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Preparation and Properties of Mg/Al Layered Double Hydroxide–Oleate and –Stearate Intercalation Compounds

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Mg/Al layered double hydroxide–oleate and –stearate intercalation compounds were successfully synthesized by the reconstruction method under hydrothermal conditions from calcined hydrotalcite. The intercalation compounds were characterized by the high structural regularity as evidenced by the sharp and intense X-ray diffraction peaks. The oleate intercalated layered double hydroxide exhibits unique physicochemical properties such as a reversible thermoresponsive change in the basal spacing and swelling in organic solvents such as *n*-alkanes.

Intercalation of organic guest species into layered inorganic solids is a way of producing ordered inorganic–organic assemblies with unique microstructures controlled by host–guest and guest–guest interactions.[1] Layered double hydroxides (LDHs) are a class of layered materials consisting of a positively charged brucite like layer, where some M^{2+} cations are substituted with M^{3+} cations to give a positive charge, and charge compensating interlayer exchangeable anions.[2] Besides the mineralogical and structural interests, studies on the possible applications of LDHs as materials such as catalysts,[3] adsorbents,[4] ceramic precursors,[5] reaction media for controlled photochemical[6] and electrochemical reactions,[7] bioactive nanocomposites,[8] and pharmaceutical uses[9] have been conducted. Intercalation of various guest species into LDHs has been investigated in order to functionalize LDHs further or to modify the properties of LDHs. So far, various organic guest species ranging from molecular anions, organometallic species and inorganic complex anions to polymers and biomolecules have been intercalated to LDHs and the structures and properties of the resulting hybrids have been investigated.[3,4,6–11]

For cation exchangeable layered materials, cationic surfactants have been intercalated and the properties of the resulting intercalation compounds have been investigated extensively.[12,13] Quaternary ammonium surfactant intercalated smectites are notable examples that show the merits of surface modification by such complexations. Hydrophilic smectites become strongly organophilic by replacing the interlayer cations (sodium or calcium) with cationic surfactants. Organophilic clays thus obtained have been utilized as rheology controlling reagents, adsorbents for environmental purification, catalyst supports, precursors for pillared clays, fillers for organic polymers to improve the properties, and so on.[13] As for LDHs, the intercalation of anionic surfactants, such as dodecyl sulfate and aliphatic carboxylates, has been reported previously.[14–19] The applications of surfactant modified LDHs include filler to organic polymers[20] and adsorbents to nonionic organic contaminants in water.[21] However, if compared with smectite systems, studies on the intercalation of surfactants into LDHs are still limited. Further systematic studies on the structures and properties of LDH–surfactant intercalation compounds using LDHs with different composition and particle size, and surfactants with different chemical structures are worth conducting.

Here, we report the synthesis of oleate and stearate intercalated Mg/Al LDHs by the reconstruction method and the properties of the intercalation compounds. The intercalation of unsaturated alkylammonium ions into smectite and the effects of unsaturation on the nanostructures have been reported so far.[22] Unsaturation in the alkyl chains significantly affects the packing of the intercalated surfactants so that the nanostructures and their thermal transformation vary depending on the presence and the position of the unsaturation in the alkyl chain. The intercalation of surfactants with unsaturation in the alkyl chains have scarcely been investigated. Recently, the synthesis of oleate intercalated LDHs by an ion exchange reaction was reported as the first example of unsaturated aliphatic carboxylate intercalated LDH.[16] However, the properties of the resulting intercalation compounds were not documented. In the present study, the reconstruction method was employed to synthesize LDH–oleate and –stearate intercalation compounds according to our preliminary communication.[19] The swelling properties of the LDH–oleate intercalation compound were investigated to show its organophilic nature. Reversible thermal nanostructural changes of the LDH–oleate and –stearate intercalation compounds were investigated by means of differential scanning calorimetry combined with X-ray diffractometry.

Experimental

Materials. Urea (Extra pure grade, >99.0% Wako Pure Chemical Industries, Ltd.), magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$, Kanto Chemical Co., Inc.), and aluminum chloride hexahydrate ($AlCl_3 \cdot 6H_2O$, Kanto Chemical Co., Inc.) were used without further purification. Sodium oleate and sodium stearate were purchased from Tokyo Kasei Ind. and used as received.

Sample Preparation. The following is a typical synthetic procedure. 0.20 g of hydrotalcite, which was synthesized by the hydrothermal method reported previously[23] (the chemical compo-

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sition is $Mg_{0.65}Al_{0.35}(OH)_2 0.18CO_3 \cdot nH_2O$), was calcined in air at 600 °C for 24 h. The calcined hydrotalcite was allowed to react with 70 mL of an aqueous solution of sodium oleate (the concentration was 3.5×10^{-4} mol L^{-1}) or sodium stearate in a Teflon-lined autoclave at 150 °C for 24 h. After cooling to room temperature, product was collected by centrifugation and washed with deionized water three times and dried at 60 °C. As a control, the reconstruction of calcined hydrotalcite in an aqueous solution of sodium oleate was conducted at room temperature and 60 °C.

Characterization. X-ray powder diffraction patterns were obtained on a Rigaku Rad IB diffractometer using monochromatic Cu Kα radiation operated at 40 kV and 20 mA. The X-ray diffraction pattern was also recorded during heating and cooling in the temperature range between −50 °C and room temperature on a Rigaku Rint Ultina$^+$ + DSC system. Differential scanning calorimetry (DSC) curves were recorded on a Rigaku DSC 8230L at a heating rate of 2 °C min^{-1} and using α-alumina (α-Al_2O_3) as the standard material. Infrared spectra of the samples were recorded on a Shimadzu FT-IR 8200PC Fourier transformed infrared spectrophotometer by the KBr disk method with the wavenumber resolution of 2 cm^{-1}. Solid-state ^{13}C CP/MAS NMR spectra were recorded on a JEOL JNM-CMX400 spectrometer. Scanning electron micrographs were obtained on a HITACHI S-2380N scanning electron microscope for the samples coated with Au. CHN analysis was performed on a Perkin-Elmer 2400 II instrument. Mg and Al contents were determined by inductively coupled plasma emission spectroscopy (Rigaku Spectro Ciros CCD) for the solution prepared by dissolving the products in HCl.

Results and Discussion

Ion exchange, coprecipitation, and reconstruction are the three methods that have been used for the synthesis of the intercalation compounds of LDH.[2,11] The reconstruction method, which is usually conducted under ambient pressure, was investigated under hydrothermal conditions in the present study. The powder X-ray diffraction pattern (XRD) of the product obtained by the hydrothermal reaction of the calcined hydrotalcite with aqueous sodium oleate is shown in Fig. 1 (trace a). As a reference, the XRD pattern of the as synthesized hydrotalcite used as the starting material is also shown in Fig. 1. A sharp diffraction peak with the *d* value of 3.9 nm accompanying higher reflections (up to 4th order) was observed in the X-ray diffraction pattern of the product (Fig. 1a), indicating the formation of a layered material by reconstruction under hydrothermal conditions.

The infrared spectrum of the product obtained by the hydrothermal reaction of the calcined hydrotalcite with aqueous sodium oleate is shown in Fig. 2 together with that of the as synthesized hydrotalcite. The absorption bands characteristic to the oleate anion, such as C–H stretching vibration (2935 and 2863 cm^{-1}) and COO$^-$ (1450 and 1400 cm^{-1}), were observed in the spectra together with the bands due to the brucite-like layer. The absorption bands due to the carbonate anion were not observed. In the ^{13}C solid-state NMR spectrum, signals due to carbon atoms in C=C and COOH were observed at 183 and 130 ppm, respectively. From the chemical composition of the product (Mg: 10.6, Al: 5.5, and C: 45.8 mass %, which was determined by CHN analysis and ICP), the product was expressed as the following chemical formula $Mg_{0.68}Al_{0.32}(OH)_2 \cdot 0.33(C_{18}H_{34}O_2^-)$. All of these observations confirmed the successful formation of the LDH–oleate intercalation compound, where positive charge was quantitatively compensated by the oleate anion (molar Al:oleate = 1:1).

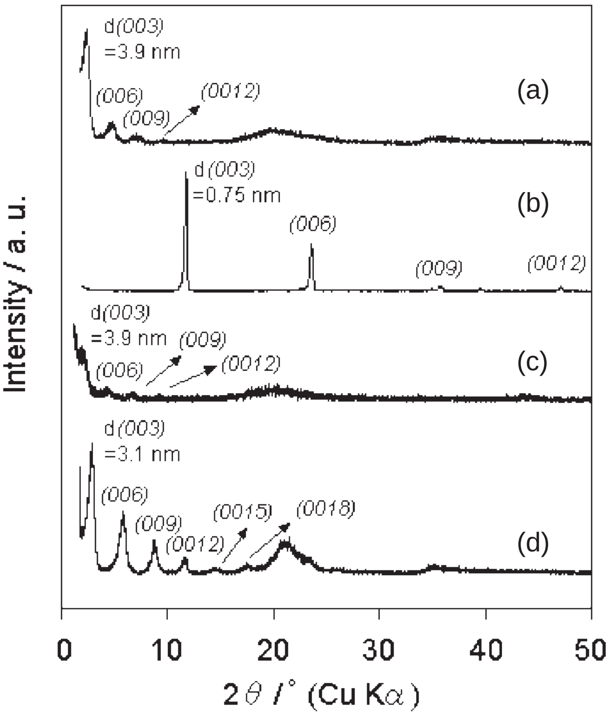

Fig. 1. X-ray powder diffraction patterns of (a) the LDH–oleate intercalation compounds prepared under hydrothermal condition (b) as synthesized hydrotalcite, (c) the LDH–oleate intercalation compounds prepared at room temperature. Trace (d) was the XRD pattern of the LDH–stearate intercalation compound prepared under the hydrothermal condition.

By the reconstruction method under ambient pressure at room temperature, intercalation compounds with similar basal spacings (3.9 nm) were obtained. The X-ray diffraction pattern of the product prepared at room temperature for 24 h are shown in Fig. 1c. The diffraction peaks were weak, as shown in Fig. 1, when compared with those of the LDH–oleate intercalation compound prepared under hydrothermal conditions (Fig. 1a). Thus, the importance of hydrothermal conditions to prepare intercalation compounds with high structural regularity was demonstrated. Considering the results of the ion exchange under hydrothermal conditions, it seems to be possible to exclude the carbonate anion, which usually has high selectivity as interlayer anions. As a result, intercalated species are thought to take a regular arrangement to give high structural regularity. The versatility of the present hydrothermal reconstruction will be confirmed by the experiment on the intercalation of stearate.

The infrared spectrum of the product obtained by reconstruction at room temperature is shown in Fig. 2. The infrared absorption spectrum (trace c of Fig. 2) is identical to that (Fig. 2b) obtained for the product prepared under hydrothermal conditions. The chemical composition of the product is determined to be $Mg_{0.67}Al_{0.33}(OH)_2 \cdot 0.21(C_{18}H_{34}O_2^-)$ from the CHN analysis and the ICP results for the dissolved sample

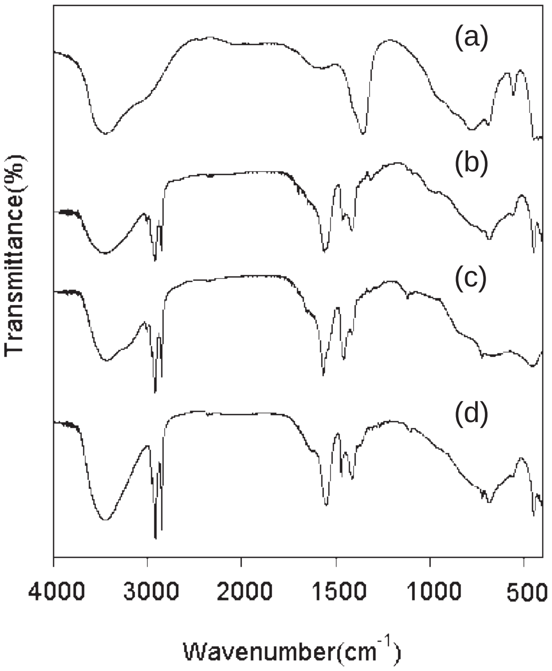

Fig. 2. Infrared spectra of (a) as synthesized hydrotalcite, (b) the LDH–oleate intercalation compound prepared under the hydrothermal condition, and (c) the LDH–oleate intercalation compound prepared at room temperature. Trace (d) was the IR spectrum of the LDH–stearate intercalation compound prepared under the hydrothermal condition.

(Mg: 12.8, Al: 6.9, and C: 38.5 mass %). If compared with that of the hydrothermally synthesized material, the oleate content is smaller. This difference suggests incomplete reconstruction. A prolonged reaction time seems to be required to complete the reaction at lower temperatures to obtain LDH that is quantitatively exchanged with the oleate anion. The weak X-ray diffraction peaks seen in Fig. 1 was thought to be due to the low oleate content. The product yields were smaller when the reconstruction reactions were conducted at room temperature and 60 °C, supporting the above idea.

Recently, it was reported that the intercalation of metal oxalato complexes into LDHs occurred under hydrothermal conditions.[24] The solvothermal ion exchange was also reported to be a possible method to introduce aliphatic α,ω-dicarboxylates into LDH.[25] Due to the high selectivity,[2] the carbonate anion is usually difficult to exclude from the interlayer space even when carbonate is carefully removed in the reactions. However, it was reported that the intercalation compounds prepared under hydrothermal ion-exchange reactions did not contain carbonate anions.[24] The present LDH–oleate intercalation compounds also contained no carbonate anions as evidenced by the IR and CHN analysis. Though the origin is difficult to explain at present, the affinity between carbonate and oleate may be related.

A LDH–stearate intercalation compound was also synthesized by the reaction of the calcined hydrotalcite with an aqueous solution of sodium stearate in a Teflon-lined closed vessel at 150 °C for 24 h. The X-ray diffraction pattern of the LDH–stearate intercalation compound is shown in Fig. 1d. The basal spacing is 3.1 nm, which is similar to those reported for the analogous intercalation compounds prepared by the coprecipitation and reconstruction methods.[14,15] The chemical composition of the LDH–stearate intercalation compound was expressed as the following chemical formula $Mg_{0.67}Al_{0.33}(OH)_2 \cdot 0.34(C_{18}H_{36}O_2{}^-)$ as determined by CHN analysis and ICP (Mg: 9.3, Al: 5.5, and C: 41.9 mass %). The LDH–stearate intercalation compound also contained no carbonate anions as shown by the CHN analysis and the IR spectrum (Fig. 2d). The positive charge was quantitatively balanced by the stearate anion.

It should be noted that the basal spacings are apparently different for the two intercalation compounds (3.9 and 3.1 nm for the oleate and stearate intercalated compounds, respectively), while the chemical compositions of the LDH–oleate and –stearate intercalation compounds were similar. The difference was thought to have arisen from the density (or molecular packing) of the carboxylates in the interlayer space of LDH. Ionic species with long chain alkyl groups tend to form paraffin-type aggregates in the interlayer space of layered solids with relatively high layer charge density.[12,13] The paraffin-type aggregates are thought to be one of the densely packed forms of the intercalated species. On the other hand, due to the bent molecular structure of oleate, the intercalated oleate could not take such a paraffin-type arrangement. Consequently, the basal spacing of the LDH–oleate intercalation compound is larger than that of the present stearate intercalated compound. This idea is supported by the sharpness of the X-ray diffraction peaks for the stearate intercalated compound shown in Fig. 1d.

Figure 3 shows SEM images of the products. As reported previously, hydrotalcite particles obtained by the hydrothermal reaction using urea hydrolysis are hexagonal plates with the lateral size of a few tens of a µm and the thickness of less than 1 µm, as shown in Fig. 3a.[23] The hexagonal platy morphology of the hydrotalcite used as the precursor was retained even after the thermal decomposition of the hydrotalcite and the subsequent reconstruction with oleate and stearate, as shown in Figs. 3b–3d. These observations indicate that the reconstruction occurred topotactically under hydrothermal conditions. Curled small granules were seen at the particle surface for the hydrothermal synthesized products; however, the origin of the texture is not clear at present.

As a characteristic of the present LDH–oleate intercalation compound, thermal change in the nanostructure was investigated by an in situ XRD study in the temperature range between −50 °C and room temperature. Figure 4A shows the DSC curve of the LDH–oleate intercalation compound. It has been reported for the dialkyldioctadecylammonium–smectites that the intercalated species show phase transition between gel and liquid crystalline state, as confirmed by the DSC as well as the spectroscopic probe studies.[26–30] Dialkyldimethylammonium–micas showed a similar phase transition and the phase-transition temperature corresponded to the alkyl chain length.[28] As for the LDH-surfactant intercalation compounds, there are no reports of reversible phase-transition behavior. In the DSC curve recorded upon cooling, there is an exothermic peak at −35 °C. An endothermic peak was seen at −13 °C in the DSC curve recorded upon heating. These reactions are reversible and were observed repeatedly. Thus, it is

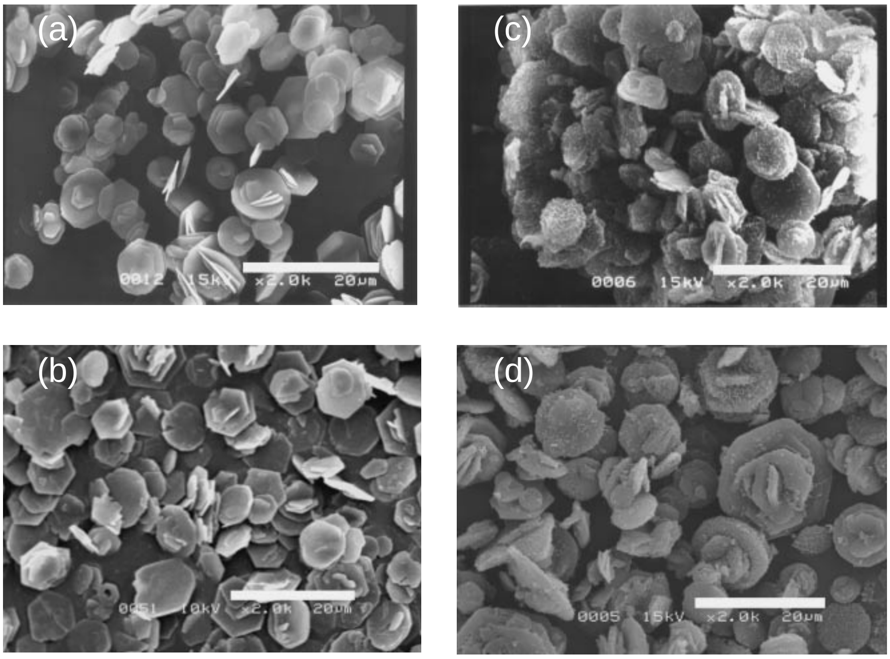

Fig. 3. Scanning electron micrographs of (a) as synthesized hydrotalcite, (b) the LDH–oleate intercalation compound prepared at room temperature, (c) the LDH–oleate intercalation compound prepared under the hydrothermal condition, and (d) the LDH–stearate intercalation compound prepared under the hydrothermal condition.

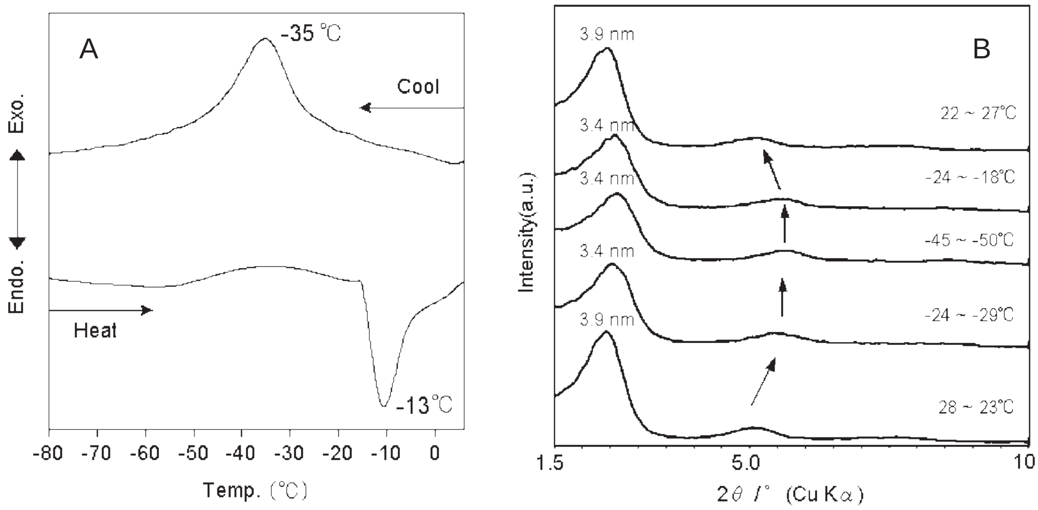

Fig. 4. A. DSC curve of the LDH–oleate intercalation compound prepared under the hydrothermal condition. B. The in-situ XRD patterns of the LDH–oleate intercalation compound at the temperature range between −50 °C and room temperature.

thought that the reaction corresponded to the nanostructural changes, including the changes in the molecular conformation, intermolecular interactions, and the packing.

Figure 4B shows the variation of the X-ray diffraction pattern of the LDH–oleate intercalation compound recorded during the heating and cooling. The basal spacing decreased upon cooling (3.4 nm at −50 °C) from room temperature and subsequent heating resulted in the recovery of the basal spacing to the original value (3.9 nm at room temperature).

Thermal phase transition was also seen for the LDH–stearate intercalation compound. Figure 5 shows the DSC curve and the variation of the X-ray diffraction pattern of the LDH–stearate intercalation compound. Phase transition was observed at 78 °C upon heating and at 66 °C upon cooling. The basal spacing of the LDH–stearate intercalation compound changed between 3.2 (at lower temperature) and 4.1 nm (above the phase-transition temperature).

Thus, phase transition was observed for the present two surfactant intercalated LDHs and the phase-transition temperature varied reflecting the presence of unsaturation. Further systematic studies on the thermal behavior of the series of surfactant intercalated LDHs are worth conducting to understand the phase transition more quantitatively. These thermal changes are reversible and they have been observed repeatedly during the heating and cooling cycles. The thermal behavior observed in the present system reminds researchers to investigate the

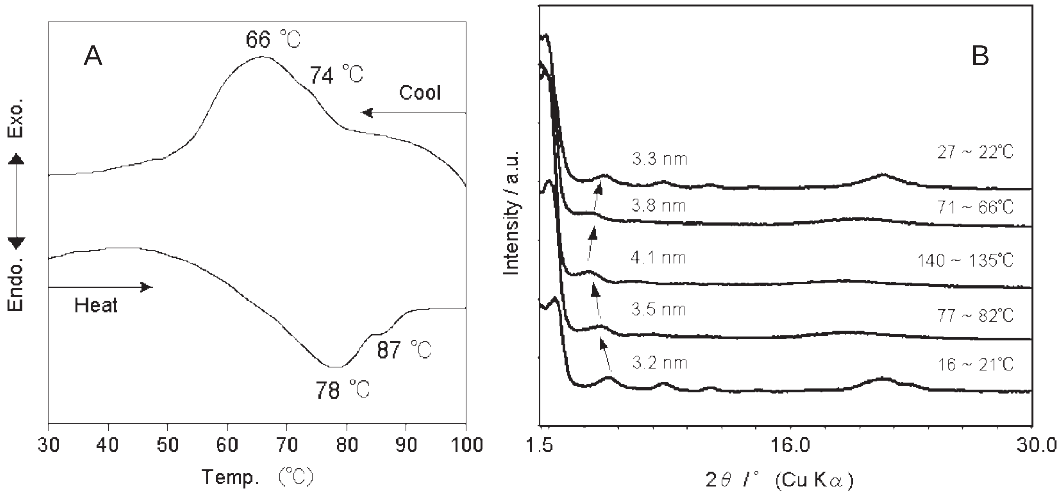

Fig. 5. A. DSC curve of the LDH–stearate intercalation compound prepared under the hydrothermal condition. B. The in-situ XRD patterns of the LDH–stearate intercalation compound at the temperature range between 16 and 140 °C.

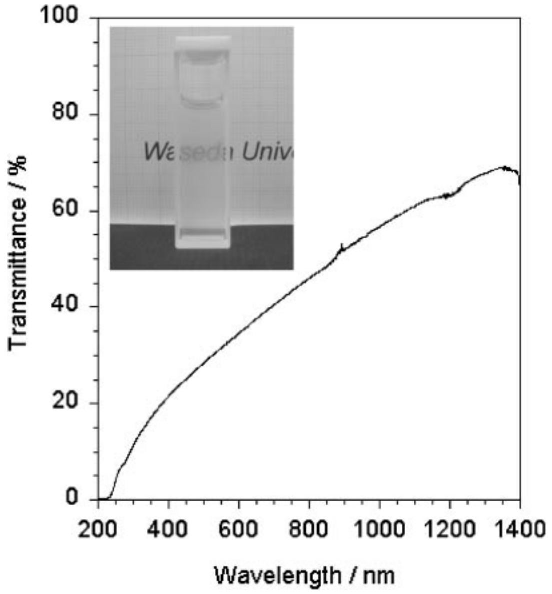

Fig. 6. Transmission spectrum of the suspension of the LDH–oleate intercalation compound prepared under hydrothermal condition in *n*-hexane. Inset. Photograph of the *n*-hexane suspension of the LDH–oleate intercalation compound prepared under hydrothermal condition.

effects of temperature on the properties of LDH–organic intercalation compounds, especially when the compounds are used as fillers to organic polymers because the intermolecular interactions between polymer chains and the organically modified surface are very important factors to control the degree of dispersion and the consequent performance of the resulting hybrids.

It is worth noting that the present LDH–oleate intercalation compound swells in organic solvents such as *n*-alkanes, toluene, and chloroform. A photograph of the *n*-hexane suspension is shown in the Fig. 6 inset. Figure 6 was taken for a suspension containing 0.1 g of the LDH–oleate intercalation compound in 20 mL of *n*-hexane after magnetic stirring for 24 h. When the suspension was stored without stirring for a day, the LDH–oleate intercalation compound precipitated to some extent. This is a clear difference when compared with the swelling of organophilic clays derived from smectites by cation exchange with long-chain alkylammonium ions. Some of them swell to give very stable suspensions and have been utilized as rheology controlling reagents in paints and greases.[31,32] For certain kinds of applications, the degree of swelling and the stability of the suspension should be optimized for the present LDH–oleate intercalation compound. At present, we expect LDHs with different particle sizes and layer charge densities to exhibit different swelling behavior.

In order to assess the swelling observed in the present study, slurries were prepared by mixing the LDH–oleate intercalation compound with *n*-decane in a sample holder for the XRD measurement. The samples were covered with miler films to suppress the evaporation of *n*-decane during the measurement. Figure 7 shows the X-ray diffraction patterns of the slurries and the relationship between the basal spacing and the added amount of *n*-decane (Fig. 7 right). There is a linear relationship between the basal spacing and the amount of *n*-decane added, showing that the added *n*-decane was intercalated to expand the interlayer space. The basal spacing increased to 5.2 nm and further expansion was not observed when the amount of *n*-decane added was greater than 0.5 mL/100 mg. Thus, the adsorption capacity of *n*-decane was determined to be 0.5 mL/100 mg.

The intercalation of a series of *n*-alkylalcohols into the octylsilylated-magadiites has been reported.[33] As for LDH, the swelling of the Zn/Cr LDH–dodecylsulfate intercalation compound with aliphatic alcohols and amines has also been reported.[15,34] The orientation of the intercalated species has been estimated from the variations of the basal spacings for the products as a function of the alkyl chain lengths. It has been reported that the basal spacings correlate with the alkyl chain length of the intercalated ionically neutral aliphatic compounds.[15,33,34] On the other hand, such a general tendency toward larger basal spacing with increased alkyl chain length has not been observed when unsaturation has existed in the alkyl

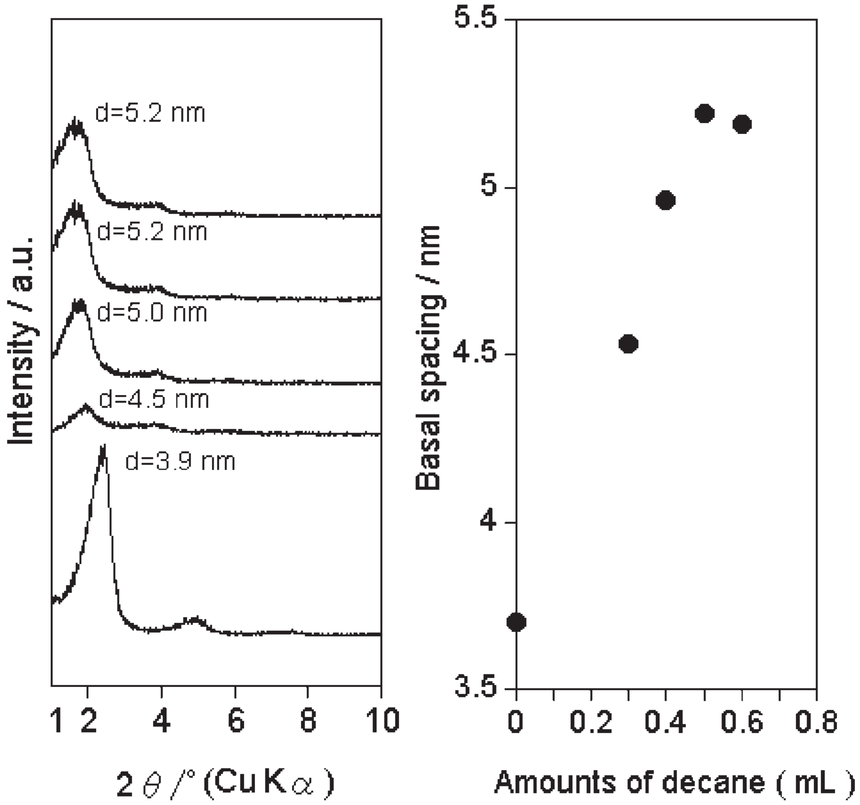

Fig. 7. (Left) The X-ray diffraction patterns of the LDH–oleate intercalation compound prepared under hydrothermal condition (the lowest) before and after the addition of *n*-decane (from the bottom) 0.3, 0.4, 0.5, and 0.6 mL of *n*-decane/100 mg of the LDH–oleate intercalation compound. (Right) The variation of the basal spacing as a function of the added amount of *n*-decane.

chains.[22] By the intercalation of *n*-hexadecanol, the basal spacing of the LDH–oleate intercalation compound increased to 5.3 nm, which is similar to that observed upon the intercalation of *n*-decane. It was thought that a regular paraffin-type arrangement of the intercalated species is implausible due to the bent molecular structure of the oleate anion as a result of the presence of unsaturation. Consequently, a direct correlation between the basal spacing and the molecular size of the guest was not observed for the LDH–oleate intercalation compounds incorporating aliphatic compounds. This result is consistent with the idea given by Lagaly.[22]

Starting from such suspensions, the LDH–oleate intercalation compound can be processed into films by solvent evaporation. Efforts are being made in our laboratory to fabricate films from suspensions and the results will be reported subsequently. It should be noted here that the LDH–stearate did not exhibit such a swelling behavior.

Conclusion

We have successfully synthesized Mg/Al LDH–oleate and –stearate intercalation compounds by the reconstruction method under hydrothermal conditions. The LDH–oleate and –stearate intercalation compounds exhibited reversible thermal nanostructural change as evidenced by the DSC curves and the variation of the X-ray diffraction patterns during heating and cooling. The LDH–oleate intercalation compound swells in organic solvents such as *n*-alkanes as a result of the interlayer expansion.

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