Formation of Mesoporous Silica from a Layered Polysilicate Makatite

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Mesoporous silicas with highly ordered and less ordered mesopores were formed through the reaction of a crystalline layered polysilicate makatite with hexadecyltrimethylammonium (C_{16}TMA) chloride. The uniqueness of makatite as a starting material for the formation of mesostructured silica is verified.

Layered polysilicates, such as kanemite ($NaHSi_2O_5 \cdot 3H_2O$), have attracted much attention because unique mesoporous silicas (KSW-1,[1] FSM-16,[2,3] and KSW-2[4]) including lamellar mesophases[5] are obtained by the reactions with alkyltrimethylammonium (C_nTMA) surfactants. FSM-type mesoporous silica was also prepared from silinaite ($LiNaSi_2O_5 \cdot 2H_2O$),[6] the crystal structure of which is analogous to that of kanemite. Recently, we have found that mesoporous silicas with varied orderings are synthesized by the reaction of hydrated α-$Na_2Si_2O_5$ with C_{16}TMACl. Mesoporous silicas (less ordered SSW-1 and highly ordered SSW-2) with higher thermal stability can be prepared under the conditions of wide C_{16}TMA/Si molar ratios.[7,8] However, the precise structure of hydrated α-$Na_2Si_2O_5$ has not fully been determined yet. Further studies on the reactions between well-defined layered polysilicates and surfactants are essential for understanding the crucial role of layered polysilicates for the synthesis of surfactant-templated mesoporous silicas.

Makatite ($Na_2Si_4O_8(OH)_2 \cdot 5H_2O$) is a layered polysilicate composed of single silicate sheets that are constructed by highly distorted boat-type six-membered rings of SiO_4 units (Supporting Figure S1).[9] The periodicity and arrangement of SiO_4 units in the silicate sheets are different from those in kanemite, being important for understanding the formation of mesoporous silicas. Si–O$^-$ sites on the layer surface of makatite directly interact with interlayer sodium cations, whereas those of kanemite interact with interlayer-hydrated sodium cations.[9,10] These differences should cause a different intercalation behavior of makatite, which may induce a diversity of mesoporous silica derived from layered polysilicates. Here, we report the formation of mesoporous silicas from makatite with comparison with those derived from kanemite and hydrated α-$Na_2Si_2O_5$.

The purity of makatite, supplied by Kurosaki Hakudo Kogyo Co.,[11] was checked by powder XRD, ^{29}Si MAS NMR, and ICP. Pulverized makatite powders were allowed to react with a 0.1 M solution of C_{16}TMACl at 70 °C for 3–5 days in the range of the C_{16}TMA/Si molar ratios of 0.2–2.0. Solid products were recovered by centrifugation and dried at 40 °C. The following post-treatment was conducted when the C_{16}TMA/Si molar ratios were 0.2 and 0.5. The solid products were dispersed in distilled water and then the pH value of the suspensions was adjusted to 8.5 by adding 2 M HCl under stirring. The stirring was kept at 70 °C for 6 h under the same pH condition. The products were centrifuged and dried at 40 °C.

The powder XRD patterns of as-synthesized and calcined products without post-treatment are shown in Figure 1. For the samples prepared at the C_{16}TMA/Si ratios of 0.2 and 0.5, four peaks assignable to 2-D hexagonal phase ($d_{10} = 4.0$ nm) were observed clearly in low diffraction angles and the peaks due to makatite disappeared. The mesostructure was not retained after calcination. With the increase in the C_{16}TMA/Si ratio, only ill-resolved XRD peaks were observed before and after calcination at 550 °C for 6 h. The results indicate the formation of less ordered materials. The N_2 adsorption–desorption isotherm of the calcined product (C_{16}TMA/Si $= 2.0$) was type IV (Supporting Figure S2) typical for those observed for silicas with uniform mesopores. The BET surface area, pore volume, and BJH pore diameter were 1240 m^2 g^{-1}, 0.76 cm^3 g^{-1}, and 2.5 nm, respectively. The TEM images strongly support the formation of less ordered mesoporous silica (Figure 2).

Highly ordered mesoporous silicas can be obtained in the present system through post-treatment (Supporting Figure S3) as in the case of SSW-2 prepared from hydrated α-$Na_2Si_2O_5$.[8] The TEM images of the calcined product (C_{16}TMA/Si $= 0.2$) exhibit hexagonally arranged 1-D mesopores (Figure 2). The N_2 adsorption–desorption isotherm also showed the presence of mesopores (pore size: 2.1 nm) (Supporting Figure S2), and the pore diameter became smaller than that observed for the above mesoporous silica (2.5 nm). The BET surface area and pore volume were 1010 m^2 g^{-1} and 0.47 cm^3 g^{-1}, respectively. The ^{29}Si MAS NMR spectra of the as-synthesized and post-treat-

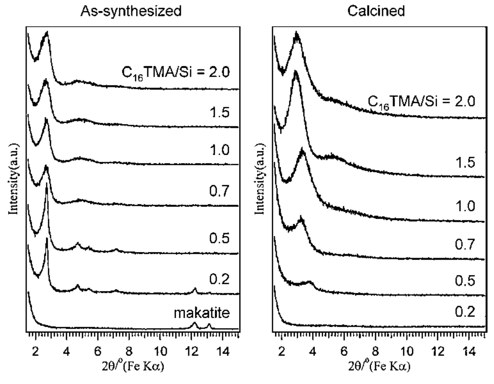

Figure 1. XRD patterns of as-synthesized and calcined products without post-treatment.

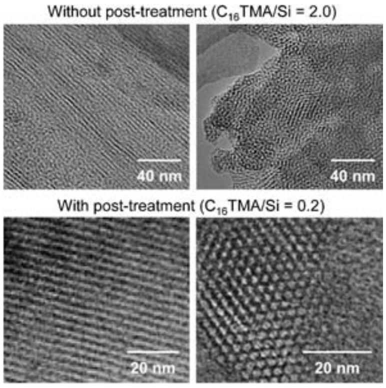

Figure 2. TEM images of the calcined products.

ed products indicate further condensation of the silicate framework during the post-treatment (Supporting Figure S3).

The SEM images of makatite and the 2-D hexagonal mesoporous silica (C_{16}TMA/Si $=$ 0.2) show that rectangular crystals were present homogeneously in makatite and that the morphology was retained after the reaction with C_{16}TMACl and the subsequent post-treatment (Figure 3), indicating that the silicate structure was not completely dissolved after the reaction. An FSM-type mesostructured precursor is proposed to be formed via a layered C_{16}TMA–silicate intermediate with fragmentation of silicate sheets.[12,13] The present results suggest that the fragmentation and mesostructural transformation occur inside the individual particles. In accordance with the previous reports,[12,13] the present results support that the mesostructured precursor is not formed from soluble silicate species but formed through a route different from that of MCM-type materials.[14,15]

Lamellar mesostructured materials are not obtained under the conditions used in the present makatite system, whereas lamellar mesophases are formed under the same conditions for the kanemite system.[5] This difference can be ascribable to the different reactivities with C_{16}TMA cations. The reactivity of makatite with surfactants is lower than that of kanemite, which was confirmed by the incomplete reaction of makatite with surfactants at the C_{16}TMA/Si ratio of 0.2 after 5 days, although the complete reaction of kanemite was achieved even after 3 h.[5] The basal spacing of makatite (0.91 nm) is shorter than that of kanemite (1.02 nm), and the interaction between Si–O^- sites and Na^+ ions in makatite is stronger than that of kanemite, which is evidenced by the lower chemical shifts (-93–-95 ppm) of Q^3 sites in makatite than that (-98 ppm) in kanemite.

Single-layered silicates are gradually fragmented under high-pH and high-temperature conditions.[7,8] The reaction of kanemite with surfactants at the C_{16}TMA/Si ratio of 0.2 causes a larger extent of the fragmentation of the layered silicate due to a high-pH condition. Fragmented silicate species reassemble via the interactions with C_{16}TMA surfactants, resulting in the formation of highly ordered 2-D hexagonal phases. At the C_{16}TMA/Si ratios higher than 0.5, the reaction of kanemite prevents the fragmentation because of the relatively low pH values and the high intercalation reactivity. The prevention preferentially induces the formation of lamellar phases. On the other hand, the reaction of makatite with C_{16}TMA cations requires much longer reaction time, which allows fragmentation to a larger extent during the reaction. Accordingly, less ordered phases are formed through fragmentation during the reactions before C_{16}TMA cations are accommodated in the interlayer space for possible formation of lamellar phases. Consequently, the reaction of makatite at higher C_{16}TMA/Si ratios than 1.0 yields not layered but less ordered mesostructures.

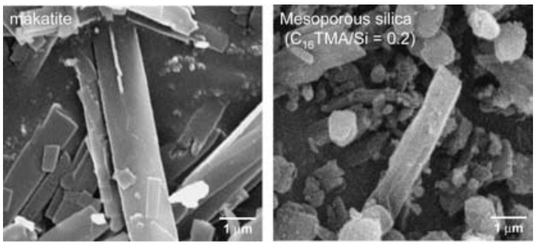

Figure 3. SEM images of makatite and the calcined product.

In conclusion, the mesoscale ordering of the products derived from makatite depends on the C_{16}TMA/Si ratios. The range of the ratio for the formation of highly ordered and less ordered mesostructured silicas from makatite is quite different from that of kanemite. Both the layered structures and the reactivities toward surfactants are crucial for the formation of the silica-based mesostructures. These results are quite useful for the understanding of the layered polysilicate systems to obtain ordered mesoporous silicas having molecularly ordered pore walls.

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16 Supporting Information is also available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.