Preparation and Intercalation reactions
Of Zn-Sn LDH and Zn-Al-Sn LDH

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Abstract. Layered double hydroxide (LDH) is synthesized conventionally only with divalent and trivalent cations. In this study, Zn-Sn LDH consisting of di- and tetra-valent cations and Zn-Al-Sn LDH consisting of di-, tri- and tetra-valent cations were prepared and reacted with organic monocarboxylic, dicarboxylic and aromatic acids at 60°C. The 003 spacing of the prepared LDH (Zn-Sn-CO_3) is 0.67 nm which is smaller compared to that of the usual LDH (Zn-Al-CO_3) with 0.76 nm in the case of carbonate anion as the guest. Zn-Al-Sn-CO_3 LDH has two 003 spacings i.e., 0.67 and 0.75 nm which belong to Zn-Sn-CO_3 and Zn-Al-Sn-CO_3 LDH, respectively. Analysis by DTA, TG and DTG indicated that the electrostatic force between the Zn-Sn layers and carbonate anions is larger than that of Zn-Al LDH. The carbonate anions in Zn-Sn LDH decomposed at 261°C while in the usual LDH they decomposed at 230-240°C.
Keywords. Layered double hydroxide, Intercalation, Thermal characteristics, XRD patterns, SEM image

INTRODUCTION

Layered double- metal hydroxides (LDHs), can be used as catalysts, photo catalysts, catalyst supports, adsorbents, anion exchangers, medicine and bonding materials [1-4]. We have been interested in the application of layered materials for preferential intercalation of isomers and as novel, cost effective and environmentally friendly separation materials [5,6]. LDHs are constituted by infinite sheets of brucite-type material which is charged positively because some divalent cations are replaced by trivalent cations in the octahedra. 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 interlayer anion that leads to electrical neutrality of the compound. Velu et al [7] have reported the effect of the presence of tetravalent metal (Zr and Sn) into the layers of LDH and Tichit et al [8] have recently studied the effect of inclusion of Zr into the hydrotalicite-like structures (Mg/Al), (Ni/Al), (Zn/Al).

We recently reported that the preparation of Zn-Ti LDH consisting of di- and tetra-valent LDHs is possible [9]. The present work examines the possibility of preparation of other examples of LDH consisting of di- and tetra-valent cation or consisting of di-, tri- and tetra-valent cations. We have synthesized a series of LDH, one containing Zn^{2+} and Sn^{4+} cations and the other containing Zn^{2+}, Al^{3+} and Sn^{4+} cations in the brucite-like layers and simple anion (CO_3^{2-}) in the gallery region as the guest. Also, changes in structure and the possibility of exchange of the interlayer anion with different kinds of organic acids were examined.

EXPERIMENTAL
Materials

The Zn-Sn LDH and Zn-Al-Sn LDH were prepared by co-precipitation of zinc, tin and/or aluminum salts from homogeneous solution. In the case of Zn-Sn LDH, a solution of zinc chloride and tin chloride were mixed with urea solution under vigorous stirring and heated for 18h at 90°C. After filtration and washing, the samples were dried at 90°C. The percentage of tin is 14 mole%. In the case of Zn-Al-Sn LDH, the total percentage of tin and aluminum is 14 mole%. Zn-Al-CO_3 LDH was prepared by the same method for comparison. Also, $SnCl_2$ salt was used instead of $SnCl_4$ for comparison.

Intercalation

Typically, appropriate amount of sodium salt of organic acid (0.002 mole) was dissolved in 10 ml of deionized and distilled water (concentration about 0.2 M) with ultrasonic treatment. The LDH (0.24g) was mixed with 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 CuKα (filtered) radiation (λ = 0.154 nm) at 40 kV and 20 mA between 1.8 and 50°. Thermal analyses (TG, DTG and DTA) of powdered samples up to 800°C were carried out at a heating rate of 10 °C/min in flowing 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

X-ray diffraction

The XRD pattern of Zn-Sn-CO_3 LDH has the main peak at 0.67 nm that corresponded to a 003 spacing of the LDH as shown in Figures 1c.   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. Weak reflections at d=0.36 and 0.32 nm were observed as shown in Figure 1c. We assign these reflections to impurities of zinc hydroxide.

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. When $SnCl_2$ instead of $SnCl_4$ was used at the same condition for comparison, XRD indicated another structure of zinc and tin as shown in Figure 1d. Figure 1d shows peaks at 0.3, 0.27, 0.69, 0.32 nm which agree with the peaks previously reported for $(Cu_{0.1}Zn_{0.9})_5(CO_3)_2(OH)_6$ [10] and therefore, this compound may be a $Zn^{2+}Sn^{2+}$hydroxy carbonate.

The d_{003} spacing of 0.67 nm for Zn-Sn-CO_3 LDH is smaller than the 0.76 nm spacing of Zn-Al-CO3 LDH. In Zn-Sn-CO_3 LDH, tin cation replaced trivalent cation indicating the production of high positive charge (+2). It appears that the electrostatic force between inorganic layers and guest compounds in this Zn-Sn LDH is stronger than that in case of Zn-Al LDH because of higher charge density in the former. This speculation is supported by the comparison of the thermal characteristics of Zn-Sn LDH and Zn-Al-Sn LDH with Zn-Al LDH as described later.
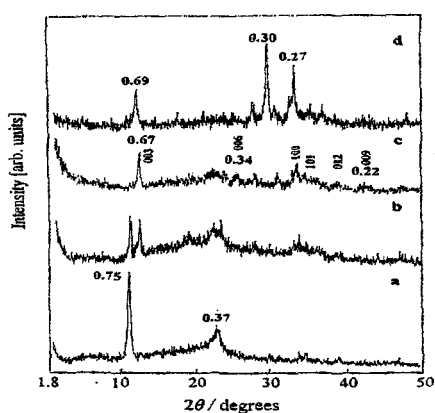

Fig.1 X-ray diffraction patterns of (a) Zn-Al-CO_3LDH (b) Zn-Al- Sn-CO_3 LDH (c) Zn-Sn-CO_3LDH and (d) $Zn^{2+}Sn^{2+}$ hydroxyl carbonate
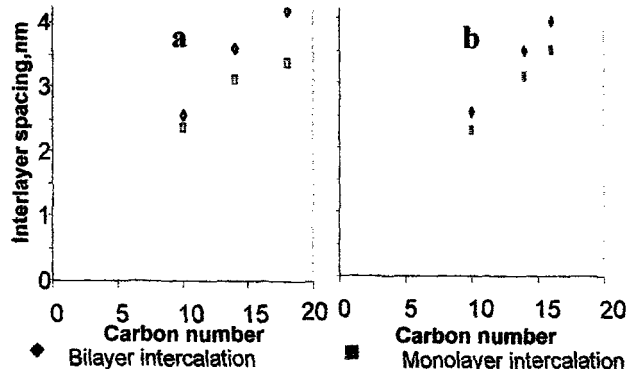

Fig.2 Effect of carbon numbers of intercalated monocarboxylic acids on interlayer spacings (nm) of (a) Zn-Sn LDH and (b) Zn-Al-Sn LDH
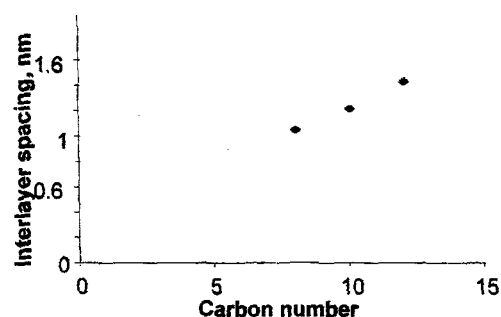

Fig.3 Effect of carbon numbers of intercalated dicarboxylic acids on interlayer spacings (nm) of Zn-Sn LDH

The XRD pattern of Zn-Al-Sn LDH showed two d_{003} spacings, 0.75 and 0.67 nm. This means that Zn-Al-Sn LDH is composed of two kinds of layered double hydroxides, one is Zn-Al-Sn LDH and the other is Zn-Sn LDH. By the treatment of Zn-Sn LDH and Zn-Al-Sn LDH with sodium salts of aliphatic acids such as *n*-capric, myristic and stearic acids, the XRD results showed two new peaks, and the d_{003} peak of LDH itself (0.67 nm) disappeared suggesting complete intercalation. The presence of two new peaks was considered that intercalation compounds of LDHs with monocarboxylic acids have two orientations, monolayer and bilayer structure.   These structures indicate later in discussion section.

In the reaction of the Zn-Sn LDH and Zn-Al-Sn LDH with monocarboxylic acids whose carbon number were 10 to 18 and dicarboxylic acids whose carbon numbers were 8 to 12, the d_{003} spacing of LDHs increased linearly with the chain length of organic acids as shown in Figures 2 and 3. This agreed with the results previously published in case of divalent-trivalent LDH [1,10]. This indicates that the intercalation of all kinds of organic acids is possible into Zn-Sn LDH and Zn-Al-Sn LDH.

Thermal Analysis

Thermal characteristics of the LDH were determined by TG and DTA as shown in Figure 4.   The comparison among Zn-Sn LDH, Zn-Al-Sn LDH and Zn-Al LDH in TG diagram showed that the weight loss for Zn-Al LDH and Zn-Al-Sn LDH up to 200°C are 7% and 5%, respectively, whilst the weight loss for Zn-Sn LDH up to the same temperature is only 3%. This means that the amount of interlayer water of Zn-Sn LDH is small compared to Zn-Al LDH. The interlayer space of Zn-Sn LDH is narrower than that of Zn-Al LDH (Figure 1) and hence there is less amount of water in the former.

The main weight loss occurs from 200 °C to 285 °C that corresponded to the decomposition of carbonate anions and water produced from the dehydroxylation process.   DTA diagram shows that Zn-Al LDH has three endothermic peaks as shown in Figure 4a. The first 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 the case of Zn-Sn LDH, only one sharp peak was observed at 261 °C as shown in Figure 4c. This peak corresponded to decomposition of carbonate anions and dehydroxylation process.

These results suggest that the carbonate anions in Zn-Sn LDH have stronger interaction with brucite
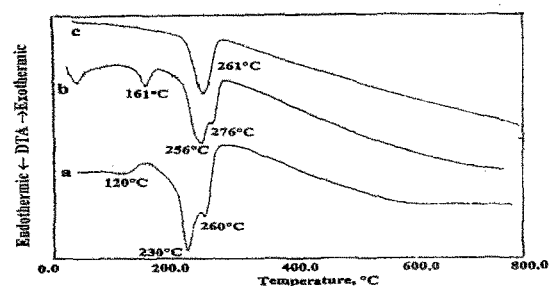

Fig.4 Differential thermal analysis (DTA) of (a) Zn-Al-CO₃ LDH, (b) Zn-Al-Sn-CO₃ LDH and (c) Zn-Sn-CO₃ LDH.

layers than those in Zn-Al LDH.

This suggestion is supported by the smaller interlayer spacing of Zn-Sn LDH compared to Zn-Al LDH.

While, in case of Zn-Al-Sn LDH (Figure 4b), three peaks were observed at 161°C, 256°C and 276°C indicating that the decomposition of carbonate anions of Zn-Al-Sn LDH occurred at higher temperature than that of Zn-Al LDH and at lower temperature than that of Zn-Sn LDH. These facts supported that the Zn-Al-Sn LDH is composed of both Zn-Al LDH and Zn-Sn LDH.

The intercalation compounds were measured by thermal analysis (TG and DTA). The experimental data indicated that decomposition temperature of organic acids Shifted to higher temperatures by intercalation as shown in Figure 5 in case of intercalation reactions of n-capric acid.
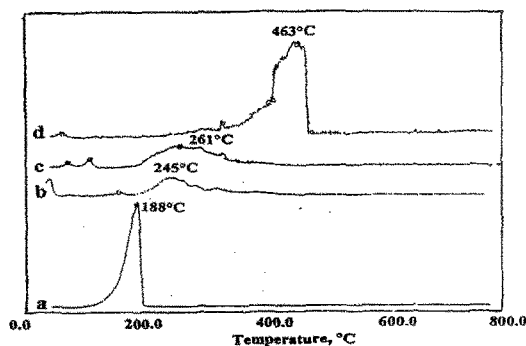

Fig. 5 Differential thermo-gravimetery (DTG) of (a) *n*-capric acid and the reaction product of *n*-capric acid sodium salt with (b) Zn-Al-Sn-CO₃ and (c) Zn-Sn-CO₃, and (d) *n*-capric acid sodium salt alone.

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-Al-Sn and Zn-Sn LDHs 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-Sn LDH and Zn-Al-Sn LDH, 3435 cm⁻¹, is similar to Zn-Al LDH and the extreme broadness of the OH band may be owing to the presence of hydrogen bonding [1,13-15].

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
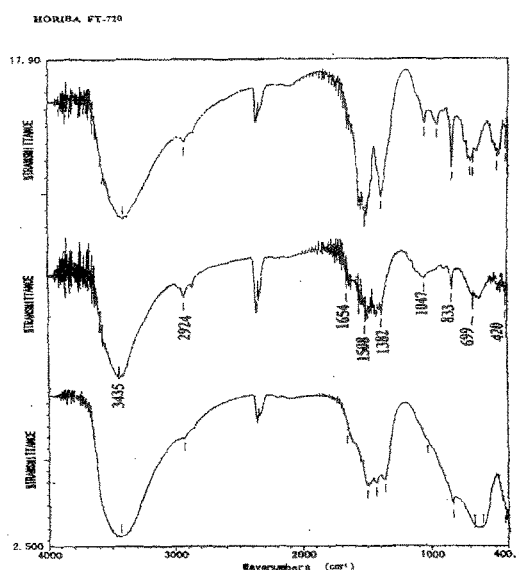

Fig. 6 IR Spectra of (a) Zn-Al LDH,(b) Zn-Al-Sn LDH and (c) Zn-Sn LDH.

interlayer carbonate anions [10,13-15]. The bending mode band of water molecules, usually observed close to 1600 cm⁻¹, 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-Sn LDH, no band was observed in this position. This means that the amount of interlayer water inside Zn-Sn LDH is very small. This speculation was also supported by the results of XRD, DTA and TG.

The band, 1508 cm⁻¹, together with its companion at 1382 cm⁻¹, should be due to mode v_3 of interlayer carbonate species [15]. The splitting is probably due to the restricted symmetry in the interlayer space.

The weak band observed at 1047 cm⁻¹ for Zn-Sn LDH can be ascribed to the v_1 mode of carbonate. 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 833 cm⁻¹, can be ascribed to mode v_2 of carbonate anion. Mode v_4 of carbonate anion could be responsible for bands at 669 and 707 cm⁻¹ [15].

These results indicate that the prepared samples Zn-Sn and Zn-Al-Sn LDHs have similar structure with usual (Zn-Al) LDH structure and it was confirmed the presence of carbonate anions and small amount of water inside the interlayer space of Zn-Sn LDH.

Scanning electron microscopy (SEM)

SEM images of Zn-Sn LDH and Zn-Al-Sn LDH before and after intercalation of organic compounds are shown in Figures (11 and 12). Zn-Sn LDH and Zn-Al-Sn 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

The X-ray diffraction of Zn-Sn-CO3 LDH (Figure 1c) showed the basal peaks of planes (003), (006) and (009) and non-basal peaks (100), (101), (012) and (104) with
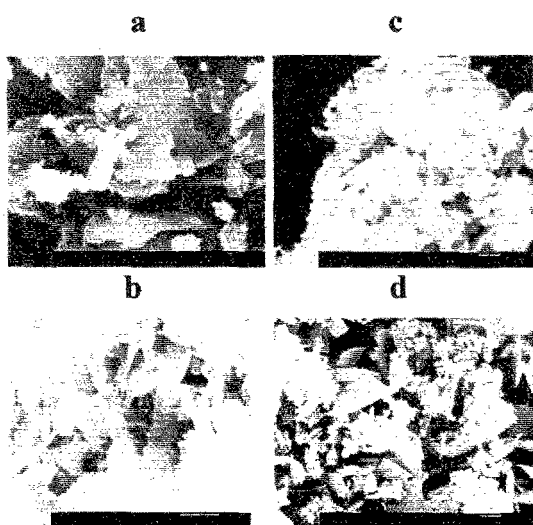
a   c

b   d

Fig.7. SEM images of (a) Zn-Al-Sn LDH, (b) Zn-Sn LDH and the reaction products of Zn-Sn LDH with (c) n-capric acid and (d) sebacic acid

little shifting for basal peaks to higher scattering angles (2θ) compared with those of Zn-Al LDH or 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.
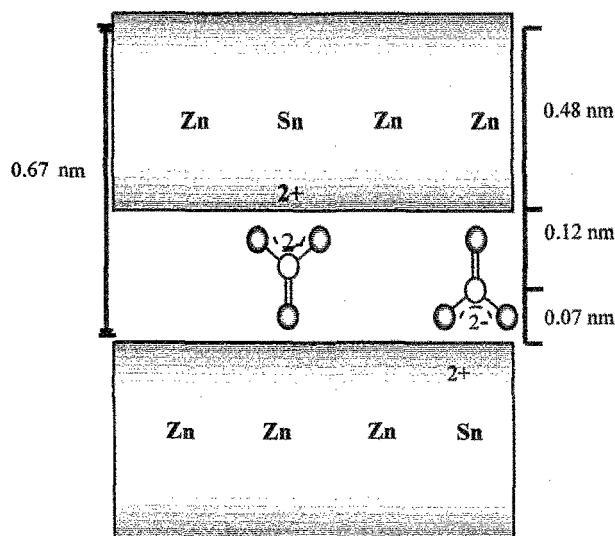

Fig.8 Schematic representation of Zn-Sn-Carbonate LDH

Gastuche et al. [10] showed that the non-basal reflections in synthetic Mg-Al hydrotalcite at d=0.273, 0.265, 0.259 and 0.246 nm were considered to be relative to the (100),(101),(012) and (104) planes and the presence of both sharp and diffuse non-basal reflections was taken as indication of a partially disordered structure.

For Zn-Sn-CO3 LDH, interlayer spacing was calculated from the thickness of the brucite layer and the size of carbonate ion as shown in Figure (8). The observed d_{003} spacing, 0.67 nm, agrees well with the calculated value. Pinnavaia et al. [12] and Yun et al. [13] have reported that basal spacing of the LDH consisting of divalent and trivalent cations (Mg-Al-CO$_3$ 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-Sn LDH and also, suggested that the presence of small amount of interlayer water.

The experimental results show that the fatty acids such as stearate anion are intercalated into the interlayer spacing and bound to the host matrix by electrostatic force with two interlayer spacings, 4.19 nm and 3.37 nm. 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 were calculated as 3.71 nm and 2.89 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 In the intercalation of dicarboxylic acids, bridging structure between the layers was suggested.

CONCLUSION

In this study, Zn-Sn layered double hydroxide consisting of bivalent and tetravalent cations has been prepared for the first time. The Zn-Sn-CO$_3$ LDH has small interlayer d_{003} spacing, 0.67 nm compared to usual Zn-Al-CO$_3$ LDH. The Zn-Al-Sn-CO$_3$ LDH showed two d_{003} spacings, 0.75 and 0.67 nm, coinciding with Zn-Al-Sn-CO$_3$ LDH and Zn-Sn-CO$_3$ LDH. Anion-exchange reactions were successful in replacing the carbonate anions with monocarboxylate, dicarboxylate and phthalate anions. The preparation and characterization of Zn-Sn-organic anion LDH have been accomplished in this study.

REFERENCE

1 F. Cavani, F. Trifiro and A. Vaccari, Catal. Today, 11, 173(1991)
2 H. Tagaya, S. Ogata, S. Nakano, J. Kadokawa, M. Karasu and K. Chiba, J. Inclusion Phenomena., 31, 231(1998).
3 S. Ogata, H. Tagaya, M. Karasu, J. Kadokawa and K. Chiba, Trans. MRS-J., 24, 501(1999).
4 S. Ogata, H. Tagaya, M. Karasu and J. Kadokawa, J. Mater. Chem., 10, 321(2000).
5 T. Takahashi, H. Adachi, J. Kadakawa and H. Tagaya, Trans. Mater Res. Soc. Jpn., 26, 2, 491(2001).
6 H. Tagaya, S. Sato, T. Kuwahara, J. Kadokawa, M. Karasu and K. Chiba, J. Mater. Chem., 4, 1907(1994).
7 S. Velu, K. Suzki, M. Okazaki, T. Osaki, S. Tomura, and F. Ohashi Chem. Mater., 11, 2163(1999).
8 D. Tichit, N. Das, B. Coq and R. Durand, Chem.Mater. 14, 1530(2002).
9 O. Saber and H. Tagaya, J. Inclusion Phenomena and Macrocyclic Chem. 45, 109(2003).
10 M. C. Gastuche, G.Brown and M.Mortland, Clay minerals, 7, 172(1967).
11 JCPDS file no. 20-1437
12 Constantino and T. Pinnavaia, Inorg. Chem., 34, 4, 883(1995).
13 S. Yun and T. Pinnavaia, Chem. Mater., 7, 348(1995).
14 A. Vaccari, Appl. Clay Sci., 14, 161(1999).
15 N. Nakamoto, Infrared and Raman Spectra of inorganic and coordination compounds, John Wiley&Sons, New York, 4th edn.(1986).