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Preparation of Layered Double Hydroxide–Organic Intercalation Compounds by Solid–Solid Reactions

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Layered double hydroxide–organic intercalation compounds were successfully synthesized by the solid–state reactions of magnesium hydroxide, aluminum hydroxide, and the guest species (*p*-toluenesulfonic acid, malonic acid, and oxalic acid) at room temperature. The present very simple synthesis is potentially applicable to a variety of layered double hydroxide–organic intercalation compounds.

Layered double hydroxides (LDHs; the general formula of $M^{2+}{}_{1-x}M^{3+}{}_{x}(OH)_2(A^{n-})_{x/n}\cdot mH_2O$) are a class of layered materials consisting of positively charged brucite-like layers and the charge compensating interlayer exchangeable anions.[1] In addition to studies on the mechanism of LDH formation and their structures, the applications of LDHs in such fields as catalysts,[2] photochemical reaction media,[3] electrodes,[4] bioactive nanocomposites,[5] and polymer additives,[6] have been reported so far. The functions can be modified by the introduction of guest species. The modification of the interlayer space to be hydrophobic by the introductions of anionic surfactant is a known example for the applications as adsorbents and polymer additives. One can also expect functions from the intercalated guest species; catalytically active species such as polyoxometalates[2b] and metal complexes[2c] have successfully been immobilized in the interlayer space. The wide range of applications of LDHs and their intercalates motivate researchers to develop a simple and economically viable synthetic method.

For the introduction of guest species into the interlayer space of LDHs, three methods, i) coprecipitation from homogeneous solution containing the anions to occupy the interlayer space by pH adjustment and subsequent aging, ii) anion exchange of the preformed LDHs, and iii) so-called reconstruction, where calcined LDH (dehydroxylated and decarbonated form) is suspended in a solution containing the anion to occupy the interlayer space to restructure the layered structure, have been used.[1–7] We have developed a simple synthetic method using magnesium hydroxide (brucite) and aluminum hydroxide (gibbsite) as the inorganic sources for the synthesis of the Mg–Al LDH–deoxycholate[8] and –polysulfides[9] intercalation compounds, where aqueous suspension of magnesium hydroxide, aluminum hydroxide, and deoxycholate (or thioacetoamide) was hydrothermally treated in a closed vessel.[8,9] The reaction was also applied to prepare Zn–Al LDH–benzenesulfonate intercalation compound.[10] Similarly, LDH–acetates have been synthesized from an aqueous slurry.[11]

Recently, the preparation of LDH by solid-state reactions from magnesium hydroxide, aluminum hydroxide, and magnesium nitrate was reported.[12] If compared with reported LDH syntheses using aqueous media,[1–10] the solid-state syntheses of LDH has such advantages as i) solid–liquid separation of product is not necessary, ii) carbonate contamination is less plausible, iii) the starting materials are not expensive if compared with those (soluble salts) used for the conventional syntheses. Accordingly, the preparation of organic anion intercalated LDHs by solid–solid reactions is worth investigating. Here, we report the preparation of LDHs containing *p*-toluenesulfonate, malonate, and oxalate by solid–solid reactions of brucite, gibbsite, and the guest species.

A planetary ball mill (Planet M2-3, Gokin Planetaring, Japan), which has two mill pots (80 cm^3 inner volume each) and 30 zirconia-balls with 10 mm diameter, was used for the synthesis. Mill speed was 700 rpm (revolution) and 1750 rpm (rotation). The ball/sample weight ratio was 30 (=90 g/3.0 g). The mixture of brucite (1.180 g) and gibbsite (0.529 g) was milled for 1 h, to this mixture was added 1.290 g of *p*-toluenesulfonic acid (abbreviated as TS), where the molar ratio of Mg:Al:TS = 3:1:1, and the mixture was subsequently milled for another 1 h.

The XRD pattern of the product obtained by the reaction of brucite, gibbsite, and *p*-toluenesulfonic acid is shown in Figure 1Aa. Diffractions due to the starting materials (brucite, gibbsite, and *p*-toluenesulfonic acid) were not detected. The new diffraction peak with the *d* value of 1.77 nm, which corresponded to the basal spacing reported for the LDH–TS intercalation compound,[13] was observed, indicating the formation of LDH by the present solid–solid reactions and the intercalated TS formed a bilayer as reported previously.[13] When the solid–solid reaction was conducted by heating at

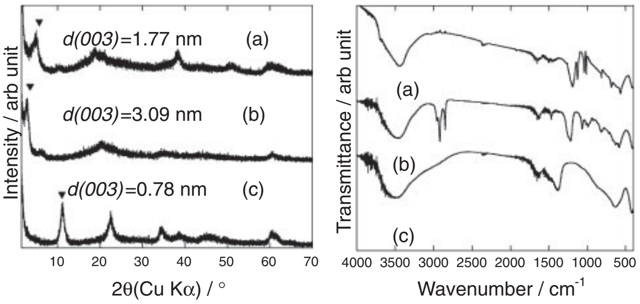

Figure 1. (A) XRD patterns and (B) infrared spectra of (a) the product prepared from brucite, gibbsite, and *p*-toluenesulfonic acid monohydrate, (b, c) after the ion exchange of (a) with dodecyl sulfate (b) and carbonate (c).

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100 °C, pressing and manual grinding the starting mixtures, LDH–organic intercalation compounds were not obtained. Therefore, it is suggested that mechanochemical effects by planetary milling may be concerned for the present LDH formation.

On the other hand, it is difficult to quantify the remaining starting materials as well as the by-products. The absence of XRD diffractions due to the starting materials and by-products indicated the main component was LDH–TS intercalation compound. While in the IR spectra, the absorption band due to brucite (OH stretching vibration) was observed at 3693 cm^{-1}. From the IR spectrum, the amount of unreacted brucite was estimated to be 11%. This fact suggested the presence of other by-products or starting materials in the product, while it is very difficult to isolate or quantify them.

The morphology of LDHs is a key issue for the applications of LDHs in such fields as pharmaceutics and catalysis. A scanning electron micrograph (SEM) of LDH–TS intercalation compound is shown in Figure 2a. Platy particles with the lateral size of 1–10 μm were observed. The starting materials (brucite; hexagonal platy particles with the lateral size of 500 nm and gibbsite; hexagonal platy particles with the size of 450 nm) were not seen in the SEM image of the product showing the solid-state formation of LDH–TS intercalation compound. In addition, particle aggregates with the size of about 700 nm were observed in the transmission electron micrograph (TEM) (Figure 2b) for the sample prepared by casting the aqueous suspension on a grid. A disk-like particle with the lateral size of 250 nm was observed in the TEM image (Figure 2c), suggesting that the primary particle is in the size range of several hundred of nm and they tend to aggregate. It is worth investigating further to correlate the particle morphology, starting materials and reaction conditions. Recently, Tongamp et al. reported the solid–solid reactions to prepare Ni-doped LDH ($Mg_xNi_yAl_2(OH)_{18}\cdot 4H_2O$) from $Mg(OH)_2$, $Ni(OH)_2$, and $Al(OH)_3$, where a small amount of water was added to promote the reaction.[14] This kind of modification of the reaction is possible for the preparation of LDH–organic intercalation compounds and the modification may cause differences in structural regularity and particle morphology of the products.

In order to show the anion-exchange ability, the product (0.20 g) was allowed to react with aqueous solutions (100 mL) of sodium dodecyl sulfate and sodium carbonate (the amount is 10 times of anion-exchange capacity). The products were collected by centrifugation and dried at 60 °C. The XRD patterns (Figures 1Ab and 1Ac) of the products showed the diffraction peaks with the *d* values of 3.09 (dodecyl sulfate-exchanged product) and 0.78 nm (carbonate-exchanged product). These *d* values were in good agreement with those reported for the LDH–dodecyl sulfate intercalation compound[15] and hydrotalcite.[16] In the IR spectra (Figure 1B), the absorption bands due to C–H stretching vibration at 2920 and 2848 cm^{-1} for dodecyl sulfate and that due to C=O stretching vibration at 1382 cm^{-1} for carbonate were observed. In addition, the absorption bands due to aromatic ring ascribable to TS at 1120 and 1040 cm^{-1} were not observed after the ion exchange. All these observations confirmed the possible anion-exchange reactions of the present LDH–TS intercalation compound prepared by the solid–solid reactions.

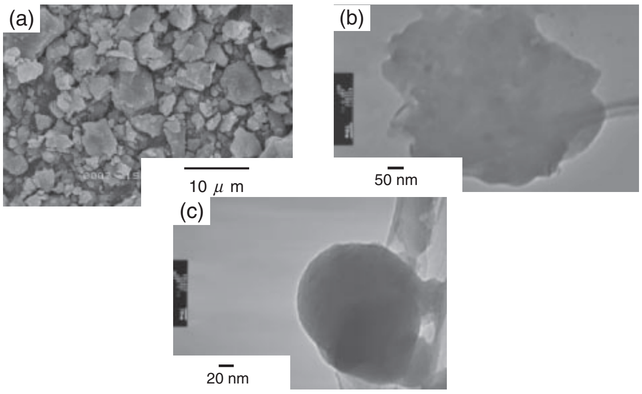

Figure 2. (a) SEM and (b and c) TEM images of the product prepared from brucite, gibbsite, and *p*-toluenesulfonic acid monohydrate.

In order to show the versatility of the present syntheses, oxalic acid and malonic acid were used as guest species. The composition of the starting mixture was as follows; 1.656 g of brucite, 0.743 g of gibbsite, 0.600 g of oxalic acid dihydrate and 1.712 g of brucite, 0.769 g of gibbsite, 0.513 g of malonic acid. The XRD patterns of the products are shown in Figures 3Aa and 3Ab. Being the same as the case of the reaction with TS, diffraction peaks due to the starting materials were not detected, and new diffraction peaks with the *d* values of 0.88 and 0.86 nm, for oxalic acid and malonic acid systems, respectively, appeared in the XRD patterns. Considering the thickness of the brucite-like layer (0.48 nm), the molecular size and geometry of oxalate and malonate, oxalate and malonate anions were intercalated to form monolayers. The infrared spectra of the products are shown in Figure 3B. The absorption bands ascribable to asymmetric and symmetric C=O stretching vibration of $R–CO^{2-}$ group were observed at 1360 and 1590 cm^{-1} (Figures 3Bc and 3Be). Compared with the infrared absorption bands of pristine oxalic acid dihydrate or malonic acid, the absorption bands observed for the products shifted to a lower wavenumber due to the dissociation of carboxy group. All these results confirmed the formation of LDH containing

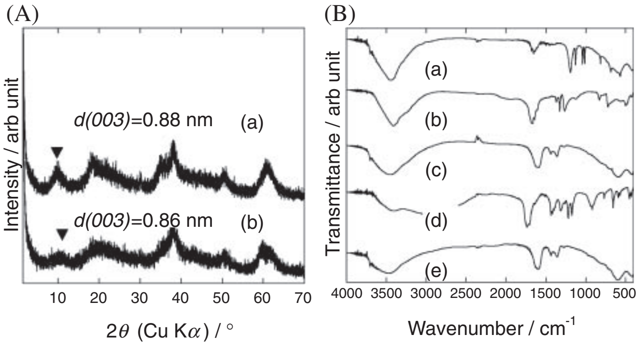

Figure 3. (A) XRD patterns of the products prepared from brucite, gibbsite, and (a) oxalic acid dihydrate and (b) malonic acid. (B) Infrared spectra of the products prepared from brucite, gibbsite, and (a) *p*-toluenesulfonic acid monohydrate, (c) oxalic acid dihydrate, (e) malonic acid and the starting materials (b) oxalic acid dihydrate and (d) malonic acid.

oxalate and malonate anions in the interlayer space by the present solid–solid reactions.

It is worth mentioning as a merit of the present solid-state syntheses that the absorption bands due to carbonate anions at 1360, 874, and 672 cm^{-1} were not observed in the IR spectrum (Figure 3Ba) of the LDH–TS intercalation compound. It is known that carbonate anion is preferentially adsorbed in the interlayer space of layered double hydroxide,[1c] therefore, special caution is required to avoid the carbonate contamination for the preparation of LDH–organic intercalation compounds. In the IR spectra of LDH–oxalate and –malonate intercalation compounds, (Figures 3Bc and 3Be) the bands characteristic to bending nonplanar and angular vibration of carbonate anion at 874 and 672 cm^{-1} were not detected.[17]

In summary, LDH–toluenesulfonate, oxalate, and malonate intercalation compounds were successfully prepared by solid–solid reactions of the mixtures of brucite, gibbsite, and guest species. The present simple solid–solid reactions is versatile way to synthesize LDH–organic intercalation compounds.

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