A Novel Synthetic Route to Layered Double Hydroxides Using Hexamethylenetetramine

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For the homogeneous precipitation of hydrotalcite-like compounds (layered double hydroxides; LDHs), HMT (hexamethylenetetramine) was used and the conditions for obtaining the LDHs were investigated. The well-crystallized 1–5 μm LDHs were obtained in a pressure vessel after a 1-day treatment at 140 °C. The resulting LDHs contained a carbonate anion, which was successfully deintercalated using an NaCl–HCl mixed solution without any morphological change.

The layered double hydroxides (LDHs) are composed of positively charged metal hydroxide layers and interlayer anions.[1] The divalent and trivalent cations such as Mg^{2+} and Al^{3+} constitute the metal hydroxide layer and the general formula for MgAl–LDH is $Mg_{1-y}Al_y(OH)_2(X^{n-})_{y/n}\cdot mH_2O$, where $y = 0.1$–0.34, $m = 1 - 3y/2$ and X^{n-} is an n-valent anion.[2] The LDHs are anion-exchangeable and synthesized for use as catalysis, substrates, etc.[3]

The LDHs have been prepared by precipitation from an aqueous solution of Al and Mg salts by adding NaOH solution with maintaining the pH of the solution slightly alkaline.[4,5] The obtained precipitates are not well-crystallized, so aging at a high temperature is needed to obtain higher quality LDHs.[1] Recently, the LDHs with a homogeneous size and a well-defined hexagonal shape were prepared by the urea method.[6,7] The hydrolysis of urea at a high temperature releases ammonia, which causes a homogeneous nucleation of the LDHs. Such LDHs are very interesting from the viewpoint of nanotechnolgy because the LDHs supply nano-order 2-dimesional spaces for anionic functional materials. However, the LDHs prepared by the urea method usually contain carbonates, CO_3^{2-}, which cannot be easily deintercalated because of their high affinity to LDHs.

In this study, we attempted a homogeneous preparation of the LDHs using another reagent, hexamethylenetetramine (HMT). The HMT was expected to hydrolyze at a high temperature in an aqueous solution with releasing ammonia, which makes the solution alkaline. So far, the HMT has been used for preparing metal hydroxides and oxides.[8] The hydrolysis of HMT produces ammonia and formaldehyde, which would not be incorporated into the LDH.

The reagents, $MgCl_2\cdot 6H_2O$, $AlCl_3\cdot 6H_2O$, and HMT (Kanto Chemical Co., Ltd.), were used for preparing the starting solution. The typical synthesis process is as follows: The $MgCl_2$ and $AlCl_3$ in a mol ratio Mg/Al = 2.0 were used with different concentrations, [Mg + Al] = 0.03, 0.15, and 0.25 M. HMT were used 2.625 or 3.5 times of [Al]. To prepare the solutions, degassed deionized water was used and the resulting 12.5 mL of mixture was placed in a 25-mL-Teflon inner vessel within a stainless steel outer vessel (Sanai Kagaku). The mixture was allowed to react at 100–140 °C for 24 h in air-tight conditions. The resulting product was filtrated with a membrane filter (0.2 μm, Millipore) and dried in a vacuum. The pH of the solution was monitored using a TOKO TPX-90 pH meter with a glass electrode. The pH of the initial mixture was about 5 and that of the resulting solution was in the range of 7.5–9.5 depending on the amount of HMT.

The obtained precipitates were characterized as follows: The contents of Mg and Al were analyzed using a Seiko SPS1700HVR ICP-AES instrument after acid decomposition. The FT-IR transmittance spectra were recorded using a Perkin-Elmer 1600 FT-IR spectrometer at room temperature from 4000 to 450 cm^{-1}. The powder X-ray diffraction (XRD) of the products was conducted using a Rigaku RINT 1200 diffractometer with Ni-filtered Cu Kα radiation ($\lambda = 0.15418$ nm). The basal spacing corresponds to the d_{003} for the unit cell. The scanning electron microscopy (SEM) images were obtained on a Hitachi S-5000 scanning electron microscope.

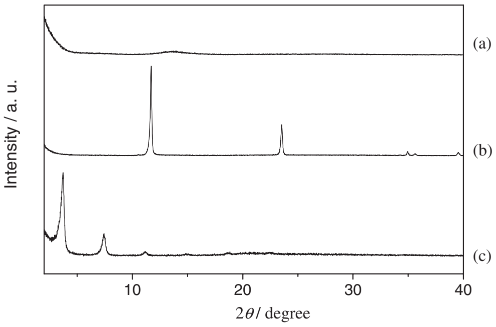

Figure 1. XRD profiles for the products (a) prepared at 100 °C for 24 h, (b) prepared at 140 °C for 24 h, and (c) prepared using the starting mixture containing sodium dodecanoate (C12).

For [Mg + Al] = 0.15 M, at 100 °C for 24 h, we could only obtain a gel-like solid in 23% yield which showed a very broad peak at $2\theta = 13.6°$ ($d = 0.65$ nm) in the XRD profile (Figure 1a). This is probably due to Al hydroxide assumed to form in the initial stage of the urea method.[7] The FT-IR spectrum is shown in Figure 2a. At 120 °C, even after 24 h, a peak with $d = 0.65$ nm still remained (yield = 66%). At 140 °C, the samples treated for 24 h showed only peaks attributable to LDH in the XRD profile for all [Mg + Al] concentrations (yield = 81%; Figure 1b), though a 3-h reaction was not enough (yield = 38%). The basal spacing was 0.757 nm. The Mg/Al ratio determined by chemical analysis was 1.91, which was almost the same as that of the initial mixture. In a few cases, a weak peak due to a secondary phase with $d = 0.275$ nm appeared. For the dilute conditions, the yield tended to decrease.

The FT-IR spectra of the obtained LDH (Figure 2b) showed a strong absorption at 1354 cm^{-1}, which is close to the

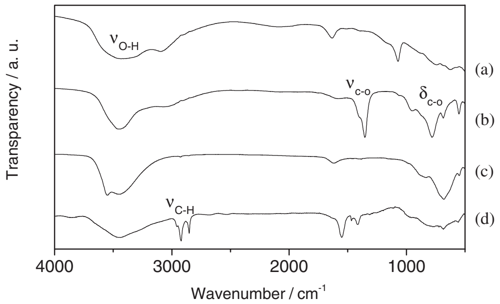

Figure 2. FT-IR spectra of the compounds (a) prepared at 100 °C for 24 h, (b) prepared at 140 °C for 24 h, (c) obtained by treating the LDH using HCl–NaCl, and (d) prepared using the starting mixture containing sodium dodecanoate (C12).

1368 cm^{-1} usually observed for the CO_3^{2-}–LDH. In the 450–1000 cm^{-1} region, a 780-cm^{-1} absorption predominated instead of the 668 cm^{-1} absorption usually observed for the CO_3^{2-}–LDH. We assumed the two possibilities for the incorporated anion, $HCOO^-$ and CO_3^{2-}. To determine either, we synthesized $HCOO^-$– and CO_3^{2-}–LDHs by ion exchange of the deintercalated LDHs as will be described later. The FTIR spectrum of the starting LDH is identical to the CO_3^{2-}–LDH, not to the $HCOO^-$–LDH. The spectrum is also the same as that of the LDH we prepared by the urea method.[6,7] The SEM photos showed that the products were in the shape of the hexagonal plates of the 1–5 µm size (Figure 3a), which is comparable to the LDHs made by the urea method.[6,7] No clear dependence of the crystal size on the reaction conditions was observed. The CO_3^{2-} may be formed by the further oxidation of HCOOH formed by the oxidation of HCHO, which has been formed by the reductive methylation of ammonia into methylamine (*Leuckart reaction*).[9]

The deintercalation of the obtained LDH was conducted as follows: The LDH (10 mg) was placed in a glass vessel, to which 10 mL of an aqueous solution adjusted to 0.005 N HCl and 13 wt % NaCl concentration was added. After purging with nitrogen gas, the glass vessel was tightly capped. The vessel was stored at 25 °C for 1 day with a constant shaking. After filtrated through a menbrane filter, the specimen was dried in a vacuum. The weight loss was negligible. By this treatment using the salt-acid mixed solution[10] (SAM treatment), we could obtain a LDH without any carbonate ions, judging from the FT-IR (Figure 2c). The SEM photo (Figure 3b) indicates that no morphological change took place by this treatment. Using only 0.005 N HCl or 13% NaCl, the ion exchange was barely attained. The basal spacing was 0.772 nm after the treatment, which might indicate the incorporation of Cl^- into the interlayer space.

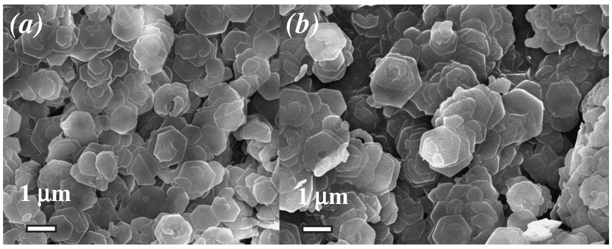

Figure 3. SEM photos of (a) the as-grown LDH and (b) that after deintercalation treatment.

The direct incorporation of organics was attempted by adding the sodium salts of carboxylic acids of different carbon numbers (C2, 4, 6, 8, 10, 12, 14; number indicates n for the formula $CH_3(CH_2)_{n-2}COOH$) to the starting solution. The carboxylic acids were used in 1.5 times of the [Al]. The reaction was conducted at 140 °C for 1 day. The obtained solids were thoroughly washed with water and ethanol to eliminate the intersalated carboxylic acid salts.[11] For C2, 4, and 6, the obtained LDHs exhibited the same IR-profile as that for the LDH prepared without any carboxylates; however, for C10, 12, and 14, the absorption at 1354 cm^{-1} due to CO_3^{2-} disappeared. Instead, strong IR absorptions at 2852, and 2920 cm^{-1} due to the C–H stretching vibration and those at 1553, 1470, and 1415 cm^{-1} attributable to COO^- were observed (Figure 2d). The basal spacing of C12–LDH was 2.40 nm, and its sheet-like shape was observed by SEM. The spectrum for C8 was a mixture of the two features. The LDHs containing C10, 12, and 14 carboxylates were probably separated in an aqueous solution because of their high hydrophobicity, making the LDHs barely ion-exchanged by the carbonate anion generated later.

And also we successfully conducted the ion exchange of the SAM-treated LDH using the sodium C10 carboxylate (20 times the LDH amount in mol) in the usual manner at 25 °C for 6 h. The SEM photos showed that the resulting C10-LDH retained the defined hexagonal contour.

To summarize, we developed a synthetic route to the well-crystallized LDH using HMT. The obtained LDH was successfully decarbonated and thus-treated LDH would be a promising starting material for high-quality nanocomplexes because of its successful incorporation of organic anions by ion exchange without any morphological change.

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