Preparation of hectorite-like swelling silicate with controlled layer charge density

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Smectite like layered silicates with cation exchange capacity ranges from 60 to 90 mequiv/100g clay were synthesized from LiF, Mg(OH)₂ and colloidal silica. The controlled cation exchange capacity achieved by changing the composition of the starting mixture (namely the added LiF amount) successfully influenced the nanostructures of intercalation compounds prepared by the ion exchange with diotadecyldimethylammonium ion.

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1. Introduction

Host-guest complexation has extensively been investigated to control the physicochemical characteristics of both host and guest and to construct hybrids with unique functions to which both host and guest alone cannot access. Layered solids offer two dimensional nanospaces to accommodate guest species (Intercalation). Inorganic–organic hybrid materials with varied chemical composition and nanostructures have been synthesized by the intercalation reaction. Among possible layered materials capable of accommodating guest species, smectite group of layered clay minerals have most widely been investigated due to their stability, large surface area, natural abundance, and rich host-guest chemistry. To avoid problems such as qualitative and quantitative differences of impurities and inconsistent quality stemming from the natural smectites, the syntheses of layered silicates which possess swelling properties similar to natural smectites have been conducted. One of the known example is “Laponite”, which is a synthetic hectorite-like silicate. Na-fluorotetrasilicic mica, which is prepared by sintering and flux melt reaction, is another manufactured example of synthetic expandable silicate. The thermal reaction of talc and sodium fluorosilicate or lithium fluoride has been reported to obtain expandable 2:1 type silicate. In addition to those commercialized products, there are several reports on the preparation of smectite-like silicates and intercalation compounds.

One of the advantages of smectites as host material for the nanocomposite and hybrid materials is the variation of cation exchange capacity (CEC). In addition to the vast variety of available smectites with different CECs, it is possible to reduce the CEC by the thermal treatment of Li exchanged forms (Hofmann–Klemen Effect). It has been recognized that the CEC is a key factor to determine many important properties of smectites and their intercalation compounds. The variation of CEC has been used to control the distances of adjacent interlayer cations, resulting in the controlled molecular sieving functions of pillar clay and photoprocesses of adsorbed cationic dyes. While smectites with varied CEC are available, other characteristics such as the composition, and particle size also vary to potentially affect the properties of smectites and their intercalation compounds. Therefore, there is a need to prepare smectites with a series of CEC without modifying other characteristics such as position of isomorphous substitution and particle size in order to discuss the effects of CEC on the physicochemical properties of smectites and their intercalation compounds. Here, we report the successful preparation of smectites (triocahedral group, hectorite-like) with the CEC ranges from 60 to 90 meq/100 g clay. It is worth noting as a merit of preparing hectorite-like layered silicates because this can be obtained under ambient pressure and a relatively lower temperature (~100°C) than that for other synthetic smectites as saponite.

2. Experimental procedure

2.1 Materials

LiF and Mg(OH)₂ were obtained from Kanto Kagaku Ind., Co. Silica sol (SiO₂:20.3 mass%, SiO₂/Na₂O = 95) was kindly donated from Nissan Chemical Ind., Co. Diododecyldimethylammonium (abbreviated as 2C₁₈₂CN⁺) chloride and 1,1'-dimethyl-4,4'-bipyridinium (abbreviated as MV₂⁺) chloride were purchased from Tokyo Kasei Ind., Co. All these chemicals were used without further purification.

2.2 Sample preparation

Sample preparation was conducted based on the reports by Carrado et al. and Mg(OH)₂ was added to an aqueous solution of LiF and the mixture was vigorously mixed with magnetic stirrer for 30 min at room temperature. To which suspension was added silica sol, and the suspension was mixed with homogenizer for another 30 min at room temperature. The slurry brought to reflux with stirring for 2 d. The product was separated by ultracentrifugation (25,000 rpm for 20 min) and dried at 60°C. In order to vary CEC, the molar ratios of LiF:Mg(OH)₂:SiO₂ in the starting mixture were changed as summarized in Table I.

The ion exchange reactions of the silicates thus obtained were examined using diotadecyldimethylammonium (abbreviated as 2C₁₈₂CN⁺) chloride and 1,1'-dimethyl-4,4'-bipyridinium chloride and 1,1'-dimethyl-4,4'-bipyridinium...
(abbreviated as MV²⁺) chloride. The aqueous solution of the organic salt was mixed with an aqueous suspension of the silicates and the mixture was mixed with stirring at room temperature for 1 d. After the ion exchange, the product was collected by centrifugation and dried.

2.3 Characterization
X-ray powder diffraction (XRD) patterns were obtained by a Rigaku RAD IB diffractometer (monochromatic Cu Kα radiation) operated at 20 mA, 40 kV. UV-Visible (UV-vis) absorption spectra were recorded on a Shimadzu UV–3100PC spectrophotometer. Thermogravimetric-differential thermal analysis (TG–DTA) curves were recorded on a Rigaku TG8120 instrument at a heating rate of 10° C/min and using α-alumina as the standard material. Fourier transform infrared spectra (FT-IR) were recorded on a Shimadzu FT-IR8200 by the KBr disk method.

3. Results and discussion
The XRD patterns of the products are shown in Fig. 1. In the XRD patterns, reflections ascribable to smectite were observed. The (00l) and (hk0) reflections were observed at 8–9°(2θ) for (001) and 20 and 40°(2θ) for (hk0) reflections for all the samples. The intensities of the reflections are low and the reflections are broad, indicating that the products are composed of finite par-

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Adsorbed amt. MV²⁺/meq (100 g clay)⁻¹</th>
<th>Basal spacing (MV²⁺ form)/nm</th>
<th>Adsorbed amt. 2C₁₈2CN⁺/meq (100 g clay)⁻¹</th>
<th>Basal spacing (2C₁₈2CN⁺ form)/nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (2.8:4.6:8)</td>
<td>83</td>
<td>1.31</td>
<td>94</td>
<td>2.88</td>
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<tr>
<td>B (1.4:5.3:8)</td>
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<td>1.31</td>
<td>62</td>
<td>2.26</td>
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<tr>
<td>C (0.7:5.65:8)</td>
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<td>1.31</td>
<td>57</td>
<td>2.03</td>
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<tr>
<td>D (0.35:5.83:8)</td>
<td>44</td>
<td>1.30</td>
<td>47</td>
<td>1.79</td>
</tr>
<tr>
<td>E (0.14:5.93:8)</td>
<td>42</td>
<td>1.30</td>
<td>39</td>
<td>nd*</td>
</tr>
</tbody>
</table>

*nd*: not determined.

Fig. 1. XRD patterns of the products prepared from the varied chemical composition (Table 1).

Fig. 2. IR spectra of the products, (a) sample A, (b) sample B, (c) sample C, (d) sample D and (e) sample E.

Fig. 3. XRD patterns of samples after the ion exchange with MV²⁺. Traces (a) sample A, (b) sample B, (c) sample C, (d) sample D and (e) sample E.
particles with poor crystallinity. This is consistent with the reported characteristic features of the synthetic smectites-like minerals prepared under relatively mild conditions.13)–18) The FT-IR absorption spectra are shown in Fig. 2, where the absorption bands such as OH stretching at 3666 cm⁻¹, Si–O stretching at around 1000 cm⁻¹, and Mg–O at 650–670 cm⁻¹, which are characteristics to smectites,27) are observed. All the samples expand their basal spacings to ca. 1.8 nm after the reaction with ethylene glycol. All these data indicate the formation of hectorite-like swelling silicate.

The cation exchange reactions of the present hectorite-like silicate with two organic cations, dioctadecyldimethylammonium (abbreviated as 2C182CN⁺) and 1,1'-dimethyl-4,4'-bipyridinium (abbreviated as MV2⁺), were examined to see the variation of CEC. Figure 3 shows the variation of the XRD patterns of the products obtained by the ion exchange reactions with MV2⁺. The basal spacing of all the MV2⁺ ion exchanged products were 1.31 nm, which was consistent with the value reported for the MV2⁺-smectite intercalation compounds.28),29) Judging from the interlayer expansion (Table 1) and the size of MV2⁺ (0.63 × 1.34 × 0.3 nm),30) the adsorbed MV2⁺ are thought to be arranged as a monomolecular layer with their molecular planes of pyridinium rings (0.3 nm) parallel to the silicate layers.

The adsorbed amounts of MV2⁺ were determined by the difference in the concentration of MV2⁺ in aqueous phase by means of UV absorption spectra (absorption maximum at around 250 nm) and the results are summarized in Table 1. In our previous reports, the adsorbed amounts of MV2⁺ were shown to be close to the CECs of smectites.22),29),31) The adsorbed MV2⁺ amounts varied from 42 to 83 mequivalent/100 g clay, suggesting that the variation of layer charge density was achieved by the composition of the starting mixture for the synthesis.

The ion exchange with dioctadecyldimethylammonium (abbreviated as 2C182CN⁺) was also examined. The ion exchange with a series of n-alkylammonium ions (of the type RNH₃⁺) has been utilized to estimate the layer charge density and the internal surface area of smectites and other layered materials.6),7) Jumps were observed in the relationships between the basal spacing and the size of intercalated n-alkylammonium ions, which indicate monolayer to bilayer and bilayer to pseudotrimolecular layer transitions of intercalated n-alkylammonium ion’s arrangements. The intercalation of quaternary ammonium (of the type R₄N⁺) has also been used to determine the internal surface area of smectites.32) Here, we used 2C182CN⁺ as the probe to estimate the layer charge density. The 2C182CN⁺-smectites have been investigated so far for permeation and electrochemical studies as well as to immobilize catalytically and optically active species in the nanospaces.33)–42) Due to the large size of 2C182CN⁺, the intercalated 2C182CN⁺ ions tend to take paraffin type arrangements when intercalated in the interlayer space of smectites. (Fig. 4(d)) Then, the basal spacing, which corresponds to the inclination of the alkyl chains, should increase with the CEC of clays, reflecting the inclination.

The variation of the XRD patterns after the ion exchange with 2C182CN⁺ is shown in Fig. 5 and the basal spacings determined from the XRD data are summarized in Table 1. The adsorbed amounts of 2C182CN⁺ are derived from the weight loss in the TG curve (Fig. 6) of the products. In the TG–DTA curves, weight losses due to the decomposition of the adsorbed 2C182CN⁺ were seen at the temperature range between 200 and 500°C, where exothermic peaks were observed in the corresponding DTA curve. A typical example of the TG–DTA curves of 2C182CN⁺ exchanged samples is shown in Fig. 6. The adsorbed 2C182CN⁺ amounts are close to those of the MV2⁺ listed in Table 1, confirming the successful control of CEC. Figure 7 shows the rela-
reflect the bilayer arrangements of the intercalated 2C\textsubscript{182}CN\textsuperscript{+} ions and the structural analogues,\textsuperscript{33}–\textsuperscript{42} the basal spacing of 1.8 nm, which are worth noting as a merit of the present synthesis to form silicate (sample B).

The layer charge density has been recognized as a key parameter to determine the useful properties (such as adsorptive and swelling) of smectites and their intercalates. The application of the silicates synthesized in the present study is worth conducting especially for the optical studies\textsuperscript{23}–\textsuperscript{25},\textsuperscript{36},\textsuperscript{37} due to their whiteness and purity.

4. Conclusions

Smectite like layered silicates were synthesized by the reaction of LiF, Mg(OH)\textsubscript{2} and colloidal silica in aqueous suspension at 100°C for 2 d. The silicate was ion exchangeable by conventional method. The cation exchange capacity was successfully controlled by changing the composition of the starting mixture from 60 to 90 mequivalent/100 g clay. The samples are possible candidates of host materials to immobilize cationic species in systematically controlled spatial separation.

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References


Fig. 6. A typical example of TG–DTA curve of the samples before (dotted lines) and after (solid line) the ion exchange with 2C\textsubscript{182}CN\textsuperscript{+} (sample B).

Fig. 7. Relationship between the basal spacings and the adsorbed 2C\textsubscript{182}CN\textsuperscript{+} amounts of the 2C\textsubscript{182}CN\textsuperscript{+} exchanged samples. 1) M. J. Carrizosa, et al. Clays Clay Miner., 52, 643 (2004); 2) L. P. Meier et al. J. Colloid Interface Sci., 238, 24 (2001); 3) M. Ogawa et al. Langmuir, 9, 1529 (1993); 4) M. A. Osman et al. J. Phys. Chem. B, 108, 2580 (2004); 5) D. Voulgaris and D. Petridis, Polymer, 43, 2213 (2002).

Fig. 7. Relationship between the basal spacings and the adsorbed 2C\textsubscript{182}CN\textsuperscript{+} amounts of the 2C\textsubscript{182}CN\textsuperscript{+} exchanged samples. 1) M. J. Carrizosa, et al. Clays Clay Miner., 52, 643 (2004); 2) L. P. Meier et al. J. Colloid Interface Sci., 238, 24 (2001); 3) M. Ogawa et al. Langmuir, 9, 1529 (1993); 4) M. A. Osman et al. J. Phys. Chem. B, 108, 2580 (2004); 5) D. Voulgaris and D. Petridis, Polymer, 43, 2213 (2002).