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The mesoporous silica based materials invented by scientists of the Mobil Corporation have attracted considerable interest since the first scientific publications appeared in 1992. Recently a detailed mechanism was suggested how these materials can be formed via a layered intermediate. Although already in the first publications transmission electron micrographs have been published, it is yet not clear whether the pore shape is hexagonal or round. A model describing the intensities of the X-ray diffraction patterns is favoring a hexagonal pore shape. 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.

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High Resolution Transmission Electron Microscopy of Mesoporous MCM-41 type Materials

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The mesoporous silica based materials invented by scientists of the Mobil Corporation (1) have attracted considerable interest since the first scientific publications appeared in 1992 (2,3). Recently a detailed mechanism was suggested how these materials can be formed via a layered intermediate (4). 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 favoring a hexagonal pore shape (5). 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. (6). Calcination of the samples was performed in air at 813 K with a heating rate of 1 K/min for 8 h. MCM-41 samples prepared following this procedure showed four peaks in the diffractogram below 5° (2 theta) which are characteristic for a high quality material. The sorptive properties are similar to published data (7). 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 center of the micrograph. Since this photograph was recorded at conditions far from optimum (scherzer focus), the contrast

is reversed. This hexagonal shape is energetically most favourable, since this is the only way to maintain a constant wall thickness (8) which in turn maximizes surfactant-silicate surface interaction.

Figure 1 does not only show the hexagonal pore shape, but also is a direct proof for the transformation from a layered material to a hexagonal phase which was inferred based on X-ray data in ref. (4). In the right part of fig. 1 the material is still predominantly in the lamellar state which gradually transforms to the hexagonal phase towards the left side of the micrograph. On a somewhat larger scale this can be seen in fig. 2: Most of the pores in fig. 2 are arranged in the hexagonal phase, but in the upper right quadrant a layered structure is clearly visible. At some points (arrows) first bridges between the silicate sheets seem to have formed. In the transition region the hexagonal phase is still relatively disordered, since the structure is not completely relaxed. In the left part of the figure, where the transformation is complete, a perfect hexagonal arrangement of the pores can be seen.

However, since 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, the observation of structures as described above is no definite proof for the presence of a lamellar phase. Depending on the direction, the repeat distances can be as small as half the a -axis (beam parallel to (110)). In fig. 2 the layered part is certainly not another crystal, since the transition between the hex and the layered part is smooth. A different crystallite seen along a different axis can thus not be the reason for the appearance of the layered structure. Nevertheless, 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 might be observed. This can be ruled out, though, by the structure observed in fig. 3 which also shows a transition region left of the center.

However, the closed loop structure in the upper right quadrant of the micrograph can not be explained assuming winding tubes, but only with the presence of a layered phase. One can thus infer that indeed a real layered structure is observed in the micrographs. Moreover, the closed loops as a termination of the layers are perfectly understandable in terms of the model put forward by Monnier et al. (9): In order to avoid an energetically highly unfavorable 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 (10). Thus, instead of forming a high curvature "end cap" between subsequent layers, larger loops as seen in fig. 3 are formed.

The micrographs, especially fig. 1, also allow the discrimination between two transformation models, the one described by Monnier et al. which implies formation of the hexagonal structure with the (100) direction parallel to the layers, and the one suggested by Kuroda et al. (11) for the transformation of Kanemite in which a transformation to a hex phase with the (110) direction parallel to the layers occurs. Fig. 1 and also fig. 2 clearly support the model of Monnier et al.: Near the transition region the (100) axis of the hex structure is parallel to the layers.

The pure layered phase described by Monnier et al. (12) 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 hex 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. (13)). 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 (14). However, here a material has been analyzed 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 (arrows in fig. 2). 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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