Synthesis and exfoliation of layered hydroxide zinc aminobenzoate compounds

Lifang ZHAO,^{*,**} Jianying MIAO,^{*} Hongshe WANG,^{*} Yoshie ISHIKAWA^{**} and Qi FENG^{**,†}

^{*}Department of Chemistry and Chemical Engineering, Baoji University of Arts and Science, Baoji, Shanxi, 721007 P. R. China

^{**}Department of Advanced Materials Science, Faculty of Engineering, Kagawa University,
2217-20 Hayashi-cho, Takamatsu-shi, 761-0396

Two types of layered hydroxide zinc *o*-aminobenzoate compounds with structures of layered basic metal salt (LBMS) were prepared by reacting of zinc hydroxide and *o*-aminobenzoic acid solution in a temperature range of 40–110°C. The formation reactions, structures, chemical compositions, and exfoliation behavior in alcohol solvents of the layered compounds were investigated by using XRD, TG-DTA, SEM, and TEM. The layered phase with a basal spacing of 1.33 nm has an α -Ni(OH)₂-like structure, and its chemical formula can be written as Zn(OH)_{1.27}(*o*-NH₂C₆H₄COO)_{0.73}·*n*H₂O. The 1.33 nm layered phase shows plate-like particle morphology. The plate-like crystals can be exfoliated into nanosheet-like particles in alcohol solvents.

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1. Introduction

Low-dimensional nanomaterials, such as zero-dimensional nanoparticles, one-dimensional nanofibers and nanotubes, and two-dimensional nanosheets, attract much attention due to their special physical and chemical properties and potential applications to nanotechnologies in wide fields. Exfoliation techniques for layered compounds are interesting and useful for the preparation of the two-dimensional nanosheets. Since the nanosheets of the elementary layer with uniform thickness can be obtained by using this low cost process, many studies have been carried on the exfoliations of the layered compounds.^{1–3)} Up to now, many types of cation-exchangeable layered metal oxides, e.g. layered titanates,⁴⁾ and layered manganese oxides,⁵⁾ have been exfoliated by using organic amine intercalation reactions, which offer variety of two-dimensional semiconductor nanomaterials.

For anion-exchangeable layered compounds, only layered double hydroxides (LDHs) have been successfully exfoliated. The anion-exchangeable LDHs have a brucite-like structure with a general formula of [M^{II}_{1–z}M^{III}_z(OH)₂](A^{m–})_{z/m}·*n*H₂O, where M^{II} is a divalent cation such as Mg²⁺, Mn²⁺, Fe²⁺, Ni²⁺, Zn²⁺, Cu²⁺, or Co²⁺, M^{III} is a trivalent cation such as Al³⁺, Co, Mn³⁺, Cr³⁺, Fe³⁺, V³⁺, or Ga³⁺, and A^{m–} is an exchangeable anion such as CO₃^{2–}, NO₃[–], OH[–], X[–], etc. The *z* is the molar ratio of M³⁺/(M²⁺+M³⁺), generally ranges between 0.2 and 0.4, and it determines the positive-layer charge density and the anion-exchange capacity.⁶⁾ The LDHs are a very attractive class of lamellar solids capable of producing various intercalation compounds and nanocomposites using their anion-exchange properties and the wide possibility of manipulation. Recently much attention has been attracted on the LDHs exfoliation, and LDHs with the interlayer anions of dodecyl sulfate,⁷⁾ glycine,⁸⁾ amino acids,⁹⁾ lactate,¹⁰⁾ benzoate, 2,4-dichlorobenzoate-, hydroxybenzoate,¹¹⁾ and nitrate¹²⁾ have been successfully exfoliated.

Another type of anion-exchangeable brucite-like layered metal hydroxide compounds is known as layered basic metal salts (LBMSs), and can be represented by a general formula of [M^{II}(OH)_{2–x}](A^{m–})_{x/m}·*n*H₂O.¹³⁾ In the LBMS structure, the OH[–] anions on the brucite hydroxide layer are partially replaced by A^{m–} anions, and A^{m–} anions are anion-exchangeable. Some studies on synthesis and structure of layered hydroxide zinc carbonate compounds have been reported, and found that these layered compounds have the LBMS structure.^{14,15)} Very recently we have reported that layered hydroxide zinc benzoate compounds can be prepared by the hydrothermal reaction of ZnO with benzoic acid, and these compounds belong to LBMSs.^{16,17)} Two types of structures, zinc hydroxide-nitrate-like structure and α -Ni(OH)₂-like structure, have been found in the layered hydroxide zinc benzoate compounds. We have achieved also the exfoliation of the layered hydroxide zinc benzoate compounds in alcohol solvents, which is first time success in the exfoliation of LBMSs. The exfoliated LBMS nanosheets are interesting two-dimensional organic-inorganic nanocomposite, where the organic anions coordinate directly to the metal ions in the metal hydroxide nanosheet, which is different to the ionic binding between the LDH nanosheets and anions.

In the present article, we described synthesis of a new type of layered hydroxide zinc aminobenzoate compound and its exfoliation reaction. To our best knowledge, no any study has been reported on the synthesis and exfoliation of the layered hydroxide zinc aminobenzoate compound yet. The results of the exfoliation study will help us to understand the exfoliation reaction of LBMSs and effect of anion in the interlayer on the exfoliation reactions, and furthermore the exfoliation will give a new category for the nanosheets.

2. Experiment procedure

A 0.4 M NaOH solution (250 mL) was added dropwise into a 0.2 M Zn(NO₃)₂ solution (250 mL) at 10°C under stirring conditions for a period of 0.5 h. The product was aged in the reaction solution at 10°C for 4 h, and then was filtered, washed with dis-

[†] Corresponding author: Q. Feng; E-mail: feng@eng.kagawa-u.ac.jp

tilled water, and dried at 40°C for 1 d. This sample was used as the starting material for the preparation of the layered hydroxide zinc aminobenzoate compounds. For the preparation of the layered hydroxide zinc aminobenzoate compounds, 0.5451 g of the starting material containing 3.2 mmol of Zn, *o*-aminobenzoic acid (*o*-NH₂C₆H₄COOH), and 15 mL distilled water were sealed into a Teflon-lined autoclave with inner volume of 75 mL, and then hydrothermally treated at 40, 70, 90, 110 or 130°C for 12–24 h under autogenous pressure. In this hydrothermal reaction, 0.132, 0.219, 0.395, 0.526, and 0.658 g of *o*-aminobenzoic acid were used to adjust the *o*-NH₂C₆H₄COOH/Zn molar ratios in the reaction system to 0.3, 0.5, 0.9, 1.2 and 1.5, respectively. The product was filtered and washed with distilled water, and dried at 50°C for 1 d.

The layered hydroxide zinc *o*-aminobenzoate compound (0.015 g) was added into an organic solvent (10 mL), and then ultrasonicated for 20 min or stirred for 1 d at room temperature for exfoliation treatment. After standing for 1 d, supernatant colloidal solution was collected by pipetting off to separate the exfoliated nanosheet colloid solution from the unexfoliated solid particles. The purified colloidal solution was dried using a freeze-drier to obtain an exfoliated solid sample for the XRD and TG-DTA analyses. Saturation concentration (g·L⁻¹) of the exfoliated nanosheet sample was evaluated from the volume of the colloidal saturation solution and the weight after the freeze-drying treatment.

Powder X-ray diffraction (XRD) analysis was carried out on a Shimadzu Co., XRD 6100 X-ray diffractometer with Cu K α ($\lambda = 0.15418$ nm) radiation. Thermogravimetry (TG) and differential thermal analysis (DTA) data were obtained on a Shimadzu Co., DTG60H thermal analyzer at a heating rate of 10°C/min in air. Scanning electron microscope (SEM) observation was carried out using a JEOL Ltd., JSM5500S. Transmission electron microscope (TEM) observation was performed on a JEOL Ltd., JEM3010 at 300 kV. In the TEM study of exfoliated sample, the exfoliated colloidal solution was supported on a microgrid, and dried at room temperature.

3. Results and discussion

3.1 Synthesis of layered hydroxide zinc *o*-aminobenzoate compounds

Figure 1 shows the XRD patterns of starting material and the products obtained by reacting the starting material with *o*-aminobenzoic acid at 40°C. The starting material was obtained by reacting NaOH solution and Zn(NO₃)₂ solution, and showed a XRD pattern of β -Zn(OH)₂ phase (JCPDS No. 20-1435) (Fig. 1(a)). When the starting material was reacted with *o*-aminobenzoic acid at 40°C, new diffraction peaks with *d*-values of 2.668, 1.332, 0.6638, 0.4419 and 0.3377 nm were observed. The peaks with *d*-values of 1.332, 0.6638, 0.4419 and 0.3377 nm can be assigned to a layered phase of hydroxide zinc *o*-aminobenzoate compound with a basal spacing of 1.33 nm, and the peak with *d*-value of 2.668 nm maybe corresponds to another layered phase with a basal spacing of 2.67 nm. The peaks intensity of 1.33 nm layered phase increased, and that of 2.67 nm layer phase decreased with increasing the concentration of *o*-aminobenzoic acid in the reaction system.

The formations of the layered hydroxide zinc *o*-aminobenzoate compounds are dependent on the concentration of *o*-aminobenzoic acid and also on the reaction temperature. **Figure 2** shows the XRD patterns of products obtained at 70°C. Under these conditions the 1.33 nm layered phase was formed. Without the 2.67 nm layered phase was formed under the high tempera-

Fig. 1. XRD patterns of (a) the starting material, and (b–d) products obtained by hydrothermal reaction of the starting material with *o*-aminobenzoic acid at 40°C for 24 h. The *o*-NH₂C₆H₄COOH/Zn molar ratios in the reaction system are (b) 0.9, (c) 1.2, (d) 1.5, respectively. ●: 1.33 nm layered phase; ■: 2.67 nm layered phase; *: Zn(OH)₂ phase.

Fig. 2. XRD patterns of products obtained by reacting the starting material with *o*-aminobenzoic acid at 70°C for 12 h. The *o*-NH₂C₆H₄COOH/Zn molar ratios in the reaction system are (a) 0.3, (b) 0.5, (c) 0.9, (d) 1.2 and (e) 1.5, respectively. ●: 1.33 nm layered phase; ◆: ZnO layered phase.

ture conditions, suggesting the 2.67 nm layered phase is unstable at high temperature. A small amount of ZnO phase was observed also, due to the unreacted Zn(OH)₂ phase was unstable and transformed to ZnO phase under these conditions.

The dependence of formations of the layered hydroxide zinc *o*-aminobenzoate compounds on the *o*-NH₂C₆H₄COOH/Zn molar ratio and the reaction temperature are summarized in a phase diagram of **Fig. 3**. The 2.67 nm layered phase tend to be formed under low temperature conditions. The 2.67 nm layered phase is difficult to be obtained in single phase under the present study conditions. Because the unreacted Zn(OH)₂ phase is remained under low *o*-NH₂C₆H₄COOH/Zn molar ratio conditions, and the 1.33 nm layered phase is formed under high *o*-NH₂C₆H₄COOH/Zn molar ratio conditions in the low temperature range. The single 1.33 nm layered phase can be obtained around *o*-NH₂C₆H₄COOH/Zn molar ratio range of 1.2 to 1.5 in a temperature range of 70 to 90°C. When the temperature was higher than 110°C, except the 1.33 nm layered phase ZnO phase was observed also around *o*-NH₂C₆H₄COOH/Zn molar ratio

range of 1.2 to 1.5, suggesting above 110°C the 1.33 nm layered phase became unstable and decomposed into ZnO phase.

3.2 Characterization of layered hydroxide zinc *o*-aminobenzoate compounds

The thermal stability and chemical composition of the layered hydroxide zinc *o*-aminobenzoate compounds were investigated using TG-DTA analysis. **Figure 4** is TG-DTA curves of sample A, a single 1.33 nm layered phase sample prepared at *o*-NH₂C₆H₄COOH/Zn molar ratio of 1.2 and 70°C (Fig. 2(d)). The sample shows an endothermic peak at 370°C, and two exothermic peaks at 455 and 465°C. Each of the endothermic and the exothermic peaks correspond to a weight loss. An XRD study indicates that the layered structure is stable up to 300°C (**Fig. 5**). At 400°C the layered phases disappeared completely, and the destruction of the layered phase accompanied formation of ZnO phase. The 1.33 nm layered phase shows a higher thermal stability than that of the layered hydroxide zinc benzoate compounds.¹⁶⁾

The endothermic peak at 370°C can be assigned to the dehydration of the hydroxide groups binding on Zn(II) from the layered compound. The exothermic peaks at 455 and 465°C can be assigned to the decomposition and oxidation of *o*-aminobenzoate groups to CO₂ in air. The dehydration of the hydroxide groups at 370°C accompanies the destruction of the layered structure. From the weight loss around 460°C (32%) of the decomposition and

Fig. 3. Phase diagram for the formation of layered hydroxide zinc *o*-aminobenzoate compounds. ♦: ZnO phase; ●: 1.33 nm layered phase; ■: 2.67 nm layered phase; ▲: Zn(OH)₂ phase.

Fig. 4. TG-DTA curves of sample A prepared under the conditions of 70°C, 12 h and *o*-NH₂C₆H₄COOH/Zn molar ratio of 1.2.

oxidation of *o*-aminobenzoate groups, the *o*-NH₂C₆H₄COO⁻/Zn molar ratio in the sample A can be evaluated as 0.73. Since the sample A is single phase, the chemical formula for the 1.33 nm layered phase can be written as Zn(OH)_{1.27}(*o*-NH₂C₆H₄COO)_{0.73}·*n*H₂O, where has some interlayer water in the compound.

An SEM study indicates that the 1.33 nm layered phase has plate-like particle morphology (**Fig. 6**), and the particle size is much larger than the size of the starting material (about 0.1 μm). The plate-like particle size is dependent on the reaction conditions. The thickness of plate-like particles decreases with inc-

Fig. 5. XRD patterns of (a) sample A and samples obtained by heat-treatment of sample A at (b) 200, (c) 300, (d) 400 and (e) 500°C, respectively. ▲: 1.33 nm layered phase; ◆: ZnO phase.

Fig. 6. SEM images of samples prepared at the *o*-NH₂C₆H₄COOH/Zn molar ratio of 1.2 and different temperature. (a) 40°C for 24 h; (b) 70, (c) 90, (d) 110 and (e) 130°C for 12 h; (f) 90°C for 6 h. (a): 1.33 nm layered phase containing small amount of Zn(OH)₂ phase; (b), (c), (f): 1.33 nm layered phase; (d) and (e): 1.33 nm layered phase containing small amount of ZnO phase.

reasing reaction temperature and decreasing reaction time. These results suggest that the 1.33 nm layered phase easily grows under the low temperature conditions by a dissolution-deposition reaction. Some small stick-like particles were formed in samples prepared at high temperature, such as at 130°C (Fig. 6(e)). These small stick-like particles correspond to ZnO phase, revealing that the layered phase becomes unstable at high temperature above 110°C, which is agree with the results of XRD study.

3.3 Exfoliation of layered compound and characterization of exfoliated sample

The sample A was treated in methanol, ethanol, *n*-propyl alcohol, *i*-propyl alcohol, *n*-butyl alcohol, *t*-butyl alcohol, β -propylene-glycol, and formamide solvents, respectively, to exfoliate the layered compound into its elementary nanosheets. After treatments in the organic solvents, the colloidal solutions were obtained in methanol, *i*-propyl alcohol, *n*-butyl alcohol, *t*-butyl alcohol, and β -propylene-glycol solvents, suggesting the layered phase can be exfoliated in these solvents. The concentrations of the colloidal solutions were high in *n*-butyl alcohol, *t*-butyl alcohol, and β -propylene-glycol solvents, and were low in methanol and *i*-propyl alcohol solvents. The exfoliation is due to the swelling of the layered structure by intercalation of the solvent molecules into the interlayer space of the layered structure.^{5),12)} The swelling causes expansion of the interlayer space, and finally exfoliation into the elementary sheets. The driving force of intercalation reaction of the solvent molecules is due to the affinity between the interlayer of the layered compound and solvent molecules. Hibino et al. have reported that amino acid-form LDH compounds can be exfoliated in formamide solvent.⁹⁾ However, the layered hydroxide zinc aminobenzoate compound prepared in this study cannot be exfoliated in formamide solvent, although aminobenzoate has a amine group, suggesting that the exfoliation reaction is dependent not only on the interlayer anions, but also strongly on the structure and composition of host layers.

The formation of the nanosheets by the exfoliation reactions can be confirmed by a TEM study. **Figure 7** shows the TEM images of the exfoliated sample A in the *n*-butyl alcohol solvent. The nanosheet-like particles were observed, and the nanosheets were much thinner than the original crystal of sample A, revealing that the exfoliation reaction occurs in the *n*-butyl alcohol solvent. The thickness of the nanosheet-like particles suggests that the nanosheet-like particles are constructed by stacking several elementary layers of the layered structure. The single layer nanosheet of the layered compound was not observed in this exfoliation system. This result reveals that layered hydroxide zinc *o*-aminobenzoate compound is more difficult to be exfoliated than layered hydroxide zinc benzoate compounds which can be exfoliated into the elementary layers.¹⁶⁾ The saturation concentration of the exfoliated sample in the *n*-butyl alcohol solvent is 0.12 g/L that is smaller also than 0.7 g/L of the layered hydroxide zinc benzoate compound. The reason may be due to formation of hydrogen bond between amine groups of *o*-aminobenzoates in the interlayer that will be discussed in next section.

An XRD study indicated that when the nanosheet colloidal solution was dried, the nanosheets restack to the 1.33 nm layered structure again. **Figure 8** shows TG-DTA curves of the restacked sample (sample B) obtained by drying the nanosheet colloidal solution. The sample B shows an endothermic peak at 345°C, and a broad exothermic peak at 441°C, and each peak corresponds to a weight loss. Since the exothermic peak 441°C is broad, it overlaps with the endothermic peak at 344°C. Similar

Fig. 7. TEM images of nanosheet samples obtained by exfoliation treatment of sample A in *n*-butyl alcohol solvent.

Fig. 8. TG-DTA curves of samples B obtained by drying exfoliated nanosheet solution.

to the original sample A, the endothermic peak at 345°C can be assigned to the dehydration of the hydroxide groups from the layered compound, and the exothermic peak at 451°C to the decomposition and oxidation of *o*-aminobenzoate groups to CO₂ in air. In comparison with the original sample A (Fig. 4), the endothermic and exothermic peaks shift to low temperature after the exfoliation treatment, suggesting some damage to the layered structure after the exfoliation-restacking reaction.

From the weight loss around 441°C (27%) of the decomposition and oxidation of *o*-aminobenzoate groups, the *o*-NH₂C₆H₄COO⁻/Zn molar ratio in the sample B can be evaluated as 0.35. Therefore, the chemical formula for the sample B can be written as Zn(OH)_{1.65}(*o*-NH₂C₆H₄COO)_{0.35}·*n*H₂O. The *o*-NH₂C₆H₄COO⁻/Zn molar ratio decreased after the exfoliation, indicating loss of *o*-NH₂C₆H₄COO⁻ group from the nanosheets in the exfoliation process, which causes the damage on the layered structure.

3.4 Structure of layered hydroxide zinc *o*-aminobenzoate compounds

We have reported that two kinds of layered hydroxide zinc benzoate compounds can be obtained by reacting ZnO and benzoic acid under the hydrothermal conditions, and they belong to LBMS compound.¹⁶⁾ In LBMS compounds, two types of structures have been reported.¹³⁾⁻¹⁵⁾ One is α -Ni(OH)₂-like structure, in which without vacancy in the octahedral sites in the brucite hydroxide layer, and anions in the interlayer space coordinate to metal ions at octahedral sites, as shown in **Fig. 9(a)**. Another is zinc hydroxide-nitrate-like structure (Zn₅(OH)₈(NO₃)₂·2H₂O). In this structure, 1/4 octahedral metal ion sites in the brucite

Fig. 9. Structural models of the layered hydroxide zinc *o*-aminobenzoate compounds with (a) α -Ni(OH)₂-like structure and (b) zinc hydroxide-nitrate-like structure.

hydroxide layer are vacancies, and two metal ions occupy tetrahedral sites locating above and below the vacant octahedral site, as shown in Fig. 9(b). The anions in the interlayer space coordinate to the metal ions at tetrahedral sites, and then it has a larger basal spacing than that of α -Ni(OH)₂-like structure.

The layered hydroxide zinc benzoate compounds with α -Ni(OH)₂-like structure and zinc hydroxide-nitrate-like structure have basal spacings of 1.47 and 1.93 nm, respectively.¹⁶⁾ The α -Ni(OH)₂-like phase has smaller basal spacing and higher benzoate content than the zinc hydroxide-nitrate-like phase. In the present study, two types of layered compounds with basal spacings of 1.33 and 2.67 nm, respectively, were obtained also in the hydroxide zinc *o*-aminobenzoate system. We think that the 1.33 nm layered phase of the hydroxide zinc *o*-aminobenzoate compound can be assigned to the α -Ni(OH)₂-like structure, in which *o*-aminobenzoate groups coordinate to zinc ions at octahedral sites with *o*-NH₂C₆H₄COO-Zn(II) bond (Fig. 9(a)), because its basal spacing and *o*-aminobenzoate content are close to those of the hydroxide zinc benzoate compound with α -Ni(OH)₂-like structure.

The smaller basal spacing of the hydroxide zinc *o*-aminobenzoate compound than that of the hydroxide zinc benzoate compound may be due to formation hydrogen bond between amine groups of *o*-aminobenzoates which coordinate to different zinc hydroxide layers in the interlayer space, as shown in Fig. 9(a), which causes the increase of stability of the layered structure. This may be the reasons why the hydroxide zinc *o*-aminobenzoate compound has higher thermal stability and is more difficult to be exfoliated into its elementary layers than the hydroxide zinc benzoate compounds. We think that the hydroxide zinc *o*-aminobenzoate compound with basal spacing of 2.67

nm maybe has the zinc hydroxide-nitrate-like structure (Fig. 9(b)), but further detail study is necessary to confirm it.

4. Conclusion

The layered hydroxide zinc *o*-aminobenzoate compound with basal spacing of 1.33 nm can be formed by the hydrothermal reaction of Zn(OH)₂ and *o*-aminobenzoic acid. The layered compound has α -Ni(OH)₂-like structure and can be exfoliated in the alcohol solvents. The exfoliation reaction is dependent on the properties of the alcohol solvents. The exfoliation reaction accompanies partial loss of *o*-aminobenzoate in the layered compound.

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