Cubosome Description of the Inorganic Mesoporous Structure MCM-48

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Received January 24, 1997. Revised Manuscript Received July 16, 1997[⊗]

The cubic mesoporous hydroxylated silicate MCM-48 is shown to consist of sub-micron-sized particles which display "crystal-like" faces. This well-defined particle habit is described in terms of cubosome behavior, and a complete representation of the particle structure is given as an analytical function. This function combines, in an exponential manner, both the minimal surface nature of the internal structure and the polyhedral nature of the peripheral structure. The consequences of a cubosome nature for MCM-48 are discussed in terms of possible chirality.

Introduction

MCM-48 is the cubic member of the new class of mesoporous material first synthesized by the Mobil company.[1] The Mobil scientists reported three phases,[2] a lamellar (MCM-50), a hexagonal (MCM-41), and a cubic (MCM-48), but other structures have since been synthesized.[3,4] The synthesis proceeds via a liquid templating mechanism with a surfactant, typically cetyltrimethylammonium chloride (CTACl) acting in some manner as template. It is thus natural to see a connection between lyotropic liquid crystals and these mesoporous sieves. To our knowledge, all phases discovered so far except one have a corresponding liquid-crystal phase.

It has been suggested[5] and later confirmed[6] that the structure of MCM-48, although essentially amorphous on a microscopic scale, is defined on a mesoscopic scale by a so-called minimal surface, with the midplane of the silicate wall sitting on the surface. On a minimal surface every point is a saddle point and the average curvature is zero. Minimal surfaces and their mathematically more easily described analogues, nodal surfaces,[7] have been successfully used in the description of the structures of crystals, such as for example zeolites and liquid crystals, e.g., lipids.[8] The surface defining

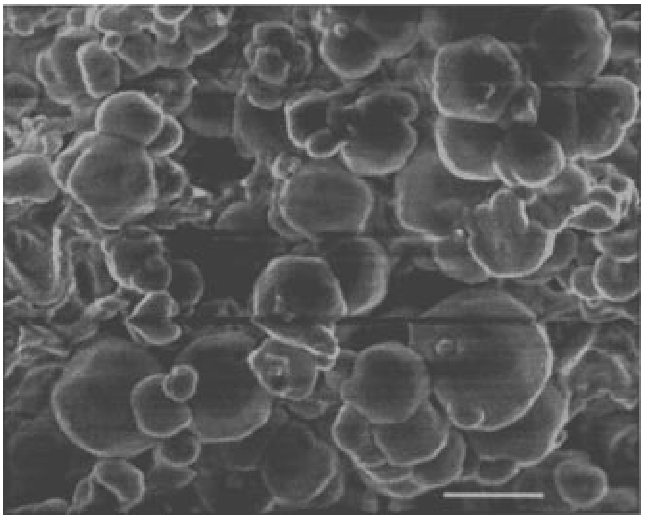

Figure 1. High-resolution SEM image of uncalcined MCM-48 (the size bar is 1 mm).

[⊗] Abstract published in *Advance ACS Abstracts,* September 1, 1997.

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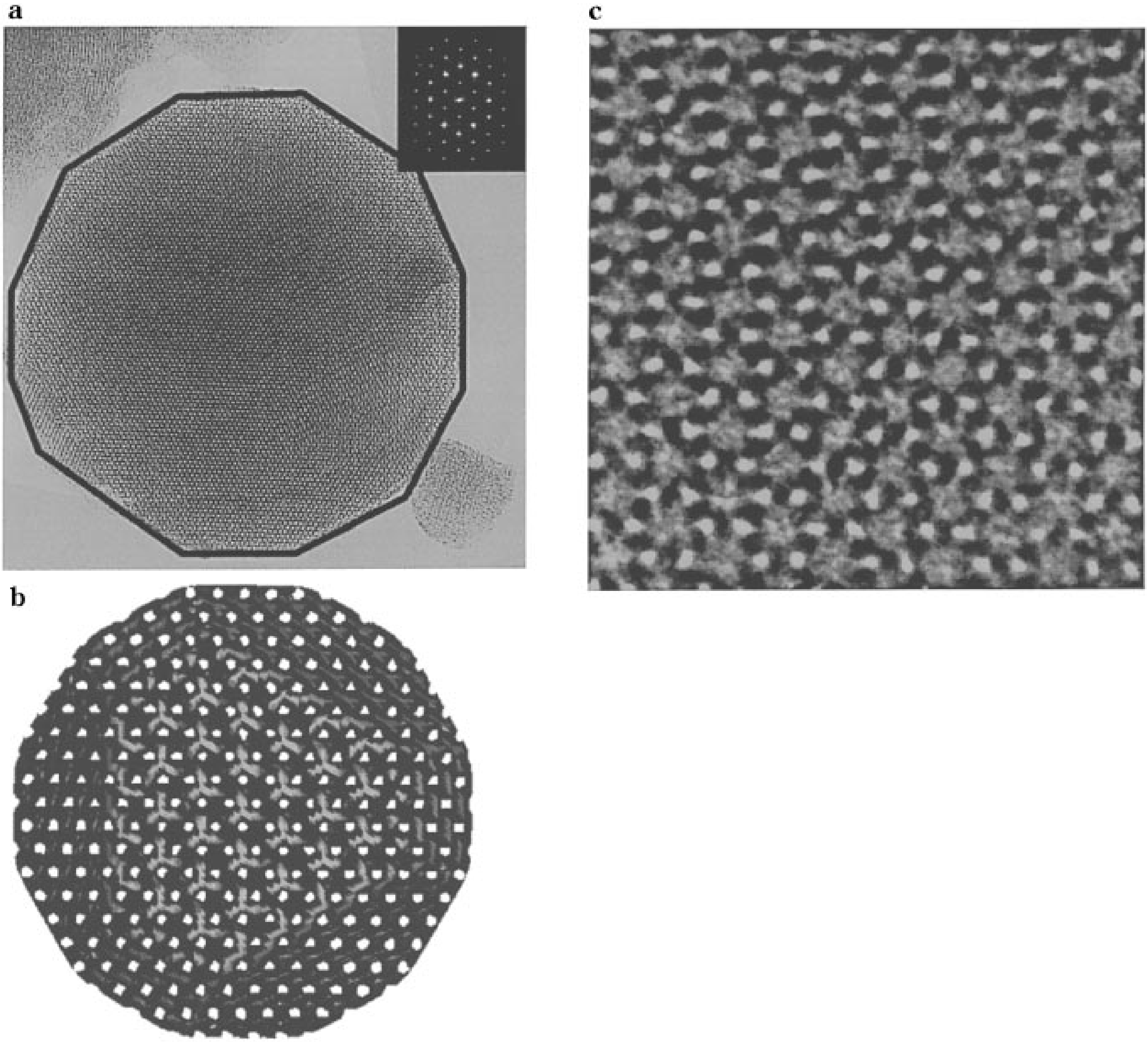

Figure 2. (a) TEM image of calcined MCM-48 along [111] with 12 edges shown. Inserted is the corresponding Fourier transform. (b) Calculated cubosome along [111]. The cubosome is defined by a truncated octahedra. (c) Closeup of the [111] direction of the image in (a). with the channels clearly seen.

MCM-48 is the gyroid or G-surface.[9] This minimal surface divides space into two identical but separate compartments. The structure contains a three-dimensional channel network with channels running along [111] and [100]. A structure defined by the gyroid surface will have the space group $Ia\bar{3}d$. This space group is frequently observed in water−surfactant and water−lipid systems[10] and has for example been found for water−CTABr.[11]

In an earlier work[6] we noticed by imaging in a TEM that MCM-48 has a very well-defined structure, and we have so far been unable to detect any irregularities or defects in the structure. In this work we will show that not only is the structure regular and well defined but also to a large extent is the morphology of the particles.

It seems natural to make a comparison between these mesoporous silicates and lipids based on the fact that the structures are equivalent in both size and shape. Lipids have a tendency to form regular bodies, so-called cubosomes,[12,13] in a water solution. A cubosome is defined as a particle formed by dispersing a minimal surface-shaped infinite lipid bilayer in water. The cubosome is thus built up by a periodic surface structure and terminated by outer boundaries, defined for example by a polyhedral shape, in such a way that the surface is continuous. The outer boundaries close one of the two identical channel systems of the minimal surface, leaving only the other one exposed to the exterior. For the description of cubosomes mathematical functions on the exponential scale can advantageously be used.[14] By using such mathematics, it is possible to exponentially add the function of the nodal

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surface to that of the polyhedron and obtain a continuous surface defined by a single mathematical function.

Experimental Section

The reactants (tetraethylortosilicate (TEOS), cetyltrimethylammonium chloride (CTACl), NaOH, and water) were mixed to a homogeneous gel at room temperature and transferred to a Teflon bottle, and subsequently placed in an oven for 4 days at 95 °C. The MCM-48 sample was synthesized in accordance with the molar ratio given in ref 6 (1 mol of TEOS:0.25 mol of Na_2O:0.65 mol of CTACl:62 mol of H_2O). The product was washed with distilled water and, for the TEM sample, calcined in air at 300 °C. During calcination the unit cell parameter is slightly reduced, from about 97 Å to about 85 Å. XRD patterns of both the uncalcined and the calcined specimen confirms the product to be MCM-48.

The TEM sample was crushed under methanol and placed on a holey carbon grid. The images were recorded with a JEM-4000EX microscope operated at 400 kV. The particles were rarely tilted. Most frequently only particles already aligned along main crystallographic axes were imaged.

The Fourier transform of the TEM images were calculated with the Semper image-processing system.

The SEM sample was sputtered with carbon to avoid charging and high-resolution SEM images were recorded utilizing a field emission gun. As the particles are small (less than 1 μm in diameter) a normal SEM does not provide the necessary resolution.

The cubosomes were calculated and displayed on a Silicon Graphics Indigo 2 Extreme using the following equation:

$$10^{x} + 10^{y} + 10^{z} + 10^{-x} + 10^{-y} + 10^{-z} + \\ 10^{0.75(x+y+z)} + 10^{0.75(-x+y+z)} + 10^{0.75(x+y-z)} + 10^{0.75(-x+y-z)} + \\ 10^{0.75(x-y+z)} + 10^{0.75(-x-y+z)} + 10^{0.75(x-y-z)} + 10^{0.75(-x-y-z)} + \\ 10^{25(\sin((3\pi/2)x)\cos((3\pi/2)y)+\sin((3\pi/2)y)\cos((3\pi/2)z)+\sin((3\pi/2)z)\cos((3\pi/2)x))} = \\ 10^{10}$$

This equation represents the gyroid surface with polyhedral outer boundaries. The polyhedron has the shape of an octahedron with its vertexes truncated by a cube. The first line of the equation defines a cube, the second and third an octahedron, and the fourth the gyroid nodal surface. The factor of 0.75 in lines 2 and 3 is chosen to match the experimentally observed particle shape and defines the size of the {111} faces with respect to the {100} faces. The factor 25 in line 4 defines the particle size and is limited by computing restrictions. To calculate the full equation for a 1 μm in particle would be too computer intensive. The constant, the last line, is the isosurface constant which defines the smoothing of the particle vertexes. For example, a smaller value of this constant would generate a particle with rounder edges and vertexes whereas a larger value would generate a sharper and more well-defined polyhedron.

Results

When examining an MCM-48 specimen in both SEM and TEM, we realized that the particles had a “crystal” or a cubosome shape associated with them. Although all the particles are not perfect polyhedra we noticed that a prevailing shape is the truncated octahedron. The SEM images show that the particles are determined by “crystal” surfaces (cf. Figure 1). However as the size of the particles is so small it is difficult to say anything of the actual shape or morphology even though a high-resolution SEM was used. Although TEM images only give a projection of the particles it is possible from looking along different directions to deduce the morphology. Naturally, as the TEM specimens were ground in a mortar, it could be argued that what the images show are only particle fragments. This is however not very likely as the size of the particles is so small (less

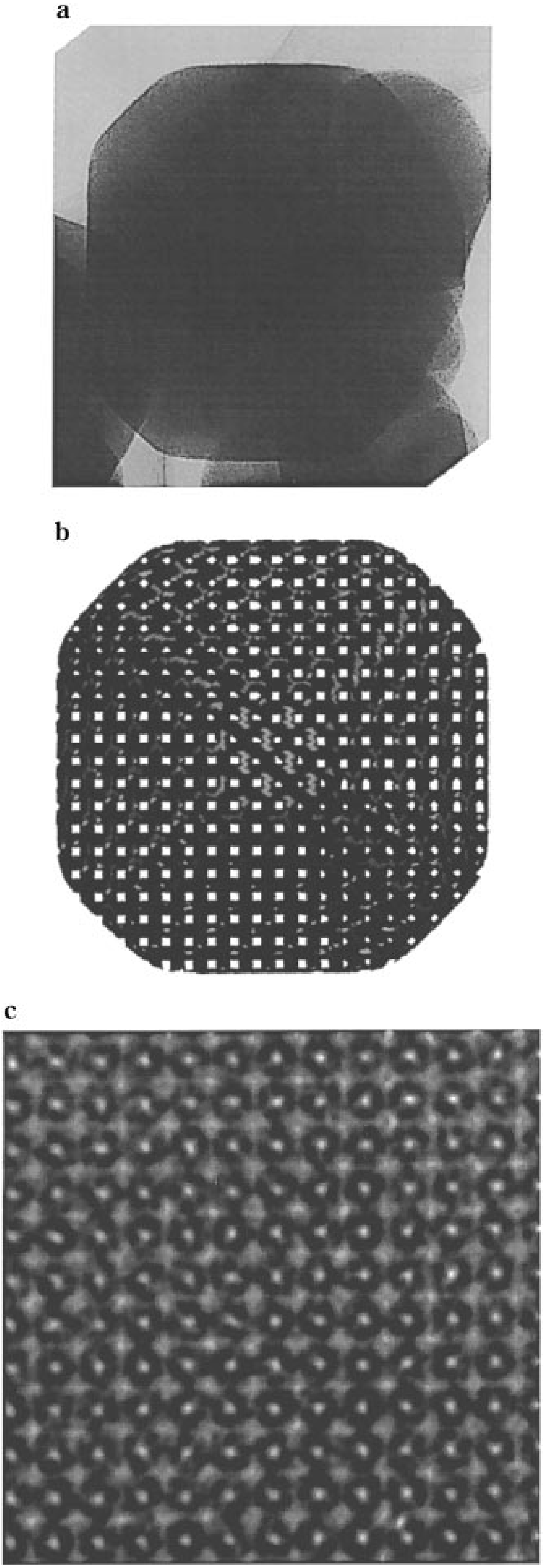

Figure 3. (a) TEM image of calcined MCM-48 along [100]. (b) Calculated cubosome along [100]. (c) Closeup of a particle exactly aligned along [100].

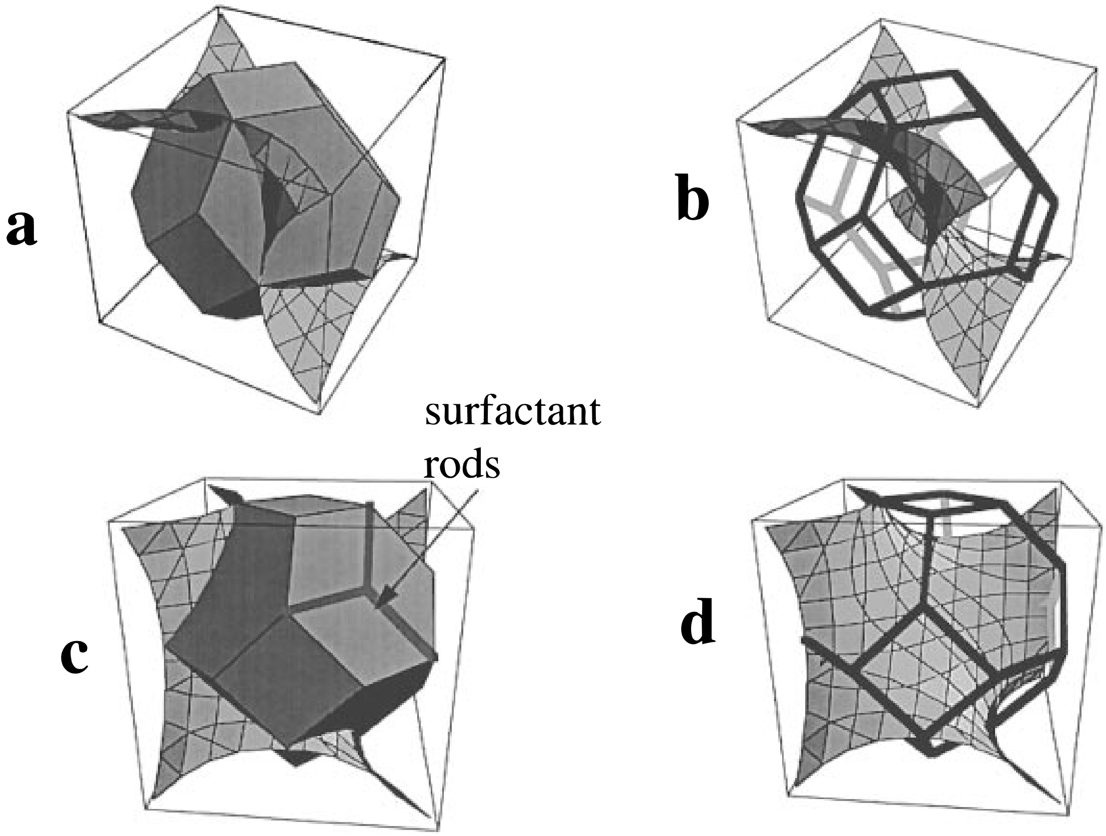

Figure 4. Schematic representation of the gyroid surface (MCM-48). The asymmetric unit for the gyroid surface can best be described as a section of a regular truncated octahedron (sodalite cage). The gyroid surface divides the sodalite cage in two, cutting six of the eight hexagonal faces of the sodalite cage. The remaining two hexagonal faces, located on opposite sides of the sodalite cage, provide the location for the surfactant rods during synthesis (Figure 4c). By repeating this sodalite unit 16 times via a series of 2-fold rotations, the unit-cell volume is constructed. The sodalite cage itself is not the fundamental repeating unit (asymmetric volume) which is achieved by further subdividing the sodalite cage into six parts (first divide in half perpendicular to [111], then in three along (−12−1) and (11−2) planes). This basic unit has a volume $^{1}/_{96}$ of a unit cell and replicates to produce the gyroid surface according to space group $Ia\bar{3}d$.[15] (a) and (b) from one viewpoint and (c) and (d) from a slightly different viewpoint. The origin is taken as the center of the sodalite cage. See ref 15 for more detail.

than 1 μm in diameter), and thus it would be difficult to actually crush them. Furthermore the shape of the particles shown here is very regular, which implies that the surfaces shown are the actual growth surfaces.

To deduce the morphology of the particles with 100% certainty is very difficult. Many particles are malformed or lying along a direction that cannot be identified. However we believe that the prevailing shape is an octahedron with truncated vertexes. As the symmetry of MCM-48 is cubic it is natural to believe the particles to be determined by some type of polyhedron with cubic symmetry. The SEM images show that the particles are definitely not spheres but have crystal faces.

A particle aligned almost exactly along [111] is shown in Figure 2a. At a first glance the projection of this particle might look round, but after closer examination the 12 edges determining the shape can be seen (marked in the figure). It is not possible from one direction to understand the three-dimensional nature of the particle. For example, in this direction, both a truncated cube or a truncated octahedron would look exactly the same. Both have 12 edges in projection along [111]. In Figure 2b the truncated octahedron is shown. Figure 2c shows a close up of a selected area of the image in Figure 2a. As can be seen, the structure is very well defined and regular. The whiter spots in the image corresponds to the channels running along this direction.

To better understand the shape of the particles, we also imaged MCM-48 along [100]. Along this direction we could see that the particles were determined by eight edges (cf. Figure 3a). This immediately rules out the truncated cube as a model for the particles as this polyhedron would look like a square in projection along this direction. However the truncated octahedron, shown in Figure 3b, is a very likely candidate. Figure 3c shows a closeup of a particle lying almost exactly along [100]. There are straight channels running along this direction, and they can be seen as white spots in the image.

The truncated octahedral shape of particles of MCM-48 is a reflection of the underlying symmetry of the gyroid surface (see Figure 4) combined with the growth mechanism of the particulates. The growth mechanism is still a matter of some speculation at both the mesoscopic and macroscopic scale. It is generally accepted that the cationic long-chain surfactant molecules form an ordered liquid-crystalline mesophase in conjunction with the anionic silicate species in solution. It is also known that the silicate species begin to condense rapidly (within minutes at room temperature and within seconds at elevated temperatures). Consequently, there is a transition from a "soft" material to a relatively "hard" material within seconds at elevated temperatures. Whether the particulates of MCM-48 nucleate and grow or whether they preform their final particulate size while still “soft” before condensation of silicate units is unknown. In the latter scenario, if the particulates form a thermodynamic equilibrium shape, then that shape will be a “Wulff body” and will be a true reflection of the relative surface energies of different facets as observed in liquid crystals.[16] In the case of MCM-48 the surface energy of the {111} face would be 0.77 times that of the {100} face and all other faces would have a higher surface energy. [The factor of 0.77 for the relative surface energies comes from the relative distance of the [111] and [100] facets from the center of the particle. This distance is given by the factor 0.75 in the second line of the equation describing the cubosome.] If, on the other hand the particles nucleate and then grow to their final size, the particle is unlikely to have a thermodynamic equilibrium shape and the exact shape of the particle would be a reflection of the growing rates on different facets with the {100} and {111} facets being those with slowest growth.

It is also interesting to speculate whether the structure of MCM-48 follows a continuous surface at the particle periphery as in a cubosome. This requires that the surface wraps back on itself forming a closed body. The implication of such a folding would be that one channel system in MCM-48 would be closed, and one would be open to the exterior. As each channel system is chiral—but with opposite handedness—such an eventuality would lead to chiral particles with spiral channels. In other words the open channel would be chiral with symmetry $P4_132$ or $P4_332$. Of course different particles would have spiral channels with different handedness. However, if particles could be synthesized of sufficient size, perhaps by methods akin to those recently described for fabricating macroscale structures,[17,18] then particles of different chirality could be separated by hand. It seems to us likely that such a continuous surface property exists for MCM-48. This is not observable in the TEM images such as Figure 2a as the surface wrapping does not change the electron density appreciably in projection (a hexagonal distribution of pores are observed). We have tried to image the surface of MCM-48 by atomic force microscopy to prove or disprove this conjecture by observing for instance the triangular pattern of pores along [111] as shown in Figure 2b but have not, as yet, been successful. If MCM-48 does turn out to be a closed surface then this would have ramifications for our understanding of the termination of the tunnel structure in MCM-41.

Since initial submission of this paper Yang et al. have published on exotic particle morphologies in MCM-41.[19]

Acknowledgment. The authors would like to thank Zoltan Blum, Sten Andersson, and Kåre Larsson for valuable discussions. Financial support is also acknowledged by V.A. from the Swedish Research Council for Engineering Sciences (TFR), by M.J. from the Swedish Natural Science Research Council (NFR), and by V.A, M.W.A., and O.T. from the British Council.

CM970052W

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