Trimethylsilyl Derivatives of Alkyltrimethylammonium-Kanemite Complexes and Their Conversion to Microporous SiO_2 Materials

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Synopsis. Alkyltrimethylammonium-kanemite complexes, having three dimensional SiO_2 networks, were allowed to react with a trimethylsilylating reagent to form the trimethylsilylated derivatives. The three dimensional SiO_2 networks were retained after trimethylsilylation. The calcined products obtained from the trimethylsilylated products had about 840—880 $m^2 g^{-1}$ in specific surface areas and micro pores with 22—33 Å in average pore diameter. These values were slightly smaller than those of the calcined products obtained from alkyltrimethylammonium-kanemite complexes, which indicated the effect of the trimethylsilyl groups.

Kanemite ($NaHSi_2O_5 \cdot 3H_2O$),[1] one of the layered polysilicates,[2,3] is known to form intercalation compounds by cation-exchange reaction with organoammonium ions. Since kanemite consists of single layers connected with SiO_4 tetrahedra[1] like $KHSi_2O_5$[4] and δ-$Na_2Si_2O_5$,[5] they are so sensitive that delamination or interlayer condensation occurs during the cation-exchange reaction.

Alkyltrimethylammonium-kanemite complexes were synthesized by cation-exchange reaction in our previous study.[6] In these complexes, three dimensional networks of SiO_2 were formed by delamination of SiO_4 tetrahedra layers during cation exchange. The three dimensional SiO_2 networks had a high heat stability, and the calcined products of the alkyltrimethylammonium-kanemite complexes had pores of 20—40 Å diameter.

The variation in pore sizes in zeolites has been attempted by the reaction between silylating reagents and silanol groups on their surfaces.[7—9] It can be expected that pore sizes on the SiO_2 porous materials obtained from alkyltrimethylammonium-kanemite complexes could also be varied by reaction with silylating reagents.

In this study, chlorotrimethylsilane, one of the most common silylating reagents, was allowed to react with the alkyltrimethylammonium-kanemite complexes to estimate the effects of trimethylsilyl groups (abbreviated as TMS groups) on their pore size distributions of the calcined products.

Experimental

Materials. The starting material kanemite was synthesized by a method described by Beneke et al.[1] The alkyltrimethylammonium-kanemite complexes were synthesized by the reaction between kanemite and alkyltrimethylammonium chloride solutions.[1,6] The formation was checked by X-ray powder diffraction and ^{29}Si-MASNMR. Dodecyltrimethyl-, tetradecyltrimethyl-, hexadecyltrimethyl-, and octadecyltrimethylammonium chloride (Tokyo Kasei Kogyo, extra pure) were used as the alkyltrimethylammonium chlorides. Commercially available chlorotrimethylsilane and hexamethyldisiloxane (Tokyo Kasei Kogyo, extra pure) were used in this study.

Trimethylsilylating Reaction and Calcination of the Silylated Products. The alkyltrimethylammonium-kanemite complexes were mixed with an excess amount of a 1:1 mixture of chlorotrimethylsilane and hexamethyldisiloxane. These mixtures were refluxed for 48 h. The silylated products were washed thoroughly with acetone and air-dried. The trimethylsilylated products were next calcined at 700 °C by a DTA apparatus under the same conditions as in our previous study.[6]

Analyses. X-Ray powder diffraction patterns, IR spectra, ^{29}Si-MASNMR spectra, specific surface areas, and pore size distributions were obtained in the same manner as in our previous study.[6]

Results and Discussion

The IR spectrum of the trimethylsilylated product from the hexadecyltrimethylammonium-kanemite complex is shown in Fig. 1c. The trimethylsilylated

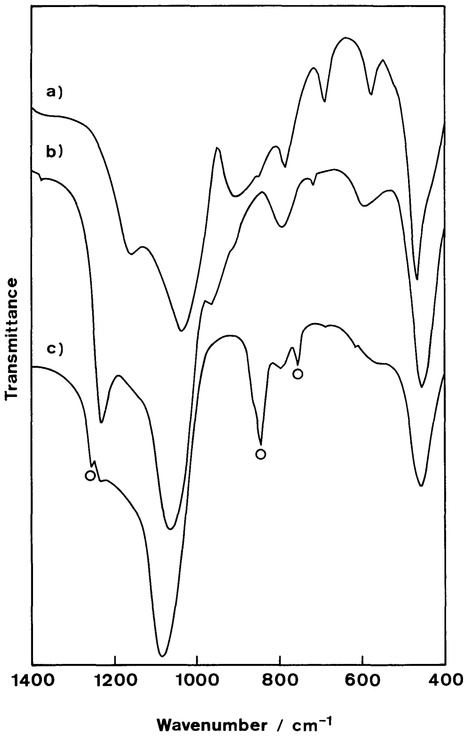

Fig. 1. IR spectra of a) kanemite, b) hexadecyltrimethylammonium-kanemite complex, and c) the trimethylsilylated derivative. (○=trimethylsilyl groups.)

product showed the absorption bands attributed to TMS groups at 1250 cm^{-1}, 850 cm^{-1}, and 750 cm^{-1}. These bands remained after heat-treatment at 300 °C. The absorption bands due to hexadecyltrimethylammonium ions disappeared after trimethylsilylation.

The ^{29}Si-MASNMR spectra of kanemite and the products are shown in Fig. 2. In the spectrum of the hexadecyltrimethylammonium–kanemite complex (Fig. 2b), the peak due to Si atoms in Q^3 environment (O$\underline{\text{Si}}$(OSi≡)$_3$) appeared at −100.8 ppm and a peak due to Si atoms in Q^4 environment ($\underline{\text{Si}}$(OSi≡)$_4$) appeared at −110.2 ppm. The peak due to the Q^4 environment did not appear in the spectrum of the original kanemite. (Fig. 2a) This means that interlayer condensation of neighboring SiO$_2$ layers occurred during ion-exchange reaction to form the Q^4 environment as described in our previous study.[6] The ^{29}Si-MASNMR spectrum of the trimethylsilylated product obtained from the complex showed the peak due to Si atoms in M^1 environment (R$_3\underline{\text{Si}}$(OSi≡)) at 13.3 ppm (Fig. 2c). The peak due to the Q^3 environment decreased considerably after trimethylsilylation. This means that new Q^4 environment sites were formed from Q^3 environment sites by the following reaction,

$$\equiv\text{Si-OH} + \text{Cl-Si(CH}_3)_3 \longrightarrow \equiv\text{Si-O-Si(CH}_3)_3 + \text{HCl}. \quad (1)$$

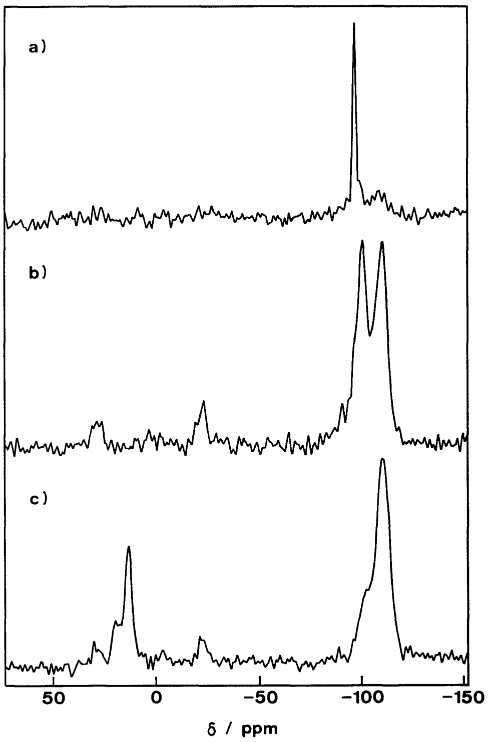

Fig. 2. ^{29}Si-MASNMR spectra of a) kanemite, b) hexadecyltrimethylammonium–kanemite complex, and c) the trimethylsilylated derivative.

From these results, it was confirmed that trimethylsilylation of hexadecyltrimethylammonium–kanemite complex took place. Since the trimethylsilylated products obtained from the other alkyltrimethylammonium–kanemite complexes exhibited similar IR spectra and ^{29}Si-MASNMR spectra, they were also trimethylsilylated by the same method applied for the hexadecyltrimethylammonium–kanemite complex.

The basal spacings of the trimethylsilylated alkyltrimethylammonium–kanemite complexes are shown in Table 1. The basal spacings of the trimethylsilylated products were very similar to those of the original alkyltrimethylammonium–kanemite complexes. Moreover, the XRD peaks which appeared in the range of 2θ=10–60° in the XRD patterns of the original alkyltrimethylammonium–kanemite complexes were retained. This means that the three-dimensional networks of SiO$_2$ in the alkyltrimethylammonium–kanemite complexes were still retained during trimethylsilylation. Elemental analysis of all the trimethylsilylated products showed that they contained 0.1—0.2 mol TMS groups per 1 mol SiO$_2$.

These trimethylsilylated products were calcined at 700 °C. The X-ray diffraction patterns of the calcined products indicated the same XRD patterns as the products before calcination. The specific surface areas of the products had nearly the same value of about 840—880 m^2 g^{-1}, which was slightly lower than those of the calcined alkyltrimethylammonium–kanemite complexes (890—910 m^2 g^{-1}). However, the values were much larger than that of calcined kanemite (about 50 m^2 g^{-1}).

The pore size of the calcined product obtained from the trimethylsilylated hexadecyltrimethylammonium complex was somewhat reduced in comparison with that obtained from the hexadecyltrimethylammonium–kanemite complex (Fig. 3). The calcined trimethylsilylated products from the other alkyltrimethylammonium–kanemite complexes similarly showed reduced pore sizes. In fact, the average pore diameters of the calcined products decreased by about 2—2.5 Å after trimethylsilylation (Fig. 4). From the decrease in the specific surface areas and the pore sizes in the calcined products, it was assumed that the pores of the calcined products were partly occupied with silica which was formed by oxidation of attached TMS groups.

In conclusion, alkyltrimethylammonium–kanemite

Table 1. Basal Spacings of Alkyltrimethylammonium–Kanemite Complexes and Their Trimethylsilylated Derivatives

	Original/Å	Trimethylsilylated derivatives/Å
Dodecyltrimethylammonium–kanemite complex	38	38
Tetradecyltrimethylammonium–kanemite complex	42	41
Hexadecyltrimethylammonium–kanemite complex	46	44
Octadecyltrimethylammonium–kanemite complex	50	49

Basal spacing of kanemite=10.4 Å.

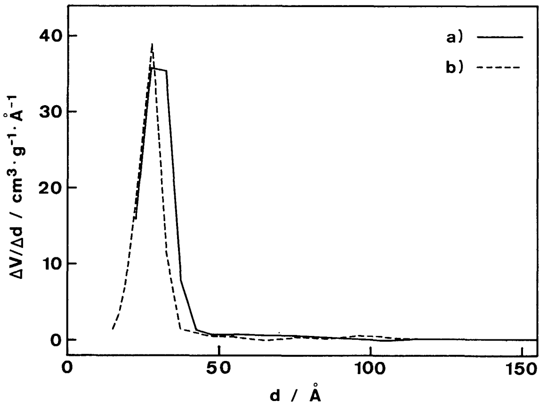

Fig. 3. Pore size distributions of a) calcined product obtained from hexadecyltrimethylammonium-kanemite complex and b) calcined product obtained from the trimethylsilylated derivative.

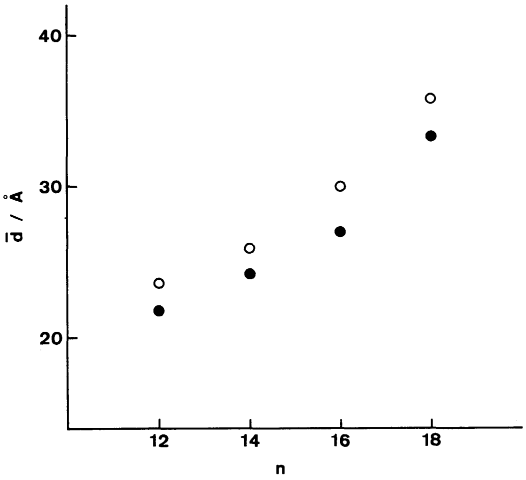

Fig. 4. Average pore diameters $\bar{d}$ of ○: calcined products from alkyltrimethylammonium-kanemite complexes and ●: calcined products from trimethylsilylated derivatives. (n=the number of carbon atoms in alkyl chain).

complexes, which have three dimensional SiO_2 networks, can be trimethylsilylated by the reaction with a trimethylsilylating reagent. The three dimensional SiO_2 networks in the alkyltrimethylammonium-kanemite complexes were still retained after trimethylsilylation. By calcination of these trimethylsilylated products, porous SiO_2 materials with high surface area were formed. The calcined products had slightly smaller surface areas and pores than the calcined products obtained from the original alkyltrimethylammonium-kanemite complexes, indicating the effect of trimethylsilyl groups.

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