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Preparation of M^{2+}/M^{3+} Layered Double Hydroxides (M^{2+}=Zn, Ni, M^{3+}=Fe): Effect of Different M^{2+} to the Layer Formation

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Abstract. Two different layered double hydroxides (LDH) materials, namely Ni-Fe LDH and Zn-Fe LDH, have been synthesized by the coprecipitation method under alkaline conditions. The prepared materials were characterized by X-ray diffraction and FT-IR in order to analyze the formation of LDH layer. Although both LDHs contains different M^{2+} metal, they consist of the same M^{3+} metal cation, i.e., Fe. Hence, in this work, the effect M^{2+} metal composition on the formation of LDH layer was investigated. According to the X-ray diffraction analysis, the synthesized ZnFe LDH showed a typical diffraction peak at 2θ of 11.08° with the basal spacing value of 7.98 Å. While for the NiFe LDH exhibited a typical diffraction peak at 2θ around 11.41° with a basal spacing value around 7.74 Å.

Keywords: layered double hydroxides, NiFe LDH, ZnFe LDH

INTRODUCTION

Layered double hydroxides (LDH) refer to a synthetic clay that consists of positively charged metal hydroxides layer encountered by a negative anion lied in the interlayer space [1]. The general formula of LDH material can be written as following [2]:

$$M^{2+}_{(1-x)}M^{3+}_{x}(OH)_2]A^{n-}_{x/n}\cdot mH_2O$$

Where M^{2+}_{1-x} is the divalent metal like Zn, Fe, Mg, Ni, and Co, M^{3+}_{x} is the trivalent metal such as Fe, Cr, and Al, while the A^n related to the inorganic and even organic anion located in the interlayer space of the LDH layer such as NO_3^-, CO_3^{2-}, OH^-, or Cl^-[3]. Basically, the structure of LDH was derived from the structure of brucite mineral ($Mg(OH)_2$) in which some part of divalent (M^{2+}) metal cations were replaced by the trivalent (M^{3+}) cations and induced a positive charge layer [4].

Compared to the other functional materials [5],[6], LDHs have various compositions and structures that can be tailored by modifying the metal ion composition and the bulkiness of the interlayer anions [7]. Moreover, by varying the metal cation composition and the native anions located in the interlayer distance, it possible to control the layer formation and the distance of the basal space of the formed LDH material [6-7]. For instance, Varga et al. [10] have synthesized LDH composed of Ca as M^{2+} metal cation and Al as M^{3+} metal cation. It was observed that the prepared material exhibited the basal spacing of 0.857 nm and the interlayer distance of 0.623 nm. On the other case, Ravuru et al. [11] also prepared the LDH material with the same M^{3+} metal cation (Al) but with different M^{2+} metal cation composition (Ni). The results reveal the formation of layered material with a basal spacing of 0.8 nm. According to

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these phenomena, in this work, we have investigated the effect of M^{2+} metal cation to the formation of two different LDH material called NiFe LDH and ZnFe LDH.

EXPERIMENTAL SECTION

Materials

All the materials used in this experiment, including iron (II) nitrate nonahydrate ($Fe(NO_3)_3.9H_2O$), nickel nitrate nonahydrate ($Ni(NO_3)_2.9H_2O$), sodium bicarbonate (Na_2CO_3), zinc nitrate tetrahydrate ($Zn(NO_3)_2{\cdot}4H_2O$) and sodium hydroxides (NaOH) were in reagent grade and used as received without further purification. All the mentioned reagents were purchased from Sigma-Aldrich and Merck. The distilled water used in all processes of materials preparation was produced by using Pureit water purification technology.

Preparation of ZnFe and NiFe LDH

NiAl layered double hydroxides (LDH) was prepared by following the work done by Ravuru et al. (2019) with slight modification [11]. The material was synthesized by the coprecipitation method as follows. Approximately 50 mL of 0.3 M nickel nitrate hexahydrate was added into 50 mL of 0.1 M iron nitrate nonahydrate in a 250 mL of beaker flask under vigorous stirring. After homogeneously stirred, the obtained mixed metal solution was transferred into other beaker flask containing 10 mL of 2 M sodium hydroxides solution and 0 mL of 1 M sodium bicarbonate under vigorous stirring while the pH of the solution was maintained at 10-11. After the mixed metal solution was totally added, the obtained solid was separated by vacuum filtration and followed by rinsing by distilled water for three times. The synthesized solid was then dried at 60 ºC for 18 h.

Another LDH material named ZnFe LDH was synthesized by the coprecipitation method according to work reported by Parida and Mohapatra (2012) [12]. In brief, 20 mL of 0.75 M zinc nitrate tetrahydrate was added into 20 mL of 0.25 M iron nitrate nonahydrate solution under vigorous stirring for 10 minutes. The prepared mixed metal lution then transferred dropwise into a 250 mL beaker flask containing 20 mL of 2M sodium hydroxides solution under vigorous stirring while the pH of the solution was kept constant at pH 10. After all the mixed metal solution was entirely transferred, the solid precipitate was collected by vacuum filtration and rinsed with stilled water for several times in order to remove the excess metal solution. After then, the wet collected solid was dried in an oven at 60 ºC for 24 h.

Materials characterization

In order to investigate the effect of M^{2+} metal cation on the formation of the LDH layer, the as-synthesized materials were characterized by X-ray diffraction analysis and FT-IR. X-ray diffraction analysis was performed using a Rigaku Mini x 600 instrument equipped with CuKα irradiation at 30 kV and 10 mA. The samples were scanned from 2θ range 5° to 80° with a scanning rate of 5°/min. The FT-IR analysis was conducted using a Shimadzu Prestige-21 FT-IR instrument. The samples were prepared using the KBr pellet method, and the spectra were recorded from the wavenumber range 400 cm^{-1} to 4000 cm^{-1}.

RESULTS AND DISCUSSION

The degree of crystallinity and the properties of layers structure of both synthesized samples were investigated by X-ray powder diffraction analysis. The obtained results were demonstrated in **FIGURE 1**. As can be observed, both XRD patterns showed a typical XRD pattern of double-layered material where three symmetric diffraction peaks were observed in the low 2θ angle. In particular, the typical reflection peaks of ZnFe LDH were observed at 2θ around 11.08°, 23.18°, 33.07°, 39.11°, 59.59°, and 61.69°. All these reflection peaks correspond to the lattice plane of (003), (006), (101), (015), (110), and (113), respectively [13],[14].

In the case of NiFe LDH, the obtained X-ray diffraction pattern also exhibited a typical double-layered material. The XRD pattern of NiFe LDH showed reflection peaks at 2θ around 11º, 23º, 35º, 40º and 61º which corresponds to the lattice plane of (003), (006), (101), (015), and (110) [15]. The lattice plane of (003) and (006) are the typical plane of layered material in which (003) indicated the interlayer distance of the layered structure. According to the Bragg

equation, it can be obtained that the interlayer distance or basal space of the synthesized material is 7.74 Å and 7.98 Å for NiFe LDH and ZnFe LDH respectively. This result exhibited that ZnFe LDH gives rise to a higher interlayer distance than NiFe LDH.

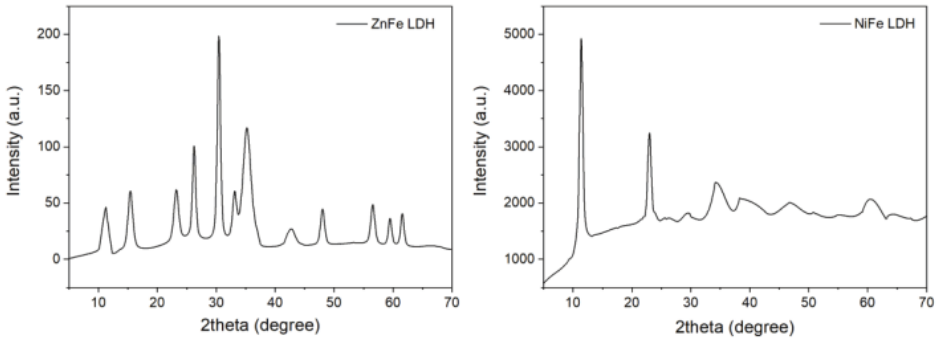

FIGURE 1. X-ray diffraction pattern of ZnFe LDH and NiFe LDH

Accordingly, the lattice parameters of *c* and *a* can be calculated from the diffraction peak of the (003) and (110) lattice plane. The lattice parameter of *c* refers to the three times of basal spacing of (003) plane while the lattice parameter of *a* refers to the two times of the basal spacing of (110) plane.

$$c = 3d(003)$$
$$a = 2d(110)$$

The obtained lattice parameter of both ZnFe and NiFe LDH are listed in **TABLE 1**. The results exhibited that the difference of M^{2+} metal cation composition affecting the layer formation of LDH material. Basically, nickel is a member transition metal as well as zinc. However, they are different in size. Nickel with higher atomic radii (163 pm) than zinc (139 pm) possibly give rise to the higher positively charged of the LDH layers. Consequently, it gave a higher attraction to the interlayer anions.

TABLE 1. Structural parameters of the synthesized materials

Samples	Lattice parameters			
	***d*(003) Å**	***d*(110) Å**	***a* (Å)**	***c* (Å)**
ZnFe LDH	7.98	1.57	3.14	23.94
NiFe LDH	7.74	1.51	3.02	23.22

For further confirming the layered formation of both ZnFe and NiFe LDH, FT-IR analysis was conducted. The FT-IR spectra of ZnFe LDH and NiFe LDH were displayed in **FIGURE 2**. As can be seen in the figure, both ZnFe LDH and NiFe LDH showed similar spectra as the typical spectra of double-layered material. The strong absorption band observed at wavenumber around 3425 cm^{-1} correspond to the existence of water molecule in the interlayer space of ZnFe and NiFe LDH as well as relatively weak absorption band observed at wavenumber around 1635 cm^{-1} which correspond to the bending vibration of H-O-H group of the interlayer water molecule [16].

The sharpest peak of both materials observed at wavenumber around 1381 cm^{-1} is a characteristic peak of the LDH material that is indicating the presence of interlayer anion [17]. According to Saftel et al. [18], that peak corresponds to the NO_3^- anion. Since both spectra showed a similar characteristic absorption band of NO_3^- anion, it can be assumed that interlayer distance of the both LDH is profoundly affected by the composition of the metal cation. The absorption band that appeared below wavenumber of 1000 cm^{-1} are the characteristic absorption band of M—O bonding of the both ZnFe LDH and NiFe LDH. For instance, the absorption band that was indicating the vibration of Zn—O bond was observed at a wavenumber of 408 cm^{-1}.

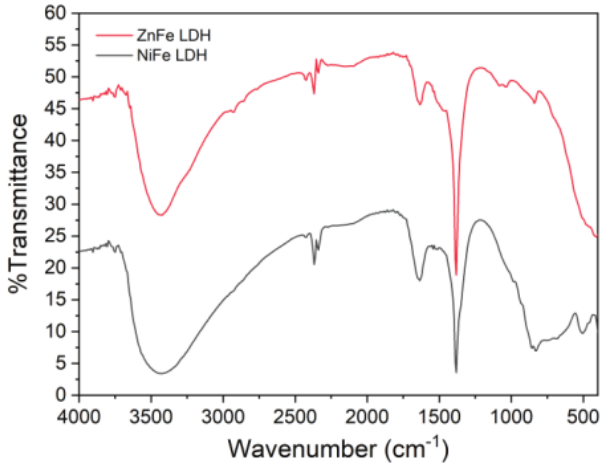

FIGURE 2. FT-IR spectra of ZnFe LDH and NiFe LDH

CONCLUSION

Two different layered double hydroxides (LDHs) material composed of Ni or Zn as M^{2+} metal cation and Fe as M^{3+} metal cation has been successfully synthesized by the coprecipitation method under alkaline condition. The obtained materials have a well crystalline structure with a typical layer structure of *brucite-like* material. The result of the crystal lattice parameter indicated that the ZnFe LDH has higher interlayer distance than the NiFe LDH although according to the FT-IR result, both materials containing the same interlayer anion species i.e., NO_3^-.

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