Intercalation behavior of amino acids into Zn–Al-layered double hydroxide by calcination–rehydration reaction

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Abstract

The intercalation of amino acids for the Zn–Al-layered double hydroxide (LDH) has been investigated by the calcination–rehydration reaction at 298 K using mainly phenylalanine (Phe) as a guest amino acid. The Zn–Al oxide precursor prepared by the calcination of Zn–Al-carbonated LDH at 773 K for 2 h was used as the host material. The amount of Phe intercalated by the rehydration was remarkably influenced by the initial solution pH and reached ca. 2.7 times for anion exchange capacity (AEC) of the LDH at neutral and weak alkaline solutions, suggesting that Phe was intercalated as amphoteric ion form into the LDH interlayer. As Phe is intercalated for the LDH as monovalent anion in alkaline solution, the amount of Phe intercalated at pH 10.5 corresponded with AEC of the LDH. The solid products were found to have the expanded LDH structure, which confirmed that Phe was intercalated into the LDH interlayer as amphoteric ion or anion form. The basal spacing, d_{003}, of the Phe/LDH was 1.58 nm at pH 7.0 and 0.80 nm at pH 10.5; two kinds of expansion suggested for Phe in the interlayer space as vertical (pH 7.0) and horizontal (pH 10.5) orientations. The intercalation behavior of various amino acids for the LDH was also found to be greatly influenced by the feature of the amino acid side-chain, namely, its carbon-chain length, structure and physicochemical property. In particular, α-amino acids possessing a hydrophobic or negative-charged side-chain were preferentially intercalated for the LDH.
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Keywords: Zn–Al-layered double hydroxide; Intercalation; Calcination–rehydration reaction; Amino acids

1. Introduction

Clay minerals are well known as layered materials and employed in their potential technological applications as catalysis, ion-exchanger, adsorbent, biosensor [1–6], and a synthesis of organic–inorganic nanocomposites [7–11]. Especially, the synthesis of novel organic–inorganic nanohybrid materials has received extensive research in recent years [12–15]. The conjunction of layered material and intercalation technique has a possibility of providing new organic–inorganic nanohybrid materials. Layered double hydroxide (LDH), one of layered materials, is known as hydrotalcite-like compounds and has anion exchange property [16–18]. LDH is a two-dimensional layered compound and anionic clay comparing with more conventional cationic clays. The chemical composition of LDH is represented by general formula $[M_{1-x}^{2+}M_x^{3+}(OH)_2][A_{x/n}^{n-} \cdot y H_2O]$, where M^{2+} is a divalent cation such as Mg^{2+}, Zn^{2+}, Co^{2+}, Mn^{2+}, and Cu^{2+}, M^{3+} is a trivalent cation such as Al^{3+}, Cr^{3+}, Fe^{3+}, and Co^{3+}, and A^{n-} is an ion-exchangeable anion such as OH^-, Cl^-, NO_3^-, CO_3^{2-}, SO_4^{2-}, and various organic anions. The x-value is equal to the ratio $M^{3+}/(M^{2+} + M^{3+})$, generally ranging between 0.20 and 0.33, and its value indicates charge density of the hydroxide basal layer, namely, anion exchange capacity (AEC). LDH has a positively charged hydroxide basal layer due to the trivalent cation substituted for the divalent cation in the hydroxide basal layers and are neutralized by the

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intercalated anion with water molecules into the occupying interlayer space. The intercalation of various anions for LDH has been accomplished by the following methods: coprecipitation, ion-exchange, calcination–rehydration (reconstruction method), thermal reaction, and hydrothermal reaction [19–24]. The most interesting feature of carbonated LDHs is the calcination–rehydration reaction. LDH oxide precursor prepared by the calcination of a carbonated LDH at various temperatures can rehydrate and intercalate various anions from aqueous solution with a reconstruction of the LDH structure [25–28].

Since, there are few studies on the intercalation of amino acids into LDHs. The intercalation of glutamic acid, aspartic acid, and poly-aspartic acid for the Mg–Al LDH by the coprecipitation has been reported [29,30]. The intercalation of phenylalanine (Phe) and tyrosine for the Zn–Al LDH by the ion exchange has also been investigated [31]. However, there was no quantitative analysis for the intercalation. We have quantitatively investigated the intercalation of various amino acids for the M^{2+}–M^{3+} (M^{2+}: Mg, Mn, Zn, M^{+3}: Al, Cr) LDHs by the coprecipitation [32,33]. Newman et al. reported the molecular dynamics simulation of the Phe/Mg–Al LDH [34]. Recently, Nakayama et al. described the intercalation of amino acids and peptides for the Mg–Al LDH by the calcination–rehydration reaction in alkaline solutions [35]. Then, we investigated the intercalation behavior of amino acids for the Zn–Al LDH in order to compare the calcination–rehydration reaction with the coprecipitation. In this study, the quantitative intercalation behavior of various amino acids for the Zn–Al LDH in neutral and weak alkaline solutions has been investigated by using the calcination–rehydration reaction. As the Zn–Al LDH is known to be stable in wide pH region from weak alkaline solutions, it is quite convenient for investigation on the intercalation amino acids for LDH in wide pH region.

2. Experimental

2.1. Materials

Amino acids and other inorganic reagents were purchased from Wako Pure Chemical Industries, Ltd, Japan and used without purification.

2.2. Synthesis of CO_3/Zn–Al LDH

The CO_3/Zn–Al LDH (CO_3/LDH) was prepared by a standard coprecipitation method as follows [18]. A mixture solution of 1 M $ZnCl_2$ and $AlCl_3$ (Zn/Al molar ratio = 2/1) was added to 1 M Na_2CO_3 solution at 317 K with stirring and the suspension was aged at 317 K for 1 h. The pH of the reaction mixture was

adjusted 9 ± 0.2 by dropwise addition of 2 M NaOH solution. The white precipitate was separated, washed with distilled water several times and added to 1 M Na_2CO_3 solution again. The slurry was incubated again for 5 h with boiling. The resulting precipitate was collected by centrifugation, washed with distilled water several times and dried at 333 K for 24 h in a vacuum oven. The chemical composition of the synthesized CO_3/LDH was $[Zn_{0.67}Al_{0.33}(OH)_2][(CO_3)_{0.16} \cdot 0.55H_2O]$.

2.3. Intercalation of amino acid for Zn–Al LDH by calcination–rehydration reaction

The Zn–Al oxide precursor used for the intercalation reaction of amino acids was obtained by the calcination of the CO_3/LDH at 773 K for 2 h in a muffle furnace. The Zn–Al oxide (0.2 g) was added to amino acid solution (50 cm^3) with various concentrations in a 100 cm^3 Erlenmeyer flask and shaken in a water bath at 298 K on proper times under a nitrogen atmosphere to prevent the formation of the CO_3/LDH. The solid product was separated by filtration and washed with distilled water several times to remove excess adsorbed amino acid. The supernatant solution was subjected for the measurement of amino acid concentration using a Shimadzu TOC-5000 total organic carbon analyzer. The solid product was dried at 333 K for 24 h in a vacuum oven.

2.4. Characterization of solid products

Powder X-ray diffraction (XRD) patterns of the solid products were obtained using a Rigaku 2013A powder X-ray diffractometer, using a Cu-$K\alpha$ radiation with Ni filtered at 10 mA and 35 kV. The crystallite size of the resulting LDH was calculated from the Scherrer equation. Fourier-transform infrared (FT-IR) spectra were recorded on the sample pressed into KBr disc using a JASCO WS/IR 7300 FT-IR spectrophotometer. Chemical analysis data for Al and Zn were obtained using a Hitachi 180-80 atomic absorption spectrometer after dissolution of the solid product in 0.1 M HCl solution.

3. Results and discussion

3.1. Intercalation behavior of phenylalanine

The intercalation behavior of amino acids for the Zn–Al LDH was investigated using 50 mM L- or D-phenylalanine (L- or D-Phe) as a guest amino acid. The time dependence of the amount of Phe intercalated at pH 7.0 and 10.5 is shown in Fig. 1. The intercalation rate and amount of Phe intercalated were considerably different by the initial solution pH. At pH 7.0, the
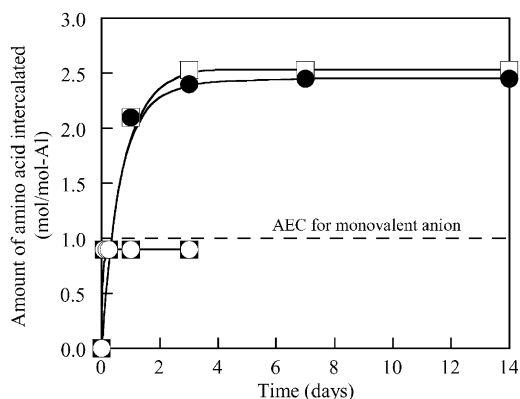
Fig. 1. Time dependence of amount of D- and L-Phe intercalated by Zn–Al oxide precursor. □: D-Phe (pH 7.0), ●: L-Phe (pH 7.0), ■: D-Phe (pH 10.5), ○: L-Phe (pH 10.5).

Fig. 2. Influence of pH for intercalation of L- and D-Phe by Zn–Al oxide precursor. □: D-Phe, ●: L-Phe. Broken line: amphoteric ion, dot–dash line: anion.

Fig. 3. Intercalation isotherms of (●) L-Phe (pH 7.0), (○) L-Phe (pH 9.5) by Zn–Al oxide precursor at 298 K after 120 h.

amount of Phe intercalated was increased gradually until the equilibrium was reached after 3 days and the maximum amount of L- and D-Phe intercalated was almost the same as 2.45 and 2.53 mol/mol-Al in oxide, respectively, which are unexpectedly high values. However, the intercalation equilibrium of L- and D-Phe at pH 10.5 was quickly attained only after 12 h, and both the amount of Phe intercalated became relatively lower as 0.90 mol/mol-Al. This result supports that the intercalation behavior of Phe for the LDH was greatly influenced by the solution pH, and the difference in the intercalation of Phe enantiomer was not observed.

The influence of the initial solution pH for the intercalation of L- and D-Phe was further examined, and the results are shown in Fig. 2 with the calculated fraction of Phe forms in the pH 7–12 range. The amount of Phe intercalated was reached at maximum in the pH 7–8 region. Acid–base equilibrium constants of Phe are $pK_1 = 2.16$ and $pK_2 = 9.18$ at 298 K in aqueous solution, namely, Phe exists as amphoteric ion form in this pH region. AEC of LDH is determined by the amount of a trivalent cation substituted for LDH basal layer, namely, 1.00 mol/mol-Al for monovalent anion and 0.5 mol/mol-Al for divalent anion. Assuming that Phe exists as anion form, the measured amount of Phe intercalated at pH 7.0 was found to be ca. 2.7 times that of AEC of LDH, suggesting that a majority of Phe was intercalated as amphoteric ion form into the LDH interlayer in this pH region. Nakayama et al. compared the chemical shift values of amino acids between in aqueous solution and in solid state by using the ^{13}C NMR and demonstrated that a part of amino acids were intercalated as amphoteric ion in the interlayer space of the Mg–Al LDH in alkaline solutions [35]. In the intercalation of Phe in neutral and weak alkaline solutions, Phe molecule was predicted to form some molecular aggregates by the hydrophobic interaction between each phenyl group. The intercalation behavior of amino acids for LDH has been investigated by some
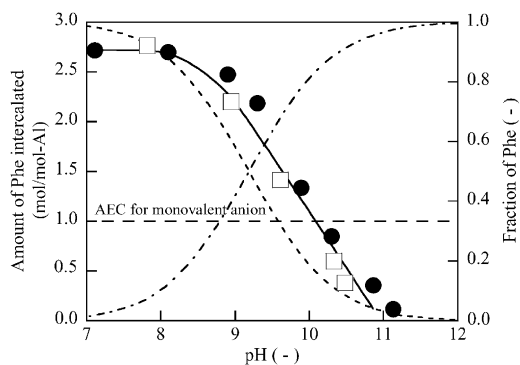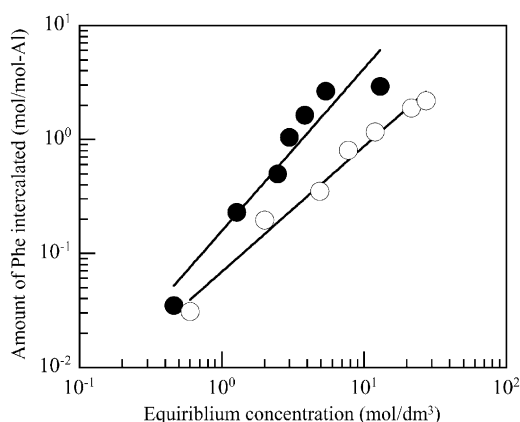
researchers [29–35]. However, such extraordinary intercalation behavior of amino acids far excess of AEC has not been reported hitherto. On the other hand, the amount of Phe intercalated at pH 10.5 was corresponding to AEC, because the most of Phe is existed as monovalent anion form. The amount of Phe intercalated was diminished with increasing the initial solution pH, because the competing OH⁻ was increased in Phe solution. It is generally known that anions having a high charge density such as CO_3^{2-}, OH⁻, and Cl⁻ are readily intercalated for LDH. As compared the charge density of OH⁻ with Phe anion, it is easily understand that OH⁻ is predominantly intercalated for the LDH.

The amounts (X/M) of L-Phe intercalated at pH 7.0 and 9.5 were determined using various initial concentrations of L-Phe, and the results are shown in Fig. 3. The amount of L-Phe intercalated was found to increase slightly with increasing the equilibrium concentration in solution. In all cases, the Freundlich isotherm, log (X/M) = $1/n$ (log C) + log k, is applicable. The X mol is the amount of adsorbed guest, M mol-Al is the amount of the LDH and C mol/dm³ is equilibrium concentration of guest. The k mol/mol-Al and n-values indicate the

adsorption amount and the adsorption strength, and these values are calculated to the intercept and slope of the isotherm, respectively. The k and n values of L-Phe for the LDH were $k = 0.16$ mol/mol-Al and $n = 0.70$ at pH 7.0 and $k = 0.07$ mol/mol-Al and $n = 0.91$ at pH 9.5, respectively. The amount of amphoteric ion form of Phe intercalated was approximately two times higher than that of anion form of Phe intercalated.

These results confirmed that amphoteric ion form of Phe was preferentially intercalated for the LDH over AEC value in neutral and weak alkaline solutions by the rehydration reaction using Zn–Al oxide precursor.

3.2. Characterization of Phe/Zn–Al LDH

The XRD patterns of the CO_3/LDH, Zn–Al oxide precursor and solid products are shown in Fig. 4. The main diffraction peaks of the CO_3/LDH ($d_{003} = 0.76$ and $d_{006} = 0.38$ nm) were observed in Fig. 4a, which values are in good agreement with that of the synthetic hydrotalcite-like compound and the crystallite size of

Fig. 4. XRD patterns of solid products. (a) CO_3/LDH, (b) Zn–Al oxide precursor, (c) OH/LDH, (d) L-Phe/LDH (pH 7.0), (e) L-Phe/LDH (pH 9.5) and (f) L-Phe/LDH (pH 10.5).

the CO_3/LDH is 33.2 nm. The destruction of the CO_3/LDH structure was achieved by heating at 773 K for 2 h, which can be seen by the disappearance of (003) and (006) reflections and the appearance of broad peaks of ZnO in Fig. 4b. As a reference, the solid product was observed to have the LDH structure ($d_{003} = 0.76$ and $d_{006} = 0.38$ nm) with the disappearance of ZnO reflection when the Zn–Al oxide precursor was rehydrated in distilled water (non-containing Phe) in Fig. 4c, meaning that the Zn–Al oxide precursor regenerated the LDH structure (OH/LDH) by the rehydration reaction. The XRD patterns of the Phe/LDH showed the expanding LDH structure with a sharp (003) spacing of 1.58 nm in Figs. 4d and e. The crystallite sizes of the Phe/LDH (pH 7.0 and 9.5) were 26.8 and 22.6 nm, respectively. Sharp (006) and (009) reflections were also observed at 0.79 and 0.54 nm, supporting that Phe/LDH was single phase with significant order. However, the diffraction peaks, $d_{003} = 0.76$ and $d_{006} = 0.38$ nm, were also observed, indicating that a part of the Zn–Al oxide precursor reconstructed the OH/LDH. The broad diffraction peaks with LDH structure ($d_{003} = 0.80$ and $d_{006} = 0.40$ nm) were observed for the Phe/LDH (pH 10.5) in Fig. 4f. The crystallite size of the Phe/LDH (pH 10.5) was 15.2 nm, suggesting that the crystallite size of the Phe/LDH was increased with increasing the amount of Phe intercalated. Assuming a thickness of 0.48 nm for the LDH hydroxide basal layer, the interlayer space is calculated as 1.10 (pH 7.0 and 9.5) and 0.32 nm (pH 10.5), respectively. Molecular size of Phe is 0.88 nm in length, 0.59 nm in width, and 0.31 nm in thickness, therefore, the interlayer space is larger than the molecular size of Phe. As shown in Fig. 1, the amount of Phe intercalated was substantially differed, supporting that the orientation of Phe in the LDH interlayer space was altered by the amount of Phe intercalated. These expanded basal spacing of both the Phe/LDH confirmed the intercalation of Phe for the LDH interlayer space.

The FT-IR spectra of the solid products are shown in Fig. 5. A broad absorption peaks in the 2800–3600 cm^{-1} region and 1560 cm^{-1} are assigned to O–H group stretcher and deformation vibration of the hydroxide basal layer or interlayer water molecule. The strong peak at 1375 cm^{-1} is attributed to the stretching mode of CO_3^{2-}. The lattice vibration modes of the LDH sheets are observed by M–O (550, 590, and 840 cm^{-1}) and O–M–O (430 cm^{-1}) vibrations. The strong absorption peaks of alkyl C–H stretch and amine N–H stretch are observed in the 2900–3030 cm^{-1} region, and the absorption peaks of R–COO$^-$ antisymmetric and symmetric stretches at 1590 and 1400 cm^{-1} are observed in Fig. 5c. In Fig. 5d, the absorption peaks of alkyl C–H stretch and amine N–H stretch are hardly observed due to a smaller amount of Phe intercalated, and the absorption peak of R–COO$^-$ antisymmetric is shown at 1590 cm^{-1}. These
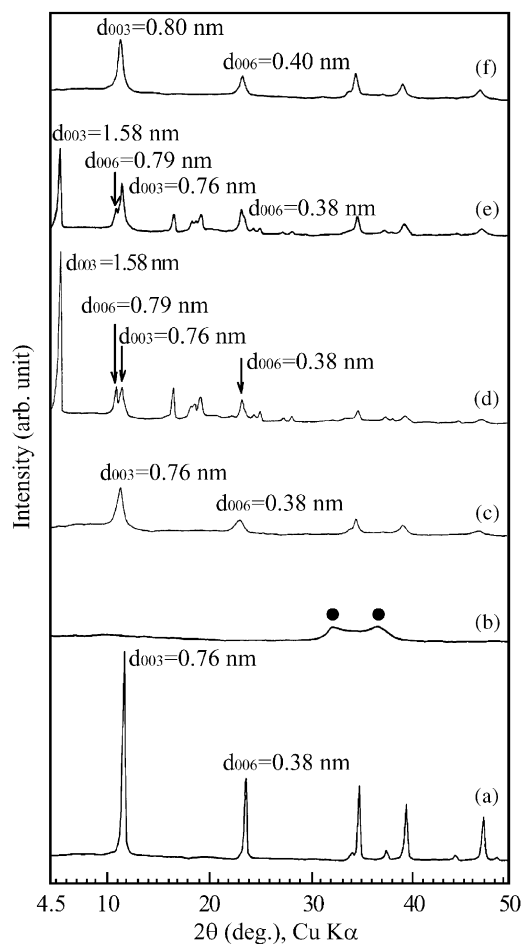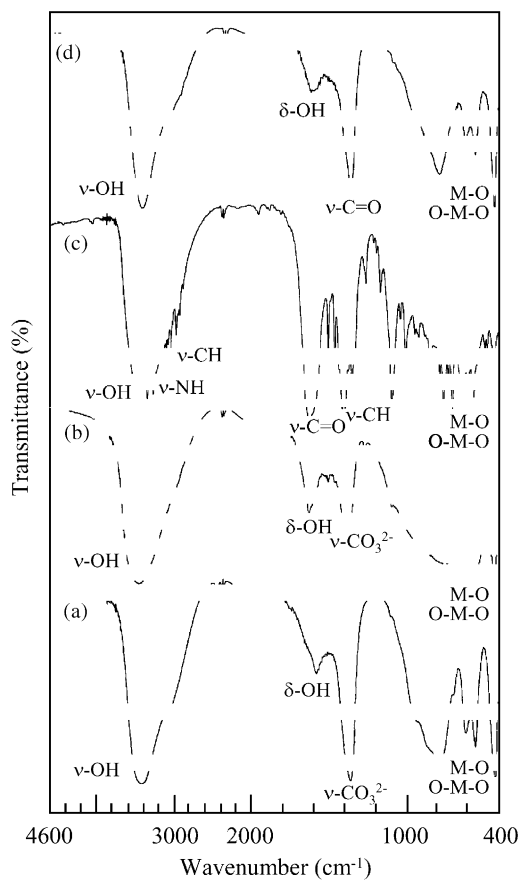
Fig. 5. FT-IR spectra of solid products. (a) CO_3/LDH, (b) OH/LDH, (c) L-Phe/LDH (pH 7.2) and (d) L-Phe/LDH (pH 10.5).
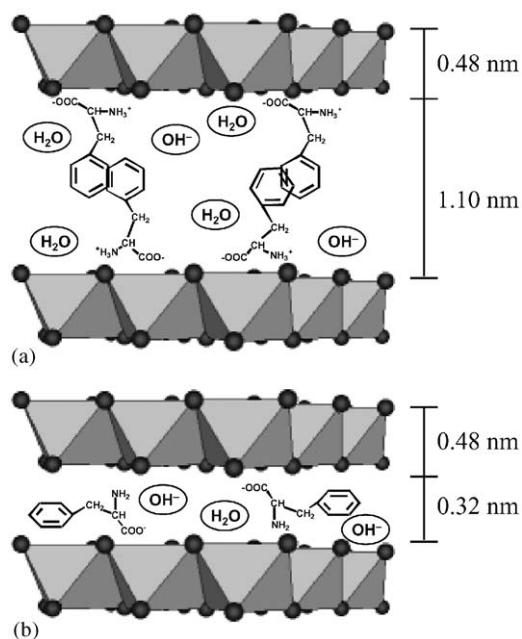

Fig. 6. Spatial orientation of Phe/LDH. (a) pH 7.0 and (b) pH 10.5.

Table 1
Maximum intercalated amount of various amino acids for Zn–Al LDH and XRD data for solid products

Amino acid		Time (days)	Amount of amino acid intercalated (mol/mol-Al)	d_{003} (nm)
D-phenylalanine	(D-Phe)	14	2.53	1.58
L-phenylalanine	(L-Phe)	14	2.45	1.58
L-leucine	(Leu)	14	2.04	1.38
L-norleucine	(n-Leu)	14	1.99	1.58
L-norvaline	(n-Val)	14	1.75	1.42
L-α-amino butylic acid	(Aba)	14	1.40	1.12
L-β-amino butylic acid	(β-Aba)	1.0	0.04	0.76
γ-amino butylic acid	(γ-Aba)	1.0	0.08	0.76
L-α-alanine	(Ala)	0.5	0.28	0.76
β-alanine	(β-Ala)	1.0	0.08	0.76
Glycine	(Gly)	0.5	0.38	0.76
L-arginine	(Arg)	6.0	0.15	0.76
L-histidine	(His)	6.0	0.28	0.76
L-aspartic acid	(Asp)	6.0	0.59	1.25
L-glutamic acid	(Glu)	6.0	0.69	1.27

peaks demonstrated that Phe was intercalated into the LDH interlayer.

The spatial orientations of the Phe/LDH are shown in Fig. 6. As a possible model, Phe bilayer was considered to be arranged vertically to the LDH basal layer, in which Phe side-chain was overlapped by hydrophobic interaction, namely, $\pi - \pi$ overlap of phenyl group (pH 7.0) as shown in Fig. 6a. As shown in Fig. 6b, the expanded interlayer space of the Phe/LDH (pH 10.5) suggested that anion formed monolayer Phe was horizontally oriented for the LDH basal layer together with the coexistence OH^- to compensate the excessive positive charge on the LDH basal layer.

3.3. Intercalation behavior of various amino acids

In this section, the intercalation behavior of various amino acids for the Zn–Al LDH has been investigated. The abbreviation of amino acid is shown in Table 1. The time dependence of various amino acids intercalated for the Zn–Al oxide precursor is shown in Fig. 7. This result indicated that the intercalated amounts of the amino acids having an aliphatic group such as Gly, Ala, Aba, n-Val, and n-Leu were influenced by the structure and

carbon number of side-chain, and increased with increasing the carbon number of side-chain. In the case of the amino acid having a long alkyl group such as Aba, n-Val, n-Leu, and Leu, the amount of amino acid intercalated was increased continuously until the equilibrium was reached after about 6 days being 1.4, 1.8, 2.0, and 2.0 times of AEC, respectively. This result indicated that the intercalation of amino acid for the LDH was influenced by the guest–guest hydrophobic interaction of side-chain. On the other hand, the amino
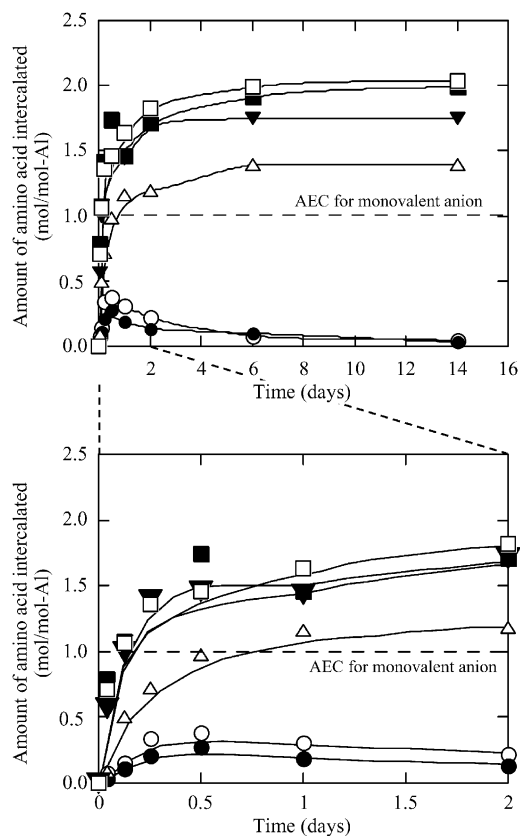
Fig. 7. Time dependence of amount of amino acids intercalated by Zn–Al oxide precursor. ○: Gly, ●: Ala, △: Aba, ▼: n-Val, □: n-Leu and ■: Leu.

Fig. 8. XRD patterns of amino acids/LDH. (a) Gly, (b) Ala, (c) Aba, (d) n-Leu and (e) n-Val.

acids having a short alkyl group such as Gly and Ala were hardly intercalated for the LDH. The maximum amount of Gly and Ala intercalated was 0.38 and 0.28 mol/mol-Al after 12 h, respectively, and these amounts were decreased with the elapse of reaction time. During the reaction process, Gly and Ala were thought to be gradually ion-exchanged with OH^- because the higher charge density anion is easily intercalated for LDH. These amino acids does not exhibit the hydrophobic interaction due to the possessing a short alkyl group such as –H and $-CH_3$.

3.4. Characterization of various amino acids/Zn–Al LDH

The XRD patterns and FT-IR spectra of the various amino acids/LDH are indicated in Figs. 8 and 9. The amount of various amino acid intercalated for the LDH and the basal spacing, d_{003}, of the amino acid/LDH are also presented in Table 1. The main diffraction peaks, $d_{003} = 0.76$ and $d_{006} = 0.38$ nm, were observed in Figs. 8a and b, and the crystallite size of the Gly and Ala/LDH was 20.5 and 15.5 nm, respectively. The expanding interlayer space suggests that a small amount of Gly and Ala was intercalated for the LDH, and OH^- was
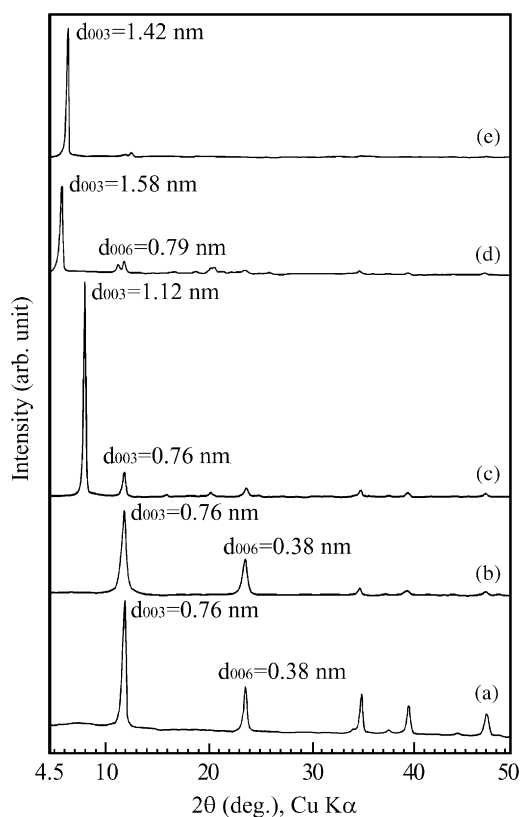
included as a competing anion. Nakayama et al. indicated that the Gly and Gly–Gly/Mg–Al LDH were not expanded the interlayer distance in spite of the intercalation of Gly and Gly–Gly. The maximum amount of Gly and Ala intercalated was 0.38 and 0.28 mol/mol-Al after 0.5 day which were less than AEC, because the hydrophobic interaction of amino acid did not occur between side-chains. The broad absorption peak due to $R-COO^-$ was observed at $1590 cm^{-1}$ in Figs. 9a and b. On the other hand, the XRD patterns of the Aba, n-Val, and n-Leu/LDH indicated the expanding LDH structure. The basal spacing, d_{003}, of the amino acids/LDH was 1.12 (Aba), 1.42 (n-Val), and 1.58 nm (n-Leu) and increased linearly with an increase in the methylene chain length of side-chain, and the interlayer space was estimated to 0.64, 0.94, and 1.10 nm, respectively. The crystallite sizes of the Aba, n-Val, and n-Leu/LDH were 26.8, 207, and 257 nm, respectively. The molecular size of amino acid is not corresponded to the interlayer distance. As a possible model, the bilayer amino acids are vertically oriented to the LDH basal layer, namely, long alkyl side-chains were also overlapped by hydrophobic interaction as same as in Fig. 5a. The amount of basic amino acids intercalated, Arg ($pK_1 = 1.82$, $pK_2 = 8.99$, and

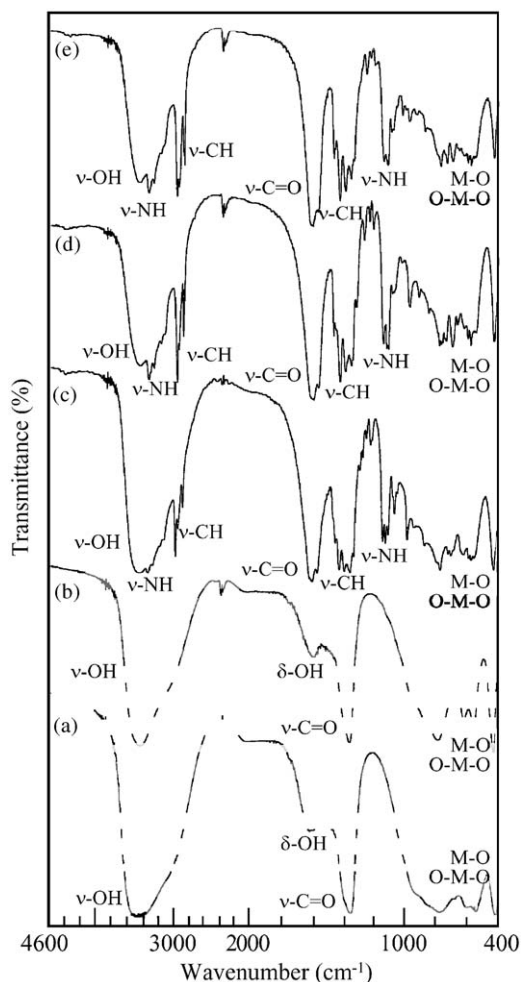Fig. 9. FT-IR spectra of amino acids/LDH. (a) Gly, (b) Ala, (c) Aba, (d) n-Leu, and (e) n-Val.

pK_R = 12.48) and His (pK_1 = 1.80, pK_2 = 9.33, and pK_R = 6.04), was 0.15 and 0.28 mol/mol-Al, respectively. Arg and His are existed as cation and amphoteric ion. In particular, Arg was difficult to be intercalated into the LDH interlayer due to the charge repulsion occurring between the LDH basal layer and the side-chain of Arg. In the case of acidic amino acids such as Asp and Glu, the amount of amino acids intercalated was 0.59 and 0.69 mol/mol-Al, respectively. As these amino acids existed as monovalent anion form, they were easily intercalated by the electrostatic force of attraction between anionic amino acid and the positive basal layer. The basal spacing, d_{003}, of the Asp and Glu/LDH was 1.25 and 1.27 nm, suggesting that the intercalated Asp and Glu was oriented vertically for the LDH basal layer with cross-linking the LDH basal layers by their carboxylate groups. Moreover, β- and γ-amino acids were failed to be intercalated into the LDH interlayer. It can be said that LDH has the preferential intercalation ability for α-amino acids.

4. Conclusions

This investigation has led to new findings for the intercalation of amino acids for the Zn–Al LDH by the calcination–rehydration reaction. Some of the important findings of this study were summarized as follows. (1) The intercalation of Phe was influenced by the solution pH, and the amount of Phe intercalated was reached ca. 2.7 times of AEC in neutral and weak alkaline solutions. (2) The intercalated Phe was oriented horizontally for the LDH basal layer in neutral solutions and vertically in alkaline solutions. (3) The intercalation of various amino acids was also influenced by the kind of side-chain of the amino acids. The amino acids having hydrophobic side-chain or negative charged were preferentially intercalated into the LDH interlayer. In future, the amino acids/LDH would be used for separation, concentration techniques, and synthesis of new organic–inorganic hybrid material.

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