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Synthesis and characterization of zinc-aluminum and zinc-chromium LDHs intercalated citrate anion

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Abstract. In this study, the preparation of Zinc-Al and Zinc-Cr LDH intercalated by citrate anion conducted using co-precipitation method at room temperature. The characterization of Zinc-Al and Zinc-Cr LDHs intercalated citrate anion was performed using XRD and FTIR. The result of XRD pattern and FTIR spectra confirmed that Zinc-Al and Zinc-Cr intercalated citrate anion were successfully prepared. The vibration of citrate anion observed at 1590 cm^{-1} and 1390 cm^{-1} , respectively, correspond to the characteristic of the carboxylate group ($-\text{COO}^-$). Structure of Zinc-Al and Zinc-Cr LDHs were shown by reflection at 2 theta (003) that indicated the interlayer space was higher than before intercalation.

Keywords: Zinc-Al, Zinc-Cr, intercalation, LDH, citrate

1. Introduction

Layered double hydroxide is well-known as potential material with broad applications in various fields [1]. In recent years, these materials get attention from researchers with their potential applications such as adsorbent, catalysis, membrane, flame retardants and also anionic changes [2, 3]. Layered double hydroxide is an anionic material with lamellar structure, its ability as ion exchanger makes LDH easy modification [4]. The layered double hydroxide has a general formula $[\text{M}^{2+}/\text{M}^{3+}(\text{OH})]_x[\text{A}^{n-}]_y \cdot m\text{H}_2\text{O}$ from stacking brucite-like layers metal oxide containing a positive charge due to partial substitution of divalent metal cation by trivalent metal cation [5]. The positive charge represented by anions located in the interlamellar spaces. Interlamellar space is also known as interlayer, can exchange species A^{n-} to other anions. The interlayer can be expanded to an adapted wide range of interlayer anion [6]. Therefore, A^{n-} can be exchangeable with inorganic or organic anionic compounds, such as carboxylic [7], halides [8], oxo-anion [9], and polyoxometalate [10].

Layered double hydroxide was considered as a class of materials that is easy to synthesize among several methods [11]. Various methods have been prepared depending on the intended usability and purpose for which the layered double hydroxide used. Many procedures were used to synthesize the layered double hydroxide using precipitation method by varying ratio molar and adjusting pH [12], anion exchange [13], hydrothermal synthesis [14], sol-gel process [15], structure reconstruction [16]. The most conventional method used is precipitation, which can be performed at constant pH depending on the applied conditions. The co-precipitation method was studied in this research. Co-precipitation has more advantages than other methods. The benefits of this method are easy preparation, high



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crystallinity, and high purity of material [15, 16]. Zhang et al. reported that Zn-Al LDH was synthesized and modified by intercalating EDTA in interlamellar space using co-precipitation method [17]. Rahmanian et al. reported Zn-Fe LDH intercalated by citrate anion and applied as sorbent [18]. The research by Meyn et al. reported that several LDHs intercalated organic acid anions using co-precipitation method has different interlayer distances [19]. In nature, citric acid is widely found. Similar with ethylenediaminetetraacetic acid (EDTA), they have advantages as an excellent chelating agent in binding toxic metal cations. Therefore, the citrate anions-intercalated LDHs are expected in various applications especially as adsorbent [18]. In this research, Zinc-Al and Zinc-Cr LDHs intercalated citrate anion using co-precipitation method with constant pH. The surface morphology and chemical structure of LDHs were analyzed by XRD and FTIR.

2. Materials and method

2.1. Materials and instrumentation

The materials used including zinc nitrate, aluminum nitrate, chromium nitrate and sodium carbonate were purchased from Merck. Sodium hydroxide and citric acid were purchased from Sigma Aldrich. Aquadest was obtained by Purite Instruments. The material was characterized by XRD Rigaku Miniflex-600, and FTIR Shimadzu FTIR Prestige- 21.

2.2. Methods

2.2.1. *Synthesis of Zinc-Al LDH.* The synthesis of Zinc-Al LDH was conducted by co-precipitation method [20]. A 100 mL of 0.75 M zinc nitrate (14.202 g) was added to 100 mL of 0.25 M aluminum nitrate (5.324 g) by vigorous stirring for an hour. Sodium hydroxide was prepared by diluting 0.8 g NaOH into 100 mL of water. Alkaline solution of LDHs was added dropwise to 2 M sodium hydroxide until pH reached 10 with continuous stirring at 340 rpm. The white gel was obtained and temperature synthesis was kept at 80 °C for 4 h. The material was washed and kept in the oven overnight at 60 °C. The dried Zinc-Al LDH was characterized by XRD and FTIR.

2.2.2. *Synthesis of Zinc-Cr LDH.* According to Sun et al., the synthesis of Zinc-Cr LDH was conducted by mixing 0.4 M zinc nitrate (7.57 g; 100 mL) and 0.2 M chromium nitrate (10.004 g; 100 mL), and added to 2.5 M sodium carbonate and 3 M sodium hydroxide under vigorous stirring for 2 h. pH of the mixture solution was adjusted to 10 using sodium hydroxide [21]. The mixture solution was kept at 60 °C overnight with moderate stirring. The gray solution was kept in the oven at 80 °C until gray gel obtained. The dried Zinc-Cr LDH was characterized by XRD and FTIR.

2.2.3. *Preparation of Zinc-Al and Zinc-Cr LDH intercalated citrate anion.* Under nitrogen atmosphere, 2 g of LDH gel was diluted by 50 mL deionized water. Another beaker with 10 g of citric acid was diluted by 50 mL deionized water. The solution of LDH was added dropwise into citric acid with continuous stirring for 24 h, then pH was adjusted to 10. The mixture solution was kept at room temperature. The material was washed, dried and characterized by XRD and FTIR.

3. Results and discussion

Zinc-Al and Zinc-Cr LDH were successfully synthesized by co-precipitation method. The result is shown in figure 1. Figure 1 shows the powder form of LDHs. The LDHs results remained in white and grey powder, same as the color of LDH before intercalation. Zinc-Al and Zinc-Cr were intercalated by citrate anion by co-precipitation method. This method was conducted by mixing LDH gel and citric acid with a ratio of g 1:10. The mixing solution was adjusted to pH 10. The schematic of LDH intercalated by citrate anion is shown in figure 2.



Figure 1. Powder of (a) Zinc-Al LDH, (b) Zinc-Al Intercalated, (c) Zinc-Cr LDH, and (d) Zinc-Cr Intercalated.

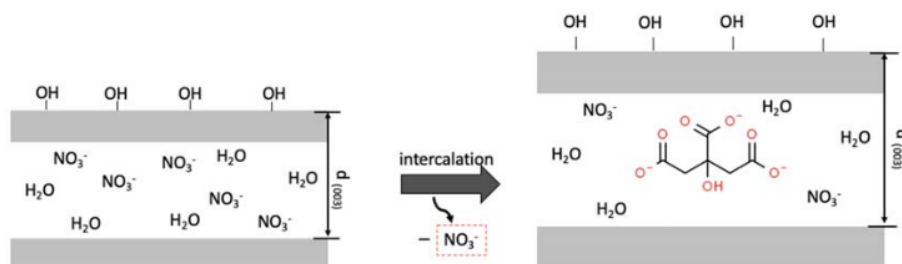


Figure 2. The scheme of LDH intercalated by citrate anion.

The FTIR spectra of the Zinc-Al, Zinc-Cr LDH, and LDH intercalated are shown in figure 3. Figure 3 shows the broad vibration at 3400 cm^{-1} which represents the O-H stretching vibration of water molecules and also hydroxide layers. The sharp peak shown in figure 3a and figure 3b at 1380 cm^{-1} are denoted as nitrate anion vibration in the interlayer space of LDH. Another lower peak at 1635 cm^{-1} corresponds to bending O-H. Figure 3 c and figure 3d show the differences prominent peaks at 1590 cm^{-1} and 1390 cm^{-1} which are the characteristics of C=O bonds and -COO- (carboxylate group). The nitrate anion stretching at 1380 cm^{-1} is not observed because of the decreased intensity and the appearance of carboxylate groups from figure 3c and figure 3d. The spectrum of Zinc-Al intercalated by citrate anion is similar to LDH, which yielded by Zhang et al. [17]. Zhang reported that after intercalation using citrate anion, Zn-Al/citrate has a vibration at 1394 and 1600, which is the characteristic of the COO- groups vibration. Based on FTIR measurements, Zinc-Al and Zinc-Cr have been successfully inserted citrate anion into the interlayer [17]. These materials were characterized by XRD powder analysis.

Figure 4, shows the XRD pattern of Zinc-Al, Zinc-Cr, and intercalated LDH. LDH materials have a similar layered structure. LDH has a unique reflection $d_{(003)}$ which represents the interlayer structure and corresponds to the distances between up and down cations layers. When the interlayer anions in a LDH changed, a corresponding change in the $d_{(003)}$ spacing should be observed. This change will be indicated if the new anions have been successfully intercalated into the LDH. Figure 4 shows Zinc-Al intercalated by citrate has a diffraction 2 theta of $d_{(003)}$, which shifting to a lower angle from 10° to 8° . Zinc-Cr intercalated citrate does not shift, but the interlayer space is higher than before intercalated. The increasing data of Zinc-Al and Zinc-Cr before and after intercalating are shown in table 1.

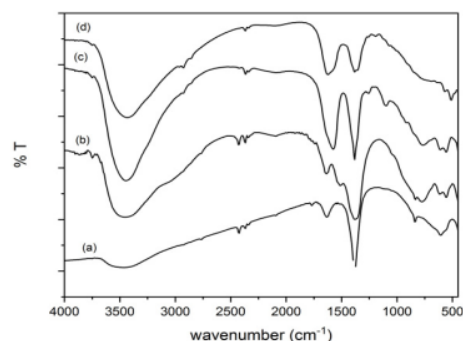


Figure 3. FTIR spectra of a) Zinc-Al LDH, b) Zinc-Cr LDH, c) Zinc-Al Intercalated, and d) Zinc-Cr Intercalated.

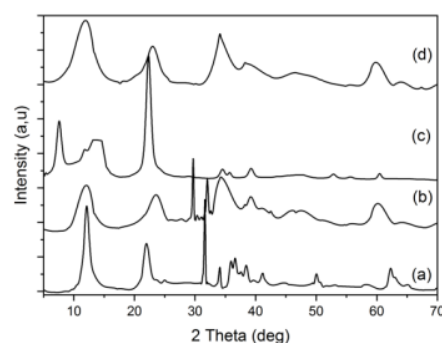


Figure 4. XRD Pattern of a) Zinc-Al LDH, b) Zinc-Cr LDH, c) Zinc-Al Intercalated, and d) Zinc-Cr Intercalated.

Table 1. Data of interlayer Zinc-Al and Zinc-Cr LDH.

	Zinc-Al LDH	Zinc-Cr LDH
Before Intercalated	7.57 Å	7.53 Å
After Intercalated	11.68 Å	10.94 Å

The increasing interlayer distances of Zinc-Al and Zinc-Cr LDH indicated the successful preparation of these materials. Figure 4 also shows other diffraction, which represents by sharp peaks at 22°, 30°, and even 60° for reflection (003), (006) and (110). This unique reflection is useful for identifying the crystallography of LDH. According to Baliarsigh et al., based on Bragg's Laws, LDH can be determined as hexagonal structure by unit cell parameters [22].

The expanded interlamellar region (003) was continued with the intercalation of citrate anions into the interlayer space of LDH. Moreover, the intensity of other reflections such (003), (006) and (110)

decreased after the intercalation. As reported by Meyn et al. [19] and Perera et al. [23], the result of citrate pillaring LDH has the lowest value in this research. Meyn showed the interlayer distance after intercalated by Zn-Cr and Zn-Al 8.9 Å and 9.0 Å [19]. Perera showed the interlayer after intercalated by a citrate amount of 8.8 Å [23]. However, the materials were successfully synthesized and ready to apply in various fields.

4. Conclusion

Zinc-Al and Zinc-Cr LDH intercalation by citrate anion has been prepared by the co-precipitation method. The FTIR spectra showed the vibration of the carboxylate group at wavenumber 1390 and 1590 cm^{-1} after intercalation. The nitrate vibration was decreased after the intercalation and was not observed at 1380 cm^{-1} . XRD pattern showed that interlayer space of Zinc-Al and Zinc-Cr LDH was increased after the intercalation from 7.57 Å and 7.53 Å to 11.68 Å and 10.94 Å, respectively.

Acknowledgments

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