Influence of the Kind of Layered Disodium Disilicates on the Formation of Silica−Organic Mesostructured Materials

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Silica-based mesostructured materials are formed using hydrated α-sodium disilicate and hexadecyltrimethylammonium (C_{16}TMA) chloride at various C_{16}TMA/Si molar ratios, and compared with those from kanemite. When the C_{16}TMA/Si ratios are 0.2, 0.5, 0.7, and 1.0, 2-D hexagonal structures are formed from hydrated α-sodium disilicate though the structures are collapsed on calcination. Less ordered hexagonal structures with straight channels arranged in one direction are formed when the C_{16}TMA/Si ratio exceeds 1.0. In the case of the reactions of kanemite with C_{16}TMA ions, lamellar mesostructures are formed at the ratios higher than 0.5, whereas a 2-D hexagonal structure is formed only at the ratio of 0.2. Mesoporous silica (SSW-1) derived from hydrated α-sodium disilicate is prepared at lower pH without acid treatment when the C_{16}TMA/Si ratio is 2.0. The volume occupied by the headgroups of C_{16}TMA ions in hydrated α-sodium disilicate should be larger than that in kanemite because the distance between Si−O$^-$ sites in the bending direction of hydrated α-sodium disilicate is longer than that of kanemite due to the unique layered silicate structure.

Introduction

Silica−organic mesostructured materials can be prepared by the reaction of a layered polysilicate kanemite ($NaHSi_2O_5 \cdot 3H_2O$)[1−3] with surfactant molecules as templates.[4] By calcining the mesostructured materials, mesoporous silica with narrow pore size distribution (denoted as KSW-1 at a later stage[5]) was obtained. FSM-16 (2-D hexagonal mesoporous silica derived from kanemite) was also formed by optimizing the reaction conditions.[6] Since the report on M41S mesoporous silicas such as 2-D hexagonal MCM-41 by the Mobil group,[7,8] a huge number of studies on this type of materials has been reported in this decade. The char-

acteristic points of ordered mesoporous materials are controllable morphology, structure, and composition, which makes the materials very promising in diverse fields of applications including not only separation and adsorption but also photonics and electronics materials.

Davis et al. compared MCM-41 with mesoporous silica derived from kanemite (KSW-1) and reported that the thermal and hydrothermal stabilities of KSW-1 are higher than those of MCM-41.[9] Inaki et al. also compared both types of the materials from the point of photometathesis of propene in mesopores and reported that the activity of FSM-16 is higher than that of MCM-41 because of the unique arrangements of surface Si−OH groups originated from kanemite.[10] The in situ XRD analysis of mesostructured materials also clarified that the formation process of the as-synthesized precursor for FSM-16 is different from that of MCM-41.[11] It has

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been described several times that fragmented silicate sheets wrap rodlike micelles to form a 2-D hexagonal structure in the formation of FSM-16.[9,11,12] Recently we have reported the presence of fragmented silicate sheets in the formation process of mesostructured materials for FSM-16,[13] and the finding is consistent with the report by O'Brien et al.[11] On the other hand, a structurally different mesoporous silica called KSW-2 is also formed from kanemite.[5] An intercalation compound composed of kanemite-derived silicate sheets and hexadecyltrimethylammonium (C_{16}TMA) ions[14] can be transformed into silica-based mesostructured materials containing squared mesopores by acid treatment which induces the structural deformation. This reaction uses surfactant assemblies but the porous structures are not governed by the packing, which is only observed for the unique kanemite system. The powder XRD patterns of mesostructured precursors for KSW-2 exhibit several peaks at higher diffraction angles, suggesting the partial retention of the silicate framework of kanemite. On the basis of these findings, it is reasonable to say that mesoporous silicas derived from layered disilicates are structurally superior to those using soluble silicate species in thermal and hydrothermal stabilities as well as catalytic activity, and that the formation mechanisms between them are different. However, kanemite has never retained its intact crystalline structure after the formation of mesoporous materials. Therefore, it would be quite interesting to survey the influence of the diversity of the crystalline silicate structures on the formation of mesostructured materials.

Layered disodium disilicates have several crystal structures which are composed of single-layered silicate sheets with interlayer sodium ions, and the silicate layers consist of six-membered rings of SiO_4 tetrahedra with only Q^3 environments of Si (O*Si*(OSi)$_3$).[15−17] Among them, δ-$Na_2Si_2O_5$ (precursor for kanemite) and α-$Na_2Si_2O_5$ have different framework structures: the δ phase has silicate sheets with boat-type six-membered rings, whereas the α phase possesses silicate sheets with chair-type six-membered rings (Figure 1).[17,18] Therefore, we can expect that the degree of condensation during the formation of mesostructured materials should be different and that the assembling structure of surfactants should also be different, which may affect the structure of mesoporous silica after calcination.

However, there have been no reports on the formation of mesostructured materials derived from α-$Na_2Si_2O_5$ and related materials, though Lagaly et al. reported that acid-treated $H_2Si_2O_5$−I reacted with some alkylamines to form intercalation compounds.[19,20] In the present study, based on the synthetic procedure established for
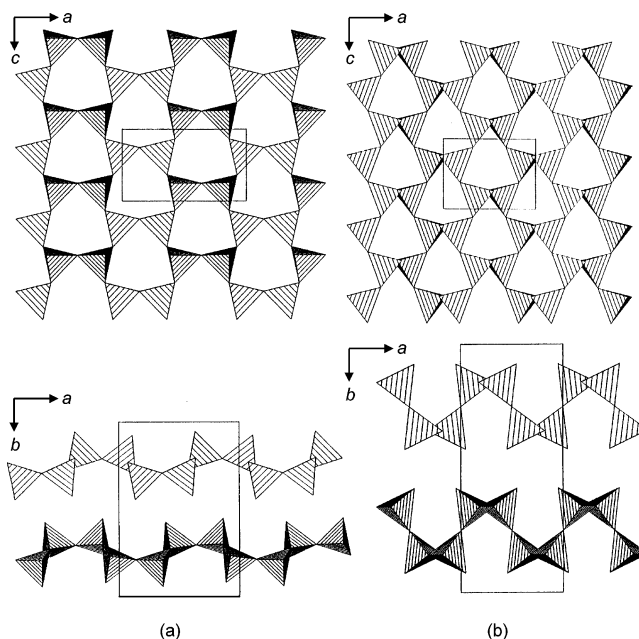
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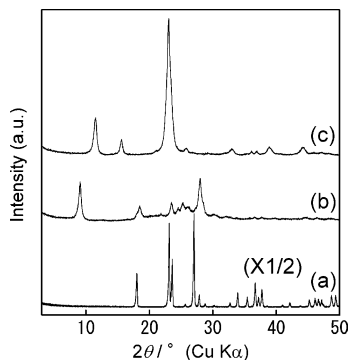

Figure 1. Crystal structures of α- and δ-disodium disilicates[17]: (a) δ-$Na_2Si_2O_5$ and (b) α-$Na_2Si_2O_5$.

FSM-16, hydrated α-sodium disilicate was used as a starting layered polysilicate for the formation of mesostructured materials, and the products were characterized to find the influences of the different structural features of layered disodium disilicates on the formation of mesostructured materials.

Experimental Section

1. Synthesis of α-$Na_2Si_2O_5$, Its Hydrate, and $H_2Si_2O_5$− I. An aqueous solution of NaOH (2 M) was added to a high-purity sodium silicate solution (SiO_2/Na_2O = 3.51, Nissan Chemical Ind., Ltd.) to adjust the ratio of Na/Si to 1.0. The mixed solution was stirred at room temperature for 1 day. After drying the solution, the resultant solid was pulverized and then heated at 800 °C for 12 h in an air atmosphere to form α-$Na_2Si_2O_5$. According to the method of preparing kanemite from δ-$Na_2Si_2O_5$, 1 g of α-$Na_2Si_2O_5$ was dispersed in 50 mL of water and the mixture was stirred for 30 min. The suspension was then centrifuged and air-dried to form hydrated α-sodium disilicate. Wet slurries of hydrated α-sodium disilicate were used without drying when mesostructured materials were synthesized. Disilicic acid ($H_2Si_2O_5$−I) was prepared by treating α-$Na_2Si_2O_5$ (1 g) with HCl (2 M) at room temperature for 3 h, centrifuged, and air-dried.

2. Formation of Hydrated α-Sodium Disilicate−C_{16}TMA Mesostructured Materials. Wet slurries of hydrated α-sodium disilicate were added to a hexadecyltrimethylammonium chloride (C_{16}TMACl) solution (0.1 M) with the C_{16}TMA/Si molar ratio of 2.0. The mixture was stirred at room temperature (for 3 h to 7 d) or 70 °C (for 3 to 6 h). Stirring at 70 °C for 6 h was needed to complete the reaction. The suspensions were then centrifuged, washed with distilled water, and air-dried to form hydrated α-sodium disilicate−C_{16}TMA mesostructured materials. A different C_{16}TMA/Si molar ratio of 4.0 was also employed to form a hydrated α-sodium disilicate−C_{16}TMA mesostructured material. The resultant solids were calcined at 550 °C for 6 h in an air atmosphere (heating rate 5 °C min^{-1}).

The lower ratios of C_{16}TMA/Si (0.2, 0.5, 0.7, and 1.0) were also applied for the formation of hydrated α-sodium disilicate−C_{16}TMA mesostructured materials. Wet slurries of hydrated α-sodium disilicate were reacted with C_{16}TMACl solutions and the mixtures were stirred at 70 °C for 3 h. The suspensions were treated similarly, as described above. The resultant solid

Figure 2. XRD patterns of (a) α-Na$_2$Si$_2$O$_5$, (b) hydrated α-sodium disilicate, and (c) H$_2$Si$_2$O$_5$−I.

at the C$_{16}$TMA/Si molar ratio of 0.2 was calcined at 550 °C for 6 h in an air atmosphere (heating rate 5 °C min^{-1}).

3. Formation of Kanemite−C$_{16}$TMA Mesostructured Materials. Kanemite was synthesized according to our previous report.[14] Wet slurries of kanemite were used without drying when mesostructured materials were synthesized. Kanemite was added to C$_{16}$TMACl solutions (0.1 M) with C$_{16}$-TMA/Si molar ratios of 0.2, 0.5, 0.7, 1.0, and 2.0. The mixtures were stirred at 70 °C for 3 h. The suspensions were then centrifuged, washed with distilled water, and air-dried to form kanemite−C$_{16}$TMA mesostructured materials.[14] The resultant solids at the C$_{16}$TMA/Si molar ratios of 0.2 and 2.0 were calcined at 550 °C for 6 h in an air atmosphere (heating rate 5 °C min^{-1}).

4. Characterization. Powder XRD patterns were recorded on Mac Science MXP^3 (Cu Kα) and M03XHF[22] (Fe Kα) diffractometers with a scanning speed of 2°/min. The diffraction angles were calibrated by using phlogopite as a reference. Solid-state ^{29}Si MAS NMR spectra were measured by a JEOL CMX-400 spectrometer, using a resonance frequency of 79.4 MHz, a rotation speed of 5 kHz, accumulation of 500−800 scans, pulse delays of 200 s for the inorganic substances (disilicates and their hydrates) and 100 s for mesostructured materials, and a pulse angle of 45°. Tetramethylsilane was used as a reference (0 ppm). Nitrogen adsorption−desorption isotherms were obtained by a BELSORP 28SA (Japan Bel Co.) and samples were outgassed at 120 °C under 10^{-2} mmHg for 3 h prior to the measurement. Specific surface areas, pore volumes, and pore size distributions were calculated by the BET method,[21] the t-plot method, and the BJH method using adsorption isotherms.[22] TEM images were taken by a JEM2010EX electron microscope (JEOL) at an accelerating voltage of 200 kV. Powdery samples were dispersed in acetone and mounted on microgrids. The chemical compositions were determined by ICP, CHN, and TG. ICP analysis was performed with an IRIS-AP spectrometer (Jarrell Ash) and samples were prepared by a melting method with lithium metaborate. The surfactant/silicon ratio (C$_{16}$TMA/Si) was determined by CHN analysis using a Perkin-Elmer PE-2400II instrument. Thermogravimetry was conducted by a TG-DTA2000S apparatus (Mac Science Co.) in the temperature range from RT to 1000 °C at a heating rate of 10 °C min^{-1} and an air flow of 200 mL min^{-1}.

Results and Discussion

1. α-Na$_2$Si$_2$O$_5$ and Its Hydrate. All the powder XRD peaks of α-Na$_2$Si$_2$O$_5$ (Figure 2a) are consistent with those reported by Williamson[23] and no impurity phases were observed. The ^{29}Si MAS NMR spectrum of α-Na$_2$Si$_2$O$_5$ (Figure 3c) shows a single signal at −95 ppm

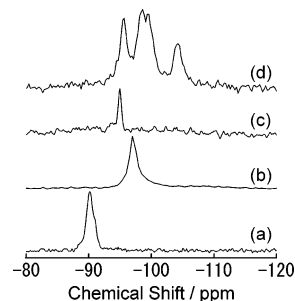**Figure 3.** ^{29}Si MAS NMR spectra of α- and δ-Na$_2$Si$_2$O$_5$ and their hydrates: (a) δ-Na$_2$Si$_2$O$_5$, (b) kanemite, (c) α-Na$_2$Si$_2$O$_5$, and (d) hydrated α-sodium disilicate.

due to Si atoms with a Q^3 environment, which coincides with the report by Heidemann.[24] The Na/Si ratio, determined by ICP, was 1.03. All these data confirm the formation of α-Na$_2$Si$_2$O$_5$.

Figure 2b shows the powder XRD pattern of hydrated α-sodium disilicate obtained by dispersing α-Na$_2$Si$_2$O$_5$ in water. The pattern is different from those of α-Na$_2$Si$_2$O$_5$ and H$_2$Si$_2$O$_5$−I.[25] The appearance of the new peak at $d = 0.96$ nm ($2\theta = 9.2°$) indicates the expansion of the interlayer spacing. The composition of hydrated α-sodium disilicate prepared here was Na$_{1.2}$H$_{0.8}$Si$_2$O$_5$·2.5H$_2$O. Ai et al. also reported the formation of a hydrated product of α-Na$_2$Si$_2$O$_5$ by allowing the disilicate to stand under the humidity of 35−50% at room temperature for 6 months.[26] The XRD pattern shows a peak at $d = 0.94$ nm with some peaks due to unreacted α-Na$_2$Si$_2$O$_5$ and some other peaks inconsistent with those observed by us. They do not provide the crystal structure of the substance.

Figure 3 shows the ^{29}Si MAS NMR spectra of δ-Na$_2$Si$_2$O$_5$ and α-Na$_2$Si$_2$O$_5$, and their hydrates. Kanemite exhibits a sharp signal ascribable to the Q^3 units at −97 ppm. The spectrum of hydrated α-sodium disilicate (Figure 3d) shows several signals in the region of Q^2 and Q^3 units, indicating the diversity of Si environments, which is basically consistent with the previous reports.[26,27] The hydrated behavior is quite different from that of kanemite. The previous papers[26,27] report the presence of the peaks at −110 ppm due to Q^4 that we did not observe, possibly because of the differences between the hydration conditions. The Raman spectra of α-Na$_2$Si$_2$O$_5$ and hydrated α-sodium disilicate (Figure 4) show similar patterns, suggesting the retention of the original silicate framework in the hydrated form.

The layered nature of the hydrate was also supported by the intercalation behavior with C$_{16}$H$_{33}$NH$_2$. The powder XRD pattern of the reaction product (Supporting Information Figure S1) shows the peaks at $d = 5.55$, 2.76, and 1.86 nm assignable to (001), (002), and (003) reflections, respectively, indicating the large expansion by the intercalation, which confirms the lamellar structure of hydrated α-sodium disilicate.

2. Mesostructured Products Derived from Hydrated α-Sodium Disilicate and Kanemite. The powder XRD patterns of the reaction products of hydrated α-sodium disilicate or kanemite with C$_{16}$TMA ions, prepared at the ratio of C$_{16}$TMA/Si = 2.0, are

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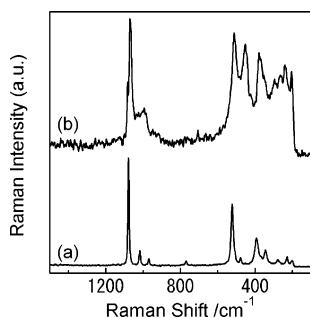
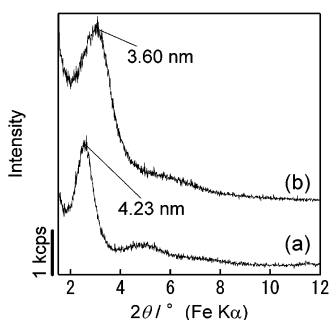**Figure 4.** Raman spectra of (a) α-$Na_2Si_2O_5$ and (b) hydrated α-sodium disilicate.

Figure 5. XRD patterns of (a) the hydrated α-sodium disilicate$-C_{16}$TMA compound and (b) the product after calcination of (a) (C_{16}TMA/Si = 2.0).
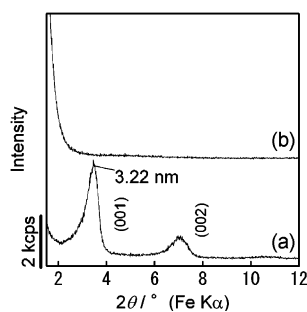

Figure 6. XRD patterns of (a) the kanemite$-C_{16}$TMA intercalated compound and (b) the calcined product of (a) (C_{16}TMA/Si = 2.0).
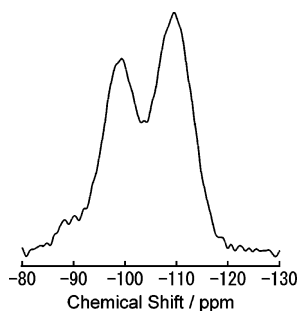

Figure 7. ^{29}Si MAS NMR spectrum of the hydrated α-sodium disilicate$-C_{16}$TMA compound (C_{16}TMA/Si = 2.0).

shown in Figures 5 and 6, respectively. When kanemite was used, the peak at $d = 3.22$ nm and the higher order peaks are observed (Figure 6a). These peaks disappeared after calcination, which means the formation of a lamellar mesophase, as reported previously by us.[14] On the other hand, the peak at $d = 4.23$ nm and a broad peak at $2\theta = 4$–$6°$ (Figure 5a) are observed when hydrated α-sodium disilicate was used. These peaks were preserved after calcination (Figure 5b), indicating the formation of a three-dimensional (3-D) silica net-
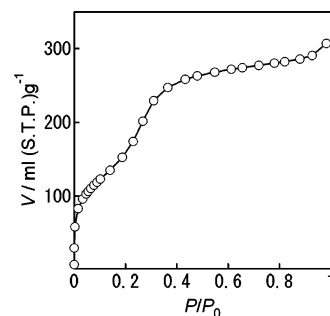

Figure 8. N_2 adsorption isotherm of the hydrated α-sodium disilicate$-C_{16}$TMA compound (C_{16}TMA/Si = 2.0) after calcination (SSW-1).

work. The finding of the formation of the 3-D silica network at the C_{16}TMA/Si ratio of 2.0 is important because the C_{16}TMA/Si ratio induces the formation of a lamellar mesophase from kanemite.

The ^{29}Si MAS NMR spectrum (Figure 7) revealed the degree of condensation of the silicate network of the hydrated α-sodium disilicate$-C_{16}$TMA compound (C_{16}TMA/Si = 2.0) before calcination, and the ratio of $Q^4/(Q^3 + Q^4)$ was 0.57. Though the compound was not acid-treated, the value is quite high—being similar to that found for the pH-adjusted precursor for FSM-16. Consequently, the structure of the compound was retained after calcination without pH adjustment. Compared with the pH of the solution before acid treatment in the synthesis of FSM-16 (higher than 11.5),[28] the pH of the solution at the C_{16}TMA/Si ratio of 2.0 was relatively low (10.2). Therefore, the silicate sheets do not tend to be fragmented by dissolution and the interlayer condensations are liable to occur, leading to a stable 3-D silica network. This is the reason for the high degree of condensation of the silicate network under the high C_{16}TMA/Si ratio.

The surfactant/silicon ratio (C_{16}TMA/Si) was 0.20 in the hydrated α-sodium disilicate$-C_{16}$TMA compound when the starting ratio of C_{16}TMA/Si was 2.0, whereas the contents were 0.24–0.28 in lamellar mesophases derived from kanemite under the same C_{16}TMA/Si ratio. The smaller organic content of the hydrated α-sodium disilicate$-C_{16}$TMA compound results from a higher degree of condensation of the silicate network; that is, there are many Q^4 environments of Si which do not interact with C_{16}TMA.

The nitrogen adsorption isotherm of the porous material derived from the hydrated α-sodium disilicate$-C_{16}$TMA compound (C_{16}TMA/Si = 2.0) after calcination (denoted as SSW-1 hereafter) is shown in Figure 8. A type IV isotherm is observed,[29] and the pore size is 2.7 nm though the pore size distribution is broad (Supporting Information Figure S2).

The TEM image of SSW-1 is shown in Figure 9. A disordered structure (Figure 9a) is observed, which corresponds to the broadness of the diffraction peaks shown in Figure 5b. On the other hand, when we look at the arrangement of the channels, the uniformly arranged straight channels are observed (Figure 9b). This is characteristic of the system using hydrated α-sodium disilicate which should bend along the a axis.[30] Even under the higher C_{16}TMA/Si ratio of 4.0, the XRD peak of the solid after calcination at 550 °C was

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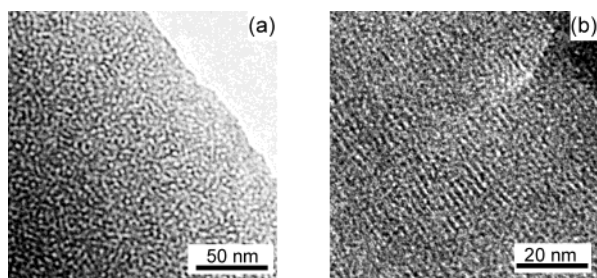(29) Kruk, M.; Jaroniec, M. *Chem. Mater.* **2001**, *13*, 3169.

Figure 9. TEM images of the hydrated α-sodium disilicate–C_{16}TMA compound (C_{16}TMA/Si = 2.0) after calcination (SSW-1).
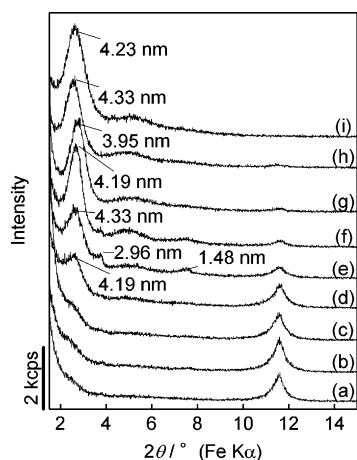

Figure 10. XRD patterns of the hydrated α-sodium disilicate–C_{16}TMA compounds (C_{16}TMA/Si = 2.0) prepared at RT for (a) 3 h, (b) 6 h, (c) 12 h, (d) 1 d, (e) 3 d, (f) 5 d, and (g) 7 d, and 70 °C for (h) 3 h and (i) 6 h.

Figure 11. XRD patterns of the hydrated α-sodium disilicate–C_{16}TMA compounds at the C_{16}TMA/Si ratios of (a) 0.2, (b) 0.5, (c) 0.7, and (d) 1.0.

Figure 12. XRD patterns of the kanemite–C_{16}TMA mesostructured compounds at the C_{16}TMA/Si molar ratios of (a) 0.2, (b) 0.5, (c) 0.7, and (d) 1.0.

observed (Supporting Information Figure S3), showing the formation of a 3-D silica network in the case of hydrated α-sodium disilicate.

To examine the initial stage of formation of the hydrated α-sodium disilicate–C_{16}TMA compound (C_{16}-TMA/Si = 2.0), the reaction was conducted at room temperature and the XRD patterns of the resultants are shown in Figure 10. A broad peak with *d* value of ca. 4 nm began to appear in the XRD pattern of the product at 6 h. As shown in Figures 5 and 6, when C_{16}TMA was used as a template, the peak with *d* value of ca. 3 nm was observed in the lamellar mesostructure, whereas the peak with *d* value of ca. 4 nm was observed in a less ordered hexagonal structure. Therefore, the appearance of the peak with *d* value of ca. 4 nm even at the very initial stage of 6 h indicates that the hydrated α-sodium disilicate forms a 3-D silica network at the initial stage. In the formation of hexagonal mesostructured silica from kanemite, it is reported that a 3-D silica network is formed by way of a lamellar mesophase at the initial stages,[13] though hydrated α-sodium disilicate–C_{16}TMA does not take such a process. Moreover, the peak at 2θ of 11.6° due to hydrated α-sodium disilicate was observed at the initial stages and the peak intensity gradually weakened as the reaction proceeded. The pH values of the reaction solutions were less than 11 at any reaction condition, therefore, the possibility

of dissolution of hydrated α-sodium disilicate is low. However, only a halo peak resulting from the very poorly crystalline structure was observed at higher diffraction angles in the XRD pattern (Figure S4), indicating that the intact crystal structure was not preserved in the hydrated α-sodium disilicate–C_{16}TMA compound. Several peaks at 2θ of 9°, 24°, and 28° were also observed, and these were due to a very small amount of unreacted hydrated α-sodium disilicate detectable by a high-power XRD apparatus (50 kV, 300 mA).

The powder XRD patterns of the reaction products of hydrated α-sodium disilicate and kanemite with C_{16}-TMA ions, prepared at C_{16}TMA/Si molar ratios less than 2.0 (C_{16}TMA/Si = 0.2, 0.5, 0.7, and 1.0) are shown in Figures 11 and 12. When kanemite was used, four diffraction peaks were observed at the C_{16}TMA/Si molar ratios of 0.2 (Figure 12a). These are characteristic of a hexagonal structure, corresponding to (100), (110), (200), and (210) reflections. At the C_{16}TMA/Si molar ratio of 0.5, in addition to the four peaks characteristic of the hexagonal structure, a peak at *d* value of 3.18 nm and the higher order peaks were observed (Figure 12b). This shows the mixture of the hexagonal and lamellar structures. At the ratios of 0.7 and 1.0, only lamellar mesophases were formed (Figure 12c and d). In the report by us,[14] the diffraction peaks resulting from a lamellar structure are observed though a hexagonal structure mainly formed at the ratio of 0.2. The slight difference between these reports is supposed to be due to the reaction conditions.

On the other hand, when hydrated α-sodium disilicate was used, four peaks characteristic of 2-D hexagonal structures were observed in all the XRD patterns at the C_{16}TMA/Si molar ratios of 0.2–1.0 (Figure 11). No clear diffraction peaks were observed at higher diffraction angles (Figure S5), indicating the substantial loss of the crystal structure of the framework. When the ratio was

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(30) The bending direction is limited to the *a* axis. Our recent calculation of the stiffness of kanemite sheet shows that the energy required to strain the sheet in kanemite is much higher in the *c* axis than that in the *a* axis. This finding is in good agreement with our experience using a structural model kit. The same tendency was observed for hydrated α-sodium disilicate.
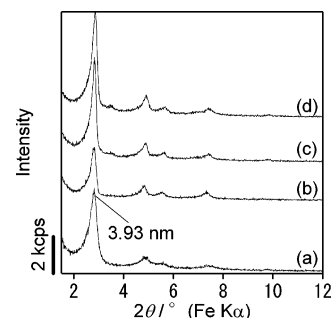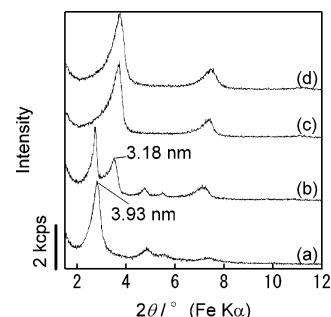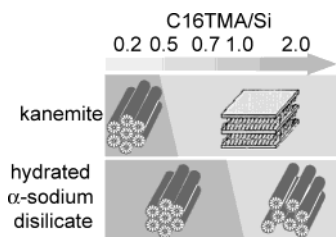
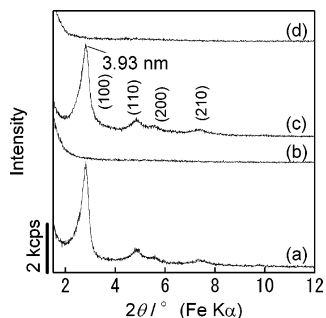**Figure 13.** Structural variation with the C_{16}TMA/Si ratio.

Figure 14. XRD patterns of (a) the hydrated α-sodium disilicate−C_{16}TMA compound (C_{16}TMA/Si = 0.2), (b) the calcined product of (a), (c) the kanemite−C_{16}TMA compound (C_{16}TMA/Si = 0.2), and (d) the calcined product of (c).

Figure 15. ^{29}Si MAS NMR spectra and the integrated intensity ratios of wet slurries of (a) hydrated α-sodium disilicate and (b) kanemite.

1.2, the structure was less ordered, which is similar to the results on the product at the ratio of 2.0.

The relation between the C_{16}TMA/Si molar ratio and the structural variation is shown in Figure 13. A lamellar mesostructure was formed at the C_{16}TMA/Si molar ratios higher than 0.5 in the case of kanemite, whereas 2-D hexagonal structures were formed at the C_{16}TMA/Si molar ratios of 0.2−1.0 in the case of hydrated α-sodium disilicate. The reason for this difference will be discussed later. When hydrated α-sodium disilicate−C_{16}TMA prepared at the C_{16}TMA/Si molar ratio of 0.2 was calcined at 550 °C, no diffraction peaks were observed, meaning the collapse of the mesostructure (Figure 14b). The reason of the collapse is that this mesostructured material was not acid-treated and the degree of condensation was low ($Q^4/(Q^3 + Q^4)$) = ca. 0.35). The collapse of the mesostructure was prevented by acid treatment, as in the case of FSM-16, and the stability was higher than that of FSM-16, which is under investigation and will be reported in near future.

From these results, it is easier for hydrated α-sodium disilicate to form mesoporous materials than for kanemite. The reason why hydrated α-sodium disilicates tend to form mesoporous materials is discussed here. The ^{29}Si MAS NMR spectra of the wet slurries of hydrated α-sodium disilicate and kanemite, as well as their integrated intensity ratios, are shown in Figure 15. The signals due to Q^3 environment were observed mainly in both of them, suggesting hydrated α-sodium disilicate did not dissolve completely, though the ratios of Q^1 and Q^2 were higher for the hydrated α-sodium disilicate than for kanemite.

Inagaki et al. have recently reported the successful preparation of ordered mesoporous materials with uniform organic−inorganic hybrid frameworks.[31] They commented that the low anion charge density plays a role in making the headgroups of alkyltrimethylammonium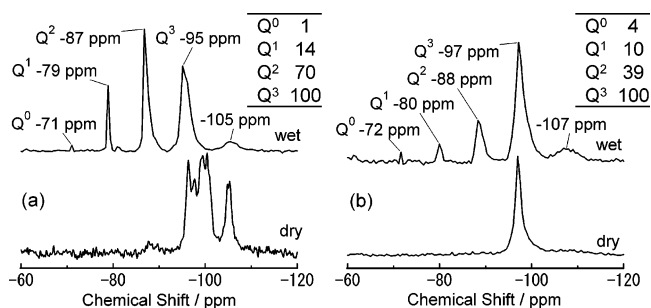 (C_nTMA) ions apart and that a 3-D hexagonal structure is formed. In our report, lamellar mesostructures were formed at the C_{16}TMA/Si molar ratios higher than 0.5 in the case of kanemite, whereas 2-D hexagonal structures were obtained at the C_{16}TMA/Si ratios of 0.2−1.0 in the case of hydrated α-sodium disilicate. This is probably due to the fact that the distances between Si−O$^-$ sites along the bending direction are longer for the hydrated α-sodium disilicate than those for kanemite. The distances between the Si−O$^-$ sites for sodium disilicate are shown in Figure 16. These layers are considered to bend along the *a* axis,[30] and the distance between Si−O$^-$ sites along the *a* axis is longer for α-sodium disilicate (Figure 16b) than for δ-sodium disilicate (Figure 16a). If we assume that the structures similar to the parent silicates are preserved in the hydrates, the headgroups of C_{16}TMA ions become larger, as shown in Figure 16d, in the case of hydrated α-sodium disilicate, leading to the formation of a hexagonal structure.

Although the distance between Si−O$^-$ sites is longer along the bending direction, the hexagonal structure of the product obtained from the hydrated α-sodium disilicate at the C_{16}TMA/Si molar ratio of 2.0 was less ordered. Because the pH value of the reaction solution was not high enough to fragment the silicate sheets, obviously those sheets cannot form an ordered hexagonal structure due to their structural restriction. When C_nTMA ions are used as a template, a highly ordered 2-D hexagonal structure is formed at various pH values from soluble silicate species,[7,8,32,33] whereas it is not formed from a layered silicate unless the pH of the solution is high enough to fragment the sheets. This is a distinctive difference between a layered disilicate and soluble silicate species as the silica sources.

The most important thing for using hydrated α-sodium disilicate is that mesoporous silica can be prepared at lower pH than in the case of kanemite and without acid treatment when the ratio was increased to 2.0. From this point of view, it is expected that the silicate structure would be retained partly in the framework of mesostructured silica when hydrated α-sodium disilicate is used. Further structural control during the formation remains to be tackled. If the *intra*layer condensation observed for the C_nTMA-kanemite systems[5,14] is ideally controlled depending on both the kind of layered polysilicates and the reaction conditions, the deformation of the silicate frameworks would be suppressed. Introduction of heterogeneous atoms such as Al into the

(31) Inagaki, S.; Guan, S.; Fukushima, Y.; Ohsuna, T.; Terasaki, O. *J. Am. Chem. Soc.* **1999**, *121*, 9611.

(32) Huo, Q.; Leon, R.; Petroff, P. M.; Stucky, G. D. *Science* **1995**, *268*, 1324.
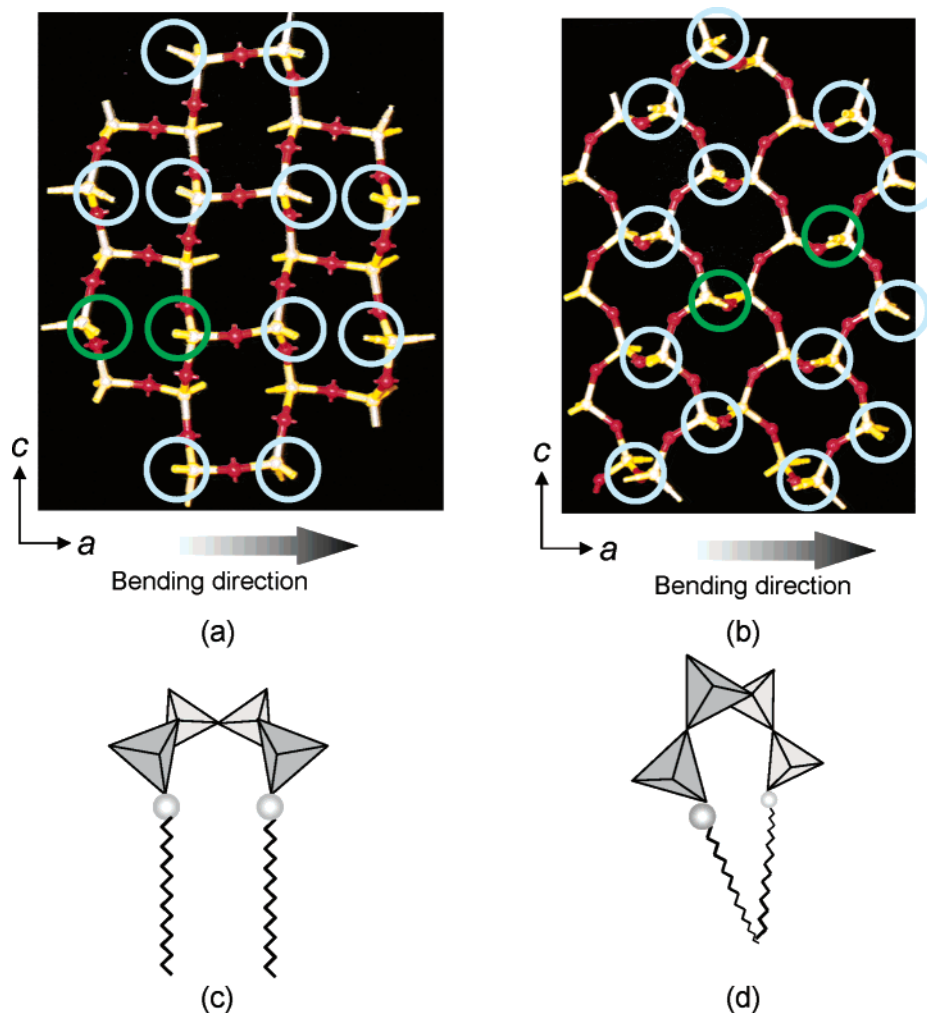(33) Huo, Q.; Margolese, D. I.; Stucky, G. D. *Chem. Mater.* **1996**, *8*, 1147.

Figure 16. Distances between the Si–O⁻ sites of (a) kanemite and (b) hydrated α-sodium disilicate and the difference of the mesostructures derived from (a) and (b) (c and d, respectively).

framework will also be one of the most interesting themes.

Conclusions

Silica-based mesostructured materials were formed using two different disilicates of hydrated α-sodium disilicate and kanemite as the silica sources. The influence of the different structural features of layered disodium disilicates on the formation of mesostructured materials was verified. The original silicate framework of α-$Na_2Si_2O_5$ is probably preserved in its hydrated α-sodium disilicate. In the C_{16}TMA/Si molar ratios of 0.2–1.0 (C_{16}TMA/Si = 0.2, 0.5, 0.7, and 1.0), 2-D hexagonal structures were formed from hydrated α-sodium disilicate, though a less ordered structure was formed when the ratio was 2.0. The uniformly arranged straight channels are observed in the TEM image. This is characteristic of the system using hydrated α-sodium disilicate which should bend along the *a* axis. On the other hand, in the case of kanemite, lamellar meso-structures were formed at the ratios higher than 0.5, and a 2-D hexagonal structure was formed only at the ratio of 0.2. Longer distance between Si–O⁻ sites along the bending direction in hydrated α-sodium disilicate than that in kanemite, making the headgroups of C_n-TMA ions apart, may be the reason for these differences.

Mesoporous silica (SSW-1) derived from hydrated α-sodium disilicate is prepared at lower pH than that from kanemite at the C_{16}TMA/Si ratio of 2.0. More importantly, the acid treatment, which is normally required for the preparation of mesoporous silica from kanemite, was not needed for the formation of 3-D silica network from hydrated α-sodium disilicate at the ratio of 2.0. These findings are quite useful for future design of the framework of mesostructured silica, because, by an appropriate selection of disilicate, mesostructured materials can be prepared under lower pH conditions that are advantageous for retaining the original silicate structures to some extent.

Supporting Information Available: Powder XRD patterns and pore size distributions of the materials discussed (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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