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Research Paper

Synthesis and Characterization of Zn/Al, Zn/Fe, and Zn/Cr Layered Double Hydroxides: Effect of M^{3+} Ions Toward Layer Formation

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Abstract
Layered double hydroxides are composed by substitution of metal cation divalent and trivalent. Metal cation divalent and trivalent can be changed. In this work, effect metal cation trivalent (M^{3+}) toward layer formation were studied. Synthesis of LDHs has used co-precipitation methods with molar ratio 3:1 and kept pH at 10. The result of synthesis was characterized by X-ray Diffraction (XRD) and Fourier Transform Infrared (FT-IR) analyses.

Keywords
layered double hydroxides, LDHs, co-precipitation, Zn/Al LDHs, Zn/Cr LDHs, Zn/Fe LDHs

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1. INTRODUCTION

Inorganic materials can be classified by layered materials (Ma et al., 2009) and porous materials (Abdelrahman, 2018). Each of these materials has advantages as adsorbents (Taher et al., 2018; Palapa et al., 2018c), catalyst (Jadhav et al., 2007), ion exchangers (Lins et al., 2018) and sensors (Xu et al., 2018b). One of the most interesting material is layered materials (Mishra et al., 2018). Based on its existence, nature layered materials such as kaolinite and bentonite (Taher et al., 2018, 2017) then synthesized layered material such as layered double hydroxides or hydrotalcite (Jadhav et al., 2007; Lesbani et al., 2018; Palapa et al., 2018b). Nowadays, researchers had been interesting to layered materials especially layered double hydroxides. Layered double hydroxides are more effective to be modified because layered double hydroxides have a flexible structure (Takei et al., 2014) and easy to handle (Li et al., 2017). LDHs has many physical and chemical properties which are similar to cationic clay minerals (Zhao et al., 2011). Their layered structure, extensive chemical composition (due to isomorphic variable metal cation substitution), ion exchange properties Chen (2011), reactive interlayer space (Xu et al., 2018a), swelling in water, rheological properties and colloids have made LDH like mineral clay (Zhao et al., 2011).

Generally, layered double hydroxides have a general formula of M^{2+} M^{3+} $(OH)_2(An\text{-})x/n.yH_2O$ where M^{3+} and M^{2+} are represented the trivalent metal and divalent metal, respectively (Tichit et al., 2019; Lins et al., 2018). Formed as 1 – xx layered double

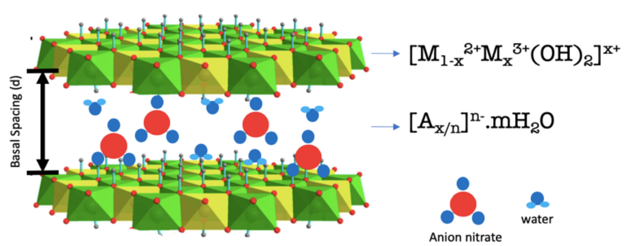

Figure 1. Structure of Layered Double Hydroxides was had nitrate anion

hydroxides (LDHs) and prepared by two metal salts (divalent and trivalent metal) (Islam and Patel, 2010; Palapa et al., 2018a). In this case, the trivalent metal that essentially can be Al, Fe, Ni, Cr, Ga, and Mn (Elmoubarki et al., 2017). While, the divalent metals cation such as Mg, Mn, Co, Cu, Zn, and Fe. An interlayer anion as counterbalancing the metals cations (Lesbani et al., 2018). The anion can be taken up by layered double hydroxides uses three mechanisms such as anion exchanges in interlayer, surface adsorption and reconstruction layered double hydroxides calcined by 'memory effect' (Gaini et al., 2009).

In this research, the effect of the comparison of ion M^{3+} metal cation trivalent from Zn/Al, Zn/Fe, and Zn/Cr layered double hydroxides. The LDHs has been successfully prepared and characterized by XRD and FT-IR analyses.

2. EXPERIMENTAL SECTION

2.1 Chemicals and Instrumentation

All chemicals material was used analytical reagents grade such as zinc nitrate, aluminum nitrate, chromium nitrate, iron nitrate were obtained by Merck. Sodium hydroxide and sodium carbonate were obtained by from Sigma-Aldrich. The solution was prepared by deionized purity water. Then characterized by XRD Diffractometer Rigaku Miniflex-600 and Spectrophotometer FT-IR Shimadzu FT-IR Prestige-21.

2.2 Synthesis of Zn/M^{3+} (M^{3+}: Al, Fe, and Cr) LDHs

Zn/Al, Zn/Fe, and Zn/Cr LDHs material have been prepared by co-precipitation method at constant pH. The synthesized of LDHs were used the molar ratio 3:1 was conducted zinc nitrate (100 mL, 0,3 M) and a trivalent metal cation such as aluminum nitrate, iron nitrate, chromium nitrate (100 mL, 0.1 M), respectively. This solution was called A solution. Then A solution was stirring for an hour. B solution was prepared by 10 mL of sodium solution 2.5 M and 10 mL of NaOH 3 M. then B solution was added slowly to A solution under vigorous stirring of 2 hours and adjust pH at 10 by addition of NaOH and temperature kept at 60 °C for 24 hours to obtain layered double hydroxides. After that, Layered double hydroxides were washed and kept at room temperature.

3. RESULTS AND DISCUSSION

Synthesis of Zn/Al, Zn/Cr, and Zn/Fe layered double hydroxides were obtained from metal cation divalent e.g. zinc nitrate and metal cations trivalent such as aluminum nitrate, iron nitrate, and chromium nitrate. Layered double hydroxides have successfully prepared by co-precipitation method with molar ratio and adjust pH at 10 by adding NaOH. Co-precipitation method is based on the complex condensation to build the brucite layers with exchanges of metal cation divalent and trivalent and balancing by anion in the interlayer. The result of Zn/Al, Zn/Fe, and Zn/Cr LDHs was shown in Fig. 2. The result has remained white powder, brown powder and grey powder, respectively. Then, Zn/Al, Zn/Fe, and Zn/Cr LDHs were characterized by XRD Diffractogram.

According to Forano et al. (2006) layered double hydroxides (LDHs) has an octahedral-hydroxyl layer which has a positive charge because of substitution of metal cation divalent and metal cation trivalent (Lesbani et al., 2018). This brucite layer described the close packing structure of metal cation and hydroxyl anion. Brucite layers balanced by anion and water molecules namely interlayer. X-Ray diffraction is one of the most effective methods to determine the synthesis process. The result of X-Ray Diffraction shows in Fig. 3.

The pattern of Zn/Al, Zn/Fe, and Zn/Cr LDHs was shown in Fig 3. Fig. 3 shows a similar characteristic of layered double hydroxides has sharp peaks at 2θ amount 10°, 22°, 30°, 35°, 49° and overlapping peaks at 60° are responding to (003), (006), (012), (104), (018) and (110) reflections, respectively. The sharp peak amount 10o for all compounds was indicated interlayer of layered

Figure 2. Powder of Zn/AL LDHs (a), Zn/Fe LDHs (b) and Zn/Cr LDHs (c)

double hydroxides. The higher value of interlayer is Zn/Cr (7.68 Å) > Zn/Al (7.57 Å) > Zn/Fe (5.80 Å). in this case, the effect of ionic radii affects the distance between layers (interlayer) due to the difference in ionic radii where metal cation trivalent Cr^{3+} (0.64 Å), Al^{3+} (0.53 Å) and Fe^{3+} (0.61 Å). According to Forano et al (2006) the influence of the biggest metal ionic radii will be transformed interlayer higher than interlayer of smaller metal ionic radii [24]. However, in this study, the assumption was not answered because Zn/Fe LDHs had the smallest interlayer due to the synthesis of Zn/Fe LDH experiencing impurities and calcite formed due to the temperature that is not kept constant in the synthesis process.

According to Parida and Mohapatra (2012), (003), (006) and (110) reflections are most important characteristic based on a crystallographic parameter. The crystallographic parameter is the first reflection diffraction pattern for layered double hydroxides. Based on Braag's Law, layered double hydroxides have a hexagonal structure, to determining hexagonal structure used unit-cell parameters. However, the hexagonal structure has a rule which a=b≠c parameters, its equation:

$$1/d^2(hkl) = ((h^2 + k^2)/a^2) + l^2/c^2 \tag{1}$$

Data digital of XRD was showed the value of d-spacing (003), (006) and (110) reflection. (003) and (006) reflection was used to calculate the 'c' parameter. 'c' parameter is a parameter that shows the size of the crystal structure using equation c = 3/2 [(d (003)) + (2d (006))] (Benito et al., 2010). Diffraction (110) reflection were used to calculated 'a' parameter using equation a = 2d (110). The data of crystallographic parameter were shown in Table 1.

Table 1. Crystallography Parameters of LDHs

Parameters	Zn/Cr	Zn/Al	Zn/Fe
(003) (Å)	7.68	7.57	5.8
(006) (Å)	3.81	3.79	3.41
(110) (Å)	1.53	1.53	1.49
'a' parameter (Å)	3.06	3.06	2.99
'c' parameter (Å)	22.962	22.725	18.933

Table 1. were showed the unit cell of parameter crystallographic such a and c parameter. The value of 'a' parameters

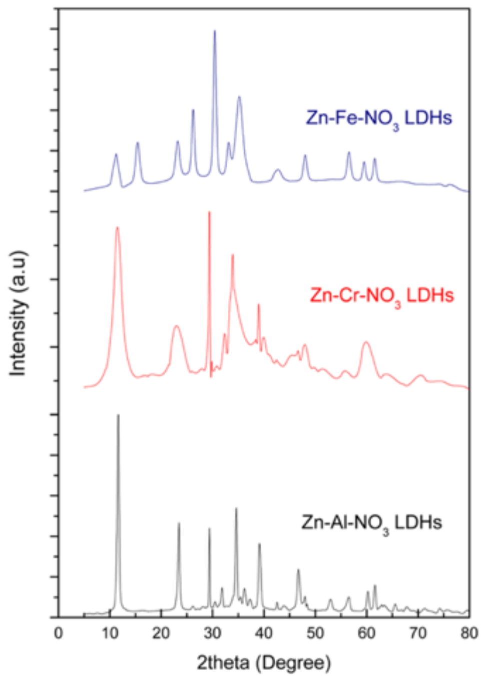

Figure 3. XRD Diffractograms of LDHs

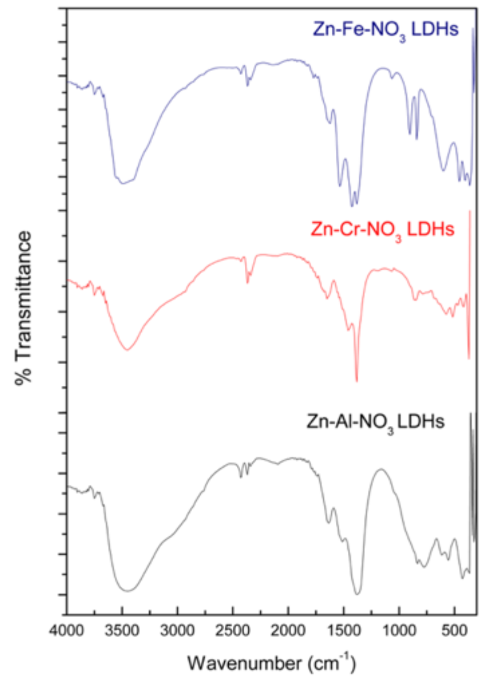

Figure 4. FT-IR spectrum of LDHs

was obtained similar because of the presence of nitrate anion in interlayer for all LDHs. 'c' parameter has denoted that size and crystal structure. The value of 'c' parameter of Zn/Cr LDHs higher than others its means the basal spacing of Zn/Cr LDHs biggest.

Zn/Al, Zn/Cr, and Zn/Fe LDHs have been characterized by FT-IR spectrophotometer analyses. The purpose of characterized by FT-IR is to determine the functional groups from layered double hydroxides (LDHs). The spectra of Zn/Al, Zn/Cr, and Zn/Fe LDHs was shown in Fig. 4. All compounds had identical spectra where a broadband vibration from -OH stretching amount wavenumber 3400-3600 cm^{-1} while the weak vibration from water molecules in interlayer at wavenumber 1635 cm^{-1}. Then, the sharp vibration at wavenumber 1380 cm^{-1} denotes the anion of nitrate as balancing in the interlayer. The M-O bonding vibration was identified at wavenumber under 1000 cm^{-1}.

4. CONCLUSIONS

In this research has been successfully prepared Zn/Al, Zn/Cr and Zn/Fe layered double hydroxides (LDHs) by co-precipitation method with ratio molar 3:1 and kept pH at 10. The result has been characterized by X-Ray Diffractograms and FT-IR spectrophotometer analyses. XRD data obtained the value of interlayer Zn/Cr LDHs (7.68 Å) highest than Zn/Al LDHs (7.57 Å) and Zn/Fe (5.80 Å). So, this study can be presented a synthesis of layered double hydroxides and its characterization.

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