after etching, characterizing the presence of an amorphous polymer. Elemental analysis on the silica/polymer composite sample gave 45% carbon content. For an ideal complete filling of the channels, the required carbon content needed to be 59%, and hence the channels can be assumed to be *ca.* 75% filled. This degree of mesopore filling is consistent with the results of 77 K N_2 adsorption isotherms recorded for calcined mesoporous silica before and after polymer encapsulation in the channels which show that the accessible pore volume of the mesoporous silica has diminished to about 85 vol%. ^{13}C CP MAS NMR spectra of the extracted polymer displayed two broad signals at 40 and 130 ppm. These peaks can be assigned to the presence of the methylene and aromatic groups, respectively. Aside from some slight line narrowing in the aromatic region and small intensity changes in the methylene region, the spectrum of the extracted polymer was more-or-less the same as that of bulk poly(phenolformaldehyde). Further evidence of the presence of the polymer was obtained by FTIR spectroscopy. Characteristic bands for poly(phenolformaldehyde) at *ca.* 3500 cm^{-1} were assigned to νOH stretching modes and several sharp bands at *ca.* 1500 cm^{-1} were attributed to C—O, C—C groups similar to those found for the bulk poly(phenolformaldehyde). The combination of the NMR and FTIR results indicated that the mesoscale size constraint afforded by the channels did not cause extensive deviation in polymer connectivity and dynamics from that of the bulk. Nevertheless, NMR relaxation studies and the measurement of the elastic constants of the fibres by, for example, AFM will be needed to explore whether there exists any alteration in the dynamical and mechanical properties between the mesofibre and bulk forms of the polymer.

The most interesting information was gained by HRTEM. It should be emphasized that because of the low electron contrast of the extracted sample, HRTEM studies of the polymer necessitated the use of direct imaging on ultrathin 'holey' carbon film (*ca.* 7 Å thick), and indirect imaging using heavy metal negative staining using a dilute solution of uranyl

Fig. 1 Transmission electron micrograph (using negative staining technique with uranyl acetate solution) of polymer mesofibres supported on a carbon film. Magnification bar = 100 nm.

acetate on thin carbon-support film, Fig. 1. From the micrograph, it is obvious that only fibre-like morphology is seen for the extracted poly(phenolformaldehyde). The width of the fibres, as determined through the micrographs, is found to be *ca.* 20 Å with an effective resolution of 7 Å (combination of uranyl acetate stain and other specimen parameters). These are comparable to the pore diameter of the host taking into consideration that only between 75 and 85% of the available volume is occupied. Furthermore, depending on extraction, sonication and solvent protocols both single and bundles of polymer strands are observed. These bundles are discernible from single fibres by their size and texture. These display extensive regions of curvature thereby indicating appreciable flexibility of the poly(phenolformaldehyde) mesofibres. The mesofibres were found to display extensive lengths which were comparable to the particle size of the mesoporous silica host, and the aspect ratios (ratio of the length to the diameter) of the extracted polymer fibres were found to exceed 10^3. This suggests that for the mesoporous silicas, the channels run practically the entire length of the particles (whose sizes are in the range 1–10 μm, depending on the synthesis conditions).

Control TEM experiments have been performed for bulk forms of poly(phenolformaldehyde), as well as samples synthesized on the surface of non-porous Cab-O-Sil silica that had been pre-treated under identical conditions to those used for the mesoporous silica channel host material. The TEM images of the polymer mesofibres show distinct morphologies, Fig. 1, while only shapeless polymer particulates are extracted from Cab-O-Sil, Fig. 2, and only non-descript polymer agglomerates are obtained for the bulk form of the polymer.

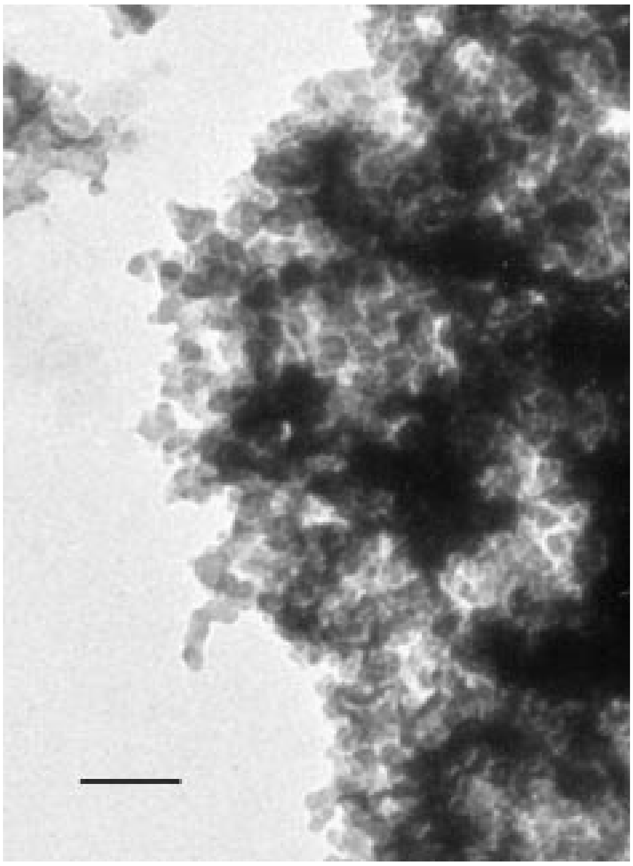

Fig. 2 Transmission electron micrograph of control sample—polymer deposited on amorphous silica (Cab-O-Sil). Magnification bar = 100 nm.

We wish to emphasize that while mesoporous silica encapsulated polymers, metals and semiconductors have been previously reported,[4,6,7] no studies have been described on the extraction of these materials and their structural characterization. Hence, the concept of synthesizing copies of the channels of mesoporous silica and extracting them provides access to a diversity of mesofibres with a range of compositions and size-tunable properties.

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