C.2a.1.21-Intercalated layered double hydroxides.pdf

By Risfidian Mohadi

WORD COUNT	2428	TIME SUBMITTED	22-JAN-2022 11:08AM
		PAPER ID	81673334

Intercalated layered double hydroxides M^{2+}/M^{3+} (M^{2+}: Mg, Ca, Ni; M^{3+}: Al) with tungstosilicate polyoxometalate

Cite as: AIP Conference Proceedings **2242**, 040002 (2020); https://doi.org/10.1063/5.0007910
Published Online: 01 June 2020

A. Lesbani, T. Taher, N. R. Palapa, et al.

Intercalated Layered Double Hydroxides M^{2+}/M^{3+} (M^{2+}: Mg, Ca, Ni; M^{3+}: Al) with Tungstosilicate Polyoxometalate

A. Lesbani[1, a)], T. Taher[2], N. R. Palapa[1], R. D. Tarmizi[1], S. V. Aseri[1], Y. Irianty[1], M. Mardiyanto[3] and R. Mohadi[1]

[1]*Department of Chemistry, Faculty of Mathematics and Natural Sciences (FMIPA), Sriwijaya University, Palembang 30662, South Sumatra, Indonesia*
[2]*Department of Environmental Sciences, Graduate School, Sriwijaya University, Palembang 30139, South Sumatra, Indonesia*
[3]*Department of Pharmacy, Faculty of Mathematics and Natural Sciences (FMIPA), Sriwijaya University, Palembang 30662, South Sumatra, Indonesia*

[a)]Corresponding author: aldeslesbani@pps.unsri.ac.id

Abstract. Layered materials consist of M^{2+}/M^{3+} (M^{2+}: Mg, Ca, Ni ; M^{3+}: Al) were synthesized using coprecipitation method at pH constant to form Mg/Al-NO_3, Ca/Al-NO_3, and Ni/Al-NO_3 layered double hydroxides (LDHs). LDHs were intercalated with polyoxometalate anion $[\alpha\text{-}SiW_{12}O_{40}]^{4-}$ using ion exchange method under atmospheric nitrogen to form Mg/Al-$SiW_{12}O_{40}$, Ca/Al-$SiW_{12}O_{40}$, and Ni/Al-$SiW_{12}O_{40}$. All LDHs materials were characterized using X-Ray analyses, FTIR spectroscopy, and thermogravimetry analyses to investigate layer formation of materials. The results showed that interlayer distance of LDHs were increased after intercalation of tungstosilicate ion. IR spectrum showed that intensity vibration of nitrate at wavenumber 1600 cm^{-1} was decreased after anion intercalation due to insertion of large anion. Thermogravimetry analysis showed that there was an endothermic peak at 600 °C after intercalation due to decomposition of tungstosilicate anion.

Keywords: Layered double hydroxides, tungstosilicate, polyoxometalate, intercalation

INTRODUCTION

Layered double hydroxides (LDHs) is one of class anionic clay synthesis, which has positively charged and exchangeable anion in the interlayer [1]. Layers were formed as octahedral coordinated divalent (i.e., Ni, Zn, Ca, Cu, Mg) and trivalent (i.e., Al, Cr, Fe) metal cations, sharing edges to obtain the brucite layers [2]. LDHs has a unique structure and their ability in interlayer gallery and ion-exchangeable properties of interlayer guest ions make layered double hydroxide are widely useful applications. Layered double hydroxides have attracted attention due to their high anion-exchange capacities [3-4]. Layered double hydroxides can be represented as general formula $[M^{2+}(1\text{-}x)M^{3+}x(OH)_2](A^{n-})x/nH_2O$ [5]. Which in that positive charges are balanced by the interlayer anions such as Cl^-, NO_3^- and CO_3 [6-7]. However, the distance of basal spacing of the layered materials still has small interlayer constraints and narrow layer spacing due to the small exchange ions [8]. Layered double hydroxides need to be modified to increase its interlayer.

Recently, layered double hydroxides intercalated macroanion has been studied by researchers with an anion exchange method [3, 9]. One of the most well-known macroanion is polyoxometalate. Polyoxometalates consists of

Proceedings of the 5th International Symposium on Current Progress in Mathematics and Sciences (ISCPMS2019)
AIP Conf. Proc. 2242, 040002-1–040002-6; https://doi.org/10.1063/5.0007910
Published by AIP Publishing. 978-0-7354-2001-4/$30.00

hetero, and addenda atoms have various kind of structures, shapes, and charges are suitable anion for intercalation of LDHs.

LDHs intercalated with polyoxometalate are widely applied as adsorbent [10], catalyst [3], ion exchange [2], and also membrane [11, 12]. These properties are due to the effect of interlayer distance of LDHs. The large interlayer distance of LDHs has many advantages than small ones such as increasing adsorption capacity [13], increasing catalytic activity [14], and also increasing ion exchange properties [15]. Taher et al. reported that intercalated Ca/Al LDH with Keggin ion $[\alpha\text{-}SiW_{12}O_{40}]^{4-}$ can increase the adsorption capacity of iron(II) linear with increasing interlayer distance of that material [15]. On the other hand, that materials were also adsorbed cadmium(II) in similar capacity with iron(II) [16]. Thus Ca/Al intercalated with $[\alpha\text{-}SiW_{12}O_{40}]^{4-}$ has effective as removal divalent heavy metals.

In this work, tungstosilicate polyoxometalate $[\alpha\text{-}SiW_{12}O_{40}]^{4-}$ was used as intercalant agent. We reported here the preparation of M^{2+}/M^{3+} (M^{2+}: Mg, Ca, Ni; M^{3+}: Al) to form Mg/Al, Ca/Al and Ni/Al LDHs. These LDHs was intercalated with tungstosilicate polyoxometalate $[\alpha\text{-}SiW_{12}O_{40}]^{4-}$ to form Mg/Al-$[\alpha\text{-}SiW_{12}O_{40}]$, Ca/Al-$[\alpha\text{-}SiW_{12}O_{40}]$, and Ni/Al-$[\alpha\text{-}SiW_{12}O_{40}]$. Intercalated LDHs are widely used for various applications such as catalysts, adsorbents, and also ion exchanges. Thus, research of these materials are vital. Characterization of materials was carried out using XRD, FTIR and TG-DTA analyses to study the interlayer distance properties of these LDHs.

EXPERIMENTAL

Materials

Nickel nitrate $Ni(NO_3)_2{\cdot}6H_2O$, calcium nitrate $Ca(NO_3)_2{\cdot}6H_2O$, magnesium nitrate $Mg(NO_3)_2{\cdot}6H_2O$, aluminum nitrate $Al(NO_3)_3{\cdot}6H_2O$, sodium hydroxide (NaOH), sodium metasilicate (Na_2SiO_3), sodium tungstate (Na_2WO_4), hydrochloric acid (HCl), and potassium chloride (KCl) in analytical grade were purchased by Merck and Sigma Aldrich. Water was obtained from Purite® ion exchange water purification.

Characterization

Characterization of materials was conducted using XRD Diffractometer Rigaku Miniflex-600. The sample was scanned 1°/min. Spectrophotometer FT-IR Shimadzu FT-IR Prestige-21 was used to identify the functional groups. The sample was mixed with proportional KBr to from pellet. Characterization of thermal was conducted using Shimadzu TG/DTA 60A under the nitrogen atmosphere condition.

Preparation of Layered Double Hydroxides

LDHs were prepared by co-precipitation method at constant pH with molar ratio 3:1 [5, 11, 13, 17]. Divalent and trivalent metal solutions were stirred for an hour, and NaOH 2 M was added into the solution. The mixture was stirred for 4 hours and pH was adjusted to 10 by adding NaOH. The mixture was kept at 60 °C for 24 h followed with 80 °C for 36 h to obtain gel of layered double hydroxides. Solid materials were washed and dried at room temperature. Characterization of materials was performed using X-Ray, FTIR, and TG-DTA analyses.

Preparation of Tungstosilicate Polyoxometalate

Tungstosilicate polyoxometalate $[SiW_{12}O_{40}]^{4-}$ was prepared as follows. Sodium metasilicate (11 g) was dissolved with 100 mL water (solution A). Sodium tungstate (182 g) was dissolved with 300 mL warm water (Solution B). Into solution B, 4 M HCl was added dropwise and stirred at 350 rpm. Solution B were poured quickly into solution B followed with addition of 4 M HCl 50 mL. The mixture was stirred for an hour at 100 °C. pH solution was adjusted between 5–6. Sodium tungstate (1 M, 50 mL) was added and 4 M HCl 80 mL were poured into the mixture. The mixture was cooled to room temperature and the anion of tungstosilicate polyoxometalate were obtained [13].

Intercalation of LDHs-Tungstosilicate Polyoxometalate

The process of intercalation by ion exchange method was prepared using the mixtures of 1 g of LDHs with 50 mL NaOH 0.1 M and 2 g of tungstosilicate-polyoxometalate with 10 mL of water. The mixture was stirred under nitrogen atmosphere for 36 h at room temperature. Then, the mixture was washed and dried to obtain the intercalated LDHs. Characterization of the intercalated LDHs was conducted using XRD, FTIR, and TG-DTA analyses.

RESULTS AND DISCUSSION

The XRD powder analysis of Ca/Al, Mg/Al, Ni/Al and intercalated Ca/Al, Mg/Al, and Ni/Al LDHs are shown in Fig. 1. The XRD pattern of M^{2+}/M^{3+} LDHs (M^{2+}: Ca, Mg, Ni; M^{3+}: Al) shows almost similar diffraction peaks at around 11.51 (d_{003}), 23.30 (d_{006}), 29.38 (d_{008}), 34.77 (d_{012}), 48.15 (d_{018}), and 60.29 (d_{110}). These diffractions are specific and unique for all LHDs with various divalent and trivalent ions. Other different diffraction peaks are due to the composition of divalent/trivalent metal ions. The diffraction at d_{003} shifts to the lower 2θ values after intercalation of Ca/Al, Mg/Al, and Ni/Al LDHs with tungstosilicate $[\alpha\text{-}SiW_{12}O_{40}]^{4-}$ due to insertion of Keggin ion to form Mg/Al-$[\alpha\text{-}SiW_{12}O_{40}]$, Ca/Al-$[\alpha\text{-}SiW_{12}O_{40}]$, and Ni/Al-$[\alpha\text{-}SiW_{12}O_{40}]$. The size of anion $[\alpha\text{-}SiW_{12}O_{40}]^{4-}$ is larger than nitrate ion then diffraction of materials after intercalation was shifted to lower diffraction peaks.

Diffraction of Ni/Al-$[\alpha\text{-}SiW_{12}O_{40}]$ did not show higher crystallinity than Mg/Al-$[\alpha\text{-}SiW_{12}O_{40}]$ and Ca/Al-$[\alpha\text{-}SiW_{12}O_{40}]$ probably due to high water of crystallization content in Ni/Al LDHs before intercalation.

The gallery height of Ca/Al, Mg/Al and Ni/Al LDHs was increased after the intercalation with $[\alpha\text{-}SiW_{12}O_{40}]^{4}$. Table 1 shows the interlayer distance of LDHs before and after intercalation with tungstosilicate ion and schematic illustration of increasing interlayer space is shown in Fig. 2.

The layer of LDHs was increased in the range of 0.08–2.7 Å. Ni/Al LDH has a larger interlayer distance after the intercalation process than Ca/Al and Mg/Al LDHs. The role of transition metal element plays an important key for

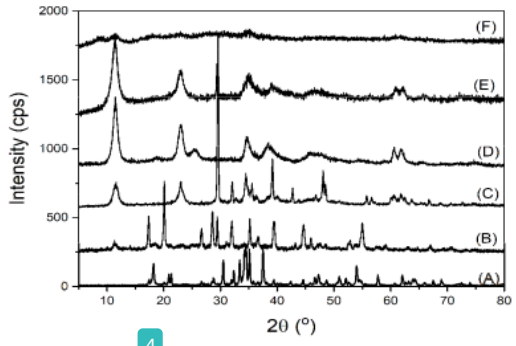

FIGURE 1. XRD powder pattern of (a) Ca/Al LDH, (b) Ca/Al-$[\alpha\text{-}SiW_{12}O_{40}]$, (c) Mg/Al LDH, (d) Mg/Al-$[\alpha\text{-}SiW_{12}O_{40}]$, (e) Ni/Al LDH, (f) NiAl-$[\alpha\text{-}SiW_{12}O_{40}]$.

TABLE 1. The interlayer distance of LDHs.

LDHs	Intercalation Process	
	Before	After
Ca/Al	4.25	4.41
Mg/Al	7.59	7.67
Ni/Al	7.66	10.36

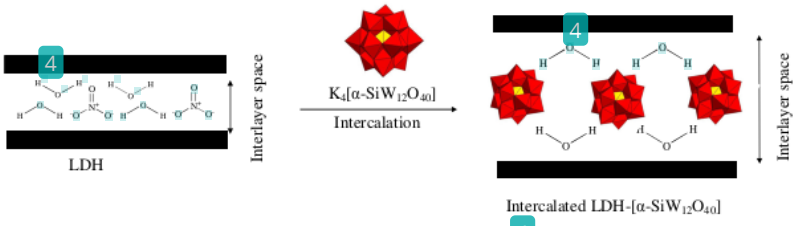

FIGURE 2. Schematic illustration of LDHs intercalation with Keggin ion $[\alpha\text{-}SiW_{12}O_{40}]^{4}$.

interlayer flexibility than an essential element. Thus, Ni/Al LDH has higher interlayer distance after intercalation compared with Ca/Al and Mg/Al.

The IR spectra of Ca/Al, Mg/Al, Ni/Al, and intercalated LDHs with Keggin ion are shown in Fig. 3. The peak at wavenumber 1380 cm^{-1} is attributed to the nitrate ion. The nitrate ion still remains in intercalated ZnCr LDH with boarder peaks suggesting that the anion exchange occurred. Another peak is appeared at 3480 cm^{-1} from the stretching vibration of OH. Vibration at 1380 cm^{-1} of Ca/Al LDHs was split into two peaks due to the cooperation of carbonate ion with nitrate ion between the interlayer of LDHs.

As shown in Fig. 4, the TG-DTA analysis is conducted of all LDH. Two endothermic peaks are identified for all LDH. In general, the first peak shows an endothermic peak at 110 °C is attributed to loss of water of the LDHs surface. The second peak at around 320 °C is due to the decomposition of the layer structure. On the other hand, the TG-DTA curve after intercalation shows three endothermic peaks at 100, 200 and around 640 °C. Peak at 640 °C is assigned as

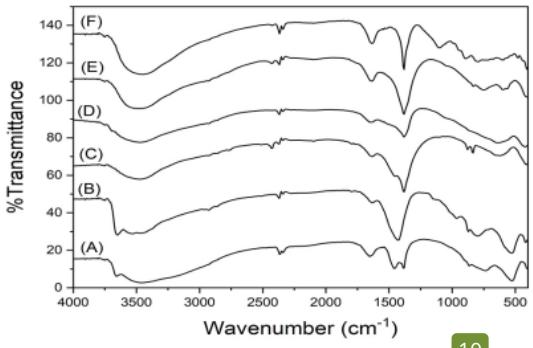

FIGURE 3. FTIR spectra of (a) Ca/Al LDH, (b) Ca/Al-[α-$SiW_{12}O_{40}$], (c) Mg/Al LDH, (d) Mg/Al-[α-$SiW_{12}O_{40}$], (e) Ni/Al LDH, (f) NiAl-[α-$SiW_{12}O_{40}$].

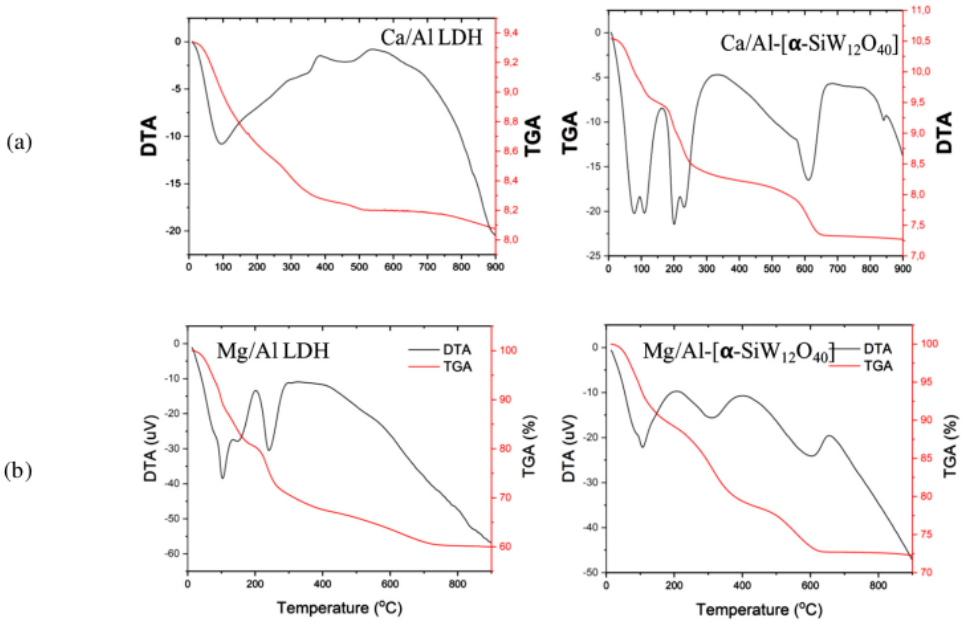

FIGURE 4. TG-DTA profile of (a) Ca/Al, (b) Mg/Al, and (c) Ni/Al LDHs with intercalated LDHs.

(c)

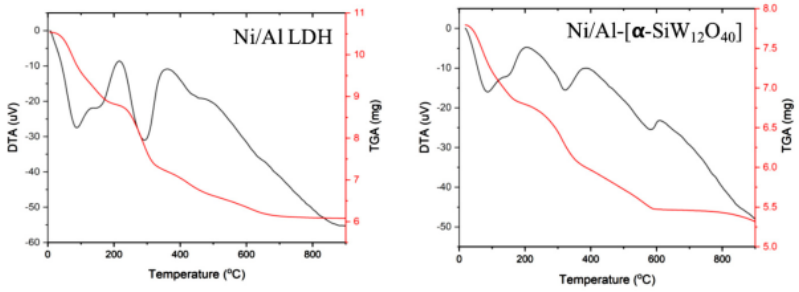

FIGURE 4 (continued). TG-DTA profile of (a) Ca/Al, (b) Mg/Al, and (c) Ni/Al LDHs with intercalated LDHs.

decomposition of tungstosilicate ion. The decomposition of Ca/Al LDHs did not show two endothermic peaks. Probably due to the small water of crystallization content of Ca/Al LDHs than Mg/Al and Ni/Al LDHs. This result shows that the intercalation of tungstosilicate ion on the interlayer distance of Ca/Al, Mg/Al, and Ni/Al LDHs were successfully conducted.

CONCLUSION

The XRD analysis showed that unique diffraction of LDHs was appeared at 11.51 (d_{003}), 23.30 (d_{006}), 29.38 (d_{009}), 34.77 (d_{012}), 48.15 (d_{018}), and 60.29 (d_{110}). Diffraction was shifted to a lower angle after intercalation with $[\alpha\text{-}SiW_{12}O_{40}]^{4-}$. The interlayer distance of LDHs was increased in the range 0.08–2.7 Å. IR spectrum showed that wavenumber at 1600 cm^{-1} was assigned as tungstosilicate ion intercalated to LDHs. TG-DTA profile shows there was endothermic peak at 650 °C which was identified as decomposition of tungstosilicate polyoxometalate. LDHs Mg/Al, Ca/Al, and Ni/Al was successfully synthesized and intercalated with tungstosilicate polyoxometalate $[\alpha\text{-}SiW_{12}O_{40}]^{4-}$ to form Mg/Al-$[\alpha\text{-}SiW_{12}O_{40}]$, Ca/Al-$[\alpha\text{-}SiW_{12}O_{40}]$, and Ni/Al-$[\alpha\text{-}SiW_{12}O_{40}]$.

ACKNOWLEDGMENTS

The authors are grateful to Kemenristek DIKTI, Republik Indonesia through "Hibah Penelitian Dasar 2019" contract no. 0057.10/UN9/SB3.LP2M.PT/2019. This research is also a small part of Hibah Profesi 2019 supported by Universitas Sriwijaya contract No. 0014/UN9/SK.LP2M.PT/2019.

REFERENCES

1. M. Laipan, H. Fu, R. Zhu, L. Sun, J. Zhu and H. He, Sci. Rep. **7**, 7277 (2017).
2. K. Cermelj, K. Ruengkajorn, J.-C. Buffet, D. O'Hare, J. Energy. Chem. **35**, 88-94 (2019).
3. F. Malherbe and J. P. Besse. J. Solid State Chem. **155**, 332-341 (2000).
4. Y. Saria, T. Taher, P. L. Hariani and A. Lesbani, AIP Conf. Proc. **2026**, 0200043 (2018).
5. N. R. Palapa, T. Taher, R. Mohadi and M. Said, AIP Conf. Proc. **2026**, 020033 (2018).
6. Y. Guo, Z. Zhu, Y. Qiu and J. Zhao, J. Environ. Sci. **25**, 944-953 (2013).
7. X. Han, K. Fang, J. Zhou, L. Zhao and Y. Sun, J. Colloid Interface Sci. **470**, 162-171 (2016).
8. M. Asif et al., Sensor Actuat. B: Chem. **239**, 243-252 (2017).
9. Y. Jia, Y. Fang, Y. Zhang, H. N. Miras and F-Y Song, Chem. Eur. J. **21**, 14862-14870 (2015).
10. S. Zhao, J. Xu, M. Wei and F. Y. Song, Green Chem. **13**, 384-388 (2011).
11. N. R. Palapa et al., Sci. Technol. Indones. **4**, 36–39 (2019).
12. M. Zubair, N. Jarrah, S. A. Manzar, and M. Al-harthi, J. Mol. Liq. **230**, 344-352 (2017).
13. A. Lesbani, R. Kawamoto, S. Uchida and N. Mizuno, Inorg. Chem. **47**, 3349- 3357 (2008).

14. T. Taher, D. Rohendi, R. Mohadi and A. Lesbani, Arab J. Bas. Appl. Sci. **26**, 125-136 (2019).
15. T. Taher et al., Bull. Chem. React. Eng. Cat. **14**, 260-267 (2019).
16. T. Taher et al., Indones. J. Chem. **19**, 873-881 (2019).
17. A. Lesbani et al., AIP. Conf. Proc. **2026**, 020011 (2018).

C.2a.1.21-Intercalated layered double hydroxides.pdf

ORIGINALITY REPORT

21%
SIMILARITY INDEX

PRIMARY SOURCES

1	puima.mipa.unsri.ac.id Internet	69 words — 3%
2	journal.ugm.ac.id Internet	58 words — 3%
3	aip.scitation.org Internet	57 words — 3%
4	ejournal2.undip.ac.id Internet	50 words — 2%
5	sciencetechindonesia.com Internet	46 words — 2%
6	seap.taylors.edu.my Internet	25 words — 1%
7	worldwidescience.org Internet	25 words — 1%
8	doaj.org Internet	17 words — 1%
9	www.ect-journal.kz Internet	17 words — 1%
10	repository.kulib.kyoto-u.ac.jp Internet	

16 words — 1%

11	budi.ristekdikti.go.id Internet	14 words — 1%
12	www.mdpi.com Internet	14 words — 1%
13	pubs.rsc.org Internet	13 words — 1%
14	mafiadoc.com Internet	12 words — 1%
15	cpk-front-devel.mzk.cz Internet	11 words — 1%

EXCLUDE QUOTES	OFF	EXCLUDE MATCHES	< 1%
EXCLUDE BIBLIOGRAPHY	ON		