

High-resolution Transmission Electron Microscopy of Mesoporous MCM-41 Type Materials

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High-resolution transmission electron microscopy of MCM-41 shows for the first time clearly the hexagonal shape of the pores, and allows direct observation of the transition from a lamellar to the hexagonal phase.

The mesoporous silica-based materials invented by scientists of the Mobil Corporation¹⁻³ have attracted considerable interest since the first scientific publications appeared in 1992.^{4,5} Recently a detailed mechanism was suggested how these materials can be formed *via* a layered intermediate.⁶ Although already in the first publications transmission electron micrographs have been published, it is as yet not clear, whether the pore shape is hexagonal or round. A model describing the intensities of the X-ray diffraction patterns is favouring a hexagonal pore shape.⁷ This was, however, not confirmed by other techniques. Here we present for the first time a direct observation of the transition between the layered and the hexagonal phase which also allows to discriminate between two possible mechanisms for this transformation, as well as direct evidence of the hexagonal pore shape.

The materials were synthesized according to a procedure given by Beck *et al.*⁵ A solution A was prepared by adding aluminium oxide (Pural SB) to a 25% solution of hexadecyltrimethylammonium chloride (Aldrich) and stirred for approximately 20 min until the alumina was thoroughly dispersed. A second solution B was prepared by dissolving tetramethylammonium bromide (Aldrich) in water and then adding sodium silicate solution (Woellner). This solution was stirred for 5 min and then added to solution A under continuous stirring. This intermediate solution was stirred for another 10 min then fumed silica (Aerosil 200) was added and the final mixture stirred for another 15 min. The molar composition of the final reaction mixture is 1 SiO₂:0.034 Al₂O₃:0.065 Na₂O:0.11 NMe₄Br:0.24 NMe₃(C₁₆H₃₃)Cl:35 H₂O. This mixture was reacted for 96 h at 423 K in a Teflon-lined 50 ml stainless steel autoclave in a preheated oven. The reaction products were filtered and allowed to dry in air at room temp. Calcination of the materials was performed in air at 813 K with a heating rate of 1 K min⁻¹ for 8 h. MCM-41 samples prepared following this procedure showed four peaks in the diffractogram below 5° (2θ) which are characteristic for a high quality material. The sorptive properties are similar to published data.⁴ For analysis in the transmission electron microscope the samples were crushed under acetone and dispersed on a holey carbon copper grid. Micrographs were recorded with a JEOL 4000 EX microscope operated at 400 kV.

Fig. 1 clearly shows the hexagonal shape of the pore openings in the centre of the micrograph. Since this photograph was recorded at conditions far from optimum (Scherzer focus), the contrast is reversed. The defocus, however, does not alter the symmetry of the structure observed so that the hexagonal shape of the pores in the micrograph represents the true geometry of the pores. This hexagonal shape is energetically most favourable, since this is the only way to maintain a constant wall thickness⁶ which in turn maximizes surfactant-silicate surface interaction.

Fig. 1 does not only clearly show the hexagonal pore shape for the first time, but might also directly show the transformation from a layered material to a hexagonal phase which was inferred based on X-ray data in ref. 6. In the right-hand side of Fig. 1 the material seems to be still predominantly in

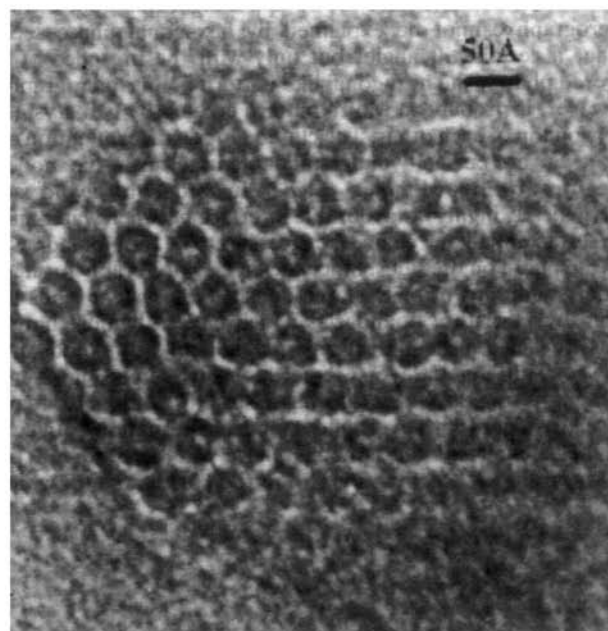


Fig. 1 Transmission electron micrograph showing the hexagonal pore shape of MCM-41. Lamellar to hexagonal phase transition visible from right to left. Pore diameter of approximately 4.4 nm agrees well with X-ray diffraction data and sorption experiments.

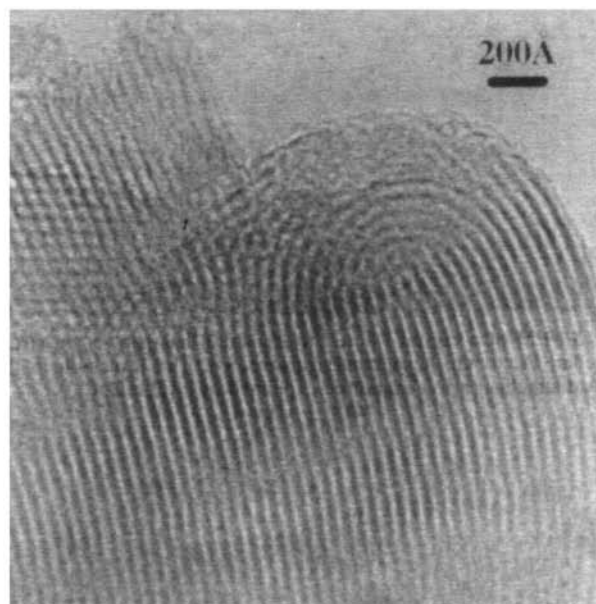


Fig. 2 Larger lamellar region of an MCM-41 sample. The layers are terminated by rounded structures, thus avoiding high curvatures.

the lamellar state which gradually transforms to the hexagonal phase towards the left side of the micrograph.

We cannot completely exclude the possibility that the observed layered structure is created by a tilting effect. A hexagonal crystal lying with the tubes perpendicular to the electron beam, or even tubes slightly off the zone axis, would give an image similar to a lamellar phase. Depending on the direction, the repeat distances can be as small as half the a -axis (beam parallel to $[110]$). If the channels in the structure were not always straight, but also winding which would bring the tubes slightly off the zone axis, such a layer pattern or a transition region between a layer and a hexagonal structure might be observed. This, however, seems to be fairly improbable, if one considers the structure observed in Fig. 2. The closed loop structure in the upper right quadrant of the micrograph cannot be explained by hexagonal phase seen under a certain tilt angle, but only with the presence of a layered phase. The hexagonal like pattern in this micrograph, however, is probably a Moiré pattern created by two crystals lying on top of each other. The closed loops as a termination of the layers are perfectly understandable in terms of the model put forward by Monnier *et al.*⁶ In order to avoid an energetically highly unfavourable interface between water and the surfactant alkane chain, the layer has to be terminated by a silicate phase on the sides. Since the layer is preferably formed under conditions of high charge density, the system tends to form low-curvature boundaries which have a higher charge density.⁸ Thus, instead of forming a high-curvature 'end cap' between subsequent layers, larger loops as seen in Fig. 2 are formed. A region where the layer structures are not completely straight, but nevertheless the transformation between the hexagonal and the lamellar phase can be observed, is shown in Fig. 3. Region A is still in the lamellar state, while

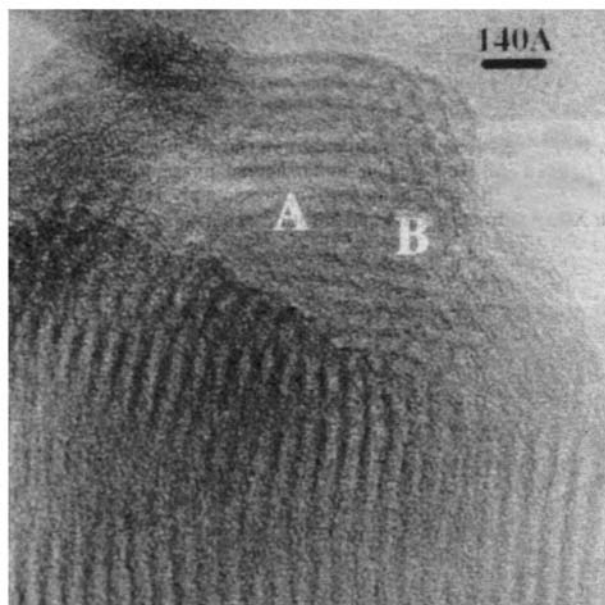


Fig. 3 TEM of a crystal where the transition has just set on (from lamellar, A, to the hexagonal structure, B). The transition in the curved lamellar region cannot be explained by a tilt effect.

towards the right in region B the hexagonal structure has already formed. The occurrence of a transition region in a curved lamellar structure cannot be explained by a tilt effect, since a tilt against two axes would result in a completely structureless picture.

The micrographs, especially Fig. 1, also allow the discrimination between two transformation models, the one described by Monnier *et al.*⁶ which implies formation of the hexagonal structure with the $[10]$ direction parallel to the layers, and the one suggested by Kuroda and coworkers⁹ for the transformation of Kanemite in which a transformation to a hex phase with the $[1 - 1]$ direction parallel to the layers occurs (using the conventional cell with $\gamma = 120^\circ$). Fig. 1 and also Fig. 3 clearly support the model of Monnier *et al.* Near the transition region the $[100]$ axis of the hexagonal structure is parallel to the layers.

The pure layered phase described by Monnier *et al.*⁶ has a smaller lattice spacing than the hexagonal phase. In the present study, however, the spacing between the layers is only slightly smaller than the d -spacing of the hexagonal phase. This can also be rationalized in terms of the transition model: during the transformation from the layer to the hexagonal phase an expansion of the layer spacing has been observed (Fig. 2 of ref. 6). At the transition point, which is observed in the present study, the spacing of the hexagonal and the layered phase should be approximately equal which is indeed observed.

The question remains, how the layer can maintain its stability after the template has been removed, since the features described above are observed on calcined samples. For the pure layered phase amorphization has been observed on calcination.⁶ However, here a material has been analysed which was almost completely converted to the hexagonal phase. The layered fractions are relatively small, at some points first silicate bridges between the layers can be identified. It is thus feasible that these comparatively small layered parts of the structure are stabilized by the surrounding hexagonal phase and the first bridges which are formed between the layer sheets.

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