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Preparation of Ni-Al LDH: Influence of Intercalated Polyoxometalate Anion $(\alpha\text{-}SiW_{12}O_{40})^{4-}$ on the Interlayer Gallery Distance

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Abstract. Layered double hydroxides (LDH) have gained high attention as a promising material to be applied in various fields owing to their flexibility and controllable interlayer anion and composition. In this study, NiAl based layered double hydroxides were successfully prepared by the coprecipitation method. Furthermore, its intercalated form was prepared by an ion-exchange method using $(\alpha\text{-}SiW_{12}O_{40})^{4-}$ anion. The prepared materials were characterized by X-ray diffraction and FT-IR. X-ray diffraction analysis showed that after intercalated by $(\alpha\text{-}SiW_{12}O_{40})^{4-}$, the typical diffraction peak of NiAl LDH shifted to the lower angel, indicating that the interlayer distance expanded. The pristine NiAl LDH showed a typical pattern at the diffraction angle of 11.52° with basal distance 7.66 Å. While, after intercalated by $(\alpha\text{-}SiW_{12}O_{40})^{4-}$ the diffraction angle of the typical pattern moved to 8.52° with the basal distance increased to 10.36°.

Keywords: Layered double hydroxides, intercalated, polyoxometalate

INTRODUCTION

In the recent decade, the development of functional materials for various purposes like environmental remediation, organic and inorganic reaction catalysts, drug support, and energy storage, has attracted much attention worldwide [1]. Among the most studied inorganic materials, layered based materials are one of the most promising materials to be developed for versatile application [2–5]. Layered based clay mineral-like montmorillonite and kaolinite even have been studied from the ancient time due to their unique properties such as high thermal stability, high swelling properties, cation exchange capability [3],[6].

The novel synthetic clays called layered double hydroxides (LDH) or hydrotalcite-like material are a group of layered material that gained much attention recently [7]. It also mentioned as an anionic clay owing to its anion exchange capability [8]. Layered double hydroxides based material has the general formula of $[M^{2+}_{1-\chi}M^{3+}_{\chi}(OH)_2]^{\chi+}(A^{n-})_{\chi/n}\cdot mH_2O$ [9]. Where the M^{2+} represents the divalent metal cation such as Mg^{2+}, Co^{2+}, Ni^{2+}, etc, and M^{3+} represents the trivalent metal cation such as Al^{3+}, Co^{3+}, Mn^{3+}, etc. While A^{n-} correspond to the anion located in the interlayer space of the LDH layered structure like Cl^-, NO^{3-}, CO_3^{2-}, SO_4^{2-} [10]. LDH can be prepared by a facile method such as co-precipitation, urea hydrolysis, hydrothermal, sol-gel, and even electrodeposition.

One of the most advantageous developments of LDH materials is owing to their versatile composition and structure flexibility. LDH could be prepared in various metal cation composition of M^{2+}/M^{3+} combination. Moreover, their anionic interlayer species could be easily exchanged and modified with another functional species. For instance, recently we have developed LDH material with different compositions of M_{2+} (Ca, Mg, Zn) and M^{3+} (Al, Fe) [11]–

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[13] and found that the obtained material exhibited excellent properties as an adsorbent material for environmental remediation purpose. Moreover, owing to their high anion exchange properties, various organic and inorganic anion species have been studied to be intercalated into the interlayer distance of LDH. As reported by Candu et al. (2018), levulinic acid can be intercalated into the interlayer space of MgAl LDH and leads to increasing its basal distance and enlargement of the pore size [14].

In this work, we have developed an LDH material composed of Ni as M^{2+} metal cation and Al as M^{3+} metal cation. For further investigating its anion exchange capability, we have also investigated the possibility of inorganic cation of polyoxometalate, named α-$SiW_{12}O_{40}^{4-}$, to be intercalated into its interlayer space by using a simple ion-exchange method. The possibility of the intercalation process was evaluated from the interlayer distance of the NiAl LDH before and after intercalated by α-$SiW_{12}O_{40}^{4-}$.

EXPERIMENTAL SECTION

Materials

All the chemicals used in this work, including aluminium nitrate nonahydrate ($Al(NO_3)_3.9H_2O$), nickel nitrate hexahydrate ($Ni(NO_3)_2.6H_2O$), hydrochloric acid (HCl), sodium hydroxides (NaOH), sodium bicarbonate (Na_2CO_3), potassium chloride (KCl), sodium metasilicate (Na_2SiO_3), and sodium tungstate ($Na_2WO_4.2H_2O$), were in reagent grade then used as received without further purification.

Preparation of NiAl LDH

NiAl layered double hydroxides (LDH) material was synthesized by the coprecipitation method. Notably, 100 mL of 0.3 M $Ni(NO_3)_2.6H_2O$ solution was added into a 500 mL beaker flask containing 100 mL of 0.1 M $Al(NO_3)_3.9H_2O$ under vigorous stirring for 10 min. The obtained mixed metal solution was then transferred into another beaker flask containing 100 mL of 0.3 M Na_2CO_3 dropwise under vigorous stirring at 80 ºC.While adding the mixed metal solution, the pH of the total solution was kept constant at pH 10 by the addition of 2 M NaOH. After completed, the obtained solid was collected by vacuum filtration and dried at 80 ºC for one night. The obtained solid was then labeled as NiAl LDH.

Preparation of α-$SiW_{12}O_{40}^{4-}$

Polyoxometalate compound ($K_4[\alpha\text{-}SiW_{12}O_{40}]\cdot nH_2O$) was synthesized by the following method. As much as 11 g of sodium metasilicate was dissolved into 100 mL of distilled water. On the other flask, 182.5 of sodium tungstate was dissolved into 300 mL of boiled water under vigorous stirring. Into the sodium tungstate solution, 165 mL of 4 M hydrochloric acid solution was added under vigorous stirring for 5 min. Next, the sodium metasilicate solution that previously prepared was added into the sodium tungstate solution while another 50 mL of hydrochloric acid solution was also added simultaneously. The mixed solution was further stirred for 1 h at 100 ºC while the pH of the mixed solution was kept constant at pH 5-6. After finished, the mixed solution was aged at room temperature in order to cool down the solution temperature. After that, 50 g of potassium chloride was added into the solution in order to obtain a solid $K_4[\alpha\text{-}SiW_{12}O_{40}]\cdot nH_2O$.

Preparation of α-$SiW_{12}O_{40}^{4-}$ intercalated NiAl LDH

NiAl LDH intercalated by α-$SiW_{12}O_{40}^{4-}$ was prepared by a facile ion exchanged method according to the following procedure. 1 g of as-synthesized NiAl LDH was dissolved into 50 mL of distilled water. On the other flask, 1 g of the prepared $K_4[\alpha\text{-}SiW_{12}O_{40}]\cdot nH_2O$ was added into 25 mL of 1 M sodium hydroxide solution. Both prepared solutions then were added vastly under N_2 atmosphere condition under vigorous stirring for 24 h. After finished, the final suspension was cooled down at room temperature and separated by vacuum filtration. The obtained solid was further rinsed with distilled water several times and dried in an oven at 80 ºC for one night. The obtained solid then labeled as NiAl-Inter.

Materials characterization

The characteristic of the synthesized NiAl LDH and the properties of the intercalated sample were investigated by conducting X-ray diffraction analysis as well as FT-IR spectra analysis. X-ray diffraction analysis was performed using a Rigaku Miniflex 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 result of the X-ray diffraction analysis of NiAl LDH and intercalated NiAl LDH was displayed in **FIGURE 1**. The X-ray diffraction pattern of NiAl LDH showed a sharp and robust reflection peak at 2θ around 11.52° that corresponds to the lattice plane of (003) with basal distance around 7.66 Å. Other characteristic peaks of the LDH material were observed as reflection peak at 2θ around 22.8°, 35.14°, 39.47°, and 61.4° that corresponds to the lattice plane of (006), (012), (015) and (110) [15]. Since the lattice plane (003) referees to the distance of the interlayer space, then it can be calculated that the interlayer distance of the synthesized NiAl LDH was around 7.66 Å.

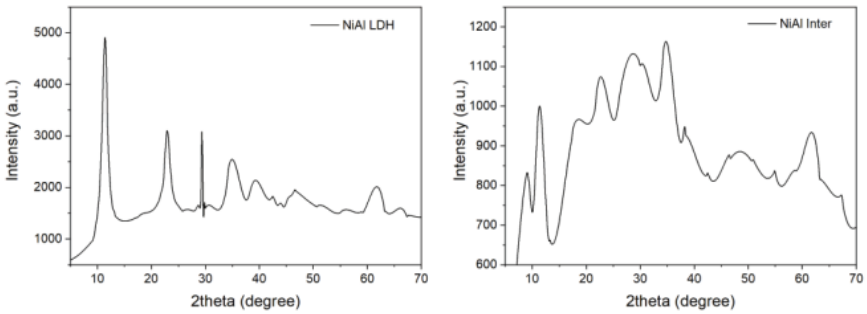

FIGURE 1. XRD pattern of NiAl LDH and intercalated NiAl LDH

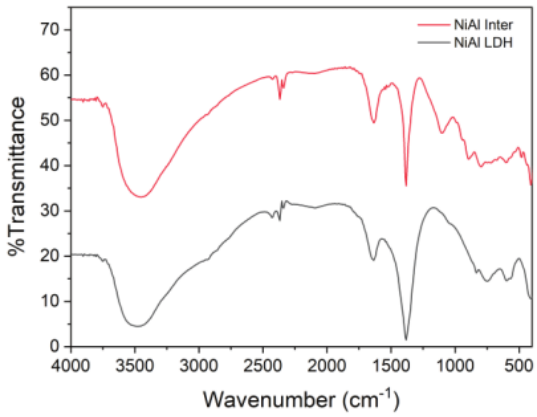

FIGURE 2. FT-IR spectra of NiAl LDH and intercalated NiAl LDH

After intercalated by α-$SiW_{12}O_{40}^{4-}$, it can be observed in the diffraction pattern of NiAl inter that the typical reflection peak of (003) lattice plane slightly shifted to the lower 2θ angle. This result was indicating the enlargement of the basal distance or the interlayer space [16]. According to the magnitude of the angle shifting, it can be calculated

that the peak of (003) lattice plane moved from 11.52° to 8.52°. From the Bragg' Equation then it can be observed that the interlayer distance of intercalated NiAl LDH increased from 7.66 Å to 10.368 Å.

The FT-IR spectra of NiAl LDH and intercalated NiAl LDH were presented in **FIGURE 2**. FT-IR spectra of pristine NiAl LDH exhibited the characteristic absorption band of LDH material in which the strong band observed at wavenumber around 3400 cm^{-1} correspond to the stretching vibration of H-O-H bond of the water molecule located the interlayer space of LDH [17]. Furthermore, the moderate absorption band observed at the wavenumber around 1635 cm^{-1} related to the O-H bending vibration of the interlayer water molecule as well as the metal hydroxyl group on the LDH structure [18].

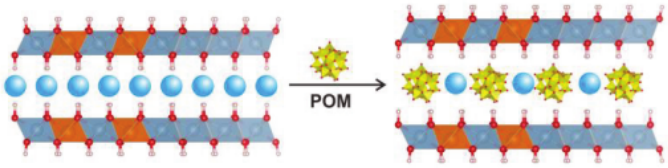

FIGURE 3. Intercalation process of polyoxometalate (POM) α-$SiW_{12}O_{40}^{4-}$ into interlayer space of NiAl LDH

The other characteristic band of the LDH material observed as a strong and sharp band at wavenumber around 1381 cm^{-1}. That band corresponds to the absorption band of NO_3^- anion that located in the interlayer space of the NiAl LDH structure [9]. After intercalated with α-$SiW_{12}O_{40}^{4-}$, it can be seen there is no significant change of the absorption band of the water molecule. However, the absorption band of NO_3^- anion decreased after the intercalation process. This phenomenon probably induced by the incorporation of α-$SiW_{12}O_{40}^{4-}$ anion into interlayer space of NiAl LDH and causes the decreasing of the NO_3^- anion in the interlayer space of the pristine NiAl LDH. Since α-$SiW_{12}O_{40}^{4-}$ anion has a bigger size than the pristine NO_3^- anion, then the interlayer distance of the intercalated NiAl LDH increased as described in the X-ray diffraction analysis. In a simple figure, the mechanism of the α-$SiW_{12}O_{40}^{4-}$ intercalation into the interlayer space of the NiAl LDH can be illustrated in **FIGURE 3**.

CONCLUSION

NiAl LDH material has been successfully synthesized by a facile coprecipitation method. The synthesized material has also successfully intercalated by α-$SiW_{12}O_{40}^{4-}$ anion through ion exchange method. According to the X-ray diffraction analysis, the basal spacing or interlayer distance of the NiAl LDH can be increased by incorporating a larger anion into the interlayer space.

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REFERENCES

1. H. Zhou, Z. Jiang, and S. Wei, Appl. Clay Sci. **153**, 29 (2018).
2. B. Caglar, B. Afsin, E. Koksal, A. Tabak, and E. Eren, Quim. Nova **36**, 955 (2013).
3. G.K. Sarma, S. SenGupta, and K.G. Bhattacharyya, Sep. Sci. Technol. **46**, 1602 (2011).
4. J. Ma, M. Yang, Q. Chen, S. Zhang, H. Cheng, S. Wang, L. Liu, C. Zhang, Z. Tong, and Z. Chen, Appl. Clay Sci. **150**, 210 (2017).
5. N. Rahayu Palapa and M. Said, Sci. Technol. Indones. **1**, 25 (2016).
6. T. Taher, R. Mohadi, D. Rohendi, and A. Lesbani, in *AIP Conf. Proc.* (American Institute of Physics Inc., 2017), p. 020028.
7. V. Rives and M.A. Ulibarri, Coord. Chem. Rev. **181**, 61 (1999).
8. A. Chatterjee, P. Bharadiya, and D. Hansora, Appl. Clay Sci. **177**, 19 (2019).
9. F.P. De Sá, B.N. Cunha, and L.M. Nunes, Chem. Eng. J. **215–216**, 122 (2013).

10. N. Zhao, H. Fan, M. Zhang, C. Wang, X. Ren, H. Peng, H. Li, X. Jiang, and X. Cao, J. Alloys Compd. **796**, 111 (2019).
11. N.R. Palapa, Y. Saria, T. Taher, R. Mohadi, and A. Lesbani, Sci. Technol. Indones. **4**, 36 (2019).
12. N.R. Palapa, T. Taher, M. Said, R. Mohadi, and A. Lesbani, Sci. Technol. Indones. **3**, 189 (2018).
13. N.R. Palapa, T. Taher, R. Mohadi, M. Said, and A. Lesbani, in *AIP Conf. Proc.* (2018), p. 20033.
14. N. Candu, D. Paul, I.-C. Marcu, V.I. Parvulescu, and S.M. Coman, Catal. Today **306**, 154 (2018).
15. R. Extremera, I. Pavlovic, M.R. Pérez, and C. Barriga, Chem. Eng. J. **213**, 392 (2012).
16. T. Taher, D. Rohendi, R. Mohadi, and A. Lesbani, in *IOP Conf. Ser. Mater. Sci. Eng.* (Institute of Physics Publishing, 2018).
17. K. Nejati, A.R. Akbari, S. Davari, K. Asadpour-Zeynali, and Z. Rezvani, New J. Chem. **42**, 2889 (2018).
18. D. Zhao, Z. Bai, and F. Zhao, Mater. Res. Bull. **47**, 3670 (2012).

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