# The Preparation of Alkyltrimethylammonium-Kanemite Complexes and Their Conversion to Microporous Materials

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Single layered polysilicate kanemite ($NaHSi_2O_5 \cdot 3H_2O$) was allowed to react with alkyltrimethylammonium chloride solutions to form alkyltrimethylammonium-kanemite complexes. During the organic intercalation, the $SiO_2$ layers in the complexes were condensed to form three-dimensional $SiO_2$ networks. The calcined products of the complexes had micro pores 2—4 nm in diameter, and the surface areas were ca. 900 $m^2 g^{-1}$. The pore size of the calcined products was altered with the variation in the alkyl-chain length of the alkyltrimethylammonium ions employed.

Kanemite ($NaHSi_2O_5 \cdot 3H_2O$), one of the layered polysilicates, has been found by Johan et al.[1] A synthetic method has been developed by Beneke and Lagaly.[2] The layers of kanemite are composed of single-layered sheets of $SiO_4$ tetrahedra, such as $KHSi_2O_5$[3] and $\alpha$-$Na_2Si_2O_5$,[4] although the precise crystal structure has not yet been determined. A report on organic intercalation compounds of kanemite has already been presented by Beneke and Lagaly.[2] According to this report, it was possible to exchange $Na^+$ ions in the interlayer space of kanemite with organic cations. The intercalation of alkylamines into the interlayer space of acid-treated kanemite was also possible.

$^{29}Si$-MAS NMR spectroscopy is a useful method for the structural study of silicates. Chemical shifts of $^{29}Si$ atoms in silicates depend mainly on the number and kind of atoms connected with $SiO_4$ tetrahedra.[5] In previous studies,[6–8] the $^{29}Si$-MAS NMR spectra of layered polysilicates, such as $\delta$-$Na_2Si_2O_5$, $KHSi_2O_5$, and kanemite, indicated only the signals due to $Q^3$ environments in $SiO_4$ tetrahedra ($-O\underline{Si}(OSi\equiv)_3$), for these layered polysilicates consist of single-layer sheets of $SiO_4$ tetrahedra. However, the $^{29}Si$-MAS NMR spectrum of $H_2Si_2O_5$-III,[6,8] which is the acid derivative of $\delta$-$Na_2Si_2O_5$, $KHSi_2O_5$, and kanemite, showed the signal due to the $Q^4$ environment in $SiO_4$ tetrahedra ($\underline{Si}(OSi\equiv)_4$) in addition to the signal due to the $Q^3$ environment. This means that $H_2Si_2O_5$-III is relatively unstable and that interlayer condensation between SiOH groups on the surface of the $SiO_2$ layers in this layered polysilicic acid occurs. In our preliminary study,[9] it was confirmed by means of $^{29}Si$-MAS NMR that the delamination of kanemite also occurred during the ion-exchange of interlayer $Na^+$ ions with alkyltrimethylammonium ions. With regard to $KHSi_2O_5$, it has been confirmed very recently that delamination and interlayer condensation occurred during the ion-exchange of interlayer $K^+$ ions with alkylammonium ions.[8]

On the other hand, there has been growing interest in the so-called pillared clays because of their possible use for catalysts and molecular sieves, since the pore sizes can be designed to be larger than those of zeolites.[10] It seems that, by varying the size of the pillars and the spacing between pillars, porous silicates with adjusted pore sizes can be prepared. However, in general, the ion- exchange capacities of clays are not variable in a broad range, and the kinds of polyoxocations or clusters which can be intercalated are also limited.[11] Thus, the pore sizes and the pore-size distribution of pillared clays can not be regulated freely. Since the deformation of the layers in kanemite can be expected on organic intercalation, a specific $SiO_2$ network would form if organic guest substances were selected appropriately.

Therefore, in the present study, we used kanemite as the starting material and investigated the $SiO_2$ structure of the alkyltrimethylammonium complexes. Furthermore, we discussed their conversion to inorganic porous materials by means of calcination.

## Experimental

**Starting Materials.** The kanemite was prepared by the method described by Beneke and Lagaly.[2] A mixture of amorphous silica and NaOH ($SiO_2$:NaOH=1:1) was dispersed in 100 ml of methanol with cooling; it was then dried at 100 °C for 2 weeks. After this dried material had then been calcined at 700 °C for 5.5 h, the product was dispersed in water, filtered, and air-dried. The formation was checked by means of X-ray powder diffraction and $^{29}Si$-MAS NMR. The chemical analysis also showed that the composition was the same as that of $NaHSi_2O_5 \cdot 3H_2O$.

**Preparation of Alkyltrimethylammonium-Kanemite Complexes and the Thermal Treatment.** Alkyltrimethylammonium-kanemite complexes were prepared by cation-exchange, as has been described by Beneke and Lagaly.[2] One hundred ml of a 0.1 mol dm$^{-3}$ alkyltrimethylammonium chloride ($C_nH_{2n+1}(CH_3)_3N^+Cl^-$, $n$=12, 14, 16, or 18) aqueous solution was added to 1 g of kanemite, and then the suspension was stirred for one week at 65 °C. While the suspension was being stirred, this pH was kept between 8 and 9. After the filtration of the product, the same procedure was repeated. Then, the product was washed with an excess of acetone and air-dried.

The complexes were calcined up to 700 °C in air by means of a thermal analyzer, in which the alkyltrimethylammonium ions were pyrolyzed completely.

**Analyses.** The X-ray powder diffraction patterns were obtained with a Rigaku Rad-IB diffractometer using Ni-filtered Cu *Kα* radiation. The $^{29}$Si-MAS NMR spectra were obtained with a JEOL GSX-270 spectrometer at 53.67 MHz. The external standard was tetramethylsilane, and a gated high power proton decoupling technique without cross polarization was employed with a 45° pulse. The $^{29}$Si-CP MAS NMR spectra were obtained with a JEOL GSX-400 spectrometer at 79.42 MHz. The matched radiofrequency field amplitude of CP was 38.46 kHz, the 90° pulse was 6.5 μs, the CP contact time was 2 ms, and the pulse repetition time was 5 s. The IR spectra were recorded on a Shimadzu IR-435 infrared spectrometer. The Brunauer-Emmet-Teller (BET) surface areas of the calcined products were determined by means of $N_2$ adsorption at the temperature of liquid nitrogen using a Shimadzu Digisorb 2600 apparatus. The pore-size distributions of the calcined products were determined by use of a cylindrical capillary model[12] from $N_2$ adsorption-desorption isotherms using a Digisorb 2600. Some calcined alkyltrimethylammonium-kanemite complexes were also examined by means of transmission electron microscopy (TEM), using a thin-section technique. The powder samples were first embedded in Quetol 651[13] and then sectioned with a glass knife. Micrographs were taken with a Hitachi H-700H electron microscope at 200 kV.

## Results and Discussion

**Alkyltrimethylammonium-Kanemite Complexes.** The X-ray powder diffraction patterns of kanemite and the product obtained by the reaction with dodecyltrimethylammonium ions are shown in Fig. 1. Only the peaks at $d$=0.433 nm, 0.406 nm, and 0.250 nm were observed after the reaction. These peaks could be attributed to dehydrated kanemite.[2] This means that the single-layered silicate structure derived from kanemite was partly retained in the product. The broad peak at around $2\theta$=15—30° indicated that the crystallinity of the product decreased drastically and that delamination proceeded. The products prepared by the reaction with other alkyltrimethylammonium ions also exhibited similar X-ray powder diffraction patterns.

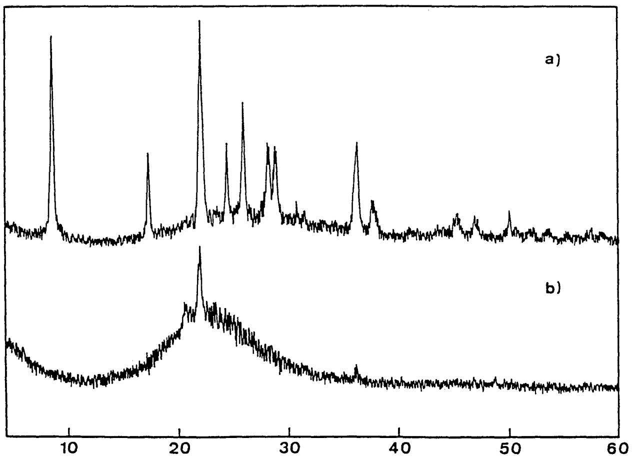

Fig. 1. X-Ray powder diffraction patterns of a) kanemite and b) dodecyltrimethylammonium-kanemite complex.

A similar pattern has been reported in the $KHSi_2O_5$–ethyl- or heptylammonium system, in which broad reflections are observed in the 5—10° $2\theta$ range and in the 20—30° $2\theta$ range, accompanied by some sharper peaks.

Figures 2c—e show the variation in the X-ray powder diffraction patterns of the dodecyltrimethylammonium reaction products with the reaction time. Each pattern shows two peaks at 3.7 nm and 3.1 nm. The latter peak agreed with the result obtained by Beneke and Lagaly.[2] Thus, this peak was ascribable to dodecyltrimethylammonium intercalated kanemite, which has no interlayer condensation. In fact, the peak at 3.1 nm disappeared after washing with acetone. Figures 2c—e show that the intensity of the peak at 3.7 nm, which was possibly attributable to the interlayer condensed product, increased with the reaction time. This result agreed with that from $^{29}$Si-CP MAS NMR, which will be described below. In fact, after a reaction time of 2 weeks, the peak at 3.1 nm disappeared. (Fig. 2b) The powder X-ray diffraction patterns of the products obtained by the reaction with other alkyltrimethylammonium ions for 2 weeks indicated similarly large d-spacings: 4.1 nm, 4.6 nm, and 5.0 nm in the tetradecyl-, hexadecyl-, and octadecyltrimethylammonium kanemites respectively.

The $^{29}$Si-MAS NMR spectrum of kanemite (Fig. 3a)

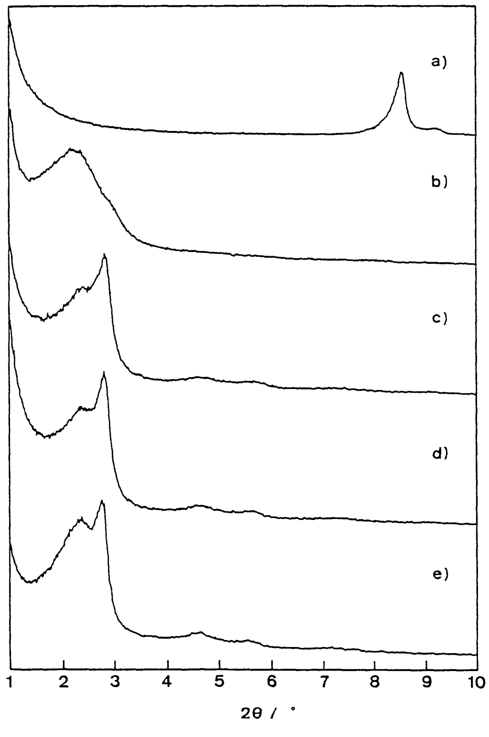

Fig. 2. X-Ray powder diffraction patterns in lower $2\theta$ region of a) kanemite and b—e) dodecyltrimethylammonium-kanemite complexes.
(Reaction time: b) 2 weeks, c) 1 h, d) 3 h, and e) 1 d.)

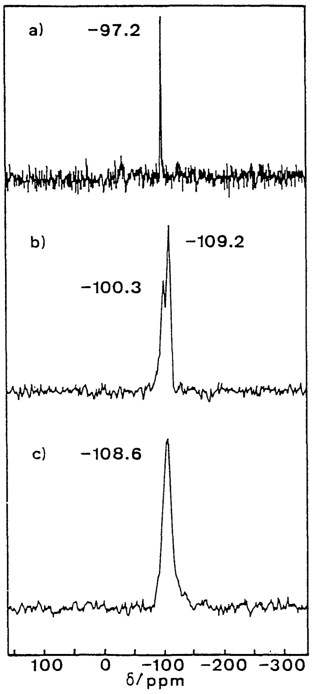

Fig. 3. $^{29}$Si-MAS NMR spectra of a) kanemite, b) dodecyltrimethylammonium-kanemite complex, and c) calcined (700 °C) dodecyltrimethylammonium-kanemite complex.

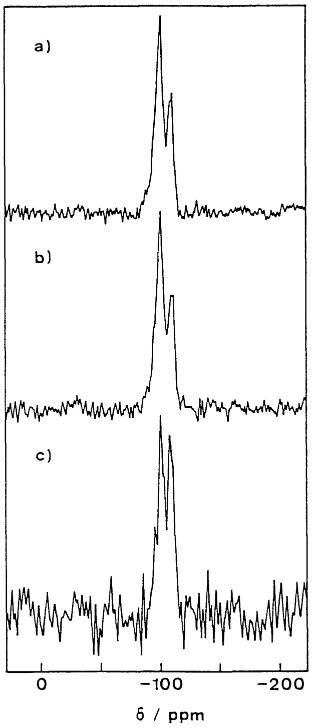

Fig. 4. $^{29}$Si-CP MAS NMR spectra of dodecyltrimethylammonium-kanemite complexes. (Reaction time: a) 1 h, b) 3 h, and c) 1 d.)

showed only one peak, at −97.2 ppm, which was assigned to the $Q^3$ environment in $SiO_4$ tetrahedra ($\mathrm{O\underline{Si}(OSi{\equiv})_3}$),[5] similar to the result reported by Pinnavaia et al.[7] This result supported the single-layered silicate structure of kanemite. However, the spectrum of the dodecyltrimethylammonium-kanemite complex (Fig. 3b) showed a further peak at −109.2 ppm, which was definitely assigned to the $Q^4$ environment in $SiO_4$ tetrahedra ($\mathrm{\underline{Si}(OSi{\equiv})_4}$). When magadiite and kenyaite were used as starting layered polysilicates, the $^{29}$Si-MAS NMR spectra showed no changes between the original layered polysilicates and their alkyltrimethylammonium ion-exchanged forms.[14,15] Judging from these results, some of the silicate layers of kanemite were condensed during the ion exchange reaction, and a three-dimensional $SiO_2$ network was formed. Other alkyltrimethylammonium-kanemite complexes also exhibited similar $^{29}$Si-MAS NMR spectra.

Figure 4 shows the $^{29}$Si-CP MAS NMR spectra of the complexes which were prepared by the reaction with dodecyltrimethylammonium chloride solutions for various reaction times. Even the spectrum of the product which was treated for 1 h shows the $Q^4$ peak; the intensity of this $Q^4$ peak increased with the reaction time. These results show that the interlayer cross-linking occurred partially, even during the initial cation exchange, and that it proceeded gradually.

The IR spectra of these alkyltrimethylammonium products indicated the absorption peaks due to the alkyltrimethylammonium ions. ICP results showed that these products contained no $Na^+$ ions. From these results, it can be said that the $Na^+$ ions in the interlayer spaces of kanemite were exchangeable with alkyltrimethylammonium and that alkyltrimethylammonium-kanemite complexes were formed.

Elemental analysis of all the alkyltrimethylammonium-kanemite complexes showed that they contained about 0.1 mol of alkyltrimethylammonium ions per mol of $SiO_2$. This result indicated that not all the $Na^+$ ions were exchanged with alkyltrimethylammonium ions. As has been described above, alkyltrimethylammonium-kanemite complexes contained no $Na^+$ ions. A previous report[2] indicated that about 70% of the $Na^+$ ions were exchanged with protons at pH=8.5 when kanemite was titrated with dil. HCl. Therefore, some of the $Na^+$ ions must have been exchanged with protons to form Si-OH groups. Silanol groups on neighboring $SiO_4$ tetrahedra layers are thought to be condensed with each other, because the cation-exchange was conducted under the conditions of 65 °C and pH=8—9.

Since kanemite is made up of single layers composed of $SiO_4$ tetrahedra, the layers are easily deformed. Therefore, it is considered that the neighboring bent layers in the alkyltrimethylammonium-kanemite complexes are able to be condensed with each other. The alkyltrimethylammonium ions in the complexes were surrounded by these bent layers.

Therefore, it was considered that the layered structure derived from kanemite was still retained, at least in part, in the three-dimensional structure of the complexes. The fact that the X-ray diffraction peaks due to dehydrated kanemite appeared at 0.433 nm, 0.406 nm, and 0.25 nm supported this model. However, since the detailed structure of kanemite has not yet been clarified, a concrete structural model of the complexes can not be displayed at present.

**Heat Treated Products of the Alkyltrimethylammonium-Kanemite Complexes.** The $^{29}$Si-MAS NMR spectrum of the heat-treated product of the dodecyltrimethylammonium-kanemite complex indicated a broadened peak whose top was at −108.6 ppm (Fig. 3c). Although this peak was mainly due to the $Q^4$ environment, judging from the chemical shift, the broadening and the low symmetry of this peak suggested some presence of the $Q^3$ peak. From this finding, it appears that the structure of the dodecyltrimethylammonium-kanemite complex changed further. However, the X-ray powder diffraction pattern of the calcined product indicated a pattern similar to that of the untreated dodecyltrimethylammonium-kanemite complex. From this result, it can be assumed that the three-dimensional $SiO_2$ network in the calcined dodecyltrimethylammonium-kanemite complex was still retained after the heat treatment. In the calcined products obtained from other alkyltrimethylammonium-kanemite complexes, the three-dimensional $SiO_2$ networks were retained after calcination, since their X-ray powder diffraction patterns indicated d values similar to those of the alkyltrimethylammonium-kanemite complexes.

Each specific surface area of the calcined products has almost the same value; about 900 $m^2 g^{-1}$. On the other hand, the specific surface area of H-kanemite ($H_2Si_2O_5$-III) calcined at 700 °C was only about 50 $m^2 g^{-1}$. This means that adsorption by $N_2$ molecules was introduced to the inner surface of the calcined products. Judging from the results obtained by means of the Cranston-Inkley method,[12] most of the surface areas in the calcined products resulted from the surface of mesopores less than 10 nm in diameter. If the large surface area arises from the pores among the surfaces of small aggregated, non-porous $SiO_2$ particles, the diameter of the particles should be about 2.9 nm. However, as is shown in the transmission electron micrograph to be described below, such aggregated particles could not be found. Therefore, the influence of the external surface of the particles on the surface areas was estimated to be very low. That is to say, even after the alkyltrimethylammonium ions in the complexes had been eliminated by calcination, the three-dimensional $SiO_2$ networks were well retained and micro pores were formed.

The pore-size distribution of the calcined products was then calculated by means of the Cranston-Inkley method[12] (Fig. 5), from these results, the range of the pore-size distribution of each calcined product was very narrow; the pore size increased from about 2 nm to about 4 nm with the length of the alkyl chain in the alkyltrimethylammonium ions employed. This fact indicated the synthesis of porous $SiO_2$, whose pore size was controlled by varying the kind of alkyltrimethyl-

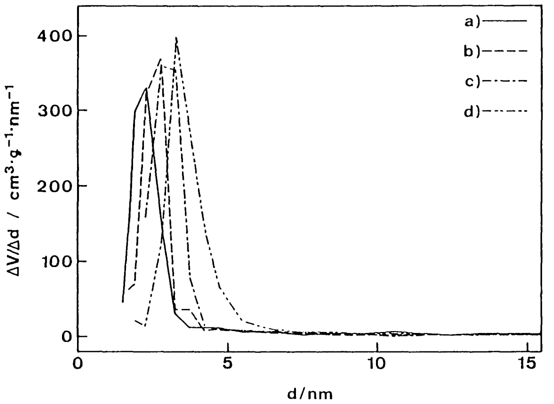

Fig. 5. Pore size distributions in the calcined products obtained from a) dodecyl-, b) tetradecyl-, c) hexadecyl-, and d) octadecyl-trimethylammonium-kanemite complexes.

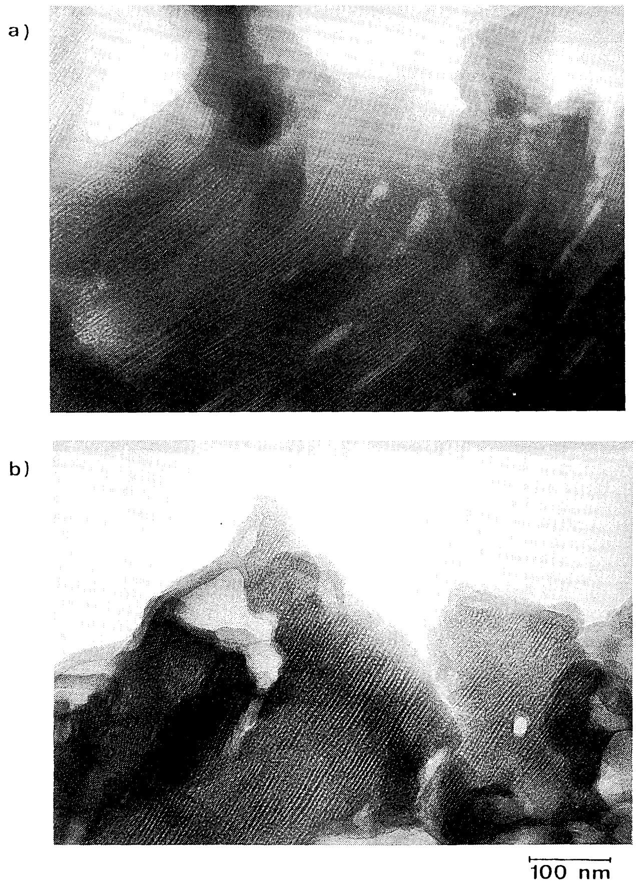

Fig. 6. Transmission electron micrographs of the a) octadecyltrimethylammonium-kanemite complex and b) calcined (700 °C) octadecyltrimethylammonium-kanemite complex.

ammonium ion.

The transmission electron micrographs of the octadecyltrimethylammonium-kanemite and its calcined product are shown in Fig. 6. Although the alkyltrimethylammonium-kanemite has seemingly retained its layer structure (Fig. 6a), the single-layered silicate sheet is so thin that the lines in the TEM image can not correspond to the single layered sheet itself. The precise observation of the image suggested that the lamellar lines indicated the formation of uneven layers. Since the other data, obtained by means of $^{29}$Si-MAS NMR and X-ray powder diffraction, indicated the formation of a three-dimensional $SiO_2$ network, the image probably exhibited just the overall arrangement of the condensed $SiO_2$ skeleton at its macromolecular level. The micrograph of the calcined product (Fig. 6b) showed a form similar to that of the uncalcined complex. The image also suggested that the uneven $SiO_2$ layers were retained in a similar manner. This finding was in agreement with the XRD results for the calcined product, in which the large d spacing remained. The TEM images of other alkyltrimethylammonium kanemites before and after calcination were also similar.

In conclusion, alkyltrimethylammonium-kanemite complexes were synthesized by the treatment of kanemite with alkyltrimethylammonium chloride solutions. $^{29}$Si-MAS NMR and X-ray powder diffraction clarified that $SiO_2$ layers in the complexes were condensed with each other to form three-dimensional $SiO_2$ networks. The calcined products of the complexes have micropores whose sizes increased with the length of the alkyl chain in the alkyltrimethylammonium ions used. These facts indicated the synthesis of porous $SiO_2$ with a controlled pore size.

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