Indonesian Journal of Material Research
e-ISSN: 2987-1654
Vol. 1, No. 2, July 2023

Indonesian Journal of
MATERIAL RESEARCH

Research Paper

Preparation of Layered Double Hydroxide-Polyoxometalate Based Composite

Yulizah Hanifah[1]*, Amri Amri[2]

[1] *Graduate School, Faculty of Mathematics and Natural Sciences, Sriwijaya University, Palembang, 30139, Indonesia*
[2] *Research Center of Inorganic Materials and Coordination Complexes, Faculty of Mathematics and Natural Sciences, Sriwijaya University, Palembang, 30139, Indonesia*
***Corresponding author**: yulizahanifah@gmail.com

Abstract

Material NiAl-$K_3[\alpha\text{-}PW_{12}O_{40}]$, NiAl-$K_4[\alpha\text{-}SiW_{12}O_{40}]$, ZnAl-$K_4[\alpha\text{-}SiW_{12}O_{40}]$ and ZnAl-$K_3[\alpha\text{-}PW_{12}O_{40}]$ were created. FTIR, XRD and SEM were used to characterize the substance. The findings of the successfully completed synthesis showed that peak diffraction angle for NiAl-LDH were at 11.58°, 23.18°, 35.01°, 39.41°, 46.70°, 60.94°, and 62.26° and diffraction at 10.29°, 20.07°, 34.02°, and 60.16° for ZnAl-LDH. The composite material LDH-polyoxometalate NiAl-$PW_{12}O_{40}$ that was at angles 10.76°, 26.59°, 30.8° and 63.1° and 8.61°, 25.27°, 33.8°, 66.34° for ZnAl-plyoxometalate. The typical polyoxometalate band on the composite material's FTIR spectrum proved tha intecalation of the substance. SEM examination revealed the aggregat for nearly all intercalated and synthesized materials.

Keywords
Layered Double Hydroxide, Polyoxometalate, Composite

Received: 19 May 2023, Accepted: 17 July 2023
https://doi.org/10.26554/ijmr.20231210

1. INTRODUCTION

The unique characteristics of self-assembled catalysts are utilized in heterogeneous catalysis. Therefore, the development of new structured catalysts and reactors can benefit from the utilization of these materials. Self-assembled catalysts can increase heat and mass transfer by avoiding the Ende for An inert binder to isolator crystals in catalytic beds. Therefore, it is reasonable to anticipate that one will be able to increase catalytic activity, which may also increase selectivity.

Polyoxometalate (POM) with the Keggin structure is frequently employed in acid catalysis because of its straightforward production process and chemical stability (Xu et al., 2018). The general formula for these acid polyoxometalates is a molecular cluster comprising several metal oxides. Twelve MO6 octahedral (M= P, W) are placed around a core PO_4 tetrahedron four groups of three edge-sharing MO_3O_{13}. The central PO_4 tetrahedron and an oxygen atom are shared by each group. When MO^+ or W^+ ions are replaced by V^{5+}, an excess of negative change results, which must be made up for (Pope, 2008). Ionic crystals known as hetepolyacids are composed of massive polyanions (the fundamental structure), opposing cations, and crystallization water. The so-called secondary structure is produced as a result.

Current research aims to establish an appropriate synthesis method while producing an orderly tertiary structure of POM that contains V. We have concentrated our efforts on using tests and PM6 calculations to understand the assembly process. Mixed metal oxides known as polyoxometalate are gaining attention due to their unique characteristics and several uses as electrocatalysts, adsorbents, photodegrades, and catalysts (Jia et al., 2014). According to Lu et al. (2019), polyoxometalates exhibit good thermal and oxidative stability as well as tunable acid-base characteristics. The vacant d-orbitals in polyoxometalates are also there to catch electrons (Umapathi et al., 2019). Keggin, Anderson, and Dowson kinds of polyoxometalates exist (Liu et al., 2016). The type Keggin-polyoxometalate has received the greatest attention in this area of research lately. Studies on polyoxometalate, dye-sensitized solar cells, adsorption, and photocatalysis (Zhao et al., 2020) among other applications, have all been described.

The elimination of contaminants, layered double hydroxide (LDH), which has positively charged multimetal cations and interlayers in brucite-like layers compensatory anions, has been used. Energy storage, heavy metal ions, adsorbents, and other techniques to remove pollutants from wastewater have been the focus of recent LD research (Behbahani et al., 2020). By modifying the active centers and shape of LDHs utilizing a variety of control synthesis, techniques, such as intercalated and immobilized, it's possible to significantly improve photodegradation performance.

In summary, polyoxometalate $K_3[\alpha\text{-}PW_{12}O_{40}]$ and $K_4[\alpha\text{-}SiW_{12}O_{40}]$ was investigated. Material composite layered double hydroxide (NiAl-LDH and ZnAl-LDH) on Keggin polyoxometalate (NiAl-$K_3[\alpha\text{-}PW_{12}O_{40}]$, NiAl-$K_4[\alpha\text{-}SiW_{12}O_{40}]$, ZnAl-$K_4[\alpha\text{-}SiW_{12}O_{40}]$ and ZnAl-$K_3[\alpha\text{-}PW_{12}O_{40}]$) modified material was characterized using analysis FTIR, XRD, and SEM.

2. EXPERIMENTAL SECTION

2.1 Chemical

We used hydrogen peroxide, sodium hydroxide, sodium tungstate, sodium phosphate, concentrated hydrogen chloride, aluminum nitrate monohydrate, zinc nitrate hexahydrate distilled water, sodium carbonate, and concentrated hydrogen chloride were purchased from Merck and Sigma Aldrich.

2.2 Synthesis of ZnAl-LDH

In 50 mL of distilled water, 0.75 M of zinc nitrate hexahydrate and 0.25 M of aluminum nitrate nonahydrate were dissolved, respectively. A beaker containing 20 mL of distilled water received the mixture. To get ZnAl-LDH, the mixture was then added to 2 M sodium hydroxide at pH 8 and agitated for 4 hours at 343 K.

2.3 Synthesis of NiAl-LDH

In 50 mL of distilled water, 0.75 M of nickel nitrate hexahydrate and 0.25 M of aluminum nitrate monohydrate were dissolved, respectively. The combination was added to a beaker that already had 20 mL of distilled water in it. To obtain NiAl-LDH, the mixture was added to 2 M sodium hydroxide at pH 8 and agitated for 4 hours at 343 K.

2.4 Synthesis of Polyoxometalate

Solution A was created by dissolving 2 g of sodium phosphate in 100 mL of distilled water. Solution B a created by dissolving 125 g of sodium tungate in 300 mL of boiling water. Then, 10 mL of concentrated 37% HCl kept at 322 K was added to solution B, followed by the addition of solution A. This solution has been dried and filtered. A white precipitate of polyoxometalate $K_4SiW_{12}O_{40}$ and $K_3PW_{12}O_{40}$ was produced by the addition of 50 g of $KCl.nH_2O$.

2.5 Characterization

The determination of the functional groups, compounds, and chemical bonds used Fourier transform infrared in range wavenumber 4000−500 cm^{-1} (Shimadzu). X-ray diffractometer in 2θ= 5−80° to determine the crystallinity of material synthesis and preparation (Rigaku, Japan), Scanning electron microscope in 2500 times magnification was carried out to determine the morphological structure (Quanta, England). All were used to characterize the $K_4[\alpha\text{-}SiW_{12}O_{40}]$, $K_3[\alpha\text{-}PW_{12}O_{40}]$, NiAl-LDH, ZnAl-LDH, NiAl-$K_3[\alpha\text{-}PW_{12}O_{40}]$, NiAl-$K_4[\alpha\text{-}SiW_{12}O_{40}]$, ZnAl-$K_4[\alpha\text{-}SiW_{12}O_{40}]$ and ZnAl-$K_3[\alpha\text{-}PW_{12}O_{40}]$.

2.6 Preparation of Composite

To make solution A, which is 2 g of prepared material of polyoxometalate, 50 mL of distilled water was utilized. In solution, B, 25 mL of sodium hydroxide 1 M is combined with 2 g of pure and composite LDH, a material catalyst. The suspension was immediately combined with N_2 gas for 24 hours to produce the composite LDH. XRD analysis, FTIR spectrometer, and SEM analysis. Water molecules $K_3PW_{12}O_{40}$ and $K_4SiW_{12}O_{40}$ polyoxometalate were produced, according to previously published research (Lesbani and Mohadi, 2014).

3. RESULTS AND DISCUSSION

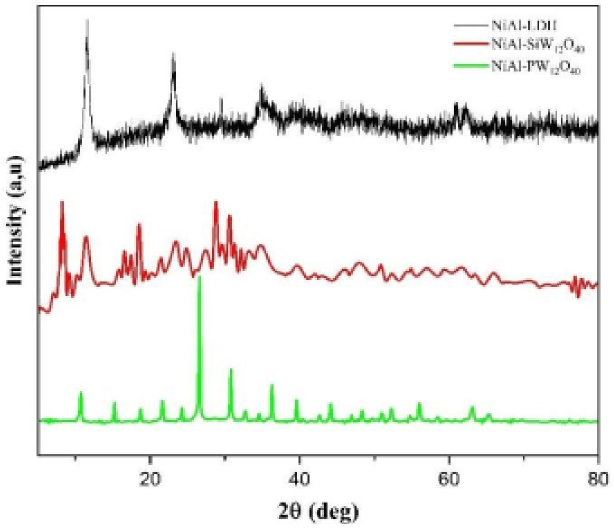

Figure 1. XRD Diffraction of NiAl-LDH Pristine and NiAl-LDH Composite

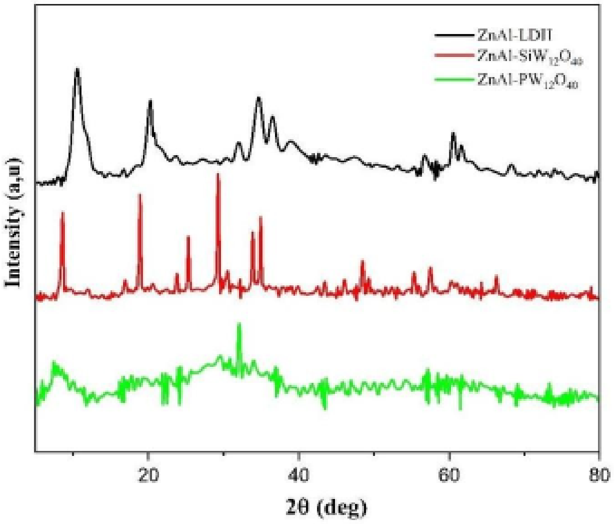

Figure 2. XRD Diffraction of ZnAl-LDH Pristine and ZnAl-LDH Composite

XRD analysis of LDH pristine and LDH composites was made. The X-ray diffraction pattern of pure polyoxometalate. compounds which are $K_4[\alpha\text{-}SiW_{12}O_{40}]$, $K_3[\alpha\text{-}PW_{12}O_{40}]$, LDH pristine NiAl-LDH, NiAl-$SiW_{12}O_{40}$, and NiAl-$PW_{12}O_{40}$ are shown in Figure 1. The LDH crystal plane is shown by LDH pristine diffraction peaks at 11.58°, 23.18°, 35.01°, 39.41°, 46.70°, 60.94°, and 62.26° which correspond to the (003), (006), (012), (015), (018),

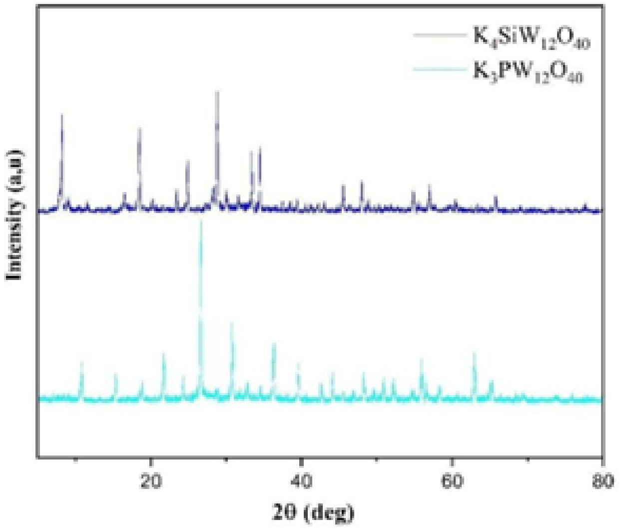

Figure 3. XRD Diffraction of $K_3PW_{12}O_{40}$ and $K_4SiW_{12}O_{40}$

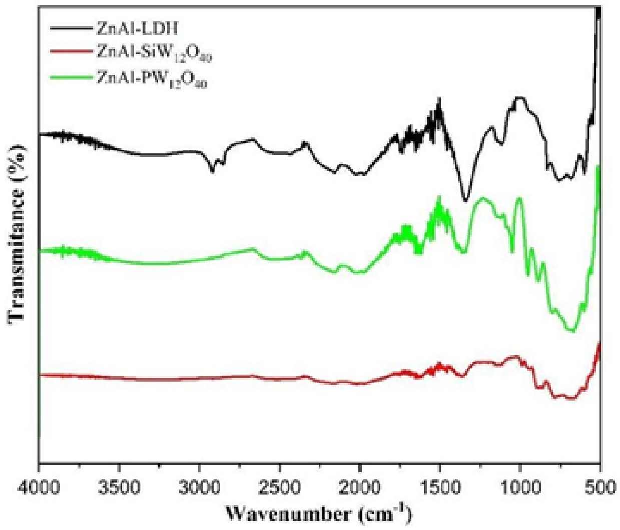

Figure 5. FTIR Spectra of ZniAl-LDH Pristine and ZnAl-LDH Composite

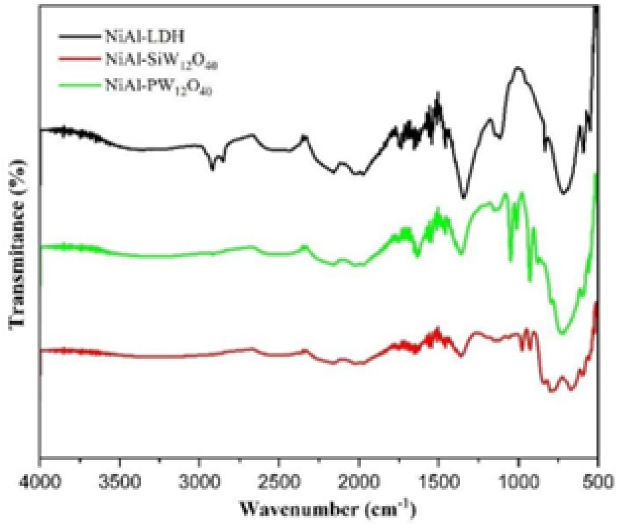

Figure 4. FTIR Spectra of NiAl-LDH Pristine and NiAl-LDH Composite

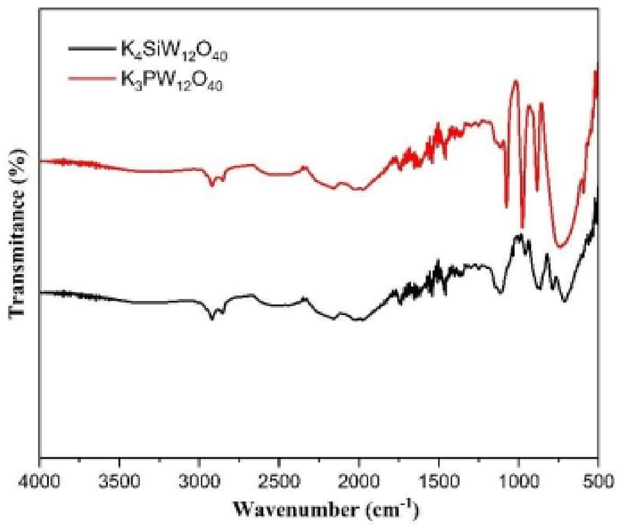

Figure 6. FTIR Spectra of $K_3PW_{12}O_{40}$ and $K_4SiW_{12}O_{40}$

(110) and (113) correspondingly, indicate the LDH crystal plane (JCPNDF No. 22-0452). The diffraction of polyoxometalate compounds $K_3PW_{12}O_{40}$ and $K_4SiW_{12}O_{40}$ was shown at 2θ angles of 8-20°, and 26-32° (Wang et al., 2021a; Wang et al., 2021b). Owing to the utilization of composite LDH which polyoxometalate on NiAl-LDH. According to Figure 1, each polyoxometalate peak in NiAl-$PW_{12}O_{40}$ that was at angles 10.76°, 26.59°, 30.8° and 63.1° which correspond to the (003), (006), (009), and (110) is still visible. $K_4SiW_{12}O_{40}$ is present in LDH. The synthesis of the composites was successful. The successfully intercalated of NiAl composite material by showing angles at 10.76°, 26.59°, 30.8° and 63.11°. Each material was shown the LDH pristine by peak 003 indicating that the polyoxometalate was intercalated on interlayer of layered material LDH which showed by peak shift towards the lower.

ZnAl-LDH, ZnAl-$SiW_{12}O_{40}$, and ZnAl-$PW_{12}O_{40}$ X-ray diffraction are shown in Figure 2. ZnAl-LDH was found at 10.29°, 20.07°, 34.02°, and 60.16°, which correspond to the lattice planes (012), (110), (003), and (006). The PW has diffraction peaks at 7.73°, 28.6°, and 35.6° which correspond to (003), (006), and (110). The peaks of $PW_{12}O_{40}$ are still present in ZnAl-PW. The diffraction ZnAl-$SiW_{12}O_{40}$ was located at 8.61°, 25.27°, 33.8°, 66.34°. The peaks of composite ZnAl-$SiW_{12}O_{40}$ are present in polyoxometalate $SiW_{12}O_{40}$ in layered ZnAl-LDH. Nevertheless, the typical polyoxometalate compound in this study showed diffraction at angles 8.26°, 11.34°, 29°, and 35.1° that shown in Figure 3.

Figure 4 presents FTIR spectra of NiAl-LDH, NiAl-$SiW_{12}O_{40}$, and NiAl-$PW_{12}O_{40}$. FTIR spectra of NiAl-$SiW_{12}O_{40}$ in the range

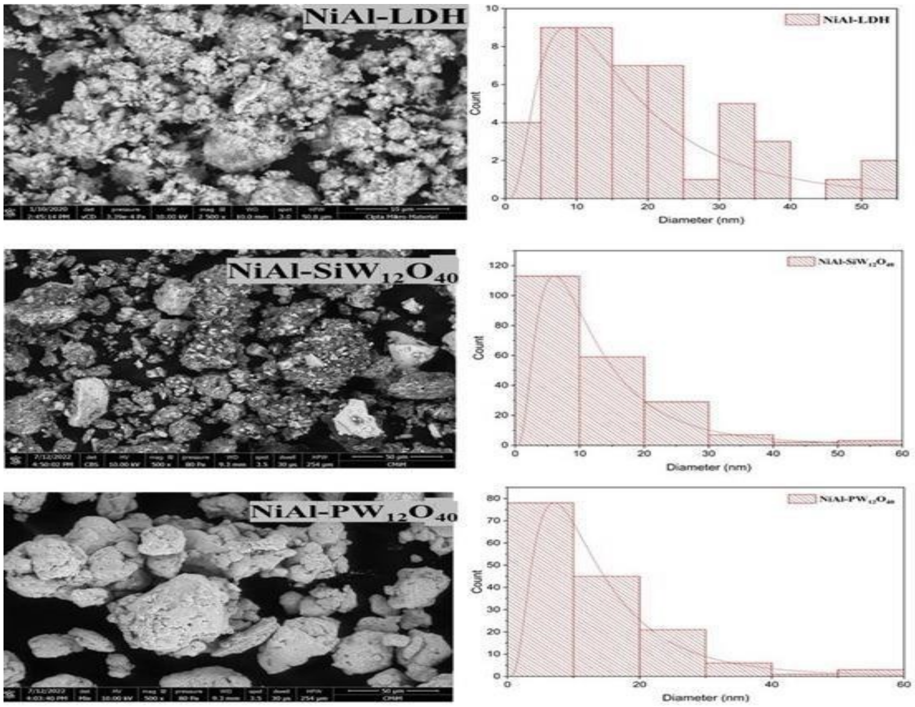

Figure 7. SEM of NiAl-LDH Pristine and NiAl-LDH Composite

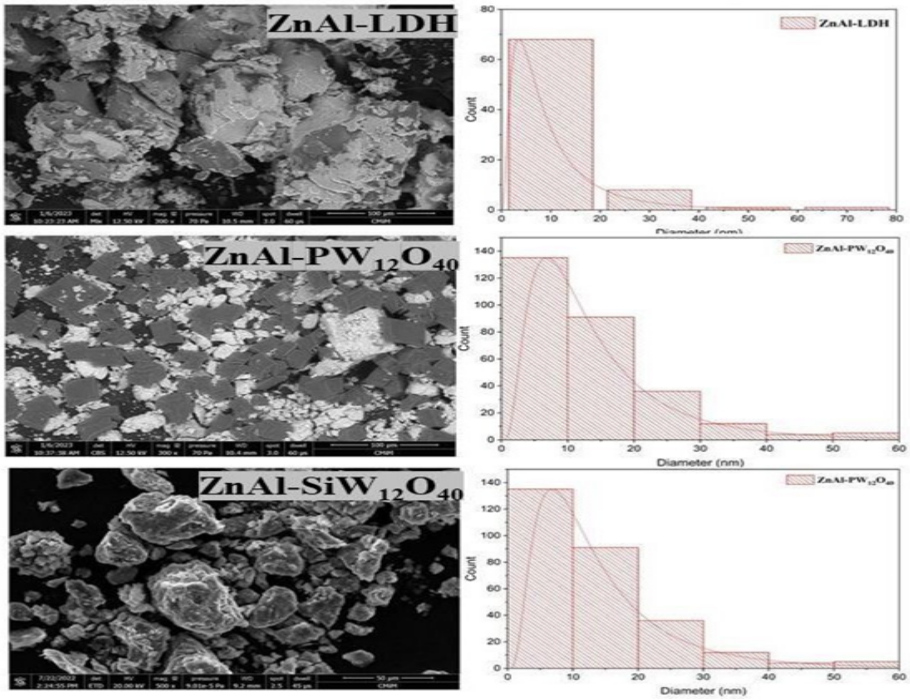

Figure 8. SEM of ZnAl-LDH Pristine and ZnAl-LDH Composite

wavenumber 3178, 1541, 1363, and 769.9 cm^{-1}. NiAl-PW$_{12}$O$_{40}$ in wavenumber of 3317, 1560, 929, 717 cm^{-1}. O-H stretching from the interlayer of NiAl-LDH may be caused by the band at 3178 cm^{-1}. The hydroxyl and NO$_3^-$ vibrations were ascribed to the absorption peaks at 1541 and 1363 cm^{-1}. According to Xu et al. (2018), the broad bands at 769.9 cm^{-1} are due to the asymmetric stretching of M-O from M (metal = P, W, Zn, Al) from NiAl-LDH, ZnAl-LDH pristine, LDH composite, and both polyoxometalate.

Figure 5 shows the infrared spectrum of ZnAl-LDH pristine and ZnAl-LDH composite. The spectrum of the polyoxometalate compound was measured. The alfa-Keggin SiW_{12} exhibits four distinctive asymmetric vibration bands that correspond to 927, 973, 882, and 813 cm^{-1} in the range 780-980 cm^{-1} indicated by W-O (Mirzaei et al., 2019). Figure 6 shows the FTIR spectra of $K_3PW_{12}O_{40}$ in wavenumber 2917, 1685, 1076, 976, 884, 740, 594 cm^{-1}, and for FTIR $K_4SiW_{12}O_{40}$ showed a peak at 2918, 1654, 1399, 1114, 958, 865, 787, and 714 cm^{-1}. Figure 6 shows the successfully synthesized. Figure 6 Using FTIR analysis, the surface groups of LDH were identified. The composites synthesis was successfully prepared by shown in wavenumber at 3244, 1637, 1363, 863, and 666 cm^{-1} for ZnAl-$SiW_{12}O_{40}$. FTIR spectra at wavenumber 3276, 1685, 1363, 952, 887 cm^{-1}. The composite ZnAl-LDH showed the characteristic of polyoxometalate that identified the intercalation process was successful. The spectrum band FTIR between 3110-2980 cm^{-1} showed white molekul in the interlayer and brucite-like layers. This band was shown for all material pristine and material composite. The H_2O from interlayer water is banded at 1630 cm^{-1}. The spectrum band at 1381 cm^{-1} represents the CO_3 vibrations (Zhao et al., 2020). The bands of 983-870 cm^{-1} and 804.84 cm^{-1}, respectively, represent the W-O and W-O-W bands (Wang et al., 2021b). These bands can still be seen in their typical LDH-polyoxometalate catalyst state.

SEM analysis was used to analyze the morphology of the subsequently synthesized NiAl- LDH, as seen in Figure 7 and Figure 8. The NiAl-LDH and ZnAlLDH samples showed morphology, demonstrating the validity of the LDH microsphere to the layered framework. LDH composite and LDH are pristine and have different heterostructures. The morphology which appears to be created by the assembly of the two-layered materials is proof that LDH intercalated heterostructures are present. When $[SiW_{12}O_{40}]$, the aggregate appeared on the surface material, according to the morphological structure. It is feasible to understand that platelet-shaped microcrystals exist. If the LDH composite is compared to the LDH pristine, was polypore which means introducing polyoxometalate added to the blending solution has the potential to bond to the composite's surface.

4. CONCLUSIONS

In conclusion, we described a quick, low-cost, and easy approach for producing effective co-precipitation on the materials LDH pristine and LDH composite. Investigation of the molecular and crystal structure of the composite, as well as the chemical composition and surface morphology, using characterizing techniques like FTIR, XRD, and SEM. The results showed that material pristine (NiAl-LDH and ZnAl-LDH) and material composite (NiAl-$K_3[\alpha\text{-}PW_{12}O_{40}]$, NiAl-$K_4[\alpha\text{-}SiW_{12}O_{40}]$, ZnAl-$K_4[\alpha\text{-}SiW_{12}O_{40}]$ and ZnAl-$K_3[\alpha\text{-}PW_{12}O_{40}]$) were successfully synthesized and prepared. Characterization of polyoxometalate using spectra FTIR showed the characteristic band of polyoxometalate in both NiAl-polyoxometalate and ZnAl-polyoxometalate. Resulted analysis using XRD confirmed that characteristic peak that showed the successful of intercalated polyoxometalate on layered double hydroxide which showed there are SiW or PW on polyoxometalate.

5. ACKNOWLEDGEMENT

The authors thank to Research Center of Inorganic Materials and Complexes Universitas Sriwijaya for valuable discussion, apparatus, and chemical analysis.

REFERENCES

Behbahani, E. S., K. Dashtian, and M. Ghaedi (2020). Fe/Co-Chalcogenide-Stabilized Fe_3O_4 Nanoparticles Supported MgAl-Layered Double Hydroxide As a New Magnetically Separable Sorbent for the Simultaneous Spectrophotometric Determination of Anionic Dyes. *Microchemical Journal*, **152**; 104431

Jia, Y., S. Zhao, and Y. F. Song (2014). The Application of Spontaneous Flocculation for the Preparation of Lanthanide-Containing Polyoxometalates Intercalated Layered Double Hydroxides: Highly Efficient Heterogeneous Catalysts for Cyanosilylation. *Applied Catalysis A: General*, **487**; 172–180

Lesbani, A. and R. Mohadi (2014). Brönsted Acid of Keggin Type Polyoxometalate Catalyzed Pinacol Rearrangement. *Bulletin of Chemical Reaction Engineering & Catalysis*, **9**(2); 136

Liu, C. G., T. Zheng, S. Liu, and H. Y. Zhang (2016). Photodegradation of Malachite Green Dye Catalyzed by Keggin-Type Polyoxometalates under Visible-Light Irradiation: Transition Metal Substituted Effects. *Journal of Molecular Structure*, **1110**; 44–52

Lu, D., X. Zhang, H. Chen, J. Lin, Y. Liu, B. Chang, F. Qiu, S. Han, and F. Zhang (2019). A High Performance Solid-State Asymmetric Supercapacitor Based on Anderson-Type Polyoxometalate-Doped Graphene Aerogel. *Research on Chemical Intermediates*, **45**; 3237–3250

Mirzaei, M., H. Eshtiagh-Hosseini, and A. Hassanpoor (2019). Different Behavior of Pda As a Preorganized Ligand Versus Pca Ligand in Constructing Two Inorganic-Organic Hybrid Materials Based on Keggin-Type Polyoxometalate. *Inorganica Chimica Acta*, **484**; 332–337

Pope, M. T. (2008). *Chapter 240 Polyoxometalates*, volume 38. Handbook on the Physics and Chemistry of Rare Earths

Umapathi, A., N. P. Nagaraju, H. Madhyastha, D. Jain, S. P. Srinivas, V. M. Rotello, and H. K. Daima (2019). Highly Efficient and Selective Antimicrobial Isonicotinylhydrazide-Coated Polyoxometalate-Functionalized Silver Nanoparticles. *Colloids and Surfaces B: Biointerfaces*, **184**; 110522

Wang, J., G. Lv, and C. Wang (2021a). A Highly Efficient and Robust Hybrid Structure of CoNiN@NiFe LDH for Overall Water Splitting by Accelerating Hydrogen Evolution Kinetics on NiFe LDH. *Applied Surface Science*, **570**; 151182

Wang, J., G. Wang, B. Cheng, J. Yu, and J. Fan (2021b). Sulfur-Doped $g\text{-}C_3N_4/TiO_2$ S-Scheme Heterojunction Photocatalyst for Congo Red Photodegradation. *Chinese Journal of Catalysis*, **42**(1); 56–68

Xu, M., B. Bi, B. Xu, Z. Sun, and L. Xu (2018). Polyoxometalate-Intercalated ZnAlFe-Layered Double Hydroxides for Adsorbing Removal and Photocatalytic Degradation of Cationic Dye. *Applied Clay Science*, **157**; 86–91

Zhao, M., Y. Fang, L. Ma, X. Zhu, L. Jiang, M. Li, and Q. Han (2020). Synthesis, Characterization and in Vitro Antibacterial Mechanism Study of Two Keggin-Type Polyoxometalates. *Journal of Inorganic Biochemistry*, **210**; 111131