Delamination of Layered Double Hydroxides Containing Amino Acids

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Various amino acids were intercalated into Mg−Al layered double hydroxides (LDHs) as interlayer anions. The goal of this approach was to create an interlayer environment that was attractive to formamide, because of hydrogen bonding, so that penetration of formamide would lead to delamination. Some of the amino acid intercalates were successfully delaminated in formamide, but others were not. The intercalates that could not be delaminated had a high amino acid content, exceeding 15−20% of the charge occupation rate. At that rate, closely packed amino acids were likely to be tightly connected to one another and to the host layers via hydrogen bonds, and therefore formamide presumably could not open or penetrate the interlayers in large volume. In contrast, there was not a clear lower threshold for charge occupation of amino acid; even LDH intercalates with charge occupations of less than 1% underwent delamination. Finally, M^{2+}−Al LDH systems other than the Mg−Al system also underwent delamination.

Introduction

Layered double hydroxides (LDHs), also known as hydrotalcite-like compounds, are ionic lamellar compounds that consist of positively charged hydroxide sheets and interlayers filled with anions and water molecules. The most common group of LDHs can be represented by the general formula $[M^{2+}{}_{1-x}M^{3+}{}_{x}(OH)_2]$-$[A^{n-}{}_{x/n}\cdot mH_2O]$, where M^{2+} and M^{3+} are di- and trivalent metal cations occupying octahedral positions within the host layers of hydroxide sheets, and A^{n-} is an interlayer anion that compensates for the charge on the layers. Positive charge on the host layers arises from isomorphous replacement of a fraction of the divalent cations with trivalent cations. The combination of Mg and Al has been studied most frequently, with a variety of Mg: Al ratios and interlayer anions.

Delamination, a process unique to lamellar compounds, is the most useful and versatile method for building nanocomposite materials. There have been many reports on the delamination of lamellar solids other than LDHs, such as smectite clays,[1−4] graphite oxides,[5−7] dichalcogenides,[8−12] metal phosphates,[13−16] and layered oxides.[17−21]

Delamination into single sheets or packets of a few sheets has facilitated the use of lamellar solids as precursors in the production of nanocomposites. For example, smectite clays have been extensively studied for the preparation of polymer−clay nanocomposites.[4,22−26] These nanocomposites show various excellent reinforcement properties, and, unexpectedly, they also show excellent flame-retardant performance, despite the fact that smectite clays are not flame retardant as such.[27] Considering the fact that LDHs are among the components of flame-retardant agents, dispersion of delaminated LDHs in a polymer could allow the preparation of a more effective alternative to brominated flame retardants, which will be banned in the future.

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(1) Norrish, K. *Discuss. Faraday Soc.* **1954**, *18*, 120.

(2) van Olphen, H. *An Introduction to Clay Colloid Chemistry: For Clay Technologists, Geologists, and Soil Scientists*; Wiley: New York, 1977; pp 150−161.

(3) Fukushima, Y. *Clays Clay Miner.* **1984**, *32*, 320.

(4) Lagaly, G. *Appl. Clay Sci.* **1999**, *15*, 1.

(5) Matsuo, Y.; Tahara, K.; Sugie, Y. *Carbon* **1997**, *35*, 113.

(6) Matsuo, Y.; Hatase, K.; Sugie, Y. *Chem. Mater.* **1998**, *10*, 2266.

(7) Liu, P.; Gong, K. *Carbon* **1999**, *37*, 706.

(8) Joensen, P.; Crozier, E. D.; Alberding, N.; Frindt, R. F. *J. Phys. C: Solid State Phys.* **1987**, *20*, 4043.

(9) Kanatzidis, M. G.; Bissessur, R.; DeGroot, D. C.; Schindler, J. L.; Kannewurf, C. R. *Chem. Mater.* **1993**, *5*, 595.

(10) Tsai, H.-L.; Schindler, J. L.; Kannewurf, C. R.; Kanatzidis, M. G. *Chem. Mater.* **1997**, *9*, 875.

(11) Heising, J.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **1999**, *121*, 638.

(12) Bezverkhy, I.; Afanasiev, P.; Lacroix, M. *Inorg. Chem.* **2000**, *39*, 5416.

(13) Alberti, G.; Casciola, M.; Costantino, U. *J. Colloid Interface Sci.* **1985**, *107*, 256.

(14) Kim, H.-N.; Keller, S. W.; Mallouk, T. E.; Schmitt, J.; Decher, G. *Chem. Mater.* **1997**, *9*, 1414.

(15) Nakato, T.; Furumi, Y.; Terao, N.; Okuhara, T. *J. Mater. Chem.* **2000**, *10*, 737.

(16) Alberti, G.; Cavalaglio, S.; Marmottini, F.; Matusek, K.; Megyeri, J.; Szirtes, L. *Appl. Catal., A* **2001**, *218*, 219.

(17) Sasaki, T.; Watanabe, M.; Hashizume, H.; Yamada, H.; Nakazawa, H. *J. Am. Chem. Soc.* **1996**, *118*, 8329.

(18) Wang, L.; Schindler, J.; Kannewurf, C. R.; Kanatzidis, M. G. *J. Mater. Chem.* **1997**, *7*, 1277.

(19) Sasaki, T.; Watanabe, M. *J. Am. Chem. Soc.* **1998**, *120*, 4682.

(20) Saupe, G. B.; Waraksa, C. C.; Kim, H.-N.; Han, Y. J.; Kaschak, D. M.; Skinner, D. M.; Mallouk, T. E. *Chem. Mater.* **2000**, *12*, 1556.

(21) Kim, J.-Y.; Chung, I.; Choy, J.-H. *Chem. Mater.* **2001**, *13*, 2759.

(22) Fukusima, Y.; Okada, A.; Kawasumi, M.; Kurauchi, T.; Kamigaito, O. *Clay Miner.* **1988**, *23*, 27.

(23) Vaia, R. A.; Jandt, K. D.; Kramer, E. J.; Giannelis, E. P. *Chem. Mater.* **1996**, *8*, 2628.

(24) LeBaron, P. C.; Wang, Z.; Pinnavaia, T. J. *Appl. Clay Sci.* **1999**, *15*, 11.

(25) Alexandre, M.; Dubois, P. *Mater. Sci. Eng.* **2000**, *28*, 1.

(26) Cho, J. W.; Paul, D. R. *Polymer* **2001**, *42*, 1083.

(27) Giannelis, E. P. *Adv. Mater.* **1996**, *8*, 29.

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The delamination-restacking process is useful for inserting bulky guests into interlayers. This strategy has already been demonstrated for smectite clays and metal phosphates.[16,28,29]

The delamination of LDHs has been reported more recently than that of other lamellar materials and has not yet been fully investigated. It was long believed that LDHs could not undergo delamination, because they have high charge densities on their sheets, and strong interaction between sheets hinders delamination in solvents.[30] Although there are few reports on the delamination of LDHs, some methods have been developed to make delamination of LDHs possible. Modification of LDHs with organic anions has been found to be effective for delamination. LDHs modified with dodecyl sulfate can be delaminated in butanol after 16 h of refluxing at 120 °C,[31] and the dodecyl sulfate intercalate also undergoes delamination, with shearing, in acryl monomer during heat treatment at 70 °C.[32] In addition, the dodecyl sulfate intercalate has been reported to be well dispersed in a polyethylene matrix after a refluxing procedure in xylene medium.[33,34]

We have reported the delamination in formamide of LDHs containing glycine.[35] We believe that, because of hydrogen bonding, intercalated glycine attracts a large volume of formamide into the interlayers, which causes the LDH sheets to come apart in the solvent. This delamination method is more effective than other methods, because the reaction occurs instantly and spontaneously and does not need any heat or refluxing.

This paper describes the extension of this method to various other amino acids as interlayer anions for the purpose of finding other LDHs that can be delaminated and that have better affinity for polymers. The affinity of glycine, the simplest amino acid, for polymers may not be sufficient for use as a modifier for LDHs: it has been reported that polymers are extracted from polymer−LDH hybrids by solvents when delaminated glycine-containing LDHs are used.[36,37] Amino acids with longer side chains may be more desirable as modifiers.

Other M^{2+}−Al LDH systems (M = Ni, Co, or Zn) containing glycine were tested to explore and expand the potential of these novel delamination systems, which might show some conductivity and catalytic properties. On the basis of the results of these investigations, the mechanism of delamination is also discussed.

Experimental Section

Preparation of LDHs. LDHs containing amino acids were synthesized by coprecipitation. Common L-α-amino acids were used. Amino acids fall into three classes based on the nature of the side chains: nonpolar, polar but neutral, and acidic or basic. Several amino acids from each group were investigated.

Table 1. Synthesis pH Values and Basal Spacings of Amino Acid-Containing LDHs

		LDH basal spacing (nm)[a]	
amino acid	synthesis pH	preparation condition #1	preparation condition #2
glycine (Gly)	10.0	0.81	0.81
alanine (Ala)	10.0	0.81	0.80
leucine (Leu)	10.0	0.82	0.80
phenylalanine (Phe)	10.0	(1.80) and 0.85	(1.75) and 0.86
serine (Ser)	10.0	0.81	0.81
tryptophan (Trp)	10.0	(1.75) and 0.89	(1.75) and 0.86
tyrosine (Tyr)	11.5	0.79	0.79
lysine (Lys)	10.5	0.80	0.80
arginine (Arg)	11.0	0.81	0.81
histidine (His)	10.0	0.80	0.79
aspartic acid (Asp)	10.0	(1.22) and 0.76	(1.23) and 0.76
glutamic acid (Glu)	10.0	(1.26) and 0.78	(1.23) and 0.77
asparagine (Asn)	10.0	0.80	0.80
glutamine (Gln)	10.0	0.80	0.79

[a] The values in parentheses are the basal spacings observed when samples were wet; these reflections were indistinct after drying.

A mixed solution of magnesium and aluminum nitrates was added dropwise to a stirred aqueous alkaline (NaOH) solution of the amino acid. During the addition of the metal solution, the reaction mixture was maintained at the starting pH by adding NaOH solution. The pH was maintained at 10.0, unless the highest pK_a of the amino acid used exceeded 10.0, in which case the pH was higher than the pK_a (Table 1). This pH ensured that the majority of the amino acid molecules existed as monovalent anions, except for the acidic amino acids aspartic and glutamic acids, which existed as divalent anions.

The Mg:Al ratio was set at a constant 3:1 for all LDHs, so that the effects of the Mg:Al ratio on delamination, already described in our previous report,[35] could be eliminated. Moreover, so that the amino acids would be intercalated well, they were used at a concentration higher than that of competing anions. Consequently, the amino acid quantities were much higher than the stoichiometric quantities. Either 1 (condition #1) or 2 (condition #2) molar equivalents relative to the total nitrates from the magnesium and aluminum nitrates was used. These two series were employed to determine the effect of amino acid content.

All of the synthetic procedures were carried out under nitrogen in a glovebag to minimize contamination from carbonate in the air. The resulting LDH slurries were washed several times by repeated centrifuging and replacement of the washing water. During the centrifuging, sealed containers were used to avoid contact with air, and the deionized−distilled water used for synthesis and washing was decarbonated by boiling and subsequent cooling in the absence of CO_2 by means of a gas-washing bottle filled with KOH solution. After coprecipitation and washing, LDHs were dried at room temperature in a glovebag filled with nitrogen. Therefore, LDHs used in this work were not exposed to air until they were dry.

Delamination. A small portion of each gently dried sample of LDH containing amino acids was mixed with formamide. To determine whether delamination would occur, 10 mg of LDH powder was first mixed with one droplet of formamide to see whether the mixture became a viscous gel. Next, 3 mL of formamide was added, and the mixture was stirred well. After standing overnight, the mixture was observed to see whether it remained a translucent colloidal solution.

To confirm delamination of LDH in colloidal solution, microscopic analysis was carried out using the colloidal solution from Gly-LDH. The colloidal solution was diluted to 5.0×10^{-4} wt % with formamide, and one droplet of this mixture was placed on a mica substrate and air-dried. Atomic force microscope (AFM) images were obtained in the contact

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(28) Toranzo, R.; Vicente, M. A.; Bañares-Muñoz, M. A.; Gandía, L. M.; Gil, A. *Microporous Mesoporous Mater.* **1998**, *173*, 173.

(29) Rodríguez-Castellón, E.; Jiménez-López, A.; Maireles-Torres, P.; Mérida-Robles, J.; Braos-García, P.; Aguilar-Armenta, G.; Flores-Loyola, E.; Marmonttini, F.; Felici, E. *Langmuir* **2001**, *17*, 3769.

(30) Albiston, L.; Franklin, K. R.; Lee, E.; Smeulders, J. B. A. F. *J. Mater. Chem.* **1996**, *6*, 871.

(31) Adachi-Pagano, M.; Forano, C.; Besse, J.-P. *Chem. Commun.* **2000**, 91.

(32) O'Leary, S.; O'Hare, D.; Seeley, G. *Chem. Commun.* **2002**, 1506.

(33) Chen, W.; Qu, B. *Chem. Mater.* **2003**, *15*, 3208.

(34) Chen, W.; Feng, L.; Qu, B. *Chem. Mater.* **2004**, *16*, 368.

(35) Hibino, T.; Jones, W. *J. Mater. Chem.* **2001**, *11*, 1321.

(36) Li, B.; Hu, Y.; Fan, W.; Li, B.; Liu, J.; Chen, Z. *Colloid Polym. Sci.* **2003**, *281*, 998.

(37) Li, B.; Hu, Y.; Zhang, R.; Chen, Z.; Fan, W. *Mater. Res. Bull.* **2003**, *38*, 1567.

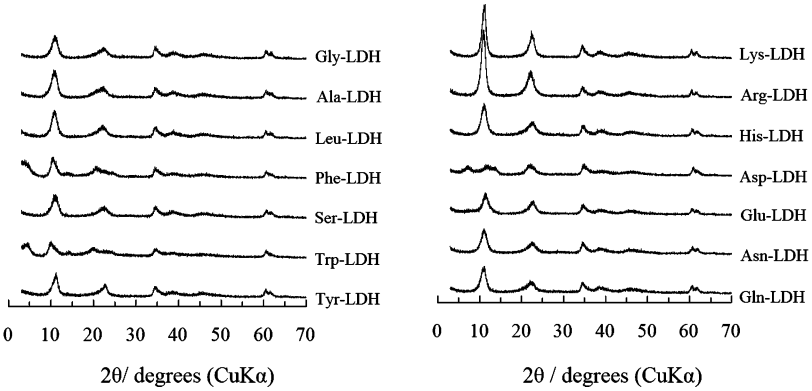

Figure 1. XRD patterns of amino acid-containing LDHs prepared under condition #1.

mode using a Seiko Instruments SPI3700/SPA300 with triangular, 100-μm-long Si_3N_4 cantilevers (spring constant = 0.2 N m^{-1}, Seiko Instruments SN-AF01). In addition, to further investigate the causes of delamination, various other polar solvents and the effect of adding salt were studied.

Characterization. LDH morphology was observed with a Hitachi S-4700 field emission scanning electron microscope (FE-SEM), which has a much higher resolution and magnification than conventional SEMs. Samples were directly observed rather than being coated with a conductive substance such as gold.

Simultaneous thermogravimetry and differential thermal analysis (TG-DTA) was carried out in air or under a nitrogen flow using a Rigaku Thermo Plus TG8120 at a heating rate of 10 °C/min^{-1}, mainly to distinguish combustion reactions in exothermic reactions. Differential scanning calorimetry (DSC) was performed in air at a heating rate of 10 °C/min^{-1} using a Rigaku Thermo Plus DSC8270, which provided data having better baselines than the DTA. X-ray diffraction (XRD) data were collected on a Rigaku MultiFlex equipped with a graphite monochromator, using Cu Kα radiation.

The amino acid content of the LDHs was measured by soaking them in an aqueous Na_2CO_3 solution for 1 day to extract the amino acid by means of ion exchange with carbonate anions. The amount of extracted amino acid in the solution was measured by electrophoresis (Ostuka Electronics CAPI-3200) and then interpolated from a calibration curve for each amino acid. Mg and Al content was determined by means of EDTA chelate titration after the LDHs were dissolved in an aqueous HCl solution.

Results and Discussion

Synthesis and Structure of Amino Acid-Containing LDHs. When the entire synthetic procedure, including drying, was carried out under nitrogen, no phase other than LDH was observed for every sample (Figure 1). In contrast, when the LDHs were dried in air, extraction of amino acids during drying was observed for some samples.

The XRD patterns of LDHs prepared under conditions #1 and #2 were almost identical. The basal spacings for all of the LDHs, except Phe-, Trp-, Asp-, and Glu-LDHs, were approximately 0.8 nm (Table 1), which means that the interlayer spacing was about 0.32 nm (the basal spacing minus the thickness of the host layers, 0.48 nm). This narrow gap is almost equivalent to the diameters of C, N, and O atoms and indicates that the amino acid molecules were horizontally oriented in the interlayers.

Phe-, Trp-, Asp-, and Glu-LDHs showed two sets of basal spacings after drying. Reflections from the larger spacings were more clearly observed when the samples were wet. Judging from their molecular lengths estimated by summation of bond lengths, the amino acid molecules in these LDHs adopted some vertical monolayer or bilayer arrangement, as previously reported (Figure 2).[38,39] Among the LDHs showing about 0.8-nm basal spacing after drying, moist Gly-LDH, for example, showed a larger basal spacing of about 1.0 nm without a change in glycine content when hydrothermal treatment was performed after coprecipitation. The larger basal spacings indicate that amino acids were successfully intercalated by the present coprecipitation method.

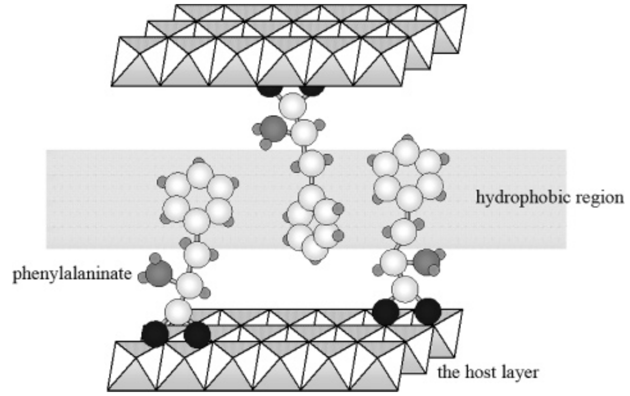

Figure 2. Schematic of Phe-LDH.

All of the tested LDHs containing amino acids showed similar morphology (Figure 3), regardless of their susceptibility to delamination. Small platelets cohered relatively tightly, lying on top of one another and forming a pielike structure like that of mille-feuille. This structure contrasts markedly with the roselike morphology of LDH containing carbonate, which is frequently studied and does not show any change in the presence of formamide.

The charge occupation rates by amino acids in the LDHs varied over a wide range, even under identical synthetic conditions (Table 2). The original goal was to obtain two series of LDHs containing similar amounts of amino acids, but the fluctuation among amino acids was far beyond the original goal. Amino acids having aromatic (phenylalanine and tryptophan) or acidic (aspartic acid and glutamic acid) side chains were highly intercalated. The same tendency has been observed for LDHs prepared from dilute amino acid solutions.[38]

In the synthesis of Arg-LDHs, the pH was set below the pK_a because the pK_a of arginine exceeds the pH at

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(38) Aisawa, S.; Takahashi, S.; Ogasawara, W.; Umetsu, Y.; Narita, E. *J. Solid State Chem.* **2001**, *162*, 52.

(39) Newman, S. P.; Cristina, T. D.; Coveney, P. V.; Jones, W. *Langmuir* **2002**, *18*, 2933.

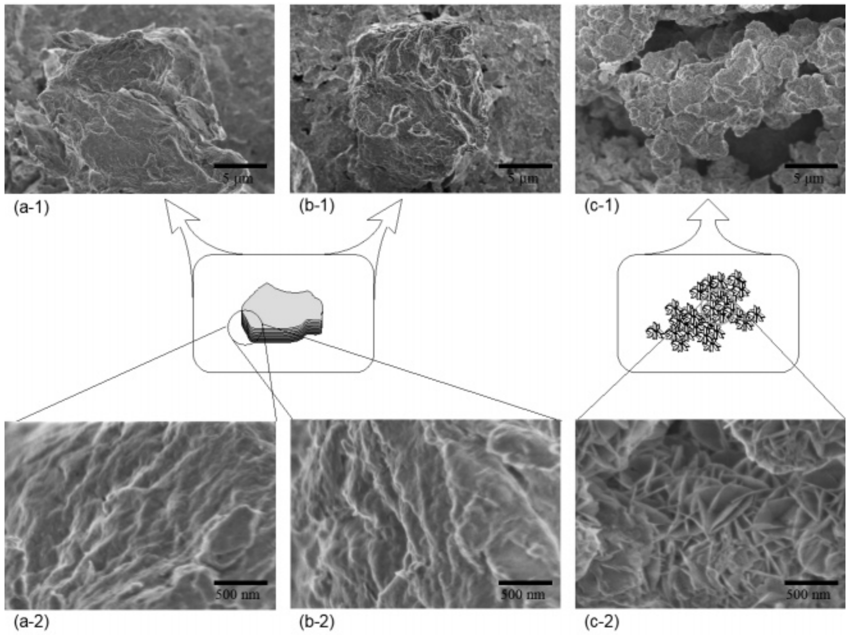

Figure 3. FE-SEM photos of (a-1 and a-2) Ala-LDH(#1), which can delaminate; (b-1 and b-2) Phe-LDH(#1), which cannot delaminate; and (c-1 and c-2) CO_3-LDH.

Table 2. Delamination of LDHs Containing Amino Acids

inserted amino acid	preparation condition #1			preparation condition #2		
	delamination test	Mg/Al	charge occupation by amino acid[a] (%)	delamination test	Mg/Al	charge occupation by amino acid[a] (%)
glycine	delaminated	2.60	6.4	delaminated	2.37	14.7
alanine	delaminated	2.70	4.8	delaminated	2.63	8.8
leucine	delaminated	2.74	10.0	no	2.59	24.9
phenylalanine	no	2.78	66.9	no	2.67	73.9
serine	partly delaminated[b]	2.74	22.0	no	2.44	29.8
tryptophan	no	2.86	71.6	no	2.79	74.4
tyrosine	no	3.00	26.0	no	2.91	18.9
lysine	delaminated[c]	2.92	2.2	delaminated[c]	2.98	5.5
arginine	delaminated[c]	2.97	0.7	delaminated[c]	2.97	0.3
histidine	delaminated[c]	2.52	18.0	no	2.49	26.5
aspartic acid	no	2.52	89.4	no	2.25	84.2
glutamic acid	no	2.84	78.1	no	2.64	87.5
asparagine	nearly delaminated[d]	2.69	15.2	no	2.34	19.8
glutamine	delaminated	2.75	0.7	delaminated	2.57	1.3

[a] Charge occupation by amino acid = molar quantity of amino acid × valence/molar quantity of aluminum × 100%. Acidic amino acids were calculated as divalent anions, and the others were calculated as monovalent. [b] The LDH became a viscous gel when a small amount of formamide was added, but most of the powder remained on the bottom after the addition of more formamide. [c] These samples lost the susceptibility to delamination after 6 months of storage but regained it upon rehydration. [d] A very small amount of the powder remained after the addition of enough formamide.

which Al redissolves.[40] This low pH may have caused poor intercalation of arginine because most of the arginine molecules were not in anionic form.

The Mg:Al ratio was fixed at 3:1 in the original solution, but the Mg:Al ratios observed in the LDH products were slightly smaller, because some of the Mg was consumed to form metal chelates with the amino acids, and these chelates remained in the solution.

Delamination of Amino Acid-Containing LDHs in Formamide. Some of the amino acid-containing LDHs were found to delaminate in formamide (Table 2). When LDHs containing amino acids were delaminated in formamide, the delamination behavior was similar to that of Na-type smectite in water. In both cases, the addition of a small amount of solvent led to the formation of a viscous gel, and the mixture turned into a translucent colloidal solution after the addition of a large amount of solvent. Moreover, the reaction occurred instantly and spontaneously.

An AFM image of delaminated Gly-LDH(#1) on mica over a large scanning area (2 μm × 2 μm) showed small aggregates consisting of a few sheets stacked stepwise. At more precise scanning (about 250 nm × 250 nm area), many thin single sheets were observed around each aggregate. The thin sheets were 0.65−0.85 nm thick and 30−100 nm wide (Figure 4). The thickness corresponds to the step interval observed for the above-mentioned aggregates and, within experimental error, falls in the range between the hydroxide sheet thickness of 0.48 nm and the basal spacing of ca. 0.8 nm estimated from XRD, indicating that the LDH was delaminated into single sheets.

Differences in Delamination Behavior among Amino Acid-Containing LDHs. A slight fluctuation

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(40) Cavani, F.; Trifirò, F.; Vaccari, A. *Catal. Today* **1991**, *11*, 173.

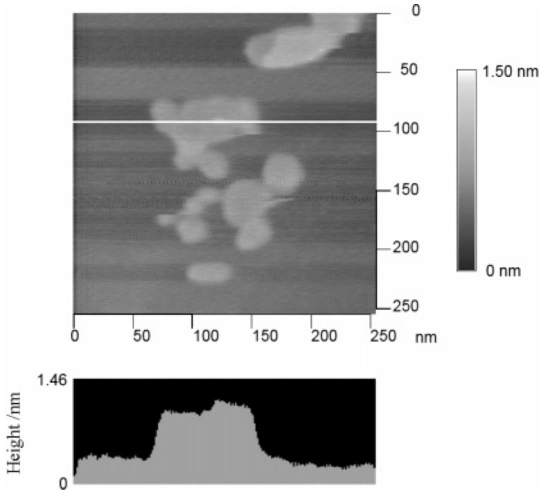

Figure 4. AFM image of delaminated LDH sheets (Gly-LDH(#1)) on a mica substrate. The white line in the image shows where the height profile was measured.

in the Mg:Al ratio in the products was observed, as mentioned earlier, but it did not seriously affect the delamination behavior. However, differences in amino acid content did. At first, it was assumed that LDHs having a high amino acid content would readily delaminate, and it was therefore expected that condition #2 would yield the greater number of intercalates that underwent delamination. However, the opposite occurred. Overall, the upper limit of amino acid content for delamination was 15−20% charge occupation.

These results can be explained by invoking a model in which the interlayers are tightly shut because of a hydrogen-bonding network. As the amino acid content is increased, amino acid molecules become closely packed. Neighboring amino acid molecules likely make tight connections among themselves and with the host layers via hydrogen bonds. Divalent anions of acidic amino acids can connect the host layers above and below via the two carboxyl groups, and this type of connection may be stronger than the other types.

The original goal was to intercalate amino acids into the LDHs to attract a large volume of formamide by means of hydrogen bonding, and it was expected that the influx of formamide would lead to delamination. However, it turned out that so many hydrogen bonds were formed during synthesis of the intercalates that formamide penetration was hampered. In addition, the hydrophobic regions created by hydrophobic moieties in the side chains (Figure 2) seemed to repel the polar solvent formamide (in the same way that Phe-LDH repels water, as reported by Newman et al.[39]), and this repulsion may also have hindered delamination.

These mechanistic speculations do not imply a clear lower threshold for amino acid content. Indeed, even arginine and glutamine at charge occupations of less than 1% worked well for delamination, although when formamide was added to Arg- and Gln-LDHs, they took longer (about 5 min) to become viscous gels than the other LDHs did.

To confirm that hydrogen bonding is the driving force for delamination, the following tests were carried out. First, several solutions were prepared by adding a polar solvent (methanol, ethanol, acetone, propylene carbonate, water, or *N*-methylformamide) in 1:1 volumetric ratio to the colloidal solution in which Gly-LDH had been delaminated with formamide. All mixtures were stable colloidal solutions just after mixing, but a gellike sediment was obtained from some of the mixed media after centrifuging at 1500 rpm for 10 min. Sedimentation occurred when methanol, ethanol, acetone, and propylene carbonate were used, whose relative dielectric constants ($D = 20-65$) are much smaller than that of formamide ($D \approx 110$). When solvents with higher D (ca. 80−180), water and *N*-methylformamide, were used, no sediment was obtained. The relative dielectric constant D reduces the Coulombic force between charged particles by a factor of $1/D$. Thus, delaminated sheets of LDH in colloidal solution are stabilized by a balance of electrostatic interactions. Next, Gly-LDH was added to formamide containing 0.001−0.5 M NaCl. At greater than 0.1 M NaCl, a large amount of LDH was not delaminated and was deposited immediately. This result indicates that NaCl disturbs coordination of Gly-LDH with formamide, a process known as solvation. Solvation is usually induced by electrostatic interaction, such as dipole−dipole attraction or hydrogen bonding. Finally, a variety of polar solvents were tested for their ability to induce delamination. The solvents ranged from amphiprotic solvents to aprotic solvents and included water, methanol, ethanol, methylene glycol, ethylenediamine, triethanolamine, *N*-methylformamide, *N*,*N*-dimethylformamide, ethyl formate, methyl acetate, propylene carbonate, and acetone. Among these solvents, formamide was the only solvent to induce delamination. Hydrogen bonding is an especially strong type of dipole−dipole attraction between molecules in which hydrogen is covalently bonded to atoms of strongly electronegative elements such as oxygen or nitrogen. The formamide molecule contains one oxygen atom and one nitrogen atom, and, among the organic solvents tested, the formamide molecule has the highest ratio of strongly electronegative elements to other elements. These facts strongly imply that hydrogen bonding is the driving force for delamination.

For some LDH intercalates, a change with the passage of time was observed: after 6 months of storage, intercalates of lysine, histidine, and arginine lost their ability to undergo delamination but regained that ability upon rehydration in a humid atmosphere for 12 h. This result indicates that LDHs did not undergo delamination because of the loss of some interlayer water.

When droplets of delaminated LDHs in formamide were repeatedly cast onto glass slides and subsequently dried at about 30 °C, crystalline, highly oriented LDHs were obtained, and they showed almost the same basal spacings of about 0.8 nm as before delamination. This result indicates that the LDHs were not decomposed by the delamination procedure. No intermediate state such as crystalline swelling was observed during drying. The swelling state may not be stable because of the high charge density on the LDH sheets. Interestingly, some restacked LDHs after drying showed two sets of basal spacings that were close to each other.

Thermal Decomposition Behavior of Amino Acid-Containing LDHs. LDHs that could not be delaminated in formamide had large, sharp exothermic peaks on their DSC curves before or during the collapse of the layered structure occurring at 350−450 °C (Figure 5).

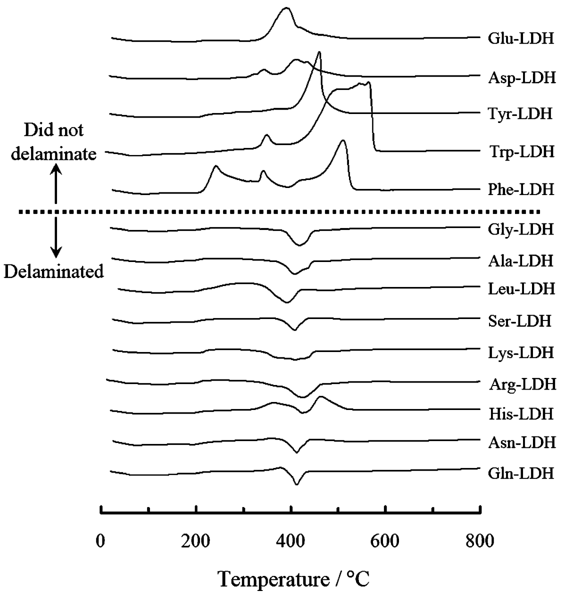

Figure 5. DSC curves measured in air for amino acid-containing LDHs prepared under condition #1.

That most of these exothermic reactions were combustive reactions was confirmed by comparison of DTA measurements in air and in nitrogen. Careful examination of the DSC curves for the LDHs that could be delaminated reveals differences in peak temperatures, broadness of peaks, and shoulders on the peaks. Peak temperatures can be shifted when Mg:Al ratios are changed.[41,42] However, peak temperatures varied even among Ala-, Leu-, and Ser-LDHs, which have nearly the same Mg:Al ratio. Therefore, unique DSC curves were obtained for LDHs that could be delaminated as well as for those that could not be delaminated.

In general, amino acids show large endothermic decomposition peaks at 200−300 °C, and, for some amino acids, decomposed remainders show broad exothermic peaks at temperatures higher than 500 °C. However, sharp and large exothermic peaks were observed for LDHs that could not be delaminated. Moreover, LDHs having amino acid contents at or just below the upper limit under condition #1, Leu-, Ser-, His-, and Asn-LDHs, had small exothermic peaks on their DSC curves, and the corresponding peaks became larger when the amino acid content was higher than the upper limit under condition #2. Exothermic peaks were not observed until the amino acid content reached 15−20% of anion occupation, and this turning point was exactly matched to the threshold of amino acid content for delamination. It is reasonable to assume that amino acids in the interlayers would tend to aggregate with increasing amino acid content and that a hydrophobic region would form as a result. Therefore, formation of the hydrophobic region, whose role in delamination was discussed earlier, is strongly associated with exothermic decomposition of the LDHs.

Investigation of Various M^{2+}−Al LDH Systems. In addition to the Mg−Al system, Zn−Al, Ni−Al, and Co−Al LDHs containing amino acids were synthesized. The M^{2+}:Al ratio was set at 3:1, and glycine was used as the amino acid. Synthesis was carried out by coprecipitation at a pH of 10.0. The quantity of added glycine was considerably decreased, to twice the stoichiometric quantity ([glycine] = 2[Al]), because the chelate compounds formed by these divalent metals in aqueous solution are much more stable than those formed by Mg ions, and the compounds do not precipitate easily if a large amount of amino acid is present in the solution. Furthermore, it was anticipated that a decrease in the amount of glycine would not be an obstacle for delamination, on the basis of the finding in this study of Arg- and Gln-LDHs that even a very low amino acid content can work well for delamination. As part of this series, Mg−Al−Gly LDH was also prepared with the smaller amount of glycine.

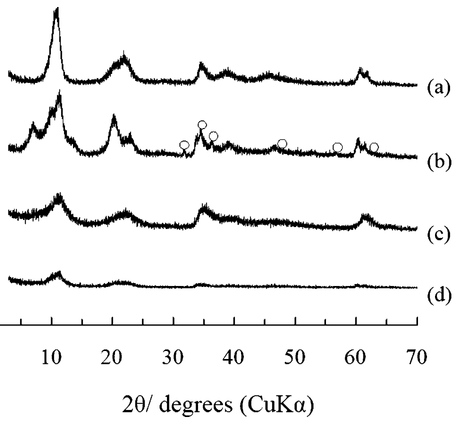

Figure 6. XRD patterns of (a) Mg−Al−Gly LDH, (b) Zn−Al−Gly LDH, (c) Ni−Al−Gly LDH, and (d) Co−Al−Gly LDH. Diffraction peaks corresponding to ZnO are labeled with open circles.

All four of the LDHs became viscous gels when a small amount of formamide was added. After the addition of more formamide, Mg−Al−Gly and Co−Al−Gly LDHs were completely delaminated. Zn−Al−Gly LDH was almost completely delaminated, and a very small amount of powder remained. Nearly half of the Ni−Al−Gly LDH was delaminated. The XRD pattern of Zn−Al−Gly LDH had multiple basal spacings and showed that this LDH contained ZnO (Figure 6). Some phase other than LDH might remain as a powder when formamide was added. Although the amount of delamination depended on the M^{2+} metal in the host layers, these results indicate that delamination occurs in a similar manner in various M^{2+}−M^{3+} LDH systems other than Mg−Al LDH.

Conclusions

Some amino acid intercalates of LDHs other than Gly-LDH were found to undergo delamination in formamide. This result indicates that amino acids with greater affinity for polymers can be used to prepare LDHs that can be delaminated, and this result is promising for the preparation of polymer−LDH nanocomposites. In addition, this study provided the following insights into the mechanism of delamination:

As the amino acid content was increased, a tight hydrogen-bonding network was presumably created among the closely packed amino acids and the host layers, and this network made opening and delamination of the interlayers impossible.

The divalent anions of acidic amino acids likely connected the host layers above and below them, which

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(41) Miyata, S. *Clays Clay Miner.* **1980**, *28*, 50.

(42) Xu, Z. P.; Zeng, H. C. *Chem. Mater.* **2001**, *13*, 4564.

was implied by the fact that the divalent anions had a vertical orientation in interlayers when wet, and this tight connection also seemed to prevent delamination.

When amino acids were closely packed, hydrophobic regions were created, which may have repelled formamide and assisted in preventing LDH delamination.

The proposed mechanis, that intercalated amino acids attract formamide by means of hydrogen bonding, does not imply a lower limit for amino acid content. Indeed, less than 1% of charge occupation rates of amino acid worked for delamination.

Some amount of interlayer water was indispensable for delamination, as implied by the fact that the ability to undergo delamination could be restored by rehydration after the loss of interlayer water during long storage.

Finally, $M^{2+}-M^{3+}$ systems other than Mg−Al could also undergo delamination in formamide completely or to some extent when glycine was intercalated. This result suggests that delaminated LDHs may be applicable to the preparation of novel functional materials requiring conductivity or catalytic activity, because Ni, Co, and Zn in the host layers have these properties.

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