SYNTHESIS AND THERMAL DECOMPOSITION OF PHENYLALANINE INTERCALATED LAYERED DOUBLE HYDROXIDES

SUMIO AISAWA, MASAHIRO IZUMI, SATOSHI TAKAHASHI, HIDETOSHI HIRAHARA, YOSHIO UMETSU and EIICHI NARITA*

Department of Chemical Engineering, Faculty of Engineering, Iwate University, 4-3-5 Ueda, Morioka 020-8551, Japan

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ABSTRACT

The synthesis and thermal decomposition behavior of the phenylalanine/M\(^{2+}\)-Al layered double hydroxides (Phe/Mg-Al, Mn-Al and Zn-Al LDHs) have been investigated. The Phe/LDH was easily synthesized by the conventional coprecipitation method. The basal spacing of the Phe/LDHs was expanded to 0.86 (Mg-Al), 1.80 (Mn-Al) and 1.86 nm (Zn-Al), respectively, which supported that Phe was intercalated into interlayer space of the LDH as an anion or an amphoteric ion form. The thermal decomposition of the intercalated Phe was influenced by the kind of a divalent metal ion in the LDH basal layer. In particular, the Mn-Al LDH was found to have the strong catalytic action for the decomposition of the intercalated Phe. From the FT-IR, HPLC and NMR measurements, it was proved that the intercalated Phe was decomposed via the formation of N-benzoylbenzamide (NBBA) regardless of the kind of LDHs, which compound never formed in the thermal treatment of Phe itself. Therefore, it is expected that the two dimensional LDH interlayer space can be used as a novel nano-scale reactor for the synthesis or the decomposition reaction of organic compounds.

Key words: Layered double hydroxides, Intercalation, Phenylalanine, Thermal decomposition, N-benzoylbenzamide

INTRODUCTION

The nano-technology has received considerable attention in recent years (Sanchez et al., 2001), and layered materials has been used for the development and synthesis of the novel organic–inorganic nano-hybrid materials (Leroux and Besse, 2001; Carrado et al., 2001). The combination of layered material and intercalation technique will have a possibility of providing new nano-hybrid materials. Layered double hydroxide (LDH), one of the two dimensional layered compounds, has anion exchange ability and is so-called an anionic clay or a hydrotalcite-like compound (Miyata and Kumura, 1973; Cavani et al., 1991). The LDH has received considerable interests due to their potential technological applications such as a catalyst, an electrode, an optical memory and a separator (Sels et al., 1999; Kaneda et al., 1998; Qu and Villemure, 1997; Kuwahara et al., 1996; Seida and Nakano, 2000). The LDH consists of positively charged octahedral hydroxide layers and an exchangeable interlayer anion with water molecules. The general chemical composition of LDH is represented as \[[M^{2+}_{1-x}M^{3+}_x(OH)_2][A'^{-}\times_nyH_2O]\], where \(M^{2+}\) is a divalent cation (Mg\(^{2+}\), Zn\(^{2+}\), Co\(^{2+}\), Mn\(^{2+}\) and Cu\(^{2+}\)), \(M^{3+}\) is a trivalent cation (Al\(^{3+}\), Cr\(^{3+}\), Fe\(^{3+}\) and Co\(^{3+}\)), \(A'^{-}\) is an anion (Cl\(^{-}\), CO\(_3^{2-}\), NO\(_3^{-}\), SO\(_4^{2-}\) and various organic anions), and \(x\) value can be varied between 0.20 and 0.33 (Allmann, 1968; Taylor, 1973). In particular, hydrotalcite \[[Mg_{0.66}Al_{0.34}(OH)_2][(CO_3)_{0.17} \cdot 0.33H_2O]\] is the most frequently investigated LDH and is found in nature.

The intercalation of the biomolecule into LDHs such as a nucleotide, a deoxyribonucleic acid, an amino acid and a polypeptide has been investigated in order to prepare the biomolecule/LDH nano-hybrid material (Choy et al., 1999, 2000 and 2001; Whilton et al., 1997; Fudala et al., 1999). We have also studied quantitatively on the intercalation of various amino acids for LDHs by the coprecipitation method (Aisawa et al., 2000 and 2001). The purpose of this paper is to elucidate the synthesis of phenylalanine/M\(^{2+}\)-Al LDH (Phe/LDHs, M\(^{2+}\) = Mg, Mn and Zn) and the thermal decomposition behavior of the Phe/LDHs.

* To whom correspondence should be addressed, Tel & Fax: +81-(0)19-621-6331, e-mail: enarita@iwate-u.ac.jp
EXPERIMENTAL

Materials

Reagents (Al(NO₃)₃, Mg(NO₃)₂, Mn(NO₃)₂, NaOH, Phe and Zn(NO₃)₂) were purchased from Wako Pure Chemical Industries, Ltd., and used without further purification.

Synthesis of Phe/LDHs

The Phe/LDHs precipitate was prepared by hydrolysis of M²⁺ and Al³⁺ ions in the presence of Phe. The mixed solution of 1 M M²⁺(NO₃)₂ and Al(NO₃)₃ (M²⁺/Al³⁺/Phe molar ratio = 2/1/1, M²⁺ = Mg²⁺, Mn²⁺ or Zn²⁺) was added dropwise to 50 mM Phe solution with stirring under a nitrogen atmosphere to minimize the contamination with atmospheric CO₂. The solution pH was adjusted by dropwise addition of 1 M NaOH solution, and the temperature was kept at 313 K in a thermostat set. The synthesis pH of the Phe/LDHs was indicated in Table 1. The precipitate was collected by centrifugation after aging for 1 h. The supernatant solution was subjected to the measurement of Phe concentration by using a Shimadzu TOC-5000 total organic carbon analyzer. The solid product was washed with distilled water several times and dried in a vacuum oven at 333 K for 24 h.

Thermal treatment of Phe/LDHs

The thermal treatment of the Phe/LDHs was carried out using a ULVAC infrared image furnace HPC-7000. All samples were heated with a rate of 10 K/min and kept at desired temperature for 90 min under an air atmosphere. In the case of the Phe/Mn–Al LDH, the thermal treatment was also carried out under a nitrogen atmosphere. A part of the solid product was dissolved in 0.1 M HCl solution after the thermal treatment. The dissolved solution was analyzed by using a reverse phase high performance liquid chromatography (HPLC) Shimadzu SCL-6 with Shodex C18-5B (4.6 by 250 mm), and the detection was performed with a UV detector at 210 nm. The column was equilibrated with 0.1% trifluoroacetic acids solution (TFA), and the dissolved solution was analyzed by a linear gradient of 60% acetonitrile solution with 0.1% TFA solution from 0 to 100% for 40 min. On the other hand, the dissolved solution was separated by a column chromatography with silica gel packing (15.0 by 150 mm, eluent: chloroform/ethyl acetate = 5/1). Nuclear magnetic resonance (NMR) spectra of the isolated solution were recorded on a Bruker AC-400P, and resonance frequencies of ¹H and ¹³C were 400 and 100 MHz, respectively.

Characterization of solid products

Powder X-ray diffraction (XRD) measurements were performed on a Rigaku Rint 2200 powder X-ray diffractometer, using a Cu-Kα radiation (λ = 0.15405 nm) with Ni filtered at 20 mA and 40 kV, a scanning rate of 2°/min and a 2θ angle ranging from 2 to 50°. Fourier-transform infrared (FT-IR) spectra were obtained by a JASCO WS/IR 7300 FT-IR spectrophotometer with the standard KBr disks method. Thermogravimetry (TG) and differential thermal analysis (DTA) were carried out in the temperature range 298–1073 K under an air atmosphere at a heating rate of 10 K/min by a Seiko TG/DTA 320. Chemical analysis data for the solid

![FIG. 1. XRD patterns of Phe/LDH precipitates. (a) Mg–Al LDH, (b) Mn–Al LDH and (c) Zn–Al LDH.](image)

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<th>TABLE 1. Chemical composition of Phe/LDH precipitates</th>
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<td>Solid product</td>
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<tr>
<td>Phe/Mg–Al LDH</td>
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<td>Phe/Mn–Al LDH</td>
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products were determined by a Hitachi 180-80 atomic adsorption spectrometer (metal ion), TOA Electronics IA-100 ion analyzer (NO₃⁻ ion) and Shimadzu TOC-5000 (Phe) after dissolution of the solid products in 0.1 M HCl solution.

RESULTS AND DISCUSSION

Synthesis and Characterization of Phe/LDHs
The chemical composition of the Phe/LDHs obtained by the coprecipitation method is indicated in Table 1. The molar ratio M²⁺/Al³⁺ of the Phe/LDHs was found to agree with the initial mixed ratio, being 1.94–2.13 in all the Phe/LDHs. In the case of the Phe/Mn–Al and Zn–Al LDH, the amount of the intercalated Phe and NO₃⁻ ion disagreed with that of the positive charge on the LDHs basal layer. The anion exchange capacity (AEC) of LDH is normally 1.00 mol/mol-M³⁺ for a monovalent anion. However, the molar ratio guests/Al³⁺ was calculated as 1.38 and 1.55 mol/mol-Al³⁺, indicating that Phe was intercalated as an amphoteric ion form into the LDHs, because the synthesis pH of the Phe/Mn–Al and Zn–Al LDH was 9 and 8 (pKᵢ = 2.17 and pK₂ = 9.14), respectively. In the Phe/Mg–Al LDH, the molar ratio guests/Al³⁺ was lower than other LDHs, estimating as 0.59 mol/mol-Al³⁺. The most of Phe existed as the anion form at pH 10 in solutions, and the remaining positive charge of the LDH basal layer was supplemented by OH⁻ ion.

The XRD patterns of the Phe/LDHs are shown in Fig. 1. The diffraction peaks (d₀₀₃ = 0.86 nm and d₀₀₆ = 0.43 nm) were observed with the LDH structure for the Phe/Mg–Al LDH in Fig. 1(a). As the thickness of LDH basal layer is 0.48 nm, the interlayer space is estimated as 0.38 nm. Molecular size of Phe is 0.88 nm in length and 0.31 nm in thickness, suggesting that Phe was horizontally intercalated for the LDH basal layer. The XRD patterns of the Phe/Mn–Al and Zn–Al LDH showed the expanding LDH structure, in which the main diffraction peak (d₀₀₃ = 1.80 nm and d₀₀₆ = 1.86 nm) was observed in Fig. 1(b) and (c), respectively. The gallery height of the Phe/Mn–Al and Zn–Al LDH was estimated as 1.32 nm and 1.38 nm, suggesting that Phe was vertically oriented to the LDH basal layer as the bilayer arrangement by the hydrophobic interaction between phenyl groups.

Figure 2 shows the FT-IR spectra of the Phe/LDHs. The weak absorption peaks of alkyl C–H stretch and amine N–H stretch were observed in the region 2900–
The strong absorption peaks for antisymmetric and symmetric stretches of R−COO− were observed at 1590 and 1400 cm⁻¹, and the weak absorption peaks for the mono substituted benzene were observed at 750 and 695 cm⁻¹, indicating that Phe was incorporated for the LDHs. The strong absorption peak at 1385 cm⁻¹ was due to stretching vibration of N−O by the co-intercalated NO₃⁻ ion. A broad absorption peak in the region 3000–3600 cm⁻¹ was assigned to O−H group stretches of both hydroxides for the basal layer and the interlayer water molecule. In the low-frequency region, the absorption peaks of the spectra corresponded to the lattice vibration modes were attributed to M−O vibration at 840 and 650 cm⁻¹ and O−M−O vibration at 430 cm⁻¹, respectively.

The TG-DTA curves of the Phe/LDHs are shown in Fig. 3. Three weight losses due to the decomposition of Phe itself in the temperature range 473–546 K (weight loss 70%) and two-step combustion of Phe itself were observed in the temperature ranges 546–672 K (weight loss 20%) and 685–801 K (weight loss 10%) as a reference sample. The thermal decomposition of the intercalated guest Phe was found to be influenced by the kind of the host LDHs layer. Total weight loss of the Phe/LDHs was ca. 50% and major weight loss indicated three steps. The first step corresponding to the removal of adsorbed water and interlayer water was observed for all the Phe/LDHs from room temperature to 523 K. The second step due to both the dehydroxylation of the hydroxide basal layer in the temperature region 523–723 K and the decomposition of the intercalated Phe at between 473 and 523 K were observed successively. Third step corresponding to the combustion of the intercalated Phe was followed in the temperature region 543–753 K. In particular, the combustion weight loss of the intercalated Phe was observed at 556 K for the Phe/Mn–Al LDH. This decomposition temperature was the lowest in all the Phe/LDHs, suggesting that the Mn–Al LDH has an excellent catalytic action for the decomposition of the intercalated guest organic compounds in the LDH interlayer space. The DTA curves indicated that an endothermic peak at 527 K for the decomposition of Phe itself and two exothermic peaks at 657 and 801 K for the combustion of Phe itself were observed in Fig. 3(a). In the case of the Phe/LDHs, the combustion of the intercalated Phe was shown as the main exothermic peaks in the temperature region 461–750 K, which are lower than the combustion temperature of Phe. 

![XRD patterns of solid products obtained after thermal treatment. (a) Phe/Mg–Al LDH and (b) Phe/Zn–Al LDH. ▼: MgO and ■: ZnO.](image-url)
itself. In particular, the combustion temperature of the intercalated Phe was shifted from 801 K to 556 K in the Phe/Mn–Al LDH. In other LDH systems, such phenomenon did not occur, and this is the potential feature of the Mn–Al LDH.

**Thermal treatment of Phe/LDHs**

The XRD patterns of the Phe/Mg–Al and Zn–Al LDH after the thermal treatment are shown in Figs. 4(a) and 4(b), respectively. In the case of the Phe/Mg–Al LDH, the solid product kept the LDH structure with decreasing the crystallinity in the temperature range 373–573 K. The LDH structure was destroyed at 673 K, in which the solid product formed MgO (JCPDS-ICDD, PDF-45-946). As can be seen in the TG-DTA curves, the thermal decomposition process of the Phe/Mg–Al LDH was slower than other LDHs. In the case of the Phe/Zn–Al LDH, the expanded LDH structure has been kept until 373 K with declining the crystallinity. At 573 and 673 K, the LDH structure was completely destroyed with increasing temperature, and the solid product formed ZnO (JCPDS-ICDD, PDF-36-1451). The XRD patterns of the Phe/Mn–Al LDH after the thermal treatment are shown in Figs. 5 (5(a): air atmosphere and 5(b): nitrogen atmosphere). Both of the diffraction peaks with the LDH structure (d = 0.82 nm) were observed at 373 K. The reduction of gallery height indicates that the intercalated Phe was horizontally oriented for the LDH basal layer. Furthermore, the (003) diffraction peak shifted to higher angles from 1.80 nm to 1.00 or 1.05 nm. The schematic model of the Phe/Mn–Al LDH after the thermal treatment is shown in Fig. 6. The orientation angle of the intercalated Phe changed from 90° to 70° for the LDH basal layer, because a part of the interlayer water was removed by the thermal treatment. In the case of the air atmosphere, the clear diffraction peaks were not observed in the XRD pattern of the solid product at 473 K. Then, the solid product was crystallized to Mn$_3$O$_4$ (JCPDS-ICDD, PDF-24-73) with increasing temperature. Mn ion of the LDH basal layer was oxidized by the combustion of the intercalated Phe. The XRD patterns of the solid products after the thermal treatment at 473 and 573 K did not show the clear peaks in the nitrogen atmosphere. However, the broad peaks due to amorphous Mn$_3$O$_4$ were observed at 673 K. Moreover, the weak diffraction peaks by the crystallized MnO (JCPDS-ICDD, PDF-4-32) were observed at 873 K, namely, Mn$_3$O$_4$ was reduced by the.

![Fig. 5. XRD patterns of solid products obtained after thermal treatment of Phe/Mn–Al LDH precipitates. (a) air atmosphere and (b) N$_2$ atmosphere ●: Mn$_3$O$_4$ and ◆: MnO.](image)
organic carbon from the intercalated Phe.

The FT-IR spectra of the solid products at 473 K are shown in Fig. 7. The absorption peaks of alkyl C–H stretch, amine N–H stretch, the strong absorption peaks of R–COO\(^{-}\) were disappeared as shown in Fig. 2. The stretching vibration of N–O by NO\(_3^{-}\) ion and O–H group by the LDH basal layer were also decreased. In particular, the Phe/Mn–Al LDH, the broad peak in the region 3000–3600 cm\(^{-1}\) by O–H group stretch was remarkably decreased compared with other LDHs. However, the new weak peak appeared at 1655 cm\(^{-1}\) by the stretch mode of –CONH at all the samples, meaning that the intercalated Phe was condensed by the thermal treatment.

The HPLC chromatograms of the Phe/Zn–Al LDH obtained after the thermal treatment at various temperatures are shown in Fig. 8(a–e). As a reference
In this paper, the synthesis and thermal decomposition behavior of the Phe/M²⁺-Al LDHs have been investigated. Phe was easily intercalated into the LDHs as an amphoteric ion form in the Mn-Al and Zn-Al LDH and an anion form in the Mg-Al LDH by the coprecipitation method. From the expanding interlayer space, the intercalated Phe was oriented horizontally or vertically for the LDHs basal layer. The thermal decomposition of the intercalated Phe was remarkably influenced by the divalent cation in the LDH hydroxide layers. The decomposition temperature was lower in the following order: Mg-Al > Zn-Al > Mn-Al LDH, especially, the Mn-Al LDH possess the excellent catalytic action for the decomposition of the intercalated Phe. The decomposition process of the intercalated Phe was also found to proceed via the formation of NBBA regardless of the kind of LDHs, which never form in the thermal treatment of Phe itself. It is expected that the two dimensional LDH interlayer space can be used as a
novel nano-scale reactor for synthesis or decomposition reaction of organic compounds.

ACKNOWLEDGEMENT

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