Biomimetic Templating of Porous Lamellar Silicas by Vesicular Surfactant Assemblies

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A biomimetic templating approach to the synthesis of lamellar silicas is demonstrated. The procedure is based on the hydrolysis and cross-linking of a neutral silicon alkoxide precursor in the interlayered regions of multilamellar vesicles formed from a neutral diamine bola-amphiphile. Unlike earlier surfactant-templating approaches, this method produces porous lamellar silicas (designated MSU-V) with vesicular particle morphology, exceptional thermal stability, a high degree of framework cross-linking, unusually high specific surface area and pore volume, and sorption properties that are typical of pillared lamellar materials. This approach circumvents the need for a separate pillaring step in building porosity into a lamellar host structure and offers new opportunities for the direct fabrication of adsorbents, catalysts, and nanoscale devices.

Templating processes that mimic biomineralization have attracted considerable attention because of their potential uses in the design of valuable inorganic materials (*1*, *2*). Similar processes based on the hydrolysis and cross-linking of inorganic precursors at the surfaces of supramolecular surfactant assemblies have been used to prepare new families of hexagonal and cubic mesoporous molecular sieves (*3*–*6*). Unfortunately, however, all of the related surfactant-templated lamellar phases prepared to date collapse to an amorphous oxide upon template removal (*7*, *8*). Lamellar phases have been recognized for their ability to form continuous films (*8*) that could be useful for the direct fabrication of membranes, sensors, and other nanostructured devices (*9*), provided that the framework remains intact in the absence of the template.

The instability of surfactant-templated lamellar phases represents an important gap in the chemistry of porous metal oxides prepared by direct synthesis. Porous derivatives of lamellar MCM-50 frameworks can be prepared by a postsynthesis cross-linking treatment with tetraethyl orthosilicate (TEOS) (*10*). This approach, however, suffers a major drawback because it requires, by analogy to conventional pillaring methods (*11*, *12*), a second postsynthesis step to intercalate inorganic oxide pillars in the gallery of the lamellar host. In addition, the charged quaternary ammonium template is strongly bound to the framework and is difficult to recover by nondestructive methods. Therefore, a one-step direct synthesis approach to the formation of stable, porous lamellar silicas that would allow for efficient removal of the template is highly desirable.

Here, we report the preparation of porous lamellar silicas that have vesicular particles, a high degree of thermal stability and framework cross-linking, very high specific surface area and pore volume, and sorption properties that are like those of pillared lamellar solids. Our approach is based on the hydrolysis and cross-linking of a neutral inorganic alkoxide precursor in the interlayered regions of multilamellar vesicles of a neutral bola-amphiphile surfactant that contains two polar head groups linked by a hydrophobic alkyl chain. In addition, the method provides for the efficient and environmentally benign recovery of the template by solvent extraction. This biomimetic approach eliminates the need for a separate pillaring step that would build porosity into a lamellar host structure and can be used to fabricate adsorbents, catalysts, and nanoscale devices.

A neutral inorganic precursor is hydrolyzed in the presence of neutral diamines with alkyl chain lengths from C_8 to C_{12} and a cosolvent [ethanol (EtOH)]. The preparation with 1,12-diaminododecane (DADD) illustrates the novelty of the synthetic strategy. In a typical preparation, TEOS was added to a templating solution of DADD in EtOH and deionized water; the reaction mixture had the molar composition 1.0 TEOS : 0.26 DADD : 9.09 EtOH : 50.8 H_2O. The reaction mixture was vigorously stirred at ambient temperature for 18 hours to obtain the templated lamellar product with vesicular morphology, denoted MSU-V. The crystalline product was recovered by filtration, washed with deionized water, and air-dried. Template was removed either by calcination in air at 630°C for 4 hours or by solvent extraction. The solvent extraction was performed as described in (*6*), but the temperature of the extraction was set at ~40°C. Complete cross-linking of the structure of the EtOH-extracted product was accomplished by subsequent calcination in air at 630°C for 4 hours.

The powder x-ray diffraction (XRD) patterns of the as-synthesized, EtOH-extracted, and EtOH-extracted and calcined MSU-V products prepared with DADD (*13*) are shown in Fig. 1. The as-synthesized sample exhibits an XRD pattern typical for lamellar material. Two well-expressed 00ℓ reflections, corresponding to a basal spacing of 2.3 and 1.2 nm, are resolved. The absence of additional reflections of the lamellar phase could be attributed to limited order in the lamellar framework of this silicate. A few reflections were also reported for the hexagonal MCM-41 and related hexagonal mesoporous silica (HMS) materials; these were attributed to the limited local order in the framework walls (*3*, *6*).

The removal of the template by EtOH extraction slightly altered the corresponding XRD pattern (Fig. 1). A new reflection centered at an interplanar distance or *d* spacing of 1.3 nm and a weak shoulder at ~1.2 nm were observed. These reflections nearly coincide with a hexagonal 110 and 200 subset rather than with the expected lamellar one. However, the possibility of reorganization of our lamellar surfactant–inorganic arrays into a hexagonal structure during solvent extraction [similar to that observed for kanemite (*4*)] is precluded on the basis of the corresponding transmission electron microscopy (TEM) images that are similar to those shown in Fig. 2, B and C. Also, corresponding electron diffraction patterns of the most ordered regions of the sample exhibited diffraction

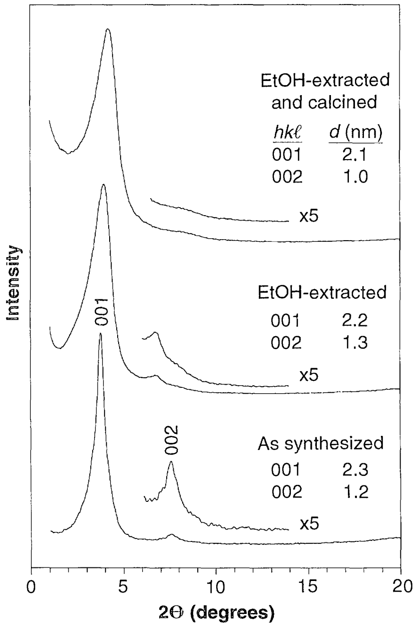

Fig. 1. Powder XRD patterns of as-synthesized, EtOH-extracted, and EtOH-extracted and calcined MSU-V samples. The patterns were measured on a Rigaku Rotaflex diffractometer equipped with a rotating anode and using Cu K_α radiation (wavelength, 0.15418 nm).

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maxima typical of a lamellar structure.

In contrast to all previously reported bilayer quaternary ammonium–templated lamellar phases (*3, 5, 7, 8, 10*), our EtOH-extracted MSU-V samples and our EtOH-extracted and calcined MSU-V samples clearly retained their crystallinity (see Fig. 1). The XRD pattern of the MSU-V material in which the template was removed by calcination (not shown) was similar to that exhibited by the EtOH-extracted and calcined MSU-V sample. In addition, the as-synthesized MSU-V and EtOH-extracted MSU-V exhibited superior thermal stability relative to the conventional pillared lamellar materials. Our experiments indicate that the thermal stability of MSU-V materials is comparable to that of hexagonal MCM-41 and HMS molecular sieves; these materials retain their XRD patterns upon calcination in air up to 800°C for 4 hours.

A low-magnification TEM micrograph of a thin section of the as-synthesized MSU-V is shown in Fig. 2A. Elliptical multilamellar vesicles of ~300 to 800 nm are evident in this image. The multilamellar regions near the vesicle surface are populated by a dense inorganic phase. The presence of layerlike patterns in the central parts of some vesicles is most likely the result of damage caused by ultrathin sectioning. The lamellar character of the MSU-V structure is clearly evident from the TEM images in Fig. 2, B and C. The basal spacings measured from the micrograph in Fig. 2B (~2.5 to 2.9 nm) agree well with the value obtained from XRD data (d_{001} = 2.3 nm). The thickness of the layers is ~1.0 to 1.3 nm, which is similar to that observed for smectite clays (*11*) and the layered silicic acids magadiite and kenyaite (*14*). Figure 2C shows an ultrathin section of a few adjacent vesicles that have multilamellar regions entirely populated by a well-ordered lamellar phase. This is evident from the multiple parallel dark lines (layers) that surround the vesicle cores (see arrows). This structural feature is indicative of biomimetic nucleation and growth of a lamellar silica material in the interlayered regions of the multilamellar bola-amphiphile vesicles.

The vesicular particle morphology of the

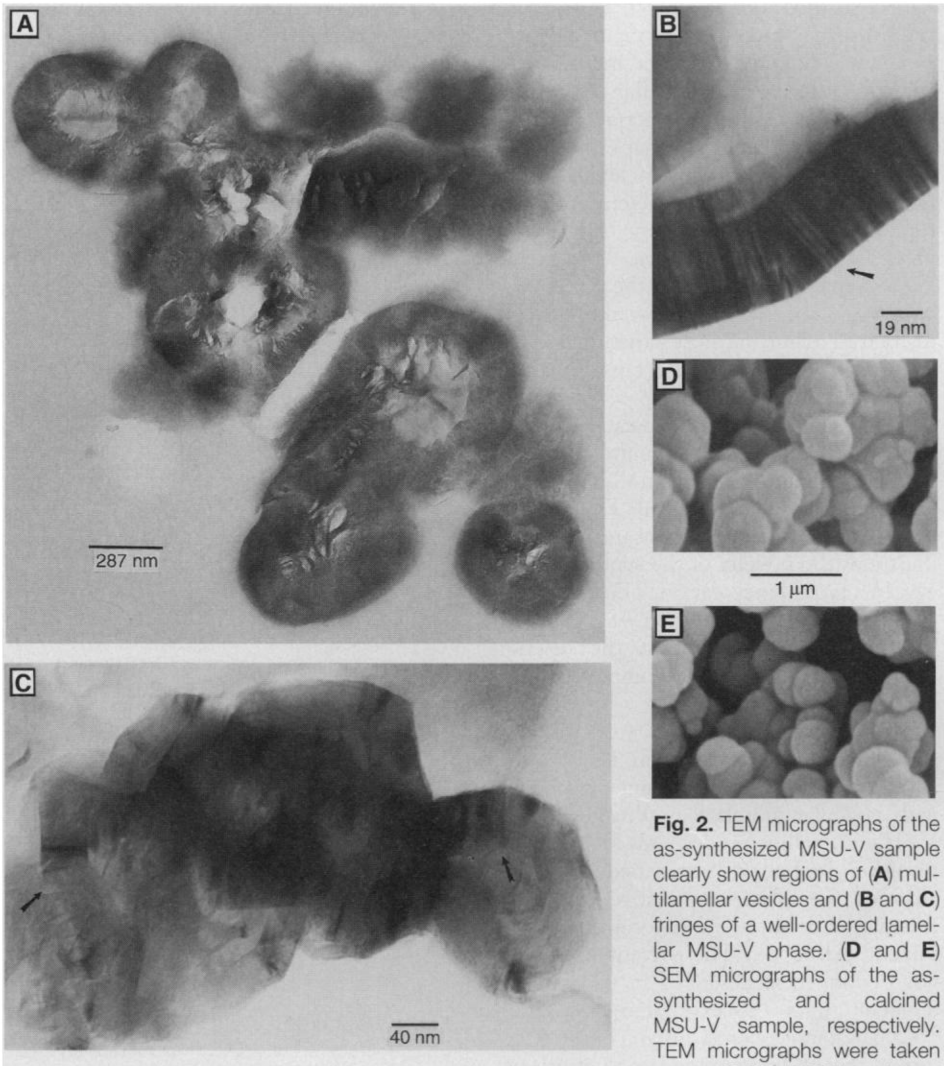

Fig. 2. TEM micrographs of the as-synthesized MSU-V sample clearly show regions of (**A**) multilamellar vesicles and (**B** and **C**) fringes of a well-ordered lamellar MSU-V phase. (**D** and **E**) SEM micrographs of the as-synthesized and calcined MSU-V sample, respectively. TEM micrographs were taken on a JEOL 100CX equipped with a lanthanum hexaboride gun using an accelerating voltage of 120 kV and an aperture of 20 µm for the objective lens. SEM micrographs were taken on a JEOL JSM 6400V using an accelerating voltage of 8 kV and a working distance of 16 mm.

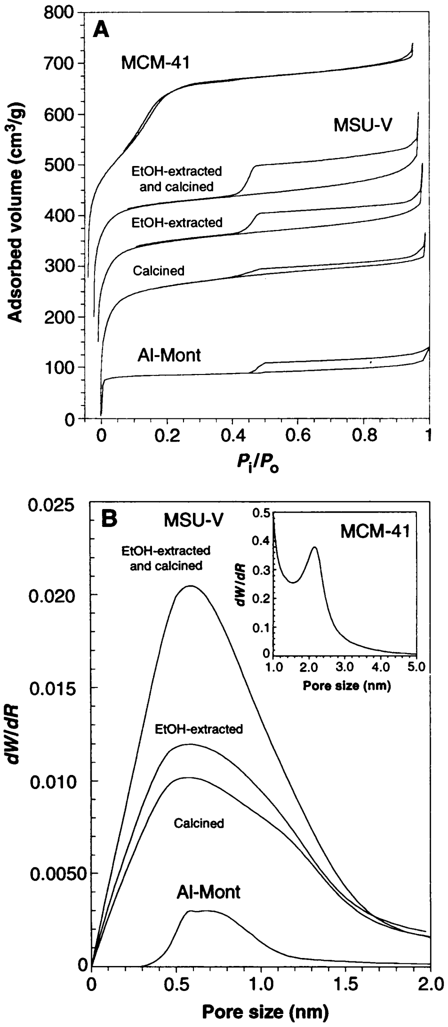

Fig. 3. (**A**) N_2 adsorption-desorption isotherms of Al-Mont, MSU-V, and MCM-41 (P_i/P_o, partial pressure of nitrogen). (**B**) Corresponding Horvath-Kawazoe pore size distribution curves. (Inset) Horvath-Kawazoe pore size distribution of mesoporous MCM-41. We measured the N_2 adsorption-desorption isotherms at −196°C on a Coulter Omnisorp 360CX Sorptometer, using a continuous adsorption procedure. Before measurement, samples were evacuated overnight at 150°C and 10^{-6} torr. The volume adsorbed is at standard temperature and pressure (*dW/dR*, derivative of the normalized nitrogen volume adsorbed with respect to the pore size of the adsorbent). The isotherms were shifted from the origin for improved clarity. The micropore size distribution was estimated from the adsorption branch of the isotherms by the method of Horvath and Kawazoe (*15*).

as-synthesized MSU-V product (containing the template) is confirmed by the corresponding scanning electron microscopy (SEM) image presented in Fig. 2D. The size of the vesicles determined from this SEM image is in agreement with that obtained from TEM. The calcined MSU-V phase inherits the vesicular morphology of the original organic-inorganic complex (Fig. 2E). This again suggests that the self-assembly process occurs in the interlayered regions of these multilamellar vesicles.

The N_2 adsorption-desorption isotherms and corresponding Horvath-Kawazoe (*15*) pore size distribution (PSD) curves of the MSU-V samples are shown in Fig. 3, A and B, respectively. Included for comparison are the curves for typical MCM-41 and Al-pillared montmorillonite (Al-Mont). The corresponding parameters of the pore structure are summarized in Table 1. All MSU-V samples exhibit type I isotherms with hysteresis loops of type H4 (*16*) (see Fig. 3A). These isotherms are very different from the isotherm of the hexagonal MCM-41. The sharp adsorption feature at P_i/P_o of 0.08 to 0.25, which is characteristic for MCM-41 (*3*), is absent in our isotherms. In addition, the corresponding PSD curves for MSU-V samples show maxima centered in the micropore size region (0.6 and 1.2 nm), whereas the curve for MCM-41 shows a maximum at a framework-confined mesopore size of 2.2 nm (see Fig. 3B).

Comparison of the data in Table 1 shows that MSU-V and MCM-41 have similar specific surface areas. However, MCM-41 exhibits only framework-confined mesoporosity and little or no microporosity or textural mesoporosity. In contrast, lamellar MSU-V exhibits well-developed intergallery framework microporosity and complementary textural or interparticle mesoporosity, as evidenced by the significant micropore volumes (V_{micro}) and mesopore volumes (V_{meso}) and by the large C_{BET} constants, which give an indication of the magnitude of the adsorbent-adsorbate interaction energy. The similar sorption properties of calcined and EtOH-extracted MSU-V signify that the neutral template can be efficiently removed from the pore network by solvent extraction. In addition, the isotherm of the EtOH-extracted and subsequently calcined MSU-V is similar to that exhibited by the EtOH-extracted product. The N_2 adsorption-desorption isotherms and pore size distribution curves of MSU-V resemble those of Al-Mont and related pillared clays (*17*, *18*). These results suggest that our materials are structurally similar to pillared clays and preclude the possibility of an analogy with the templated hexagonal M41S phases.

We postulate that the formation of MSU-V materials occurs in a manner reminiscent of natural biomineralization processes. As illustrated in Fig. 4, our biomimetic templating synthesis most likely occurs through the assembly of neutral diamine surfactants into multilamellar vesicles. The multilamellar regions of the vesicles are composed of closely packed layers of surfactant separated by water layers. The addition of TEOS to the template solution affords hydrolyzed $Si(OC_2H_5)_{4-x}OH_x$ species. These neutral species penetrate the vesicle interface, diffuse into the multilamellar regions, and participate in H-bonding interactions with the lone electron pairs on the surfactant head groups. The lack of electrostatic repulsions between the neutral silica oligomer species, the absence of charge-matching surfactant-inorganic interactions, the close proximity of the layers, and the further cross-linking and polymerization of adjacent silica species leads to the simultaneous growth of the parallel silica layers and the intergallery pillars. Further support for the proposed mechanism is obtained from the Q^4/Q^3 ratios of $Si(OSi)_4$ to $Si(OSi)_3OH$ silicon sites [obtained from ^{29}Si magic angle spinning nuclear magnetic resonance (MAS NMR) spectra (*19*)] exhibited by the as-synthesized MSU-V and EtOH-extracted MSU-V (1.16 and 1.63, respectively), which are much higher than the ratios reported for bilayer templated lamellar silicas (from 0.73 to 1.0) (*3*, *5*). This result indicates a much higher degree of cross-linking for noncalcined MSU-V samples.

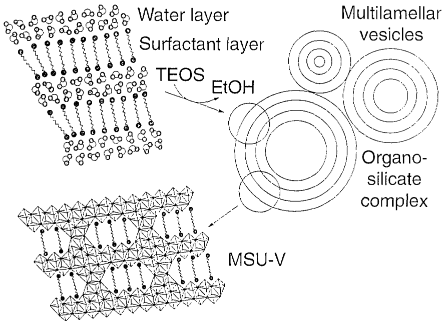

Fig. 4. Proposed biomimetic vesicular templating mechanism for the formation of MSU-V.

Table 1. Sorption properties of MSU-V silicas prepared by biomimetic diamine vesicle templating. The specific surface area, S_{BET}, and the C_{BET} constant were calculated from the linear part of the Brunauer-Emmett-Teller (BET) plot according to International Union of Pure and Applied Chemistry recommendations (*16*). The total pore volume, V_{total}, was taken from the desorption branch of the isotherm at P_i/P_o = 0.98, assuming complete surface saturation. The volume of micropores, V_{micro}, was determined by the *t*-plot method (*16*). The volume of mesopores, V_{meso}, was estimated from the equation $V_{meso} = V_{total} - V_{micro}$. All volumes were expressed in terms of adsorbed liquid nitrogen. The average pore size, d_p, was determined from the maxima of the corresponding Horvath-Kawazoe pore size distribution curves (*15*) (see Fig. 3B).

Sample	S_{BET} (m^2/g)	C_{BET}	V_{total} (cm^3/g)	V_{micro} (cm^3/g)	V_{meso} (cm^3/g)	d_p (nm)
MCM-41	1104	84	0.70	0	0.70	2.2
MSU-V (EtOH-extracted and calcined)	838	765	0.562	0.078	0.484	0.6
MSU-V (EtOH-extracted)	756	177	0.468	0.121	0.347	0.6, 1.2
MSU-V (calcined)	984	282	0.526	0.169	0.357	0.6, 1.2
Al-Mont (*17*)	365	*	0.25	0.12	0.13	0.6, 0.8

*Not reported.

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