Silica-Based Mesostructured Materials Induced by Surfactant Assemblies in the Two-Dimensionally Limited Space of a Layered Polysilicate Kanemite

Tatsuo Kimura, Daigo Itoh,[1] Tetsuro Shigeno,[1] and Kazuyuki Kuroda*,[1,2,3]

Ceramics Research Institute, National Institute of Advanced Industrial Science and Technology (AIST),
Shimoshidami, Moriyama-ku, Nagoya 463-8560

[1]Department of Applied Chemistry, Waseda University, Okubo, 3, Shinjuku-ku, Tokyo 169-8555

[2]Kagami Memorial Laboratory for Materials Science and Technology, Waseda University,
Nishiwaseda 2, Shinjuku-ku, Tokyo 169-0051

[3]CREST, Japan Science and Technology Corporation, Kawaguchi-shi, Saitama 332-0012

Received August 12, 2003; E-mail: kuroda@waseda.jp

Silica-based mesostructured materials derived from a layered polysilicate kanemite were prepared by reactions with *gemini*-type diammonium ($C_{16-3-16}$, $C_{16-5-16}$, C_{16-3-1}) surfactants. The surfactants were assembled in the two-dimensionally limited space between the silicate layers of kanemite, leading to the formation of lamellar, 2-d hexagonal, and disordered mesophases. Lamellar phases were formed by using $C_{16-3-16}$ and $C_{16-5-16}$ surfactants. An acid treatment of the lamellar $C_{16-5-16}$–silicate complex induced the transformation into a 2-d hexagonal phase, whereas the $C_{16-3-16}$–silicate complex retained its lamellar structure after the treatment. A disordered phase was obtained through the reaction of kanemite with C_{16-3-1} surfactants whose assembly shows a larger surface curvature. The formation of layered surfactant–silicate intermediates under various conditions and the transformation to other mesophases lead to the conclusion that the formation of ordered and disordered mesostructured materials derived from kanemite simply depends on the surfactant assemblies in the two-dimensionally limited space.

Since the discovery of ordered mesoporous silicas prepared by using surfactant molecules,[1,2] the self-assembling ability of surfactants has attracted much attention in the field of porous materials design.[3,4] Periodic mesoporous materials with various structures, morphologies, and compositions have been reported during these past 15 years.[5–9] These materials are useful for catalysts, catalyst supports, and adsorbents for relatively large molecules, and the potential applications include use as confined reaction media and functional materials for electronics and photonics. Surfactant molecules, themselves, are uniformly assembled in aqueous solutions, depending on the conditions, such as concentration and temperature,[11] while the presence of inorganic species attached to the hydrophilic headgroups plays an important role in the mesostructural variation. The geometrical packing of surfactant molecules containing attached inorganic species should be considered for the formation of mesostructured materials because the charge density of the inorganic framework is changed by condensation, corresponding to the variation in the amount of accommodated surfactants.[12] However, the mesostructures of ordered mesoporous silicas (FSM-16[13] and KSW-2[14]) derived from a layered polysilicate kanemite cannot be understood in the same manner as those derived from soluble silicate species, because kanemite has two-dimensionally connected silicate networks.[15,16] The formation of FSM-16 and KSW-2 is much more complicated than those of other ordered mesoporous silicas (MCM-41,[2,10] SBA-15,[17] etc.). In the present study, kanemite was allowed to react with aqueous solutions of *gemini*-type diammonium surfactants. The obtained mesostructures (such as, lamellar, 2-d hexagonal, and disordered phases), which are different from those derived from soluble silicate species,[18–21] can be explained by combining both the geometrical packing of surfactants and the interactions of the cationic headgroups of surfactants with silicate sheets.

Kanemite is an attractive layered polysilicate applicable for the synthesis of ordered mesoporous silicas. The single-layered silicate sheets in kanemite are composed of only tetrahedral SiO_4 units.[15,16] By the presence of two-dimensionally connected silicate networks, ordered mesoporous silicas with three-dimensionally connected mesopores that are observed for MCM-48, SBA-1, and SBA-2 have never been synthesized in the surfactant–kanemite systems.[22] The formation of disordered (KSW-1) and 2-d hexagonal mesoporous silicas (FSM-16) by the direct reaction of kanemite with alkyltrimethylammonium (C_nTMA) surfactants has been well recognized.[1,13,23] In addition to TEM and in situ XRD investigations on the formation of the mesostructured precursor for FSM-16,[24–26] which suggests the different formation processes between FSM-16 and MCM-41, the formation mechanism has recently been proved by using docosyltrimethylammonium (C_{22}TMA) or docosyltriethylammonium (C_{22}TEA) surfactants that are likely to be assembled as lamellar phases.[27] The 2-d hexagonal mesophases are formed by the transformation of the lamellar intermediates composed of C_{22}TMA or C_{22}TEA cations and fragmented silicate sheets. Lamellar surfactant–silicate mesostructured ma-

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terials can also be obtained from kanemite by using C_{16}TMA cations under the appropriate synthetic conditions (C_{16}TMA/Si ≥ 0.5).[22] Condensation within the individual silicate sheets (*intralayer* condensation) occurs, depending on the reaction temperature.

A layered C_{16}TMA–kanemite complex retaining the silicate structure can be converted to a mesostructured precursor for orthorhombic KSW-2 by a mild acid treatment.[14] The formation of the orthorhombic mesostructure is understood on the basis of both the geometrical packing of C_{16}TMA and the interactions of the cationic headgroups with the silicate sheets. The assemblies of C_{16}TMA molecules within the semi-squared spaces cannot simply be explained by using the geometrical packing. The semi-squared arrangement of mesopores had never been found before our publication. All of the mesostructures, except for KSW-2, are governed by the geometrical packing of surfactant molecules used.[11] The orthorhombic mesostructure is formed through bending of the individual silicate sheets, unlike monomeric and/or oligomeric silica species. Thus, the surface curvature of the silicate sheets does not match that of the C_{16}TMA assemblies completely, and the C_{16}TMA molecules are encapsulated within the semi-squared spaces because of the interactions of the cationic headgroups of the C_{16}TMA molecules with the silicate sheets. Therefore, studying the reactions of kanemite with cationic surfactants with a range of the packing parameters, such as *gemini*-type diammonium surfactants, is quite important for further understanding the surfactant–kanemite systems.

Experimental

Kanemite was synthesized as described previously.[22] *Gemini*-type diammonium surfactants, such as $C_{16}H_{33}(CH_3)_2NBr$-$C_3H_6NBr(CH_3)_2C_{16}H_{33}$ ($C_{16-3-16}$), $C_{16}H_{33}(CH_3)_2NBrC_5H_{10}NBr$-$(CH_3)_2C_{16}H_{33}$ ($C_{16-5-16}$) and $C_{16}H_{33}(CH_3)_2NBrC_3H_6NBr(CH_3)_3$ (C_{16-3-1}), were prepared according to the literature.[28] These surfactants were synthesized by the reactions of hexadecyldimethylamine with 1,3-dibromopropane, 1,5-dibromopentane, and 3-bromopropyltrimethylammonium bromide, respectively, and then purified by recrystallization in chloroform/methyl acetate.

The reaction conditions of kanemite with *gemini*-type diammonium ($C_{16-3-16}$ and $C_{16-5-16}$) surfactants were decided based on the solubility of the surfactants. In the $C_{16-3-16}$– and $C_{16-5-16}$–kanemite systems, 1 g of kanemite was added to aqueous solutions of 0.08 M $C_{16-3-16}$ (N/Si = 0.32) and 0.05 M $C_{16-5-16}$ (N/Si = 0.2), respectively, and the reactions were performed at 70 °C for 3 h. Acid-treatments of the lamellar phases obtained by the reactions with $C_{16-3-16}$ and $C_{16-5-16}$ were conducted by the addition of 2 M HCl; the pH values of the suspensions were adjusted to 8.5 and the stirring was kept at 70 °C for 3 h. Reactions of kanemite with C_{16-3-1} were also performed at 70 °C for 3 h. When the N/Si molar ratio was 0.2, 1 g of kanemite was added to 20 mL of 0.1 M C_{16-3-1}. After the resultant was separated by centrifugation, the product was dispersed in 20 mL of distilled water. The pH value of the suspension was adjusted to 8.5 by the addition of 2 M HCl. After stirring at 70 °C for 3 h, the as-synthesized material was dried at 60 °C and calcined at 550 °C for 6 h. When the N/Si molar ratio was 2.0,[19] 1 g of kanemite was added to 200 mL of 0.1 M C_{16-3-1}. After the reaction, the product was centrifuged and air-dried. All of the products were characterized by powder X-ray diffraction. Powder XRD patterns were obtained by using a Mac Science M03XHF[22] diffractometer with monochromated Fe Kα radiation. The identification of various mesophases was based on the peak assignments.

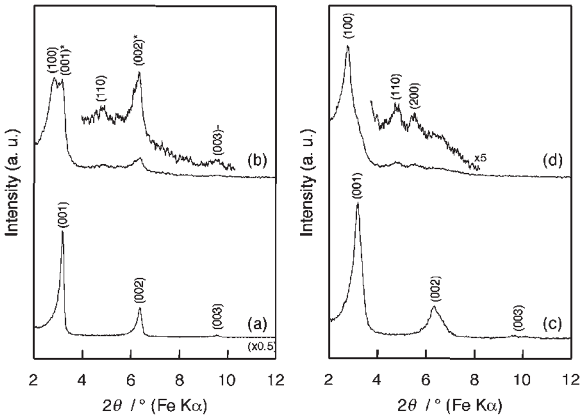


Fig. 1. XRD patterns of the products obtained during the synthesis of (a), (c) $C_{16-3-16}$– (N/Si = 0.32) and (b), (d) $C_{16-5-16}$–silicates (N/Si = 0.2); (a), (b) before and (c), (d) after the pH adjustment.

Results and Discussion

Reactions with *Gemini* Surfactants. The XRD patterns of the as-synthesized materials prepared by using $C_{16-3-16}$ and $C_{16-5-16}$ surfactants are shown in Fig. 1. The peaks at *d*-spacings of 3.5 nm and the higher order diffractions are observed in the XRD patterns of $C_{16-3-16}$–silicates recovered before and after the pH adjustment. $C_{16-3-16}$ surfactants have a tendency to be assembled as a lamellar phase or rod-like micelles according to the conditions, being useful for the synthesis of mesostructured silicate with lamellar (MCM-50) and 2-d hexagonal phases (MCM-41, SBA-3).[12] In the limited interlayer space of kanemite, where the anionic charge is arranged in a flat manner, it is feasible for the surfactants to form a lamellar phase. Therefore, the formation of the layered $C_{16-3-16}$–silicate is predominant. In contrast, in the $C_{16-5-16}$–kanemite system, both lamellar ($d_{001} = 3.5$ nm) and 2-d hexagonal phases ($d_{100} = 3.9$ nm) were obtained as the mixed products, and the 2-d hexagonal phase ($d_{100} = 4.0$ nm, $d_{110} = 2.3$ nm, $d_{200} = 2.0$ nm) was mainly observed after the pH adjustment. The result indicates that the layered $C_{16-5-16}$–silicate is transformed into the 2-d hexagonal phase by the acid treatment as well as layered C_{22}TMA– and C_{22}TEA–silicates.[23] The use of $C_{16-4-16}$ and $C_{16-6-16}$ surfactants is practical for the formation of mesostructured silicates with 2-d hexagonal phases (MCM-41, SBA-3, space group; *p*6*mm*) mainly.[12] By increasing the alkylene chain length between the diammonium groups (spacer) in *gemini*-type surfactants, $C_{16-5-16}$ molecules are assembled as rod-like micelles in the present case.

The XRD patterns of the as-synthesized materials prepared by using C_{16-3-1} surfactants and those of the calcined materials are shown in Fig. 2. In both cases (N/Si = 0.2, 2.0), the broad peaks were observed for as-synthesized materials. In addition to the main peaks, higher order diffractions with very weak intensities were observed. In spite of the same alkyl chain lengths as C_{16}TMA, the d_{100}-spacings of the C_{16-3-1}–silicates were ca. 4.5 nm, being larger than that observed for 2-d hexagonal C_{16}TMA–silicate (ca. 4 nm, Fig. 3).[13] Although it is possible

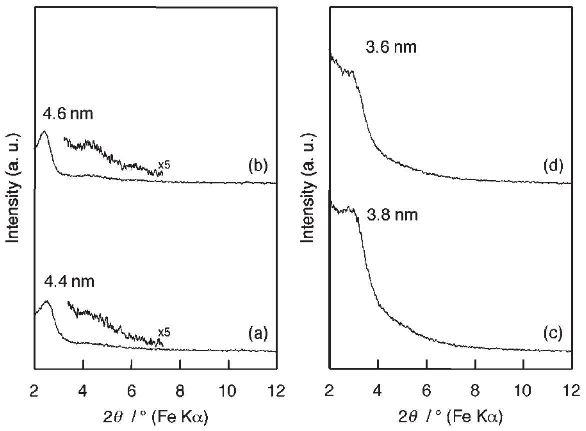


Fig. 2. XRD patterns of the products obtained during the synthesis of C_{16-3-1}–silicates where the N/Si molar ratios were (a), (c) 0.2 and (b), (d) 2.0; (a), (b) after the pH adjustment and (c), (d) the calcined material.

to index the peaks to 2-d hexagonal phases, the peaks were further broadened after calcination. C_{16-3-1} surfactant molecules are assembled spherically, being useful for the synthesis of mesostructured silicate with a 3-d hexagonal phase (SBA-2, space group; $P6_3/mmm$).[12] The formation of such spherical assemblies is not conceivable within the two-dimensionally limited space of kanemite. Because the surface curvature of the spherical assemblies is higher than that of rod-like micelles composed of C_nTMA molecules, disordered C_{16-3-1}–silicates are formed in the present C_{16-3-1}–kanemite system. Similar mesophases appeared under both conditions of N/Si ratios of 0.2 and 2.0. When C_{16}TMA ions were used, a hexagonal phase appeared if the ratio was 0.2, whereas a lamellar phase was observed when the ratio was 2.0. This finding also supports the unique assemblies in the interlayer space.

Formation of Mesostructured Materials Derived from Kanemite. The schematic formation routes of ordered mesostructured materials derived from kanemite are summarized in Scheme 1 based on the present and previous results on the C_nTMA–kanemite systems (Fig. 3).[14,22,27] The 2-d hexagonal phase (FSM-16) can be obtained by the transformation of the layered C_nTMA–silicate intermediate composed of fragmented silicate sheets.[27] Layered surfactant–silicates derived from kanemite are unique because the silicate framework contains condensed and ordered silicate species. The formation of the condensed silicate species has already been proved;[22] *intralayer* condensation occurs within the individual silicate sheets of kanemite, and the degree of condensation is controllable by the reaction temperature. A reaction of kanemite with C_{16}TMA

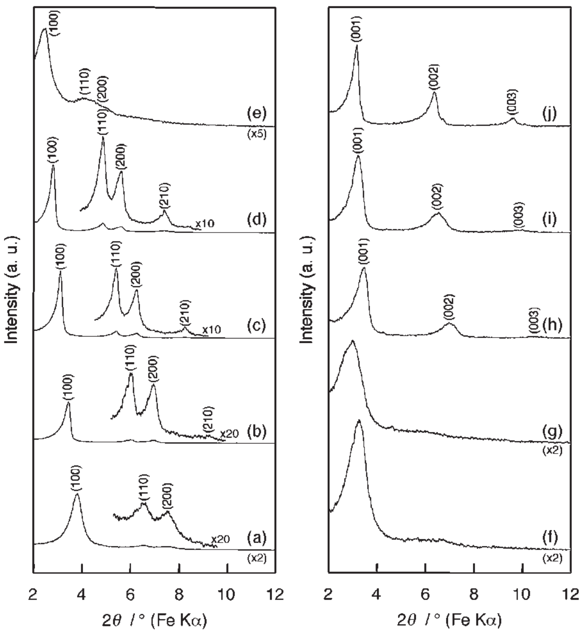
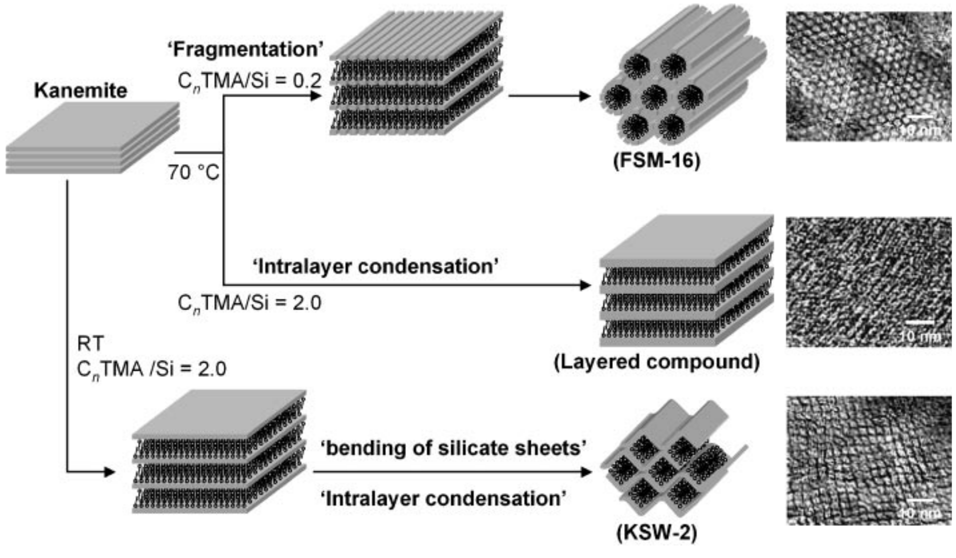


Fig. 3. (left) XRD patterns of calcined materials prepared by using (a) C_{12}TMABr, (b) C_{14}TMABr, (c) C_{16}TMABr, (d) C_{18}TMABr, and (e) C_{22}TMABr where the N/Si molar ratios were 0.2. (right) XRD patterns of as-synthesized materials prepared by using (f) C_{12}TMABr, (g) C_{14}TMABr, (h) C_{16}TMABr, (i) C_{18}TMABr, and (j) C_{22}TMABr where the N/Si molar ratios were 2.0. The pattern of (e) is adapted from Ref. 28.



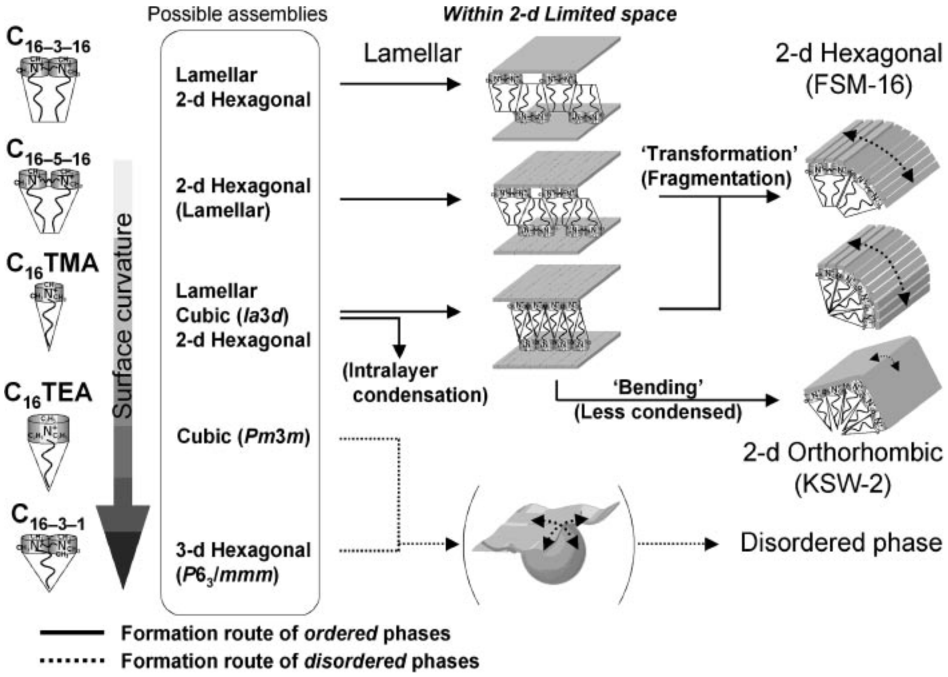
Scheme 1. Schematic formation routes of ordered mesostructured and mesoporous materials derived from kanemite.

cations at room temperature leads to the formation of a layered C_{16}TMA–silicate composed of mainly Q^3 silicate species. A mild acid treatment of the layered C_{16}TMA–silicate retaining the kanemite structure induces a mesostructural transformation into an orthorhombic phase (KSW-2, space group; *C*2*mm*).[14]

In MCM-type mesostructured materials, a mesostructural transformation is also observed during thermal and hydrothermal post-treatments.[29,30] However, various chemical reactions occur in those systems; silicate species are solubilized and linked again, surfactant molecules are partly degraded, the degraded organic molecules are solubilized in the remaining surfactant assemblies, and so on. In contrast, in the C_nTMA–kanemite systems, layered C_nTMA–silicate phases are present as the key materials during the formation of mesostructured materials. The silicate frameworks of the layered C_nTMA–silicate phases, containing the structural units of kanemite through fragmentation of the silicate sheets or newly formed structural units by *intralayer* condensation within the individual silicate sheets of kanemite, have already been investigated in detail.[23,28] Consequently, the mesostructural transformations can be simply summarized by using the structural change of the silicate frameworks of kanemite, such as fragmentation, *intralayer* condensation and bending. The schematic model is also supported by the present results obtained by the $C_{16-3-16}$– and $C_{16-5-16}$–kanemite sytems; the formation of layered surfactant–silicate complexes in both systems and the transformation into the 2-d hexagonal phase only in the $C_{16-5-16}$–kanemite system are observed.

Surfactant Assemblies in the Two-Dimensionally Limited Space. In the synthesis of MCM-type mesoporous silicas, the mesostructures formed through cooperative organization have often been explained by the geometrical packing of the surfactant molecules.[11] Newly formed amphiphilic ion pairs composed of surfactant molecules and attached inorganic species are self-organized and the attached inorganic species are condensed. In the surfactant–kanemite systems, the 2-d silicate networks originated from kanemite always affect the formation of mesostructured materials because of the interactions of the silicate frameworks with surfactants. The formation of an orthorhombic mesostructure (KSW-2) is a good example, proving that surfactant molecules are not freely assembled in accordance with the geometrical packing within the limited space.[14] C_{16}TMA molecules are accommodated in the semi-squared spaces because of the interactions of the cationic headgroups with the silicate sheets.

The formation of disordered phases is also discussed based on both the geometrical packing of the surfactants used and the interactions of the silicate frameworks with the surfactants. The formation routes of ordered and disordered materials derived from kanemite are summarized in Scheme 2. Disordered phases are formed by the reactions of kanemite with C_{16-3-1} surfactants. These surfactant molecules cannot be assembled as lamellar phases,[12] though layered materials are normally very important for the formation of ordered phases in the surfactant–kanemite systems. C_{16-3-1} surfactants tend to be assembled spherically because of the geometrical packing. One-directional bending of the silicate sheets is probable for the formation of ordered mesostructured precursors (KSW-2).[14] However, two-directional bending of the silicate sheets in order to match the surface curvature of the spherical surfactant assemblies with the bent silicate sheets is not rational, because the spherical surfactant assemblies cannot be surrounded by silicate sheets with long-range networks.[15,16] Thus, the disordered phases that afford mesoporous silicas are obtained through the bending of the silicate sheets according to the interactions of the silicate frameworks with those surfactants. Disordered phases can also be obtained by using alkyltriethylammonium (C_nTEA) surfactants with shorter alkyl chains ($n < 20$) (Fig. 4) because the C_nTEA surfactants are also likely to be assembled spherically. Even under the conditions for the forma-



Scheme 2. Schematic formation routes of ordered and disordered materials derived from kanemite.

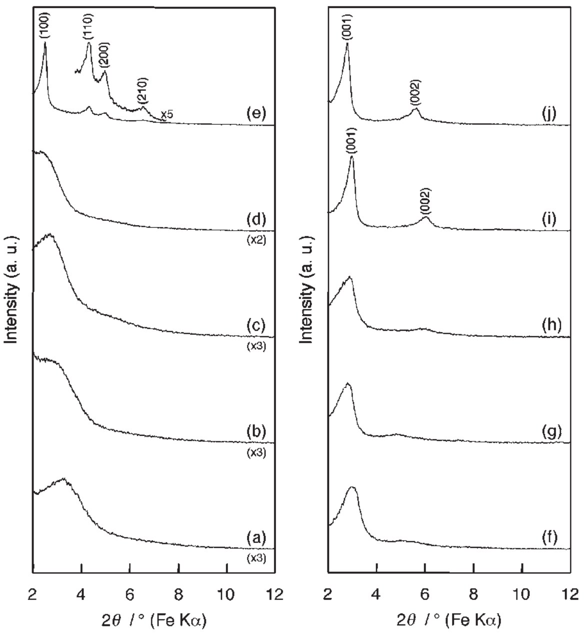


Fig. 4. (left) XRD patterns of calcined materials prepared by using (a) C_{14}TEABr, (b) C_{16}TEABr, (c) C_{18}TEABr, (d) C_{20}TEABr, and (e) C_{22}TEABr where the N/Si molar ratios were 0.2. (right) XRD patterns of as-synthesized materials prepared by using (f) C_{14}TEABr, (g) C_{16}TEABr, (h) C_{18}TEABr, (i) C_{20}TEABr, and (j) C_{22}TEABr where the N/Si molar ratios were 2.0. The pattern of (e) is adapted from Ref. 28.

tion of lamellar mesopohases (Surf/Si = 2.0), disordered mesophases are produced when the alkyl chain lengths are short. When the number of n is 12 and 14, both the C_nTEA and C_nTMA–kanemite systems produce disordered mesophases. The C_nTEA system also yields a disordered mesophase even under the condition of $n = 16$.

Conclusions

Silica-based mesostructures are derived from a layered polysilicate kanemite, and the formation is induced by reactions with various cationic surfactants with different geometrical packings. In surfactant–kanemite systems, several reactions, such as the interactions of cationic surfactants with the silicate sheets, the fragmentation or bending of the silicate sheets, and the geometrical packing of the surfactant molecules are interrelated in a complicated manner. However, the formation of ordered (lamellar, 2-d hexagonal, and 2-d orthorhombic) and disordered mesostructured materials can simply be summarized based on the presence of layered surfactant–silicate intermediates. Being different from the formation of MCM- and SBA-type mesophase silicates using soluble silicates, 2-d silicate networks are originally present in the starting kanemite. The formation of lamellar phases is understood as in the case of intercalation compounds using layered polysilicates. Depending on the synthetic conditions, the 2-d hexagonal phases can be formed through the fragmentation of silicate sheets. Disordered phases are formed when the interactions of surfactant molecules with silicate sheets prevent the surfactant molecules from self-assembling according to the geometrical packings. The findings and insights obtained here are potentially applicable for the simultaneous control of short-range (framework) and long-range (mesostructure) orderings in mesostructured materials derived from layered polysilicates.

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