

# Assembly of Mesoporous Lamellar Silicas with Hierarchical Particle Architectures

Peter T. Tanev, Ying Liang, and Thomas J. Pinnavaia\*

Contribution from the Department of Chemistry and Center for Fundamental Materials Research, Michigan State University, East Lansing, Michigan 48824-1322

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**Abstract:** A family of silica molecular sieves with lamellar frameworks and hierarchical structure (denoted MSU-V) was assembled from homogeneous solutions of neutral  $\text{H}_2\text{N}(\text{CH}_2)_n\text{NH}_2$  bolaamphiphiles ( $n = 12-22$ ) as the structure directors and tetraethylorthosilicate as the inorganic precursor. Optimal lamellar order was observed for four *as-synthesized* and *calcined* (550 °C) mesostructures when they were assembled at the following reaction temperatures ( $T$ , °C) and surfactant/silica ratios ( $R$ ) of  $T = 25$  °C,  $R = 0.26$  ( $\text{C}_{12}$ );  $T = 45$  °C,  $R = 0.20$  ( $\text{C}_{16}$ );  $T = 55$  °C,  $R = 0.15$  ( $\text{C}_{18}$ );  $T = 55$  °C,  $R = 0.11$  ( $\text{C}_{22}$ ). MSU-V silica assembled from the short  $\text{C}_{12}$  alkyl chain bolaamphiphile exhibited gallery-confined *micropores* (1.3 nm), but the derivatives prepared from the longer  $\text{C}_{16}$ – $\text{C}_{22}$  diamines showed gallery-confined *mesopores*. As the alkyl chain length of the bolaamphiphile surfactant increased from  $\text{C}_{16}$  to  $\text{C}_{22}$ , the size of the gallery-confined mesopores increased from 2.0 to 2.7 nm. The described synthetic strategy afforded hierarchical MSU-V structures with biomimetic multilamellar vesicular particle architectures. Distorted vesicular, plate, and spiral-ribbon shaped particles also were observed, particularly for the lamellar silica assembled from the  $\text{C}_{16}$  bolaamphiphile. The variation in morphologies was attributed to agitation effects during synthesis. MSU-V silica assembled from the  $\text{C}_{22}$  diamine was the least stable member of the series and partially decomposed upon calcination. Remarkably, surfactant removal by calcination did not affect the biomembrane-like, hollow disk morphology of the original *as-synthesized*  $\text{C}_{22}$  product. This bolaamphiphile assembly approach provides new opportunities for the preparation of *lamellar* mesoporous molecular sieves with hierarchical structures specifically tailored to applications as diverse as sorbents, catalysts, sensors, bone implants, and nanoscale devices.

## Introduction

The preparation of inorganic frameworks in the presence of assemblies of surfactant species as structure directors was recently elevated to an exciting new level by reports of hierarchical structures having ordered motifs on at least two different length scales.<sup>1–9</sup> The ability to control the assembly and patterning of inorganic frameworks not only on a nanoscale but also on micrometer and/or millimeter length scales can have enormous implications for the design of sorbents, membranes, catalysts, ceramics, sensors, and bone implants with hierarchical structures tailored for optimal performance.<sup>10–13</sup>

In a remarkable experiment Mann and his co-workers have demonstrated<sup>1</sup> that a bacterial superstructure, consisting of a tread of coaligned multicellular filaments of *Bacillus subtilis*, can be used as a macrotubular array template to extend the

length scale of MCM-41 silica<sup>14</sup> mesostructure patterning. Dipping air-dried bacterial tread into a typical  $\text{S}^+ \text{I}^-$  MCM-41 synthesis mixture they have succeeded in preparing ordered macroporous silica fibers with uniform MCM-41 type mesopore channels in the walls of the fibers.

Hollow silica tubules of 0.3 to 3  $\mu\text{m}$  in diameter which exhibited coaxial cylindrical MCM-41 type mesopore channels in their walls were reported by Lin and Mou.<sup>2</sup> The  $\text{S}^+ \text{I}^-$  preparation of this hierarchical structure was accomplished via careful control of the surfactant–water content and the rate of silica condensation at high pH values.

Transparent silica spheres with diameters from 0.1 to 2  $\mu\text{m}$  and mesoporous structure, similar to that of the hexagonal MCM-41 (pore diameters in the range of 1 to 5 nm), were reported recently by Stucky and co-workers.<sup>3</sup> The ambient reaction temperature preparation of the spheres was accomplished via the  $\text{S}^+ \text{I}^-$  electrostatic templating pathway,<sup>14</sup> using an oil-in-water emulsion formed from the hydrophobic tetrabutyl orthosilicate (TBOS) silica precursor and the water-immiscible BuOH. The yield of spheres was reported to be close to 100% when the synthesis was conducted at stirring speeds in the range of 200 to 400 rpm.<sup>3</sup>

Mann *et al.*<sup>4</sup> have also prepared hollow mesoporous shells of crystalline calcium carbonate (aragonite) that resemble the cocospheres of certain marine algae. These hierarchical and biporous (non-uniform mesopores and uniform micrometer-size pores) aragonite shells were obtained by dipping gold-coated

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micrometer-size polystyrene beads in bicontinuous microemulsions of cationic quaternary ammonium surfactant, tetradecane, and supersaturated aqueous calcium bicarbonate solution. The removal of the polystyrene beads from the product by dissolution in acetone/ethanol mixtures followed by thermal treatment at 400 °C revealed the biporous nature of the aragonite shells.<sup>4</sup>

Schüth *et al.*<sup>5</sup> synthesized hexagonal mesoporous MCM-41 products with fibrous, spherical, and/or sheet-like morphology. These materials were obtained from acidic ( $S^+X^-I^+$ ) MCM-41 reaction mixtures in the presence of simple organic co-surfactants (primarily mesitylene). The formation of an oil-in-water emulsion interface by the co-surfactant was responsible for the observed morphologies. The preparation of materials with a particular morphology was controlled by the rate of agitation of the reaction mixture.<sup>5</sup>

Using the acidic  $S^+X^-I^+$  electrostatic assembly pathway and quiescent reaction conditions Ozin *et al.*<sup>6</sup> have obtained hexagonal MCM-41 products with toroidal, disk-like, spiral, and spheroidal particle morphology. Certain acid concentrations in the reaction mixture favored low-curvature ropes and related particle shapes (70HCl:1TEOS), while others (35HCl:1TEOS) led to larger-curvature gyroids, spheroids, and related forms. The formation of these curved particle architectures was attributed to growth of a silicate "liquid crystal embryo" with hexagonal cross-section that, under different initial reaction conditions, is subject to increasing degrees of curvature.<sup>6</sup>

A vesicular lamellar aluminophosphate with mesoscale *d*-spacing (3.0 nm) and surface patterns that mimic diatom and radiolarian microskeletons has been reported by Ozin *et al.*<sup>7</sup> This material was obtained by hydrothermal treatment of aluminophosphate precursors in the presence of bilayers of protonated primary amine template and tetraethylene glycol (TEG) co-surfactant. Some particles of the material exhibited micrometer scale surface bowls and honeycomb patterns with hexagonal micrometer scale pores. Mesolamellar aluminophosphates with coaxial cylindrical morphology also were assembled by Sayari *et al.*<sup>8</sup> in the presence of bilayers of protonated primary or tertiary amines. The above lamellar aluminophosphate materials with hierarchical structure collapsed upon the removal of the organic templates.

We recently demonstrated a novel assembly approach for the preparation of a porous lamellar silica with a hierarchical structure (denoted MSU-V).<sup>9</sup> This synthetic strategy involved the cooperative formation of multilamellar vesicular surfactant-silica complexes. The cooperative assembly process was accomplished by H-bonding interactions between  $H_2N(CH_2)_{12}NH_2$  as the bolaamphiphile and the hydrolysis products of tetraethylorthosilicate as the silica precursor. The obtained lamellar MSU-V silica exhibited sorption properties similar to pillared lamellar clays, a gallery-confined framework microporosity, vesicular morphology, a high degree of framework cross-linking, and a high specific surface area and pore volume. In contrast, all previously reported *as-synthesized* lamellar mesophases prepared by electrostatic liquid crystal templating from quaternary ammonium ion surfactants and ionic inorganic precursors are unstable and undergo structural collapse upon surfactant removal.<sup>14-16</sup>

Although the properties of MSU-V silicas prepared from  $H_2N(CH_2)_{12}NH_2$  as the structure director are unique, the pore sizes are limited to the micropore region. A much wider range of catalytic and materials applications can be anticipated for mesoporous MSU-V derivatives assembled from larger bolaam-

phiphiles. However, our assembly method originally used to obtain the *as-synthesized* lamellar MSU-V was not directly applicable to the assembly of well-ordered lamellar analogs from bolaamphiphiles containing longer alkyl spacer groups. This unanticipated result has led us to develop an assembly pathway from homogeneous solutions. We are now able to demonstrate the existence of an entire family of lamellar MSU-V materials with pore structures extending into the desired mesopore range. In addition to multilamellar vesicular hierarchical particle morphology, intriguing plate, spiral-ribbon, and disk-like particle architectures can be obtained depending on the choice of bolaamphiphile.

## Experimental Section

**Chemicals.** Tetraethylorthosilicate (TEOS), obtained from Eastman Kodak, was used as a silica precursor. The 1,12-diaminododecane was purchased from Aldrich and used without further purification. The long alkyl chain  $H_2N(CH_2)_nNH_2$  bolaamphiphiles (where  $n = 16, 18,$  and  $22$ ) were not available commercially and were synthesized as described in the following section. The corresponding  $HOOC(CH_2)_nCOOH$  dicarboxylic acids (where  $n = 16, 18,$  and  $22$ ) were obtained from TCI America and Aldrich. Absolute ethanol (EtOH) was used as a co-solvent for the MSU-V synthesis.

**Surfactants Synthesis.** The diamine bolaamphiphiles with long alkyl spacer groups were synthesized by converting dicarboxylic acids to diamines by using a modification of previously described procedures.<sup>17</sup> In a typical diamine synthesis a dicarboxylic acid of the type  $HOOC(CH_2)_nCOOH$  (0.0146 mol), where  $n = 16, 18, 22$ , was dissolved in 230 mL of chloroform. A 62-mL quantity of concentrated  $H_2SO_4$  was added, and the mixture was placed in an oil bath and heated to 50 °C. Sodium azide (0.107 mol) was slowly added to the above mixture over a period of 2 h. Following the addition, the mixture was heated and stirred at 50 °C for another 2 h. The lower acidic layer was separated and poured into 60 mL of ice water to obtain a suspension of the protonated base sulfate. The suspension at the boiling point was treated with 10 N NaOH until a clear solution of surfactant was obtained (pH 11.0). In contrast to the previously described procedures,<sup>17</sup> we did not isolate the diamine reaction products as hydrochloride salts. Instead, the neutral diamine was extracted with chloroform and purified by two consecutive ethanol recrystallizations. The identity and the quality of the diamines was confirmed by <sup>1</sup>H NMR, mass spectrometry, and melting point analyses.

**MSU-V Synthesis.** The synthesis of MSU-V materials here was accomplished from homogeneous solutions of bolaamphiphile as the structure director. A wide range of reaction temperatures (from ambient to 75 °C) and reaction mixture molar compositions of the general formula  $1.0TEOS:nR(NH_2)_2:mEtOH:xH_2O$ , where  $n = 0.07$  to  $0.43$ ,  $m = 4.0$  to  $27.0$ , and  $x = 32.0$  to  $84.0$ , were employed in an attempt to find the optimum conditions for the preparation of MSU-V products with the best long-range lamellar framework order *before* and *after* the removal of bolaamphiphile. The following synthesis procedures provide the optimum conditions for the preparation of MSU-V molecular sieves with the best lamellar framework order, as judged by XRD, using diamine bolaamphiphiles with different spacer chain lengths.

**MSU-V C12 25 °C.** This derivative was prepared as described previously<sup>9</sup> from 1,12-diaminododecane (denoted  $C_{12}$ ) at ambient temperature (25 °C), except that the mesostructure was formed from a homogeneous solution of the structure director, rather than from a heterogeneous gel. In a typical preparation a  $1.4 \times 10^{-3}$  mol quantity of 1,12-diaminododecane was mixed with  $5.0 \times 10^{-2}$  mol of EtOH and 0.278 mol of deionized water. The mixture was sealed in a 10-mL glass bottle and warmed until a transparent solution of surfactant was obtained. The glass bottle was opened in order to inject  $5.47 \times 10^{-3}$  mol of TEOS, and then sealed. The molar composition of the reaction mixture was 1.0TEOS:0.26( $CH_2$ )<sub>12</sub>(NH<sub>2</sub>)<sub>2</sub>:13.1EtOH:50.8H<sub>2</sub>O. The reaction mixture was placed in a thermostated water bath (25 °C)

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under moderate shaking and allowed to react for 48 h. The obtained product was filtered and washed with deionized water, and air dried.

**MSU-V C16 45 °C.** For this derivative  $6.32 \times 10^{-4}$  mol of 1,16-diaminohexadecane (denoted C<sub>16</sub>) was mixed with  $2.73 \times 10^{-2}$  mol of EtOH and 0.152 mol of deionized water, sealed in a 10-mL glass bottle, and heated in a furnace at 100 °C until a transparent solution of surfactant was obtained. The bottle was removed from the furnace, quickly opened to inject  $3.22 \times 10^{-3}$  mol of TEOS, and then sealed. The molar composition of the reaction mixture was 1.0TEOS:0.20-(CH<sub>2</sub>)<sub>16</sub>(NH<sub>2</sub>)<sub>2</sub>:12.5EtOH:47.2H<sub>2</sub>O. The reaction mixture was placed in a water bath at 45 °C under moderate shaking and allowed to react for 48 h. The product was filtered, washed with deionized water, and air dried.

**MSU-V C18 55 °C.** The same procedure as described above for MSU-V C<sub>16</sub> was employed, except that  $1.14 \times 10^{-3}$  mol of 1,18-diaminooctadecane (denoted C<sub>18</sub>),  $7.8 \times 10^{-3}$  mol of TEOS,  $7.16 \times 10^{-2}$  mol of EtOH, and 0.394 mol of deionized water were used and the reaction was carried out at 55 °C for 48 h. The reaction mixture composition was 1.0TEOS:0.15(CH<sub>2</sub>)<sub>18</sub>(NH<sub>2</sub>)<sub>2</sub>:13.2EtOH:50.6H<sub>2</sub>O.

**MSU-V C22 55 °C.** The quantities of reagents used to prepare this analog were as follows:  $7.97 \times 10^{-3}$  mol of TEOS;  $8.81 \times 10^{-4}$  mol of 1,22-diaminodocosane (denoted C<sub>22</sub>);  $7.3 \times 10^{-2}$  mol of EtOH; 0.407 mol of deionized water. The reaction mixture composition was 1.0TEOS:0.11(CH<sub>2</sub>)<sub>22</sub>(NH<sub>2</sub>)<sub>2</sub>:13.2EtOH:51.0H<sub>2</sub>O, and the reaction time at 55 °C was 48 h. The product was filtered, washed with deionized water, and air dried.

**Surfactant Removal.** The removal of surfactant from the above mesostructures was achieved by calcination in air at 550 °C for 4 h with a heating rate of 2 °C/min.

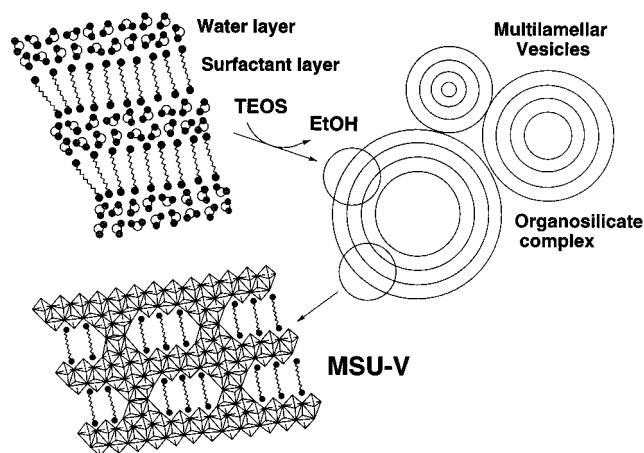
**Analytical Techniques.** Powder X-ray diffraction (XRD) patterns were measured on a Rigaku Rotaflex diffractometer equipped with a rotating anode and using Cu K $\alpha$  radiation.

Samples for transmission electron microscopy (TEM) studies were prepared by embedding in L. R. White acrylic resin (hard) and sectioned on an ultramicrotome. The thin sections (~80 nm) were supported on 300 mesh copper grids. The transmission electron micrographs were taken on a JEOL JEM-100CX II microscope equipped with a cerium hexaboride gun, using an accelerating voltage of 120 kV and 20  $\mu$ m objective lens aperture. The optical diffraction patterns of the samples were obtained from the TEM images by using NIH 1.6 image processing software.<sup>18</sup> The scanning electron micrographs were taken on a JEOL JSM 6400V, using an accelerating voltage of 8 kV and a 16 mm working distance.

The N<sub>2</sub> adsorption-desorption isotherms were measured at -196 °C on a Micromeritics ASAP 2010 instrument by using a static adsorption procedure. Before measurement, samples were evacuated overnight at 150 °C and 10<sup>-5</sup> Torr. The BET surface area was calculated from the linear part of the BET plot according to IUPAC recommendations.<sup>19</sup> Pore size distributions were determined by a recently developed method based on Density Functional Theory.<sup>20</sup>

## Results and Discussion

**Mechanistic Considerations.** Figure 1 shows a schematic representation of our proposed mechanism of formation of MSU-V materials. For H<sub>2</sub>N(CH<sub>2</sub>)<sub>n</sub>NH<sub>2</sub> bolaamphiphile with  $n = 12-22$  MSU-V formation involves primarily the cooperative assembly of the neutral diamine surfactant and the TEOS hydrolysis products into multilamellar vesicular aggregates.<sup>9</sup> Although neutral surfactants are capable of forming multilamellar vesicles spontaneously,<sup>21,22</sup> the initial surfactant solutions under our reaction conditions are completely clear and devoid



**Figure 1.** Proposed assembly mechanism for the formation of MSU-V.

of phase segregated vesicles of the size observed for the mesostructures. Phase segregation and vesicle formation does not occur until the TEOS precursor is added to the solution of the bolaamphiphile. The hydrophobic nature of TEOS and the surfactant appears to initiate a hydrophilic-hydrophobic phase separation and the creation of a curved water-organic interface which triggers the formation of vesicles. The partially hydrolyzed Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4-x</sub>OH<sub>x</sub> species at the interface may also contribute to vesicle formation by participating in H-bonding interactions with the lone electron pairs on the N atoms of the surfactant head groups. In this case the multilamellar regions of the vesicles will consist of closely packed layers of surfactant separated by water/Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4-x</sub>OH<sub>x</sub> layers. The predominantly neutral character of the assembly process,<sup>9</sup> the close proximity of the layers, and the further cross-linking and polymerization of adjacent silica species lead to the simultaneous growth of the lamellar and interlamellar silica components.

**Synthesis.** Our initial demonstration of the assembly of biomimetic lamellar MSU-V mesostructures made use of H<sub>2</sub>N(CH<sub>2</sub>)<sub>12</sub>NH<sub>2</sub> diamine as the structure directing agent.<sup>9</sup> This amine bolaamphiphile was relatively soluble in water-alcohol solutions at near-ambient temperatures. Consequently, the hydrolysis of TEOS in the presence of this surfactant readily afforded a well-ordered lamellar mesostructure at ambient temperature. Rather unexpectedly, our subsequent efforts to prepare MSU-V homologs from larger bolaamphiphiles containing longer C<sub>16</sub>-C<sub>22</sub> alkyl chains between the amino head groups led instead to poorly ordered products under analogous reaction conditions.

The difficulty in obtaining higher ordered products now has been traced to the low solubility of the larger bolaamphiphiles. Under ambient reaction conditions, the solubility of diamine bolaamphiphiles decreases substantially with increasing spacer chain length, and this could lead to segregation of the diamine from the solution. This limited surfactant solubility allows for the formation of sol-gel products that are difficult to order by ambient temperature aging into mesostructures that are completely stable to surfactant removal. However, this limitation to MSU-V synthesis can be circumvented by preparing a homogeneous solution of the bolaamphiphile prior to the addition of TEOS and by adjusting the surfactant to silica ratios (*R*) and the aging temperatures to optimal values. We kept in mind that at the surfactant concentrations used in this study (<6 wt %) the surfactant may form multilamellar vesicles, but not liquid crystal phases which are usually observed at much higher surfactant concentrations ( $\geq 20$  wt %).<sup>14</sup> The previously reported<sup>7,8,12</sup> mesolamellar aluminophosphates were prepared from

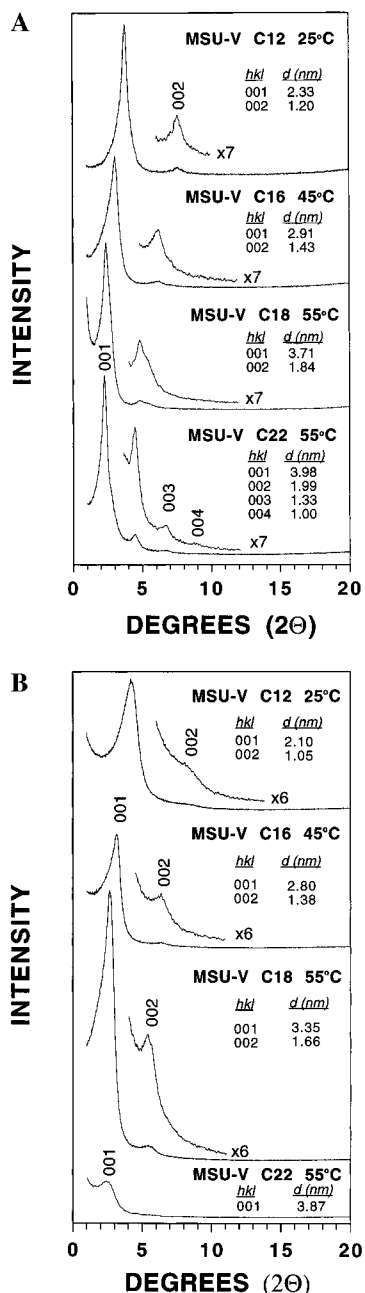
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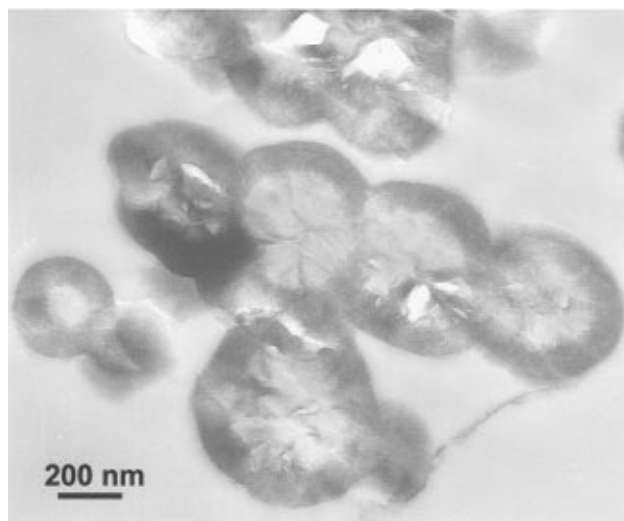
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**Figure 2.** Powder XRD patterns for MSU-V silicas assembled at reaction temperatures of 25, 45, 55, and 55 °C from homogeneous solutions of diamine surfactants with an alkyl chain length of C<sub>12</sub>, C<sub>16</sub>, C<sub>18</sub>, and C<sub>22</sub> units, respectively: (A) *as-synthesized* products and (B) *calcined* products at 550 °C for 4 h.

reaction mixtures with very high surfactant/water ratios; i.e., the assembly process occurred in the presence of bilayer liquid crystals which acted as templates affording multilamellar vesicles or coaxial cylinders.

In the present work we have explored a wide range of reaction stoichiometries and reaction temperatures for diamine surfactants with spacer chain lengths from C<sub>12</sub> to C<sub>22</sub>. The preparations with diamine bolaamphiphiles with spacer chain lengths  $\geq$  C<sub>16</sub> units were much more sensitive than the C<sub>12</sub> diamine to small variations in the molar composition of the reaction mixture and the reaction temperature. Indeed, a relatively narrow reagent concentration window exists for the preparation of well-ordered MSU-V materials with C<sub>16</sub> and C<sub>18</sub> diamines at the most favorable reaction temperatures. As the surfactant chain length was increased, the reaction temperature necessary for the preparation of MSU-V materials with optimal long range



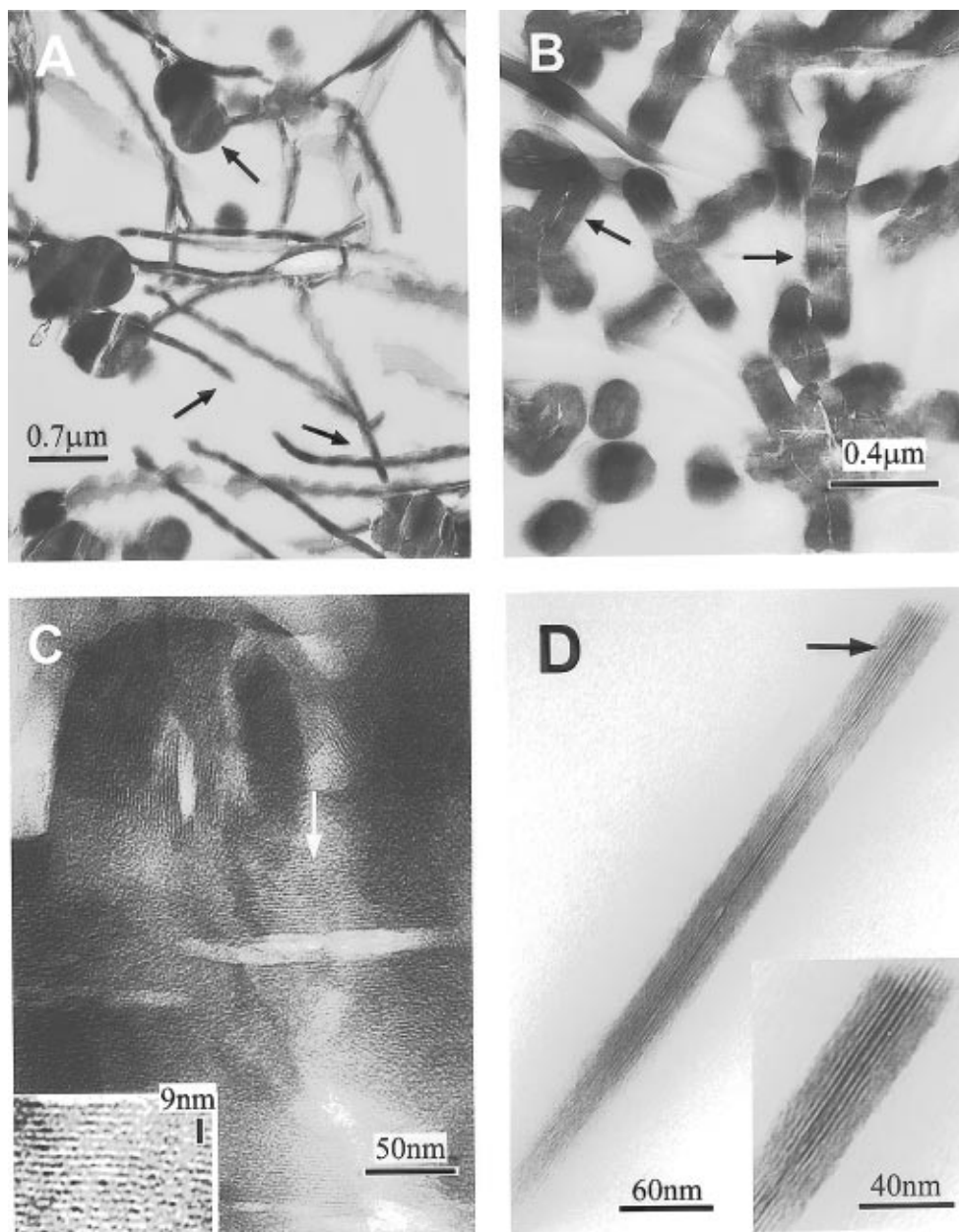
**Figure 3.** Representative TEM micrograph of an ultrathin section of *as-synthesized* MSU-V silica assembled at ambient reaction temperature from a homogeneous solution of C<sub>12</sub> diamine bolaamphiphile.

framework order after removal of surfactant also increased. Thus, well-ordered *calcined* MSU-V silicas, as determined by XRD and TEM, were obtained with C<sub>12</sub> diamine at ambient reaction temperature, C<sub>16</sub> diamine at 45 °C, C<sub>18</sub> diamine at 55 °C, and C<sub>22</sub> diamine at 55 °C. Reaction temperatures lower than the optimum temperature afforded C<sub>16</sub> to C<sub>22</sub> MSU-V derivatives that were less thermally stable, whereas reaction temperatures higher than the optimum one afforded MSU-V materials with broader XRD reflections. The loss of long range lamellar framework order, as judged from the XRD patterns, increased with increasing deviation from the optimum reaction temperature.

As the surfactant spacer chain length was increased, more TEOS (i.e., a smaller *R* value) was necessary to simultaneously assemble the layer and interlayer silica species and to obtain mesoporous MSU-V materials with long range framework order *after* calcination. Optimal lamellar order was observed for four *as-synthesized* and *calcined* (550 °C) mesostructures when they were assembled at reaction temperatures (*T*, °C) and surfactant/silica ratios (*R*) of *T* = 25 °C, *R* = 0.26 (C<sub>12</sub>); *T* = 45 °C, *R* = 0.20 (C<sub>16</sub>); *T* = 55 °C, *R* = 0.15 (C<sub>18</sub>); *T* = 55 °C, *R* = 0.11 (C<sub>22</sub>). Therefore, in the following discussion we will only consider the MSU-V silicas prepared with C<sub>12</sub> to C<sub>22</sub> diamines at the above optimum reaction mixture molar compositions and optimum reaction temperatures.

### Framework Characterization

**XRD.** Figure 2A shows the powder XRD patterns of the *as-synthesized* MSU-V materials assembled with C<sub>12</sub>, C<sub>16</sub>, C<sub>18</sub>, and C<sub>22</sub> diamines at the corresponding optimum reaction conditions. All reaction products exhibit XRD patterns with at least two 00*l* orders of reflection typical of lamellar framework structure. As the surfactant chain length increases from C<sub>12</sub> to C<sub>22</sub> units the *d*<sub>001</sub>-spacing also increases from 2.33 nm to 3.98 nm. This suggests that longer alkyl chain diamine surfactants afford *as-synthesized* MSU-V materials with a larger distance between the layers, i.e. larger gallery heights. In addition, a longer alkyl chain spacer affords MSU-V materials with better long range framework order. This is evidenced by the decrease in the XRD line widths and the increase in the number of 00*l* diffraction orders. Thus, while MSU-V prepared with C<sub>12</sub> diamine shows only two 00*l* reflections, the derivative prepared with C<sub>22</sub> diamine exhibits four sharper 00*l* reflections.



**Figure 4.** Representative TEM micrographs of an ultrathin section of *calcined* MSU-V silica assembled at 45 °C from a homogeneous solution of C<sub>16</sub> diamine surfactant showing (A) mixed vesicular, plate-like, and spiral-ribbon particle morphology (see arrows); (B) the simultaneous presence of round and elongated vesicles (see arrows); (C) a multilamellar framework patterning in an elongated vesicular fashion (see arrow); and (D) multilamellar framework patterning in a plate-like fashion (see arrow). Both Inserts represent magnified portions of images C and D illustrating the lamellar nature of the framework.

The corresponding powder XRD patterns of MSU-V silicas *calcined* at 550 °C for 4 h are presented in Figure 2B. In contrast to the *calcined* MSU-V prepared with C<sub>12</sub> diamine, which exhibits a very broad 002 reflection, the *calcined* MSU-V derivatives prepared with C<sub>16</sub> and C<sub>18</sub> diamine surfactants exhibit at least two well-defined 00*l* orders of reflection with *d*<sub>001</sub>-spacings clearly in the mesoscopic region (from 2.80 to 3.35 nm). All materials exhibit relatively small lattice contraction in the range of 0.11 to 0.36 nm upon calcination. Thus, we have succeeded in extending our assembly approach to thermally stable and more ordered lamellar mesostructures.

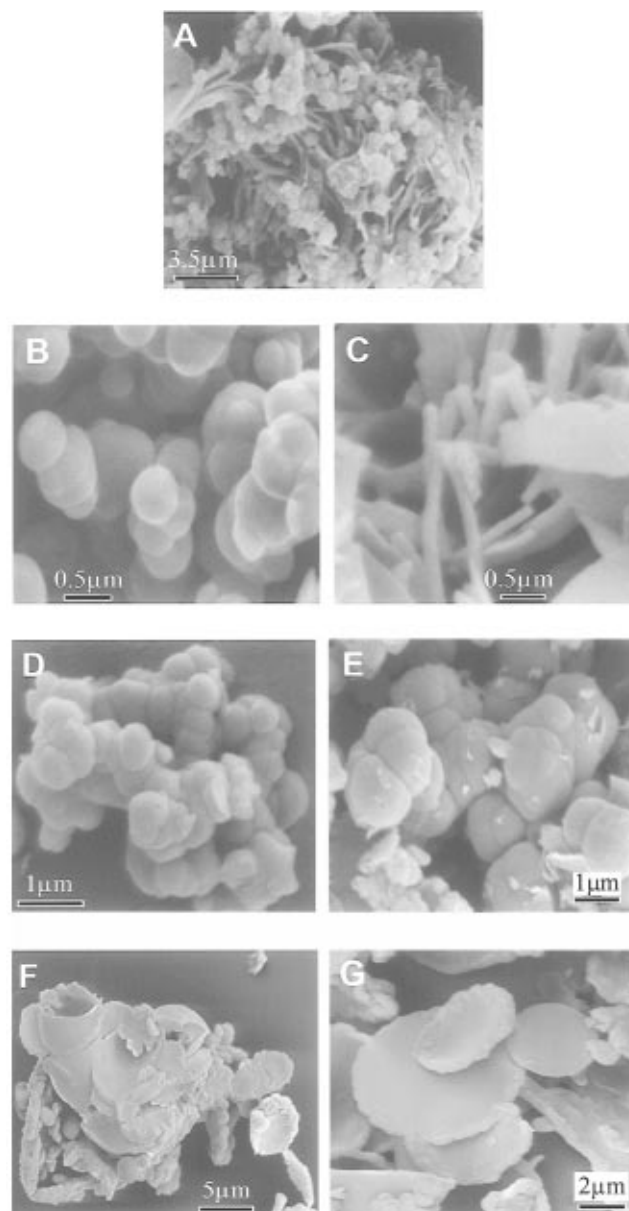
The decrease in intensity and broadening of the peaks in the XRD pattern of the *calcined* MSU-V prepared with C<sub>22</sub> diamine surfactant reveal significant collapse of the structure. This thermal instability of the C<sub>22</sub> diamine derivative could be attributed to the more biocellular rather than a vesicular hierarchical particle architecture (see below).

**TEM and SEM.** Figure 3 shows a TEM image of an ultrathin section of the as-synthesized MSU-V silica prepared at ambient reaction temperature from homogeneous solution containing C<sub>12</sub> diamine. The image of this MSU-V is very similar to that reported previously<sup>9</sup> for the MSU-V silica assembled from a nonhomogeneous C<sub>12</sub> diamine solution. Hollow multilamellar vesicles of ~300 to 600 nm in diameter are clearly evident in this image. The dark regions of the vesicles near the vesicle periphery are populated by a dense silica phase. The less dense central regions of the bisected vesicles are a consequence of the hollow central core. It is noteworthy that the vesicles tend to form cluster-like arrangements of interpenetrating vesicles rather than being separated. This fact is very interesting and could be directly responsible for the observed stability of our materials upon surfactant removal by calcination. Perhaps these structural defects facilitate the removal of the occluded surfactant and water thereby

minimizing the possibility of framework steaming and decomposition upon calcination. These hierarchical features of MSU-V ( $C_{12}$ ) are in agreement with our previous TEM and SEM observations<sup>9</sup> for the MSU-V prepared from nonhomogeneous  $C_{12}$  diamine solutions. The materials obtained from homogeneous and nonhomogeneous reaction mixtures both exhibited lattice fringes typical of lamellar structures and a vesicular particle morphology (images not shown).

Parts A and B of Figure 4 are low magnification TEM images of ultrathin sections of the *calcined* MSU-V prepared at 45 °C with  $C_{16}$  diamine. The material exhibits very interesting mixed morphology, as evidenced by the presence of multilamellar vesicles, elongated multilamellar vesicles, and plate-like and spiral-ribbon morphologies (see arrows). The size of the multilamellar vesicles is in the range of 0.2 to 1.0  $\mu\text{m}$  (see Figure 4A). The plates are about 1.0 to 3.0  $\mu\text{m}$  long with a thickness of 30 to 170 nm. The spiral-ribbon particles are about 1.0 to 2.0  $\mu\text{m}$  long and up to 0.4  $\mu\text{m}$  thick. Because there are no chiral reagents in the reaction mixture, both left- and right-handed (racemic) spiral-ribbon helical forms should be present in our reaction products. The elongated vesicles show a central slit-shaped cavity oriented parallel to the axis of elongation (see Figure 4B). The presence of elongated vesicles was also documented for solutions of other surfactant systems.<sup>23</sup> The corresponding high-magnification TEM images of the *calcined* MSU-V ( $C_{16}$  diamine) shown in parts C and D of Figure 4 verify the lamellar nature of this framework. It is important to notice that the lamellar framework is equally characteristic for both the vesicular and the plate-like morphology (compare images C and D of Figure 4). Image C shows two elongated and interpenetrating vesicles populated by multiple parallel layers (the dark dense lines). The layers run parallel to the axis of vesicle elongation and are divided by an elongated or slit-shaped central vesicle cavity. One of the vesicular areas of image C containing multiple parallel layers (pointed out with an arrow) is magnified and presented as an insert. Image D shows a cross section of a long plate that is clearly occupied by the well-ordered lamellar phase (see also corresponding insert). The average basal spacing estimated from the images shown as inserts is approximately 2.9 nm, which is in good agreement with that obtained from the corresponding XRD pattern (2.8 nm). Tilting of the sample under various angles during the TEM observation afforded always lamellar framework fringes. The SEM images of this MSU-V silica presented in Figure 5 confirm the predominantly mixed particle morphology (images A, B, and C).

The hierarchical nature of this MSU-V  $C_{16}$  diamine derivative most likely arises from patterning of the multilamellar inorganic framework. A possible framework patterning mechanism that could give rise to vesicular, elongated vesicular, plate-like, and spiral-ribbon morphologies is suggested in Figure 6. In the initial stages of synthesis, multilamellar vesicular aggregates of  $C_{16}$  diamine surfactant and more or less hydrolyzed TEOS are formed *via* a cooperative assembly. Further hydrolysis of the TEOS precursor leads to silica layer formation and layer cross-linking with silica species according to our postulated mechanism (see Figure 1). The viscosity of the reaction mixture decreases in the course of the synthesis, leading to an increase of the agitation rate. At this higher agitation rate the multilamellar vesicles could begin to elongate due to the increasing shear force giving rise to elongated vesicles which in their turn could split affording plates. Bending and twisting motions of the plates in the reaction mixture could be responsible for the

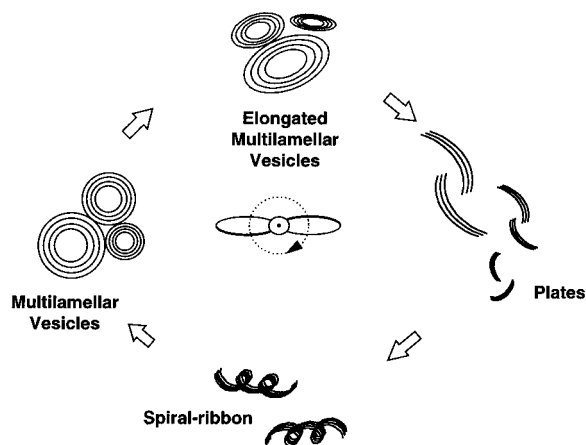


**Figure 5.** Representative SEM images for (A) *calcined* MSU-V silica prepared from a homogeneous solution of  $C_{16}$  diamine at 45 °C showing mixed vesicular and plate-like morphology. *As-synthesized* MSU-V prepared from a homogeneous solution of  $C_{16}$  diamine at 45 °C showing isolated areas of (B) vesicular and (C) plate-like morphology. SEM images of (D) *as-synthesized* and (E) *calcined* MSU-V derivative prepared from homogeneous solution of  $C_{18}$  diamine at 55 °C. The images show the predominantly vesicular morphology of the material and its tendency to form cluster-like aggregates of vesicles. SEM images of the (F) *as-synthesized* and (G) *calcined* MSU-V silica prepared from homogeneous solution of  $C_{22}$  diamine at 55 °C. The material exhibits a remarkable disk-like particle morphology that is preserved upon calcination.

observed spiral-ribbon particle morphology (see Figure 4A). The importance of shear forces on the hierarchical structures of MCM-41 has been noted in the earlier work of Stucky,<sup>3</sup> Schüth,<sup>5</sup> Ozin,<sup>6</sup> and their co-workers. It appears that related forces are capable of influencing the hierarchical structures of MSU-V materials.

Figure 7A shows a representative low magnification TEM image of an ultrathin section of the *calcined* MSU-V prepared at 55 °C with  $C_{18}$  diamine. Partially interpenetrating vesicles having a diameter of  $\sim 800$  nm and smaller vesicles with a diameter of  $\sim 250$  nm are evident in this image and in the corresponding SEM images presented in Figure 5, parts D and

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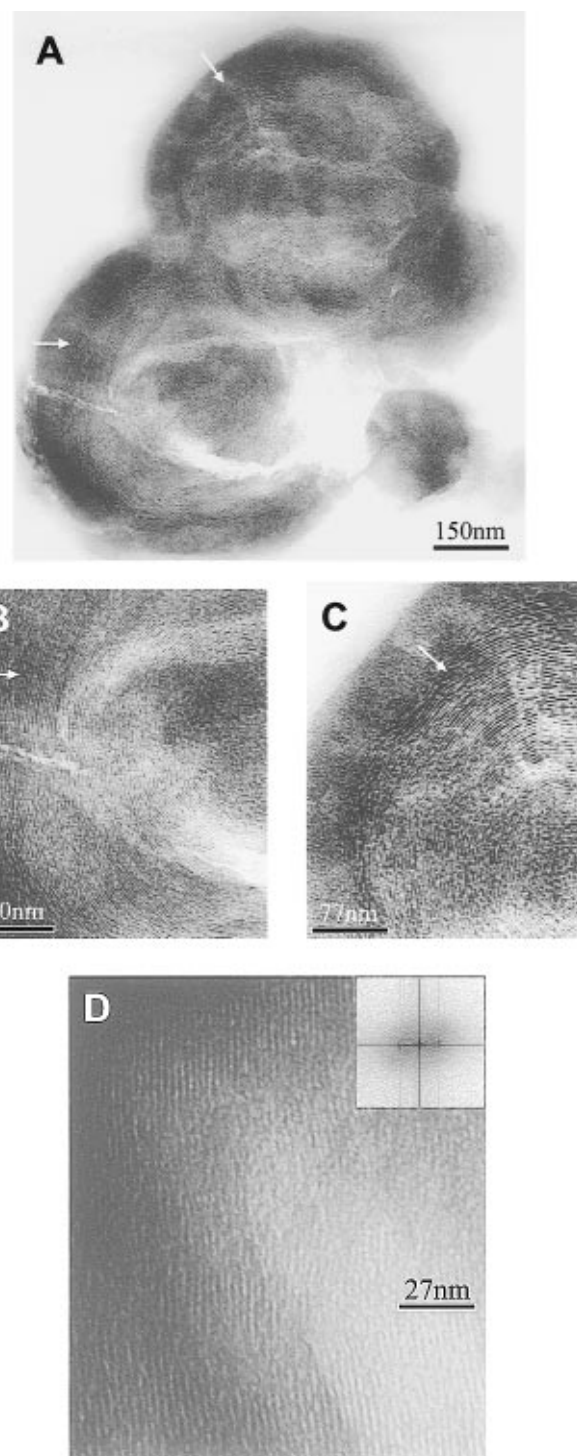
**Figure 6.** A schematic representation of the framework patterning mechanism of the MSU-V silica assembled from a homogeneous solution of  $C_{16}$  diamine surfactant at 45 °C.

E. The predominant cluster-like arrangement of the vesicles in this material may be a consequence of fusion effects due to the relatively high reactants:water ratio in the reaction mixture. Clustering of the vesicles could facilitate the removal of water and the occluded surfactant from the galleries during calcination by facilitating mass transport through interfacial cracks and other framework defects.

The presence of framework defects is apparent on the large vesicle located on the lower left corner of image A in Figure 7, but these defects are most likely due to damage caused by the ultrathin sectioning. The large vesicles are only partially populated with concentric parallel silica layers (see arrows). The vesicular patterning of the multilamellar inorganic framework is also evident from the magnified regions of image A presented in Figure 7, parts B and C. The lamellar nature of this MSU-V silica is further verified by the high magnification lattice TEM image presented in Figure 7D. The average basal spacing measured from this image is  $\sim 3.3$  nm, which is in good agreement with the 3.4 nm  $d_{001}$ -spacing obtained from XRD. The optical diffraction obtained by Fourier transform of the image (see insert) shows two diffraction spots verifying the lamellar symmetry of the mesoporous MSU-V inorganic framework.<sup>18</sup> The slightly asymmetrical character of the diffraction spots is due to the imperfect alignment of the layers. TEM observation of the sample under various tilting angles did not show evidence for any framework topology other than lamellar.

Figure 8 shows the TEM images of ultrathin sections of the *as-synthesized* MSU-V prepared at 55 °C with the  $C_{22}$  diamine surfactant. In contrast to the MSU-V derivatives prepared with  $C_{16}$  and  $C_{18}$  diamines, this derivative exhibits large biocell-like, nonspherical, and hollow aggregates. The dark areas near the interface are occupied by a dense silica (see images A, B, and C). In addition, the extent of layer stacking of the inorganic phase in these dense areas is very limited (see image C). The internal brighter areas of the material are almost devoid of silica, indicating the presence of a cavity formed by  $C_{22}$  surfactant solution. The average basal spacing estimated from Figure 8 (image C) and the corresponding insert is approximately 4.0 nm, which correlates well with that obtained from XRD. The patterning of the multilamellar inorganic framework here occurs only near the surfactant–water interface, affording remarkable aggregates that resemble biological membranes.<sup>23,24</sup> The predominantly disk-like particle morphology of the material is

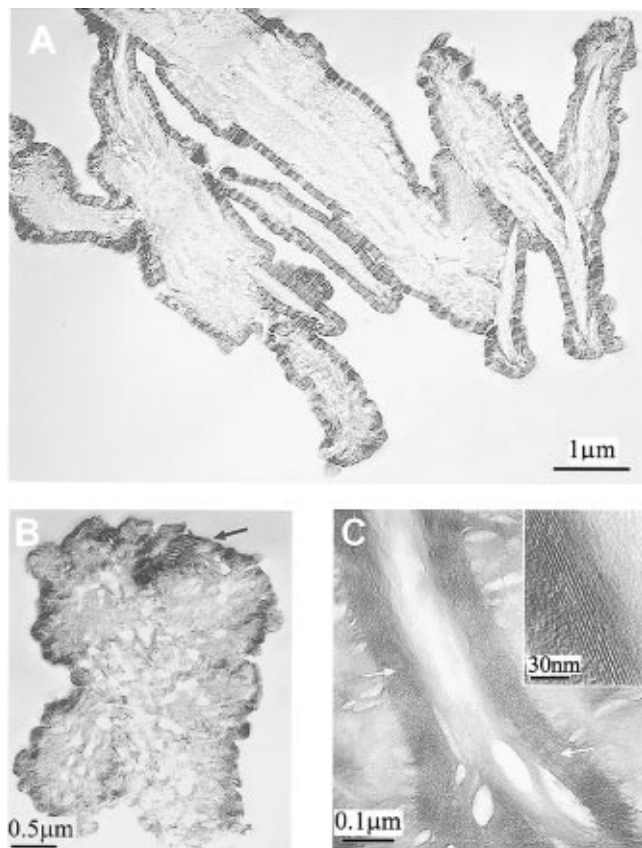
(24) Ross, M.; Pote, K. G. In *Mineral Phases in Biology*; Miller, A., Phillips, D., Williams, R. J. P., Eds.; The Royal Society: London, 1984; p 35.



**Figure 7.** Representative TEM micrographs of an ultrathin section of calcined MSU-V silica assembled from a homogeneous solution of  $C_{18}$  diamine at 55 °C showing (A) a cross-section of two large and two smaller adjacent multilamellar vesicles (see arrows); (B and C) areas occupied by multilamellar framework patterned in a unique onion-like or vesicular fashion (see arrows); and (D) a high-magnification ( $\times 270\,000$  before 60% reduction for publication) image and corresponding optical diffraction image (see insert) verifying the lamellar symmetry of the material.

evident from the corresponding SEM images presented in Figure 5, images F and G. Although the lamellar framework significantly collapsed upon calcination the biocell-like morphology of the material was clearly preserved after calcination.

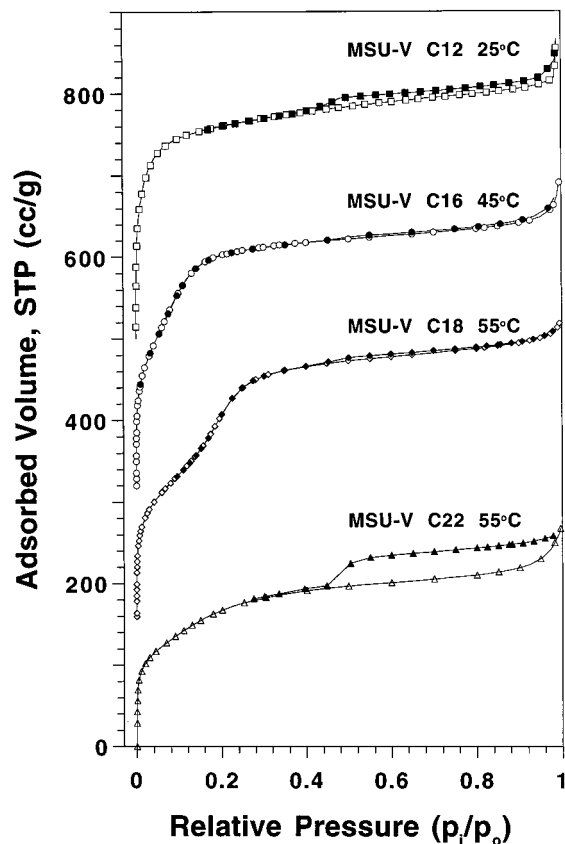
The above observations show that our multilamellar vesicular assembly approach affords silica mesostructures that are different from the lamellar aluminophosphates reported previously



**Figure 8.** Representative TEM micrographs of an ultrathin section of *as-synthesized* MSU-V silica assembled from a homogeneous solution of C<sub>22</sub> diamine at 55 °C showing (A) a biocell-like patterning of the multilamellar framework, (B) a large biocell-like aggregate, and (C) dense areas near the interface partially populated by a lamellar organic-inorganic complex. The insert on image C represents a magnified image of the section of image C pointed out with the left arrow.

by Ozin,<sup>7,12</sup> Sayari,<sup>8</sup> and their co-workers. In the first case<sup>7,12</sup> vesicles were responsible for the formation of bowl, “egg shell”, or hexagonal patterns on the surface of bilayer liquid crystal templated mesolamellar aluminophosphate spheres. In the second case<sup>8</sup> the bilayer templated mesolamellar aluminophosphates exhibited a dense concentric cylinder topology, nucleated about a central rod-like core. Ozin *et al.* have recently proposed<sup>6</sup> that “liquid crystal embryos” nucleate the diverse hierarchical structures of MCM-41 silicas formed by S<sup>+</sup> X<sup>-</sup> I<sup>+</sup> assembly. The bolaamphiphile assembly of the multilamellar vesicles in our biomimetic system does not involve liquid crystal templating or nucleation around a central rod-like core. Instead, it appears that the vesicles are formed by cooperative assembly of bolaamphiphile lamellae and hydrolyzed TEOS.

**Sorption Properties.** The N<sub>2</sub> adsorption-desorption isotherms of the *calcined* MSU-V materials prepared with C<sub>12</sub> to C<sub>22</sub> diamine surfactants are shown in Figure 9. We note that the MSU-V prepared with C<sub>12</sub> diamine exhibits a type I adsorption isotherm, and a hysteresis loop of type H4 typical of lamellar materials.<sup>9,19</sup> In contrast the MSU-V silicas prepared with the longer C<sub>16</sub> to C<sub>22</sub> diamines show type IV adsorption isotherms typical of mesoporous materials.<sup>19</sup> The derivatives prepared with C<sub>16</sub> and C<sub>18</sub> diamine exhibit a well-defined reversible adsorption step in the region of  $P_i/P_o = 0.05-0.3$  and a very little textural mesoporosity. This is evidenced by the weakly-expressed type H4 hysteresis loops at  $P_i/P_o > 0.4$ . As the surfactant chain length increases the reversible adsorption step becomes sharper and shifts toward higher  $P_i/P_o$ . However, the same trend is not continued for MSU-V prepared with C<sub>22</sub>



**Figure 9.** N<sub>2</sub> adsorption (white markers)—desorption (black markers) isotherms for *calcined* lamellar MSU-V silicas prepared from homogeneous solutions of C<sub>12</sub>, C<sub>16</sub>, C<sub>18</sub>, and C<sub>22</sub> diamine surfactants at reaction temperature of 25, 45, 55, and 55 °C, respectively. The isotherms and the origin of the  $P_i/P_o$  axis were shifted to show the starting point of each isotherm. Only 50% of the actual number of data points are shown for better clarity.

diamine due to the partial collapse of the framework mesopores upon calcination. This structural collapse is probably responsible for the much weakly-expressed adsorption step in the lower  $P_i/P_o$  range.

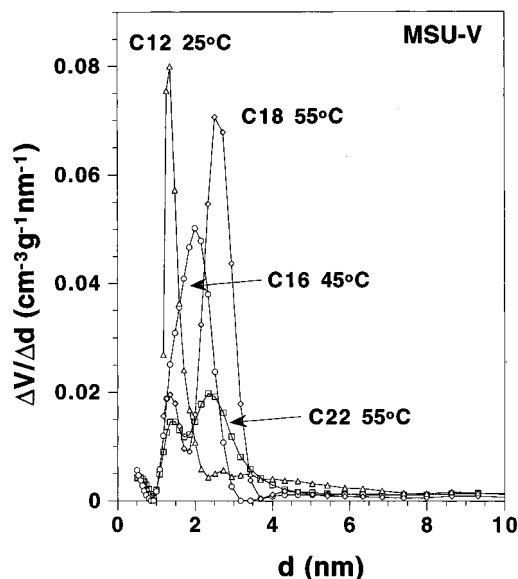
The mesoporous character of our lamellar structures is further verified by comparing their DFT<sup>20</sup> pore size distributions (PSD) and pore structure parameters presented in Figure 10 and Table 1. In contrast to MSU-V prepared with C<sub>12</sub> diamine, which shows a PSD maximum centered at a micropore size of 1.3 nm, the silicas prepared with the long chain C<sub>16</sub> to C<sub>22</sub> diamines exhibit PSD maxima centered at mesopore sizes of 2.0 to 2.7 nm. Generally, as the surfactant chain length increases from C<sub>16</sub> to C<sub>22</sub> the gallery-confined mesopore size also increases. This experimental fact is extremely important and signifies that our biomimetic assembly process is not equivalent to pillaring. If the MSU-V assembly process was pillaring, the pore size of our MSU-V materials should have been independent of the alkyl chain length of the bolaamphiphile surfactant. That is, the pore size in a pillared material should have been determined by the lateral separation between pillars and not by the gallery height. Pillared magadites formed by intragallery hydrolysis of TEOS,<sup>25</sup> and many pillared smectites,<sup>26</sup> exhibit gallery heights much larger than their micropore sizes.

The fact that the gallery pore size of our MSU-V materials increases proportionally to the alkyl chain length of the

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**Figure 10.** DFT PSD curves for calcined mesoporous lamellar MSU-V silicas prepared from homogeneous solutions of C<sub>12</sub>, C<sub>16</sub>, C<sub>18</sub>, and C<sub>22</sub> diamine surfactants at reaction temperature of 25, 45, 55, and 55 °C, respectively.

**Table 1.** Sorption Properties of Calcined MSU-V Silicas Prepared by Biomimetic Diamine Vesicle Assembly

MSU-V product	$d_{001}$ (nm)	$S_{\text{BET}}$ (m <sup>2</sup> /g)	$C_{\text{BET}}$	$V_{\text{total}}$ (cm <sup>3</sup> /g)	$d_p$ (nm)
C <sub>12</sub>	2.1	984	282	0.526	1.3
C <sub>16</sub>	2.8	1187	49	0.610	2.0
C <sub>18</sub>	3.4	926	34	0.575	2.7
C <sub>22</sub>	3.9	615	73	0.416	2.5

surfactant further verifies that the silicate layers and the intragallery silica species are simultaneously assembled. Due to the partial collapse of the mesoporous structure, the calcined MSU-V prepared with C<sub>22</sub> diamine is exempt from this trend. It is noteworthy that as the surfactant chain length increases the corresponding  $S_{\text{BET}}$  value decreases and the  $C_{\text{BET}}$  constant, which is proportional to the magnitude of adsorbent–adsorbate interactions, decreases below 100. This correlates well with the larger pore size of these MSU-V derivatives and verifies the lack of microporosity<sup>19</sup> for silicas prepared with the long chain  $\geq C_{16}$  diamines. Thus, we have succeeded in extending our assembly approach toward the mesoporous region and have prepared thermally stable and well-ordered lamellar mesoporous MSU-V molecular sieves with hierarchical structure and unique vesicular, elongated vesicular, plate-like, spiral-ribbon, and disk-like particle architectures.

## Conclusions

A family of MSU-V silica molecular sieves with lamellar frameworks and hierarchical vesicle structures is formed by an

assembly from homogeneous solutions of neutral H<sub>2</sub>N(CH<sub>2</sub>)<sub>*n*</sub>-NH<sub>2</sub> bolaamphiphiles as structure directors and tetraethylorthosilicate as the inorganic precursor. MSU-V assembly from C<sub>12</sub> diamine proceeds readily at ambient temperature, but for the longer C<sub>16</sub> to C<sub>22</sub> bolaamphiphiles, the assembly process is much more sensitive to small variations in reaction composition and temperature. Thus, as the surfactant chain length increases the quantity of inorganic framework precursor and the reaction temperature necessary for the preparation of MSU-V materials with optimal framework order also increases. As-synthesized and calcined (550 °C) MSU-V derivatives with optimal lamellar order are assembled at reaction temperatures (*T*, °C) and surfactant/silica ratios (*R*) of *T* = 25 °C, *R* = 0.26 (C<sub>12</sub>); *T* = 45 °C, *R* = 0.20 (C<sub>16</sub>); *T* = 55 °C, *R* = 0.15 (C<sub>18</sub>); *T* = 55 °C, *R* = 0.11 (C<sub>22</sub>).

Assembly from C<sub>12</sub> bolaamphiphile affords lamellar MSU-V silica with a gallery-confined micropore size of 1.3 nm and a hierarchical vesicle structure. In contrast, the C<sub>16</sub> diamine gives a MSU-V material with larger gallery-confined mesopores (2.0 nm) and remarkable hierarchical vesicular, elongated vesicular, plate-like, and spiral-ribbon particles. The presence of mixed particle architecture may arise from agitation affects during synthesis that result in elongation of the multilamellar vesicles, splitting of the elongated vesicles into plates, and further twisting of plates to afford particles with spiral-ribbon morphology. Assembly with the longer C<sub>18</sub> bolaamphiphile affords a MSU-V product with even larger gallery-confined mesopores (2.7 nm) and hierarchical vesicular structure. The as-synthesized MSU-V prepared from C<sub>22</sub> diamine exhibits the largest distance between the silica layers (4.0 nm). Its unique hierarchical structure is reminiscent of biomembrane cells, but the removal of the surfactant (by calcination) partially degrades the lamellar framework and hierarchical structure. The calcined C<sub>22</sub> diamine MSU-V product exhibits relatively little framework-confined mesoporosity centered at ~2.5 nm. This assembly approach provides new opportunities for the preparation of lamellar mesoporous molecular sieves with significant thermal stability and hierarchical particle architectures that may be specifically tailored to applications as diverse as adsorbents and membranes for separation of organic macromolecules, catalysts capable of converting bulky organic molecules, ceramics and bone implants with micro-, meso- or macroporosity, and sensor and nanoscale devices with unusual optoelectronic properties.

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