Facile synthesis of Zn–Al layered double hydroxide from aqueous suspension of zinc oxide and aluminum hydroxide

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Zn–Al layered double hydroxide containing benzenesulfonate was successfully synthesized by the hydrothermal reactions of aqueous suspension of zinc oxide and aluminum hydroxide in the presence of benzene sulfonic acid. The products were characterized by the sharp X-ray diffraction profile and platy particle morphology. The present very simple (hydrothermal reaction of the aqueous mixture) synthesis is applicable to a series of layered double hydroxides with different compositions and structures.

Key-words : Layered double hydroxide, Hydrothermal reaction, Benzensulfonate, Synthesis, Zinc oxide, Aluminum hydroxide

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The composition of the starting mixture was varied as shown in Table 1. For the mixture with the Mg:Al:BS molar ratio of 2:1:1, the reaction time was extended for 2 d.

2.3 Characterization

X-ray diffraction (XRD) patterns of the products were obtained on a Rigaku Rad II diffractometer using monochromatic Cu Kα radiation operated at 40 kV and 20 mA. 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 were recorded on a Shimadzu FT–IR8200 by the KBr disk method. Scanning electron micrographs of the Au coated samples were obtained on a Hitachi S–2380N scanning electron microscope. The coating thickness was 20 nm.

3. Results and discussion

White precipitates were obtained by the reactions. Figure 1(a) shows the XRD pattern of the product prepared by the reaction from the mixture of the composition of Zn:Al:BS = 2:1:1. A sharp diffraction peak with the d value of 1.55 nm accompanying higher reflections was observed in the X-ray diffraction pattern, indicating the formation of a layered material. The basal spacing is close to the values (between 1.55 and 1.59 nm, depending on the M2+ and M3+ of the hydroxide framework) reported for the benzenesulfonate intercalated LDHs. In addition to the reflections from the layered structure, weak reflections due to the starting materials (zinc oxide and gibbsite) were detected (Fig. 1). The infrared spectra of the products are shown in Fig. 2. The absorption bands ascribable to S = O stretching (at 1170 and 640 cm⁻¹) and aromatic ring (at 1450, 1130, 1020, and 810 cm⁻¹) were observed, indicating the incorporation of benzenesulfonate (BS) into the products. The TG–DTA curves of the product are shown in Fig. 3. In the TG curve, a weight loss was observed at the temperature ranges of 100–150, around 250, and 400–500°C due to the dehydroxylation and the oxidative decomposition of the BS was observed in the corresponding DTA curve. Thus, the weight loss corresponds to the amount of BS incorporated. All these results confirmed the formation of Zn–Al LDH containing BS in the interlayer space. Since the product contains zinc oxide and gibbsite, the chemical composition of the formed LDH phase is difficult to be determined at present. Assuming that the BS was incorporated in the LDH phase as the guest anion to compensate the positive charge (the molar Al:BS ratio is 1), the total amounts of byproducts are roughly estimated to be less than 20%. The byproducts amount thus estimated became lowest when the reaction time increase (2 d) or the molar ratio of the starting mixture was 2:1:2 (Mg:Al:BS).

It is thought that the present synthesis involved the dissolution of zinc oxide and gibbsite under the hydrothermal condition and spontaneous formation of LDH phases incorporating BS as reported previously for the deoxycholate and sulfide containing Mg–Al LDHs. The starting materials remain when the hydrothermal reaction of zinc oxide and gibbsite in aqueous slurry was conducted in the absence of BS. Thus, BS plays a role

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**Table 1.** Amounts of the Starting Materials Used for the Syntheses

<table>
<thead>
<tr>
<th>Condition No.</th>
<th>Zn:Al:BS</th>
<th>ZnO</th>
<th>Al(OH)₃</th>
<th>Benzenesulfonic acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2:1:1</td>
<td>0.8139 g</td>
<td>0.39 g</td>
<td>0.7909 g</td>
</tr>
<tr>
<td>2</td>
<td>2:1:1</td>
<td>1.6278 g</td>
<td>0.78 g</td>
<td>1.5818 g</td>
</tr>
<tr>
<td>3</td>
<td>2:1:1</td>
<td>8.139 g</td>
<td>3.9 g</td>
<td>7.909 g</td>
</tr>
<tr>
<td>4</td>
<td>2:1:1</td>
<td>1.6278 g</td>
<td>0.78 g</td>
<td>1.5818 g</td>
</tr>
<tr>
<td>5</td>
<td>1.5:1:1</td>
<td>1.2209 g</td>
<td>0.78 g</td>
<td>1.5818 g</td>
</tr>
<tr>
<td>6</td>
<td>3:1:1</td>
<td>1.2209 g</td>
<td>0.39 g</td>
<td>0.7909 g</td>
</tr>
<tr>
<td>7</td>
<td>4:1:1</td>
<td>1.6278 g</td>
<td>0.39 g</td>
<td>0.7909 g</td>
</tr>
<tr>
<td>8</td>
<td>2:1:2</td>
<td>1.6278 g</td>
<td>0.78 g</td>
<td>3.1636 g</td>
</tr>
<tr>
<td>9</td>
<td>4:1:2</td>
<td>0.8139 g</td>
<td>0.195 g</td>
<td>0.7909 g</td>
</tr>
</tbody>
</table>

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**Fig. 1.** X-ray powder diffraction patterns of the products prepared from aqueous mixture of zinc oxide, gibbsite and BS (2:1:1) by the under hydrothermal reaction at 150°C for 1 d (a) and 2 d (b) d. Trace (c) represent the XRD pattern of the product from concentrated suspension. (condition 3 in Table 1).

**Fig. 2.** Infrared absorption spectra of the product prepared from aqueous mixture of zinc oxide, gibbsite and BS (2:1:1) by the under hydrothermal reaction at 150°C for 1 d. Traces (a) and (b) are spectra for the products from conditions 1 and 3, respectively.
as the incorporating guest species as well as to dissolve zinc oxide and gibbsite. BS made the solution pH lower, so that the dissolution of zinc oxide and gibbsite was promoted. The remaining starting materials can be eliminated by employing the modified conditions such as prolonged reaction time and higher reaction temperature. This idea was supported by the fact that the reflection intensity due to zinc oxide in the XRD patterns decreased to some extent when the reaction time varied from 1 day to 2 d. The XRD patterns of the product prepared by the reaction for 2 d are shown in Fig. 1(b).

Scanning electron micrographs of BS–LDH prepared are shown in Fig. 4. Platy particles with the lateral size of several μm and the thickness of several hundreds of nm were observed. In addition, smaller particles with the size of several hundreds of nm were observed in the SEM images. The smaller particles was thought to be zinc oxide and gibbsite, whose presence was shown by XRD (Fig. 1). The amount of the smaller particles decreased as the reaction time increased as shown in Fig. 4, which was consistent with the XRD results (Fig. 1).

The XRD patterns of the products prepared from the mixtures of different compositions (Zn:Al:BS = 1.5:1:1, 2:1:1, 3:1:1, 4:1:1, 2:1:2 and 4:1:2 for traces a,b,c,d,e and f, respectively; Note that Fig. 5(b) is the same data as Fig. 1(a)) are shown in Fig. 5. All the XRD patterns were characterized by the sharp diffraction due to the BS intercalated LDH. Irrespective of the composition of the starting mixture, the d(003) values were almost same, from 1.55 to 1.58 nm. The reflections due to the remaining zinc oxide and gibbsite were detected as impurity phases, and the intensity of the reflections due to zinc oxide depends on the Zn:Al ratio of the starting mixture; the intensity weakened when the Zn/Al ratio decreased. When Zn:Al ratio was 1.5:1:1, the reflections due to zinc oxide is negligible. This difference was explained as the result of difference in the BS concentration in the starting mixture. With decreasing the Zn:Al ratio of the starting mixture, the BS concentration increase to promote the dissolution of zinc oxide and gibbsite. This idea was supported by the fact that the remaining amount of the starting materials decreased when the amount of BS was increased. Similar difference in the presence of zinc oxide was observed as seen in the XRD patterns (Fig. 5(a) and (e), where Zn:Al:BS ratio were 2:1:1 and 2:1:2).

On the other hand, no apparent difference was seen for the reactions from the mixtures of Zn:Al:BS ratio = 4:1:1 and 4:1:2. (Fig. 5(d) and (f)) Thus, it was suggested that the Zn:Al ratio of the product (LDH) is concerned for the remaining amount of the
starting materials, while we do not have direct evidence for this idea due to the difficulty of determining the composition of the formed LDH phase.

Scanning electron micrographs of the series of the Zn–Al LDH–BS intercalation compounds prepared are shown in Fig. 6. Platy particles of the lateral size of several μm and the thickness of several hundreds of nm were observed, irrespective of the composition (Zn:Al:BS ratio) of the starting mixture. In addition, smaller particles with the size of several hundreds of nm were observed in the SEM images, and the amount of the smaller particles decreased as the Zn/Al ratio of the starting mixture decreased. These SEM observations supported the above discussion based on the XRD results on the presence of zinc oxide in the products with the formed Zn–Al LDH.

Assuming that the thickness of hydroxide layer is 0.48 nm, the intercalated BS forms a bilayer in the interlayer space. This structure is similar to those reported for toluenesulfonate intercalated Mg–Al LDH. The preparation of LDH has actively been investigated from both fundamental and practical viewpoints, and several new or modified synthetic methods, which utilize sonication, microwave irradiation, colloid mill, and an in line dispersion-precipitation method, have been reported recently. Homogeneous precipitation using urea hydrolysis has been applied for the synthesis of carbonate LDHs with large and controlled particle size. On the other hand, the preparation of LDH-organic anion intercalation compounds has been done by coprecipitation, ion exchange and reconstruction methods using conventional batch reactor. The present method is a new and useful method to prepare LDH-organic anion intercalation compounds. The present method is also applied to the preparation of Zn/Al LDH-toluene sulfonate intercalation compounds with the basal spacing of 1.72 nm.

In addition, the intercalated BS was exchanged with other anions including carbonate and dodecylsulfate anions as shown by the change in the XRD pattern (Fig. 7). The resulting products gave basal spacings (2.55 and 0.76 nm for dodecylsulfate and carbonate exchanged materials, respectively) similar to those of the reported products, IR spectra (Fig. 8), where the absorption bands due to C–H stretching vibration at 2948 and 2917 cm\(^{-1}\) for the dodecylsulfate exchange product and that due to C–O stretching vibration at 1358 cm\(^{-1}\) for the carbonate exchanged product were observed in compensation with the disappearance of the absorption bands due to BS confirmed the successful ion exchange. Further variation of ion exchange with other anions and the quantitative examination are worth conducting in order to apply the present method.

Larger scale synthesis is possible using the present hydrothermal reactions starting from concentrated slurries. The scale up was examined using the same reaction vessel (100 ml Teflon lined stainless bottle) using 8.1 g of zinc oxide, 3.9 g of gibbsite, and 1.6 g of BS to give ca. 19 g product, which give XRD (Fig. 1(c)), IR (Fig. 2(b)), and TG–DTA (Fig. 3(b)) results identical to

Fig. 6. Scanning electron micrographs of the products prepared by the under hydrothermal reaction at 150°C for 1 d. The compositions (Zn:Al:BS molar ratio) of the starting mixtures were 1.5:1:1, 2:1:1, 3:1:1, 4:1:1, 4:1:2 and 4:1:2 for traces (a), (b), (c), (d), (e) and (f), respectively.
Further systematic study on the preparation of LDHs with various composition are being done in our laboratory and the results will be reported subsequently.

4. Conclusion

Highly crystalline Zn–Al LDH-benzenesulfonate intercalation compounds were successfully synthesized by the hydrothermal reaction (at 150°C) of aqueous suspension of zinc oxide, gibbsite, and benzenesulfonic acid. The Zn–Al LDH-benzenesulfonate intercalation compounds were platy particles with the size of several microns. Larger scale synthesis (ca. 20 g from 100 mL container) is possible by applying the concentrated aqueous slurry of zinc oxide and gibbsite. The occluded benzenesulfonate anions can be exchanged with anions such as carbonate and dodecylsulfate with retaining the structural regularity and particle morphology. Thus, the present hydrothermal reaction from aqueous suspension of zinc oxide and aluminum hydroxide is an effective and versatile way to synthesize LDH organic intercalation compounds.

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