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Chemical Modification of Hectorite by Interlayer-Polymerization of (3-Aminopropyl)trimethoxysilane

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Interlayer-polymerization of (3-aminopropyl)trimethoxysilane (APMS) was carried out in the interlayer of lithium hectorite(LHT), and hectorites modified by "tuning guest" such as alkylammonium hectorite(CnNHT) and pyridinium hectorite (PyHT). XRD measurements revealed that the polymer-LHT complex showed no d_{001} diffraction peaks, while the polymer-CnNHT and -PyHT complexes had definite basal spacings depending on the guest or the amount of APMS. The polymer-clay complexes were characterized by means of ^{29}Si CP/MAS NMR and FT-IR spectra.

Introduction of organic groups to an interlayer of layered compounds has been studied extensively.1) Interlayer-polymerization is one of the methods for the incorporation of organic groups in an interlayer structure. There have been some studies on polymer-clay complexes containing poly(methyl methacrylate),2) polystyrene,3) and 6-nylon.4) However, these researches are restricted to the polymerization of monomers which have no other functional groups that can be utilized for further reactions such as ligating metal complexes. The chemical modification of interlayer space with polymers which have reactive groups is attractive in the stand point of developing new catalysts5) and new composite materials.6) Introduction of organic ligands or polymer ligands in the interlayer of layer compounds can be applied to the intercalation of various neutral metal complexes and metal complex anions as well as metal clusters such as metal carbonyls which are useful precursors for versatile catalysts.7) Furthermore, these organic guests which have stereo regularity in the interlayer are expected to enhance the selectivity in shape selective reactions. Silane coupling agents are one of popular reagents for the introduction of organo-functional groups to inorganic supports. Exploring studies about the polymerization of silane coupling agents in clay interlayers have hitherto been focused on related to only physical properties of their complexes,8-10) and there are few descriptions about layered regularity. In this paper, the authors report on the preparation and characterization of the clay-polymer complexes using (3-aminopropyl)trimethoxysilane (APMS) in lithium hectorite(LHT), alkylammonium hectorite(CnNHT) and pyridinium hectorite(PyHT) with focusing on layered regularity. CnNHT and PyHT were used as starting materials to control the interlayer-polymerization of APMS, resulting in the production of an interlayer-modified hectorite with consistent regularity between layers.

The poly(3-aminopropyl)siloxane (PAPS,polymerized product from APMS) incorporated hectorite was prepared as follows. CnNHT(n=8,octyltrimethylammonium-hectorite; n=18,octadecyltrimethylammonium-hectorite) or PyHT were synthesized by cation exchange of LHT (cation exchange capacity(CEC) = 80 mequiv.(100 g)$^{-1}$, Onoda Chemicals, Inc., Japan)$^{11)}$ with the corresponding ammonium halide salts in an aqueous solution.$^{12)}$ LHT, CnNHT, or PyHT was heated at 150 °C for 2 h *in vacuo* before use. An equivalent, or excess amounts of APMS solution of toluene (20 ml) was added to the hectorite and this mixture was refluxed with stirring overnight under N_2 atmosphere. The obtained powder was filtered, and fully washed with toluene to remove unreacted and physisorbed APMS, then dried *in vacuo* for 12 h at room temperature. Samples of LHT, CnNHT, or PyHT incorporated with PAPS designated as PAPS(*x*)-LHT, PAPS(*x*)-CnNHT, or PAPS(*x*)-PyHT, respectively (*x* means equiv.-CEC mol of added APMS). Layer regularity was estimated by XRD on a Mac Science MXP^3 system using Ni-filtered, CuKα radiation. The amounts of organic components in the samples were determined by CHN analyses. Characterization of samples was performed by ^{29}Si CP/MAS NMR on a JEOL EX-270 spectrometer with ESH-27MU CP/MAS unit,$^{13)}$ and FT-IR spectra on a JASCO A-202 spectrometer.

No remarkable XRD peaks were observed for PAPS(1)-LHT and PAPS(5)-LHT. These results revealed that the PAPS-LHTs were amorphous. Figure 1 shows that each CnNHT possesses a basal spacing which corresponds to its alkyl chain length. The basal spacing changed little after the treatment with APMS. However, it is assumed that PAPS is introduced to the interlayer in PAPS-CnNHT because of the observations that a Pd complex was anchored to the amino group and the basal spacing was increased after treatment of PAPS-CnNHT with the Pd complex.$^{14)}$ Figure 2 shows XRD patterns of PAPS(*x*)-PyHTs. Each of the diffraction peaks of Fig.2-c), d), and e) can be deconvoluted to two peaks which correspond to the peaks in b) and f),$^{15)}$ and the ratio of the two peaks depends on the added amounts of APMS, *x*. The basal spacings of the peaks in Fig.2-b) and f) are 14.8 and 18.0 Å, respectively. There are two stable phases of PAPS-PyHT depending on the amount of the added APMS.

Table 1 shows the results of elemental analyses of PAPS(*x*)-PyHT. The amount of modifier increases in proportion to the amount of the APMS added. This result is consistent with the changes of XRD patterns shown in Fig.2. The ^{29}Si CP/MAS NMR spectra of PAPS(5)-LHT and PAPS(5)-PyHT are shown in Fig.3. No peak is observed at −45 ppm, corresponding to the ^{29}Si chemical shift of a neat APMS. Caravajal et al.$^{16)}$ reported the ^{29}Si spectra of the silica treated with APMS in various conditions, and they assigned that peaks at −48, −58, and −66 ppm to the mono-, bi-, and tridentate siloxane structures, respectively. According to their assignments, there remains no silanol component in PAPS(5)-LHT and thus it is concluded that APMS was polymerized completely in the layer. For PAPS(5)-PyHT, a shoulder peak was

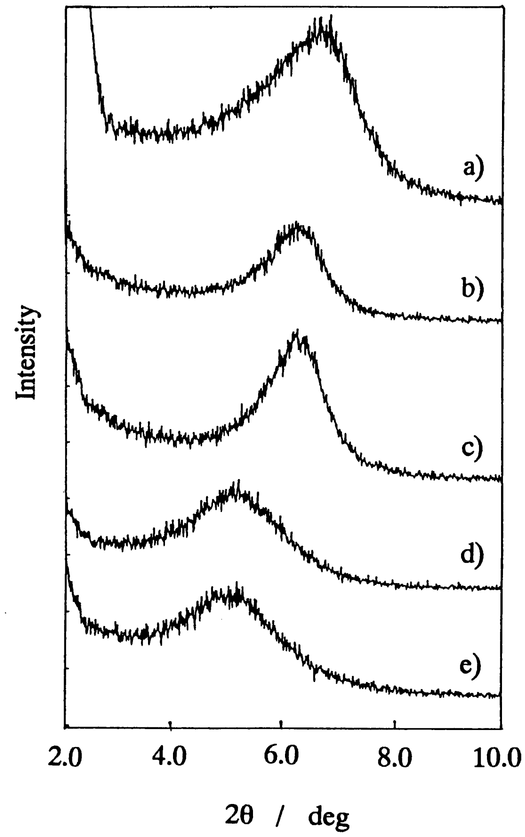

Fig. 1. X-Ray powder diffraction patterns of a) LHT, b) C_8NHT, c) PAPS(5)-C_8NHT, d) C_{18}NHT, and e) PAPS(5)-C_{18}NHT.

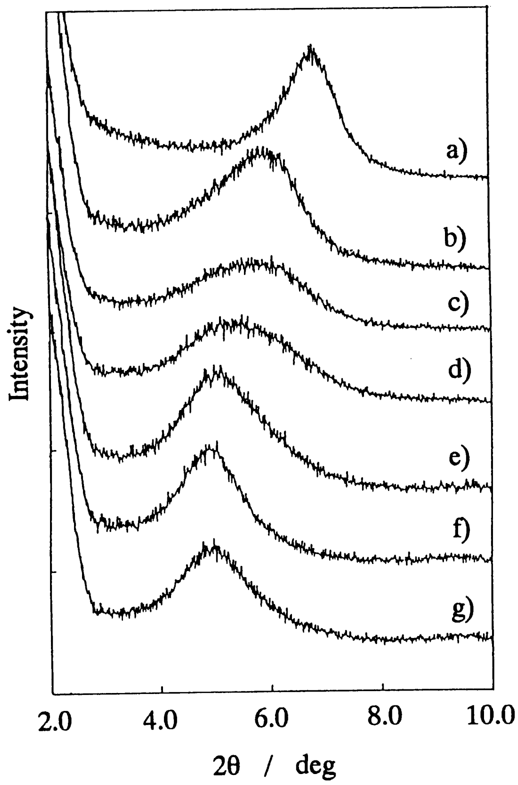

Fig. 2. X-Ray powder diffraction patterns of a) PyHT, b) PAPS(1)-PyHT, c) PAPS(2)-PyHT, d) PAPS(3)-PyHT,e) PAPS(4)-PyHT, f) PAPS(5)-PyHT, and g) PAPS(10)-PyHT.

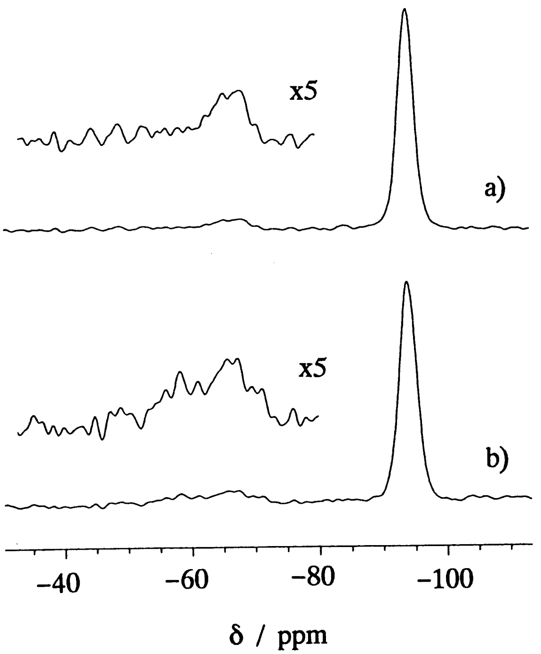

Fig. 3. ^{29}Si CP/MAS spectra of a) PAPS-(5)-LHT and b) PAPS(5)-PyHT.

Table 1. Composition of the PAPS(x)-PyHT.

Sample	C	N
	mmol(100 g)$^{-1}$	mmol(100 g)$^{-1}$
PAPS(1)-PyHT	303	85
PAPS(2)-PyHT	415	125
PAPS(3)-PyHT	614	178
PAPS(5)-PyHT	745	231

observed at -58 ppm which indicates that there partially exists bidentate structure in PAPS(5)-PyHT. IR measurements confirmed that amino group was incorporated to all of the hectorites modified by PAPS, and also that alkylammonium ion remained in the PAPS-CnNHT.[17)] On the other hand, surprisingly, there remains no peaks at 754 cm^{-1} for pyridinium ion in PAPS(x)-PyHT ($x \geq 1$). It can be speculated that the pyridinium ion was deintercalated during the polymerization of APMS.

In conclusion, intercalated alkylammonium and pyridinium ions increased the basal spacings of hectorites from the original lithium hectorite and kept the expanded basal spacings during the course of polymerization of APMS which readily intercalated and polymerized in the interlayer of hectorites. Consequently, obtained PAPS-CnNHT and PAPS-PyHT have definite basal spacings. Therefore the PAPS in CnNHT and PyHT has more regular structure than the PAPS in LHT without "tuning guest". It can be speculated that these tuning guests play an important role in tuning the interlayer-polymerization of APMS, such as a pillaring reagent to keep the basal spacing of hectorites during polymerization.

We established a novel method to obtain layered compounds which possess a definite layered structure with amino-functional polysiloxane by means of tuning guests. These novel layered compounds have a possibility in the application of two-dimensional constrained systems, especially, for catalysis.

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11) Chemical composition of LHT is as follows : SiO_2;58.48%, MgO;26.51%, Li_2O;1.16%, Na_2O;2.59%.
12) Content of octyltrimethylammmonium ion is 78 mmol(100 g)$^{-1}$, octadecyltrimethylammonium ion is 70 mmol(100 g)$^{-1}$, and pyridinium ion is 66 mmol(100 g)$^{-1}$, which was determined by elemental analysis.
13) The spectroscopic parameters were as follows: resonance frequency, 53.54 MHz; pulse width, 4.5 μs; spinning frequency, 5.0 kHz; external reference, TMS.
14) Unpublished data.
15) Deconvolution of the peaks was performed by the program in the MXP^3 system. All of the results of calculation was converged that the standard error is under 6.0%.
16) G. S. Caravajal, D. E. Leyden, G. R. Quinting, and G. E. Maciel, *Anal. Chem.*, **60**, 1776 (1988).
17) Amino group, δNH_2 1557 cm^{-1}; alkylammonium group, δCH_2, δCH_3 1490 cm^{-1}, 1476 cm^{-1}.

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