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Transformation of Layered Docosyltrimethyl- and Docosyltriethylammonium Silicates Derived from Kanemite into Precursors for Ordered Mesoporous Silicas

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The transformation of layered silicate–surfactant materials derived from a layered polysilicate kanemite into precursors for ordered mesoporous silicas was investigated. When kanemite was allowed to react with docosyltrimethylammonium (C₂₂TMA) and docosyltriethylammonium (C₂₂TEA) surfactants, layered C₂₂TMA– and C₂₂TEA–silicate materials were formed. The ²⁹Si MAS NMR spectra of the layered intermediates clearly indicated that fragmented silicate sheets were present in the silicate–surfactant materials. These layered materials can be transformed by acid treatment into mesostructured precursors with three-dimensional (3-d) silicate networks that afford uniform mesopores after the removal of the surfactants. Ordered mesoporous silica with a 2-d hexagonal structure (FSM-16) can be obtained by using C₂₂TEA with a larger headgroup. The results here successfully support the proposed formation mechanism of FSM-16, which consists of assembling of fragmented layered silicate sheets with surfactants and the subsequent structural transformation to the 2-d hexagonal mesophase.

Introduction

After the discovery of a mesoporous silica derived from kanemite with disordered mesopores (denoted as KSW-1 hereafter)¹ and the following syntheses of periodic mesoporous silicas (FSM-16 and MCM-41),^{2,3} mesoporous materials with various structures, morphologies, and compositions have been developed in the past decade.^{4–8} These materials are useful for catalysts, catalyst supports, and adsorbents for relatively large molecules. Extensive studies have also been conducted on the applications for confined reaction vessels and functional materials for electronics and photonics. Among those mesoporous materials, mesoporous silicas derived from kanemite (disordered KSW-1 and 2-d hexagonal FSM-16) have attracted much attention because the synthetic method is quite unique; the 3-d silicate networks are formed

through the reaction of a layered polysilicate kanemite and alkyltrimethylammonium (C_nTMA) surfactants. Recently, a new synthetic route to form novel orthorhombic mesoporous silica (KSW-2) was developed by utilizing a layered complex prepared by the reaction of hexadecyltrimethylammonium (C₁₆TMA) surfactant and kanemite,⁹ and the synthetic conditions of the layered complex were also investigated.¹⁰

Kanemite is composed of individual silicate sheets and interlayer hydrated sodium ions. The formation of mesoporous silica by direct reaction of kanemite with C_nTMA ions has been well recognized.^{1,3,11} However, the formation mechanism of the mesostructured precursors for FSM-16 has not been proved explicitly. It has been proposed that 2-d hexagonal mesostructured precursors are formed by the transformation of layered intermediates composed of C_nTMA ions and fragmented silicate sheets.^{12–14} Nevertheless, such layered intermediates with fragmented silicate sheets have never been isolated as a discrete phase during the transformation though layered intermediates were detected by in-situ XRD.¹³ When C₁₆TMA ions are used, a precursor with hexagonal regularity directly forms, and a layered precursor is hardly obtained under the C₁₆TMA/Si ratio of 0.2, which is explained by silicate–surfactant interactions.^{10,15,16} There are two possible approaches to prepare layered intermediates as a discrete

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phase: one is the use of a surfactant with alkyl chains longer than 16 (like C₂₂TMA ions),¹⁷ and another is the increase of the C₁₆TMA/Si ratio.¹⁰ Therefore, layered silicate–surfactant mesostructured materials derived from kanemite were prepared by the reaction with C₂₂–TMA and C₂₂TEA surfactants in the present study. The transformation of these intermediates into 3-d mesostructured precursors for FSM-16 was investigated. Layered silicate–surfactant mesostructured materials from kanemite and C₁₆TMA were also prepared under the C₁₆TMA/Si ratio of 2.0 for comparison. The presence of fragmented silicate sheets derived from kanemite was successfully proved during the formation of the mesostructured precursor.

Experimental Section

Materials. Kanemite was synthesized as described previously.¹⁰ C₂₂TMA and C₂₂TEA bromides were prepared by the reactions of 1-bromodocosane with trimethylamine and triethylamine, respectively.¹⁸ The resultants were purified by recrystallization in a mixed solvent of chloroform and methyl acetate. The purities of the bromides were checked by ¹H and ¹³C NMR and CHN analysis. C₁₆TMA bromide and chloride were obtained from Tokyo Kasei Kogyo Co. and used without further purification.

Synthesis of C₂₂TMA– and C₂₂TEA–Silicates. Kanemite was allowed to react with an aqueous solution of 0.1 M C₂₂TMABr at 70 °C for 3 h, where the C₂₂TMA/Si molar ratio was 0.2. The solid product was collected by centrifugation and denoted as C₂₂–TMA–silicate. C₂₂TEA–silicate was also prepared at 80 °C in the same manner. Wet C₂₂TMA– and C₂₂TEA–silicates were dispersed in distilled water, and the pH values of the suspensions were adjusted to 8.5 at room temperature by the addition of 2 N HCl. After being stirred for 1 h, the products were centrifuged and air-dried.

According to our previous paper (C₁₆TMA/Si = 2.0),¹⁰ layered C₁₆TMA–silicates were prepared by using C₁₆TMACl at room temperature for 3 days (C16-L-RT, where C16 = C₁₆TMA, L = lamellar, and RT = room temperature) and at 70 °C for 3 h (C16-L-70). Both C16-L-RT and C16-L-70 were gradually treated with 1 M CH₃COOH at room temperature, and the reaction mixtures were kept at pH 6.0 for 1 h, centrifuged, and air-dried.

Characterization. Powder X-ray diffraction (XRD) patterns were obtained by using a Mac Science M03XHF²² diffractometer with monochromated Fe K α radiation. Nitrogen adsorption isotherms were obtained by using a BELSORP 28 apparatus (Bel Japan, Inc.) at 77 K. Samples were heated at 120 °C for 3 h to a residual pressure of 1.3 Pa prior to the measurements. Specific surface areas were determined by BET method using the data before Kelvin condensation. Pore size distributions were calculated by BJH (Barrett, Joyner, and Halenda) method¹⁹ using adsorption branches. Solid-state ²⁹Si MAS NMR measurements were performed on a JEOL JNM CMX-400 spectrometer at a spinning rate of 5 kHz and a resonance frequency of 79.30 MHz with a 45° pulse length of 4.1 μ s and a recycle time of 100 s. The chemical shift was expressed with respect to tetramethylsilane. Intensity ratios of the signals in the ²⁹Si spectra were calculated after deconvolution of the peaks by the use of a MacFID simulation program.

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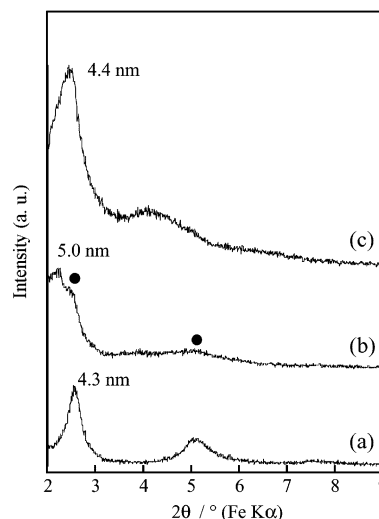


Figure 1. XRD patterns of (a) C₂₂TMA–silicate and (b) the acid-treated and (c) calcined products. Filled circles are assignable to a layered phase.

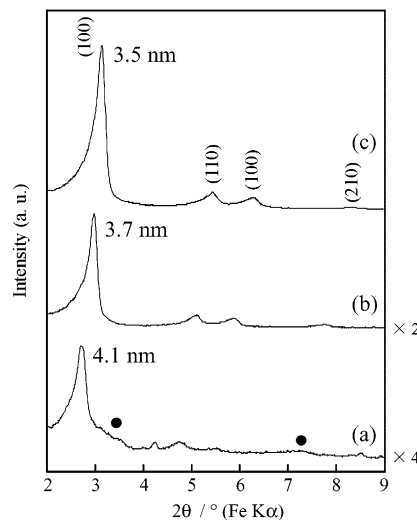


Figure 2. XRD patterns of (a) C₁₆TMA–silicate and (b) the acid-treated and (c) calcined products.

Results and Discussion

Synthesis of C₂₂TMA–Silicate and the Acid Treatment. The XRD pattern of C₂₂TMA–silicate is shown in Figure 1a. A peak with the *d* spacing of 4.3 nm and the higher-order diffractions were observed without other phases, strongly suggesting the formation of a layered phase. The *d* spacing (4.3 nm) was larger than those observed for C16-L-RT (2.9 nm) and C16-L-70 (3.1 nm), as shown later. The increase of the spacing by 1.2–1.4 nm for the case of C₂₂TMA is quite reasonable if a bimolecular layer arrangement similar to that for C₁₆TMA is assumed in the interlayer region between the silica layers. By using C_{*n*}TMA surfactants with alkyl chain lengths shorter than 18, the C_{*n*}TMA/Si ratio of 0.2 is a typical synthetic condition for the formation of ordered mesoporous silica FSM-16 with a 2-d hexagonal phase.³ During the preparation of FSM-16, layered intermediates were hardly obtained by using C₁₆TMABr (Figure 2), though in-situ XRD data of the system clearly detected the presence of a layered intermediate before the formation of a hexagonal phase.¹³ It should be emphasized that the lamellar phase was formed here for the C₂₂TMA system at the ratio of 0.2.

The layered C₂₂TMA–silicate (C22-L-70) was treated with 2 N HCl at room temperature and kept at pH 8.5 for

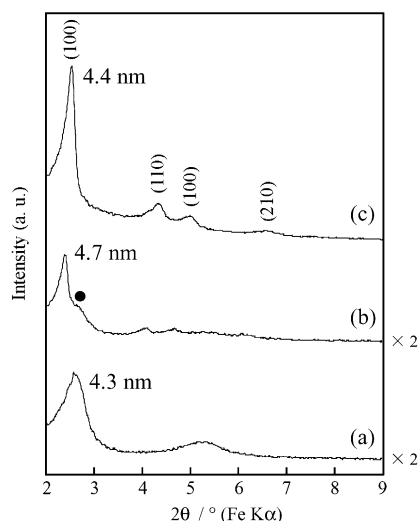


Figure 3. XRD patterns of (a) $C_{22}TEA$ -silicate and (b) the acid-treated and (c) calcined products.

1 h. This procedure was conducted without drying $C_{22}L-70$ as in the case of the synthesis of FSM-16.³ The XRD patterns of the acid-treated material and the calcined product are shown in parts b and c of Figure 1, respectively. After the pH adjustment, a new peak with the d spacing of 5.0 nm assignable to a 3-d network appeared, and the peaks due to the remaining layered material were observed. The 3-d silicate networks are present in the novel phase because the structure ($d = 4.4$ nm) was retained upon calcination. Thus, the stage of the formation of a lamellar intermediate was successfully separated from the subsequent transformation stage into a hexagonal phase, which is not possible for $C_{16}TMA$ -kanemite systems.

Synthesis of $C_{22}TEA$ -Silicate and the Acid Treatment. The XRD pattern for the $C_{22}TMA$ system described above is not so well resolved, possibly because the size of the headgroup is not large enough as compared with the longer alkyl chain. Thus, $C_{22}TEA$ with a larger headgroup was used. The XRD pattern of $C_{22}TEA$ -silicate is shown in Figure 3a. Similar to the $C_{22}TMA$ -silicate system, a peak with the d spacing of 4.3 nm and the higher-order diffractions were observed without other phases. Thus, the layered $C_{22}TEA$ -silicate was isolated though the packing parameter was different.

After the acid treatment, an ordered mesophase was successfully obtained after the pH adjustment (Figure 3b). The XRD pattern of the mesophase is typical for a 2-d hexagonal structure, and the four peaks assigned to a hexagonal structure are more distinct, compared with the pattern for the $C_{22}TMA$ system. The peaks found for the $C_{22}TEA$ system remained very sharp after calcination while the peaks for the $C_{22}TMA$ system became broad. As shown in Figure 4, the channels with hexagonal symmetry were observed by TEM, and the lattice constant ($a_0 = 5.3$ nm) was very close to that obtained from XRD ($a_0 = 5.2$ nm). Thus, the acid-treated $C_{22}TEA$ -silicate is certainly a precursor for FSM-16; the $C_{22}TEA$ surfactant with a larger headgroup was used for the preparation of a higher-ordered hexagonal mesophase than the $C_{22}TMA$ surfactant. The BET surface area, pore volume, and pore diameter of the FSM-16 derived from $C_{22}TEA$ -silicate are $820 \text{ m}^2 \text{ g}^{-1}$, 0.64 mL g^{-1} , and 3.7 nm , respectively. The formation of relatively larger periodic mesopores was achieved in the kanemite-surfactant system without auxiliary additives by the acid treatment of the layered silicates.

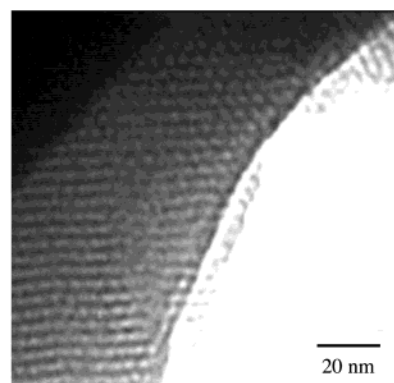


Figure 4. TEM image of the mesoporous silica obtained by acid treatment of $C_{22}TEA$ -silicate.

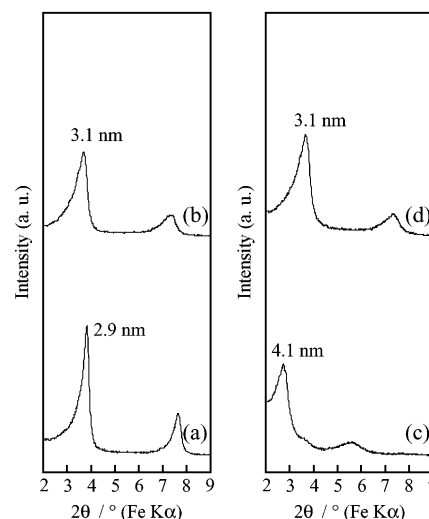


Figure 5. XRD patterns of layered $C_{16}TMA$ -silicate materials derived from kanemite and the acid-treated materials: (a) $C_{16}L-70$, (b) $C_{16}L-RT$, (c) acid-treated $C_{22}L-70$, and (d) acid-treated $C_{16}L-RT$.

Comparison of the $C_{22}TMA$ and $C_{22}TEA$ Systems with $C_{16}TMA$ Systems. The XRD patterns of $C_{16}L-RT$ and $C_{16}L-70$ are shown in Figure 5. The d spacings of $C_{16}L-RT$ (2.9 nm) and $C_{16}L-70$ (3.1 nm) were slightly different depending on the reaction temperatures. The ^{29}Si MAS NMR spectra of $C_{16}L-RT$ and $C_{16}L-70$ are shown in Figure 6. In the spectrum of $C_{16}L-RT$, several Q^8 peaks ($(\text{SiO})_3\text{SiO}$) were mainly observed in the range from -95 to -105 ppm, indicating that the structure of single silicate sheets in kanemite was almost retained. In contrast, both Q^8 and Q^4 peaks ($(\text{SiO})_4\text{Si}$) were observed at around -101 and -111 ppm for the spectrum of $C_{16}L-70$. As reported previously,¹⁰ the formation of the Q^4 silicate species is due to the structural change of kanemite; Q^8 silicate species originally present in kanemite are condensed within individual silicate sheets (*intralayer* condensation), and then silicate sheets of $C_{16}L-70$ are thickened.

The XRD pattern of $C_{16}L-RT$ changed during the acid treatment; all the peaks in the XRD pattern of the acid-treated material (Figure 5c) are assigned to an orthorhombic structure ($d_{110} = 4.1$ nm, space group $C2mm$). The results including the ^{29}Si MAS NMR data (Figure 6e) are in accordance with those reported in the previous paper.⁹ The transformation of a layered structure into an orthorhombic one is accompanied by bending of the individual silicate sheets which is induced by *intralayer* condensation and gradual leaching of $C_{16}TMA$ cations. Calcination of

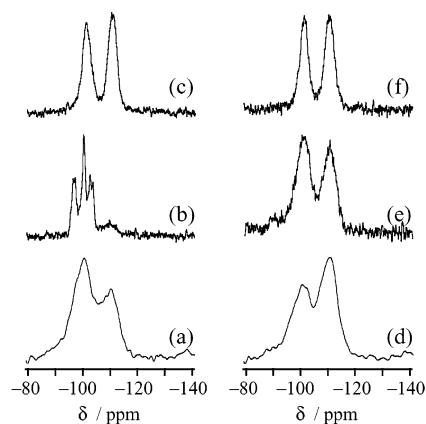


Figure 6. ^{29}Si MAS NMR spectra of layered $C_n\text{TMA}$ -silicate materials: (a) C22-L-70, (b) C16-L-RT, (c) C16-L-70, (d) acid-treated C22-L-70, (e) acid-treated C16-L-RT, and (f) acid-treated C16-L-70.

the acid-treated product leads to the formation of a mesoporous silica (KSW-2) with relatively ordered square mesopores. However, the XRD pattern (Figure 5d) and ^{29}Si MAS NMR spectrum (Figure 6f) of C16-L-70 did not change so distinctly during the acid treatment. The presence of Q^4 silicate species in C16-L-70 may prevent the bending of individual silicate sheets.

The ^{29}Si MAS NMR spectrum of C22-L-70 is shown in Figure 6a. Both Q^3 and Q^4 peaks were also detected in the spectrum of C22-L-70 as in the case of C16-L-70 although the peaks were broader than those observed for C16-L-70 (Figure 6c). Similar ^{29}Si MAS NMR data were obtained for the materials prepared using C₂₂TEA (not shown). Nevertheless, the layered materials were surely transformed into precursors for mesoporous silicas by pH adjustment. The ^{29}Si MAS NMR measurement was performed for C22-L-70 without drying and before the pH adjustment (Figure 7).²⁰ Silicate species with several environments (Q^0 (SiO_4), Q^1 ($(\text{SiO})\text{SiO}_3$), Q^2 ($(\text{SiO})_2\text{SiO}_2$), Q^3 , and Q^4) were present in the C22-L-70 slurry though the main species are Q^3 type. The formation of the Q^4 silicate species is possible by *intralayer* condensation within individual silicate sheets in kanemite and/or the reaction of the Q^3 silicate species in kanemite and soluble silicate species (Q^0 and Q^1). The presence of the Q^2 and Q^3 species is the direct evidence that single silicate sheets in kanemite composed of only Q^3 species were fragmented during the reaction of kanemite and C₂₂TMA cations. Consequently, layered intermediates that can be transformed into mesostructured precursors for mesoporous silicas are typically illustrated in Figure 7. After drying the C22-L-70 slurry, mesostructured precursors of FSM-

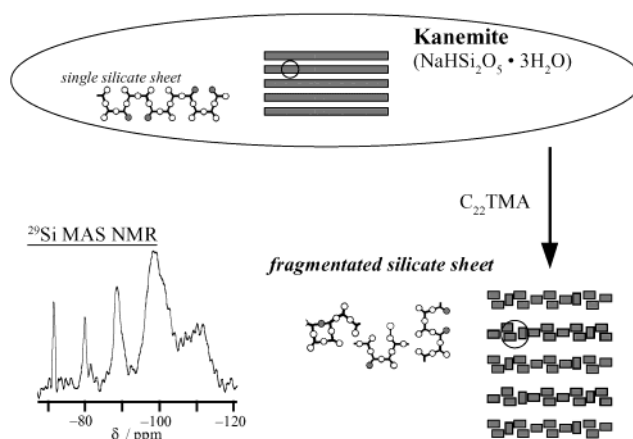


Figure 7. Schematic model of the formation of layered $C_n\text{TMA}$ -silicate materials composed of fragmented silicate sheets by the reactions of kanemite and $C_n\text{TMA}$ surfactants. ^{29}Si MAS NMR spectrum of the C22-L-70 slurry obtained during the synthesis of as-synthesized FSM-16 before pH adjustment.

16 cannot be obtained; the Q^2 and Q^3 silicate species are condensed even at room temperature during the drying process (Figure 6a). For the layered materials composed of single or fragmented silicate sheets, the structural transformation into precursors for ordered mesoporous silicas is induced by acid treatment. The results are quite reasonable for the understanding of the formation mechanism of as-synthesized FSM-16 and KSW-2 materials. In particular, the presence of fragmented silicate sheets during the formation of the as-synthesized FSM-16 material is experimentally proved for the first time.

Conclusions

Layered docosyltrimethyl- and docosyltriethylammonium silicates derived from kanemite are transformed to 3-d silicate networks after acid treatment. Fragmented silicate sheets are supposed to be used for the formation of the 3-d silicate networks. Mesostructured intermediates derived from the single layered polysilicate are strongly dependent on the preparative conditions, and the mesostructures are crucial for the formation of FSM-16, KSW-2, and layered materials even after the acid treatment. The present results are quite useful for mesoporous materials chemistry derived from layered polysilicates.

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