

Preparation of Mg/Al Layered Double Hydroxide–Oleate Intercalation Compound by a Reconstruction Method under Hydrothermal Condition

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A layered double hydroxide–oleate intercalation compound was successfully synthesized by a reconstruction method under a hydrothermal condition from calcined hydrotalcite. The LDH–oleate intercalation compound exhibits attractive properties such as the reversible thermoresponsive change in the basal spacing and the swelling in organic solvents.

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, which consist of positively charged brucite like layer, where some M^{2+} cations are substituted with M^{3+} cations to give positive charge, and the charge compensating interlayer exchangeable anions.² LDHs have extensively been investigated for such applications as catalysts,³ adsorbents,⁴ ceramic precursors,⁵ reaction media for controlled photochemical,⁶ and electrochemical reactions,⁷ and bioactive nanocomposites.⁸ For the cation exchangeable layered materials, cationic surfactants have been intercalated and the properties of the resulting intercalation compounds have been investigated extensively.⁹ The intercalation of unsaturated alkylammonium ions into smectite and the effects of unsaturation on the nanostructures have been reported.¹⁶ As to the LDHs, the intercalation of anionic surfactants has also been reported,^{10–15} however, the variation of the materials and the characterization and properties of them are still lacking. In the present study, we examined the synthesis and characterization of an oleate intercalated LDH.

Three methods, ion exchange, coprecipitation, and reconstruction have been used for the synthesis of the intercalation compounds of LDH.² The reconstruction method, which was usually conducted under ambient pressure, was conducted under a hydrothermal condition in the present study. Following is a typical synthetic procedure; 0.200 g of hydrotalcite, which was synthesized by the hydrothermal method reported previously,¹⁵ 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) in a Teflon-lined autoclave at 150 °C for 1 d. After cooling to room temperature, the solid precipitate was collected by centrifugation and washed with deionized water for three times and dried at 60 °C.

A sharp diffraction peak with the d value of 3.9 nm accompanying higher reflections was observed in the X-ray diffraction pattern²¹ of the product (Figure 1), indicating the formation of a layered material. The infrared spectrum¹⁸ of the product showed the absorption bands characteristic to oleate anion such as C–H stretching vibration (2935 and 2863 cm^{-1}) and COO^- (1450 and 1400 cm^{-1}). From the chemical composition of the product (Mg:

10.6, Al: 5.5, C: 45.8 mass %, which was determined by CHN analysis and ICP), the chemical formula was determined to be $\text{Mg}_{0.68}\text{Al}_{0.32}(\text{OH})_2 \cdot 0.33(\text{C}_{18}\text{H}_{34}\text{O}_2^-)$. These results confirmed the successful formation of the LDH–oleate intercalation compound. By the reconstruction under ambient pressure, intercalation compounds with similar basal spacings were obtained, though the diffraction peaks were weak as shown in Figure 1c for the product prepared at room temperature for 24 h. The lower oleate content of the product prepared at room temperature is a reason for the weak diffraction peaks. Thus, the importance of the hydrothermal condition to prepare intercalation compounds with high structural regularity was shown. Recently, it was reported that the intercalation of metal oxalato complexes into LDHs proceeded under a hydrothermal condition and that the products contained no carbonate contaminants.¹⁹ The present LDH–oleate intercalation compound also contained no carbonate. Thus, the complexation of LDHs with organic anions under hydrothermal conditions seems to be effective ways to synthesize intercalation compounds.

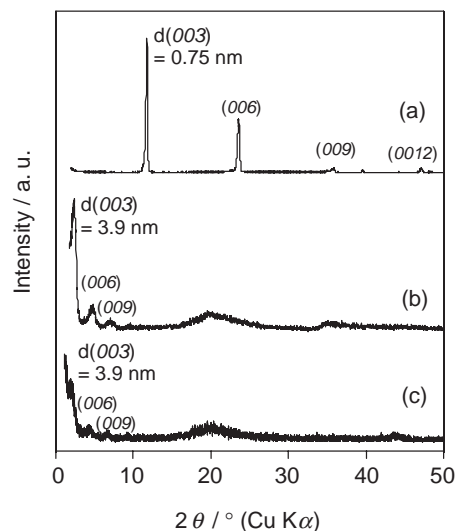


Figure 1. X-Ray powder diffraction patterns of the (a) hydrotalcite and (b and c) the LDH–oleate intercalation compounds prepared under hydrothermal condition (b) and at room temperature (c).

Figure 2a shows the SEM image of the LDH–oleate intercalation compound.²⁰ The hexagonal platy morphology (Figure 2b) of the hydrotalcite used as the precursor¹⁵ was retained.

As a characteristic of the present LDH–oleate intercalation compound, thermal change in the nanostructure was investigated using in situ XRD diffraction study in the temperature range between -50 °C and 140 °C.¹⁷ Figure 3 shows the variation of the X-ray diffraction pattern of the LDH–oleate intercalation

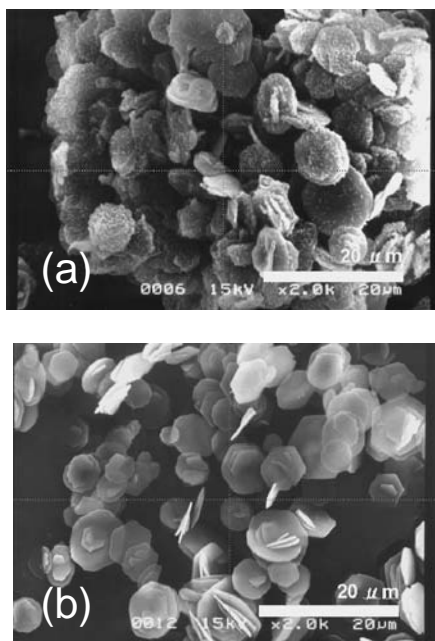


Figure 2. Scanning electron micrographs of (a) the LDH-oleate intercalation compound and (b) the LDH-CO₃²⁻ used as the precursor. Scale bar: 20 μm.

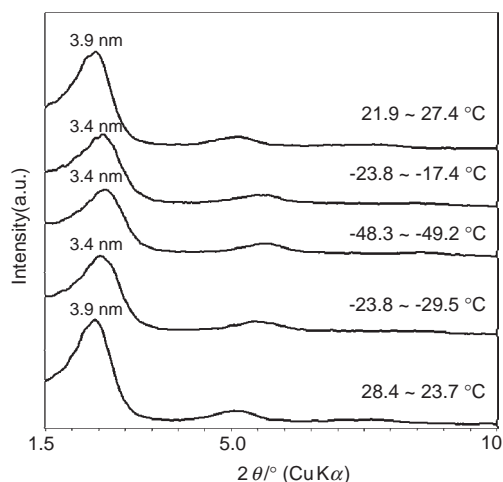


Figure 3. The *in situ* XRD patterns of the LDH-oleate intercalation compound at the temperature range between -50 and 140 °C.

compound recorded during the heating and cooling. The basal spacing decreased upon cooling (3.4 nm at -50 °C) and subsequent heating resulted in the recovery of the basal spacing to the original value (3.9 nm). The change was thought to be due to the packing density of the intercalated oleate. The thermal behavior observed in the present system reminds researchers to investigate the effects of temperature on the properties of LDH-organic intercalation compounds especially as a filler to organic polymers.

Another notable property of the present LDH-oleate intercalation compound is the swelling in organic solvents. Figure 4 is a photograph of the suspension containing 25 mg of the LDH-oleate intercalation compound in 40 mL of *n*-hexane after magnetic stirring for 60 min. The transmittance at the wavelength of

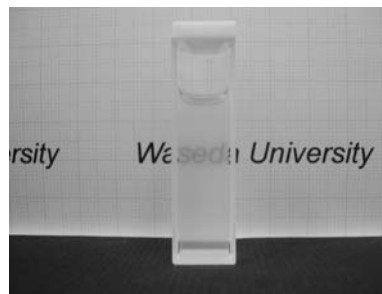


Figure 4. Photograph of the suspension of the LDH-oleate intercalation compound in *n*-hexane.

600 nm was 30% for the present suspension.

In summary, we have successfully synthesized an oleate-Mg/Al LDH intercalation compound by the reconstruction method under hydrothermal condition. The LDH-oleate intercalation compound exhibits such unique physicochemical properties as swelling in organic solvents and reversible thermal nanostructural change.

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- 17 X-Ray powder diffraction patterns were recorded on a Rigaku RADIB powder diffractometer equipped with monochromatic Cu Kα radiation, operated at 30 mA, 40 kV.
- 18 Infrared spectra were recorded on a Shimadzu FTIR8200PC by KBr disk method.
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- 20 Scanning electron micrographs were obtained on a HITACHI S-2840N scanning electron microscope.
- 21 X-ray diffraction patterns of powders were recorded on a Rigaku Rad IB powder diffractometer equipped with monochromatic Cu Kα radiation, operated at 30 mA and 30 kV.