

Incorporation Properties of Aromatic Compounds into Hydroxy Double Salt

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Hydroxy double salts (HDSs) comprise a class of layered materials that are similar to layered double hydroxide (LDH) and show a comparable intercrystalline reactivity. We already reported an incorporation reaction of alkyl carboxylate into the HDS layer and their individual conformation in the interlayer space. In this paper we report the incorporation reaction of aromatic compounds into the HDS layer and the preferential incorporation of isomers of aromatic compounds into HDS layers via an anion exchange reaction. In result, the reaction of isomers with HDS indicates that HDS compounds have the ability of recognizing molecular structure of isomers

Key words: hydroxy double salt (HDS), anion exchangeable compound, preferential incorporation

1. INTRODUCTION

Increasing interests exist in incorporation chemistry of inorganic layered compounds because incorporation compounds are candidates of functional materials such as catalysts, sorbents¹⁾. Recently, sharp-selective adsorption of some organic compounds into clay minerals were reported, indicating a novel form of molecular recognition²⁾. We already reported that Layered Double Hydroxide (LDH) incorporated preferably one isomer of naphthalene-carboxylate ions compared to its another isomer³⁾.

LDH⁴⁾ and Hydroxy Double Salt (HDS)⁵⁾ are known as anion exchangeable compounds and can incorporate various organic and inorganic compounds by electrostatic intercalation or ion exchange reactions. After all, LDH layers have positive charges although HDS layers don't have any charge. Preferential incorporation of isomeric organic anions of the same charge into HDSs has not yet been reported.

Recently, HDS has attracted much interest as anion-

exchangeable compound because of their lamellar structure. The general formula of HDS is $[(M^{II}_{1-x}, M'^{II}_{1+x})(OH)_{3(1-y)}]^+ A^{n-}_{(1+3y)/n} mH_2O$ in which M and M' correspond to divalent metal such as Cu, Co, Ni, Mg, Zn, Cd, Fe, Mn. A^{n-} is an anion situated between the cation layers of $[(M^{II}_{1-x}, M'^{II}_{1+x})(OH)_{3(1-y)}]^+$, and can be either monovalent, Cl^- , NO_3^- , Br^- , I^- , ClO_4^- , MnO_4^- , NO_2^- , or divalent, SO_4^{2-} , CO_3^{2-} . Using these compounds, we have further reported the preparation of Zn-HDS exchanged by alkyl chain, *via* anion exchange reaction⁶⁾.

Here we present some results of a selective incorporation of aromatic compounds into HDS layer, *via* anion exchange reaction.

2. EXPERIMENTAL

The parent compound, zinc-nitrate-HDS $[Zn_2(OH)_8(NO_3)_2 \cdot 2H_2O]$, was prepared by the method reported by Stählin and Oswald with some modifications⁷⁾. And another parent compounds, copper-nitrate-HDS $[Cu_2(OH)_3(NO)_3]$, was prepared by

the method reported by Meyn et al.⁸⁾

Zinc-nitrate-HDS and copper-nitrate-HDS were reacted with aromatic compounds. Aromatic mono-carboxylate such as 1- or 2-naphthoate (1- or 2-NA), and aromatic di-carboxylate such as 2, 6- or 2,7-naphthalenedicarboxylate (2,6- or 2,7-NDCA) were reacted with zinc-nitrate-HDS and copper-nitrate-HDS. The dispersion including zinc-nitrate-HDS and copper-nitrate-HDS and objective carboxylate sodium solution were occasionally shaken for 24 hr at 333 K. After the reaction, the solid was washed with degassed water and methanol for several times and dried under high vacuum.

Zinc and copper-nitrate-HDS have potential to separate aromatic carboxylate mixtures. The dispersions of aromatic carboxylate mixture were allowed to stand for several hours at 333 K. The amounts of intercalated aromatic carboxylate were determined by gas chromatography (GC), after the esterification of the acids, using calibration care of known composition. The acids were esterified by trimethyl-silyldiazomethane ($(\text{CH}_3)_3\text{SiCHN}_2$, 10 v/v% in hexane).

The XRD powder pattern of each sample was obtained using Cu K α radiation ($\lambda = 0.154$ nm) at 20 mA and 40 kV. Characterizations of all samples were performed by FT-IR spectra on a Horiba FT-200. The amount of metylester performed by GC on a Shimadzu GC-9A with a 120 (60 \times 2) m capillary column.

All other reagents were of analytical-reagent grade.

3. RESULTS AND DISCUSSION

XRD patterns of obtained compounds are shown in Figure 1. The interlayer distances of the compounds, zinc-nitrate-HDS (1) and copper-nitrate-HDS (2) are 0.976 and 0.695 nm, respectively. They show a series of (00*l*) reflections with an equivalent interval,

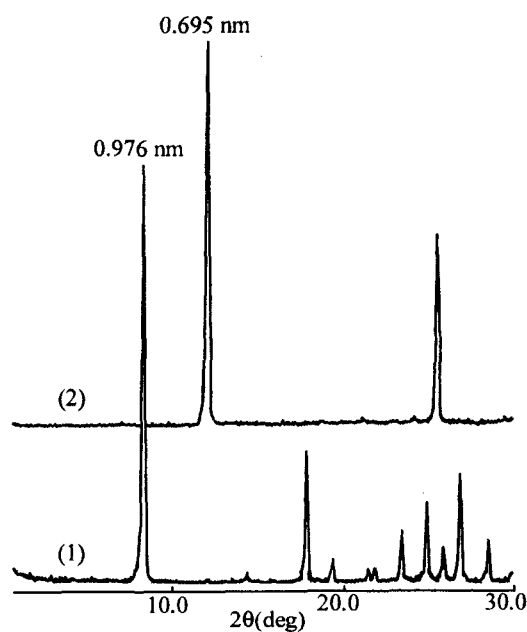


Figure 1. XRD patterns of (1) $\text{Zn}_3(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, (2) $\text{Cu}_2(\text{OH})_3\text{NO}_3$.

indicating layered structures.

We have already confirmed that nitrate anions incorporated into zinc-HDS were exchanged with alkyl mono- and di-carboxylate and interlayer spacing of zinc-alkyl mono- or di-carboxylate-HDS increased depending on the size of alkyl mono- and di-carboxylate anions⁶⁾.

Zinc-nitrate-HDS and copper-nitrate-HDS were reacted with aqueous solutions of aromatic mono- or di-carboxylic acid at 333 K for 24 hr. XRD patterns of aromatic mono- and di-carboxylic acid sodium salt did not show a series of (00*l*) reflections. By the reaction of zinc-nitrate-HDS and copper-nitrate-HDS with aromatic mono- or di-carboxylate ions, new peaks appeared in the XRD patterns. They also show a series of (00*l*) reflections with an equivalent interval suggesting that the reaction product of HDS with aromatic mono- or di-carboxylic acid was not a salt; an anion exchange reaction between nitrate ion in the HDS and aromatic mono- and di-carboxylic acid was suggested.

The interlayer spacing increased to 1.28–2.41 nm by

Table I XRD data and layer expansion of aromatic carboxylate exchanged HDS

Aromatic carboxylate (size [nm]*)	Zn ₃ (OH) ₈ (NO ₃) ₂ ·2H ₂ O		Cu ₂ (OH) ₃ NO ₃	
	Interlayer space	Layer expansion	Interlayer space	Layer expansion
	[nm]	[nm]	[nm]	[nm]
1-naphthoate (0.76)	2.09	1.54	1.58	0.89
2-naphthoate (0.93)	2.41	1.86	2.01	1.32
2,6-naphthalene di-carboxylate (1.11)	1.65	1.10	1.28	0.59
2,7-naphthalene di-carboxylate (1.02)	1.64	1.09	1.33	0.64

* Distance between two farthest hydrogen

the reaction as shown in Table I. Layer expansions were calculated from the thickness of the hydroxyl layer and interlayer spacing. In the case of aromatic mono-carboxylate, layer expansions were larger than those expected from the molecular sizes of them. It suggests the bilayer formation of organic guests between the layers. In the case of aromatic di-carboxylate, layer expansions were smaller than the molecular sizes. We postulate a bridged structure in which the two ends of the guest have reacted with surface hydroxyl groups of opposing inner planes.

Copper-nitrate-HDS was reacted with a mixture of 1-NA and 2-NA under alkaline conditions. After the reaction at 333 K for several hours, the reaction products were filtered. GC determined the amount of unintercalated carboxylate ions after the esterification of the acids in the filtrate, and the amounts of intercalated carboxylate ions were estimated.

In the case when the initial 2-NA/1-NA ratio in the solution was 1.0, 2-NA/1-NA ratio after the reaction with copper-nitrate-HDS decreased with increasing reaction time as shown in Figure 2. These results are similar to those of zinc-nitrate-HDS obtained with the 2-NA/1-NA, where 2-NA was more easily intercalated than 1-NA.

Since the interlayer space of 1-NA-HDS is much smaller than that of 2-NA-HDS, 1-NA is easily de-intercalated from the interlayer space of 2-NA-HDS.

From the present experiment, it is considered that 2-NA was strongly incorporated into HDS compounds. In the case of 2,6- and 2,7-NDCA mixture, 2,6-NDCA was preferential incorporated into the HDS layer. Since 1-NA/2-NA and 2,6-NDCA/2,7-NDCA are isomers with the same negative charge, this preferential intercalation indicates the presence of a recognition ability of the HDS.

In the previous work³⁾, we reported that the electron density of the guest is important for the incorporation, and ions having high negative charges are intercalated in preference to ions having low negative charges. This is common for clays. The amount of naphthalene-carboxylate ions incorporated in the interlayer of the LDH and the selectivity of anion uptake

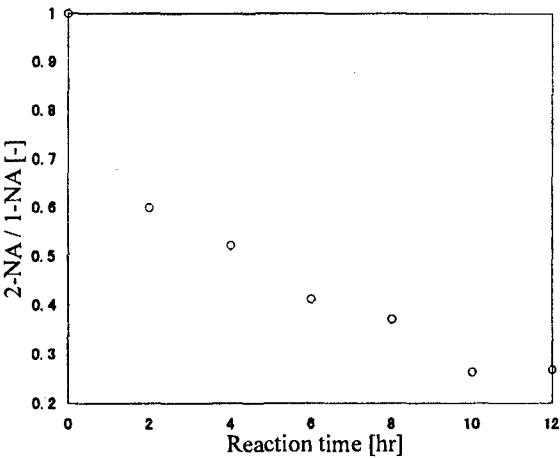


Figure 2. Recovery of naphthoate ions from reacted solution

Table II Preferential incorporation with several mixtures into copper- or zinc-HDS

Mixture	Copper-nitrate-HDS	Zinc-nitrate-HDS
1-NA and 2-NA	2-NA	2-NA
2,6-NDCA and 2,7-NDCA	2,6-NDCA	2,6-NDCA
1-NA and 2,6-NDCA	2,6-NDCA	2,6-NDCA
1-NA and 2,7-NDCA	2,7-NDCA	2,7-NDCA
2-NA and 2,6-NDCA	2-NA	2,6-NDCA
2-NA and 2,7-NDCA	2-NA	2-NA

increased with increasing charge density of the ions.

However, in the reaction of mixture of 2-NA and 2,6-NDCA or 2,7-NDCA with copper-nitrate-HDS, 2-NA was preferably incorporated into HDS layer rather than 2,6-NDCA and 2,7-NDCA. In the case of 1-NA, reverse results were obtained. In the reaction of mixture of 1-NA and 2,6-NDCA or 2,7-NDCA, 2,6-NDCA or 2,7-NDCA was preferable incorporation (Table II).

These results are quite different from those obtained with naphthalene carboxylate ions into LDH³⁾, where 2,6-NDCA was more easily incorporated than 2-NA. In the case of LDH, the amount of incorporated carboxylate ion was small, because an excess of host to guest was used; layer expansions were very few. It was interpreted that the plane of the naphthalene carboxylate ion was parallel to the plane of the host layer. Therefore, the different behavior of the preferential intercalation arises from the different incorporated geometry of incorporated compounds between LDH and HDS. In other words, preferential incorporation was caused by the difference in packing arrangement in the interlayer space. To elucidate the mechanism of preferential incorporation, an experiment using a large amount of incorporated carboxylate ion must be carried out in the case of LDH. Anyhow, while the mechanism of the molecular recognition is still not clear, we can confirm the existence of a molecular recognition ability

and preferential incorporation of HDS.

CONCLUSIONS

We succeeded in establishing a preferential incorporation of naphthalene mono- and di-carboxylate ions into the copper- and zinc-HDS indicating the existence of a molecular recognition ability of the hydroxy double salt.

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