

Preparation and characterization of a new nano layered material, Co–Zr LDH

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Received: 5 January 2006 / Accepted: 1 March 2006 / Published online: 26 August 2007
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Abstract The layered double hydroxides (LDHs) are nano-ordered layered compounds and well known for their ability to intercalate anionic compounds. Most popular LDHs are prepared conventionally only with divalent and trivalent cations. In this study, Co–Zr LDH consisting of divalent and tetravalent cations was prepared and reacted with monocarboxylic acids at room temperature. The Co–Zr LDH and intercalated compounds have been characterized by chemical analysis (C, H, N analysis, ICP, and ESCA), X-ray powder diffraction, IR spectra, thermal analysis, and Scanning electron microscope (SEM). The insertion of cyanate and carbonate anions into LDH was confirmed by chemical analysis and IR spectra. XRD patterns of the prepared Co–Zr LDH showed that the interlayer spacing of the LDH is 0.78 nm. The spacing was similar to that of usual LDH in which chloride, carbonate, or bromide anion is the guest. SEM images showed that the aging time plays a vital role in the morphology of Co–Zr LDH. The morphology of Co–Zr LDH is plate-like structure and/or fibrous structure depending on the aging time.

Introduction

Nanotechnology is one of the most dynamic and fastest growing areas of research in the fields of science, engineering, and medicine. Nanoscale materials exhibit unique properties compared to their counterpart bulk materials. Nanoscale materials have a wide range of applications that

include semiconductor processing, catalysis, optics, microelectronics, environment pollutants, biomaterials, biomedicine, food science, drug delivery, and pharmacy [1–14]. Nano structured inorganic–organic or hybrid organic–inorganic nano composites will contribute to the development of science and technology.

Layered double hydroxide (LDH) materials have been extensively studied in terms of thermal evolution [15–18], textural properties [18–20], formation of nanosized metal particles [21, 22], or for environmental purpose [23]. We have been interested in the application of layered materials for preferential intercalation of isomers [24–27] and as novel, cost effective and environmentally friendly separation materials [28].

Layered double metal hydroxides are one of the nano structural materials. LDH is the inorganic layered compound having ability to intercalate anionic compounds, because LDHs are constituted by infinite sheets of brucite-type material charged positively, where divalent cations are replaced in a fraction of x by trivalent cations in octahedral coordination. The best-known compound in this class of materials is the double hydroxide of Mg with Al, known as hydrotalcite [1, 9–12]. The general formula for these LDHs is $(\text{Mg}_{1-x}\text{Al}_x(\text{OH})_2)^{x+}(\text{A}^-)^x \cdot n\text{H}_2\text{O}$, where “A” represents the interlamellar anion that restore the electroneutrality of the compound. We call these the II–III LDHs. In the case of using Li with Al, the layers acquire the composition $(\text{Al}_{2/3}\text{Li}_{1/3}(\text{OH})_2)^{1/3+}$ and become positively charged. For charge neutrality, carbonates are intercalated into the interlayer region, resulting in a compound of the nominal composition $(\text{LiAl}_2(\text{OH})_6(\text{CO}_3)_{1/2} \cdot n\text{H}_2\text{O}$ [29, 30]. We call these I–III LDHs. Although several examples of II–III LDHs have been reported, Li–Al LDH is the only known example of I–III LDH. Attempts by the authors to prepare Fe, Cr, and Ga analogs failed to yield LDHs with Li.

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Velu et al. [31] have described the synthesis of Mg/Al/Zr LDHs and Tichit et al. [32] and Das et al. [33] have recently studied the effect of inclusion of Zr into the hydroxalcalite-like structures (Mg/Al) and (Zn/Al).

We recently reported that the preparation of Zn-Ti LDH and Co-Ti LDH consisting of di- and tetra-valent cations are possible [34, 35]. The present work examines the possibility of preparation of other example consisting of bi- and tetra-valent cations LDH. This new LDH structure contains Co^{2+} and Zr^{4+} cations in host layers and cyanate and carbonate anions as the guests. The effect of aging time on the formation of LDH structure was clarified. Also, the ability of Co-Zr LDH to perform intercalation reactions with monocarboxylic acids was investigated.

Experimental

Materials

The Co-Zr LDH was prepared by co-precipitation of cobalt and zirconium salts from homogeneous solution [34, 35]. A solution of cobalt nitrate and zirconium chloride (0.047 moles) were mixed with urea solution under vigorous stirring and heated for long time. The percentage of zirconium is 25 mol%. After filtration and washing several times in distilled water, the products were dried under vacuum at room temperature. Sodium salts of monocarboxylic acids were obtained from WAKO and T.C.I (Tokyo).

Intercalation

Typically, appropriate amount of organic acid sodium salt (0.002 mol) dissolved in 10 mL of deionized-distilled water (concentration about 0.2 M) with ultrasonic treatment. The LDH (0.24 g) was mixed with the solution of organic acid under Ar atmosphere and stirred at room temperature for 72 h. After filtration and washing, the samples were dried under vacuum at room temperature.

Characterization

Chemical analyses were obtained with a Perkin Elmer CHNS/O 2400II analyzer. Powder X-ray diffraction (XRD) spectra were recorded on Rigaku, RINT 2200 using $\text{CuK}\alpha$ (filtered) radiation ($\lambda = 0.154$ nm) 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 $10^\circ\text{C}/\text{min}$ in flow of nitrogen using a Seiko SSC 5200 apparatus. FT-IR spectra (KBr disk method) were recorded

on a Horiba FT-720. Scanning electron microscopy (SEM) was performed with JEOL: JSM-6330F, (15 kV/12 mA).

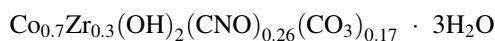
Results and discussions

Chemical analysis of Co-Zr LDH

The chemical analysis of Co-Zr LDH indicates that the percentage of carbon and nitrogen are 2.9 and 1.9, respectively. These results suggest that the Co-Zr LDH contain cyanate and carbonate anions as guests.

Elemental chemical analysis result (as determined by ICP) for Co-Zr LDH shows that the $\text{Co}^{2+}/\text{Zr}^{4+}$ mole ratio is 2.3. This means that there are some deviations comparing with the mole ratio existing in the starting solution (3). The lack of coincidence between the initial ratio of cations in the solution and the ratio in the solid isolated, is, however, rather common in the literature [36, 37] and may be ascribed to an imperfect precipitation of cobalt cation which confirmed from the color of solution after precipitation.

From chemical and elemental analysis, we can consider the structure of Co-Zr LDH as shown in the formulae:



Electron spectroscopy for chemical analysis (ESCA) supports the presence of cobalt in the solid as divalent cation. The electron binding energy of Co(2P_{3/2}) for Co-Zr LDH is 786.4 eV and this value is closer to the binding energy of Co in CoO (783.3 eV) than to the binding energy of Co in Co₂O₃ (781.2 eV).

X-ray powder diffraction

The X-ray powder diffraction for Co-Zr LDH series are given in Figs. 1 and 2. There is no XRD results reported in the literature for Co-Zr LDH. However, the XRD results of Co-Zr LDH are similar to the XRD results of the prepared Co-Al LDH, which used as a reference as shown in Fig. 1a. The measured XRD pattern of Co-Zr LDH fits well to layered structure with no evidence for other phases. 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 X-ray powder diffractions of Co-Zr LDH (Fig. 1b, c) show the basal peaks of planes hkl (003), (006), and (009). The good agreement between the values corresponding to successive diffractions by basal planes, i.e., $d(003) = 2d(006) = 3d(009)$ for Co-Zr LDH, reveals highly packed stacks of brucite-like layers ordered along axis c. Dimension c is calculated as three times the spacing for planes (003),

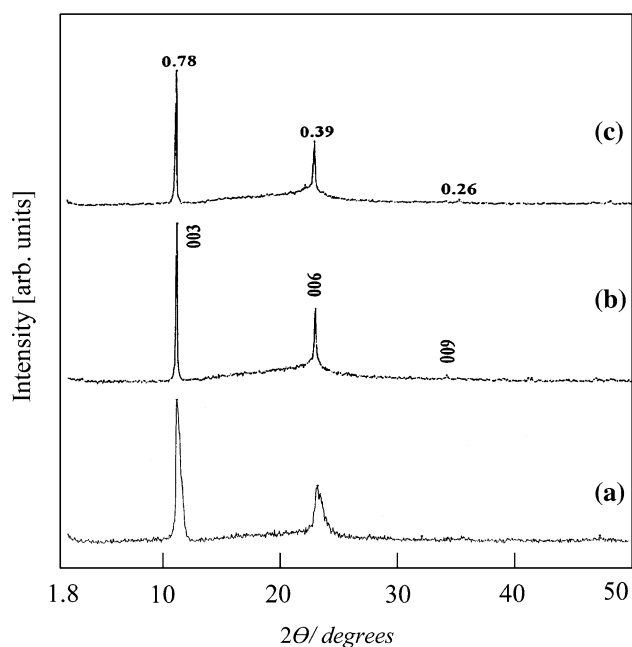


Fig. 1 X-ray diffraction patterns of (a) Co–Al LDH and Co–Zr LDH with aging time (b) 8 h and (c) 16 h

i.e., 2.34 nm. The *c* dimension is very close to that reported for natural and synthetic hydroxalcite, 2.31 nm [36, 37].

The XRD pattern of Co–Zr LDH has the main peak at 0.78 nm, which corresponded to interlayer spacing of the LDH as shown in Fig. 1b, c. This value is related to the thickness of the brucite-like layers (0.48 nm for hydroxalcite), as well as the size of the anion (and, in some cases, its orientation) and the number of water molecules existing in the interlayer.

The peaks of layered structure disappeared by the calcination at 500 °C, and appearance of new peaks at high 2θ values as shown in Fig. 2a indicates the formation of metal oxides.

By the reaction of Co–Zr LDH with *n*-capric acid at room temperature, new peaks observed at low 2θ indicating interlayer spacing 3.0 nm as shown in Fig. 2b. Also, by the treatment of Co–Zr LDH with longer organic acid, stearic acid, new peaks observed at lower 2θ indicating interlayer spacing 4.8 nm as shown in Fig. 2c. This suggests that the Co–Zr LDH can perform intercalation reactions with organic acid giving hybrid inorganic–organic nano-composites materials. Furthermore, interlayer spacing of the LDH increased with the chain length of aliphatic acids, as shown in Fig. 2, by the reaction of LDH with monocarboxylic acid.

FT-IR spectroscopy

The FT-IR technique has been used to identify the nature and symmetry of interlayer anions. The insertion of cyanate

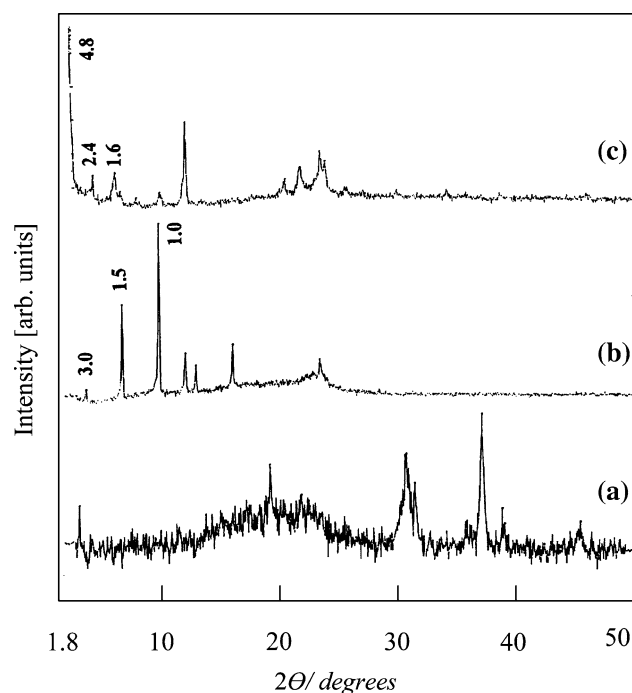


Fig. 2 X-ray diffraction patterns of Co–Zr LDH (a) after calcinations at 500 °C, and after intercalation with (b) *n*-capric acid ($\text{CH}_3(\text{CH}_2)_8\text{COOH}$), and (c) stearic acid ($\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$)

anion (NCO^-) into Co–Zr LDH is very easily demonstrated by the appearance of the ν_1 vibration in the 2230–2105 cm^{-1} region, the ν_2 vibration in the 600–650 cm^{-1} region and the ν_3 vibration in the 1190–1220 cm^{-1} region of the infrared spectrum of the materials [38].

The FT-IR spectra in Fig. 3a indicate that the interlayer (NCO^-) anions in the Co–Zr LDH are unperturbed state. This is evidenced by the strong IR absorption peak at 2221 cm^{-1} that assigned to symmetrical stretching vibration mode of CNO. As can be noted in the Fig. 3, the inclusion of carbonate anion into the interlayer space are confirmed by clear absorption peaks at 1383 and 1500 cm^{-1} [38, 39] and supported from the chemical composition.

An important phenomenon for the presence of cyanate anion into the interlayer space is the change of ν_{OH} stretching vibration at around 3500 cm^{-1} [40, 41]. It is noted that the broad OH vibration band is resolved clearly into two components which had been attributed to the presence of CN group near hydroxyl group. According to the proposed model, the hydroxyl group affected by cyanide group exhibit low wavenumber (i.e., 3467 cm^{-1}) due to the O–H bond electron density lowering, while the unaffected hydroxyl groups show high value (i.e., 3629). This phenomenon disappeared by intercalation reactions with organic acid because cyanate anion exchange with organic anion as mention later. This phenomenon agrees with the effect of nitrate into LDH as mentioned in the literature [42].

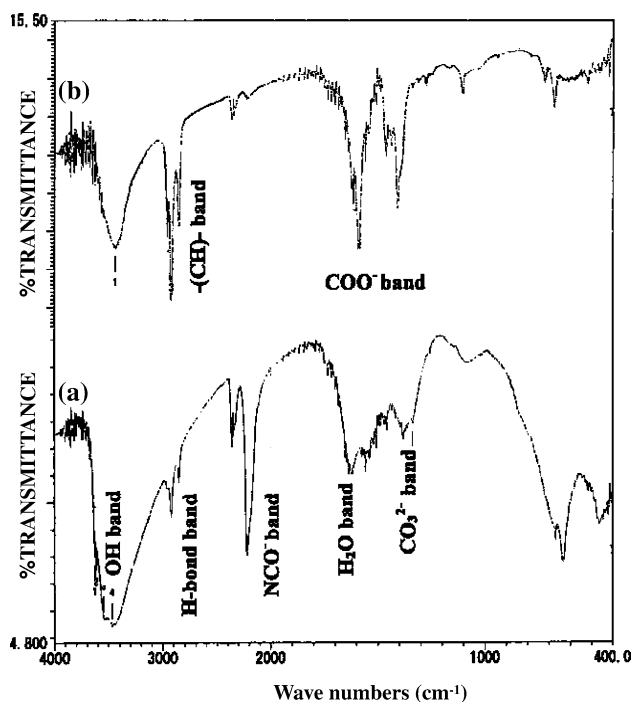


Fig. 3 IR Spectra of (a) Co-Zr LDH and (b) after intercalation with *n*-capric acid

A clear peak recorded around 2856 cm^{-1} has been ascribed to the OH stretching mode of interlayer water molecules hydrogen-bonded to interlayer carbonate and cyanate anions and supported the above-mentioned phenomenon [39, 43]. The bending mode band of water molecules observed close to 1637 cm^{-1} [44]. The weak band observed at 1055 cm^{-1} can be ascribed to the ν_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 [45]. Also, mode ν_4 of carbonate anion can be responsible for band at 690 cm^{-1} [45].

These results indicate that the prepared sample Co-Zr LDH has similar structure with usual LDH structure and it confirms the presence of carbonate anions and cyanate anions in addition to water molecules inside the interlayer space. This agrees with the chemical structure of Co-Zr LDH.

Also, the existence of organic compound into Co-Zr LDH after intercalation reactions confirmed by the results of IR spectroscopy as shown in Fig. 3b. In the IR spectrum of the reaction products of Co-Zr LDH with straight chain of aliphatic acid such as *n*-capric acid, the carbon-hydrogen stretch absorption at near 2900 cm^{-1} and the carbon-hydrogen bending band at 1470 cm^{-1} observe as shown in Fig. 3b. Furthermore, OH absorption band exist as one band because of the disappearance of the effect of cyanate anion on hydroxyl groups. Also, the new peaks at near 1540 and 1400 cm^{-1} appear. The absorption at 1540 cm^{-1}

and 1400 cm^{-1} are assigned to the symmetric and anti-symmetric stretching vibration of carboxylate. On the other hand, the carbonate and cyanate bands disappeared after intercalation reactions with organic acids.

Thermal analysis

The thermal analyses (DTA, TG, and DTG) of Co-Zr LDH are shown in Figs. 4 and 5. The presence of the divalent cation cobalt and cyanate anion, and taking into account preliminary results that indicated their oxidation (and reduction) during calcinations in air at high temperature, the thermal analysis were recorded both in air and in nitrogen, in order to identify thermal processes related to such oxidation/reduction processes.

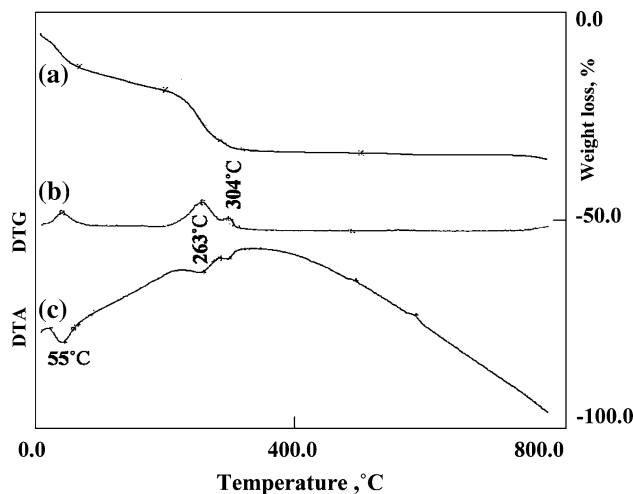


Fig. 4 Thermal analyses of Co-Zr LDH in nitrogen gas: (a) TG, (b) DTG, and (c) DTA

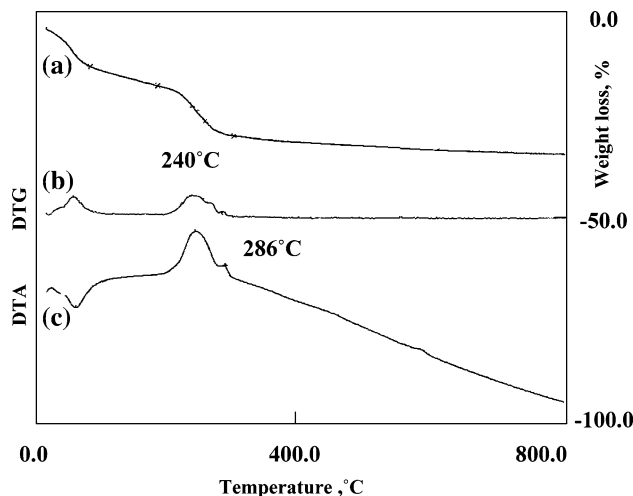


Fig. 5 Thermal analyses of Co-Zr LDH in air: (a) TG, (b) DTG, and (c) DTA

Thermal characteristics of the Co–Zr LDH in nitrogen gas were determined by TG, DTG, and DTA as shown in Fig. 4. Major losses of weight occur mainly in three steps. The TG diagram showed that the first weight loss up to 90 °C is 8% and the second weight loss up to 207 °C is 14%. These weight losses due to evaporation of surface and interlayer water. This agrees with the clear band of water which mentioned above in IR spectra of Co–Zr LDH.

The main weight loss occurs from 207 °C to 325 °C in two steps. The first step corresponded to the decomposition of cyanate anion and the second step due to the decomposition of carbonate anions and dehydroxylation process. These steps confirmed from DTG and DTA diagrams. DTA diagram shows three endothermic peaks as shown in Fig. 4a. The first peak at around 55 °C corresponds to the desorption of surface water and the second at 263 °C corresponds to the decomposition of cyanate anions. The third peak at 304 °C corresponds to the decomposition of carbonate and dehydroxylation of layers.

These processes (decomposition of cyanate, decomposition of carbonate and dehydroxylation of layers) are clearly distinguished when the analysis is performed in air instead of in nitrogen as shown in Fig. 5. The DTG of Co–Zr LDH in air showed three peaks accompanied with the main weight loss indicating three processes. Also, the DTA of Co–Zr LDH in air showed two exothermic peaks accompanied with the main weight loss. These exothermic peaks due to the oxidation of cyanate anion and Co²⁺ cation. This agrees with ESCA analysis that confirmed the presence of cobalt as divalent cation.

Differential thermal gravimetric curves of monocarboxylic acids and Co–Zr intercalation compounds of them are shown in Figs. 6 and 7. The experimental data indicated that decomposition temperature of monocarboxylic acids Shifted to higher temperatures by intercalation where the decomposition temperature of *n*-capric acid, 188 °C, and stearic acid, 249 °C shifted to higher temperatures,

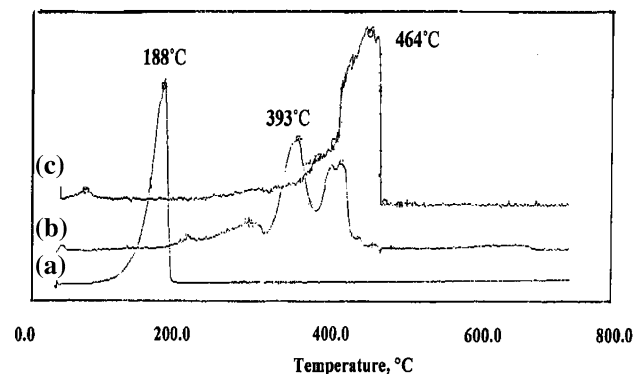


Fig. 6 Differential thermal gravimetric (DTG) of (a) *n*-capric acid only, (b) the reaction product of Co–Zr LDH with *n*-capric acid, and (c) *n*-capric acid sodium salt only

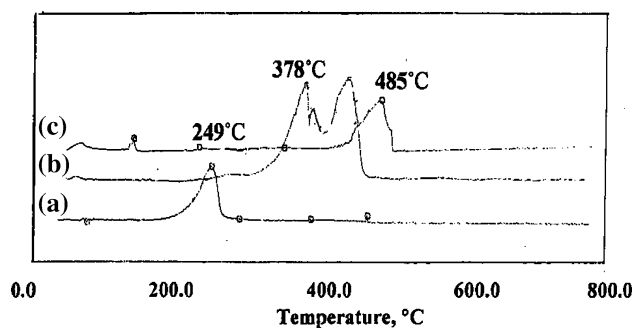


Fig. 7 Differential thermal gravimetric (DTG) of (a) stearic acid only, (b) the reaction product of Co–Zr LDH with stearic acid, and (c) stearic acid sodium salt only

393 °C and 378 °C, respectively, by intercalation. This DTG analysis agreed with TG and DTA data. These results suggest occurrence of the intercalation reaction.

Scanning electron microscope (SEM)

SEM images of Co–Zr LDH at different aging time are shown in Figs. 8 and 9. SEM images show that the

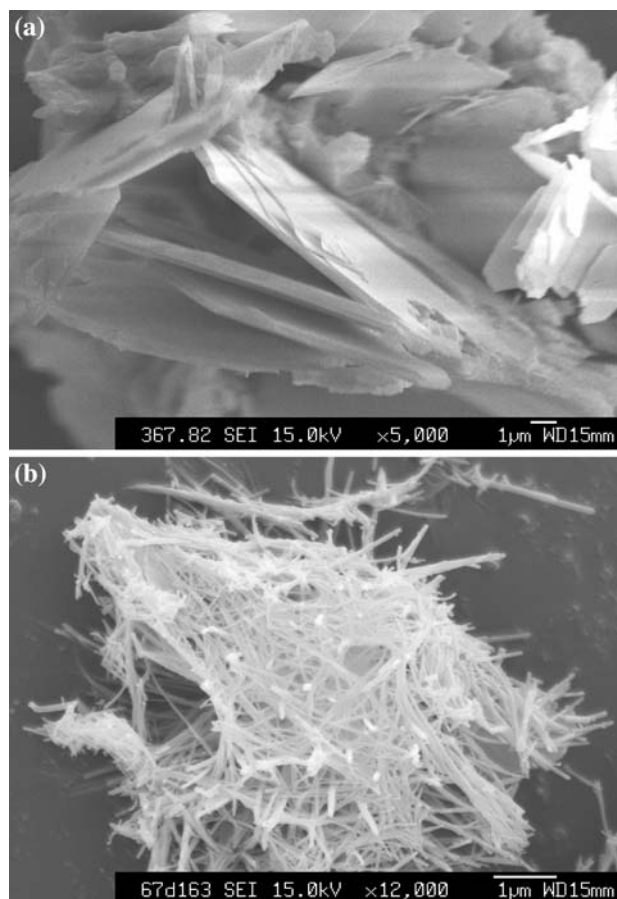


Fig. 8 SEM images of Co–Zr LDH at different aging time: (a) 8 h ×5,000 and (b) 16 h ×5,000

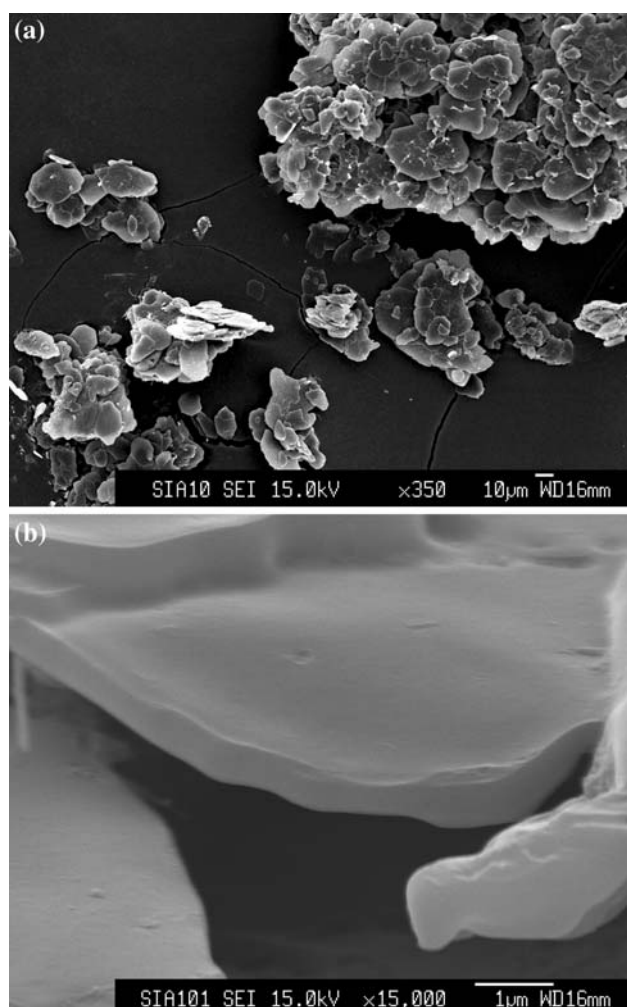


Fig. 9 SEM images of Co–Zr LDH after reaction with *n*-capric acid at different magnifications: (a) $\times 350$ and (b) $\times 15,000$

morphology of Co–Zr LDH depends mainly on the aging time of the sample.

For Co–Zr LDH at aging time 7 h, SEM image show that the sample has a clear plate-like morphology, which was typical for the LDH morphology as shown in Fig. 8a. In case of Co–Zr LDH at aging time 16 h, SEM image shows a clear fibrous morphology as shown in Fig. 8b.

However, In case of Co–Zr LDH at aging time 16 h after intercalation with organic compounds, SEM images show only plate-like morphology as shown in Fig. 9. Also, the images indicate that the average size of the organic compounds containing crystallites is much larger than that for the samples before intercalation reactions as shown in Fig. 9b. This means that the intercalation of fatty acids with LDH increases the interlayer spacing of LDH depending on the size and orientation of fatty acids inside the LDH and coincident with XRD results

In summary, it can be concluded that the best conditions for producing Co–Zr LDH having plate-like structure is 8 h

aging time or exchange the cyanate anion with organic anion and the best aging time giving Co–Zr LDH having fibrous structure is 16 h. This means that we can control the morphology of LDH by intercalation reactions which has been recently published.

Discussion

The results presented in this work show that the formation of the layer double hydroxide is not limited to the reactions between di- and trivalent cations although these are the only reactions reported by many researchers [1–18]. 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 was calculated as 0.30 nm. By comparison with the size of cyanate anion, 0.34 nm, it was considered that cyanate anion make an angle 65.7° with the Co–Zr layer and connect with Zr cation through two different sides (above and below the Co–Zr layer) in order to neutralize the positive charge as shown in Fig. 10.

The experimental results show that two anions are intercalated into the interlayer spacing of Co–Zr LDH indicating one interlayer spacing 0.78 nm. The first anion, mainly intercalated, is cyanate which produced from the decomposition of urea as shown in Eq. 1:

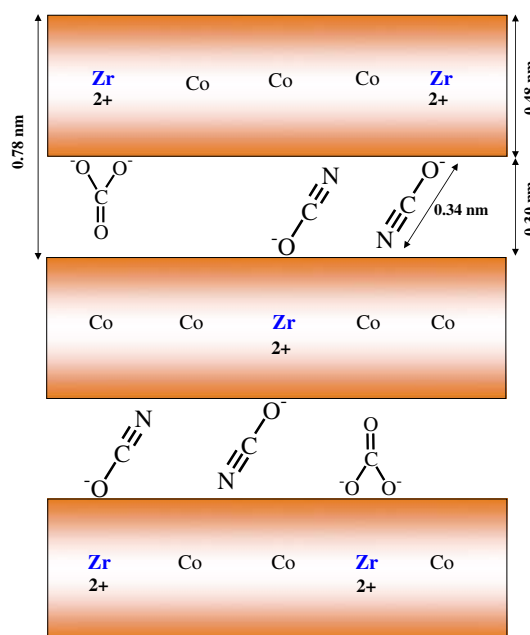
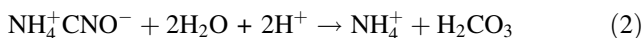


Fig. 10 Schematic representation of Co–Zr LDH for plate-like morphology



The earlier investigators [45–47] confirmed this equation and considered that the ammonium cyanate is an intermediate with decomposition of urea.

Recently, Coebel and Elsener [48] and Stradella and Argentero [49] mention that the thermal decomposition of urea can yield a variety of products; apart from ammonia and isocyanic acid. The second anion is carbonate which produced from the complete decomposition of urea as shown in Eq. 2:



The earlier investigators [45–47] indicated that the decomposition of urea is complete only in acidic conditions as shown in Eq. 2.

According to the synthetic conditions of our experiments, the decomposition of urea is not complete. This leads to the concentration of cyanate is higher than the concentration of carbonate in the interlayer spacing of Co–Zr LDH.

The schematic representation of Co–Zr LDH, Fig. 10, may be valid only for the plate-like structure while in case of fibrous structure we suggest that the above representation may be valid after some modification. According to the mechanism of our laboratory for fibrous structure, which formed from the reaction of zinc hydroxide with organic acids [28], we can apply the same idea for this fibrous structure. The presence of carbonate anions near

cyanate anions push the two cyanate anions (–1) to attack zirconium cation (+2) from only one side. So, this leads to steric repulsion between bulky cyanide groups, which cause curling of the layers giving fibrous structure as shown in Fig. 11.

Conclusion

In this study, Co–Zr layered double hydroxides consisting of bivalent and tetravalent have been prepared for the first time. The Co–Zr LDH has interlayer spacing 0.78 nm. SEM images indicate that the controlling in the morphology of LDH is possible. Where it showed that the Co–Zr LDH could exist as plate-like structure and/or fibrous structure depending on the preparation conditions. Anion-exchange reactions were successful in replacing inorganic anions with organic anions into Co–Zr LDH.

Acknowledgements The author thanks Professor H. Tagaya and Yamagata University for their cooperation.

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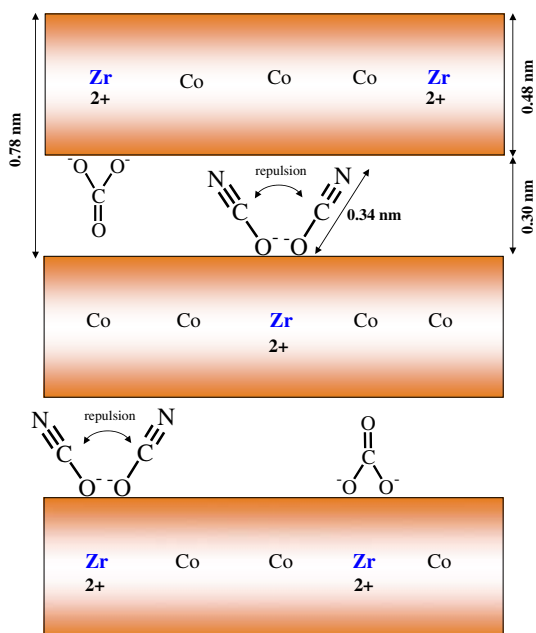


Fig. 11 Schematic representation of Co–Zr LDH for fibrous morphology

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