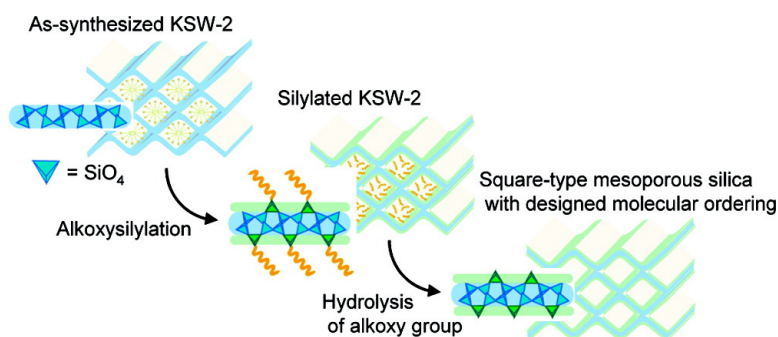


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## Design of Molecularly Ordered Framework of Mesoporous Silica with Squared One-Dimensional Channels

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**Abstract:** Mesoporous silica with squared one-dimensional channels (KSW-2-type mesoporous silica), possessing a molecularly ordered framework arising from a starting layered polysilicate kanemite, was obtained through silylation of a surfactant (hexadecyltrimethylammonium, C<sub>16</sub>TMA)-containing mesostructured precursor with octoxytrichlorosilane (C<sub>8</sub>H<sub>17</sub>OSiCl<sub>3</sub>) and octylmethyldichlorosilane (C<sub>8</sub>H<sub>17</sub>(CH<sub>3</sub>)SiCl<sub>2</sub>). The presence of the molecular ordering in the silicate framework was confirmed by XRD and TEM. Octoxy groups grafted on KSW-2 can be eliminated by subsequent hydrolysis under very mild condition, and pure mesoporous silica was obtained with the retention of the kanemite-based framework. The framework is structurally stabilized by the attachment of additional SiO<sub>4</sub> units to the framework, and the mesostructural ordering hardly changed under the presence of water vapor. A large number of silanol groups remained at the mesopore surfaces because C<sub>16</sub>TMA ions and octoxy groups can be removed *without* calcination. Octylmethylsilyl groups are regularly arranged at the mesopore surface due to the molecular ordering in the silicate framework. The molecularly ordered structural periodicity originating from kanemite is retained even after calcination at 550 °C, while that in the precursor without silylation disappeared. The synthetic strategy is quite useful for the design of the silicate framework of mesostructured and mesoporous materials with and without surface functional organic groups.

### 1. Introduction

Surfactant templated mesoporous silicas have unique structural features such as a surface area higher than 1000 m<sup>2</sup> g<sup>-1</sup>, large adsorption capacity above 1 cm<sup>3</sup> g<sup>-1</sup>, tunable uniform mesopores up to ~30 nm, and regular pore arrangements,<sup>1–8</sup> which have attracted much attention for their possible uses in catalysts, sensors, adsorbents, and electronic, optical, and

medical devices.<sup>9–16</sup> Compositional variation of ordered mesoporous materials is one of the most important topics in this field to expand their possible applications.<sup>17–25</sup> Though there are a huge number of papers on mesoporous silicas, it is very difficult to crystallize the framework of silica-based mesoporous materials and the realization of crystalline frameworks has generated a demand for possible applications including high-performance catalysts and nanoscale materials for molecular recognition.

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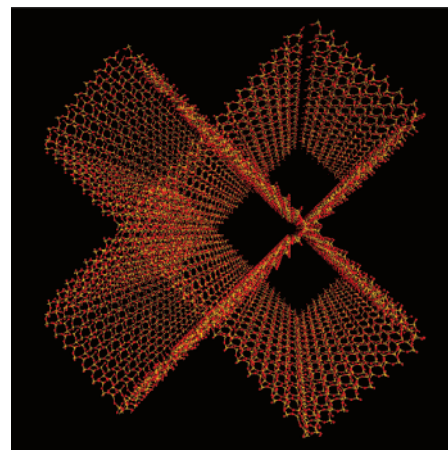
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Several attempts have been made to prepare crystalline silica-based mesoporous materials during the past decade. Following to the attempts using oligomeric silicate and aluminosilicate species like cubic octamers,<sup>26,27</sup> protozeolitic species were utilized as controlled building units.<sup>28–34</sup> Building unit structures partially remain in the mesoporous aluminosilicates, but long-range orderings in the frameworks are not confirmed by any experimental data. A mesoporous zeolite can be prepared by tiling uniform nanosized zeolitic species in the presence of surfactant molecules.<sup>35</sup> The mesoporous zeolite includes three types of pores that are surfactant templated mesopores, inter-crystalline uniform mesospaces, and micropores inside the zeolitic species. Crystallization of aluminosilicate frameworks was attempted by post-hydrothermal treatment,<sup>36–40</sup> leading to the structural collapse through complete crystallization of the frameworks. Molecularly ordered frameworks were reported only for the lamellar mesostructures prepared under hydrothermal conditions.<sup>41</sup>

Recently, a 2-D hexagonal mesoporous MFI zeolite was prepared inside replicated mesoporous carbon.<sup>42</sup> However, the walls should contain a large number of defects because connecting points of the walls from three directions in the 2-D hexagonal structure cannot be filled completely by only the five-membered ring of the MFI structure, meaning that the framework is possibly composed of semicrystalline zeolitic nanoparticles. Actually, trimodal porous silica containing two types of ordered mesopores was obtained by the reaction of uniform MFI nanoclusters with triblock copolymers.<sup>35</sup> Several types of zeolitic aluminosilicates<sup>43,44</sup> and aluminophosphate<sup>45</sup> were successfully synthesized on the basis of the amphiphilic organosilane-directed synthesis with the formation of uniform mesopores. The mesoporous zeolites showed outstanding catalytic properties arising from the crystalline frameworks and the presence of mesopores.<sup>43</sup> Wormhole mesopores are present inside the zeolite particles because highly ordered mesostructures cannot be realized because amphiphilic organosilane compounds are not highly self-assembled. Consequently, a practical strategy to synthesize mesoporous silica with both ordered mesopores and



**Figure 1.** Ideal structural model of KSW-2-based mesoporous silica with pore walls reflecting completely the crystal structure of a layered polysilicate kanemite.

crystallized frameworks has not been developed yet and has been expected for further advancement of highly architectural frameworks.

We have focused on a crucially different synthetic method to synthesize ordered mesoporous silicas utilizing crystalline layered polysilicates as starting materials.<sup>1–3,46–52</sup> Our ultimate goal in the layered polysilicate systems is to provide periodic mesoporous silicas completely reflecting the crystal structures of layered polysilicates, and an ideal possible structure is schematically shown in Figure 1. Ordered mesopores are surrounded by the original silicate sheets of layered polysilicates, and surfactant assemblies can be accommodated in the squared mesopores (not shown for clarify) with the lowest surface curvature similar to those in lamellar phases. Almost all silicate portions in the structure except for bending sites in the individual sheets and connecting sites between adjacent sheets are not curved, reflecting the periodic structure of the original silicate sheets.

Layered polysilicates with crystalline single silicate sheets can be transformed into 3-D silica networks containing uniform mesopores (KSW-1, KSW-2, FSM-16, SSW-1, and SSW-2) by the reactions with alkyltrimethylammonium ( $C_n$ TMA) surfactants.<sup>1–3,46–52</sup> KSW-1 and FSM-16 derived from a layered polysilicate kanemite show higher thermal and hydrothermal stabilities and acidity than those reported for MCM-type mesoporous silicas. However, the presence of the structural units due to the original kanemite has never been confirmed so far. We have also found an interesting character of ordered mesoporous silica named as KSW-2 with a 2-D orthorhombic structure.<sup>41</sup> The shape of the 1-D squared mesopores seems to be very close to that assumed as the ideal crystalline structure (Figure 1). The possibility to retain a molecularly ordered silicate

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structure originating from kanemite was also found in the 2-D orthorhombic mesostructured precursor (as-synthesized KSW-2) because it can be obtained through the bending of individual silicate sheets in layered C<sub>16</sub>TMA–kanemite complex during mild acid treatment. Although the molecularly ordered structure almost disappears in calcined KSW-2, we have now reached the final step to prepare ordered mesoporous silica with a crystalline framework by combining several synthetic techniques.

In the present paper, we report the successful synthesis of KSW-2-type material with a molecularly ordered silicate framework, and the squared mesopores are basically surrounded by a kanemite-based and chemically designed framework by silylation of as-synthesized KSW-2. The structural units of kanemite are basically retained in the silicate framework of as-synthesized KSW-2; the molecular ordering is based on the periodic structure along with the *a*-axis of kanemite and is parallel to the direction of the 1-D mesopores. In comparison with conventional postorganic modification, such as esterification<sup>53,54</sup> and silylation,<sup>55–58</sup> to control surface properties and pore sizes, the modification with silylating agents is absolutely useful for controlling a couple of reactions simultaneously, including the removal of surfactants and the designed capping of the silicate framework which effectively induces the stabilization of the framework. However, the periodic structural units in as-synthesized KSW-2 cannot be retained after silylation using alkyltrimethylchlorosilane,<sup>59</sup> because such a monofunctional silylating agent requires the reaction at elevated temperature and no additional ring formation to strengthen the framework is expected. Our preliminary work infers that the molecular structure of silylating agents can lead to the appropriate design of the framework.<sup>60</sup> Here we propose a novel concept to design and stabilize the periodic structure by using silylating agents with two or more reactive sites, such as alkoxytrichlorosilanes and alkylmethylchlorosilanes, affording successful synthesis of KSW-2-type mesoporous silica with a molecularly ordered framework. The well-defined silicate frameworks at the surfaces of ordered mesopores are promising for fundamental investigation of the catalytic and adsorption properties truly arising from the presence of ordered mesopores. Previously reported mesoporous silicas inevitably have several uncontrollable factors including mesopore surface roughness and unavoidable micropores, which inhibit the valid understanding of mesoporous materials.

There have been no reports on the successful preparation of pure mesoporous silica with crystalline frameworks so far though many attempts to prepare semicrystallized mesoporous aluminosilicates have been conducted as mentioned above.<sup>28–40,42–45</sup> The preparation of porous materials with pure silica frameworks is important for enhancing the thermal stability and hydrophobicity. Interesting catalytic properties have also been reported

for pure silica mesoporous materials.<sup>61–69</sup> A methodology to design silica-based frameworks of layered materials was reported by accumulating new silicate units on the original frameworks<sup>70–73</sup> and the topotactic conversion of layered silicates to zeolitic microporous silicas.<sup>74</sup> However, such attempts have never been conducted in the field of mesoporous materials. Here we present for the first time a new type of mesoporous silica with pore walls composed of a nonmicroporous silicate framework, which is quite different from zeolitic mesoporous materials. The structural feature is chemically and physically interesting for the investigation of the properties exclusively due to ordered mesopores.

## 2. Experimental Section

**2.1. Materials.** All the solvents such as dehydrated toluene, dehydrated pyridine, and tetrahydrofuran (THF) were obtained from Kanto Chemical Co. and used without further purification. Octyl alcohol, tetrachlorosilane, hexadecyltrimethylammonium chloride (C<sub>16</sub>-TMACl), and octylmethylchlorosilane (C<sub>8</sub>H<sub>17</sub>(CH<sub>3</sub>)SiCl<sub>2</sub>) were purchased from Tokyo Kasei Kogyo Co.

Octoxytrichlorosilane (C<sub>8</sub>H<sub>17</sub>OSiCl<sub>3</sub>) was prepared according to the literature for the synthesis of alkoxytrichlorosilanes.<sup>70,71</sup> C<sub>8</sub>H<sub>17</sub>OH was added dropwise to hexane containing SiCl<sub>4</sub> under vigorous stirring under flowing N<sub>2</sub> where the SiCl<sub>4</sub>/C<sub>8</sub>H<sub>17</sub>OH molar ratio was 1.0. A mixture of (C<sub>8</sub>H<sub>17</sub>O)<sub>*n*</sub>SiCl<sub>4–*n*</sub> (*n* = 0–4) obtained after the stirring was kept for 1 h at room temperature. C<sub>8</sub>H<sub>17</sub>OSiCl<sub>3</sub> was recovered through distillation (0.1 Torr, bp; ~70 °C), and the purity was checked by <sup>29</sup>Si and <sup>13</sup>C NMR (Supporting Information Figure S1).

A layered polysilicate kanemite was prepared from δ-Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> according to the literatures.<sup>46–49</sup> In a typical synthesis of δ-Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>, a sodium silicate solution was diluted by adding a sodium hydroxide solution under stirring, and the molar ratio of Na/Si was adjusted to 1.0. The aqueous solution was dried and heated at 750 °C (heating rate: 5 °C min<sup>-1</sup>) for 1 h. The solid product (1.0 g) was dispersed in 50 mL of distilled water and stirred for 30 min at room temperature to obtain kanemite. The purity of kanemite was checked by XRD (Supporting Information Figure S2 and Table S1).

**2.2. Synthesis of 2-D Orthorhombic Mesostructured Silica.** According to the literature,<sup>47</sup> 2-D orthorhombic (*c2mm*) mesostructured silica (as-synthesized KSW-2) was synthesized from kanemite using C<sub>16</sub>TMACl through mild acid treatment of a layered C<sub>16</sub>TMA–kanemite complex. Kanemite without drying was dispersed in 200 mL of 0.1 M C<sub>16</sub>TMACl aqueous solution where the C<sub>16</sub>TMACl/Si molar ratio was 2.0. The reaction of kanemite with C<sub>16</sub>TMACl proceeded at room temperature for 3 d to obtain a layered complex without impurities such as unreacted kanemite. The layered complex was recovered by centrifugation and dispersion in 150 mL of distilled water. A mild acid treatment was conducted at pH = 5.5 for 30 min by adding 1.0 M CH<sub>3</sub>COOH gradually. The powder X-ray diffraction (XRD) and

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transmission electron microscopic (TEM) results of the layered  $C_{16}TMA$ -kanemite complex (Figure S3 and Table S2) and as-synthesized KSW-2 (Figure S4) are shown in the Supporting Information.

**2.3. Silylation of As-Synthesized KSW-2.** Prior to silylation, as-synthesized KSW-2 (1.5 g) was dried under vacuum at 120 °C for 3 h. The dried precursor was dispersed in a mixture of dehydrated toluene (30 mL) and dehydrated pyridine (5 mL). The suspension was mixed with an excess of  $C_8H_{17}OSiCl_3$  (5.27 g, 20 mmol) for 1 d at room temperature under a  $N_2$  atmosphere. After filtration, the solid product was washed with toluene to remove unreacted  $C_8H_{17}OSiCl_3$  and washed with dichloromethane to remove pyridine hydrochloride and deintercalated  $C_{16}TMA$ . The resultant solid product was dried under vacuum.

Octoxy groups can be removed by hydrolysis under very mild conditions. Silylated KSW-2 with octoxytrichlorosilane (0.2 g) was added to a mixture of THF (20 mL),  $H_2O$  (2 mL), and pyridine (1 mL). After stirring for 1 d at room temperature, the solid product was recovered by centrifugation and washed with a mixture of THF and water. The resultant solid product was treated at 120 °C under vacuum for 2 h to remove adsorbed pyridine.

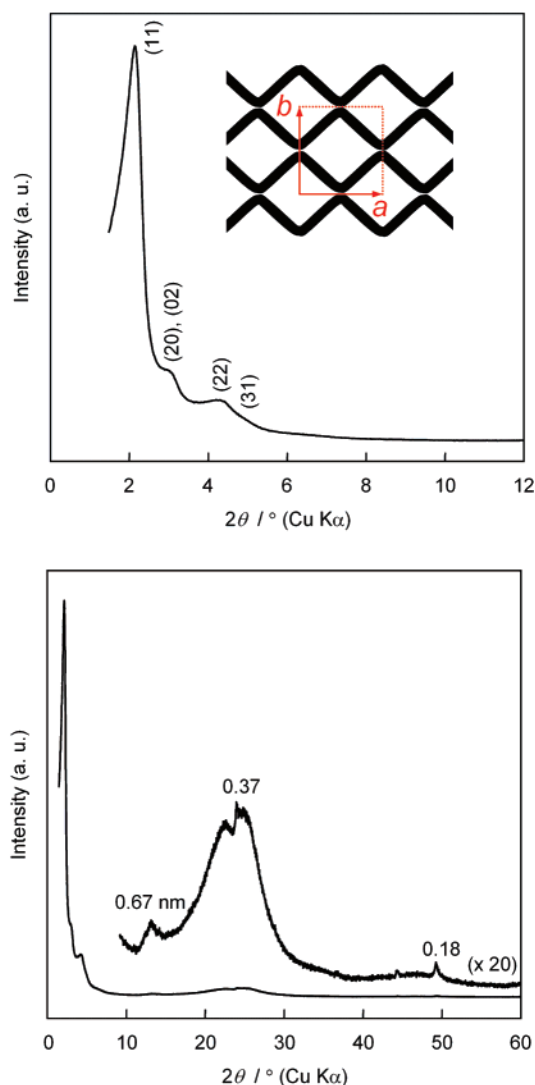
Silylation using  $C_8H_{17}(CH_3)SiCl_2$  (4.55 g, 20 mmol) was also conducted in a mixture of toluene and pyridine. After as-synthesized KSW-2 (1.5 g) was dried under vacuum, the dried precursor was dispersed in a mixture of toluene (30 mL) and pyridine (5 mL). The silylated product was washed with toluene and ethanol repeatedly and air-dried. The organic groups were removed by calcination at 550 °C for 6 h.

**2.4. Characterization.** XRD measurements were performed by using a Rigaku RINT 2000 diffractometer with monochromated  $Cu K\alpha$  radiation and a Bruker AXS M03X-HF22 diffractometer with Mn filtered  $Fe K\alpha$  radiation. TEM images were taken by a JEOL JEM 2010 instrument, operated at 200 kV.  $^{29}Si$  and  $^{13}C$  NMR measurements were performed by using a JEOL Lambda-500 spectrometer at resonance frequencies of 99.25 and 125.79 MHz, respectively. Solid-state  $^{29}Si$  MAS NMR spectra were recorded on a JEOL JNM-CMX-400 spectrometer at a resonance frequency of 79.42 MHz with a 45° pulse, a recycle delay of 200 s, and a scan of 200. Solid-state  $^{13}C$  CP/MAS NMR spectra were recorded at a resonance frequency of 100.40 MHz with a contact time of 1.5 ms and a recycle delay of 5 s. The samples were put into zirconia rotors and spun at 5 kHz. The conditions lead to full relaxation of the signals, indicating that quantitative analysis is possible.  $^{29}Si$  and  $^{13}C$  chemical shifts were referenced to tetramethylsilane at 0 ppm. Peak areas of the  $^{29}Si$  MAS NMR spectra were calculated as follows. The total areas of all  $Q^n$  peaks were set to be 1.00 in order to compare the peak areas between  $Q^n$  silicate species in the original framework of as-synthesized KSW-2 and those in silylated KSW-2, and the peak areas due to the silylating agents were also calculated on the basis of the same criterion. Compositions of the products were calculated as follows. Thermogravimetry-differential thermal analysis (TG-DTA) was carried out with a Rigaku Thermo Plus2 instrument under flowing dry air at a heating rate of 10 °C  $min^{-1}$ . Residual weights after heating up to 900 °C were treated as the amount of  $SiO_2$  fractions in the products. The amounts of organic constituents such as  $C_{16}TMA$  ions and octoxy groups were determined by using a Perkin-Elmer PE-2400 (CHN analysis).  $N_2$  adsorption-desorption isotherms were recorded by using a Quantachrome Autosorb-1 at 77 K. The samples were preheated at 110 °C for 6 h under vacuum. Total specific surface areas ( $S_{BET}$ ) were calculated by the BET method<sup>64</sup> using adsorption data. Inner surface areas ( $S$ ) and total pore volumes ( $V$ ) were estimated by the  $t$ -plot method, and then pore sizes were calculated by the equation of  $4V/S$ . Water adsorption measurements were also conducted by using a Quantachrome Autosorb-1 at 25 °C.

### 3. Results and Discussion

#### 3.1. Synthesis of KSW-2-Based Mesoporous Silica with Molecularly Ordered Framework.

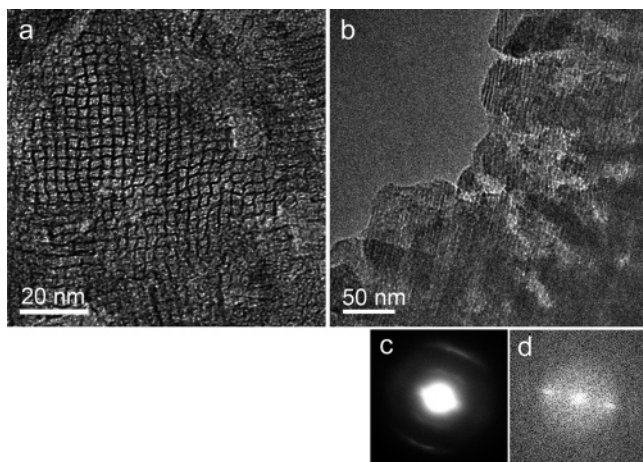
The XRD pattern of KSW-



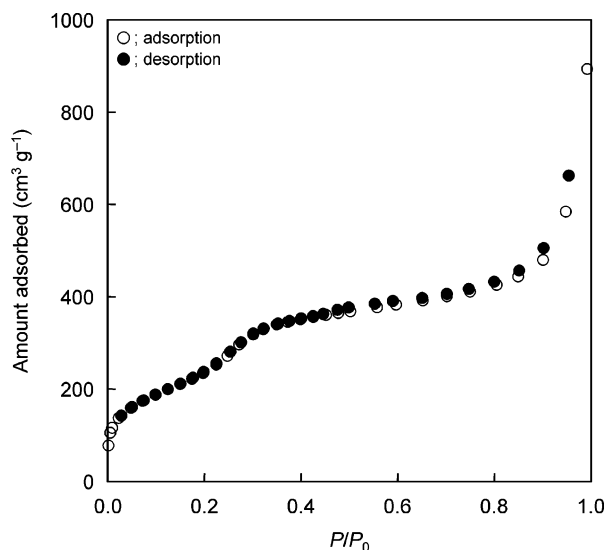
**Figure 2.** Low and high angle XRD patterns of KSW-2 silylated with  $C_8H_{17}OSiCl_3$  and hydrolyzed (Better profiles of Figure 1b in ref 60).

2-based mesoporous silica (Figure 2) that was obtained through silylation of the mesostructured precursor with  $C_8H_{17}OSiCl_3$  and subsequent hydrolysis to remove octoxy groups shows four diffraction peaks (4.09, 2.89, 2.05, and 1.79 nm) in low diffraction angles. These are assignable to (11), (20, 02), (22), and (31) peaks, respectively, due to a 2-D orthorhombic mesostructure ( $c2mm$ ) with  $a = 5.78$  nm and  $b = 5.79$  nm.<sup>47</sup> The unit cell parameters ( $a$  and  $b$ ) are almost identical, indicating the pore shape is almost square. The wide-angle XRD pattern of the material shows several peaks attributable to a periodic structure based on the crystalline framework of kanemite. In particular, two peaks with the  $d$ -spacings of 0.37 and 0.18 nm correspond to the periodic structure in kanemite along the  $c$ -axis which are possibly assignable to the (002) and (004) peaks of kanemite, as discussed later.

The TEM images also support the presence of the periodic structure in the silicate framework with the mesostructural ordering. The TEM images of KSW-2 silylated with  $C_8H_{17}OSiCl_3$  and hydrolyzed are shown in Figure 3. The corresponding selected area electron diffraction (SAED) pattern is also shown in the figure. The squared pore shape was observed clearly with the presence of one-dimensional (1-D) mesopores,



**Figure 3.** TEM images taken along with (a) parallel and (b) perpendicular directions to the 1-D mesopore of KSW-2 silylated with  $C_8H_{17}OSiCl_3$  and hydrolyzed, and (c) the corresponding SAED pattern and (d) the Fourier diffractogram of (b).



**Figure 4.**  $N_2$  adsorption–desorption isotherm of KSW-2 silylated with  $C_8H_{17}OSiCl_3$  and hydrolyzed.

and the repeat distance (ca. 4.0 nm) between pores is consistent with the  $d_{11}$  spacing. Slightly arc-shaped spots corresponding to the ordering of  $\sim 0.37$  nm were confirmed in the SAED pattern (Figure 3c). The spots were observed in the position perpendicular to the spots due to the mesostructural ordering, indicating that the  $\sim 0.37$  nm periodicity is aligned along the mesochannels.

The  $N_2$  adsorption–desorption isotherm of the material is shown in Figure 4, exhibiting a type IV behavior characteristic of ordered mesoporous materials. The BET surface area, the pore volume, and the pore diameter were  $670 \text{ m}^2 \text{ g}^{-1}$ ,  $0.43 \text{ cm}^3 \text{ g}^{-1}$ , and 2.6 nm, respectively. On the basis of the corresponding  $\alpha_s$  curve shown in Supporting Information Figure S4, the micropore volume was calculated to be  $0 \text{ cm}^3 \text{ g}^{-1}$ , which is consistent with the proposed model shown in Figures 1 and 8. Surface octoxy groups in the mesoporous silica were almost eliminated after hydrolysis under the very mild conditions (see Table 1). The surface area is smaller than that observed for ordinary KSW-2 obtained by calcination because the presence of additional surface  $SiO_4$  layers after silylation makes the silicate framework thicker.

**Table 1.** Compositions of As-Synthesized KSW-2, KSW-2 Silylated with  $C_8H_{17}OSiCl_3$ , and KSW-2-Based Mesoporous Silica Obtained after Hydrolysis

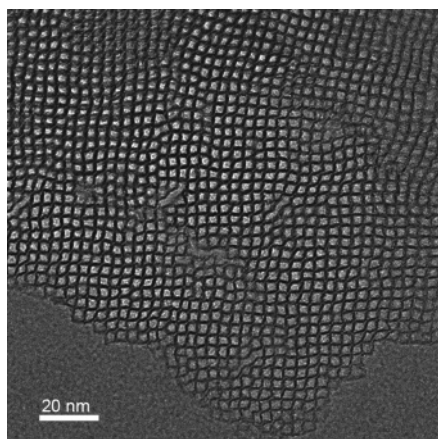
	C/mass %	N/mass %	$SiO_2$ /mass %	C <sub>8</sub> /Si ratio
as-synthesized	26.6	1.5	57.0	—
silylated	20.1	0.0	66.8	0.19
hydrolyzed	13.9	2.5 <sup>a</sup>	73.9	0.03
hydrolyzed <sup>b</sup>	5.5	0.3	82.6	0.03

<sup>a</sup> The value was due to adsorbed pyridine used in the hydrolysis. <sup>b</sup> The sample was treated at 120 °C for 2 h under vacuum to remove adsorbed pyridine.

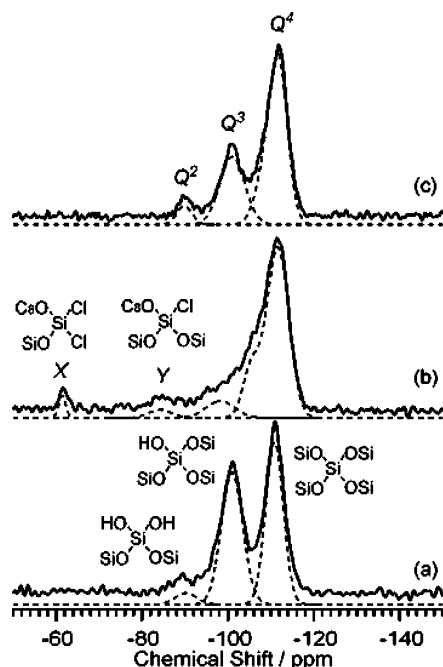
Ordered mesoporous materials with the kanemite-based framework can be obtained by silylation using alkoxychlorosilanes and alkylmethylchlorosilanes whose molecular structures are important for the design of the periodic silicate units originating from kanemite.<sup>60</sup> Difunctional and trifunctional organosilanes are suitable for smooth reactions with surface Si–OH groups. KSW-2-based mesoporous silica with the molecularly ordered framework, prepared in this way, is totally different from mesoporous zeolites reported recently.<sup>35,42–44</sup> As mentioned in the introduction, KSW-2-based mesoporous silica is composed of a nonporous silicate framework surrounding mesopores because the parent silicate sheets of kanemite are constructed with only six-membered rings of  $SiO_4$  units. In accordance with the structural feature, KSW-2-based mesoporous silica is absolutely useful for the investigation of the catalytic performance and adsorption property arising exclusively from ordered mesopores. In addition, assuming the new lattice constants ( $a = 5.78 \text{ nm}$ ,  $b = 5.79 \text{ nm}$ , and  $c = 0.74 \text{ nm}$ ) of an orthorhombic structure ( $Pbcn$ ), a peak at the  $d$ -spacing of 0.67 nm is assignable to the (111) peak. The peak was observed whenever the two peaks with the  $d$ -spacings of 0.37 and 0.18 nm were observed. Though ED spots relating to the 0.67 nm peak should be observed inside the arch contrast due to the ordering of  $\sim 0.37$  nm, we have not yet obtained such data probably because of its weak intensity. Although further study is necessary to prove this interpretation, the KSW-2-based mesoporous silica is closest to the first ordered mesoporous material with a crystalline framework and all the XRD peaks can be indexed to ( $hkl$ ) planes of one crystal structure ( $Pbcn$ ) as described above.

**3.2. Formation Process of KSW-2-Based Mesoporous Silica with Molecularly Ordered Framework.** The low- and wide-angle XRD patterns of as-synthesized, silylated, and hydrolyzed KSW-2 were quite similar to one another, indicating that the mesostructural ordering and the periodicity in the silicate framework hardly changed during the silylation and hydrolysis processes. The  $d$ -spacings of silylated KSW-2 were comparable to those observed for as-synthesized KSW-2. The mesostructural ordering with a repeated distance of ca. 4.0 nm was retained completely after silylation, being supported further by the TEM image of silylated KSW-2 (Figure 5). The image shows that squared mesopores are arranged regularly and entirely in a particle.

The variation in the  $^{29}Si$  MAS and  $^{13}C$  CP/MAS NMR spectra during the synthesis of KSW-2-based mesoporous silica obtained through silylation and subsequent hydrolysis are shown in Figures 6 and 7, respectively. The spectrum of as-synthesized KSW-2 showed three peaks due to  $Q^2$  (–90 ppm),  $Q^3$  (–100 ppm), and  $Q^4$  silicate species (–110 ppm) ( $Q^2/Q^3/Q^4 = 0.03:0.47:0.50$ ). The peak widths are narrower than those observed

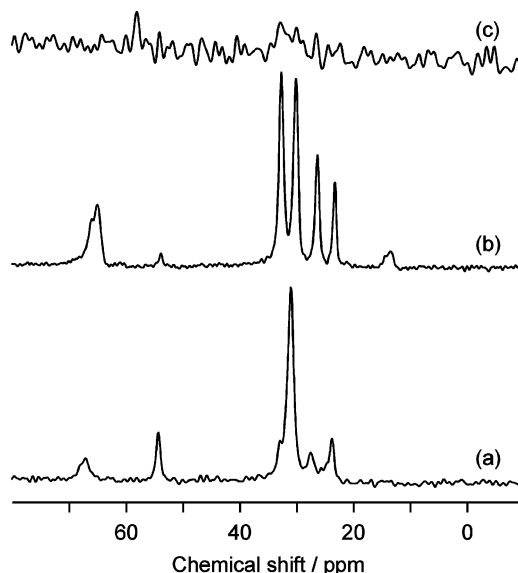


**Figure 5.** TEM image of KSW-2 silylated with  $C_8H_{17}OSiCl_3$ .



**Figure 6.**  $^{29}Si$  MAS NMR spectra (solid lines) with the deconvoluted peaks (dotted lines) of (a) as-synthesized, (b) KSW-2 silylated with  $C_8H_{17}OSiCl_3$ , and (c) KSW-2-based mesoporous silica obtained after hydrolysis. (Solid lines of (a) and (b) are reproduced from Figure 3(right)(a) and 3(b) in ref 60.)

for MCM-type mesostructured precursors. The silicate framework of as-synthesized KSW-2 is better ordered than that in MCM-type materials composed of amorphous silica networks. The presence of only a small amount of  $Q^2$  units reveals a vanishingly low fragmentation of the individual silicate sheets in kanemite. As reported previously,<sup>47</sup> the appearance of  $Q^4$  units is due to interlayer condensation of Si–OH groups between adjacent sheets through the bending and intralayer condensation within the individual silicate sheets. This structural change in the silicate sheets is vital for the formation of the 2-D orthorhombic phase from a layered complex composed of the kanemite-based crystalline framework. The periodicity in the silicate framework of as-synthesized KSW-2 is reduced gradually with the proceeding of intralayer and interlayer condensation. In the present study, further structural change in the silicate framework is suppressed completely by silylation using  $C_8H_{17}OSiCl_3$  to stabilize the periodic structural units in as-synthesized KSW-2 and subsequent hydrolysis to remove octoxy groups



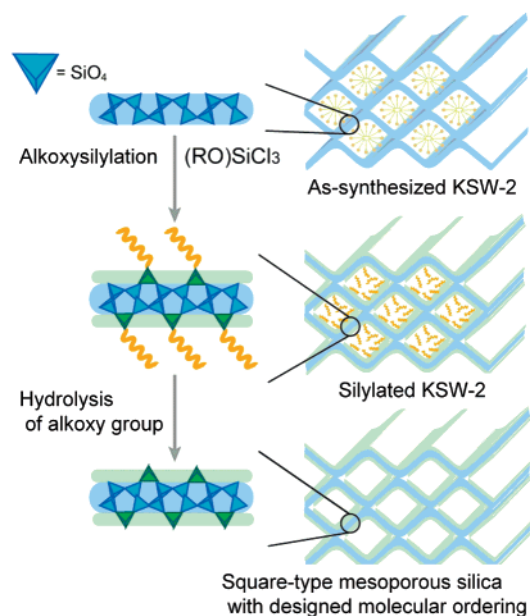
**Figure 7.**  $^{13}C$  CP/MAS NMR spectra of (a) as-synthesized KSW-2, (b) KSW-2 silylated with  $C_8H_{17}OSiCl_3$ , and (c) KSW-2-based mesoporous silica obtained after hydrolysis. (Lines (a) and (b) are reproduced from the  $^{13}C$  CP/MAS NMR spectra of Figure 3(left)(a) and 3(b) in ref 60.)

under very mild conditions, successfully affording KSW-2-type mesoporous silica with a molecularly ordered framework.

The spectrum of KSW-2 silylated with  $C_8H_{17}OSiCl_3$  exhibits new peaks at  $-62$  and  $-84$  ppm, which can be assigned to grafted species derived from  $C_8H_{17}OSiCl_3$  such as X ( $(C_8O)Cl_2Si(OSi)$ ) and Y ( $(C_8O)ClSi(OSi)_2$ ), respectively. The area of the  $Q^3$  peak decreased significantly after the silylation ( $X/Y/Q^2/Q^3/Q^4 = 0.05:0.06:0.00:0.21:0.79$ ), indicating the successful reaction of  $C_8H_{17}OSiCl_3$  with surface Si–OH groups. The  $^{29}Si$  MAS NMR spectrum of KSW-2-based mesoporous silica after hydrolysis to remove octoxy groups shows three peaks centered at  $-90$  ( $Q^2$ ),  $-100$  ( $Q^3$ ), and  $-110$  ( $Q^4$ ) ppm with the disappearance of two peaks at  $-62$  and  $-84$  ppm ( $Q^2/Q^3/Q^4 = 0.04:0.31:0.76$ ). The increase of the  $Q^2$  and  $Q^3$  peaks suggests that Si–OC<sub>8</sub> and Si–Cl groups were converted into additional Si–OH groups during hydrolysis. Considering the high  $Q^3/(X + Y)$  ratio in silylated KSW-2, it is considered that the additional Si–OH groups are condensed during silylation, hydrolysis, and drying. The relative area and the width of the  $Q^4$  peak are comparable to those observed for as-synthesized KSW-2, implying the possession of the periodic structure.

As displayed in Table 1, the carbon content of silylated KSW-2 decreased down to 20.1 mass % while that of as-synthesized KSW-2 was 26.6 mass %. The carbon content in silylated KSW-2 corresponds to the organic fractions of octoxy groups. The complete removal of  $C_{16}TMA$  ions was checked simultaneously by the nitrogen content, and then the amount of octoxysilyl groups was estimated to be 0.19 groups/SiO<sub>2</sub>. The introduction of the organic groups and the elimination of  $C_{16}TMA$  ions were proven by  $^{13}C$  CP/MAS NMR (see Figure 7). Several peaks due to carbon atoms in  $C_{16}TMA$  ions were observed in as-synthesized KSW-2, and all of the peaks disappeared completely after silylation. It has been reported that the chemical shift of the  $\alpha$  carbon atom in octyl alcohol depends on the state;<sup>75</sup>  $\alpha$  carbon atoms in octyl alcohol adsorbed

(75) Sing, K. S. W.; Everett, D. H.; Haul, R. A. W.; Moscou, L.; Pierotti, R. A.; Rouquerol, J.; Siemieniowska, T. *Pure Appl. Chem.* **1985**, *57*, 603.



**Figure 8.** Schematic formation process of KSW-2-based mesoporous silica with molecularly ordered frameworks formed by silylation.

physically on silica surfaces and octoxy groups in a Si–O–C linkage can be detected at 63 ppm and 64.5–65 ppm, respectively. The appearance of a single signal at 65 ppm strongly indicates the presence of octoxysilyl groups without the cleavage of Si–O–C linkage. Any peaks due to carbon atoms were not observed after hydrolysis, revealing the complete removal of octoxy groups.

$C_{16}$ TMA cations are eliminated during silylation, affording KSW-2-based porous silica with surface octoxy groups. As shown in Supporting Information Figure S6, the  $N_2$  adsorption–desorption isotherm of silylated KSW-2 was type I, characteristic for microporous materials. The BET surface area, the pore volume, and the pore diameter were  $580 \text{ m}^2 \text{ g}^{-1}$ ,  $0.23 \text{ cm}^3 \text{ g}^{-1}$ , and 1.6 nm, respectively. It is natural that the values are smaller than those of KSW-2-based mesoporous silica because the silicate framework is covered further with octoxysilyl groups.

The formation process of KSW-2-type mesoporous silica with the designed silicate framework is illustrated in Figure 8. As-synthesized KSW-2 with a 2-D orthorhombic structure can be formed through bending of kanemite-based silicate sheets during the mild acid treatment of the layered  $C_{16}$ TMA–kanemite complex prepared at room temperature.<sup>47</sup> The 2-D orthorhombic structure can be retained after removal of  $C_{16}$ TMA ions but the periodic structure originating from kanemite in the silicate framework vanishes by calcination, meaning the formation of ordered mesoporous silica with an amorphous framework.<sup>47</sup> As reported previously,<sup>59</sup> the periodic structure in the silicate framework is lost when as-synthesized KSW-2 is silylated with silylating agents containing only one reactive site like octyldimethylchlorosilane. Therefore, silylation using appropriate silylating agents is quite important for retaining the periodic structure originating from kanemite (wrinkled silicate sheets). As-synthesized KSW-2 is modified with silylating agents with two or more reactive sites such as alkoxytrichlorosilanes. The wrinkled silicate units are capped with the silylating agents, and the structural units are stabilized by forming new structural units such as five-membered rings of  $\text{SiO}_4$  units. Finally, KSW-2-

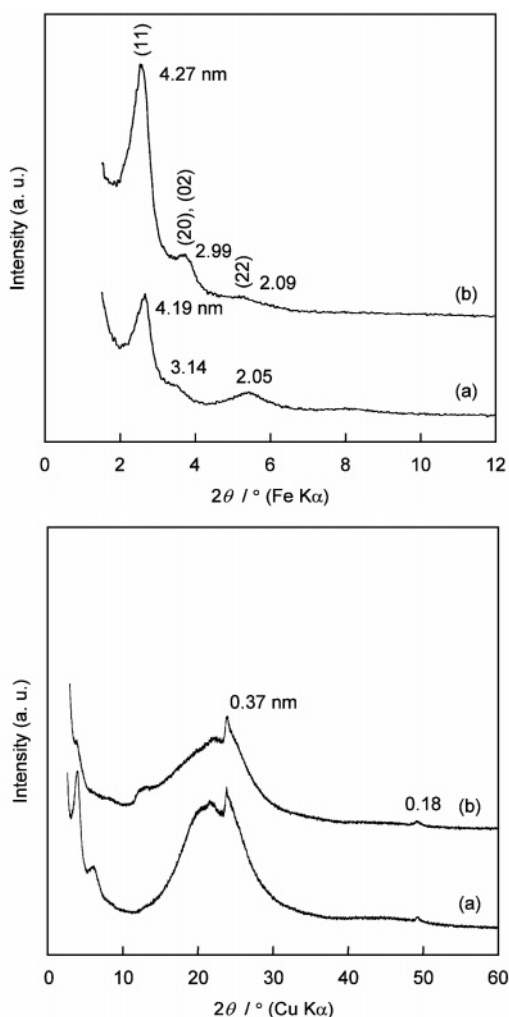
based mesoporous silica with a molecularly ordered framework can be obtained after hydrolysis to remove alkoxy groups. Further design of the surface structures is interesting because organically modified materials have attracted much attention for expanding the potential applications of silica-based mesoporous materials.

**3.3. Design of KSW-2-Based Mesoporous Silica with Molecularly Ordered Framework.** We have shown a typical synthesis for obtaining KSW-2-based mesoporous silica with the molecularly ordered framework. This crystalline KSW-2-based mesoporous silica is quite interesting and essentially different from reported mesoporous zeolites because the mesopores are surrounded by nonporous silicate walls. As described above, the KSW-2-based mesoporous silica can be obtained through several processes including the preparation of as-synthesized KSW-2, silylation using alkoxytrichlorosilanes, and subsequent hydrolysis of alkoxy groups. Although all the organic groups are eliminated by hydrolysis to obtain pure silica mesoporous material, we have introduced the possibility to further design KSW-2-based mesoporous silica by organic modification in this section.

The  $^{29}\text{Si}$  MAS NMR spectra of KSW-2-based mesoporous silica obtained through silylation of a mesostructured precursor with  $C_8H_{17}(CH_3)SiCl_2$  containing two reactive sites are shown in Supporting Information Figure S7. In the  $^{29}\text{Si}$  MAS NMR spectrum of as-synthesized KSW-2, the peaks due to  $Q^3$  and  $Q^4$  silicate species ( $Q^3/Q^4 = 0.57:0.43$ ) were observed at around  $-100$  and  $-109$  ppm with a very small peak due to  $Q^2$  species at  $-88$  ppm, respectively. The profile was changed by silylation with  $C_8H_{17}(CH_3)SiCl_2$ , and the peaks due to  $Q^4$  and  $D^2$  with small  $Q^3$  peaks ( $D^2/Q^3/Q^4 = 0.15:0.14:0.71$ ) were observed, centered at  $-110$ ,  $-13$ , and  $-100$ , respectively. The  $D^2$  peak is assignable to Si atoms in octylmethylsilyl groups derived from  $C_8H_{17}(CH_3)SiCl_2$ , and the significant decrease of the  $Q^3$  peak indicates the successful modification of the surface Si–OH groups with  $C_8H_{17}(CH_3)SiCl_2$ . The XRD patterns of as-synthesized KSW-2 and the silylated material are shown in Figure 9. Three diffraction peaks (4.19, 2.94, and 2.05 nm in as-synthesized, 4.27, 2.88, and 2.09 nm in silylated KSW-2) were observed in low diffraction angles. These are assignable to (11), (20), and (22) peaks due to a 2-D orthorhombic structure, respectively. In each wide-angle XRD pattern, two (002) and (004) peaks due to the periodic structure based on the kanemite structure were observed at the positions with the  $d$ -spacings of 0.37 and 0.18 nm, respectively. As shown in Supporting Information Figure S8, the  $N_2$  adsorption–desorption isotherm shows a behavior between type I and IV, and the BET surface area, the pore volume, and the pore diameter were  $505 \text{ m}^2 \text{ g}^{-1}$ ,  $0.16 \text{ cm}^3 \text{ g}^{-1}$ , and 1.7 nm, respectively. The presence of surface octyl groups and the absence of  $C_{16}$ TMA ions in the material were proven by  $^{13}\text{C}$  CP/MAS NMR and CHN analysis, respectively.

The grafted organic groups are more stable than octoxy groups, leading to the organic modification with stabilization of the kanemite-based framework in as-synthesized KSW-2. Silylation of the mesostructured precursor is superior to post-modification of calcined samples. A large number of the organic groups are considered to be regularly fixed on the surfaces because of the presence of the molecular ordering in the silicate framework.



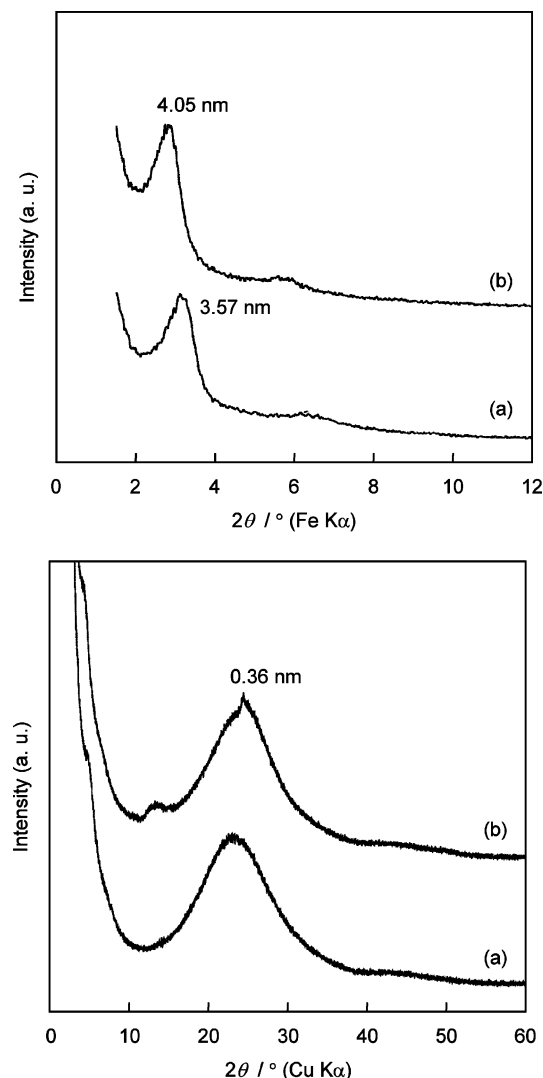


**Figure 9.** Low- and wide-angle XRD patterns of (a) as-synthesized KSW-2 and (b) KSW-2 silylated with  $C_8H_{17}(CH_3)SiCl_2$ . (Parts of the lines (a) and (b) in the right figure in wider angles than  $15^\circ$  are reproduced from the lines (a) and (b) of Figure 6 (left) in ref 60.)

Thus, we have proposed several routes to obtain a variety of KSW-2-based mesoporous silica with molecularly ordered frameworks. (1) Pure silica mesoporous material can be obtained through silylation using alkoxytrichlorosilanes and subsequent hydrolysis of alkoxy groups. (2) KSW-2-based mesoporous silica with surface organic groups can be prepared through silylation using organochlorosilanes having two or more reactive sites. (3) As a possible extension, organically modified KSW-2-based mesoporous silica may also be prepared through silylation using silylating agents containing ether bonds in grafting organic groups and the following reaction of the ether groups. A wide variety of organic groups can be grafted by using appropriate silylating agents on the surface of KSW-2-based mesoporous silica.

#### 3.4. Stability of the Molecularly Ordered Framework.

KSW-2-based mesoporous silica silylated with  $C_8H_{17}(CH_3)SiCl_2$  was calcined at  $550^\circ C$  under ambient air to check the thermal stability of the molecularly designed framework. The XRD patterns of calcined KSW-2-based mesoporous silica obtained with and without silylation are shown in Figure 10. The low- and wide-angle XRD patterns of ordinary KSW-2 obtained by calcination of as-synthesized KSW-2 indicate that the mesostructural ordering was maintained ( $d_{11} = 3.57$  nm) whereas the



**Figure 10.** Low- and wide-angle XRD patterns of calcined KSW-2-based mesoporous silicas prepared (a) without and (b) with organic modification with  $C_8H_{17}(CH_3)SiCl_2$ . (A part of line (b) (right) in the wide-angle XRD pattern higher than  $15^\circ$  is reproduced from the line (c) of Figure 6 (left) in ref 60.)

periodic structure in the silicate framework was lost after calcination. The  $N_2$  adsorption–desorption isotherm of calcined KSW-2 without modification shows a type IV behavior (Supporting Information Figure S6), and the BET surface area, the pore volume, the pore diameter, and the wall thickness were  $690\text{ m}^2\text{ g}^{-1}$ ,  $0.31\text{ cm}^3\text{ g}^{-1}$ ,  $2.3\text{ nm}$ , and  $1.3\text{ nm}$ , respectively. In contrast, although the  $N_2$  adsorption–desorption isotherm of the calcined KSW-2 after silylation using  $C_8H_{17}(CH_3)SiCl_2$  also shows a type IV behavior (Supporting Figure S6), the periodic structure in the silicate framework of silylated KSW-2 still remained even after calcination. The BET surface area, the pore volume, the pore diameter, and the wall thickness were  $786\text{ m}^2\text{ g}^{-1}$ ,  $0.34\text{ cm}^3\text{ g}^{-1}$ ,  $2.3\text{ nm}$ , and  $1.8\text{ nm}$ , respectively. The  $d_{11}$ -spacing ( $4.05\text{ nm}$ ) was larger than that observed for calcined KSW-2 without silylation. The result reveals that the molecularly ordered framework in as-synthesized KSW-2 is stabilized and designed by silylation as illustrated in Figure 8 and further condensation during calcination is suppressed. Therefore, the stability of the kanemite-based framework is drastically enhanced by silylation.

It is well-known that the stability of ordered mesoporous silica increased by organic modification because the cleavage of Si–O–Si bonds with water molecules cannot occur at the silica surface because of its strongly enhanced hydrophobicity.<sup>54,56,59</sup> The mesostructural ordering of KSW-2 is stabilized by the presence of alkyltrimethylsilyl groups.<sup>59</sup> Water vapor adsorption measurement of KSW-2, silylated with  $C_8H_{17}OSiCl_3$  and hydrolyzed, shows the stability of the molecularly ordered framework under water vapor. In comparison with calcined KSW-2 without silylation, silylated and hydrolyzed KSW-2 has a slightly more hydrophilic surface, which is reflective of the increased surface Si–OH density calculated on the basis of the  $^{29}Si$  MAS NMR and  $N_2$  adsorption data, though both of the water vapor adsorption isotherms were type V, being quite similar to those observed for ordered mesoporous silica.<sup>54,56,59</sup> The XRD pattern of silylated and hydrolyzed KSW-2 did not change after the adsorption measurement, revealing the improved hydrothermal stability due to the thicker pore walls that are designed and stabilized by additional  $SiO_4$  units.

#### 4. Conclusions

KSW-2-based mesoporous silica with the molecularly ordered framework was obtained through modification using silylating agents with two or more reactive sites such as  $C_8H_{17}OSiCl_3$  and  $C_8H_{17}(CH_3)SiCl_2$ . A structural design in the silicate frameworks of ordered mesoporous silicas is also possible by using mesostructured precursors prepared from other layered polysilicates.<sup>50–52</sup> The strategy is quite useful for designing and stabilizing the silicate frameworks of mesostructured precursors with simultaneous removal of  $C_{16}TMA$  ions without calcination, indicating the possible preparation of a wide variety of organically modified mesoporous silicas with molecularly ordered frameworks including pure silica mesoporous materials by choosing suitable silylating agents. The molecularly ordered framework of as-synthesized KSW-2 is designed and stabilized through ring formation by attaching  $SiO_4$  units to the kanemite-based framework. Further design of KSW-2-based mesoporous silica may be possible by the structural control of silylating agents with organic functions. In addition, as-synthesized metal (e.g., Al, Ti, etc.) containing KSW-2 with molecularly ordered frameworks can also be obtained through the development of synthetic procedures for incorporating metal species in the

framework of kanemite.<sup>76–80</sup> By the combination of these methods, organically and inorganically designed KSW-2-based mesoporous silicas can be synthesized, which will provide a number of unique functions.

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**Supporting Information Available:** Figures S1 ( $^{29}Si$  and  $^{13}C$  NMR spectra of  $C_8H_{17}OSiCl_3$  after distillation), S2 (crystal structure and XRD pattern of synthesized kanemite), S3 (XRD pattern of layered  $C_{16}TMA$ –kanemite complex), S4 (TEM images and SAED patterns of as-synthesized KSW-2), S5 ( $\alpha_s$ -plot curve of KSW-2 silylated with  $C_8H_{17}OSiCl_3$  and hydrolyzed), S6 ( $N_2$  adsorption–desorption isotherm of calcined KSW-2 without silylation, KSW-2 silylated with  $C_8H_{17}OSiCl_3$ , and the hydrolyzed product; filled symbols denote desorption), S7 ( $N_2$  adsorption–desorption isotherm of calcined KSW-2 without silylation, KSW-2 silylated with  $C_8H_{17}(CH_3)SiCl_2$ , and the calcined material), S8 ( $^{29}Si$  MAS NMR spectra of as-synthesized KSW-2 and the product silylated with  $C_8H_{17}(CH_3)SiCl_2$ ), and Tables S1 (XRD result on the synthesis of kanemite) and S2 (XRD result on the synthesis of layered  $C_{16}TMA$ –kanemite complex prepared at room temperature). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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