

## Observation of some pore wall ordering in mesoporous silica

Robert Mokaya

School of Chemistry, University of Nottingham, University Park, Nottingham, UK NG7 2RD.  
E-mail: r.mokaya@nottingham.ac.uk

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**Increasing the time allowed for hydrothermal crystallisation during high temperature (150 °C) synthesis of MCM-41 appears to result in some ordering (nanocrystallites) within the pore walls which is accompanied by increase in pore wall thickness, pore size, silica condensation and the formation of elongated or rod-like particles.**

The synthesis of organised inorganic materials is currently the subject of a great deal of research effort in materials science. Since the discovery of the M41S family of mesoporous silicas, prepared *via* a mechanism in which supramolecular assemblies of surfactant micelles act as templates for the organisation of inorganic silicate precursors,<sup>1,2</sup> the use of surfactant species to direct the organisation of mesoporous silica has been achieved over a wide range of synthesis conditions.<sup>3</sup> Recent advances indicate that mesoporous silica materials with a wide range of properties may be prepared by careful control of the synthesis conditions.<sup>4–7</sup> However, despite their excellent structural ordering and well defined pore size distribution, mesoporous silicas possess a largely amorphous inorganic framework; their pore walls are amorphous and in many ways exhibit properties similar to those of amorphous silica. The preparation of mesoporous silicas with semi-crystalline or crystalline walls, similar to those of zeolites, is desirable with respect to their stability and use as heterogeneous catalysts or ion exchangers.<sup>8</sup> Although the preparation of surfactant-templated mesoporous oxides (*e.g.* titania, zirconia) with semi-crystalline walls has been recently achieved,<sup>9,10</sup> there are no reports on mesoporous silica with any degree of pore wall ordering. This report describes some pore wall ordering observed in mesoporous silica materials which suggests the presence of nanocrystallites within the pore walls. The pore wall ordering, observed during the course of our work on high temperature (> 150 °C) synthesis of MCM-41, may provide some insights into the preparation of MCM-41 materials with crystallographically ordered pore walls. Materials with pore wall ordering (nanocrystallites) were obtained by extending the crystallisation time in an otherwise normal MCM-41 synthesis procedure under basic conditions. The emergence of pore wall order (*i.e.* nanocrystallites within the pore walls) was accompanied by an increase in the unit cell parameter and the formation of thick and highly condensed silica pore walls along with morphological transformation from the usual spherical shaped particles to elongated or rod-like particles. The apparent pore wall ordering was observed using transmission electron microscopy (TEM) and selected area electron diffraction (SAED).

The nanocrystallite containing MCM-41 materials were prepared using a normal procedure which was modified by increasing the time allowed for hydrothermal crystallisation from 48 to 96 h as follows; tetramethylammonium hydroxide (TMAOH) and cetyltrimethylammonium bromide (CTAB) were dissolved in distilled water by stirring at 35 °C to give a clear solution. The silica source, fumed silica (Sigma), was then added to the template solution under stirring for 1 h. After further stirring for 1 h to allow the silica to be fully dispersed, the resulting synthesis gel of molar composition SiO<sub>2</sub> : 0.25 CTAB : 0.2 TMAOH : 40 H<sub>2</sub>O was left to age for 20 h at room temperature following which the gel was transferred to a Teflon-lined autoclave and heated at 150 °C for 96 h. The solid

product was obtained by filtration, washed with distilled water, dried in air at room temperature and calcined in air at 550 °C for 8 h to obtain the final material designated as MCM-41(96).<sup>11,12</sup> We note that careful control of the crystallisation temperature was essential for obtaining nanocrystallite-containing MCM-41. In particular temperatures significantly lower than 150 °C resulted in materials with lower unit cell parameters, thinner pore walls and no evidence of pore ordering or nanocrystallites.

Fig. 1 shows typical TEM micrographs obtained for MCM-41(96). The particle morphology is consistent with the elongated or rod-like particles previously observed for this type of material.<sup>12</sup> We have previously reported that the morphology of materials (such as MCM-41(96)), which are prepared for extended crystallisation periods, differs from the normal spherical shaped particle morphology observed for MCM-41, and that they are mainly made up of elongated rod-like spheres.<sup>12</sup> Similar rod-like MCM-41 particles have also been previously obtained *via* a two-step synthesis procedure involving post-synthesis restructuring.<sup>13</sup> Fig. 2 shows representative TEMs with the corresponding SAED patterns. First we note that from the TEMs in Fig. 2, it is possible to observe the pore channels which run along the particle axis. Secondly, the SAEDs are unusual for MCM-41 in that they show several diffuse diffraction rings which is an indication that the MCM-41(96) particles exhibit some local ordering. A likely explana-

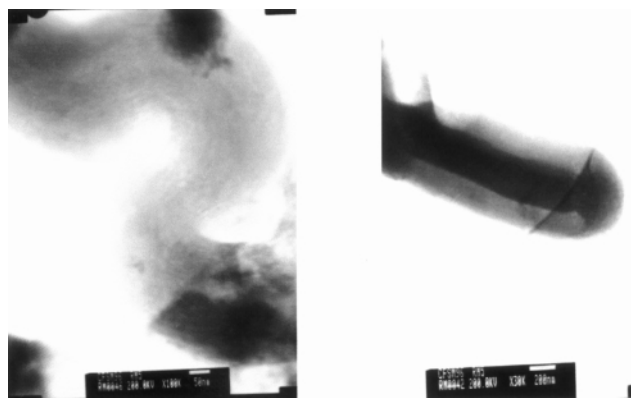


Fig. 1 Representative TEM micrographs of MCM-41(96).

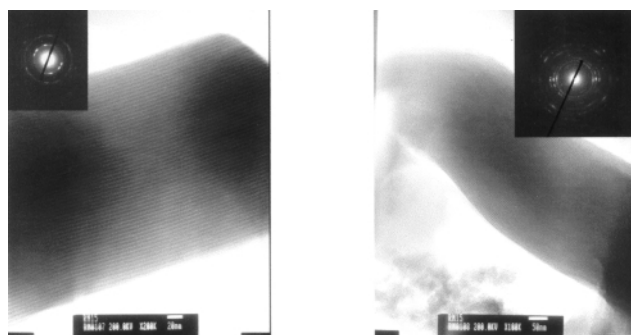


Fig. 2 Representative TEM micrographs and corresponding SAED patterns for MCM-41(96).

tion for the diffraction rings is that the pore walls of MCM-41(96) possess some crystalline character, perhaps in the form of nanocrystallites which occur within the pore walls.<sup>9</sup> We have previously shown that the pore wall thickness of materials similar to the MCM-41(96) sample reported here is much higher than that of conventional MCM-41.<sup>11</sup> The pore walls of such materials are up to twice as thick as those of conventional MCM-41 (crystallised at 150 °C for 48 rather than 96 h).<sup>11</sup> Indeed the pore walls of MCM-41(96) type materials are amongst the thickest we have encountered for any MCM-41 material. It is therefore possible that nanocrystallites can nucleate within the thick pore walls of MCM-41(96) thus resulting in semi-crystalline pore walls and the pore ordering observed in Fig. 2. Mesoporous metal oxides possessing thick pore walls and semi-crystalline frameworks have previously been reported.<sup>9</sup> The presence of thick pore walls was considered as being important in the nucleation and growth of nanocrystallites within the mesoporous metal oxide frameworks.<sup>9</sup>

The typical surface area and pore volume of MCM-41(96) materials was in the range 650–700 m<sup>2</sup> g<sup>-1</sup> and 0.70–0.8 cm<sup>3</sup> g<sup>-1</sup>, respectively. These values are rather lower than those of conventional MCM-41 presumably due to the thicker pore walls. The thick pore walls also, in part, account for the large unit cell size observed (typically 70 Å). The pore size is however not compromised by the thick pore walls and is indeed much larger than that in conventional MCM-41.<sup>11,12</sup> The powder X-ray diffraction (XRD) pattern for a typical MCM-41(96) sample is shown in Fig. 3. The XRD pattern is typical of a relatively well ordered material and shows an intense basal (100) diffraction peak and some higher order peaks. The 100 peak is shifted to lower 2θ values (compared to conventional MCM-41) indicating an expansion in the lattice parameter. We note that although we did not observe any clearly defined high angle peaks in the powder XRD patterns of MCM-41(96), the amorphous silica 'halo' peak usually present in MCM-41 materials was virtually absent. Typical N<sub>2</sub> sorption isotherms (not shown) for MCM-41(96) materials exhibit a well developed step in the relative pressure (*P/P*<sub>0</sub>) range 0.45–0.6 characteristic of capillary condensation (filling) into uniform mesopores.<sup>11,12,14</sup> The isotherms also exhibit some (triangle shaped) hysteresis which is characteristic of MCM-41 materials

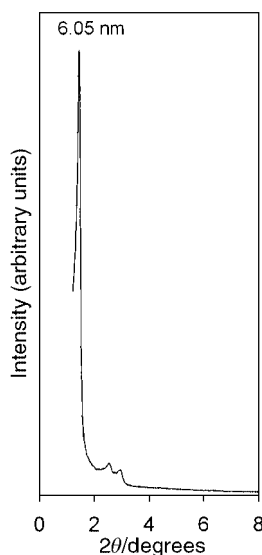


Fig. 3 Powder XRD patterns of MCM-41(96).

with pores larger than 40 Å.<sup>14</sup> It is worth noting that the thick walls of MCM-41(96) are accompanied by greater silica condensation. <sup>29</sup>Si MAS NMR spectra of as-synthesised (surfactant containing) MCM-41(96) indicated that the pore walls are primarily made up of fully condensed Q<sup>4</sup> silica units with a small contribution from incompletely cross-linked Q<sup>3</sup> units.<sup>11,12</sup> Q<sup>4</sup>/Q<sup>3</sup> ratios in the range 4.0 to 5.0 and typically *ca.* 4.5 were obtained for MCM-41(96) materials compared to a ratio of 1.4 for conventional MCM-41. As expected the Q<sup>4</sup>/Q<sup>3</sup> ratio was even higher for the calcined MCM-41(96) samples that were used for TEM analysis. It is worth noting that the thick, highly condensed pore walls and the implied presence of nanocrystallites is consistent with the improved thermal and hydrothermal stability previously observed for MCM-41(96) materials.<sup>11</sup>

We have considered other possible explanations for the origin of the diffraction rings observed in Fig. 2. A possible explanation is that the diffraction rings arise from multi-particles or particle aggregates. Although we do not rule out this possibility, we were however unable to obtain diffuse diffraction rings from multi-particles of several other MCM-41 materials that were prepared under different conditions; the diffraction rings were a feature of MCM-41(96) materials. It appears therefore, that mesoporous MCM-41 silica with semi-crystalline pore walls may be prepared by increasing the time allowed for hydrothermal crystallisation, in an otherwise normal MCM-41 synthesis procedure under basic conditions. In the present case it is likely that extending the crystallisation time allows for more extensive diffusion of additional silicate units and surfactant species into the growing surfactant/silica mesophase. Additional silicate units increase the wall thickness and extent of silica condensation while additional surfactant species increase the volume and density of the surfactant (micellar) phase thus increasing the pore size. The increased silicate accretion may favour the nucleation and growth of nanocrystallites. The findings reported here suggest that crystallisation temperature and time are likely to be important factors in attempts to prepare mesoporous silicas with semi-crystalline or crystalline pore walls.

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