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Preferential Intercalation of Isomers of Naphthalenecarboxylate Ions into the Interlayer of Layered Double Hydroxides

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Mixtures of naphthalenecarboxylate ions were intercalated into layered double hydroxides (LDHs) under alkaline conditions. In the case of the mixture of mono-, di-, and tetracarboxylate ions, nearly 90% of 1,4,5,8-naphthalenetetracarboxylic acid was intercalated, whereas only 0.1% of 2-naphthoic acid (2-NA) was co-intercalated into the interlayer of Mg/Al (0.7/0.3) LDH. 2-NA was preferably intercalated compared to its isomer, 1-NA, and the ratio of intercalated 2-NA and 1-NA reached 5. 2,6-Naphthalenedicarboxylic acid (2,6-NDCA) was preferably intercalated compared to its isomer, 2,7-NDCA. In the case of Zn/Al (0.7/0.3) LDH, more than 90% of 2,6-NDCA and only 24% of 2,7-NDCA were co-intercalated. These results indicate the existence of molecular recognition ability of layered double hydroxides.

Introduction

Layered double hydroxides (LDHs) consist of positively charged metal oxide/hydroxide sheets with intercalated anions and water molecules.[1–6] Their general composition may be represented as $[M(II)_{1-x}M(III)_x(OH)_2]^{x+}$-$[A_{x/n}{}^{n-}mH_2O]^{x-}$, where A^{n-} is an exchangeable anion. A variety of inorganic anions[7,8] may be exchanged into the LDH whose x equals 0.26–0.65, and the preferential intercalation of inorganic ions and gases have been reported.[9,10] Recently incorporation of organic acids between the layers have been reported by using calcined LDH.[11–15] However, preferential intercalation of isomeric organic anions of the same charge into LDHs have not yet been reported. In this study we have succeeded in the preferential intercalation of isomers of naphthalenecarboxylate ions into calcined LDH, $M_{1-x}Al_xO_{1+x/2}$ ($x = 0.30$ or 0.27; M = Mg, Zn). Naphthoic acid (NA), naphthalenedicarboxylic acid (NDCA), and naphthalenetetracarboxylic acid (NTCA) were intercalated into the interlayers of LDHs. These naphthalenecarboxylate ions are known to be useful raw materials for synthetic polyester resins.[16]

Experimental Section

Layered double hydroxides, $[M_{1-x}Al_x(OH)_2]^{x+}[(CO_3)_{x/2}]^{x-}$ (M = Mg, Zn), were prepared by the reaction of the mixture of $Mg(NO_3)_2$ or $Zn(NO_3)_2$ ($(1-x)/2$ mol/L) and $Al(NO_3)_3$ ($x/2$ mol/L) in Na_2CO_3 solution, whose pH was adjusted to ca. 10 with NaOH solution, at room temperature for 2 h. The products were dried for 48 h at 80 °C giving carbonate LDH. The LDH was calcined at 500 °C for 3 h to prepare Mg–Al or Zn–Al oxides. The compositions of the calcined LDHs (Mg/Al and Zn/Al ratio) were determined by ICP (inductively coupled plasma) emission spectroscopy.

Powdered, calcined LDH (15 mequiv/L) was reacted with naphthalenecarboxylate ions (7.5–30 mequiv/L) in a NaOH solution whose pH was adjusted to ca. 10 at 60 °C. The amounts of intercalated naphthalenecarboxylate ions were determined by GC, after the esterification of the acids, by calibration with esters from acids of known composition. The acids were precipitated as silver salts by reaction with silver ion and the salts were then reacted with methyliodide in benzene solution to give the methylesters.

The XRD powder pattern of each sample was obtained using Cu Kα radiation ($\lambda = 0.154$ nm) at 20 mA and 40 kV.

Results and Discussions

Intercalation of NA, NDCA, and NTCA ions. Mg–Al and Zn–Al LDHs were used in this study. An XRD pattern of the Zn/Al (0.7/0.3) LDH is shown in Figure 1a. Naphthalenecarboxylate ions were not directly intercalated into the LDHs because they already had intercalated carbonate ion. By heating at 500 °C for 3 h, the carbonate ion was decomposed to CO_2 and the calcined LDHs were obtained as shown in Figure 1b, where the peaks in the XRD patterns were broad and diffuse. We have already confirmed the reversibility of calcination and rehydration of the LDH's.[8] Naphthalenecarboxylate ions (10 mequiv/L) were reacted with calcined Mg/Al (0.7/0.3) LDH (15 mequiv/L), $Mg_{0.70}Al_{0.30}O_{1.25}$, under a nitrogen atmosphere at 60 °C for 5 h. After intercalation of 1-NA and 2-NA, other broad peaks were observed in the XRD patterns. From the peaks, the interlayer spacings were estimated as 7.6 and 7.8 Å, respectively, as shown in Table I. Dicarboxylic acids and tetracarboxylic acid were also interca-

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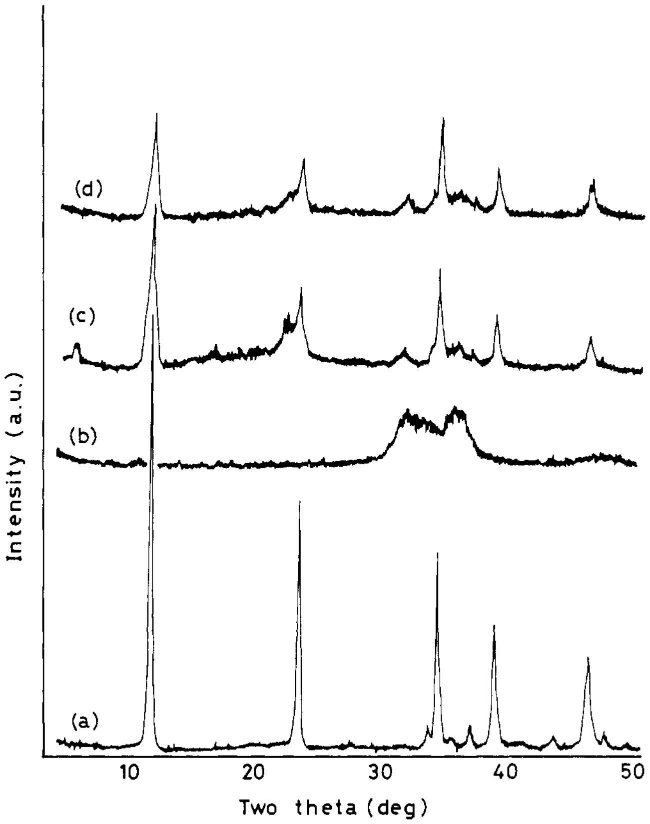

Figure 1. XRD patterns of (a) Zn/Al (0.7/0.3) LDH, (b) calcined Zn/Al (0.7/0.3) LDH, (c) 2,6-NDCA intercalate of Zn/Al (0.7/0.3) LDH, and (d) 2,6-NDCA intercalate of Mg/Al (0.7/0.3) LDH.

Table I. Interlayer Spacing of Mg/Al (0.7/0.3) LDH Intercalated Various Naphthalenecarboxylate Ions and Calculated Layer Expansions[a]

ion intercalated	interlayer spacing, Å	layer expansion, Å
1-NA	7.6	2.8
2-NA	7.8	3.0
1,8-NDCA	7.9	3.1
2,6-NDCA	7.9	3.1
2,7-NDCA	8.0	3.2
1,4,5,8-NTCA	8.2	3.4

[a] Calcined Mg/Al (0.7/0.3) LDH (15 mequiv/L) and naphthalenecarboxylate ion (10 mequiv/L) were reacted at 60 °C for 5 h under nitrogen atmosphere.

lated into Mg/Al (0.7/0.3) LDH. Figure 1d shows the XRD pattern of the 2,6-NDCA intercalate of the Mg/Al (0.7/0.3) LDH. Upon intercalation of 2,6-NDCA, 2,7-NDCA, and 1,4,5,8-NTCA into calcined LDH, the interlayer spacings measured were 7.9, 8.0, and 8.2 Å, respectively. These values are close to the value of carbonate Mg/Al (0.7/0.3) LDH. The thickness of the basic brucite layer of the Mg/Al (0.7/0.3) LDH is 4.77 Å.[17] Layer expansions were calculated from the thickness of the brucite layer yielding interlayer spacings of 2.8–3.4 Å, with a general tendency toward layer expansions as the number of carboxyl groups of the ions increase. In these cases the amount of intercalated carboxylate ion was small[18] because an excess of host to guest was used. It was assumed that the plane of the naphthalene carboxylate ions are parallel to the plane of the host layers.

Table II. Intercalation of Naphthalene Carboxylate Ions into the Interlayer of Mg/Al (0.7/0.3) LDH[a]

reaction time, min	carboxylate ion adsorbed into LDH, wt % 2-NA	2,6-NDCA	1,4,5,8-NTCA
15	19.8	63.5	100.0
60	41.3	55.3	100.0
15[b]	0.1	12.3	87.1

[a] Calcined Mg/Al (0.7/0.3) LDH (15 mequiv/L), 2-NA (2.5 mequiv/L), 2,6-NDCA (2.5 mequiv/L) and 1,4,5,8-NTCA (2.5 mequiv/L) were reacted at 60 °C under nitrogen atmosphere. [b] Concentration of each naphthalenecarboxylate ion was 10 mequiv/L.

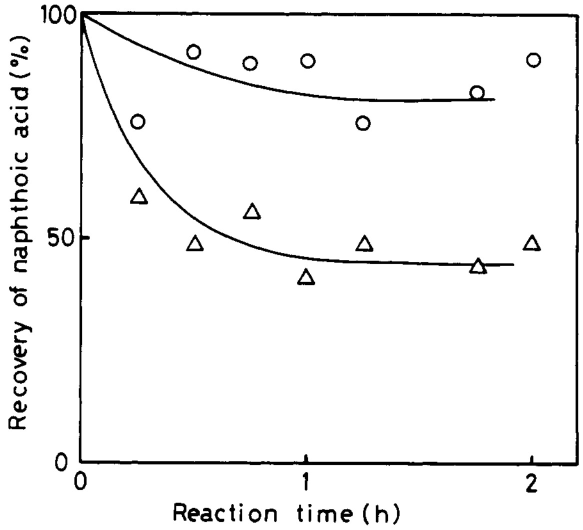

Figure 2. Preferential intercalation of naphthoic acids into the interlayer of LDH (○ 1-NA, △ 2-NA).

Intercalation of a Mixture of NA, NDCA, and NTCA Ions. The calcined Mg/Al (0.7/0.3) LDH was then reacted with a mixture of 2-NA, 2,6-NDCA, and 1,4,5,8-NTCA (2.5 mequiv/L each) under alkaline conditions. After the reaction at 60 °C for 5 h, the reaction products were filtered. The amount of unintercalated carboxylate ions was determined by GC after the esterification of the acids in the filtrate, and the amounts of intercalated carboxylate ions were estimated. In the case when the guest/host ratio was 2, 87.1% of 1,4,5,8-NTCA was intercalated, in contrast to only 0.1% of 2-NA and 12.3% of 2,6-NDCA, as shown in Table II. On the other hand, almost all of the 1,4,5,8-NTCA was intercalated after 15 min and 60 min in the case where the guest/host ratio was 0.67. These results are similar to those obtained with the benzenecarboxylate ions, where phthalic acid was more easily intercalated than benzoic acid.[14] The results indicate that the electron density of the guest is important for the intercalation, and ions having high negative charges are intercalated in preference to ions having low negative charges. This is common for clays.[19]

Intercalation of a Mixture of 1-NA and 2-NA. When the mixture of isomers of monocarboxylic acids, 1-NA and 2-NA, was reacted with the calcined Mg/Al (0.7/0.3) LDH, 2-NA was preferably intercalated as shown in Figure 2. For the reaction time from 0.5 to 2 h, about 10% of 1-NA and about 50% of 2-NA were co-intercalated. To confirm the preferential intercalation from the intercalation compound itself, the product obtained after a reaction time of 60 min was decomposed by using strong acid. Any

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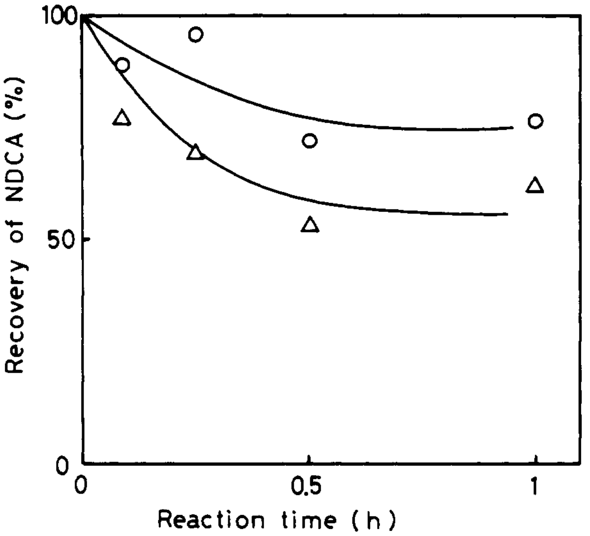

Figure 3. Preferential intercalation of naphthalenedicarboxylic acids into the interlayer of LDH (○ 2,7-NDCA, △ 2,6-NDCA).

intercalated naphthoic acids precipitated in this acid solution. Total recovery of naphthoic acids was 41.9%, and the 2-NA/1-NA ratio was 28.1/13.8, indicating a preferential intercalation. Since 1-NA and 2-NA are isomers with the same negative charge, this preferential intercalation indicates the presence of a molecular recognition ability of the LDH's.

Intercalation of the Mixture of NDCAs. A mixture of isomers of the dicarboxylic acids, 2,6-NDCA and 1,8-NDCA, in a ratio of 1.5, was reacted with calcined Mg/Al (0.7/0.3) LDH. The interlayer spacings increased to 7.9 Å upon intercalation. After reaction for 15 min, 14.2% of 2,6-NDCA and 53.3% of 1,8-NDCA were intercalated. The two carboxyl groups of 1,8-NDCA are adjacent while those of 2,6-NDCA are not. Therefore, it is possible that the difference in negative charge density causes the preferential intercalation.

The mixture of 2,6-NDCA and 2,7-NDCA was reacted for 0.125 to 1 h with calcined Mg/Al (0.7/0.3) LDH. As shown in Figure 3, 2,6-NDCA was intercalated into the LDH in preference to 2,7-NDCA. In the reaction carried out for 0.25 h, 30.3% of 2,6-NDCA was intercalated whereas only 4.4% of 2,7-NDCA was intercalated. The cationic charge of the LDH layer depends on the amount of Al and the cationic charge decreases by the reduction of the Al/(Al + Mg) ratio. It was expected that the reduction of cationic charge would cause a different preference in the intercalation. However, similar results were obtained in the case of Mg/Al (0.73/0.27) LDH, as shown in Table III.

Pronounced preferential intercalations were observed for Zn/Al (0.70/0.30) LDH. After intercalation from the mixture of 2,6-NDCA and 2,7-NDCA, a small new peak corresponding to the interlayer spacing of 16.5 Å was obtained, in addition to the large peak at 7.8 Å as shown in Figure 1c. It is possible that a mixture of products exists, including a minority product where the NDCA are intercalated perpendicular to the layers. In this case more than 90% of 2,6-NDCA and 22% of 2,7-NDCA was intercalated into the layers. The difference of charge densities between 2,6-NDCA and 2,7-NDCA is not as important because the carboxyl groups are quite separated in each case. These results show that the LDHs have the ability to recognize the nuclear isomers of NDCAs.

Table III. Selective Intercalation of NDCAs into the Interlayer of LDH[a]

LDH (atomic ratio)	reaction time, min	NDCA adsorbed into LDH, wt % 2,6-NDCA	NDCA adsorbed into LDH, wt % 2,7-NDCA
Mg/Al (0.70/0.30)	5	22.6	10.2
Mg/Al (0.70/0.30)	15	30.3	4.4
Mg/Al (0.73/0.27)	5	19.9	10.9
Mg/Al (0.73/0.27)	15	53.0	17.0
Zn/Al (0.70/0.30)	15	77.8	21.4
Zn/Al (0.70/0.30)	120	90.6	23.7

[a] Calcined Mg/Al or Zn/Al LDH (15 mequiv/L) and naphthalenecarboxylate ion (10 mequiv/L) were reacted at 60 °C for 5 h under nitrogen atmosphere.

Conclusions

There have been many attempts toward understanding the action of clay minerals in the transformation and evolution of organic and bioorganic matter.[20] Recently, shape-selective adsorptions of some organic compounds into montmorillonite were reported, indicating a novel form of molecular recognition.[20,21]

In this study we succeeded in the preferential intercalation of nuclear isomers of naphthalenecarboxylate ions into anionic clays, Mg/Al and Zn/Al LDHs. It indicates that these layered double hydroxides have the ability of recognizing molecular structure. The mechanism of molecular recognition remains unknown. A possible explanation may be due to orientation effects of intercalated naphthalenecarboxylate ions, and their subsequent intermolecular forces.

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