Intercalation of Cu²⁺ with 3-(Aminopropyl) triethoxysilane into Montmorillonite

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Siloxane Cubic Octamer (S.C.O.) prepared from of 3-(aminopropyl)triethoxysilane (APTEOS) was intercalated into the interlayer of montmorillonite. Basal spacing of S.C.O.-intercalated montmorillonite changed from 1.26 nm to 2.10 nm depending on the quantities of S.C.O., which is very similar to that by direct intercalation of APTEOS. When Cu²⁺ was intercalated into the interlayer of montmorillonite with S.C.O., basal spacing gradually decreased to 1.85 nm with an increase in intercalated Cu²⁺ for a constant S.C.O. quantity. This was explained by the change of orientations of aminopropyl groups of S.C.O. inside the interlayer: namely, there were both orientation components "parallel" and "perpendicular" without Cu²⁺ confirmed from FTIR spectra. "Perpendicular" component changed to "parallel" component due to intercalation of Cu²⁺. The orientation change was most possibly induced by the coordination of Cu²⁺ to aminopropyl groups. From the results of ESR and diffuse reflectance spectra, it was shown that aminopropyl groups of APTEOS form coordination to Cu²⁺, resulting in the complxes [Cu(propylamine)$_n$(H$_2$O)$_{6-n}$]²⁺ (n=3~5) in the interlayer of montmorillonite.
Key words: intercalation, montmorillonite, APTEOS, Cu²⁺

1. INTRODUCTION

Intercalation of montmorillonite with various compounds have been of considerable interest from various points of view.[1-8] Composites of clay-silica have been known as a silica-pillared clay. Intercalation of 3-(aminopropyl)triethoxysilane (APTEOS) was done into the interlayer of saponite,[9] montmorillonite,[10] and ZrP.[11] The intercalation of a siloxane cubic octamer prepared from hydrolysis of APTEOS was also intercalated into interlayers of montmorillonite,[12] metal hydrogen phosphate,[13] and ZrP.[14] We have previously examined the intercalation of APTEOS into montmorillonite and found that octameric species is intercalated.[15]

Analysis of structures and reaction mechanisms are important for developing and applying intercalated compounds to functional materials. In addition, when various kinds of guest species are intercalated, not only host-guest interaction but also guest-guest interaction should be discussed.

In this study, we investigated the intercalation of Siloxane Cubic Octamer (S.C.O.) and Cu²⁺ ions. It was shown that Cu²⁺ ions form complexes, [Cu(propylamine)$_n$(H$_2$O)$_{6-n}$]²⁺ (n=3~5) in the gel derived from hydrolysis of APTEOS.[16-19] Many kinds of matrices including Cu ions have been studied for various viewpoints.[20-24] Therefore intercalated compounds with S.C.O. and Cu²⁺ and the intercalation mechanisms are quite interesting. We will discuss the influence of Cu²⁺ on basal spacing of S.C.O.-intercalated montmorillonite and the intercalated state of Cu²⁺ by ESR and diffuse reflectance spectra.

2. EXPERIMENTAL

Sample preparation

Na-montmorillonite (Kunipia F) obtained from Kunimine Ind. was used. The cation exchange capacity (C.E.C.) was 119 mequiv/100 g of clay. APTEOS (Tokyo Kasei) and ethanol (EtOH, Wako) were used without further purification. Water was deionized and distilled. CuSO$_4$ 5H$_2$O (Wako) was used as-received.

For synthesis of Siloxane Cubic Octamer (S.C.O.), APTEOS, EtOH and H$_2$O were mixed and stirred for 3 h at 80 °C with the volume ratio of APTEOS : EtOH : H$_2$O=1: 9 : 0.64 as previously reported.[12] This solution was added to 100 mL of 1% aqueous suspension of montmorillonite, which was previously stirred for 4 h at room temperature, left for 1 day at room temperature and then stirred for 1 h at 60 °C before mixing. After stirring for 1h, the intercalated products were collected by centrifugation, filtered with suction, washed 10 times with water, and dried at room temperature. For further intercalation of Cu²⁺, various concentrations of CuSO$_4$ aqueous solutions were added to the clay-S.C.O. mixtures and further stirred for 1 h at 60 °C. The mixtures were also centrifuged, filtered with suction, washed 10 times with water, and dried at room temperature. As a comparison, intercalated compounds were prepared by direct mixing of APTEOS and Cu²⁺ with suspension.

Measurement

²⁹Si NMR measurements were carried out on a JEOL-JNM-GX-270 MHz spectrometer operating at 53.5 MHz. Chemical shifts are referred to external polydimethylsilane. Powdered XRD was measured

with a Rigaku RINT 2200 diffractometer using Cu Kα radiation. FTIR spectra were recorded on a JASCO FTIR-615 spectrophotometer using a KBr pellet. ESR spectra measurements were performed at room temperature with a JEOL-JES-RE1X spectrometer. Absorption spectra and diffuse reflectance (DR) spectra were recorded with JASCO spectrophotometers UBEST-50 and UV-570 at room temperature, respectively. DR spectra were converted in the Kubelka-Munk function which is proportional to the absorption coefficient. The adsorbed amounts of Cu^{2+} were spectrometrically determined by a decrease in the absorbance of the supernatant solution.

3. RESULTS AND DISCUSSIONS

Effect of intercalated Cu^{2+} for Basal spacing

²⁹Si NMR Spectrum of the solution obtained after mixing APTEOS/EtOH/H₂O is shown in Fig. 1. The strongest peak at -67.9 ppm is assigned to the Q^3 structure of Si.[9, 10] However, there are no peaks at -60 ppm assigned to the Q^2 structure. These results indicate that Siloxane Cubic Octamer (S.C.O., shown in Fig. 2) was prepared. A several side peaks around the main peak at -67.9 ppm are possibly ascribed to imperfect octameric structures.
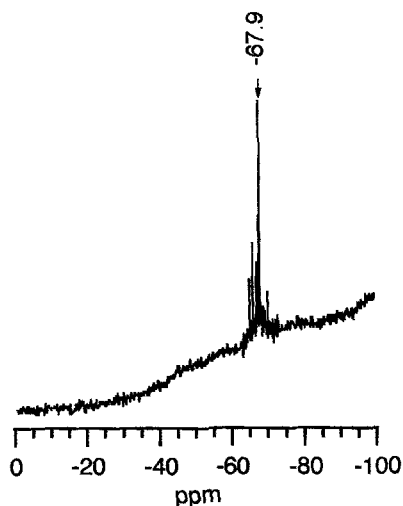

Fig. 2 Size of a siloxane cubic octamer.

Fig. 1 ²⁹Si NMR spectra of solution obtained after mixing APTEOS/EtOH/H₂O for 3 hours at 85 ℃.
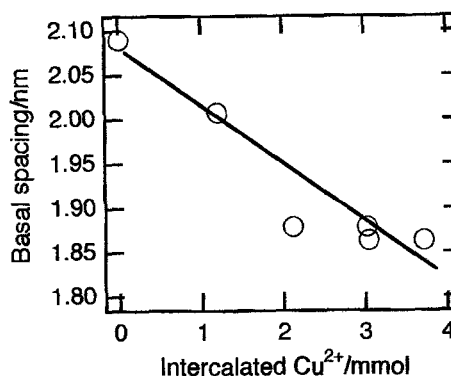
Fig. 3 Relationship between basal spacings and quantities of intercalated Cu^{2+}.

Basal spacing of S.C.O.-added compounds changed from 1.26 nm to 2.10 nm with an increase in S.C.O. in the same way with the intercalation of APTEOS,[15] indicating the intercalation of S.C.O. and that the intercalated S.C.O. changes the orientations of aminopropyl groups in S.C.O., depending on its quantity.[12] Namely, orientation of aminopropyl chains changed between "parallel" and "perpendicular" to montmorillonite layer, depending on the packing density of S.C.O. in the interlayer.[15]

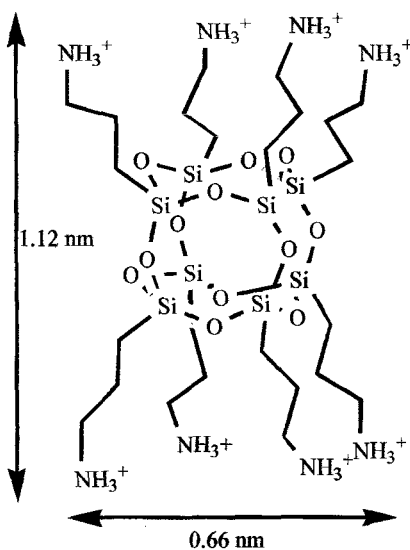When S.C.O. from 4.3 mmol of APTEOS was intercalated into montmorillonite without Cu^{2+}, the basal

spacing was 2.09 nm. However, Cu^{2+} intercalated into interlayer of S.C.O.-montmorillonite, basal spacing gradually decreased to 1.85 nm with an increase in intercalated-Cu^{2+}, as shown in Fig. 3. A quantity of intercalated Cu^{2+} is calculated from supernatant absorbance and absorption coefficient of Cu^2. The reason of the basal spacing decrease is also attributed to the orientation change of alkyl chain due to bonding between Cu^{2+} and amino groups which will be shown later.

The orientation change can be monitored by using FTIR spectra. FTIR spectra of compounds are shown in Fig. 4. In Fig. 4 (a), there are two peaks around 1500 and 1560 cm⁻¹. However there is no peak around 1560 cm⁻¹ in Figs. 4 (b) to (d); the relative peak intensity at 1510 cm⁻¹ increases with an increase in Cu^{2+}. The peaks around 1500 and 1560 cm⁻¹ are sensitive to orientations of alkyl chains.[12, 25] A peak at 1500 cm⁻¹ corresponds to "parallel" orientation, and a peak at 1560

cm^{-1} corresponds to "perpendicular" orientation for the silicate layers of clay. These results indicate that there are both orientation components "parallel" and "perpendicular" for S.C.O.-clay compounds without Cu^{2+}. The "perpendicular" component changed to the "parallel" component after Cu^{2+} intercalation because of the coordination of Cu^{2+} as shown in Scheme 1.
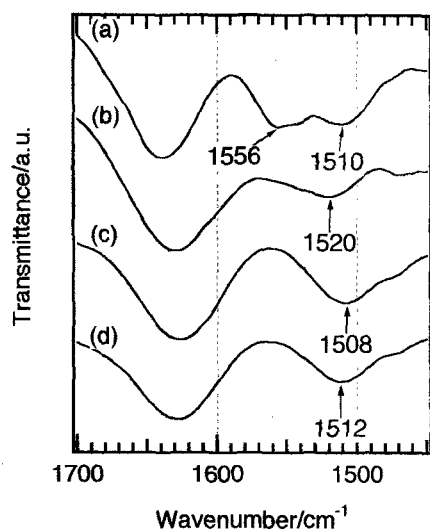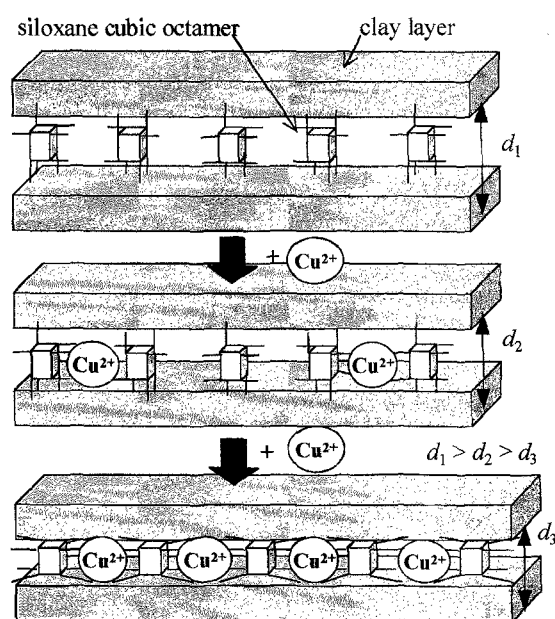

Fig. 4 FTIR spectra of intercalation compounds;
(a) without Cu^{2+}, (b) Cu^{2+} 1.2 mmol/(g clay),
(c). Cu^{2+} 3.0 mmol/(g clay) and
(d). Cu^{2+} 10.8 mmol/(g clay)

Scheme 1 Model of intercalation with siloxane cubic octamer and Cu^{2+} into interlayer of clay.

Reaction of Cu^{2+} in the S.C.O.-montmorillonite interlayer

Compared to intercalation into montmorillonite without S.C.O., Cu^{2+} is more easily intercalated into S.C.O.-montmorillonite interlayer due to the strong interaction between Cu^{2+} and amino groups.   ESR spectra of Cu^{2+}-intercalated compounds with and without APTEOS are shown in Fig. 5.   The signal in Fig. 5 (a) suggests the structure of H_2O-coordinated Cu^{2+} for direct intercalation of Cu^{2+}. On the contrary, a different spectrum was observed for montmorillonite intercalated with Cu^{2+} and APTEOS.   The spectrum in Fig. 5 (b) is assigned to NH_2-coordinated Cu^{2+} (most possibly 5 amino coordination) and very similar to signal of Cu^{2+} doped in gels derived from APTEOS.[26]
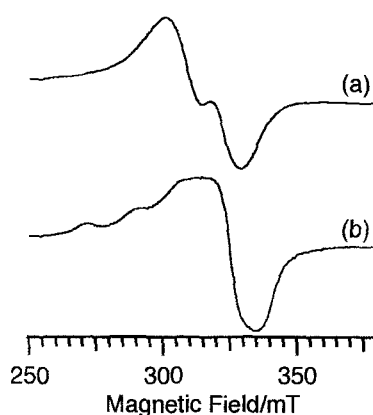

Fig. 5 ESR spectra of compounds intercalated
with Cu^{2+} and APTEOS.
(a) without APTEOS and (b) APTEOS 6.9 mmol.

Diffuse reflectance (DR) spectra of intercalated montmorillonite with Cu^{2+} and APTEOS clearly show the coordination state of Cu^{2+}.   DR spectra of compounds intercalated with Cu^{2+} and various amount of APTEOS are shown in Fig. 6.   The peak appeared at 744 nm in the spectrum of montmorillonite without APTEOS.   This peak is attributed to the absorption band of $Cu[(H_2O)_6]^{2+}$.[27]   The peak shifted to 671 nm in the spectra of compounds intercalated with Cu^{2+} and APTEOS.   Absorption bands at 600-800 nm are caused by Cu-ammonia complexes $[Cu(NH_3)_n(H_2O)_{6-n}]^{2+}$.[27]   A peak at 670 nm is assigned to the coordination with n=3 ~5 NH_3.   In addition, the gel derived from APTEOS form complexes with Cu^{2+}.[16-19]   From these results, it is concluded that aminopropyl groups of APTEOS and Cu^{2+} form complexes $[Cu(propylamine)_n(H_2O)_{6-n}]^{2+}$ (n=3~5) in the interlayer of montmorillonite.

A peak at around 350 nm gradually increased with an increase in APTEOS as shown in Fig. 6.   In order to study the origin of the peak, spectral changes were measured for the compound intercalated with APTEOS and Cu^{2+} as a function of aging time.   Peaks gradually grow at 352 and 414 nm with the ageing time as shown in Fig. 7.   It was reported that peaks appeared around at 300 and 350 nm are assigned to Cu^+ and a peak at 400 nm is assigned to Cu^+-Cu^+ dimmers.[19, 28, 29]   These results suggest the formation of Cu^+ reduced from Cu^{2+} in the interlayer.
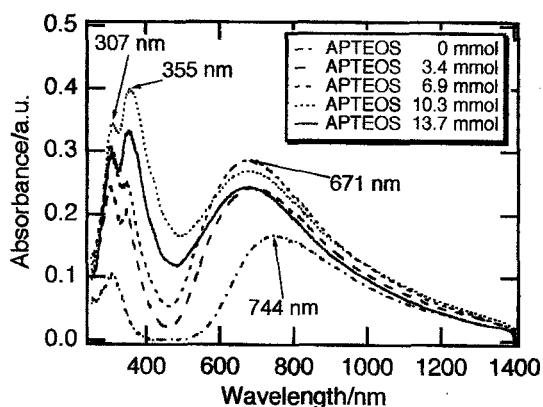
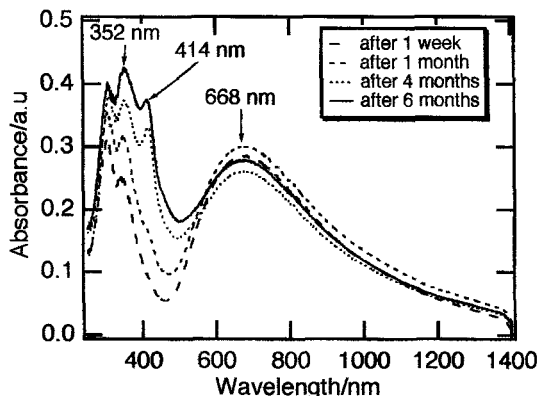Fig. 6 Diffuse reflectance spectra of compounds intercalated with Cu^{2+} and various amount of APTEOS.

Fig. 7 Diffuse reflectance spectra of compounds intercalated with 6.9 mmol/(g clay) of APTEOS and Cu^{2+} as a function of aging time.

4.CONCLUSIONS

Siloxane Cubic Octamer (S.C.O.) was intercalated into interlayer of montmorillonite. The basal spacing of intercalated montmorillonite depends on the size of S.C.O. molecules. And S.C.O. size related to the orientation of aminopropyl chains; "parallel" and "perpendicular" to clay layers. For strong interaction between Cu^{2+} and amino group of S.C.O., Cu^{2+} was easily intercalated into interlayer of montmorillonite. In the interlayer, aminopropyl groups of APTEOS coordinated to Cu^{2+} and make a coordination, $[Cu(propylamine)_n(H_2O)_{6-n}]^{2+}$ ($n=3\sim5$). Coordination of aminopropyl group to Cu^{2+} was taken priority over combination with clay layers. Basal spacing of Cu^{2+} and S.C.O. intercalated-montmorillonite decreased with increase in Cu^{2+} quantity. It was cleared that interaction between guest species have an influence on the structure of host species.

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