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# Synthesis of Silylated Derivatives of a Layered Polysilicate Kanemite with Mono-, Di-, and Trichloro(alkyl)silanes

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Interlayer modification of a layered polysilicate kanemite was performed by silylation with mono-, di-, and trichloro(alkyl)silanes. The introduction of silyl groups into the interlayer region was confirmed by XRD, IR, $^{13}$C NMR, and $^{29}$Si NMR. The layered structures of the silylated products were confirmed by swelling behavior upon adsorption of *n*-alkyl alcohols. The amounts of attached alkylsilyl groups varied with the number of functional groups as well as the alkyl chain length in the silylating agents. The products modified with alkyltrichlorosilanes exhibited various interlayer structures due to the different arrangements and/or conformations of the alkyl chains, depending on the chain lengths. The BET surface areas were relatively large (up to ∼480 m$^2$ g$^{-1}$) when short-chain alkyltrichlorosilanes were used, and decreased substantially to nonporous structures with increasing chain length. In addition to the inherent six-membered rings in the single layered silicate sheets of kanemite, new five- and six-membered rings were formed onto the silicate frameworks when dichloro- and trichlorosilanes were used for silylation. This leads to a new method for constructing novel organosilicate nanomaterials utilizing layered silicates.

## Introduction

Many efforts have recently been devoted to the design and construction of inorganic−organic nanomaterials because of their potential application in novel functional materials. Wide varieties of material combinations and synthetic strategies have been employed. Intercalation of organic species into the interlayer spaces of inorganic layered crystals provides unique nanostructures consisting of alternating layers of inorganic and organic moieties.[1,2] In general, the properties of nanocomposite materials depend on their nanostructures, in particular on the structures of the interfaces. Therefore, precise control of the interactions between inorganic and organic moieties is crucial for the construction of nanomaterials with desired functions.

The host structures of layered polysilicates are composed of silicate sheets containing reactive silanol groups arranged regularly at the interlayer surfaces. The groups are derivatized organically. Silane coupling agents, used widely for the modification of silica surfaces,[3,4] have also been employed for interlayer modification of layered polysilicates,[5,6] leading to interstratified inorganic−organic nanocomposites with directly attached interfaces. We have already reported the interlayer modification of layered polysilicates with thicker silicate sheets such as magadiite and kenyaite with various organochlorosilanes.[7−11] Some of these materials possess attractive features applicable for selective adsorbents or nanocomposites with organic polymers. However, the design of the interface at a molecular level is difficult because the exact structures of the host silicates still remain obscure. Therefore, it is very important to investigate the configurations of attached organosilyl groups on silicate frameworks by utilizing host materials with well-defined structures.

Kanemite ($NaHSi_2O_5{\cdot}3H_2O$)[12,13] is promising as a model material for the interlayer modification, because the crystal structure has recently been determined by Gies et al.[14,15] The mineral is one of the simplest types of layered polysilicates. It has been demonstrated that

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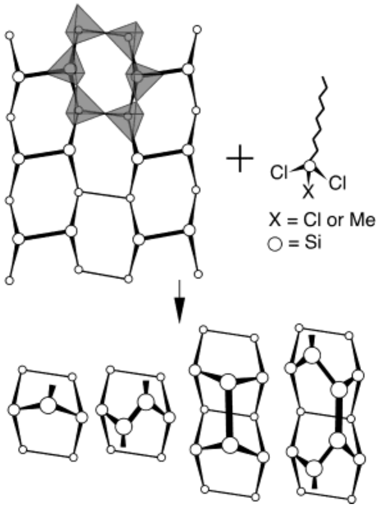
**Scheme 1. Possible Silicate Structures Formed by Silylation of Kanemite with Di- and Trichloro(alkyl)silanes**



various types of mesostructured materials can be obtained by inter- and intralayer condensations of silicate frameworks.[16−19] Silylation with di- and trifunctional silanes can also provide an opportunity to produce new silicate frameworks. Although the original silicate framework consists of only six-membered rings of $SiO_4$ tetrahedra, silylation with di- and trifunctional silanes should lead to the formation of new silicate structures, including seven-, six-, and five-membered rings (Scheme 1). It is of great interest that the silicate cage structures consisting of four five-membered rings,[20] which is a basic structural unit in some zeolites, can be formed by silylation with trifunctional silanes. This implies that the kanemite structure is available for building up novel crystalline organosilicate structures.

Although a preliminarily report described the trimethyl- and triphenylsilylation of interlayer silanol groups of kanemite using dialkyldimethylammonium kanemite as an intermediate,[21] the structural details were not elucidated. In this study, the interlayer modification of kanemite was performed with various alkylchlorosilanes for the first time. The reactivities of chlorosilanes with kanemite, the structures of the interfaces, and the arrangement of interlayer organic groups were examined in detail.

## Experimental Section

**Materials.** Kanemite ($NaHSi_2O_5{\cdot}3H_2O$) was synthesized from 1.0 g of $\delta$-$Na_2Si_2O_5$ dispersed in 50 mL of $H_2O$ with stirring for 0.5 h.[13] Hexadecyltrimethylammonium chloride [$C_{16}H_{33}N(CH_3)_3Cl$, C16TMACl] (Tokyo Kasei Co.) was used as received. Alkyltrichlorosilanes ($C_nH_{2n+1}SiCl_3$, C$n$S, $n = 1$, 2, 4, 8, 12, 16, and 18), alkylmethyldichlorosilanes [$C_nH_{2n+1}Si(CH_3)Cl_2$, C$n$$M_1$S, $n = 1$, 8, and 18], and alkyldimethylchlorosilanes [$C_nH_{2n+1}Si(CH_3)_2Cl$, C$n$$M_2$S, $n = 1$, 8, and 18] were used as silylating agents. These chemicals were obtained from Tokyo Kasei Co., except for C16S obtained from Chisso Co., and were used without further purifications. As a solvent for silylation, toluene was distilled prior to use. Toluene and ethanol for other procedures were used as received.

**Synthesis.** Alkylsilylation follows the previous procedure for magadiite, utilizing an intercalation compound with alkyltrimethylammonium ions as an intermediate,[8−11] which enables the modification of interlayer silanol groups even with bulky organosilyl groups. In this study, a layered hexadecyltrimethylammonium kanemite (C16TMA−kanemite), prepared by the ion exchange reaction of $Na^+$ with C16TMA cations,[18] was used as an intermediate. The silylation reactions were carried out at room temperature, because $Q^2$ and $Q^4$ units of $SiO_4$ tetrahedra form when C16TMA−kanemite is heated at ~110 °C in toluene, indicative of the disruption of the original silicate frameworks ($Q^3$ environment). Typically, C16TMA−kanemite (1.5 g) was dispersed in 30 mL of toluene, followed by the addition of excess amounts (50 mmol) of alkylchlorosilanes under a nitrogen atmosphere. The products reacted for 1 d were centrifuged and subsequently washed with toluene and ethanol to remove residual alkylchlorosilanes and deintercalated C16TMACl. The powdered products after drying at room temperature are designated as C$n$$M_2$S−, C$n$$M_1$S−, and C$n$S−kanemites for the products modified with alkyldimethylchlorosilane, alkylmethyldichlorosilane, and alkyltrichlorosilane, respectively. The adsorption of $n$-decyl alcohol was performed for all the products by dispersing and stirring in the alcohol for 1 d. In the case of C$n$S−kanemites, the adsorption of $n$-alkyl alcohols with the corresponding chain length ($C_nH_{2n+1}OH$, C$n$OH, $n = 1-18$) was also performed by stirring simply in liquid alcohols ($n = 1-8$) or in a diethyl ether solution of the alcohols ($n = 12-18$).

**Characterization.** Powder X-ray diffraction (XRD) measurements were conducted on a MAC Science M03XHF[22] diffractometer with Mn-filtered Fe Kα radiation. FT-IR spectra of samples in KBr pellets were obtained with a Perkin-Elmer Spectrum One spectrometer at a nominal resolution of 0.5 $cm^{-1}$. Thermogravimetry (TG) was carried out with a Mac Science 2000S instrument under a dry air flow at a heating rate of 10 °C/min, and the amounts of $SiO_2$ fractions in the products were determined by the residual weight after heating to 900 °C. The amounts of organic constituents were determined by CHN analysis (Perkin-Elmer PE-2400). Nitrogen adsorption isotherms were measured by a BELSORP 28-SA instrument (Bel Japan, Inc.) at 77 K. Samples were preheated at 120 °C for 3 h under $1 \times 10^{-2}$ Torr. 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 and a recycle delay of 200 s. The samples were put into 7.5 mm (or 5 mm) zirconia rotors and spun at 4−5 kHz. We confirmed that the signals were fully relaxed under these conditions so that quantitative analysis was possible. Solid-state $^{13}C$ CP/MAS NMR spectra were recorded on a JEOL GSX-400 spectrometer at a resonance frequency of 100.40 MHz and a recycle delay of 5 s. The $^{29}Si$ and $^{13}C$ chemical shifts were referenced to tetramethylsilane at 0 ppm.

## Results and Discussion

**Modification of the Interlayer Silanol Groups with Alkylchlorosilanes.** The XRD patterns of the layered C16TMA−kanemite as well as the reaction products with mono-, di-, and trichloro(methyl)silanes are shown in Figure 1. The peak at $2\theta = 3.5°$ ($d = 2.84$ nm) with higher order diffractions in C16TMA−kanemite disappeared, and new peaks at $d$ spacings of 1.74, 1.44, and 1.56 nm appeared in the C1$M_2$S−, C1$M_1$S−,

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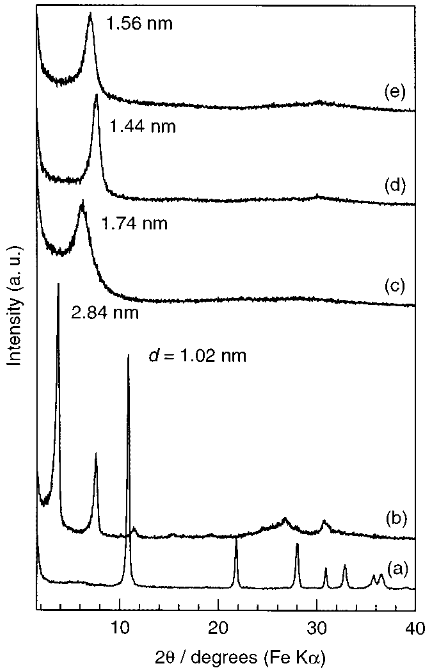

**Figure 1.** XRD patterns of (a) kanemite, (b) C16TMA−kanemite, (c) C1M$_2$S−kanemite, (d) C1M$_1$S−kanemite, and (e) C1S−kanemite.

**Table 1. Amounts of Alkylsilyl Groups in Silylated Derivatives of Kanemite**

| | | mass % C | mass % H | mass % N | % SiO$_2$ | amt of alkylsilyl groups[a]/SiO$_2$ |
|---|---|---|---|---|---|---|
| C1 | M$_2$S | 16.94 | 4.66 | 0.05 | 78.8 | 0.42 |
| | M$_1$S | 13.56 | 3.56 | 0.00 | 82.6 | 0.51 |
| | S | 10.52 | 2.75 | 0.05 | 85.8 | 0.75 |
| C8 | M$_2$S | 18.21 | 4.56 | 0.36 | 75.7 | 0.09 |
| | M$_1$S | 32.44 | 6.56 | 0.06 | 63.0 | 0.34 |
| | S | 32.73 | 6.14 | 0.09 | 58.5 | 0.40 |
| C18 | M$_2$S | 28.92 | 5.99 | 0.39 | 64.7 | 0.09 |
| | M$_1$S | 49.22 | 8.86 | 0.00 | 43.8 | 0.33 |
| | S | 47.20 | 8.70 | 0.05 | 42.1 | 0.38 |

[a] Evaluated by CHN analysis and thermogravimetry.

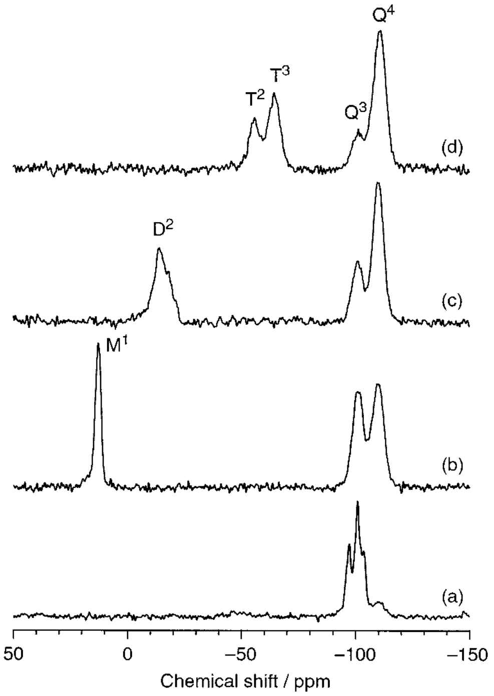

**Figure 2.** $^{29}$Si MAS NMR spectra of (a) C16TMA−kanemite, (b) C1M$_2$S−kanemite, (c) C1M$_1$S−kanemite, and (d) C1S−kanemite.

and C1S−kanemites, respectively. Desorption of C16TMA cations during the reaction was confirmed by the quantitative analysis of nitrogen (Table 1). The amounts of residual C16TMA cations were much smaller ($<$0.001 per SiO$_2$ unit of kanemite) than that in C16TMA−kanemite (ca. 0.29). The bonding of the alkylsilyl groups with the silicate layers was revealed by $^{29}$Si MAS NMR, as shown in Figure 2. C16TMA−kanemite is composed of SiO$_4$ units with their Q$^3$ environments observed at around −100 ppm and a small proportion of Q$^4$ signals observed at around −110 ppm. The reaction products exhibit signals assigned to M$^1$ (13 ppm), D$^2$ (−16 ppm), and T$^{2,3}$ (−56, −65 ppm) silicate units derived from mono-, di-, and trichloro(alkyl)silanes, respectively. The spectra also showed a substantial increase in the relative intensity of Q$^4$ signals due to newly formed Q$^4$ units by the silylation of interlayer Si−OH groups.

The layered structure of the products was confirmed by the swelling behavior upon adsorption of *n*-decyl alcohol. The *d* values of all the products increased after the adsorption, which provides strong evidence that the condensation of Si−OH groups between adjacent layers (*inter*layer condensation) did not proceed during the silylation. Furthermore, the possibility of the condensation within the individual silicate layer (*intra*layer condensation) was examined. In the $^{29}$Si MAS NMR spectrum of C1M$_2$S−kanemite (Figure 2b), the increase in the intensity of the Q$^4$ signals was almost equal to the intensity of the M$^1$ signal. In addition, the relative intensity of the Q$^4$ signal in the Q region (Q$^4$/(Q$^3$ + Q$^4$) ratio) was in agreement with the degree of silylation evaluated by thermogravimetry and elemental analysis. These results suggest that the intralayer condensation between neighboring Si−OH groups is negligible in this system.

The number of attached alkylsilyl groups per SiO$_2$ unit of kanemite was dependent on the number of functional groups, and increased in the following order: 0.42 (C1M$_2$S−kanemite) $<$ 0.51 (C1M$_1$S−kanemite) $<$ 0.75 (C1S−kanemite). The steric hindrance of the longer alkyl chains also affects the degree of silylation. As shown in Table 1, the amounts of attached silyl groups apparently decrease with increasing chain length, and exhibit similar values for the samples of $n$ = 8 and 18. Consequently, C8M$_2$S− and C18M$_2$S−kanemites exhibited the lowest degree of silylation of all the systems. These products showed very broad XRD peaks, while sharp peaks accompanying higher order diffractions were clearly observed for C*n*S− and C*n*M$_1$S−kanemites where $n = 8$ and 18. The amount of attached alkylsilyl groups in C8M$_2$S−kanemite increased from 0.09 to 0.15 by adding twice the amount of C8M$_2$S and stirring for a week during the reactions. The product showed relatively sharp diffraction peaks, indicating that the structural ordering increased with an increases in the degree of silylation.

**Interlayer Structures of C*n*S−Kanemites.** The XRD patterns of C*n*S−kanemite with $n = 1$, 2, 4, 8, 12, 16, and 18 are shown in Figure 3. Well-defined patterns due to the layered structures appear with increasing chain lengths. The variation in $d_{001}$ values as a function

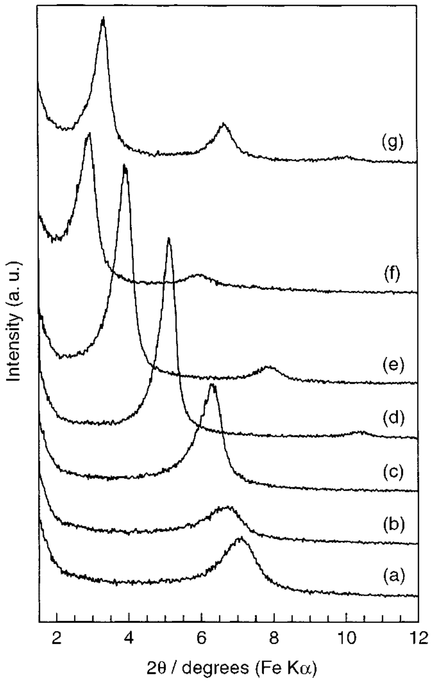

**Figure 3.** XRD patterns of C*n*S−kanemites for (a) $n = 1$, (b) $n = 2$, (c) $n = 4$, (d) $n = 8$, (e) $n = 12$, (f) $n = 16$, and (g) $n = 18$.

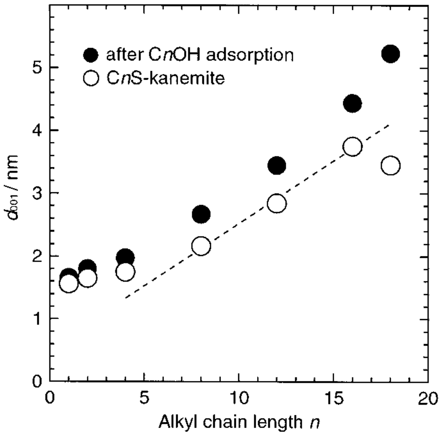

**Figure 4.** Variation in the basal spacings of C*n*S−kanemites before and after C*n*OH adsorption as a function of the number of carbon atoms in the alkyl chains.

of the number of carbon atoms in the alkyl chains is displayed in Figure 4. There is no linear relationship between the *d* values and alkyl chain length. The difference in the degree of silylation is one of the factors that affect interlayer distances. As described below, the quantity of attached alkylsilyl groups decreased from 0.75 to 0.46 per $SiO_2$ with increasing chain length from $n = 1$ to $n = 4$, and became constant (ca. 0.40) for $n = 8-18$. The *d* values of all the products were variable depending on the degree of silylation. However, it is difficult to interpret the decrease in the *d* spacing from 3.75 to 3.45 nm as the chain length increases from $n = 16$ to $n = 18$, because the amounts of attached alkylsilyl groups in both of the products are almost equal. This behavior should be attributed to the difference in the conformation and/or in the arrangement of the interlayer alkyl chains.

The conformations of the long-chain alkylsilyl groups bonded to the silica surface can be investigated by $^{13}C$ CP/MAS NMR. It is known that the signals assigned to the interior methylene carbons appear at 33 ppm for *all-trans* conformations and shift upfield to 30 ppm for *trans/gauche* conformations.[22,23] In the $^{13}C$ CP/MAS NMR spectra of the products (Figure 5), the signal due to the interior methylene carbons appears at 30 ppm (*trans/gauche* conformations) in C*n*S−kanemites ($n = 8-16$), whereas the signal is mostly detected at 33 ppm (*all-trans* conformations) in C18S−kanemite. The arrangement of the alkyl chains in the interlayer spaces was further considered. In Figure 4, the basal spacing increases linearly as the chain length increases in the range from $n = 8$ to $n = 16$. The slope of the dashed line gives an average increment of ca. 0.20 nm/$CH_2$ group, which is larger than the maximum value for the interdigitated monolayer (ca. 0.13 nm/$CH_2$). This fact, together with the $^{13}C$ CP/MAS NMR data, suggests that the alkyl chains are arranged in a bilayer structure with a disordered state. In contrast, the alkyl chains in C18S−kanemite are supposed to adopt an interdigitated monolayer because of the smaller interlayer distances regardless of longer and fully extended chains.

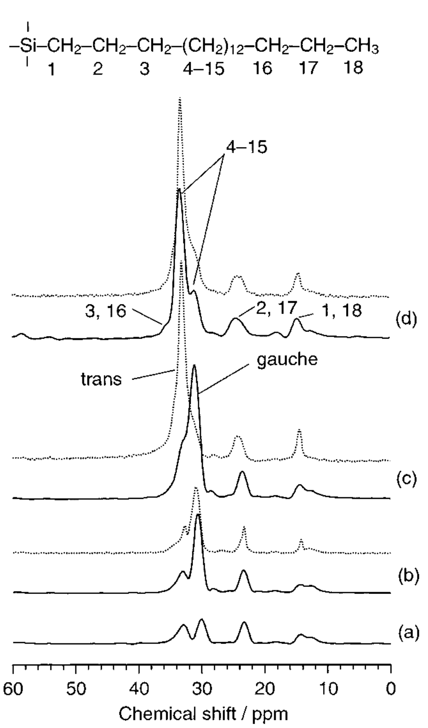

**Figure 5.** $^{13}C$ CP/MAS NMR spectra of (a) C8S−kanemite, (b) C12S−kanemite, (c) C16S−kanemite, and (d) C18S−kanemite before (solid line) and after C*n*OH ($n = 12$, 16, and 18) adsorption (dotted line).

The *d* values of all the products increased upon adsorption of *n*-alkyl alcohols with the same chain lengths as those of the corresponding alkylsilyl groups (Figure 4). Similar behavior was reported for the organic derivatives of the layered polysilicate magadiite with alkyltrichlorosilanes.[10] The driving force for intercalation is ascribed to the hydrophobic interactions and hydrogen bonding with Si−OH groups, suggesting that alcohol molecules are located between alkylsilyl groups. The increase in the *d* values can be explained in terms of the aggregation state of the mixed phases consisting

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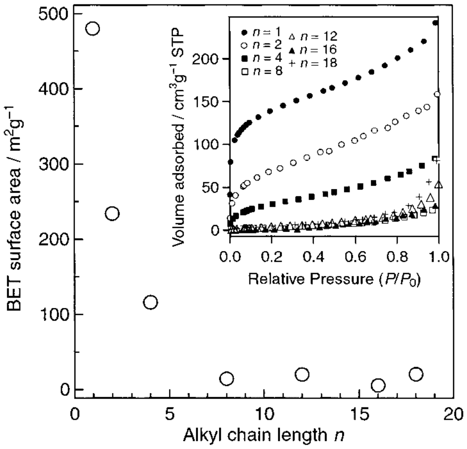

**Figure 6.** Variation in the BET surface areas of C*n*S−kanemites as a function of the number of carbon atoms in the alkyl chains. Inset: nitrogen adsorption isotherms of C*n*S−kanemites (*n* = 1−18).

of both alkylsilyl groups and alcohol molecules. The IR absorption bands due to $CH_2$ stretching vibrations of the products were slightly shifted to lower frequencies after C*n*OH adsorption (see the Supporting Information, Table S1), indicating that the interlayer chains became more rigid and extended states.[22,24] The changes in the conformation of the alkyl chains were also confirmed by $^{13}C$ CP/MAS NMR. In particular, the signal at 30 ppm for disordered chains was distinctly shifted to 33 ppm for *all-trans* chains when C16S−kanemite was treated with C16OH (Figure 5c). It is of interest that C18S−kanemite exhibited very large expansion of the basal spacing upon C18OH adsorption (~1.78 nm), while the interlayer chains did not show such a significant conformational change (Figure 5d). Considering that the basal spacing of the resulting product (5.23 nm) cannot be attained by a monolayer arrangement of C18 chains, even if fully extended chains were oriented normal to the surface, the alkylsilyl groups appear to be rearranged from a monolayer to bilayer structure by the alcohol adsorption.

Nitrogen adsorption measurements give us additional information on the interlayer structure. As shown in Figure 6, the BET surface areas of the products exhibited relatively large values (~480 $m^2\ g^{-1}$) in the case of C1S−kanemite, and decreased substantially with increases in chain length. This behavior depends essentially on the chain length, but is independent of the degree of silylation. In fact, $C1M_2S$−kanemite also exhibited porosity (~210 $m^2\ g^{-1}$), though the amount of attached alkylsilyl groups (0.42) was considerably lower than for C1S−kanemite (0.75), and was comparable to those of the C*n*S−kanemites (*n* = 8−18), which have nonporous structures. The origin of the porosity can be explained by pillaring of the interlayer spaces by the small alkylsilyl groups. As the chain becomes longer (*n* = 8−18), the interlayer space is thought to be occupied by densely packed chains, leaving less volume for $N_2$ adsorption. On the basis of all the results described above, the representative structural models for the arrangements of the alkyl chains in C*n*S−kanemite are depicted in Figure 7.

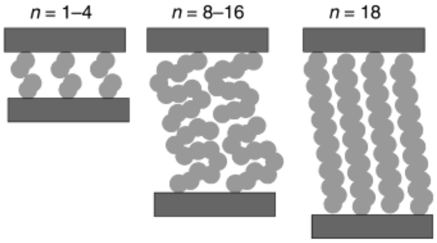

**Figure 7.** Proposed models for the arrangements of alkyl chains in the interlayer spaces of C*n*S−kanemites.

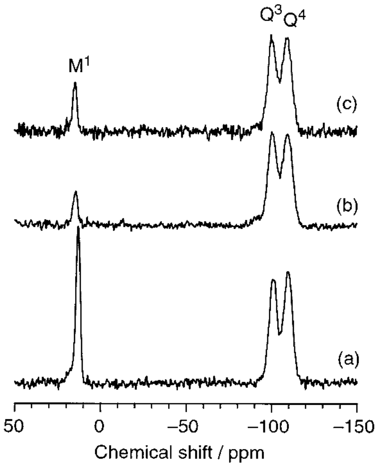

**Figure 8.** $^{29}Si$ MAS NMR spectra of (a) $C1M_2S$−kanemite, (b) $C8M_2S$−kanemite, and (c) $C18M_2S$−kanemite.

**Table 2. Relative Intensity in the $^{29}Si$ MAS NMR Spectra and the Amounts of Alkylsilyl Groups for C*n*$M_2S$−Kanemite**

| | % $M^1$ | % $Q^3$ | % $Q^4$ | $Q^4/M^1$ | $Q^4/(Q^3 + Q^4)$ | $(Q^4/(Q^3 + Q^4))$/ amt of alkylsilyl groups[a] |
|---|---|---|---|---|---|---|
| $C1M_2S$ | 30 | 34 | 37 | 1.2 | 0.52 | 1.2 |
| $C8M_2S$ | 8 | 44 | 49 | 6.3 | 0.53 | 5.9 |
| $C18M_2S$ | 11 | 42 | 47 | 4.2 | 0.53 | 5.9 |

[a] Amount of alkylsilyl groups per $SiO_2$ (Table 1).

**Structural Models of the Interlayer Surface after Silylation.** The structures of the interfaces between attached alkylsilyl groups and the silicate layers were examined. The $^{29}Si$ MAS NMR spectra of C*n*$M_2S$−kanemite (*n* = 1, 8, and 18) are shown in Figure 8. The signals assigned to the $M^1$ unit (13 ppm), due to alkyldimethylsilyl groups, were observed in addition to the signals due to the $Q^3$ and $Q^4$ silicate units. As listed in Table 2, the $Q^4/M^1$ ratio in $C1M_2S$−kanemite is 1.2, which indicates that the reaction between $C1M_2S$ molecules and Si−OH groups is predominant. It should be noted here that a small amount of $Q^4$ units was present in the C16TMA−kanemite ($Q^4/(Q^3 + Q^4)$ = ~0.1). However, $C8M_2S$− and $C18M_2S$−kanemites exhibit much larger values of 6.3 and 4.2, respectively. This result implies that the condensation between adjacent Si−OH groups in the silicate sheets also proceeds during the silylation, probably due to the relatively low reactivity of the silylating agents used.

The $^{29}Si$ MAS NMR spectra of C*n*$M_1S$−kanemites (Figure 9) suggest that the alkylmethylsilyl groups are mainly present in $D^2$ environments. As shown in Chart 1, two different structural models can be proposed for the attached alkylmethylsilyl groups in the $D^2$ environ-

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(24) Vaia, R. A.; Teukolsky, R. K.; Giannelis, E. P. *Chem. Mater.* **1994**, *6*, 1017.

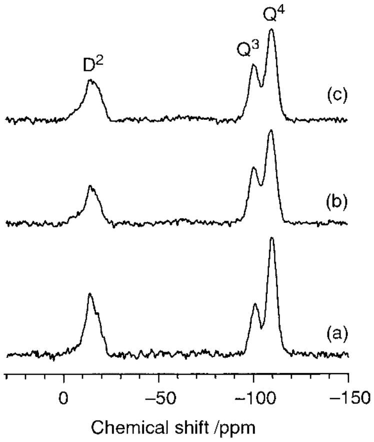
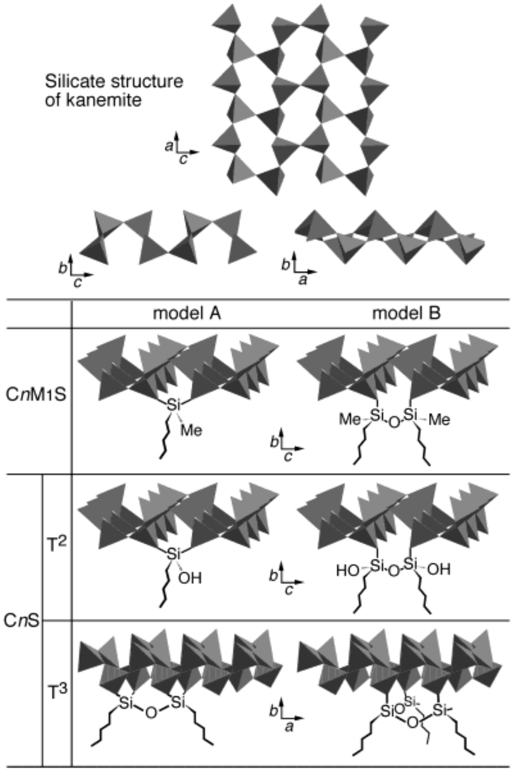


**Figure 9.** $^{29}$Si MAS NMR spectra of (a) C1M$_1$S−kanemite, (b) C8M$_1$S−kanemite, and (c) C18M$_1$S−kanemite.

**Chart 1. Proposed Structural Models for the Attached Alkylsilyl Groups in C*n*M$_1$S−Kanemite and C*n*S−Kanemite**



ment based on the crystal structure of kanemite. Model A shows that an alkylmethylsilyl group is immobilized on the silicate sheet by bridging two SiO$_4$ tetrahedra. Such a configuration is possible only when alkylmethyldichlorosilane reacts with two adjacent Si−OH groups confronting each other. The other proposed model (B) involves an alkylmethysilyl group that is bonded with one Si−OH group, and is further linked to another alkylmethysilyl group by the condensation between residual functional groups. This “dimerization” reaction is likely to occur during the washing and/or drying periods by the hydrolysis of unreacted Si−Cl groups.

Calculated values for the Q$^4$/D$^2$ ratio, which is equivalent to the (Q$^4$/(Q$^3$ + Q$^4$))/(amount of silyl groups) ratio, in models A and B are 2 and 1, respectively. In C1M$_1$S−kanemite, the experimental value for the Q$^4$/D$^2$ ratio was 1.4 (Table 3), indicating that the alkylsilyl groups are attached as depicted in both models. In contrast, the values for C8M$_1$S− and C18M$_1$S−kanemites were 1.9 and 1.8, respectively; therefore, the interface structure of model A should be predominant. The difference in the degree of silylation appears to be responsible for such variations in structure. If the alkylsilyl groups were uniformly distributed within the interlayer, dimerization (model B) should occur when the amount of attached alkylsilyl groups is above 0.5. In C1M$_1$S−kanemite, the quantity of surface silyl groups was 0.51, which is sufficient for the dimerization when the reaction proceeds randomly. On the other hand, in the cases of C8M$_1$S− and C18M$_1$S−kanemites, alkylmethylsilyl groups are likely to bridge between two adjacent SiO$_4$ tetrahedra to form two five-membered rings, due to the relatively small numbers of attached alkylsilyl groups (0.33−0.34 per SiO$_2$).

**Table 3. Relative Intensity in the $^{29}$Si MAS NMR Spectra and the Amounts of Alkylsilyl Groups for C*n*M$_1$S−Kanemite**

| | % D$^2$ | % Q$^3$ | % Q$^4$ | Q$^4$/D$^2$ | Q$^4$/ (Q$^3$ + Q$^4$) | (Q$^4$/(Q$^3$ + Q$^4$))/ amt of alkylsilyl groups$^a$ |
|---|---|---|---|---|---|---|
| C1M$_1$S | 33 | 21 | 46 | 1.4 | 0.51 | 1.4 |
| C8M$_1$S | 25 | 26 | 48 | 1.9 | 0.65 | 1.9 |
| C18M$_1$S | 26 | 26 | 47 | 1.8 | 0.64 | 1.9 |

$^a$ Amount of alkylsilyl groups per SiO$_2$ (Table 1).

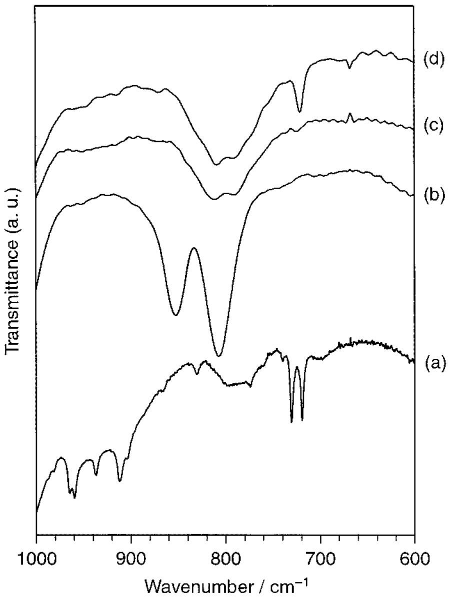


**Figure 10.** FT-IR spectra of (a) C16TMA−kanemite, (b) C1M$_1$S−kanemite, (c) C8M$_1$S−kanemite, and (d) C18M$_1$S−kanemite.

According to a recent report on the vibrational spectra of various layered silicates, including magadiite, kenyaite, and ilerite (octosilicate),[25] the absorption bands at around 800 cm$^{-1}$ are ascribed to the siloxane “cage” motions ($\nu_s$(Si−O−Si)). The IR spectra for a series of C*n*M$_1$S−kanemites are shown in Figure 10. In the spectrum of C1M$_1$S−kanemite, the absorption band due to the $\nu_s$(Si−O−Si) type of motion overlaps with strong

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(25) Huang, Y.; Jiang, Z.; Schwieger, W. *Chem. Mater.* **1999**, *11*, 1210.

**Table 4. Relative Intensity in the $^{29}$Si MAS NMR Spectra and the Amounts of Alkylsilyl Groups for C*n*S−Kanemite**

| | % $T^2$ | % $T^3$ | % $Q^3$ | % $Q^4$ | $Q^4/(T^2 + T^3)$ | $Q^4/(Q^3 + Q^4)$ | amt of alkylsilyl groups/$SiO_2$ | $(Q^4/(Q^3 + Q^4))/$ amt of alkylsilyl groups |
|---|---|---|---|---|---|---|---|---|
| C1S | 14 | 26 | 17 | 46 | 1.2 | 0.73 | 0.75 | 1.0 |
| C2S | 13 | 27 | 16 | 44 | 1.1 | 0.73 | 0.54 | 1.3 |
| C4S | 17 | 14 | 23 | 46 | 1.5 | 0.67 | 0.46 | 1.5 |
| C8S | 16 | 14 | 24 | 46 | 1.6 | 0.65 | 0.40 | 1.6 |
| C12S | 16 | 15 | 27 | 42 | 1.4 | 0.64 | 0.40 | 1.5 |
| C16S | 19 | 12 | 26 | 44 | 1.5 | 0.63 | 0.39 | 1.6 |
| C18S | 13 | 16 | 24 | 47 | 1.6 | 0.66 | 0.38 | 1.7 |

Si−$CH_3$ absorption bands at 850 and 800 cm$^{-1}$. However, an additional band was observed at 790 cm$^{-1}$ in the spectra of C8$M_1$S− and C18$M_1$S−kanemites. These bands are not observed in the spectrum of kanemite,[26] and probably arise from Si−O−Si linkages formed by silylation. A similar band at 790 cm$^{-1}$ is also observed for ilerite (observed at 789 cm$^{-1}$), indicating a structural similarity in these materials containing five-membered rings.[20]

The $^{29}$Si MAS NMR spectra of C*n*S−kanemite are shown in Figure 11. The signals assigned to the $T^2$ and $T^3$ environments were mainly observed for the attached alkylsilyl groups. Possible structural models for the alkylsilyl units in the $T^2$ and $T^3$ environments are illustrated in Chart 1. On the basis of the models for the C*n*$M_1$S−kanemite system, the structural models for $T^2$ silicate species in C*n*S−kanemite are easily obtained by the replacement of −$CH_3$ groups by −OH groups. The formation of $T^3$ silicate species requires the condensation between adjacent alkylsilyl groups in the $T^2$ environment that are located along the *a* axis to satisfy a tetrahedral coordination of organosilicate units. As listed in Table 4, the $Q^4/(T^2 + T^3)$ ratios in C1S− and C2S−kanemites were 1.2 and 1.1 (($Q^4/Q^3 + Q^4$)/(amount of silyl groups) = 1.0 and 1.3), respectively. Therefore, it is supposed that the alkylsilyl groups are predominantly attached as depicted in model B. C*n*S−kanemite ($n = 4-18$) exhibited $Q^4/(T^2 + T^3)$ ratios in the range of 1.4−1.6, and also ($Q^4/(Q^3 + Q^4)$)/(amount of silyl groups) ratios of 1.5−1.7, which indicates that the products contain substantial proportions of alkylsilyl groups that are attached as in model A. These differences in structure can also be explained by differences in the degree of silylation. Thus, new ring and cage structures were formed on the layered silicate, which implies two-dimensional nanodesign of silicate frameworks. This method can be applied to other layered polysilicates. The structures of layered polysilicates with thicker silicate layers (e.g., magadiite and kenyaite) need to be investigated further toward well-designed organosilicate nanomaterials with more condensed networks.

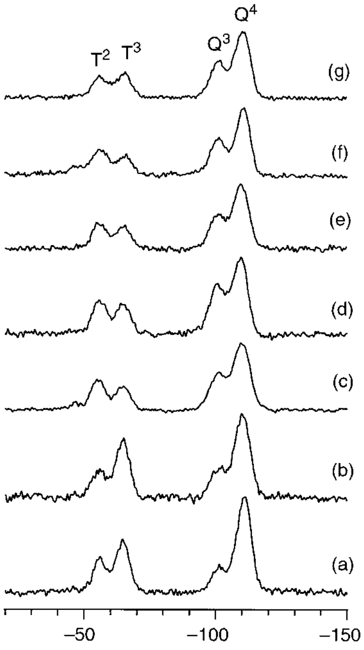

**Figure 11.** $^{29}$Si MAS NMR spectra of C*n*S−kanemites for (a) $n = 1$, (b) $n = 2$, (c) $n = 4$, (d) $n = 8$, (e) $n = 12$, (f) $n = 16$, and (g) $n = 18$.

## Conclusions

Alkylsilylation of the interlayer surface of a layered polysilicate kanemite was performed by using alkylchlorosilanes with various functionalities and alkyl chain lengths. Silylation without deteriorating the original silicate frameworks was confirmed. The variation in the chain length in alkyltrichlorosilanes results in the difference in the degree of silylation as well as the arrangements of the interlayer alkylsilyl groups. C*n*S−kanemite derived from alkyltrichlorosilanes with shorter chains ($n = 1-4$) exhibited relatively large BET surface areas, and changed to nonporous structures with $n = 8-18$. Although kanemite is composed of single layered silicate sheets of six-membered rings, silicate frameworks containing additional five- and six-membered rings are formed when dichloro- and trichloro(alkyl)silanes are used for silylation. Being completely different from pillaring of layered materials, this is the first step for the conversion of two-dimensional silicate into three-dimensional networks with a well-designed architecture by organic modification. This method will open up new possibilities for the design and construction of novel artificial crystalline microporous and mesoporous silicates.

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**Supporting Information Available:** Table giving the IR peak positions of $CH_2$ stretching vibrations for C*n*S−kanemite (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(26) Huang, Y.; Jiang, Z.; Schwieger, W. *Microporous Mesoporous Mater.* **1998**, *26*, 215.