Preparation and intercalation reactions of new layered double hydroxides

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Layer double hydroxide (LDH) is synthesized conventionally only with bivalent and trivalent cations. In this study, Zn-Zr LDH consisting of bi- and tetra-valent cations and Zn-Al-Zr LDH consisting of bi-, tri- and tetra-valent cations were prepared and reacted with organic monocarboxylic, dicarboxylic and aromatic acids at 60°C. Interlayer spacing of the prepared LDH ($Zn-Zr-CO_3$) was 0.67 nm that was small compared to usual LDH ($Zn-Al-CO_3$) of 0.76 nm in the case of carbonate anion as the guest. $Zn-Al-Zr-CO_3$ LDH has two interlayer spacing, 0.67 and 0.75 nm, that were coincidence with interlayer spacing of $Zn-Zr-CO_3$ and $Zn-Al-CO_3$ LDH. Also, DTA, TG and DTG analysis indicated that the electrostatic force between the Zn-Zr layers and carbonate anions was larger than those of Zn-Al LDH. Certainly, the carbonate anions in Zn-Zr LDH decomposed at 259°C while they in usual LDH decomposed at 230-240°C.

Keywords: Layered double hydroxide, Intercalation, Thermal analysis.

Introduction

An increasing interest exists in layered double- metal hydroxides (LDHs), which are or may be used as catalysts, adsorbents, anion exchangers, medicine and bonding materials [1-3]. We have been interested in the application of layered materials as preferential intercalation of isomers and as a novel, cost effective and environmentally friendly separation materials [4-6].

LDHs are constituted by infinite sheets of brucite-type material charged positively, where divalent cations were replaced in a fraction of x by trivalent cations in octahedral coordination. The general formula for these compounds is $(M2_{1-x}M3_x (OH)_2)^{x+} .(A^-)_x$. n H_2O, where M2 and M3 are divalent and trivalent cations, respectively and "A" represents interlamellar anion that restore the electro neutrality of the intercalation compounds. Natural LDH is known as hydrotalcite. M2, M3 and A^- of hydrotalcite are Mg, Al and CO_3^{2-}, respectively. The distance between two adjacent layers depends mainly on the nature of the interlayer species and their electrostatic interaction with the main layers. Velu et. al [7] have described the synthesis of the Mg/Al/Zr LDHs and Tichit et. al [8] have recently studied the effect of inclusion of Zr into the hydrotalicite-like structures Mg/Al, Ni/Al and Zn/Al.

We recently reported that the preparation of Zn-Ti LDH consisting of bi- and tetra-valent cations is possible [9]. The present work examines the possibility of preparation of other example consisting of bi-, tetra-valent cations Zn-Zr LDH. We have synthesized a series of LDH, one containing Zn^{2+} and Zr^{4+} cations and the other containing Zn^{2+}, Al^{3+} and Zr^{4+} cations in the brucite-like layers and simple anion (CO_3^{2-}) in the gallery region as the guest. Changes in structure and the possibility of exchange of the interlayer anion with different kinds of organic acids were examined by TG, DTG, DTA, XRD, IR and SEM.

Experimental

Materials

The Zn-Zr LDH and Zn-Al-Zr LDH were prepared by co-precipitation of zinc, zirconium and/or aluminum salts from homogeneous solution. In the case of Zn-Zr LDH, a solution of zinc chloride and zirconium chloride were mixed with urea solution under vigorous stirring and heated for long time. The percentage of zirconium is 14-20 mole%. In the case of Zn-Al-Zr LDH, the total percentage of zirconium and aluminum is 14 mole%. After filtration and washing several times in distilled water, the products were dried at 90 °C for 12 h. Zn-Al-CO_3 LDH was prepared also by the same method for comparison. For simplicity, the samples are designated here after as Zn-Zr-14 and Zn-Zr-20 depending on the percentage of zirconium in the sample.

All organic acids and sodium salts of organic acids were obtained from WAKO and T.C.I (Tokyo).

Intercalation

Typically, appropriate amount of organic acid sodium salt (0.002 mole) dissolve in 10 ml of deionized and distilled water (concentration about 0.2 M) with ultrasonic treatment. The LDH (0.24g) was mixed with the solution of organic acid under Ar-gas atmosphere and stirred at 60°C for 6h. After filtration and washing, the samples were dried under vacuum at room temperature.

Characterization

Powder X-ray diffraction (XRD) spectra were recorded on Rigaku, RINT 2200 using $CuK\alpha$ (filtered) radiation ($\lambda = 0.154$ nm) at 40 kV and 20 mA between 1.8 and 50°. Thermal analysis (TG, DTG and DTA) of powdered samples up to 800°C was carried out at a heating rate of 10 °C/min in flow of nitrogen using a Seiko SSC 5200 apparatus. FT-IR spectra (KBr disc method) were recorded on a Horiba FT-720. Scanning electron microscopy (SEM) was performed with JEOL: JSM-6330F, (15kV/12mA).

Results and Discussions

Chemical Analysis

The elemental chemical analysis result (as determined by ICP) of Zn-Zr-14 LDH shows that the Zn/Zr mole ratio is 6.1. This value agrees with the mole ratio existing in the starting solution (6.3). This means that the precipitation step was carried out effectively. The chemical analysis of Zn-Zr-14-CO_3 LDH showed that the percentage of carbon and hydrogen are 3.55 and 1.25, respectively. They were close to calculated carbon and hydrogen contents.

X-ray diffraction

The X-ray diffraction of Zn-Zr-CO_3 LDH (Figure 1c,d) showed the basal peaks of planes 00l (003), (006) and (009) and non-basal peaks (100), (101), (012) and (104) with little shift for basal peaks to higher scattering

angles (2θ) compared with those of Zn-Al LDH which has similar structure with natural and synthetic hydrotalcites [1,10]. This indicates that the thickness of the unit layer (d_{003}) decreases with the incorporation of tetravalent metal instead of trivalent metal in LDHs. Weak reflections at d=0.36 and 0.32 nm were observed as shown in Figure 1d. We assign those reflections as impurities of zinc hydroxide.

The XRD pattern of Zn-Zr-CO_3 LDH has the main peak at 0.67 nm that corresponded to interlayer spacing of the LDH as shown in Figures 1c and 1d. The peaks exhibit some common features of layered materials such as narrow, symmetric, strong peaks at low 2θ values and weaker, less symmetric lines at high 2θ values. The peak at 0.67 nm disappeared by the calcinations of the LDH at 500°C, and appearance of new peaks at high 2θ values indicates the formation of metal oxides.
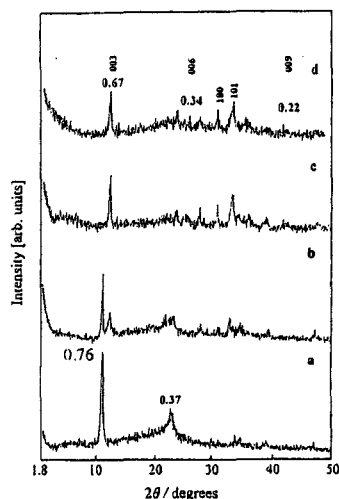

Figure 1 X-ray diffraction patterns of (a) Zn-Al-CO_3 LDH, (b) Zn-Al-Zr-CO_3 LDH, (c) Zn-Zr-14-CO_3LDH and (d) Zn-Zr-20-CO_3LDH.

Interlayer spacing, 0.67 nm of Zn-Zr-CO_3 LDH, was small compared to 0.76 nm of Zn-Al-CO_3 LDH. Pinnavaia et al. [11] and Yun et al. [12] have reported that interlayer spacing, 0.76 nm, of the LDH consisting of bivalent and trivalent cations decreased to 0.67 nm by drying the LDH at 150°C. The process was considered as desorption process of water in the space between the layers. In Zn-Zr-CO_3 LDH, zirconium cation replaced trivalent cation indicating the production of positive charge (+2). There is a possibility that electrostatic force between inorganic layers and guest compounds is stronger than that in the case of Zn-Al LDH. This speculation is supported by the comparison of the thermal characteristics of Zn-Zr LDH and Zn-Al-Zr LDH with Zn-Al LDH as described later. The XRD pattern of Zn-Al-Zr LDH showed two interlayer spacing, 0.75 and 0.67 nm. This means that Zn-Al-Zr LDH composed of two kinds of layered double hydroxides, one is Zn-Al LDH and the other is Zn-Zr LDH.

By the treatment of Zn-Zr-14 LDH with an aqueous solution of *n*-capric acid (0.002 mole) at 60 °C, two sharp peaks were observed at 2.44 and 3.01 nm and the peak of LDH itself (0.67 nm) disappeared as shown in Figure 2a suggesting complete intercalation. The interlayer ion of the LDH (carbonate) was also exchanged by various aliphatic acids. The interlayer

spacing of LDH increased to 3.39 and 4.24 nm when myristic and stearic acids whose carbon number were 14 and 18, respectively, were exchanged as shown in Figures 2b and c. Certainly, interlayer spacing of the LDH increased with the chain length of aliphatic acids as shown in Figure 2 by the reaction of LDH with monocarboxylic acid. This agreed well with that reported by Meyn et al. [2].
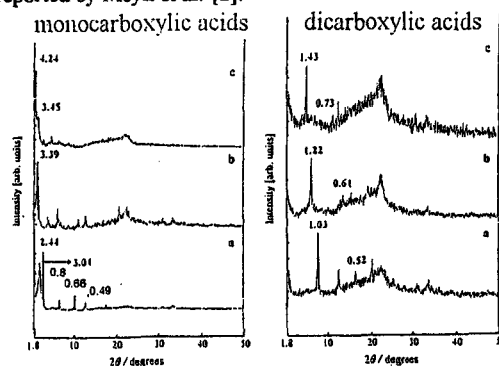

Figure 2 X-ray diffraction patterns of reaction products of Zn-Zr-14-CO_3 LDH with monocarboxylic acids (a) *n*-capric acid, (b) myristic acid and (c) stearic acid and dicarboxylic acids(a) suberic acid, (b) sebacic acid, and (c) dodecanedioic acid.

By the treatment of Zn-Al-Zr LDH with sodium salt of aliphatic acids such as *n*-capric, myristic and stearic acids, the XRD patterns (table I) showed one sharp peak and the original peaks of LDH intercalated carbonate anion were also observed. This may be due to the imperfect intercalation of aliphatic acids because of low concentration of aliphatic acids.
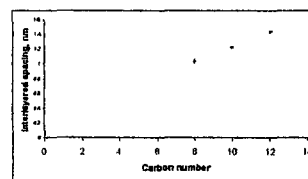

Figure 3 The effect of carbon numbers of intercalated dicarboxylic acids on interlayer spacing (nm) of Zn-Zr-14 LDH.

In the reaction of the Zn-Zr LDH with dicarboxylic acids whose carbon numbers were 8 to 12, interlayer spacing increased as shown in Figure 2, although small peak at 0.67 nm was also observed. The interlayer spacing of the dicarboxylic acid intercalation compounds increased linearly with the chain length of dicarboxylic acids as shown in Figure 3. The mean increment of interlayer spacing was 0.101 nm / CH_2 carbon. This agreed with the results previously published in case of divalent-trivalent LDH [2].
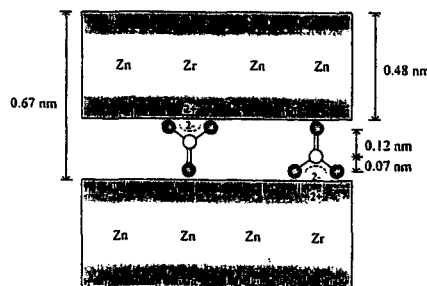

Figure 4 Schematic representation of Zn-Zr-CO_3 LDH.

Table I listed the interlayer spacing of the intercalation compound of aromatic and aliphatic acids into the LDH. In the reaction with 4-chloro phthalic acid sodium salt, interlayer increased to 1.56-1.61 nm. This indicates that the intercalation of aromatic acids is also possible into Zn-Zr LDH and Zn-Al-Zr LDH. From these XRD patterns, we can expect the orientation of carbonate anions inside Zn-Zr LDH as shown in Figure 4.

Table I: intercalation of organic acids into Zn-Zr and Zn-Al-Zr LDH at 60°C for 5h.

Host	Guest (mole%)	XRD, nm
LDH Zn-Zr-14	*aliphatic acids*	
	$CH_3(CH_2)_8COOH$ (0.002)	3.01,2.44,1.20
	$CH_3(CH_2)_{12}COOH$ (0.002)	3.39,1.81,1.24
	$CH_3(CH_2)_{14}COOH$ (0.002)	4.24,3.45,2.25
	$COOH(CH_2)_6COOH$ (0.002)	1.03,0.67,0.52
	$COOH(CH_2)_8COOH$ (0.002)	1.22,0.61,0.44
	$COOH(CH_2)_{10}COOH$ (0.002)	1.43,0.73,0.67
	aromatic acid	
	4-chlorophathlic acid (0.002)	1.56,0.48,0.66
LDH Zn-Zr-20	*organic acids*	
	$CH_3(CH_2)_8COOH$ (0.002)	2.50,2.30,1.30
	$COOH(CH_2)_6COOH$ (0.002)	1.05,0.65,0.51
	4-chlorophathlic acid (0.002)	1.61,0.91,0.66
LDH Zn-Al-Zr	*aliphatic acids*	
	$CH_3(CH_2)_8COOH$ (0.0015)	2.58,1.30,0.74
	$CH_3(CH_2)_{12}COOH$ (0.0015)	3.50,1.87,1.26
	$CH_3(CH_2)_{14}COOH$ (0.0015)	3.98,2.17,1.51
	$COOH(CH_2)_6COOH$(0.0015)	1.03,0.74,0.52
	$COOH(CH_2)_8COOH$(0.0015)	1.19,0.73,0.61
	$COOH(CH_2)_{10}COOH$(0.0015)	1.46,0.74
	aromatic acid	
	4-chlorophathlic acid (0.002)	1.56,0.48,0.66

Thermal Analysis

Thermal characteristics of the LDH were determined by TG and DTA as shown in Figure 5. The comparison among Zn-Zr LDH, Zn-Al-Zr LDH and Zn-Al LDH in TG diagram showed that the weight loss for Zn-Al LDH and Zn-Al-Zr LDH up to 200°C is 7% whilst the weight loss for Zn-Zr LDH up to the same temperature is only 1.7%. This means that the amount of interlayer water of Zn-Zr LDH is small compared to Zn-Al LDH. There is a possibility that the interlayer space of Zn-Zr LDH is narrower than that of Zn-Al LDH, and Zn-Zr LDH has no sufficient space for water.

The main weight loss occurs from 200 °C to 279 °C that corresponded to the evaporation of carbonate anions and water produced from the dehydroxylation process.
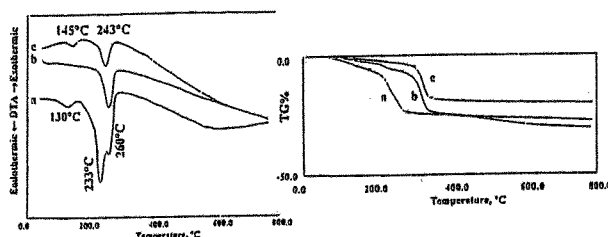
broad peak at around 130°C corresponds to the desorption of surface and interlayer water, the second sharp peak at 233°C corresponds to the decomposition of carbonate anions and the third small peak at 260°C corresponds to the dehydroxylation of hydroxide layers.

However, in case of Zn-Zr LDH, only one sharp peak was observed at 256 °C as shown in Figure 5b. This peak corresponded to desorption of carbonate anions and dehydroxylation process. These results suggested that the carbonate anions in Zn-Zr LDH have stronger interaction with brucite layers than those in Zn-Al LDH. This suggestion agreed with small interlayer spacing of Zn-Zr LDH compared to that of Zn-Al LDH.

While, in case of Zn-Al-Zr LDH (Figure 5c), two peaks were observed at 145°C and 243°C indicating that the decomposition of carbonate anions of Zn-Al-Zr LDH occurred at higher temperature than that of Zn-Al LDH and at lower temperature than that of Zn-Zr LDH. These facts supported that the Zn-Al-Zr LDH composed of Zn-Al LDH and Zn-Zr LDH.

The intercalation compounds were measured by thermal analysis (TG, DTG and DTA). The experimental data indicated that decomposition temperature of acids shifted to higher temperature by the intercalation. This data confirmed the intercalation reactions.

FT-IR Spectroscopy

The FT-IR technique has been used to identify the nature and symmetry of interlayer anions. FT-IR spectra of Zn-Al, Zn-Zr-14 and Zn-Zr-20 LDH are similar as shown in Figure 6.

Three patterns showed broad intense bands between 3600 and 3300 cm^{-1} due to the OH stretching mode of layer hydroxyl groups and of interlayer water molecules. OH band for Zn-Zr LDH, 3400 cm^{-1}, shifted to 3435 cm^{-1} for Zn-Al LDH. This shift may depend on the nature of the layer cation, as its electro-negativity will modify the electron density on the O-H bond (M-OH) and the extreme broadness of the OH band may be owing to the presence of hydrogen bonding [1].

A weak shoulder peak recorded at around 3000 cm^{-1} has been ascribed to the OH stretching mode of interlayer water molecules hydrogen-bonded to interlayer carbonate anions [13]. The bending mode band of water molecules, usually observed close to 1600 cm^{-1} [14], is recorded only as a weak shoulder on the large wavenumbers side of the stretching band at 1500 cm^{-1} in case of Zn-Al LDH, while in case of Zn-Zr LDH, no band was observed in this region. This means that the amount of interlayer water inside Zn-Zr LDH is very small. This speculation was also supported by the results of XRD, DTA and TG.
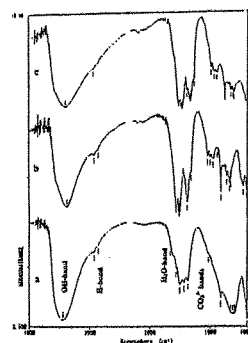

Figure 5 Thermal analysis TG and DTA of (a) Zn-Al-CO_3 LDH, (b) Zn-Al-Zr-CO_3 LDH and (c) Zn-Zr-CO_3 LDH.

DTA diagram show that Zn-Al LDH has three endothermic peaks as shown in Figure 5a. The first

Figure 6 IR Spectra of (a) Zn-Al LDH, (b) Zn-Zr-14 LDH and (c) Zn-Zr-20 LDH.

The band, 1508 cm⁻¹, together with its companion at 1382 cm⁻¹ should be due to mode v_3 of interlayer carbonate species [13,15]. This band is recorded at 1450 cm⁻¹ for free carbonate species but it splits and shifts upon a symmetry lowering. In the present case, the splitting probably due to the restricted symmetry in the interlayer space, in addition to the different electrostatic interactions because of the distortions originated by the two, different sized cations in the layers.

The weak band observed at 1045 cm⁻¹ for Zn-Zr LDH can be ascribed to the v_1 mode of carbonate. Although this band is IR-inactive in the free carbonate, it becomes activated owing to lowering of symmetry of carbonate anion in the interlayer, which is also responsible for splitting of v_3 band [16].   This band is also observed in Zn-Al LDH as a weak shoulder at 1033 cm⁻¹.

The sharp bands observed below 1000 cm⁻¹, 949 and 831 cm⁻¹, can be ascribed to mode v_2 of carbonate anion. Mode v_4 of carbonate anion could be responsible for bands at 690 and 707 cm⁻¹ [13,15].

These results indicate that the prepared Zn-Zr LDH has similar structure with Zn-Al LDH structure and it was confirmed the presence of carbonate anions and small amount of water inside the interlayer space. Also, the existence of organic compound into Zn-Zr LDH was confirmed by IR spectroscopy of intercalation compounds.
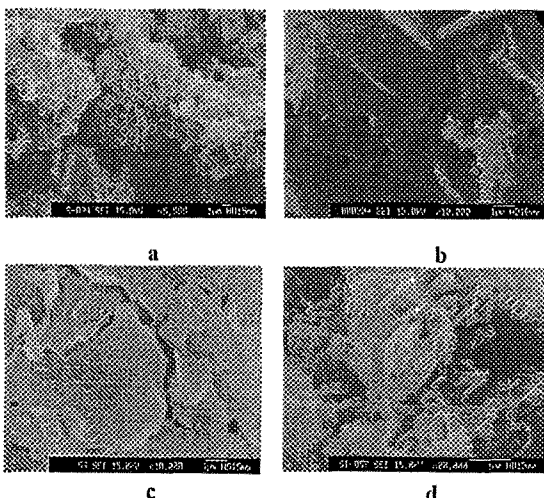

Figure 7 SEM images of (a) Zn-Zr-CO₃ LDH and (b) Zn-Al-Zr -CO₃ LDH and reaction products of Zn-Zr-14-CO₃ LDH with (c) *n*-capric acid sodium salt and (d) 4-chlorophathlic acid sodium salt.

Scanning electron microscope (SEM)

SEM images of Zn-Zr LDH and Zn-Al-Zr LDH before and after intercalation of organic compounds are shown in Figure 7.   Zn- Zr LDH and Zn-Al-Zr LDH have a clear plate-like morphology, which was typical for the LDH morphology. Also, the images indicated that the average size of the organic compounds containing crystallites is· much larger than that for the samples before intercalation reactions.

Discussion

For Zn-Zr-CO₃ LDH, interlayer spacing was calculated from the thickness of the brucite layer and the size of carbonate ion as shown in Figure 4. The observed spacing, 0.67 nm, agrees thoroughly with the calculated value. Pinnavaia et al. [11] and Yun et al. [12] have reported that basal spacing of the Mg-Al-CO₃

LDH decreased to 0.67 nm after drying at 150 °C i.e. after removing interlayer surface water. The interlayer spacing agreed with the basal spacing of Zn-Zr LDH and also, suggested that the presence of small amount of interlayer water.

The powder XRD patterns are not sufficiently high quality to allow us to carry out structure determination. However, by interlayer spacing and the size of the guest ions, orientation of guest ions was considered. From known layer thickness, 0.48 nm, the interlayer spacing available for the anion (stearate) were calculated as 3.76 nm and 2.97 nm. By comparison with the size of stearate anion, 2.25 nm, it was considered that intercalation compound has two orientations, monolayer and bilayer structure. The formation of bilayer structure can be explained by hydrophobic interaction between stearate molecules. This means that the main structure for fatty acids is bilayer structure and this consideration agrees with structures reported by K. Takagi et al. [17]. In the intercalation of dicarboxylic acids, bridging structure between the layers was suggested.

Conclusions

In this study, layered double hydroxides consisting of bivalent and tetravalent cations have been prepared for the first time. The Zn-Zr-CO₃ LDH has small interlayer spacing, 0.67 nm compared to usual Zn-Al-CO₃ LDH. The Zn-Al-Zr-CO₃ LDH showed two interlayer spacing, 0.75 and 0.67 nm, coinciding with Zn-Al-CO₃ LDH Zn-Zr-CO₃ LDH.   Anion-exchange reactions were successful in replacing the carbonate anions with monocarboxylate, dicarboxylate and phthalate anions. The preparation and characterization of Zn-Zr-organic anion LDH have been clarified in this study.

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