Chem. Mater. **2001,** *13,* 2247−2256

Phase Transitions in Mesostructured Silica/Surfactant Composites: Surfactant Packing and the Role of Charge Density Matching[†]

Sarah H. Tolbert,*,[‡] Christopher C. Landry,[§] Galen D. Stucky,[||]
Bradley F. Chmelka,[⊥] Poul Norby,[∇] Jonathan C. Hanson,[#] and Alain Monnier[†,○]

Department of Chemistry and Biochemistry, University of California at Los Angeles, Los Angeles, California 90095-1569, Department of Chemistry, University of Vermont, Burlington, Vermont 05405, Departments of Chemistry and Materials, University of California at Santa Barbara, Santa Barbara, California 93106, Department of Chemical Engineering, University of California at Santa Barbara, Santa Barbara, California 93106, Department of Chemistry, University of Oslo, P.O. Box 1033, Blindern N-0315 Oslo, Norway, Department of Chemistry, Brookhaven National Laboratory, Upton, New York 11973, and Departement de Chimie Physique Sciences II, 1211 Geneva, Switzerland

Received May 5, 2000. Revised Manuscript Received March 15, 2001

Time-resolved X-ray diffraction is utilized to follow phase transitions in nanostructured silica/surfactant composites in real time under hydrothermal conditions. The data allow us both to obtain kinetic parameters and to observe intermediate phases. In all cases, changes in the packing of the organic component of these composites drives the transformation, indicating that surfactant packing is a dominant factor in determining the overall structure of these materials. For materials heated in pure water, however, high activation energies for transformation were measured, suggesting that large kinetic barriers can stabilize structures against surfactant-driven rearrangements. Matching between the interfacial charge density of the inorganic silica framework and the charge density of the surfactant headgroups is also found to affect the kinetics of transformation. Lamellar-to-hexagonal transitions, which complement condensation-induced changes in charge density, are observed to be continuous, while hexagonal-to-lamellar transitions, which proceed contrary to these charge density changes, are discontinuous. For materials heated in their high-pH synthesis solutions, more complex phase behaviors are observed. Hexagonal (*p*6*mm*) structures transform either to a bicontinuous cubic phase (*Ia*3*d*) or to a lamellar structure. Lamellar phases are observed at either long or short polymerization times, while cubic phases dominate at intermediate polymerization times. The production of these different phases can be understood by considering the interplay between organic packing, charge density matching, and changing activation energies. At short times, high charge on the inorganic framework favors transformation to the low-curvature lamellar structures. At very long times, silica condensation both reduces this charge density and cross-links the framework. This cross-linking raises kinetic barriers for transformation and again favors the topologically simpler hexagonal-to-lamellar transition. Transformations to the cubic phase are only observed at intermediate times, when these effects are balanced.

Introduction

Self-organized silica/surfactant composite materials mark an exciting new avenue for the production of ordered nanostructured materials through simple wet-chemical techniques.[1] A wide range of 1-, 2-, and 3-dimensionally ordered porous structures can now be made,[1−9] and in most cases, the surfactant can be removed by ion exchange or calcination to produce

---

[†] This paper is dedicated to the family and memory of our colleague Alain Monnier, whose enthusiasm, expertise, and creativity had a major impact on this work. His insights and the personal and professional standards that he set will long be remembered.

* To whom correspondence should be addressed. E-mail: tolbert@chem.ucla.edu.

[‡] University of California at Los Angeles.

[§] University of Vermont.

[||] Departments of Chemistry and Materials, University of California at Santa Barbara.

[⊥] Department of Chemical Engineering, University of California at Santa Barbara.

[∇] University of Oslo.

[#] Brookhaven National Laboratory.

[○] Departement de Chimie Physique Sciences II.

(1) Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature* **1992**, *359*, 710. Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowicz, M. E.; Kresge, C. T.; Schmitt, K. T.; Chu, C. T.-W.; Olson, D. H.; Sheppard, E. W.; McCullen, S. B.; Higgins, J. B.; Schlenker, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 10834.

(2) Huo, Q.; Margolese, D. I.; Stucky, G. D. *Chem. Mater.* **1996**, *8*, 1147.

(3) Huo, Q.; Margolese, D. I.; Ciesla, U.; Feng, P.; Gier, T. E.; Sieger, P.; Leon, R.; Petroff, P. M.; Schüth, F.; Stucky, G. D. *Nature* **1994**, *368*, 317.

(4) Huo, Q.; Leon, R.; Petroff, P. M.; Stucky, G. D. *Science* **1995**, *268*, 1324.

(5) Ryoo, R.; Kim, J. M.; Ko, C. H.; Shin, C. H. *J. Phys. Chem.* **1996**, *100*, 17718.

(6) Bagshaw, S. A.; Prouzet, E.; Pinnavaia, T. J. *Science* **1995**, *269*, 1242.

10.1021/cm0003727 CCC: $20.00

ordered, nanoporous materials. These periodic porous silicas offer significant promise for a variety of size-selective applications ranging from separations to host–guest chemistry. Because the pore size and geometry are controlled by changes in organic and inorganic reagents, an exciting range of nanoscale structures can be produced.

Much progress has been made in understanding the synthesis of these complex materials. When oppositely charged silicates and surfactant are mixed under alkaline conditions (for example, when positively charged quaternary ammonium surfactants are combined with basic silicate oligomers), the formation has been shown to proceed through a cooperative self-assembly process. Ion exchange of polycharged silicate oligomers for the monovalent counterions of the surfactant is driven by electrostatic considerations.[10,11] This ion exchange reduces the repulsion between surfactant micelles and allows the system to cooperatively self-organize. At the same time, condensation of the silicate oligomers provides a route to kinetic trapping that locks the structure in place.[12] Thus, the interplay between kinetic and energetic (electrostatic) factors determines the final structure of these materials during synthesis.

The energetics of self-organization can be thought of in two parts. One part is the packing of the organic surfactant,[2,13] and the other part is charge density matching between the surfactant and the silica.[12] If the silica is highly charged, a high density of surfactant molecules is required to provide counter charges. This high density is most effectively produced by a structure with a low (or negative) curvature at the silica/surfactant interface.[13] Thus, surfactant headgroup density can help determine the overall composite structure. At the same time, the surfactant must pack to fill space and thus maximize favorable van der Waals interactions between the hydrophobic tails while avoiding high-energy repulsive interactions between the charged or polar headgroups. The packing of surfactant molecules has been quantified through the use of the packing parameter (g),[13] which is the ratio of the surfactant molecular volume (V) to the product of the effective headgroup area (a_o) and the effective surfactant length (l_c); $g = V/(a_o l_c)$. The a_o parameter is related to both the size and charge on the surfactant headgroup and is affected by the electrostatic environment around the surfactant headgroup. The l_c parameter is related to the mean length of the alkyl chain. Large surfactant headgroups tend to yield small g values (<1/3), which result in conical effective surfactant shapes. Cones can efficiently pack into spherical micellar structures with high interfacial curvatures.[3,4] A larger g value (1/3 to 1/2) results in surfactant volumes in the shape of truncated cones that efficiently pack into lower curvature rodlike structures or cylindrical micelles. Cylindrical micelles are the building blocks for the $p6mm$ 2-dimensional hexagonal structure.[2] A g value of 1 corresponds to a cylindrical molecular shape. Cylinders can effectively pack into bilayers, which are the building blocks for zero-curvature lamellar structures. Packing parameters greater than 1 produce inverse structures with negative curvatures, such as the inverse hexagonal phase. Between $g = 1/2$ and $g = 1$, some nonperiodic vesicular or spongelike structures are observed.[7] Near $g = 2/3$ to 3/4, however, the 3-dimensional periodic bicontinuous cubic phase ($Ia3d$) is found.

Synthetic studies have confirmed that many of these ideas (kinetic/energetic interplay, charge density matching, favorable packing) can be used to understand what phases will form from a given synthesis mixture.[12,14] In particular, the packing parameter formalism has provided insight into understanding what phases can be synthesized using specifically designed surfactants.[2] In this paper we address a new question: Can these same ideas be used to understand the accessible phases of already formed composites? In the experiments presented here, we follow phase transformations in already synthesized silica surfactant composites using hydrothermal conditions. X-ray diffraction experiments were performed in situ while the composite was heated to follow the course of the transformation. Previous in situ studies on mesostructured silicas have provided strong evidence that the cross-linked inorganic framework dominates the overall kinetics of transformation.[15] By modifying this framework, transition kinetics can be altered in a predictable manner. In these experiments, we show that surfactant packing and charge density matching not only are important during the initial synthesis but also play a dominant role in controlling the accessible phases in fully formed composites. By understanding factors affecting kinetic metastability of the fully formed materials, silica/surfactant composites can be optimized for specific applications, particularly in cases where reactive conditions are found (i.e., high temperature, damp or wet environments, elevated pH).

Experimental Section

Samples Heated in Water. The silica/surfactant composites used in these experiments were synthesized by established wet chemical techniques.[2] Samples were produced for two types of high-temperature diffraction experiments: those in which samples were heated in water and those in which samples were heated in their high-pH synthesis solutions. Samples that were heated in water were synthesized up to 1 month prior to the high-temperature diffraction experiments and were stored as powders. Hexagonal ($p6mm$) composites made with a 20-carbon quaternary ammonium surfactant [$CH_3(CH_2)_{19}N(CH_3)_3Br$] were synthesized by dissolving 0.23 g of the surfactant in a warmed mixture of 19.9 g of H_2O and 3.24 g of a 2 mol/kg NaOH solution. Tetraethyl orthosilicate (TEOS; 1.93 g) was added to the solution, and the mixture was stirred for 30 min at room temperature.[2] The resulting powders were filtered, washed with water, and dried in air. Lamellar composites were synthesized by dissolving 0.492 g

---

(7) McGrath, K. M.; Dabbs, D. M.; Yao, N.; Aksay, I. A.; et al. *Science* **1997**, *277*, 552.

(8) Templin, M.; Franck, A.; DuChesne, A.; Leist, H.; Zhang, Y.; Ulrich, R.; Schädler, V.; Wiesner, U. *Science* **1997**, *278*, 1795.

(9) Zhao, D. Y.; Feng, J. L.; Huo, Q. S.; Melosh, N.; Chmelka, B. F., Stucky, G. D. *Science* **1998**, *279*, 548.

(10) Firouzi, A.; Kumar, D.; Bull, L. M.; Besier, T.; Sieger, P.; Huo, Q.; Walker, S. A.; Zasadzinski, J. A.; Glinka, C.; Nicol, J.; Margolese, D.; Stucky, G. D.; Chmelka, B. F. *Science* **1995**, *267*, 1138.

(11) Firouzi, A.; Atef, F.; Oertli, A. G.; Stucky, G. D.; Chmelka, B. F. *J. Am. Chem. Soc.* **1997**, *119*, 3596.

(12) Monnier, A.; Schüth, F.; Huo, Q.; Kumar, D.; Margolese, D.; Maxwell, R. S.; Stucky, G. D.; Krishnamurty, M.; Petroff, P.; Firouzi, A.; Janicke, M.; Chmelka, B. F. *Science* **1993**, *261*, 1299.

(13) Israelachvili, J. N. *Intermolecular and Surface Forces*, 2nd ed.; Academic Press: London, 1992.

(14) Linden, M.; Schunk, S. A.; Schüth, F. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 821.

(15) Gross, A. F.; Ruiz, E. J.; Tolbert, S. H. *J. Phys. Chem. B* **2000**, *104*, 5448.

of a 16-carbon quaternary ammonium surfactant [$CH_3(CH_2)_{15}N(CH_3)_3Br$, CTAB] and 0.168 g of the cosolvent 1,3,5-trimethylbenzene in 5.4 g of water. A mixed silica solution was used that included sodium silicate (1.29 g used, SiO_2:Na_2O = 2.00, 35.96 wt % SiO_2), tetramethylammonium hydroxide [TMAOH]/silicate (1.0 g used, H_2O:SiO_2:TMAOH = 33.6:1.0:0.5), and pure cab-o-sil (0.17 g used).[2] The silica solution and surfactant solution were thoroughly mixed and then heated at 100 °C for 5.5 h. The resulting composite was filtered, washed with water, and dried in air. Immediately before X-ray diffraction experiments were performed, all composites (hexagonal and lamellar) were mixed with water at a ratio of 10:1, wt of H_2O: wt of composite.

Samples Heated in the High-pH Synthesis Solution. Hexagonal samples, which were heated in the high-pH synthesis solution, were synthesized immediately prior to high-temperature diffraction experiments. These composites were made by dissolving 0.16 g of CTAB in a solution of 7.84 g of H_2O and 1.0 g of 2 M NaOH. TEOS (0.77 g) was added, and the composite was stirred at room temperature for times ranging from 50 min to 14 h.

In Situ X-ray Diffraction. High-temperature X-ray diffraction experiments were performed on bending magnet beamline X7b at the National Synchrotron Light Source (NSLS). The details of the real time diffraction setup have been presented elsewhere and will only be summarized here.[16] Samples were loaded into a 1 mm quartz capillary fitted with a graphite ferrule so that a nitrogen back-pressure of 180 psig could be applied to the sample. The applied pressure was used to keep the sample from boiling to temperatures in excess of 180 °C. Samples were heated with a feedback-controlled hot air stream that utilized a thermocouple and a PID temperature controller. The temperature drop between the thermocouple and the sample was calibrated using the melting point of sulfur. Samples were heated under linear temperature ramps, followed in some cases by high-temperature holds. Ramp rates ranged from 0.4 to 4.5 °C/min. At ramp rates higher than 4.5 °C/min, stable heating could not be obtained. Real time powder diffraction data were obtained by scanning a Fuji image plate behind a set of fixed slits. The linear scan rate and pixel positions on the plate were converted to heating times. An X-ray wavelength of 1.41 Å was utilized for samples heated in water, while an X-ray wavelength of 1.50 Å was used for samples heated in the high-pH synthesis solutions.

Structural Rearrangements in Materials Suspended in Water

Hexagonal-to-Lamellar Transformations. Figure 1 shows an example of real time X-ray diffraction data obtained on a composite synthesized in the *p*6*mm* hexagonal structure using a 20-carbon surfactant. The composite was suspended in water, and diffraction data were obtained as the sample temperature was ramped from 25 to 160 °C under hydrothermal conditions. At early times, the silica/surfactant composite was observed to have a hexagonal structure, as indicated by the four-peak pattern with peak spacing given by 1, $\sqrt{3}$, 2, and $\sqrt{7}$. As the composite was heated (~60 min or 115 °C in this case), the hexagonal peaks disappeared and were replaced by a set of evenly spaced peaks that could be indexed to a lamellar structure. For these materials, the transformation was observed to be discontinuous. That is, even for symmetry-related peaks such as $(100)_{hex}$ and $(100)_{lam}$ or $(200)_{hex}$ and $(200)_{lam}$, there was a sharp jump in peak position at the phase transition point. Unfortunately, a unit cell volume could not be calculated from the data presented in Figure 1 because of the low dimensionality of the phases involved, and so it was not possible to determine concretely if there was a discontinuous volume change at the transition point. The sharp changes in diffraction peak positions, however, suggest some type of discontinuous change in composite structure at the structural transition point.

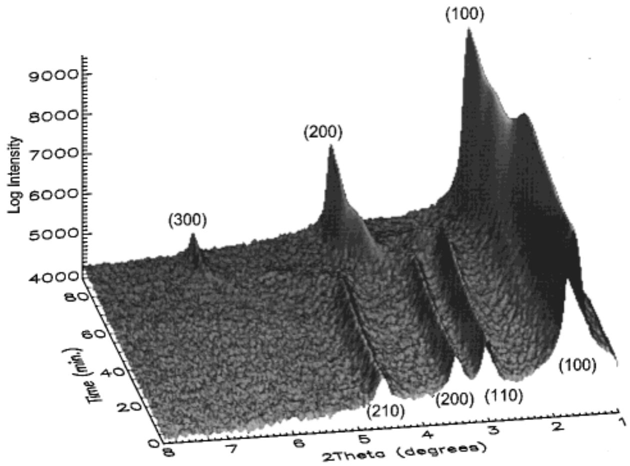

Figure 1. Real time X-ray diffraction data showing a hexagonal-to-lamellar phase transformation in a silica/surfactant composite synthesized with a 20-carbon quaternary ammonium surfactant and heated in water. The temperature was ramped from 25 to 160 °C at a rate of 1.5 °C/min. The data are plotted from right to left so that diffraction peaks do not overlap the axes. Hexagonal peaks disappear and are replaced by lamellar peaks at approximately 60 min or 115 °C. Note the discontinuous nature of the transformation.

The transformation can be understood by considering the *g* parameter of a quaternary ammonium surfactant with a 20-carbon surfactant tail. At room temperature, the *g* value is presumed to be between 1/3 and 1/2 because the composite was formed with a *p*6*mm* hexagonal periodicity. As the material was heated, however, the conformational disorder of the surfactant tail increased, increasing the surfactant molecular volume and increasing the *g* value. A schematic of this process is shown in Figure 2a, inset. At sufficiently high temperatures, a hexagonal-to-lamellar phase transformation was observed, apparently driven by changes in the surfactant packing. Support for this idea is found by examining shorter chain surfactants: no transformations are observed when similar composites made with 16-carbon or shorter surfactants are heated under hydrothermal conditions in water.[2] These results indicate that the same ideas of surfactant packing which appear to dominate silica/surfactant composite synthesis also play a major role in determining the observed phases in fully formed material.

While surfactant packing appears to provide the driving force for rearrangement, significant kinetic barriers still exist in these materials. For example, the rearrangement is completely irreversible. At any point in the heating cycle, the material can be cooled back to room temperature with no reverse transformation. Such behavior was caused in part by chemical changes in the nature of the composite (such as silica condensation) during heating and is consistent with the nonequilibrium character of this structural rearrangement.[17] Kinetic factors should also play a role in this irreversibility, and an estimate of the magnitude of such

---

(16) Norby, P. *J. Am. Chem. Soc.* **1997**, *119*, 5215. Norby, P. *J. Appl. Crystallogr.* **1997**, *30*, 21. Norby, P.; Nørlund Christensen, A.; Hanson, J. C. *Inorg. Chem.* **1999**, *38*, 1216.

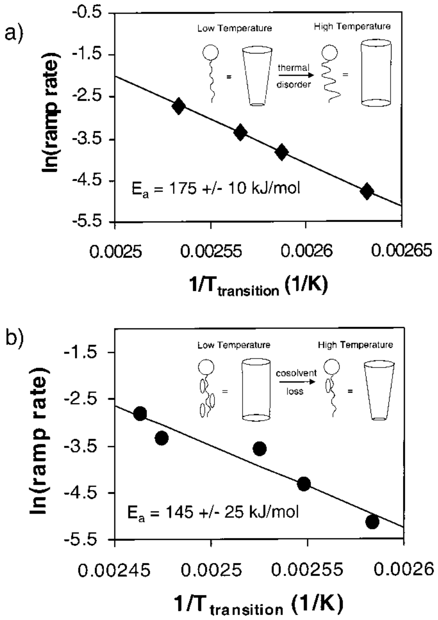

Figure 2. Plots of $1/T_{\text{transition}}$ versus ln(ramp rate) are used to calculate transformation activation energies using the Ozawa relation. (a) Data and fits obtained for a hexagonal-to-lamellar phase transition. The inset shows a schematic of the changes in surfactant geometry and packing parameter that are believed to drive the transformation from the low-temperature hexagonal structure to the high-temperature lamellar phase. (b) Data and fits obtained for a lamellar-to-hexagonal phase transition. The inset shows a schematic of the cosurfactant loss that results in a net change in shape and packing parameter for the organic component of the composite. This change is believed to drive the transformation from the low-temperature lamellar structure to the high-temperature hexagonal phase.

barriers to rearrangement can be obtained from time-dependent diffraction data.[15] The course of a transition can be monitored by following changes in diffraction peak positions with time or temperature. For these experiments, the midpoint of the sharp change in the (100) peak position (Figure 1) was assigned to the characteristic transition time or transition temperature.

Previous experiments on mesoporous silicas[15,18] and a range of other solids[19] indicate that activation energies can be estimated by following the shift in transition temperature with temperature ramp rate. At faster temperature ramp rates, the transformation cannot keep pace with the changing temperature, and so the transition is observed to occur at higher temperatures. This type of data has been used to extract activation energies for transformation in silica/surfactant composites using the Ozawa relation, which combines simple Arrhenius activation energies with a linear temperature ramp to remove the explicit time dependence. Integration over T further removes the details of the rate law and produces an equation that simply relates the activation energy for transition to the temperature ramp rate and the observed transition temperature [ln(ramp rate) $= -E_a/RT_{\text{transition}} + c$; see Figure 2 for experimental plots].[19] The idea is similar to that used to calculate activation energies for electron-transfer reactions from variable ramp rate cyclic voltammetry data. For mesoporous silicas, good agreement has been found between activation energies calculated using the Ozawa equation and those calculated from isothermal data using the Avrami equation[20] for the rate law combined with traditional isothermal Arrhenius kinetics.[18] For these experiments, a value of $E_a = 175 \pm 10$ kJ/mol was obtained.[21] This large value (a significant fraction of the Si−O bond energy)[22] is consistent with past studies on mesoporous silicas[15,18] and indicates that substantial rearrangement of the silica framework is required for the phase change to occur.

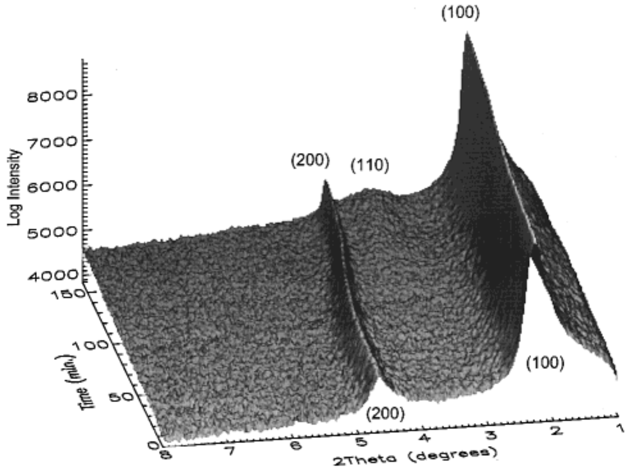

Figure 3. Real time X-ray diffraction data corresponding to a lamellar-to-hexagonal phase transformation in a silica/surfactant composite synthesized using CTAB as the surfactant and TMB as the cosurfactant. The sample was heated in water, and the temperature was ramped from 25 to 160 °C at a rate of 0.9 °C/min. The data are plotted from right to left so that diffraction peaks do not overlap the axes. The $(110)_{\text{hexagonal}}$ peak is observed to appear at approximately 120 min or 135 °C. Note the continuous nature of the transformation.

Lamellar-to-Hexagonal Transformations. When a lamellar phase synthesized using CTAB (16-carbon quaternary ammonium surfactant) and trimethylbenzene (TMB) as a cosurfactant was heated under hydrothermal conditions, a transformation to a *p*6*mm* hexagonal phase was observed (Figure 3).[2] The patterns started with two evenly spaced peaks, corresponding to the (100) and (200) reflections of a layered structure. At about 80 °C (60 min) these peaks began to shift toward smaller 2θ values, possibly indicating the appearance of a modulated lamellar phase. Although the symmetry of the composite remained lamellar, incoherent undulation of the layers resulted in a larger apparent layer-to-layer separation for the same surfactant chain length and silica wall thickness. Modulated and

---

(17) Navrotsky A.; Petrovic I.; Hu Y. T.; Chen C. Y.; et al. *Microporous Mater.* **1995**, *4*, 95. Petrovic, I.; Navrotsky, A.; Chen, C. Y.; Davis, M. E. "Zeolites and Related Microporous Materials: State of the Art 1994." *Stud. Surf. Sci. Catal.* **1994**, *84*, 677.

(18) Gross, A. F.; Le, V. H.; Kirsch, B. L.; Tolbert, S. H. *Langmuir*, **2001**, *17*, 3496.

(19) Ozawa, T. *Bull. Chem. Soc. Jpn.* **1965**, *28*, 1881

(20) Avrami, M. *J. Chem. Phys.* **1939**, *7*, 1102; **1940**, *8*, 212; **1941**, *9*, 177.

(21) The error in the linear fit is quite small (~±2 kJ/mol). The reported error is thus an estimate of both this error and of systematic errors in the slope due to the way that the characteristic transition point was chosen.

(22) West, A. R. *Solid State Chemistry and Its Applications*; John Wiley & Sons: Chichester, 1984.

perforated lamellar phases have been observed both experimentally and through simulations as intermediates in lamellar-to-hexagonal transitions in diblock copolymers.[23,24] At 130 °C (117 min) a third peak started to grow between the first two. The new peak position was $\sqrt{3}$ times the fundamental peak position. The combination of three peaks with a 1, $\sqrt{3}$, 2 spacing pattern could be indexed to the first three peaks of a hexagonal structure (100, 110, 200).

Note that the peak width in the (110) direction was much broader than that of the (100) and (200) diffraction peaks. This suggests that the newly formed hexagonal periodicity did not have as long a coherence length as the original lamellar structure.[25] As the lamellar planes corrugated to form the hexagonal structure, they apparently did so imperfectly, and so the hexagonal periodicity that developed was not well ordered. In addition, in contrast to the data presented in Figure 1 for hexagonal-to-lamellar transformation, this lamellar-to-hexagonal transformation (Figure 3) did not show any discontinuous changes, only smooth shifts in peak positions and the gradual appearance of a new diffraction peak. While the low symmetry of the phases involved again did not allow determination of whether there was a discontinuous change in composite volume upon transformation, the smooth evolution of the diffraction peaks indicated that in this transition there might be a continuous evolution from a lamellar to a modulated lamellar to a hexagonal structure, much like those observed in diblock copolymer systems.[23,24]

The lamellar-to-hexagonal transformation can also be understood by examining surfactant packing.[13] TMB is known to be effective at swelling the hydrophobic regions of liquid crystal structures and has been used extensively to swell silica/surfactant composites to form larger pore materials.[1,4] Because TMB tends to associate with the hydrophobic surfactant tail, it can change the effective “surfactant shape” (g parameter) by enlarging the surfactant volume without increasing the headgroup area or tail length. This swelled geometry (combined with some thermal disorder) results in composites with a lamellar structure, indicating a large g value (near 1). When the composite is suspended in water for hydrothermal treatment, there is initially a large concentration gradient produced because there is significant TMB in the hydrophobic region of the composite and essentially no TMB in the water phase. The solubility of small aromatic compounds in water increases rapidly with increasing temperature,[26] in part because of a decrease in dielectric constant and thus polarity of the water at higher temperatures.[27] The result of hydrothermal treatment is to drive TMB out of the composite and into the aqueous phase, a change that lowers the value of g, resulting in a transformation to a hexagonal structure. A schematic of this process is shown in the Figure 2b inset.

Changes in silica/surfactant composite structure due to the reapportioning of organic additives have been well established during composite synthesis.[28] Similar transformations have also been observed in silicate/surfactant liquid crystals, although in the liquid crystal case silicate polymerization does not occur and the transformations are reversible.[10,11] Thus, we again find that changes in surfactant packing can drive rearrangements in materials with a cross-linked inorganic framework, demonstrating the importance of surfactant packing in determining composite structure.

As with the hexagonal-to-lamellar transformations described earlier, the irreversible nature of this structural rearrangement suggests significant barriers to transformation. These barriers are again estimated by examining how the transformation temperature varies with ramp rate. As seen in Figure 3, the diffraction peaks were fairly constant until about 75 °C, at which point the peak intensity began to decrease and the peak position to shift to a lower angle, indicative perhaps of the formation of a modulated or perforated lamellar structure.[24] Just above 135 °C, the peak intensity again approached a constant value, the peak position stopped shifting, and the (110) diffraction peak appeared. We thus used changes in the fundamental diffraction peak intensity and position to assign a characteristic lamellar-to-hexagonal transition point. The shift in this transition point with temperature ramp rate can again be used in conjunction with the Ozawa relation to determine an activation energy for the transformation. The value of $E_a = 145 \pm 25$ kJ/mol is similar to that obtained for hexagonal-to-lamellar transformations.

Continuous versus Discontinuous Transformations. The activation energies for hexagonal-to-lamellar and lamellar-to-hexagonal transformations are similar; in addition the driving force for both transitions can be explained in terms of packing constraints on the organic component of the composites. As discussed above, however, the hexagonal-to-lamellar transformation was discontinuous with a clear break and discrete shift appearing between the low-temperature and high-temperature phases. By contrast, for the lamellar-to-hexagonal transformation, the diffraction peaks evolved smoothly from the lamellar to the hexagonal phase. Although the chemical details of the two systems (Figures 1 and 3) were different, the symmetry relationships between the hexagonal and lamellar phases were, obviously, the same in both cases, and both were consistent with a continuous evolution of nanoscale symmetries. We note that the cross-linked nature of the silica framework should *not* allow for a continuous evolution of atomic scale geometries. Even during a transformation that appears continuous on the nanometer length scale, abrupt changes in silica bonding must take place. Because there are no symmetry constraints linking the atomic and nanometer length scales, however, discontinuous changes in atomic scale bonding do not necessitate discontinuous changes in nanometer scale structure. Given these concepts, why was one

---

(23) Hamley, I. W.; Koppi, K. A.; Rosedale, J. H.; Bates, F. S.; Almdal, K.; Mortensen, K. *Macromolecules* **1993**, *26*, 5959.

(24) Qi, S.; Wang, Z.-G. *Phys. Rev. E* **1997**, *55*, 1682.

(25) Guinier, A. *X-ray Diffraction In Crystals, Imperfect Crystals, and Amorphous Bodies;* Lorrain, P., Lorrain, D. S−M., Translators; W. H. Freeman: San Francisco, 1963.

(26) Smith, G. A.; Christian, S. D.; Tucker, E. E.; Scamehorn, J. F. *J. Colloid Interface Sci.* **1988**, *130*, 254.

(27) *CRC Handbook of Chemistry & Physics*; Weast, R. C., Ed.; CRC Press: Boca Raton, FL, 1986.

(28) Lindén, M.; Ågren, P.; Karlsson, S.; Bussian, P.; Amenitsch, H. *Langmuir* **2000**, *16*, 5831. Ågren, P.; Lindén, M.; Rosenholm, J. B.; Blanchard, J.; Schüth, F.; Amenitsch, H. *Langmuir* **2000**, *16*, 8809. Ågren, P.; Lindén, M.; Rosenholm, J. B.; Schwarzenbacher, R.; Kriechbaum, M.; Amenitsch, H.; Laggner, P.; Blanchard, J.; Schüth, F. *J. Phys. Chem. B* **1999**, *103*, 5943.

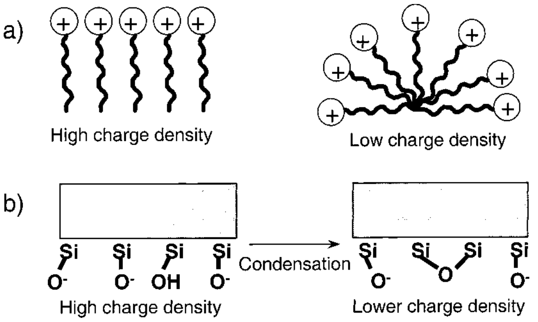

Figure 4. Schematic representation of the changes in charge density that occur in silica/surfactant composites during phase transformations. (a) Upon going from a zero-curvature lamellar structure to a higher curvature hexagonal phase, a decrease in surfactant charge density is required. (b) During heating under hydrothermal conditions, silanol groups and deprotonated silanol groups can condense to liberate hydroxide ions and reduce the interfacial charge density. When these changes in charge density (a and b) occur together, a continuous phase transition is observed (e.g., lamellar-to-hexagonal). When these changes go in opposite directions (e.g., hexagonal-to-lamellar), a discontinuous transition is observed.

transformation continuous while the other was discontinuous? While the chemical differences between the two systems might contribute to the different transition kinetics, a more general explanation can be found by considering charge density matching at the silica/surfactant interface[12] in addition to packing of the organic component and the rigidity of the inorganic framework.

One can separately consider the changes in charge density in the organic and inorganic components of the composite during a transformation. The charge density associated with the surfactant is determined largely by the interfacial curvature of the assembly. A lamellar structure has no curvature, and so surfactant headgroups are close together, resulting in a relatively high charge density (Figure 4a, left). The hexagonal structure has a higher curvature, which allows the headgroups to be farther apart while maintaining van der Waals contacts with the surfactant tail. This results in a lower interfacial charge density for the surfactant in a hexagonal phase (Figure 4a, right). The silica framework must be negatively charged to balance the positive charge on the surfactants, and the most probable anionic species are deprotonated silanol groups (Figure 4b, left). Heating in water at near neutral pH should result in the slow condensation of these groups to form Si−O−Si linkages with the liberation of OH^- and some accompanying surfactant.[29] This resulted in a decrease in inorganic charge density as the materials were heated under hydrothermal conditions. Such a decrease has been confirmed by ex situ ^{29}Si MAS NMR experiments on similar composites heated in water under hydrothermal conditions.[15]

For a lamellar-to-hexagonal transformation, both the silica and surfactant evolve from a starting state with relatively high charge density to a final state with lower charge density. Because the changes are well matched, the composite can continuously evolve from the lamellar structure into the hexagonal phase. In the case of a hexagonal-to-lamellar transformation, by contrast, the charge density on the silica will decrease with hydrothermal treatment, but at the transition point the charge density of the surfactant must increase. Thus, these two processes are not well matched, and as a result a discontinuous transition occurs in which the surfactant must redistribute between the composite and the aqueous phase during the hexagonal-to-lamellar transformation.

We note that charge density matching was not a determining factor in the kinetics of these transformations. Hexagonal-to-lamellar rearrangements occur on a reasonable time scale, although they are not facile with respect to changes in interfacial charge density. The balance of charge at the organic/inorganic interface can, however, affect the dynamics of these transitions, allowing some transitions to occur more rapidly because they require less surfactant reapportioning to accommodate changes in charge density during the transformation. Note that the activation energy for the lamellar-to-hexagonal transformation is actually lower than the activation energy for the hexagonal-to-lamellar phase change. While the difference in the numbers may not be significant within the error of the method, it should be noted that the initial lamellar phase was synthesized at 100 °C for 5.5 h while the initial hexagonal phase was synthesized at room temperature for only 30 min. Previous studies on phase transitions in silica/surfactant composites indicate that the activation barrier for rearrangement should scale with the initial degree of framework polymerization.[15] On the basis of those results, the lamellar-to-hexagonal transformation would be expected to have a much *higher* activation energy than the hexagonal-to-lamellar rearrangement. The fact that this trend was not observed testifies to the importance of charge density matching in controlling the activation energy for structural rearrangements in these composites.

Structural Rearrangements in Materials Heated in the High-pH Synthesis Solution

While the chemistry associated with transformations occurring in water is simpler, the study of phase changes occurring in the high-pH synthesis solution is, in many ways, more insightful for understanding the complicated synthesis space of these materials. For example, *Ia*3*d* cubic composites are materials that are frequently very difficult to produce, with many contradictory reports of optimal synthesis conditions. The advantages of the bicontinuous cubic structure for applications where diffusion is important can be significant, however. Because the material has 3-dimensional periodicity, pore access cannot be as easily blocked. Synthesis field maps indicate that a diverse set of phases can be formed in the region of compositional parameter space that is used to produce the *Ia*3*d* composite structure. Therefore, small differences in starting composition result in very different final products.[30] The foundation for this complex synthesis space probably lies in the fact, shown by a number of studies,

---

(29) Iler, R. K. *The Chemistry of Silica: Solubility, Polymerization, Colloid and Surface Properties, and Biochemistry*; Wiley: New York, 1979.

(30) Behrens, P.; Glaue, A.; Haggenmuller, C.; Schechner, G. *Solid State Ionics* **1997**, *101*, 255.

that the *Ia*3*d* phase is formed via a phase transition route during high-temperature hydrothermal synthesis.[31−34] The details of these phase transitions, however, appear to depend on the specific chemical systems used. Gallis[31] and McGehee[32] both reported a direct *p*6*mm* hexagonal to *Ia*3*d* cubic transition under optimized conditions. Xu[33] and Pevzner,[34] however, observed various versions of a hexagonal-to-lamellar-to-cubic transformation. Gallis[31] also observed the formation of a lamellar phase under certain conditions. Synthesis composition, reaction time, and reaction temperature were all shown to be important variables in controlling phase evolution.

In most of these cases, the transition was found to be dominated by changes in the organic packing of the composite—in this case, ethanol, liberated from the hydrolysis of TEOS.[31,33,34] The ethanol is believed to associate with the surfactant in the composite, increasing the surfactant tail volume and thus increasing *g*. A transformation from hexagonal ($g = 1/3$ to 1/2) to cubic ($g = 2/3$ to 3/4) or to lamellar ($g \approx 1$) was thus observed when samples were heated. If sodium silicate was used as a silica source[31,33] or if the ethanol was allowed to completely evaporate,[34] the hexagonal phase remained stable at high temperature and the cubic phase was not observed. If, however, ethanol was added to the synthesis mixture, the *Ia*3*d* cubic phase was again produced via a phase transition process.[31]

To examine the factors governing the hexagonal-to-cubic transformation, hexagonal composites were synthesized at room temperature using TEOS as a silica source under conditions similar to those shown by ex situ experiments to produce a hexagonal-to-cubic phase transformation.[31] The composites were allowed to react at room temperature for variable lengths of time. Nanoscale periodicity was then monitored in real time during sample heating. To observe the most diverse range of stability, samples were first ramped moderately slowly from room temperature to 145 °C. Samples were then held at 145 °C for 1/2 to 1 h. Data for the longest reaction time are shown in Figure 5. This sample was reacted at room temperature for 14 h prior to hydrothermal heating. The composite initially had a hexagonal structure; approximately 20 min after reaching 145 °C, the hexagonal peaks abruptly disappeared and were replaced by evenly spaced peaks, indicating the presence of a lamellar phase. No *Ia*3*d* cubic phase was observed. Note that, for Figures 5−8, the vertical scale is plotted as linear rather than as logarithmic intensity. Although this makes the higher order peaks harder to see, it facilitates meaningful comparisons of peak intensities.

Shorter reaction times are shown in Figures 6−8. When the room-temperature reaction time was reduced, *Ia*3*d* cubic peaks were observed in the real time X-ray diffraction profiles. Figure 6 shows data for an initially hexagonal composite heated under the same temperature program as that used in Figure 5 (1 h ramp, 1 h hold) but allowed to react at room temperature for only 3 h prior to heating. Just as the temperature reached 145 °C, a lamellar phase appeared. In this case, however, there was significant coexistence between the hexagonal and lamellar structures. After another 15 min at 145 °C, the untransformed hexagonal material converted to the *Ia*3*d* cubic structure. In the final product, however, the intensity of the lamellar (100) peak was about 70% higher than the intensity of the cubic (211) peak, showing that a large fraction of the final product did not possess the *Ia*3*d* cubic structure.

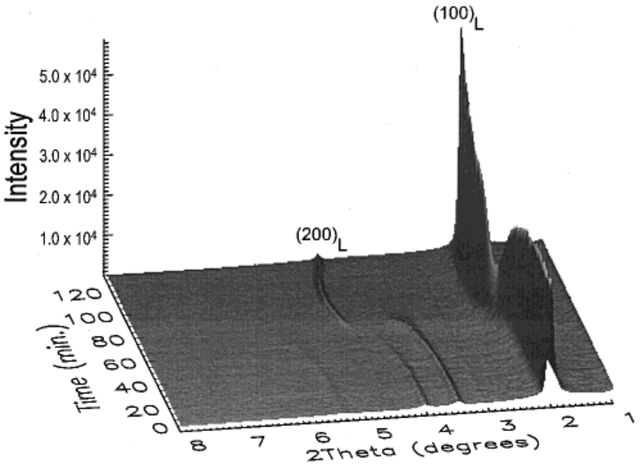

Figure 5. Real time X-ray diffraction data for a hexagonal-to-lamellar phase transformation in a silica/surfactant composite synthesized using CTAB and TEOS and heated in the high-pH synthesis solution. The sample was allowed to react for 14 h at room temperature before heating. For this experiment, the temperature was ramped from 25 to 145 °C at a rate of 2.0 °C/min, followed by a hold at 145 °C for 1 h. The data are plotted from right to left so that diffraction peaks do not overlap the axes. No reflections corresponding to the *Ia*3*d* bicontinuous cubic structure are observed.

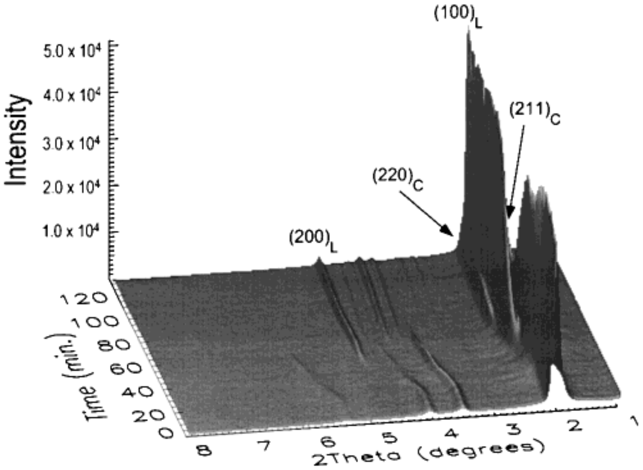

Figure 6. Real time X-ray diffraction data showing a transformation from a hexagonal phase to a mixture of cubic and lamellar structures for a silica/surfactant composite synthesized using CTAB and TEOS and heated in the high-pH synthesis solution. The sample was allowed to react for 3 h at room temperature before heating. For this experiment, the temperature was ramped from 25 to 145 °C at a rate of 2.0 °C/min, followed by a hold at 145 °C for 1 h. At the end of the experiment, reflections from both the *Ia*3*d* bicontinuous cubic structure and a lamellar phase are observed. The intensity of the lamellar (100) diffraction peak is about 1.7 times greater than the intensity of the fundamental (211) cubic peak.

---

(31) Grallis, K. W.; Landry, C. C. *Chem. Mater.* **1997**, *9*, 2035.

(32) McGehee, M. D.; Gruner, S. M.; Yao, N.; Chun, C. M.; Navrotsky, A.; Aksay, I. A. In *Proceedings of the 52nd Annual Meeting of the Microscopy Society of America*; Bailey, G. W., Garratt-Reed, A. J., Eds.; San Francisco Press: San Francisco, 1994; p 448.

(33) Xu, J.; Luan, Z. H.; He, H. Y.; Zhou, W.-Z.; Kevan, L. *Chem. Mater.* **1998**, *10*, 3690.

(34) Pevzner, S.; Regev, O. *Microporous Mesoporous Mater.* **2000**, *38*, 413.

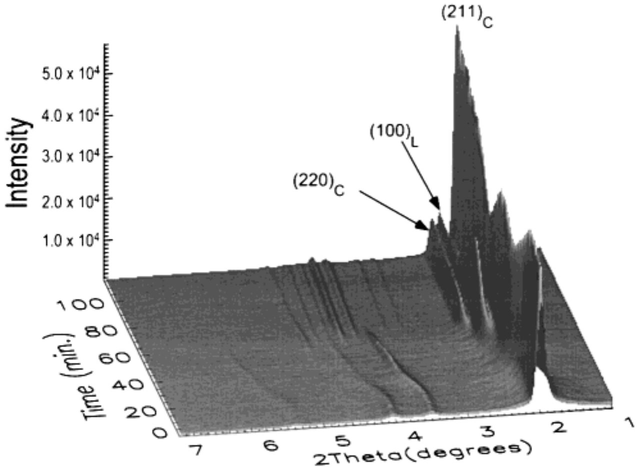

Figure 7. Real time X-ray diffraction data showing a transformation from a hexagonal phase to a mixture of cubic and lamellar structures for a silica/surfactant composite synthesized using CTAB and TEOS and heated in the high-pH synthesis solution. The sample was allowed to react for 50 min at room temperature before heating. For this experiment, the temperature was ramped from 25 to 145 °C at a rate of 2.0 °C/min, followed by a hold at 145 °C for 1 h. At the end of the experiment, reflections from both the *Ia*3*d* bicontinuous cubic structure and a lamellar phase are observed. The intensity of the fundamental (211) cubic peak is about 5 times greater than the intensity of the lamellar (100) diffraction peak.

Phase progression for a composite with a room temperature reaction time of only 1 h is shown in Figure 7. Again, the same temperature profile (1 h ramp, 1 h hold) was utilized. Like the data shown in Figures 5 and 6, a hexagonal structure was observed at low temperature. Again part of the material was observed to transform discontinuously to a lamellar phase, this time about 5 min before the composite reached 145 °C. In this case, however, the majority of the material was found to transform less than 10 min later in a continuous manner into a cubic structure. Note how the third hexagonal diffraction peak, $(200)_{\text{hexagonal}}$, smoothly evolved into the seventh cubic diffraction peak, $(422)_{\text{cubic}}$. The same trend was seen with the $(100)_{\text{hexagonal}}$ peak evolving continuously into the $(211)_{\text{cubic}}$ peak. The symmetry-allowed evolution of hexagonal liquid crystal phases into cubic phases has been well studied in pure surfactant/water systems,[35] and this type of phase epitaxy has been observed.[36,37] The details of the transformation mechanism and the symmetry relations among the hexagonal, cubic, and lamellar phases has been reported separately.[38] The final material in this experimental run was dominated by the *Ia*3*d* cubic phase, with the intensity of the fundamental $(211)_{\text{cubic}}$ peak being approximately 5 times larger than that of the lamellar fundamental, $(100)_{\text{lam}}$. The results suggested that shorter reaction times favor transformation to the cubic structure.

This simple idea does not hold up, however, when short room-temperature reaction times are combined with faster ramp rates. Figure 8 shows data obtained on a sample that was reacted at room temperature for 50 min prior to heating. To accelerate the heating process, the sample was heated quickly from room temperature to 90 °C (10 min) and then more slowly from 90 to 145 °C (30 min). The sample was finally held at 145 °C for an addition 30 min. In contrast to the trend established in Figures 5−7, no *Ia*3*d* cubic phase was observed in this reaction. Instead, a clean and discrete transformation was seen from a low-temperature hexagonal structure to a high-temperature lamellar structure. No hexagonal/lamellar phase coexistence was observed, and there was no sign of cubic material in the final product. In addition, the transformation took place before the final temperature was reached, at only 110 °C. This result contradicts the simple notion that less condensed composites favor the formation of cubic structures.

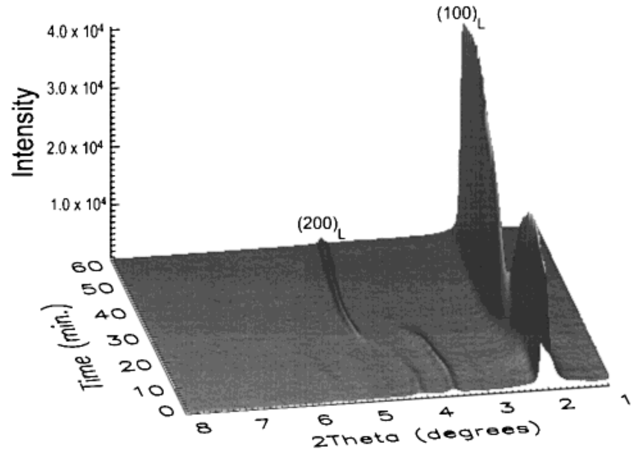

Figure 8. Real time X-ray diffraction data showing a hexagonal-to-lamellar phase transformation in a silica/surfactant composite synthesized using CTAB and TEOS and heated in the high-pH synthesis solution. The sample was allowed to react for 50 min at room temperature before heating. For this experiment, the temperature was ramped from 25 to 76 °C at a rate of 5.1 °C/min. The temperature was then increased from 76 to 145 °C at a rate of 2.3 °C/min, followed by a hold at 145 °C for 30 min. Again, no reflections from the *Ia*3*d* bicontinuous cubic structure are observed.

Previous experiments clearly indicate that partitioning of ethanol is at least in part responsible for the changes in the surfactant *g* parameter that drive the transformation.[31,33,34] Association of ethanol with the surfactant increases the hydrophobic volume, increasing the *g* parameter and driving the transformation to both the cubic and the lamellar structures. Differences in ethanol partitioning with reaction time are unlikely to completely explain the complex phase behavior observed here. Using the insight gained from following phase transformations in pure water systems, we hypothesize that the transformation to either cubic or lamellar structures must also be influenced by some combination of charge density matching effects and activation barriers.

Simple kinetic arguments can be used to explain the trends presented in Figures 5−7. After short reaction times at room temperature, silica/surfactant composites are not observed to have well cross-linked frameworks.[12] As the silica/surfactant composites are allowed to react at room temperature or high temperature (during a ramp), condensation of the framework can take place.

---

(35) Rancon, Y.; Charvolin, J. *J. Phys. Chem.* **1988**, *92*, 6339.

(36) Rancon, Y.; Charvolin, J. *J. Phys. Chem.* **1988**, *92*, 2646.

(37) Mariani, P.; Amaral, L. Q.; Saturni, L.; Delacroix, H. *J. Phys. II* **1994**, *4*, 1393.

(38) Landry, C. C.; Tolbert, S. H.; Grallis, K. W.; Monnier, A.; Stucky, G. D.; Norby, P.; Hanson, J. C. *Chem. Mater.* **2001**, *13*, 1600.

On the basis of kinetic experiments conducted on silica/surfactant composites heated in water and in fixed-pH aqueous solutions, such increased condensation should increase activation energies for transformation, resulting in higher transition temperatures and slower transition rates.[15,39] Clear signs of increasing activation energies are observed here— the hexagonal-to-lamellar transformation presented in Figure 5 began 20 min into the 145 °C hold, while that presented in Figure 8 occurred well below 145 °C (at 110 °C). Intermediate transition times are found in Figures 6 and 7.

A detailed study of the transition mechanism suggests that transformation from the hexagonal to the lamellar phase is simpler than transformation from the hexagonal to the cubic phase.[38] Fewer topological changes are needed to produce a lamellar structure, and so we hypothesize that this transition can occur even when a highly cross-linked framework results in a high activation energy for transformation. The fact that transformation from the hexagonal phase to the lamellar phase occurred at a lower temperature than transformation from the hexagonal to the cubic structure confirms the idea that the activation barrier for transformation to the lamellar phase was lower. The lamellar structure is thus the kinetically favored state. By contrast, when the activation energy was low, surfactant packing appeared to favor the cubic phase, apparently the kinetically disfavored but energetically favored product over the range of synthesis conditions used in Figures 5−7. These ideas still do not address why lamellar materials were found with short reaction times and fast heating rates, conditions that should have reduced activation barriers and favored energetically controlled products.

To explain Figure 8, additional phenomena need to be considered, in particular, the role of charge density matching. Because the reaction mixture used in these experiments was highly basic, the silica should have started out with a high charge density. Very high silica charge densities should favor transformation to a lamellar structure, which provides the highest possible surfactant charge density in a noninverted structure. The source of the high silica charge was deprotonated silanol groups, and thus the same condensation processes that increased the activation energy for transformation should also have decreased the charge density by removing silanol groups. This increase in silica condensation has been observed experimentally during the formation of *Ia*3*d* composites under hydrothermal conditions.[33] Two phenomena with opposite effects thus occur as the silica framework reacts: Reduction in silica charge density favors transformation to the cubic phase on energetic grounds on the basis of charge density matching, while increasing activation barriers make transformation to the cubic phase less favorable from a kinetic point of view. The result is the nonmonotonic trend observed in Figures 5−8.

The experiments presented here explored only one hydrothermal reaction temperature (145 °C). The interplay between kinetic and energetic factors described here suggests, however, that cubic phases could be formed with longer room-temperature reaction times if higher hydrothermal temperatures were used to overcome increasing activation energies. This result has been observed experimentally.[38]

Alternatively, higher pH in the synthesis mixture could be used to produce similar results at lower temperatures, a result that has also been observed.[33,34] In the experiments presented here, the base:silica ratio was approximately 0.20 and the final reaction temperature was 145 °C. Lower temperature, higher pH studies provide a key test of some of the ideas presented here. At higher pH, the silica charge density should be very high and thus should strongly favor the formation of a lamellar structure at early times. In agreement with this idea, experiments using base:silica ratios of 0.36−0.46 and reaction temperatures of only 100 °C clearly showed a transformation from a hexagonal structure to a lamellar phase at early reaction times.[33,34] Unlike the present case, however, where rapid silica polymerization quickly locked structures into place, the higher pH and lower temperature conditions allowed a subsequent transition back to the hexagonal structure and then on to the cubic phase as silica condensation reduced the charge density at the silica/surfactant interface. This second hexagonal structure was clearly observed in the work of Pevzner and Regev.[34] The small rise and partial fall of the lamellar phase observed in Figure 7 at intermediate times may result from a similar hexagonal-to-lamellar-to-hexagonal-to-cubic transformation. Note that, in Figure 6, where longer reaction times produce higher activation barriers, only a clean rise of the lamellar peaks was observed. The interplay between charge density reduction, changes in organic packing, and increased activation barriers for rearrangement thus appears to explain a wide range of highly complex and sometimes seemingly counterintuitive experimental data.

Conclusions

In this paper we used real time X-ray diffraction to address a range of questions concerning kinetic metastability in fully formed nanostructured silica/surfactant composites. In general, many of the same phenomena that are observed to be important in composite synthesis were found to control the accessible phases in the condensed materials. In particular, packing changes in the organic component of the composite played a dominant role, driving phase transformations under hydrothermal conditions in both pure water and high-pH synthesis solutions. While these transformations were driven by organic packing constraints, they were also inhibited by large kinetic barriers associated with the condensed silica walls. Activation energies as high as 170 kJ/mol were calculated from kinetic data for transformations occurring in water. Increases in activation energy with increased reaction time were also used to explain the dominance of hexagonal-to-lamellar phase transitions over hexagonal-to-cubic phase transformations at long reaction times.

An important concept throughout this work is the idea of charge density matching. Matching between the silica charge density and the surfactant charge density can affect both the observed phases and the dynamics of rearrangement. In transformations between hexagonal and lamellar structures, a continuous transformation

---

(39) Gross, A. F, Le, V. H., Tolbert, S. H. Unpublished data.

was observed when structural changes complemented polymerization-induced changes in charge density, while a discontinuous transition was observed if significant surfactant rearrangement was needed to accommodate a charge density change that went contrary to silica condensation. In transitions between hexagonal and cubic structures, charge density matching appeared to be responsible for destabilizing the cubic structure relative to the lamellar phase at short reaction times.

These experiments explore a range of concrete examples of the factors controlling structure in condensed silica/surfactant composites. By understanding these transformations, we hope to gain control over the observable phases of these unique nonequilibrium materials. Because of the large increase in kinetic barriers in condensed silica/surfactant composites, relative to those present during the initial synthesis process, a range of new phases may be accessible via solid−solid phase transition routes. By understanding the factors controlling these transitions, the potential for making new kinetically trapped phases continues to increase.

Acknowledgment. The research carried out at Brookhaven National Laboratory was supported under Contract DE-AC02-98CH10886 with the U.S. Department of Energy, Division of Chemical Sciences, Office of Basic Energy Sciences. This research was supported by the NSF under Grants DMR-9807180 and CHE-9626523 (S.H.T.) and Grants DMR 95-20971 and DMR 96-34396 (G.D.S.). S.H.T. is an Alfred P. Sloan Foundation Research Fellow.

CM0003727