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Formation of Intercalation Compounds of a Layered Sodium Octosilicate with *n*-Alkyltrimethylammonium Ions and the Application to Organic Derivatization

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Synopsis. In this study, *n*-alkyltrimethylammonium ions ($[C_nH_{2n+1}N(CH_3)_3]^+$; $n=12,14,16,18$) were intercalated in the interlayer space of layered sodium octosilicate ($Na_2Si_8O_{17}\cdot nH_2O$) via an ion-exchange reaction. The interlayer space was further modified by grafting of the trimethylsilyl groups via a reaction between a dodecyltrimethylammonium–octosilicate intercalation compound and chlorotrimethylsilane.

Sodium octosilicate ($Na_2Si_8O_{17}\cdot nH_2O$; $Na_2O\cdot 8SiO_2\cdot nH_2O$), which was first synthesized by Iler,[1] is one of the layered polysilicates, and consists of silicate layers formed from $Si(O, OH)_4$ tetrahedra and interlayer sodium ions. Although its structure has not yet been clarified, structural models have been proposed;[2—4] Schwieger and co-workers assumed double-layer structures on the basis of solid-state ^{29}Si nuclear magnetic resonance (NMR) spectroscopic results.[2,3] Layered polysilicates, such as kenyaite ($Na_2Si_{20}O_{41}\cdot nH_2O$) and magadiite ($Na_2Si_{14}O_{29}\cdot nH_2O$), undergo intercalative ion-exchange reactions,[5,6] whereas silicate layers of single-layered polysilicates, such as kanemite ($NaHSi_2O_5\cdot 3H_2O$), wind upon the intercalation of organic cations to form three-dimensional networks via the condensation of silanol groups (SiOH) between adjacent silicate layers.[7,8] Thus, because the layer thickness of the octosilicate is in the middle between those of magadiite and kanemite, the intercalation chemistry of sodium octosilicate is of interest. Only a few studies, however, have been reported so far; the interlayer sodium ions can be replaced with protons as well as with other inorganic cations;[1] moreover, recent work[9] has slightly mentioned the intercalation of some organic cations in the interlayer space of both sodium octosilicate and the corresponding protonated form. Furthermore, the interlayer surface of layered polysilicate can undergo grafting reactions involving silanol groups and organochlorosilanes; the trimethylsilylation of protonated octosilicate ($H_2Si_8O_{17}$) was achieved by using intercalation compounds with polar organic molecules as intermediates.[10] We have shown that the intercalation compounds of polysilicates (magadiite and kenyaite) with organoammonium ions can also be used as intermediates for silylation.[11—13] Thus, the reactions of organoammonium–octosilicate intercalation compounds with organochlorosilanes are also of interest. Here, we report on the intercalation of *n*-alkyltrimethylammonium cations into sodium octosilicate and organic derivatization by an interlayer grafting reaction using a dodecyltrimethylammonium–octosilicate intercalation compound as an intermediate.

Experimental

Materials. Sodium octosilicate was prepared from colloidal silica (Snowtex® 40, Nissan Chem. Ind. Ltd.; SiO_2 content, 40.7 mass%), sodium silicate ($Na_2SiO_3\cdot 9H_2O$), and water. These compounds were thoroughly mixed with $SiO_2:Na_2O:H_2O=4:1:25.8$ (in molar ratio). The mixture was sealed in a glass ampule (SiO_2, 72.2 mass%; B_2O_3, 10.3 mass%; Al_2O_3, 6.8 mass%; Na_2O, 6.4 mass%; BaO, 2.1 mass%; K_2O, 1.3 mass%; CaO, 0.8 mass%) and heated at 100 °C for more than two weeks. The product was washed with water; during the washing procedure, attention was paid to maintain the pH of the solution above 9 so as to avoid any possible protonation reaction. The air-dried product was a fine white powder; an X-ray powder diffraction (XRD) analysis showed that the product was single-phase sodium octosilicate.[1,9] Inductively-coupled plasma emission spectroscopy (ICP) and thermogravimetry (TG) revealed the composition of the product to be $1.1Na_2O\cdot 8SiO_2\cdot 7.5H_2O$. A slight deviation from the stoichiometry may be explained on the basis of the proposed formula.[9] Although a glass ampule contained a considerable amount of aluminum, ICP revealed that no detectable amount of aluminum was present in the product. *n*-Alkyltrimethylammonium chlorides ($C_nH_{2n+1}N(CH_3)_3Cl$, $n=4,6,8,10,12,14,16,18$) and chlorotrimethylsilane ($(CH_3)_3SiCl$) were used as received.

Intercalation of *n*-Alkyltrimethylammonium Ions. Five hundred milligrams of sodium octosilicate were dispersed in 100 ml of an *n*-alkyltrimethylammonium chloride aqueous solution (0.1 mol dm^{-3} for $n=4$—16 and 0.01 mol dm^{-3} for $n=18$), and the mixture was stirred for 24 h at ambient temperature. The procedure was repeated if the sodium ions were not fully exchanged. The centrifuged product was air-dried, but a part of product was washed with an absolute amount of acetone before drying so as to remove any excess guests for spectroscopic and compositional analyses.

Trimethylsilylation. Two hundred milligrams of a dodecyltrimethylammonium ($[C_{12}H_{25}N(CH_3)_3]^+$)–octosilicate intercalation compound were refluxed in a mixture of 10 cm^3 of chlorotrimethylsilane and 10 cm^3 of toluene for 24 h. A similar procedure was repeated to complete the trimethylsilylation. The product, separated by centrifugation, was washed with absolute amounts of acetone and ethanol, and then air-dried.

Analyses. XRD patterns were obtained using a Mac

Science MXP^3 diffractometer (monochromated Cu $K\alpha$ radiation). Scanning electron microscopy (SEM) was performed by using a JEOL JSM-T220A. Infra-red absorption (IR) spectra were recorded on a Perkin–Elmer FTIR-1640 using a KBr disk technique. Solid-state single-pulse ^{29}Si NMR spectra were obtained by using a JEOL NM-GSX400 spectrometer at 79.3 KHz with dipolar decoupling and magic-angle spinning (MAS; ca. 5 kHz). A $\pi/4$ pulse was used, and the chemical shifts were reported with respect to external tetramethylsilane. The compositions of the products were determined using ICP (Nippon Jarrell Ash ICAP-575 II) and conventional CHN analysis.

Results and Discussion

Sodium octosilicate reacted with $C_nH_{2n+1}N(CH_3)_3Cl$ aqueous solutions when $n=12,14,16,18$. Figure 1-(b) shows the XRD pattern of the reaction product with the $C_{12}H_{25}N(CH_3)_3Cl$ aqueous solution. The peak due to the basal spacing of sodium octosilicate ((001) diffraction peak[9]) (1.11 nm, Fig. 1-(a)) disappeared, and a new low-angle peak appeared at a position corresponding to a *d*-value of 2.35 nm. Although reactions with other *n*-alkyltrimethylammonium ions ($n=14,16,18$) gave very similar peaks, they had different low-angles (n=14, 2.54 nm; n=16, 2.71 nm; n=18, 2.92 nm). The *d* value increased monotonously with an increase in the number of carbon atoms in the alkyl chains. These findings strongly suggest the intercalation of $[C_nH_{2n+1}N(CH_3)_3]^+$ ions. Because of a broadening of XRD peaks and/or an overlapping of other peaks, however, we were not able to obtain evidence for the retention of the silicate layer structure by confirming the presence of ($h\,k\,0$) peaks indexed by Bobéry et al.[9] It should also be noted that, when the number of carbon atoms in the alkyl chains was equal to or less than 10, most of sodium octosilicate remained unchanged.

We further demonstrate detailed characterizations for only the reaction product with the $C_{12}H_{25}N(CH_3)_3Cl$ aqueous solution, since the XRD results indicate that the structures were very similar among all of the products with $n\geq12$. The IR spectrum of sodium octosilicate (Fig. 2-(a)) was consistent with those given in

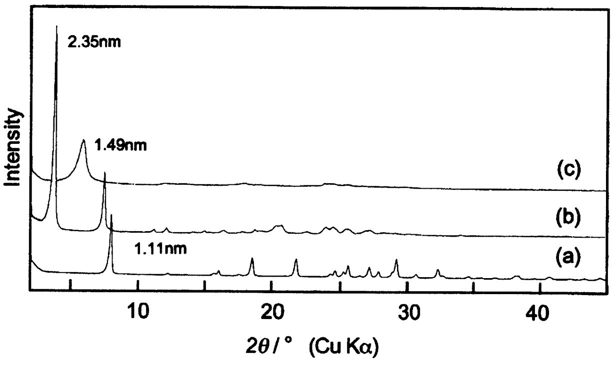

Fig. 1. XRD patterns of (a) sodium octosilicate, (b) $C_{12}H_{25}N(CH_3)_3^+$-octosilicate intercalation compound, and (c) trimethylsilylated derivative of (b).

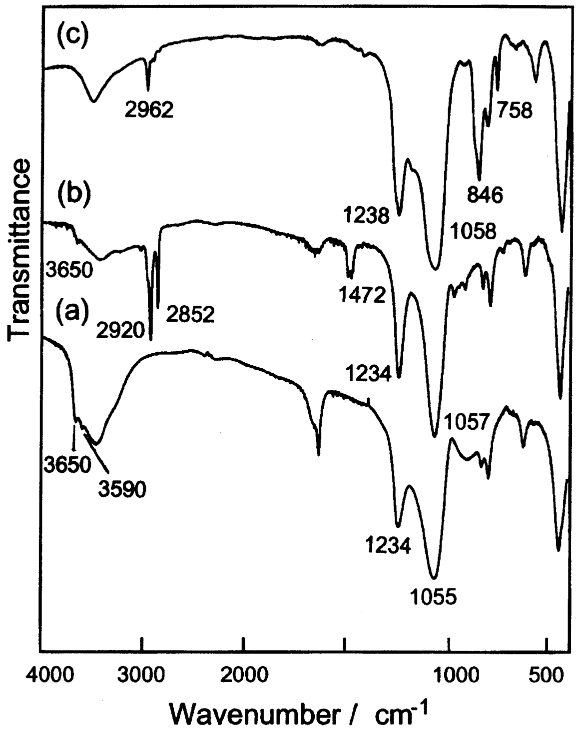

Fig. 2. IR spectra of (a) sodium octosilicate, (b) $C_{12}H_{25}N(CH_3)_3^+$-octosilicate intercalation compound, and (c) trimethylsilylated derivative of (b).

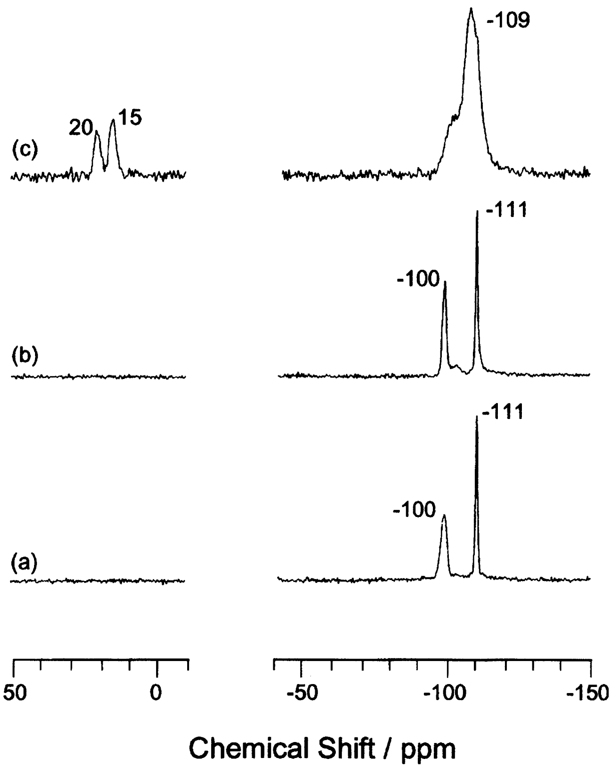

Fig. 3. Solid-state ^{29}Si NMR spectra of (a) sodium octosilicate, (b) $C_{12}H_{25}N(CH_3)_3^+$-octosilicate intercalation compound, and (c) trimethylsilylated derivative of (b).

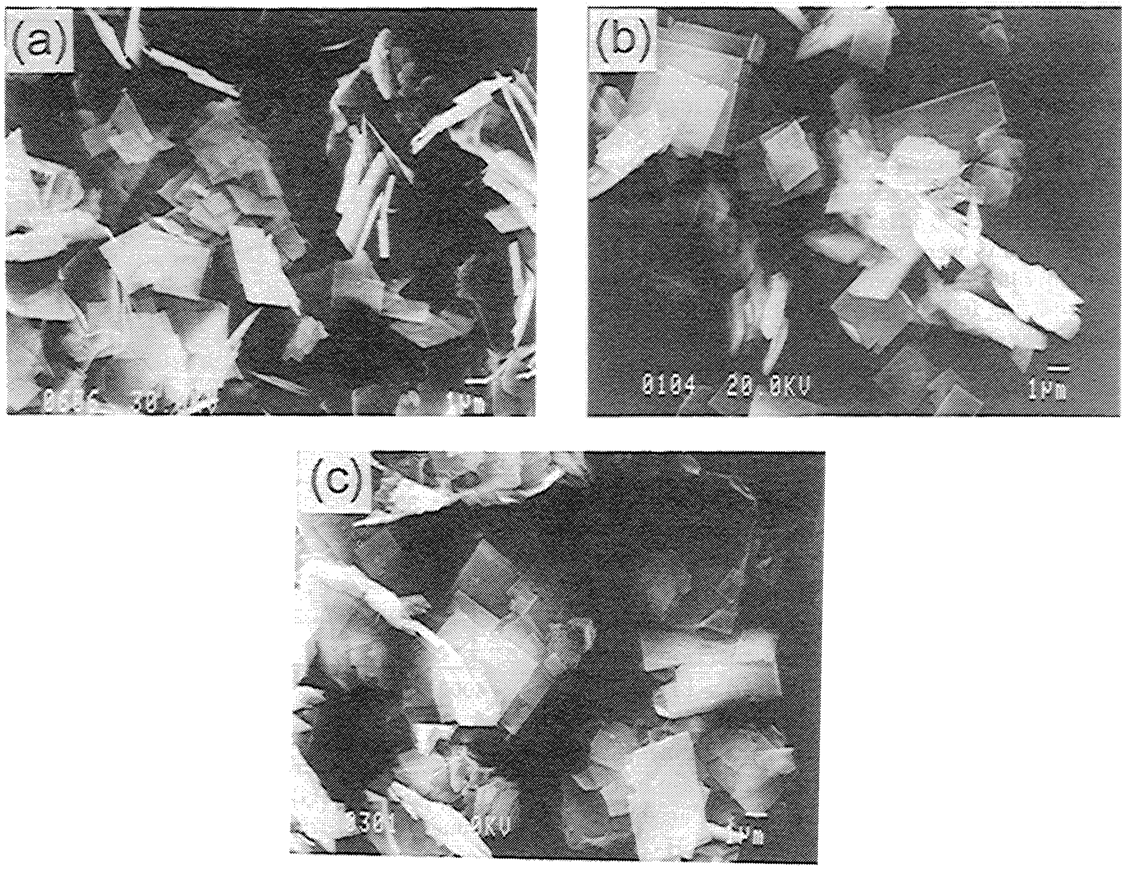

Fig. 4. Scanning electron micrographs of (a) sodium octosilicate, (b) $C_{12}H_{25}N(CH_3)_3^+$-octosilicate intercalation compound, and (c) trimethylsilylated derivative of (b).

previous reports;[4,9] after the reaction, several absorption bands characteristic of $[C_{12}H_{25}N(CH_3)_3]^+$ were detected (2960(sh), $\nu_{as(CH_3)}$; 2920, $\nu_{as(CH_3)}$; 2852, $\nu_{s(CH_2)}$; 1472, $\delta_{s(CH_2)}$), indicating the presence of $[C_{12}H_{25}N(CH_3)_3]^+$ in the product. After the reaction, one of the sharp $\nu_{(OH)}$ bands due to silanol groups (3650 cm^{-1})[4,9] was present. It should be noted that the profile of the $\nu_{(Si-O)}$ band (1055 cm^{-1}) and the 1234-cm^{-1} band (which should be related to the silicate layer structure[4]) hardly changed, suggesting that the structure of the silicate layer is maintained during the reaction.

On the basis of the CHN data (C, 33.41; H, 7.35; N, 2.72 mass%), about 1.6 mol of $[C_{12}H_{25}N(CH_3)_3]^+$ was found to be present per $Si_8O_{17}^{2-}$ unit in the product. Furthermore, an ICP analysis revealed that most of the sodium ions were lost (ca. 0.1 mol per $Si_8O_{17}^{2-}$ unit). Hence, the remaining positive charge appears to have been compensated by protons.

Information concerning the structure of the silicate layer was obtained from the NMR and SEM results. As reported earlier,[2—4,9] the ^{29}Si MAS NMR results (Fig. 3) showed two signals due to the Q^3 ($\underline{Si}(OSi\equiv)_3(O, OH)$) (−100 ppm) and Q^4 ($\underline{Si}(OSi\equiv)_4$) (−111 ppm) environments of sodium octosilicate, and the profile hardly changed after the reaction. Furthermore, the SEM observation revealed that the plate-like morphology of sodium octosilicate[4] was retained after the reaction (Fig. 4-(a) and (b)). These results indicate that the structure of the silicate layer was maintained during the reaction with the $C_{12}H_{25}N(CH_3)_3Cl$ aqueous solution.

On the basis of these results, we conclude that, as shown by Bobéry et al. for other organic cations,[9] sodium octosilicate can accommodate $[C_nH_{2n+1}N(CH_3)_3]^+$ in the interlayer space by the following ion-exchange reaction:

$$\equiv SiO^-Na^+ \xrightarrow{C_nH_{2n+1}N(CH_3)_3Cl} \equiv SiO^-[C_nH_{2n+1}N(CH_3)_3]^+ (n = 12, 14, 16, 18).$$

Silanol groups may also be involved in the ion-exchange reaction, or formed during the reactions.

When the $[C_{12}H_{25}N(CH_3)_3]^+$-octosilicate intercalation compound was allowed to react with chlorotrimethylsilane, XRD showed that the basal spacing decreased from 2.35 to 1.49 nm, which was still larger than that of sodium octosilicate (1.11 nm) by 0.38 nm and than that of its protonated form (0.74 nm) by 0.75 nm (Fig. 1-(c)).

An IR analysis showed that, after trimethylsilylation, new bands appeared at 846 and 758 cm^{-1}, characteristic of the trimethylsilyl group[11] (Fig. 2-(c)), indicating that trimethylsilyl groups are introduced in the product. Since only a trace of nitrogen was detected in the trimethylsilylated product by a compositional analysis (C, 13.74; H, 3.58; N, 0.14 mass%), most of the $[C_{12}H_{25}N(CH_3)_3]^+$ ions were released. If all of the carbon content can be ascribed to the trimethylsilyl group, 1.2 mol of the $(CH_3)_3Si$ group would have been present per $Si_8O_{17}^{2-}$ unit.

The structural change via trimethylsilylation is discussed on the basis of the spectroscopic and morphological results. Silicon-29 MAS NMR showed a relative decrease in the intensity of the Q^3 peak compared with the Q^4 peak, and the appearance of new signals due to the M^1 environment $(R_3\underline{Si}(OS\equiv))$[11] at 15—20 ppm. In addition, the profile of the $\nu_{(Si-O)}$ region was similar to that of the $[C_{12}H_{25}N(CH_3)_3]^+$-octosilicate intercalation compound (Fig. 3-(b) and (c)). Furthermore, SEM showed that the morphology of octosilicate was still preserved after trimethylsilylation (Fig. 4-(c)). These IR and SEM results indicate that the silicate layer was retained during trimethylsilylation. We thus conclude that $\equiv SiOH$ (and $\equiv SiO^-$) groups in the Q^3 tetrahedra were modified by grafting the trimethylsilyl groups to yield both Q^4 and M^1 environments.

The reaction mechanism of trimethylsilylation in the present system appears to have been similar to those reported previously for the trimethylsilylation of $[C_{12}H_{25}N(CH_3)_3]^+$-magadiite and $[C_{12}H_{25}N(CH_3)_3]^+$-kenyaite.[11] In $[C_{12}H_{25}N(CH_3)_3]^+$-octosilicate, as shown by the IR analysis (Fig. 2-(b)), silanol groups were present. Thus, chlorotrimethylsilane reacted with the silanol groups to form siloxane bonds. The liberated proton attacked the $[C_{12}H_{25}N(CH_3)_3]^+$ $O^-Si\equiv$ sites to give additional silanol groups, which were further trimethylsilylated:

$$\equiv SiOH \xrightarrow{(CH_3)_3SiCl} \equiv SiOSi(CH_3)_3.$$

In conclusion, layered sodium octosilicate and its ion-exchanged form are capable for ion-exchange and grafting reactions. The present results reveal that, as well as magadiite and kenyaite, layered sodium octosilicate is an excellent host for intercalation chemistry.

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