Flaky, Ultrathin Mesoporous Silica Laminas

Puyam S. Singh and Katsunori Kosuge*
Materials Processing Department, National Institute for Resources and Environment, 16-3 Onogawa, Tsukuba, Ibaraki 305

(Received September 26, 1997; CL-970743)

Flaky, ultrathin mesoporous silica laminas with uniform mesopores, have been synthesized by hydrolysis of acidic tetraethylorthosilicate solution with dodecylamine or, decylamine surfactant. The materials have BET surface areas of 600-850 m^2/g and mesopore diameters of *ca.* 3-4 nm after the samples were calcined at 500 °C.

As pointed out by Lehn,[1] molecular recognition may be achieved by imprinting a specific shape and size selective mark on the surface or in the bulk of a material. The synthesis of various structures of microporous zeolites by molecular templating[2] and mesoporous M41S type molecular sieves by the use of liquid crystal templates[3] or phases[4] are the typical examples. As M41S type has regular pore structure and appreciable high surface area, it has been paid considerable attention for its possible uses as efficient molecular sieves or catalysts. Since discovery of M41S with regular pore structure, many works have been published on the synthesis, modification, characterization and catalytic properties of modified mesoporous materials. Recently, M41S types which exhibit disordered mesopore channel arrangements, designated as KIT-1[5a] or MSU-1[5b] have been reported. Various morphogenesis of shapes, surface patterns and pore channel structure have also already been observed in M41S type mesoporous silica. Such diverse morphogenesis of shapes or channel arrangements in M41S has significant advantages for its uses in catalysis, separation science and technology.

Here we report that flaky, ultrathin mesoporous silica laminas with uniform mesopores can be produced by careful control of inorganic-organic interface of acidic tetraethylorthosilicate solution and dodecylamine (or, decylamine) surfactant. The mesopore channel arrangement is disordered but has uniform channel width as observed in case of KIT-1 or MSU-1. The existance of mesoporous silica with such flaky, ultrathin lamina morphology having uniform mesopore has not been reported previously.

All the synthesis experiments were performed at room temperature. A typical procedure for the synthesis of a representative sample by dodecylamine templating, is as follows: tetraethylorthosilicate (TEOS) was mixed with aqueous solution of HCl in a molar ratio of 1:0.2, followed by addition of dodecylamine (the molar ratio of dodecylamine to tetraethylorthosilicate was 1:2). The mixture was then vigorously stirred for 24 h. The solid products were separated by centrifugation, dried at 50 °C and finally calcined at 500 °C for 2 h to yield mesoporous material.

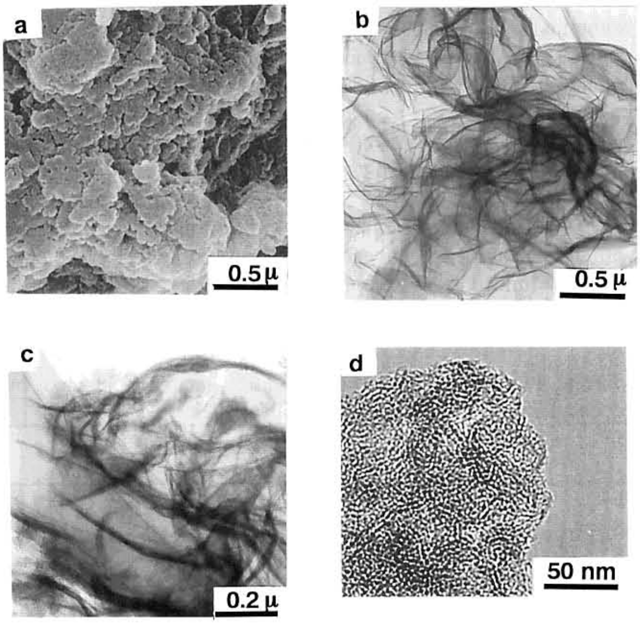
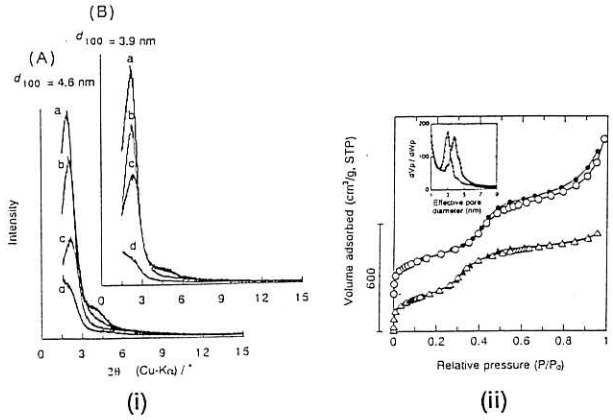


Figure 1. (a) Scanning and (b) transmission electron micrographs of Sample S3 obtained by dodecylamine templating; (c) transmission electron micrographs of Sample S7 obtained by decylamine templating; (d) High resolution transmission electron micrographs of Sample S3.



(i) (ii)

Figure 2. (i) X-ray diffraction patterns of (A) Sample S3 (B) Sample S7, upon calcination in air at (a) 500°C, (b) 800°C, (c) 900°C and 1000°C for 2 h. (ii) N_2 adsorption-desorption isotherms and the corresponding HK plots of Sample S3 (O), and Sample S7 (Δ); open and closed symbols are for adsorption and desorption branch respectively.

Scanning electron micrograph (Figure 1a) and transmission electron micrograph (Figure 1b) of a representative sample designated as S3 (see Table 1 given below for synthesis gel compositions and porous properties of the samples), obtained by dodecylamine templating shows that the sample consists of aggregates of particles having the morphology of flaky, ultrathin laminas. Similar morphogenesis of shapes are also observed in case of the sample (S7) obtained by decylamine templating (Figure 1c). The disordered, hexagonal like packing of interconnected channels with uniform channel width of *ca.* 4 nm can be seen by high resolution TEM image (Figure 1d). All the calcined samples show hexagonal symmetry of mesoporous M41S types, as signaled by the commonality of their diagnostic powder X-ray diffraction (XRD) pattern (Figure 2 (i)). Figure 2 (i) also shows the XRD patterns of the samples calcined at various temperatures (500, 800, 900, 1000 °C) indicating the degree of structural stability as a function of temperature.

Figure 2 (ii) shows the N_2 adsorption-desorption isotherms and corresponding HK plots[6] of two representative samples (S3 and S7) obtained by dodecylamine or decylamine templating. The clear adsorption step of the capillary condensation indicates the presence of framework-confined mesopores. The height and steepness of this step indicate the extent of the uniformity of framework-mesoporosity. From the HK plots of the sorption isotherms, it is revealed that dodecylamine and decylamine templating samples have uniform mesopore diameters with the size of *ca.* 3.8 nm and *ca.* 3.0 nm respectively. The pore sizes determined by sorption measurement are coincident with those evaluated from TEM and XRD.

Table 1. Porous properties of silica laminas obtained by dodecylamine or, decylamine templating

S[a]	Amine[b]	HCl[c]/ mole	BET[d] $m^2.g^{-1}$	PV[e]/ $cm^3.g^{-1}$	d[f]/ nm
S1	C_{12}	0.002	792	0.80	nd
S2	-do-	0.008	651	0.45	4.0
S3	-do-	0.010	826	0.61	3.8
S4	-do-	0.012	602	0.42	3.6
S5	C_{10}	0.002	864	0.75	nd
S6	-do-	0.008	766	0.61	3.1
S7	-do-	0.010	779	0.67	3.0
S8	-do-	0.012	755	0.63	2.9
S9	-do-	0.020	552	0.26	1.0

[a]Sample numbers, [b]alkyl chain lengh of primary amine, [c]moles of dissolved HCl in the given 20 ml of aqueous solution and it is the corresponding volume for a given 10 ml of tetraethylorthosilicate in the synthesis composition system and molar ratio of dodecylamine/decylamine to tetraethylorthosilicate is 1:2, [d]BET surface area, [e]framework pore volume is determined by *t*-plot analysis[7]; [f]pore diameter is determined by HK plots, except for the 'sample S9' which is determined by MP plots[8]; [nd]not determined.

In Table 1, examples of porous properties of flaky, ultrathin mesoporous silica laminas obtained from different reaction conditions are listed. The samples obtained from different synthesis compositions have different porous properties. For the samples obtained at very low acid concentration of synthesis composition system (Sample S1 and S5), the capillary condensation is relatively not steep, and the intensity of d_{100} reflection in the XRD patterns is considerably weak and broad indicating the unsuitability of mesostructure formation at very low acid concentration. Further, at high acid concentration (Sample S4 and S8) the mesostructure quality decreases as indicated by lower BET surface area and pore volume. The sample S9 obtained from the synthesis mixture containing 0.02 moles of HCl by decylamine templating has low BET surface area, framework pore volume of only 0.26 $cm^3.g^{-1}$, with small pore diameter of *ca.* 1 nm. In case of dodecylamine templating, tetraethylorthosilicate is not completely hydrolyzed from the synthesis mixture containing 0.02 moles of HCl. Hence, the formation of mesoporous silica laminas occur within a narrow range of the synthesis composition system.

Chemical analysis show that as-synthesized products has the molar ratio of Cl^- to template as 0.3 : 1. Furthermore the FTIR spectra of as-synthesized samples show bands in 1620-1485 cm^{-1} region due to both $R\text{-}NH_2$ and $R\text{-}NH_3^+$ bending modes. Also the spectra shows the presence of characteristic peak of the free amine at ca. 3200 cm^{-1} and broadening of spectrum in the 3800-2850 cm^{-1} range due to partially ionized hydrogen bonding. Thus it indicates that the templating amine in as-synthesized sample are only partially ionized.

The suggested formation processes of mesoporous silica laminas are as follows. The tetraethylorthosilicate hydrolyze in acidic medium to silicic acid or positively charged oligomeric intermediates, such as $\equiv Si(OH_2)^+$.[9] The positively charged silica species are attracted electrostatically to the protonated amine template through the anionic radicals coordinates. The Coulombic interaction between surfactant-coordinating ions-inorganic is the dominating factor to initiate self assembly process for the formation of mesoporous silica laminas. Depending on the degree of curvature of the surfactant-coordinating ions-inorganic, different surface pattern of mesoporous silica are resulted. With octylamine as the surfactant, we have produced silica mesoporous spheres.[10]

In summary, we have demonstrated that thermally stable, flaky, ultrathin mesoporous silica laminas with disordered channel networks can be synthesized by controlled interaction of surfactant - coordinating ions - silica. Depending on the curvature of these interacting phases, different surface morphologies of mesoporous silica can be resulted. These materials might have implications in the developement of advanced materials.

We acknowledge the support of funds provided by the New Energy and Industrial Technology Development Organization, MITI, Japan.

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