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Direct TEM Imaging of Tubules in Calcined MCM-41 Type Mesoporous Materials

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Calcined MCM-41 type mesoporous samples have been characterized by transmission electron microscopy (TEM). Samples are not crystalline at the atomic level. The existence of an array of long silicate tubules packed in honeycomb fashion, nearly always bent and curved has been evidenced. The formation of such a silicate architecture through a liquid-crystal template mechanism had been hypothesized before. Equidistant parallel lines observed in this study are shown to be related to the hexagonal repeat between tubules: the honeycomb array is sufficiently regular to give fringes in projection under proper orientation of the specimen. The existence of a hypothetical lamellar phase in the calcined material is not confirmed by our observations. Samples with different compositions all had the same general architecture.

Introduction

Considerable research effort is currently being spent on the new family of MCM-41 type mesoporous silica materials.[1-5] The large specific surface area of these materials and their adjustable pore sizes explain their great potential as catalyst support. Catalytic activity can be obtained upon incorporation of metal cations into the silicate framework, such as Al[5-10] and B,[11,12] which generate Brønsted acid sites of different strengths, or Ti[13-15] and V[16] which induce redox catalytic properties.

Additional claims were made that materials resulting from syntheses incorporating conducting polymer filaments[17] and other host molecules[18] or formation of crystalline mesostructures from transition metal oxides[19] may find applications as advanced materials. To attempt improvement of these materials for industrial use, it is then necessary to understand the mechanism responsible for the formation of pores, their sizes, and other characteristics.

Early in their discovery, Beck et al.[4,5] hypothesized that the ordered mesoporous silicates are synthesized by a liquid-crystal template mechanism. One of the models proposed assumes the formation of hexagonal arrays of cylindrical micelles, each of which is then encapsulated by the silicate species, the resulting silicate structure being preserved after calcination. More recent studies by Monnier et al.[20] suggest a mechanism via a layered phase intermediate. This mechanism stipulates that in some circumstances (i.e., high pH, low temperature, and low degree of polymerization of the silica source), a layered phase is first obtained which then transforms into the hexagonal structure as the polymerization of silica species proceeds.

Transmission electron microscopy (TEM) and diffraction have been a key method for the characterization of these materials and the identification of the various

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phase obtained, i.e., cubic (MCM-48), hexagonal (MCM-41), and lamellar (MCM-50) phases.[5,17] The most detailed TEM investigation published by Alfredsson et al.[21] for MCM-41 type materials reported two main observations. The first was that the shape of the pore channel is hexagonal rather than round. The second observation was particularly interesting as some micrographs showing equidistant parallel lines were interpreted as direct evidence of the coexistence of a layered phase with the predominant hexagonal phase after calcination, assuming that the lamellar-to-hexagonal phase transformation was not complete. The observation[21] that layered and hexagonal phases are found to have the "same *d*-spacings after calcination" does not point to the existence of two phases. In addition, we find it difficult to imagine a stable architecture constituted of only silicate slabs spaced by nearly 40 Å and with no matter in between.

The purpose of the present work is to investigate by transmission electron microscopy the microstructure of calcined MCM-41 type mesoporous materials with special attention given to the "lamellar structure". Such information is of great interest and may lead to a reinterpretation of previously published TEM micrographs of the calcined material.

Experimental Section

Silica MCM-41 material was synthesized hydrothermally using a gel with the molar composition; $SiO_2-0.085Na_2O-0.16CTAB-63H_2O$, where CTAB stands for cetyltrimethylammonium bromide. The sample was calcined in air at 873 K for 6 h. The particular sample used in this study was doped with a small amount of boron (B/Si = 0.04). It was prepared as described in detail elsewhere.[12] The presence of boron does not affect the conclusions of this work, and observations performed on materials with different doping elements were similar.

For TEM analysis, samples were dispersed ultrasonically in ethanol, and a drop of the suspension was deposited on a holey carbon copper grid. Micrographs were recorded with a 1024 × 1024 Gatan CCD camera on a Philips-CM20 microscope operated at 200 kV. The magnification was calibrated in pixels/nm on the camera, using a "MAG*I*CAL" calibration sample, consisting of a wedge of silicon with epitaxially grown calibration marks. For details see refs 22. Lengths measured in pixels on images of samples were then transformed to nanometers by multiplication with the above magnification factor, leading to an overall accuracy on length measurements better than 2%.

Results and Discussion

According to published X-ray diffraction analysis,[12] B/Si-MCM-41 mesoporous material has a hexagonal lattice with interplanar spacing $d_{100} \approx 40$ Å, similar to values already established for Si-MCM-41 and Al/Si-MCM-41 materials[4,5] prepared in the presence of the same template.

A typical particle of B/Si-MCM-41 material is shown at low magnification in Figure 1. It has the appearance of a very thin sheet, several microns long, folded and twisted. Three regions labeled A, B, and C are distinguished. A fold is seen in region A, while B and C correspond to two planar regions. With increased magnification, a honeycomb structure is seen in A (Figure 2a) and a fringe system in B (Figure 2b), similar to the "lamellar structure" reported by Alfredsson et al.,[21] while C displays no special structural features. Figure 3 shows ordered pores with regular size and presumably hexagonal outline as already described in the literature.[21] The hexagonal shape of pores is energetically most stable, because it is the best way to maintain constant wall thickness,[20] while maximizing surface interactions between surfactant and silicate. At low magnification, the particle in Figure 1 seemed to be single and homogeneous. It then becomes difficult to accept that part of it would be made of the hexagonal phase, while another part would belong to the lamellar phase. The spacings between fringes in B and layers of pores in A are both measured to be about 39 Å. This value is in line with the value reported from X-ray powder diffraction (~40 Å).[12] Many particles were observed, and their architecture was basically the same as that of the above described particle.

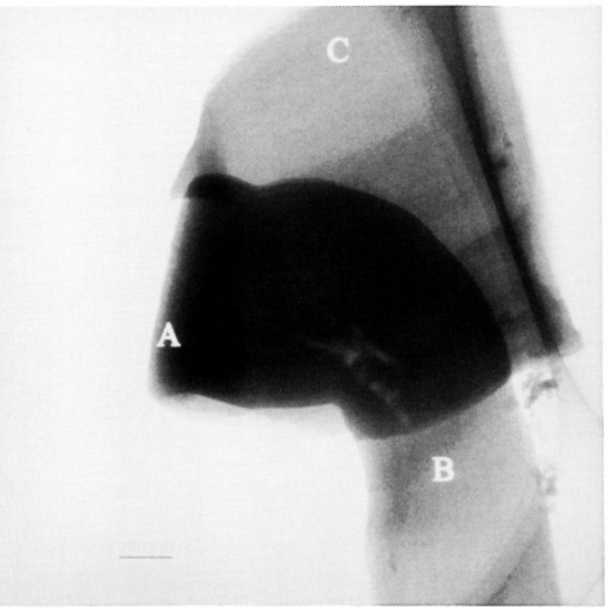

Figure 1. Transmission electron micrograph of a typical B-MCM-41 particle (bar = 200 nm).

Furthermore, the existence of a lamellar phase after calcination is unlikely, because silicate layers are too distant from one another to preserve the spacing in the silicate-organic phase without collapse or dispersion. An edifice formed only of silicate layers spaced by about 40 Å with nothing in between cannot be energetically stable. van der Waals interactions cannot maintain the layers together at this distance: for this type of interaction, the energy is proportional to r^{-6}, where r represents the interlayer distance, and would be extremely weak. An architecture of this type would either collapse under stronger forces like electrostatic attraction or disperse under repulsion or mere thermal motion under heating or gas pressure due to calcination of surfactant.

This led to think that the apparent "lamellar structure" observed in Figure 2b simply arises from tilting of the hexagonal phase. The orientation of particles with respect to the electron beam direction is not uniform. The sheet plane is mostly perpendicular to the electron beam (B and C), but the fold in A brings this plane, and the axis of tubules, mostly parallel to the beam.

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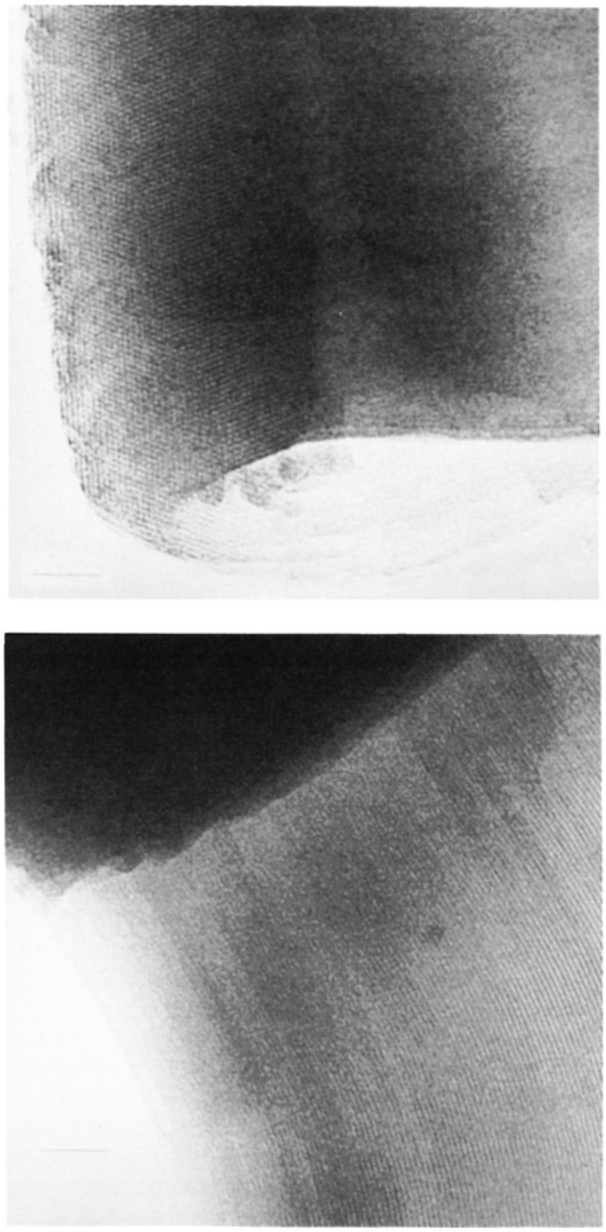

Figure 2. High-resolution TEM of (a, top) region A as defined in Figure 1 (bar = 50 nm) and (b, bottom) region B as defined in Figure 1 (bar = 50 nm).

Taking into account the above observations, it is believed that sample areas showing a fringe system represent a hexagonal array of very long silicate tubules rather than a lamellar phase as proposed in the literature.[21] A schematic drawing of parallel channels is given in Figure 4. With TEM, the image contrast in a noncrystalline sample below atomic resolution, as is the case here, arises from differences in transmission caused by interaction with a different number of atoms in the path of electrons. With this model, the aspect of micrographs will depend on the orientation of channels with respect to the electron beam direction. Lamellar appearance is expected for beam directions in the plane defined by the perpendicular to one family of channel walls and the length of tubules (Figure 4), because the projected scattering density is higher along bands corresponding to a zigzag of walls, than in between them, where half the number of walls in the zigzag are now perpendicular to the incident beam. The equidistance between darker regions is $a\sqrt{3}/2$, where a is the distance from tube center to tube center. For beam directions outside this plane, this structure disappears because the projection of scattering density is not periodical. All this is consistent with the fact that the interplanar distance is constant for every observed "layered structure" in the calcined preparation. When the electron beam propagates along the channel direction, the hexagonal structure is observed, with the distance between the centers of hexagons related to that separating the lines.

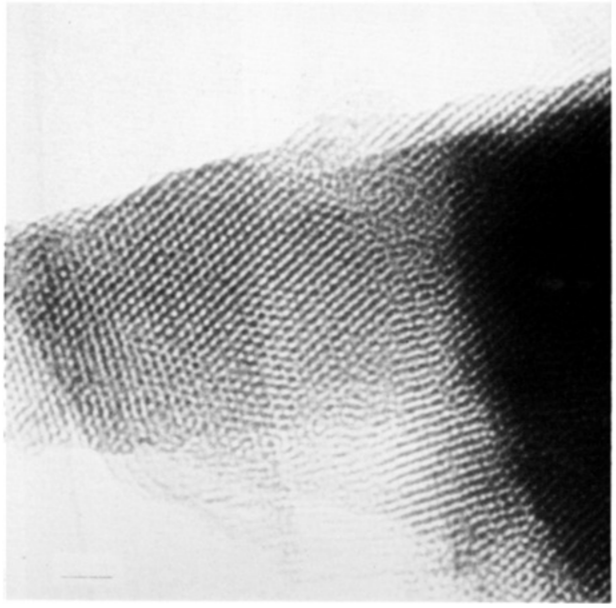

Figure 3. High-resolution TEM image of the hexagonal pore structure of B-MCM-41 (bar = 20 nm).

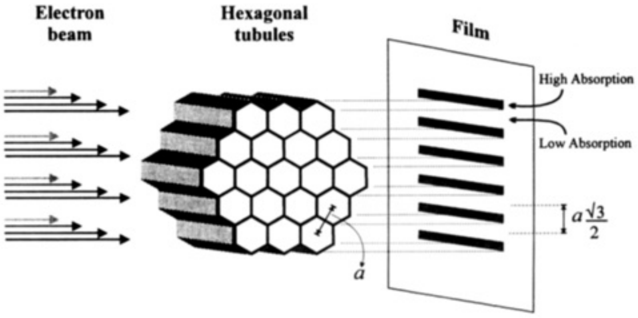

Figure 4. Schematic model showing apparent "lamellar structure" from a projection of a hexagonal array of tubules.

With the above explanations, the interpretation of Figure 1 becomes simple. We see a long, fibrous sample, made of very long hexagonal channels arranged as in Figure 4. The sample appears to be twisted, not because of marked flexibility of the solid architecture but most probably as a result of the existence of long and twisted liquid micelle rods before the silica walls thickened, giving rise to a quite rigid structure. Prior to silica condensation, the liquid micelle rods of surfactant–silicate ion pairs are not hampered from folding with extremely small curvature radius (like a bundle of spaghetti). Electronic images accordingly reveal a hexagonal structure for region A, because the beam is parallel or nearly parallel to the channels (Figure 2a), and regular fringes for region B, because the channels have appropriate orientation for periodical projection of scattering density, i.e., tube walls (Figure 2b). In the featureless region C, the channels are perpendicular to the beam, but off the appropriate orientation. This

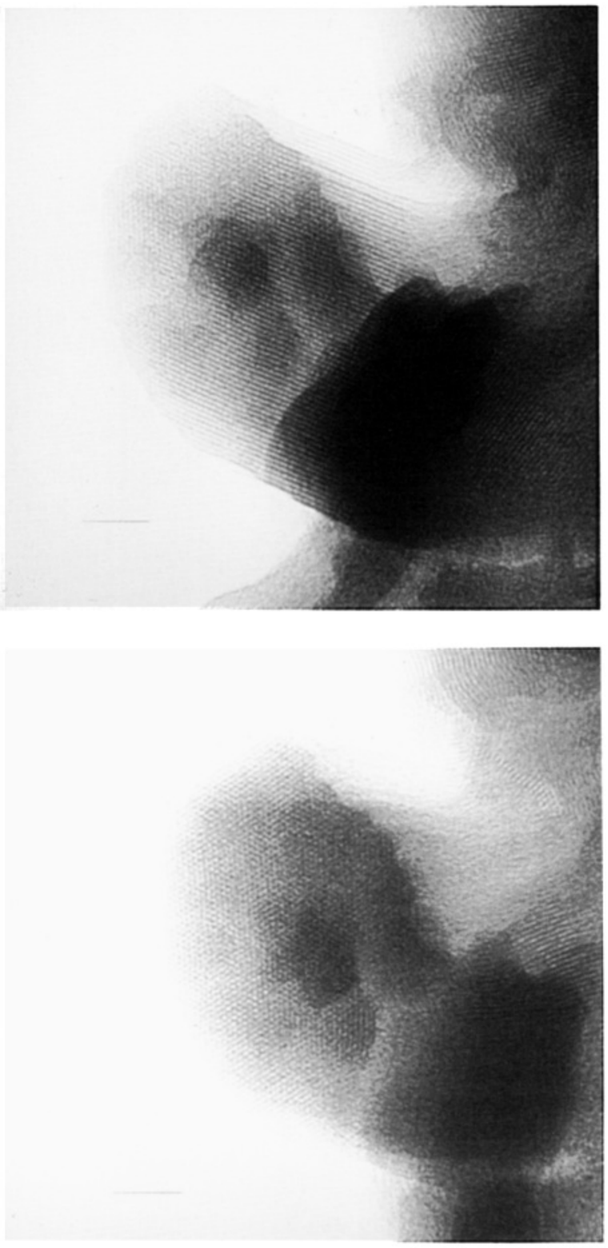

Figure 5. (a, top) TEM image showing parallel lines and honeycomb-like structure arising from channels and their extremities respectively (bar = 50 nm). (b, bottom) Lines have disappeared after slight tilt around the axis of channels (bar = 50 nm).

interpretation is in agreement with the above model of an ordered hexagonal array of very long tubules, i.e., channels.

The TEM micrographs in Figure 5 provide experimental evidence in support of this model. Hexagonal arrays of very long channels have been imaged, as shown in Figure 5a. The observed interline spacing in the region on the right is about 39.0 Å, which is related to the approximate 44.3 Å distance between pore centres by the $\sqrt{3}/2$ factor expected from the schematic model in Figure 4. With a slight tilt around the axis of channels, applied with the goniometer sample holder, the line contrast disappears, while the honeycomb stacking of channels remains (Figure 5b).

Figure 6 provides another excellent illustration of the fact that areas whose micrograph consists of honeycomb structure or a series of parallel lines belong to the same hexagonal structure. The sample of Figure 6 is the same as the vanadium-doped (Si/V = 60) silica MCM-41 described earlier(16). It was prepared in the presence of dodecyltrimethylammonium cations. The distance between hexagonal pore centres and the interline spacing were found to be 36.5 and 31.5 Å, respectively. The ratio between these two distances is again very close to $\sqrt{3}/2$ factor.

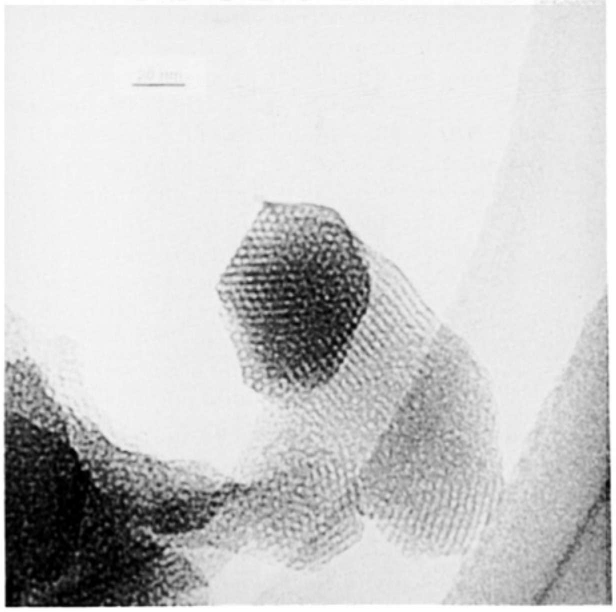

Figure 6. TEM image of a typical particle of V-MCM-41 prepared in the presence of dodecyltrimethylammonium cations (bar = 20 nm).

The formation of a silicate–surfactant mesophase as an intermediate in the production of this kind of materials is well established. In the case of MCM-41 and MCM-48 the structure of this mesophase is reflected in the structure of the resulting inorganic material after calcination. In other words, the shape and the organization of voids were imposed by the ordering of organic molecules in the silicate–surfactant mesophase, which is the key step in the synthesis of such materials.

This led to conclude that the formation of channels in B/Si-MCM-41 material is consistent with the liquid-crystal templating mechanism suggested by Beck et al.[4,5] who called upon a series of similarities between liquid-crystal phases in surfactant–water mixtures and mesoporous inorganic materials in support of their proposed mechanism. The length of created channels, reported for the first time in the present work to be several microns, can be an additional evidence favorable to the proposed mechanism, because the observation of very long channels in the calcinated material is in agreement with the existence of indefinitely long cylindrical micelles in the surfactant–water liquid crystal phase.[23,24]

Monnier et al.[20] found that the lamellar phase is a very short lived structure, favored at low temperature, high pH, and low degree of polymerization of the silica source. In contrast, the sample used in ref 21 was prepared at higher temperature and lower pH. It is therefore unlikely that the lamellar phase, if it ever formed in this sample, would have survived a long

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synthesis time, or survived calcination in air at 813 K. In addition, inspection of numerous samples with parallel lines in the micrographs in the present study did not show any silicate bridges that would have kept the layers from collapse or exfoliation.

Conclusion

The presence of a "lamellar structure" is not necessary to explain the above microscopical observations of MCM-41 type materials. Our findings are entirely consistent with the existence of a single fibrous phase made of long honeycomb arrays of tubules with silicate walls in the calcined material. These indefinitely long channels are an additional experimental observation in support of analogies previously used to hypothesize a liquid-crystal template mechanism for the formation of such materials. The mechanism, in its currently most accepted version is a cooperative process that begins by the formation of surfactant−silicate ion pairs, followed by self-organization of these ion pairs into a hexagonal mesophase and further polymerization of the silica into tube walls. The resulting silicate structure is preserved after the removal of surfactant upon calcination.

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