Mesoporous Materials

A New Minimal Surface and the Structure of Mesoporous Silicas**

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The formation of complex inorganic superstructures in nature relies on the interaction between organic and inorganic species to direct the inorganic form away from its "usual" morphology. During synthesis the superstructures are soft and dynamic which makes a study of the nature of the ephemeral interface difficult.[1] However, the inorganic skeletons formed are stable and consequently amenable to detailed examination. In 1992 researchers at Mobil[2] and in Japan[3] made the remarkable discovery that the subtle forms of mesoscopic organization of surfactant molecules could be imprinted on oxide structures. Herein we report our studies of the structure of the surfactant-templated, cubic, mesoporous silica superstructure, SBA-1[3] and provide a formulation in terms of curvature that has important repercussions for both surfactant structures and the mechanism of formation of inorganic replicas. We establish that the crucial interface that determines the inorganic structure is between the silica and water adsorbed at the micelle surface, not between silica and surfactant, thus challenging the present synthesis mechanisms.[4] We adopt a general protocol for understanding the surface curvature and energy which could be applied widely

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to the growth of inorganic structures in biology, including nonperiodic and disordered structures.

Currently there are a number of ways to address the mesophase structure of these mesoporous silicas. Terasaki and co-workers[5] adopted the direct structure elucidation approach by using electron crystallography. With this method they were able to reconstruct an electron density map directly with electron micrographs recorded along several zone axes. This has the distinct advantage that no predefined knowledge is required and that the diffraction intensities are optimized through the observation of individual particles. However, its disadvantage is that the electron density map does not easily yield clues about the synthesis mechanism. The technique is also technically very demanding and is only suitable for highly organized 3D structures that are stable in the electron microscope. It is not a routine technique and cannot be used to monitor many sample preparations, or to look at preparations in situ.

Another route, first adopted by Anderson and Alfredsson,[6] and more recently by Solovyov and co-workers,[7] and Schüth and co-workers,[8,9] involves the determination of a structural model from some known data followed by its refinement according to certain parameters, for instance, against X-ray diffraction patterns or electron micrographs. This method has the advantage that it is flexible and can be applied to a variety of preparations; the results also give information about synthesis mechanisms. The disadvantage is that the process does require input from other techniques and some prior knowledge. Also, the powder X-ray diffractogram is an average technique and as a consequence, it is important that the sample is relatively homogeneous. Herein we introduce a general mathematical approach to the modeling of mesoporous silicas, which allows easy generation of electron density maps and diffraction patterns for comparison with experimental data.

SBA-1 was synthesized in HCl (4 M) with hexadecyltriethylammonium bromide (HTEABr) as surfactant and tetraethylorthosilicate (TEOS) as a source of silica. The structure is known from electron crystallography[10] to belong to the space group $P_{m\bar{3}n}$ and consists of cages connected through windows. The corresponding surfactant phase is known as the I_1^3 (or Q^{223} referring to the space group number, or $Pm3n$ as an identifier for $P_{m\bar{3}n}$[11]) phase which is a cubic, isotropic, micellar phase. Curiously, the I_1^3 phase was not observed in the phase behavior of HTEABr,[12] in which a hexagonal phase occurs at the micellar solution boundary. Consequently, we studied the phase behavior of this surfactant with a temperature-programmed penetration scan (Supporting Information). This shows that in the presence of impurities that are likely to remain from the surfactant synthesis, such as bromohexadecane, a cubic phase is induced below ≈32 °C. Significantly, this phase occurs between the hexagonal phase and isotropic solution, which suggests a higher curvature of the micellar phase. More importantly, when HTEABr is exchanged with chloride ions to make HTEACl the penetration scan reveals the presence of three cubic mesophases. HTEACl is probably the templating agent in SBA-1 preparations owing to the large excess of chloride anions in the preparation.

The essence of our approach herein was first to build the structure essentially by hand. This requires some knowledge of the possible structures of the I_1^3 surfactant phase; some that have been discussed in the literature are illustrated in Figure 1. However, close inspection of electron micrographs reported previously[10] quickly discounts the possibility of rodlike micelles as the structure-directing agent, and consequently we choose the approach of Vargas and co-workers,[15] which uses spherical and oblate ellipsoidal micelles arranged on a cubic lattice. To describe such structures, a useful and simple exponential mathematics is available to "hand build" structures, as described in detail by Jacob and Andersson,[16] and as outlined in the Experimental Section below. A remarkably good fit is produced between experimental and theoretical diffraction patterns as shown in Figure 2. However, there is some discrepancy between the calculated void volume and that determined experimentally, suggesting that the model needs further refinement. The model works well for both as-prepared and calcined samples (Supporting Information). Upon calcination the unit cell shrinks by ≈9 % but the relative diffraction intensity changes very little. This indicates that 1) the structure remains essentially intact, and 2) there is no need to consider an electron-density profile other than silica walls and voids. The content of the void, which will be mobile, is not a significant

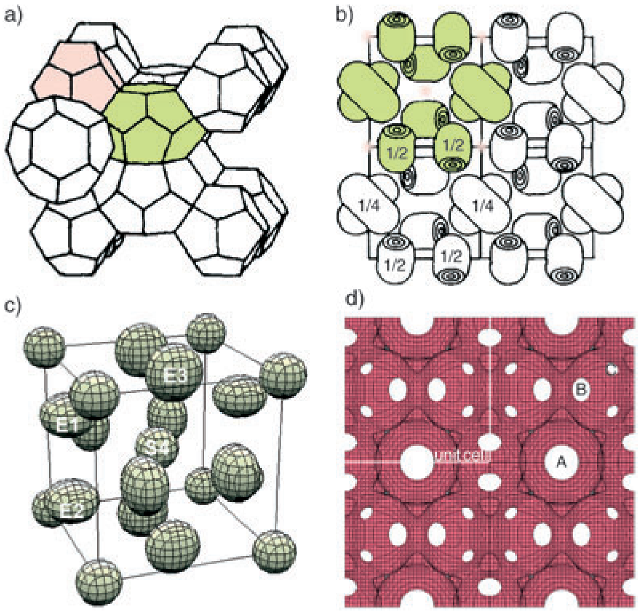

Figure 1. Various representations of the I_1^3 structure with $P_{m\bar{3}n}$ symmetry: a) model of Charvolin and Sadoc[13], which displays two polyhedra (12-hedron and 14-hedron) defining volumes that contain micelle plus associated water; b) rod-type micelles of Fontell and co-workers[14]; c) single exponential function displaying 21 micelles: 9 spherical and 12 oblate ellipsoidal, according to exponential mathematics, equivalent to model adopted by Vargas and co-workers;[15] d) continuous surface created by an exponential function as the radii of the micelles are increased, displaying the three different window types (A, B, and C) in SBA-1—2×2 unit cells viewed along [100]. To create a continuous surface, 12 extra virtual ellipsoids are placed in adjacent cells to ensure that there are no edge effects.

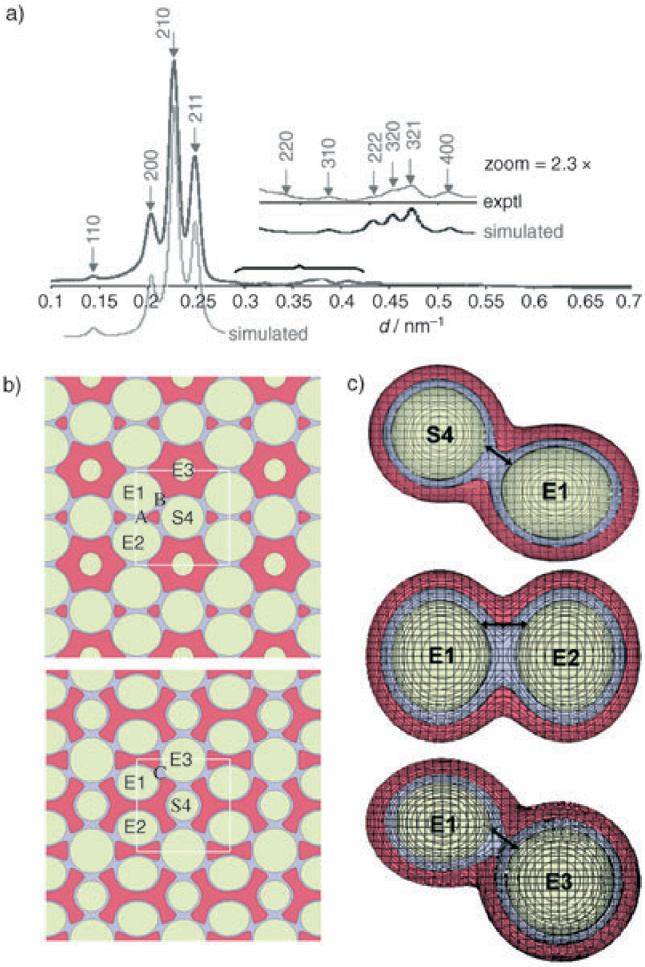

Figure 2. Calculated X-ray diffraction pattern and model from the analytical function: a) Experimental and simulated X-ray diffraction pattern for as-prepared SBA-1 with an analytical expression of $r_1 = r_2 = 0.229$ for a unit cell, for example, 19.5 Å (based on a unit cell of 85 Å) and an oblateness of 1.2; $C = 0.01$. b) Slices through the unit cell of SBA-1: red = hydroxylated silica wall structure, yellow = micellar structure, and blue = adsorbed water. The slice through the middle of the unit cell ($z = 0.5$, top) illustrates the A windows between the flat sides of two oblate ellipsoids and the B windows between a spherical and an elliptical micelle. The slice at $z = 0.375$ (bottom) shows the C windows between the tips of two ellipsoidal micelles. c) Illustration of how the window size in SBA-1 is related to the curvature in which the micelles meet, in terms of the thickness of the adsorbed water layer between the micelles; the contact angle between micelles will be different.

factor to determine the relative diffraction intensity. Nevertheless, a number of important features are immediately apparent from this approach. First, the radius of the spherical micelle must be similar to that of the short radius of the oblate ellipsoidal micelles, otherwise the [110] reflection becomes unacceptably large. This is reasonable, as these radii will both be governed by the length of the surfactant paraffin chain. Second, there is an interesting correlation between the window size and the geometry of adjacent micelles that cause the window formation. SBA-1 has three different windows and, as can be observed in Figure 1 d, the window size is greatest when the contact angle between touching micelles is smallest; alternatively, the thickness of the adsorbed water layer on the micelles which excludes the silica wall is a constant (Figure 2). This suggests mechanisms to control window size through control over the curvature of micelles.

A number of the important micellar and bicontinuous surfactant phases have been described previously in terms of infinite periodic minimal surfaces (IPMS).[17] Such surfaces are continuous in 3D space and have the property that the mean curvature at all points on the surface is zero. A number of the micellar phases have been described in this regard, but the I_1^3 structure has not yet been correlated with any known IPMS. A convenient method to explore possible IPMS structures is to use the *Surface Evolver* software from Brakke[18] which refines a surface either to minimal area or to minimal squared-mean curvature. A number of cubic IPMS have recently been explored with this approach.[19] We used this package with the "hand-built" structure as the starting point for refinement, and refined the squared-mean curvature under the constraints of defined void volume (determined from nitrogen adsorption and helium pycnometry experiments). The results are remarkable. First, without volume constraint, a new minimal surface is generated at a void volume of 55%. The surface is shown in Figure 3 and has almost exactly zero-mean curvature at every point on the surface. The surface may be characterized as a smoothed version of the analytic surface by using decreasing squared-mean curvature as a smoother. An X-ray diffraction pattern produced from such a surface is in excellent agreement with that observed experimentally. The fit is further improved by constraining the void volume to that observed experimentally (58%), and the surface produced still has close to constant and zero-mean curvature (Figure 4). In this case the surface can either be refined to constant-mean curvature or to minimal integrated-square-mean curvature. The latter approach was found to give the best agreement between experiment and simulation. The mesopore sizes are consistent with previously reported work from Terasaki and co-workers,[10] and consequently the model is consistent with X-ray diffraction, electron microscopy, and gas adsorption experiments. We have not tried to further improve the diffraction fits with the methods of Solovyov et al.,[7] as we believe that the number of variables relative to the number of fitting parameters precludes an improvement in accuracy.

This result has important repercussions for both the structure and mechanism of formation of SBA-1 and mesoporous silicas in general and also, by analogy, for the structure of surfactant mesophases. SBA-1 is formed from a low-concentration surfactant solution, which is above the critical micelle concentration (CMC) but an order of magnitude below that normally required for mesophase formation. The solution has high ionic strength which alone is not sufficient to salt out the mesophase. The precipitation only occurs in the presence of silica species. The precise nature of these silica species is unknown, although they will be positively charged at this low pH. However, the mechanism must be cooperative between the micelle species and the silica species. Before mesophase formation, the micelles must have a substantial shell formed from silica species to supply all the silica in the final product. After mesophase formation and reorganization,

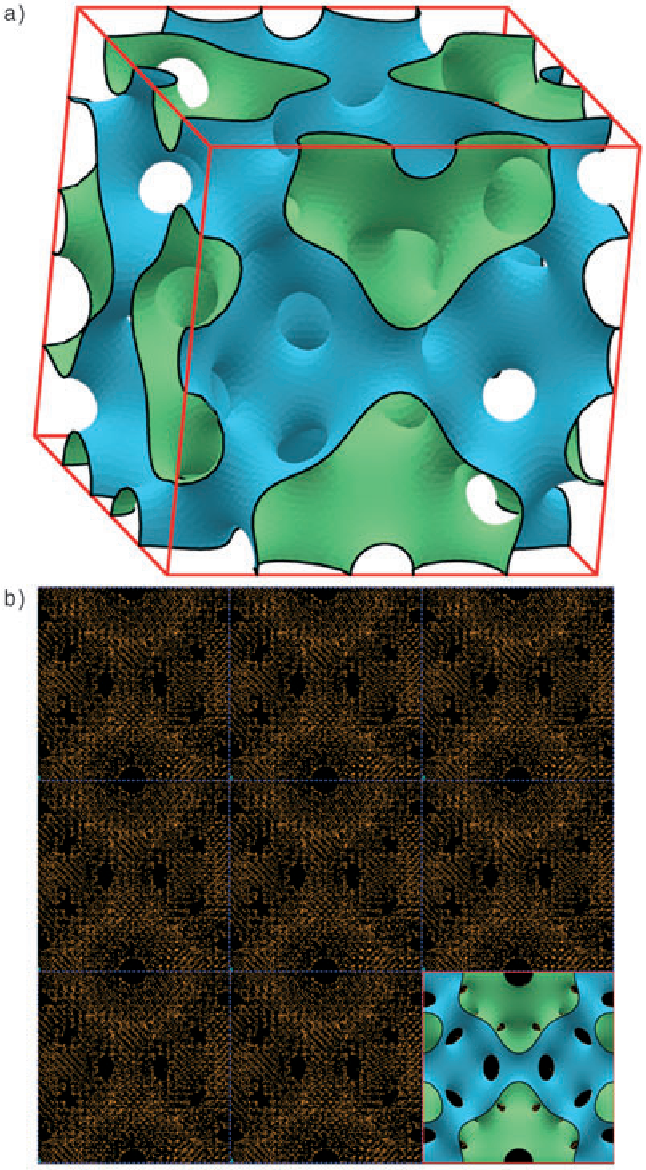

Figure 3. $P_{m\bar{3}n}$ symmetry surface with zero-mean curvature at all points: a) oblique view and b) view along [100] superimposed on 3×3 unit cells of the atomistic model used to calculate the diffraction patterns. In SBA-1 the green volume represents the inorganic hydroxylated silica wall of the material, and the blue volume contains micellar surfactant surrounded by a layer of adsorbed water. In the I_1^3 surfactant mesophase, the free water would occupy the green volume.

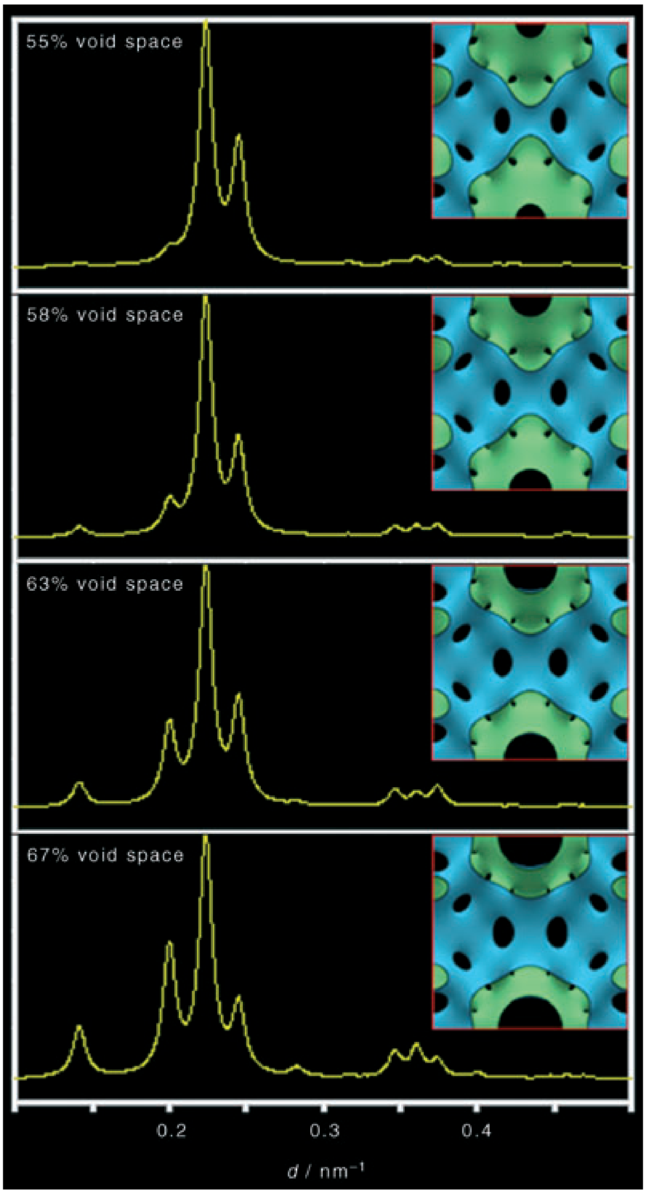

Figure 4. Calculated X-ray diffraction patterns for structures refined with *Surface Evolver.*[18] The wall volume in green is filled with uniform electron density and the void space is empty. A void volume of 55% is the surface closest to a minimal surface with near zero-mean curvature; 58% void volume represents a slightly thinner wall still, with very low curvature which most closely resembles as-prepared SBA-1.

the SBA-1 structure reveals that the silica has retracted from the micellar surface (creating windows) and that the mean curvature of the silica surface is close to zero. Yet in a micellar mesophase the mean curvature of the micelles is very large. Moreover, the Gaussian curvature (the product of the maximum and minimum curvature) of the micelles is positive, whereas the Gaussian curvature of the final structure is negative at every point. We make the assumption on geometric grounds that the micelles do not merge to form a continuous phase, as they are simply too long to be accommodated in the window region of the structure. The window sizes are less than ≈13 Å and the surfactant molecules are >20 Å, requiring a window of at least 40 Å for a bilayer (n.b.: 1) surfactant length is about 75% of all trans length; 2) the surface wrapping is complex, and therefore the notion of a bilayer is not correct, but illustrates the size that the window would need to be if the micelles were to "fuse"). Consequently, the interface of the silica is clearly not at the interface with the surfactant micelle, but at the interface with the adsorbed hydration layer surrounding the micelle (Figure 2). Although it is possible that there are other related zero-mean-curvature surfaces for such a tortuous surface, the one found fits the experimental data and is therefore a valid description for this structure in terms of curvature. As has been suggested before for other cubic micellar mesophases (specifically Q^{225} and Q^{229}) this interface between the adsorbed water and the free water, in pure surfactant/water systems, is usually a zero-mean-curvature surface (surfaces F-RD and I-WP respectively).[17] Herein we have established, through the structure of the inorganic precipitate, that a similar picture of a high-curvature micellar structure with an adsorbed water layer extending to a zero-curvature surface and then a free water region on the other side of the surface is valid for the I_1^3 or Q^{223} structure. The silica in the structure of SBA-1, and probably many other mesoporous silica structures, develops its final form in the free water. Such a mechanism would not be inconsistent with the hexagonal MCM-41 type structure in which the surfactant is present as long rods but with substantial free water between the rods (the hexagonal phase can accommodate a larger variation in water concentration than the cubic phases). The packing constraints in the hexagonal phase would also favor thicker walls simply on geometric grounds—there is less surface area to pack the silica without thickening. As a result, there are no exclusion zones in which windows will occur, and the surfactant rods are essentially covered with silica species. Such a mechanism is, however, at substantial variance with the previously proposed mechanisms of mesoporous silica formation,[4] which rely heavily upon the direct close interaction between silica species and surfactant. We suggest this interaction is crucial only in the initial precipitation process, but the combination of other interactions is far more important to the structure of the final mesophase observed. With this general method of building structures by hand followed by curvature refinement according to experimental constraints, it should be possible to derive accurate models for all inorganic mesoporous structure types. Even disordered structures could be built, as the method of constructing surfaces by hand allows any starting arrangement and micelle shape (although this would be clearly more demanding and would require information about the nature of the disorder). The same methods can also be applied toward the growth of inorganic structures in biology.

Experimental Section

Hexadecyltriethylammonium bromide (HTEABr) was prepared by mixing 1-bromohexadecane (98%, Lancaster) and triethylamine (99%, Jansen Chimica) in absolute ethanol under reflux conditions for 24 h. Ethanol was then removed with a rotary evaporator until a white, viscous paste was obtained. The resulting gel was recrystallized by minimal addition of chloroform, then ethyl acetate until the whole solid precipitated. SBA-1 was prepared with tetraethylorthosilicate (TEOS; 98%, Aldrich) as a source of silica, HTEABr (made in-house), distilled water, and aqueous HCl (33 wt%, BDH). Molar ratios for a typical SBA-1 synthesis were HTEABr/H_2O/HCl/TEOS = 1:3500:280:5. After an aging time of 1 week at 4°C, the mixture was heated to 100°C within 10 min for 1 h. These conditions were optimal for the generation of homogeneous stable materials that have probably reached an equilibrium as a soft solid before solidification in the final heating at 100°C. We have established by ^{29}Si-MAS NMR spectroscopy that at these low pH conditions, cross-linking is retarded, which is consistent with the work of Brinker and Scherer.[20] Ethanol is liberated during the hydrolysis of TEOS ($\approx$1.5 wt%) but this has little influence on the processes occurring, as the ethanol resides mainly in the water. (Low ethanol levels ($<$1 mol dm^{-3}) are known to have only a minimal influence on CMC values, hence only a small amount of ethanol is found in the micelles.) The surfactant moiety was finally burned out by calcination at 550°C for several hours, with a slow temperature-ramp rate (0.5°C min^{-1}). Hand-built structures were formulated with *Mathematica* software; the atomistic structures were generated with a *Fortran* program; X-ray diffraction patterns were calculated with *Cerius II* software from Accelerys; *Mathematica* contour surfaces were translated for input into *Surface Evolver* with a *Fortran* program.

The basis for the initial hand-built structures is that a sphere can be expressed not only as $x^2+y^2+z^2=C$ but also in the exponential scale by

$$e^{-(x^2+y^2+z^2)} = C \tag{1}$$

The radius of the sphere is determined by the constant C, and the center of the sphere can be moved to any coordinate h, k, or l by the following transformation:

$$e^{-[(x-h)^2+(y-k)^2+(z-l)^2]} = C \tag{2}$$

The sphere can be elongated or squashed in any dimension to produce, for instance, an oblate ellipsoid by the following transformation:

$$e^{-[b_1\,(x-h)^2+b_2\,(y-k)^2+b_3\,(z-l)^2]} = C \tag{3}$$

Finally, an object with a different radius can be formed by adding a constant, a, within the exponential, thus:

$$e^{a-[b_1\,(x-h)^2+b_2\,(y-k)^2+b_3\,(z-l)^2)} = C \tag{4}$$

The utility of working in the exponential scale is that multiple objects can be incorporated in a single expression by adding exponential functions together (Supporting Information). Furthermore, as isolated objects approach, a continuously wrapped surface is produced with the smoothness of the wrapping governed by the value of C. Jacob and Andersson[16] have demonstrated that this approach can be extended to describe many objects with complex shape. The arrangement of micelles in the $P_{m\bar{3}n}$, I_1^3 structure is given by adding 21 objects together according to the following equation:

$$\sum_{h,k,l} e^{-\{(x-h)^2+(y-k)^2+(z-l)^2\}} + \sum_{h',k',l'} e^{|a-\{b_1\,(x-h')^2+b_2\,(y-k')^2+b_3\,(z-l')^2\}|} = C \tag{5}$$

and this is shown in Figure 1 c. Then, by increasing the radius of the micelles relative to the unit cell size, a continuously wrapped surface is produced (Figure 1 d), which represents the structure of SBA-1. To test the validity of the model, an atomistic structure of SBA-1 was produced by placing silicon atoms randomly on one side of this continuous surface; X-ray diffraction patterns were generated for varying values of the micelle radius and the degree of oblateness of the micelles.

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