

PILLARIZATION OF DOUBLE LAYER HYDROXIDES USING $H_3[\alpha-PW_{12}O_{40}] \cdot nH_2O$: EFFECT OF PILLARIZATION TIME

Muhammad Imron^{1*}, Muhammad Said¹

¹Department of Chemistry, Faculty of Mathematics and Natural Sciences, Srijwijaya University

*Corresponding Author E-mail : muhammadimron211195@gmail.com

ABSTRACT

The pillarization of Mg/Al double layer hydroxides using polyoxometalate $H_3[\alpha-PW_{12}O_{40}] \cdot nH_2O$ by comparing the pillarization time i.e. 3 hours, 6 hours, 9 hours, 12 hours, 24 hours, 36 hours and 48 hours has been done. The product of a pillarization was characterized using an FT-IR spectrophotometer and XRD analysis. The result characterization of FT-IR spectrophotometer does not show the optimum of pillarization each time condition. Characterization using XRD shows the optimum pillarization process at 36 hours by showing the existence of double layer hydroxides material at diffraction angle 11.69° deg, 18.30° deg and 34.71° deg. Diffraction in the 60°-63° deg indicates the existence of a pillarization double layer hydroxides.

Keywords: Layered double hydroxides, pillarization, polyoxometalate $H_3[\alpha-PW_{12}O_{40}] \cdot nH_2O$.

INTRODUCTION

Inorganic materials can be classified into layered materials and porous materials. These materials have their respective advantages as absorbents, catalysts, ion exchangers, and sensors (Lin et al, 1997). The layered material is divided into two types: layered materials are in nature and coated materials are synthesized in the laboratory (Han et al, 2017). The layered material in nature has many advantages such as kaolin, halloysite (halloysite), illite, vermiculite, bentonite and much more. The layered compounds that are in the interior have a deficiency that is still a lot of impurities and is difficult to replace (Shimizu et al, 2006).

Meanwhile, the synthetic-coated and modification materials in the laboratory have many advantages i.e. fewer impurities and the structure is easy to replace so it can be modified and widely applied as adsorbent or catalyst for example double layer hydroxides. Aside from being an absorbent and a catalyst, double layer hydroxides is usually applied as ion exchangers, catalyst carriers, in industry, and medicine (Delidovich & Palkovits, 1991). For example, a double-layer hydroxides material commonly used as a catalyst for condensation reactions is Mg/Al hydrotalcite (Mg/Al mole ratio in the range of 2.1 to 3.6) with carbonate and nitrate anions in interlayer space (Hincapié et al, 2017).

In the use of layered materials still have weaknesses that are small surface area and the distance between the narrow layers due to the presence of small exchange ions (Goodarzi et al, 2016). To overcome this problem, the double layer hydroxides is modified by means of pillarization. The studies were undertaken by Zhang (2004) and Qin (2014) double layer hydroxides were inserted anion carboxylic and folic acid compounds and produced a surface area of 40-48 m²/g. This result is better than the undamaged double layer hydroxides surface area of 26 m²/g. When compared Kwon and Pinnavaia (1989) to Zhang (2012), He studied double layer

hydroxides was inserted using two types of $\alpha[SiV_3W_9O_{40}]^{4-}$ and $H_3PW_{12}O_{40}$ compounds which comprised a Keggin-type polyoxometalate compound with 155 m²/g surface area. Uncoated double layer hydroxides surface area of 26 m²/g. This suggests that the polyoxometalate compound can produce a larger surface area compared to other anion compounds so that the polyoxometalate double layer hydroxides can be effectively used as an adsorbent.

Based on the Pinnavaia (1996), the double layer hydroxides Mg/Al intercalated with anionic polyoxometalate compound with Keggin ($\alpha-H_2W_{12}O_{40}^{6-}$) has a height of 10, while the Dawson type ($\alpha-P_2W_{18}O_{62}^{6-}$) has two altitudes of 14.5 and 12.8, Finke ($Co_4(H_2O)_2(PW_9O_{34})_2^{10-}$). The double layer hydroxy Mg₃Al intercalated with anionic polyoxometalate compound with Keggin ($\alpha-H_2W_{12}O_{40}^{6-}$) has a height of 10, while the Dawson type ($\alpha-P_2W_{18}O_{62}^{6-}$) has two altitudes of 14.5 and 12.8, Finke ($Co_4(H_2O)_2(PW_9O_{34})_2^{10-}$) also has two heights of 13.3 and 12.6. The also has two heights of 13.3 and 12.6. The differences in polyoxometalates orientation are rationalized in terms of different electrostatic interactions and hydrogen bonds between the polyoxometalate pillar and the double layer hydroxide layer. In this study, a double layer hydroxides was pillarized with polyoxometalate $H_3[\alpha-PW_{12}O_{40}] \cdot nH_2O$. The pillarization time was studied in order to know the optimal time for these process.

EXPERIMENTAL SECTION

Equipments

Equipments used in this research are a set of standard laboratory, magnetic stirrer, thermometer, hot plate, oven, vacuum, desiccator, X-Ray Diffraction (Rigaku Miniflex 600), and FT-IR spectrophotometer (Shimadzu prestige-21).

Materials

The materials used in this research are sodium phosphate (Na_3PO_4), sodium tungstate (Na_2O_4W), hydrochloric acid (HCl), potassium hydroxide (KOH), potassium chloride (KCl), diethyl ether ($(C_2H_5)_2O$), sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3), magnesium nitrate ($Mg(NO_3)_2$), aluminum nitrate ($Al(NO_3)_3$).

Article History

Received: 8 December 2016

Received in revised form: 15 February 2017

Accepted: 25 February 2017

DOI: 10.26554/sti.2017.2.2.45-49

©2017 Published under the term of the CC BY NC SA license

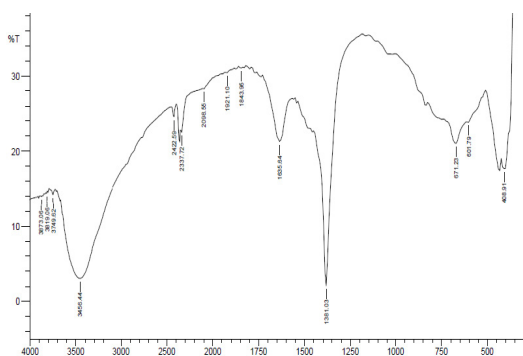


Figure 1 FT-IR spectra of Mg/Al double layer hydroxides compound

Procedures

Synthesis of Mg/Al Double Layer Hydroxides

The double layer hydroxy preparation was carried out by mixing as much as 64.01 g of $Mg(NO_3)_2 \cdot 6H_2O$ (2 mol) and 46.64 g of $Al(NO_3)_3 \cdot 9H_2O$ (1 mol) into 150 mL of aquades (solution A). A total of NaOH with 26.62 g $NaCO_3$ was dissolved in 150 mL aquades (solution B). Solution A is added to solution B and stirred slowly followed by the addition of 100 mL of aquades and a pH ranging from 9 to 10 to form a precipitate. The obtained precipitate is dried in an oven at 80 °C and ready to be characterized using FT-IR spectroscopy, and XRD analysis.

Synthesis of Polyoxometalate $H_3[\alpha-PW_{12}O_{40}] \cdot nH_2O$

A total of 125 g of sodium tungstate and 20 g of sodium phosphate were mixed with 187.5 ml of boiling water in 500 mL of a glass beaker. A total of 100 ml of concentrated hydrochloric acid was added slowly to the mixture and stirred using a magnetic stirrer. The stirring process is continuous or continuous which causes the solid to dissolve. The phosphotungstate acid will begin to separate when half of the hydrochloric acid is added then the resulting solution becomes clear and cooled. A cold solution was added 75 mL of diethyl ether and extracted. After extraction process obtained 3 layers which then separated and taken the bottom layer. The bottom layer obtained was evaporated using a rotary evaporator to obtain a white solid $H_3[\alpha-PW_{12}O_{40}] \cdot nH_2O$. Characterization of $H_3[\alpha-PW_{12}O_{40}] \cdot nH_2O$ compounds was performed using FT-IR spectrophotometer and XRD analysis.

Pillarization Double-layer hydroxides with Polyoxometalate $H_3[\alpha-PW_{12}O_{40}] \cdot nH_2O$

Two grams of double layer hydroxy were dissolved 25 NaOH and 1 g of polyoxometalate compound with 50 ml of aquades then heated to 70 °C (using a hot plate) under N_2 gas. After 1 hour of reaction, the temperature is lowered to 30 °C. Then the suspension is cooled and the product is washed with water and dried at room temperature. Characterization of pillarization compounds was done using XRD, and FT-IR spectrophotometer.

RESULTS AND DISCUSSION

Preparation and Characterization of Double Layer Hydroxides, Polyoxometalate $H_3[\alpha-PW_{12}O_{40}] \cdot nH_2O$ and Double Layer Hydroxy Pillarization with Polyoxometalate $H_3[\alpha-PW_{12}O_{40}] \cdot nH_2O$ Using FT-IR Spectrophotometer.

Synthesis of double layer hydroxides compound using magnesium nitrate and aluminum nitrate to form Mg/Al double layer hydroxides. M^{2+} charged metal cations represent magnesium and aluminum represented by M^{3+} each of which is bound to an OH⁻ anion. The results of the process of synthesis this double layer

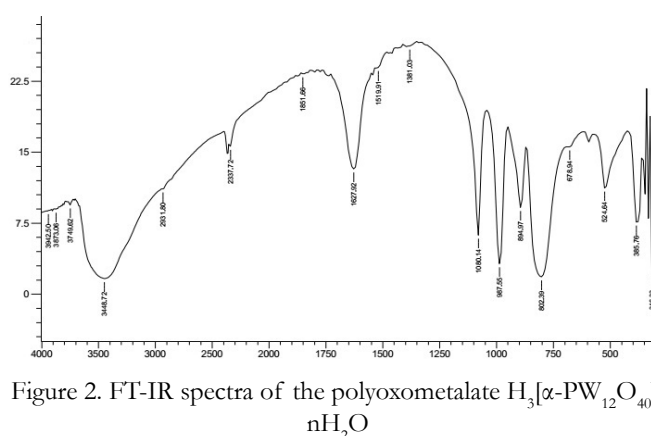


Figure 2. FT-IR spectra of the polyoxometalate $H_3[\alpha-PW_{12}O_{40}] \cdot nH_2O$

hydroxides are white solid, which is further characterized by using FT-IR spectrophotometer (Hanifah & Palapa, 2016).

The FT-IR spectra of the double layer hydroxides material is presented in Figure 1. The widespread vibration peak between the 3800-300 cm^{-1} wave numbers is the vibration of the OH strain within the structure of the double layer hydroxides. The presence of a peak detected at the wave number 1635.54 cm^{-1} is the bend vibration of OH. In the region of wavenumber 1381.03 cm^{-1} , there is a vibration which is symmetrical stretching of nitrate and 671.23 cm^{-1} is nitrate bending vibration. In the wave number 408.91 cm^{-1} is the vibration of Mg-O (Swenson et al, 2016).

Synthesis of polyoxometalate $H_3[\alpha-PW_{12}O_{40}] \cdot nH_2O$ compound using concentrated hydrochloric acid which aims to form phosphotungstate acid so as to cause the acidity of the polyoxometalate compound to increase. The result of the synthesis of polyoxometalate compound of $H_3[\alpha-PW_{12}O_{40}] \cdot nH_2O$ is in the form of white solid.

After the formation of the $H_3[\alpha-PW_{12}O_{40}] \cdot nH_2O$, the compound was then characterized using an FT-IR spectrophotometer which serves to identify functional compound groups formed on the $H_3[\alpha-PW_{12}O_{40}] \cdot nH_2O$. The FT-IR spectrum of the polyoxometalate $H_3[\alpha-PW_{12}O_{40}] \cdot nH_2O$ compound of the result of the measurement is shown in Figure 2.

Figure 2 shows the peaks of the functional groups of the polyoxometalate $H_3[\alpha-PW_{12}O_{40}] \cdot nH_2O$ compound appear at about 4000-400 cm^{-1} wavenumbers. The wave number 1081 cm^{-1} is a P-O vibration. The wave number 987 cm^{-1} denotes the vibration W = O. At the 802 cm^{-1} wavenumber is a W-Oc-W vibration (Kim et al.2009).

The double layer hydroxides pillarization process with the polyoxometalate $H_3[\alpha-PW_{12}O_{40}] \cdot nH_2O$ compound was conducted to increase the distance between the double layer hydroxides layer to wider by replacing the OH⁻ anion present in the double layer hydroxides using a larger anion of the polyoxometalate-type keggin $[\alpha-PW_{12}O_{40}]^{3-}$.

The double layerhydroxides pillar by using anion $[\alpha-PW_{12}O_{40}]^{3-}$ was carried out with aquades augmentation of the polyoxometalate $H_3[\alpha-PW_{12}O_{40}] \cdot nH_2O$ compound and the addition of sodium hydroxide to the double layer hydroxides material to form a suspension aimed at facilitating the process of anion exchange in the process the pillarization. To find out that there are other anions involved in the process of pillarization such as carbonate, the process of pillarization is done by using inert gas nitrogen. This nitrogen gas can drive and remove carbonate ions and be released as CO_2 .

Therefore, the process of pillarization of double-layer hydroxy material with polyoxometalate $H_3[\alpha-PW_{12}O_{40}] \cdot nH_2O$ compounds in this study was conducted by varying the time of pillarization

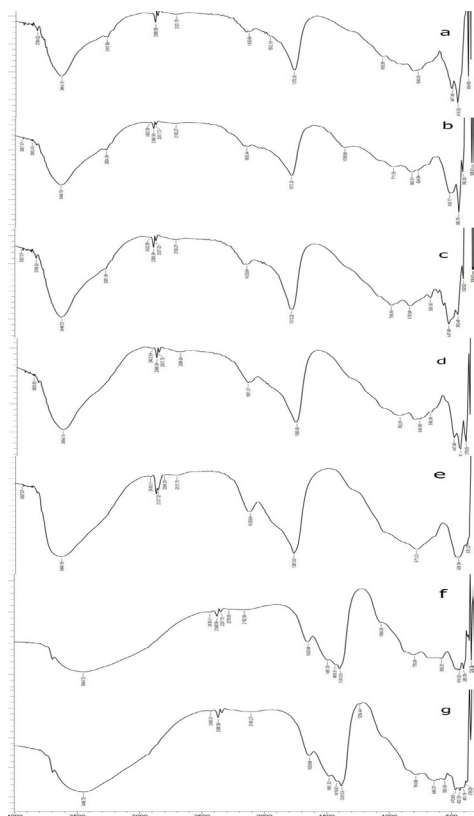


Figure 3. The FT-IR spectrum of double layer hydroxides was pillarized by polyoxometalate with a various times of pillarization (a) 3 hours, (b) 6 hours, (c) 9 hours, (d) 12 hours, (e) 24 hours, (f) 36 hours, (g) 48 hours.

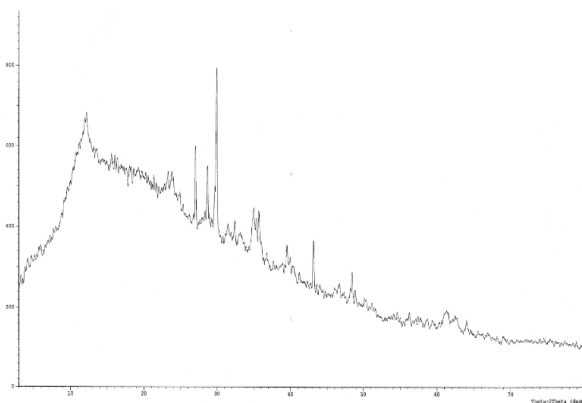


Figure 4. X-ray diffraction pattern of double layer hydroxides

for 3 hours, 6 hours, 9 hours, 12 hours, 24 hours, 36 hours, and 48 hours for the purpose of determining the double layer hydroxides material which is the most optimized pillarization of the polyoxometalate $H_3[\alpha-PW_{12}O_{40}] \cdot nH_2O$ compound. At the end of the process of pillarization of polyoxometalate compounds $H_3[\alpha-PW_{12}O_{40}] \cdot nH_2O$ obtained white solids.

The result of pillarization process of Mg-Al double-layer hydroxides material with $H_3[\alpha-PW_{12}O_{40}] \cdot nH_2O$ was characterized using FT-IR spectrophotometer to see functional group formed. FT-IR spectrum resulted from the pillaration of double layer hydroxides material with $H_3[\alpha-PW_{12}O_{40}] \cdot nH_2O$ of the measurements shown in Figure 3.

The presence of functional groups seen in the 3-hours time frame in Figure 3a indicates the presence of vibration 3463.15 cm^{-1} represents O-H stretching. At the 1635.54 cm^{-1} wavenumber

is the vibration of the O-H bond. At the wavenumber 1373.32 cm^{-1} showing the symmetric nitrate of the synthesis product of the double layer hydroxides Mg-Al. In the wavenumber 447.49 cm^{-1} shows the presence of Mg-O. These four peaks are also seen in the FT-IR spectra in Figure 3b, 3c, 3d, 3e, 3f, and 3g. These four peaks indicate the presence of a Mg-Al double-layer hydroxides material. Figure 3a shows the presence of a vibration peak for a polyoxometalate compound at an 856.39 cm^{-1} wavenumber indicating a W-Oc-W vibration. In Figure 3b shows that a vibration peak of a polyoxometalate compound appearing at 1056.99 cm^{-1} indicates the presence of P-O vibration and 771.53 cm^{-1} indicating the vibration of W-Oc-W. Figure 3c shows the presence of W-Oc-W vibration at the wave number 786.9 cm^{-1} . Figure 3d shows the presence of W-Oc-W vibration at the wave number 763.61 cm^{-1} . Figure 3e shows the presence of W-Oc-W vibration at wavenumber 671.23 cm^{-1} . Figure 3f shows the existence of P-O vibration at wavenumber 1049.28 cm^{-1} and vibration of W-Oc-W at wavenumber 779.24 cm^{-1} . Figure 3g shows the presence of W-Oc-W vibration at the wavenumber 786.96 cm^{-1} . From the results of measurements with FT-IR spectrophotometers, FTIR spectrum have not been able to show optimal pillarization results between the comparison of the time of pillarization of 3 hours, 6 hours, 9 hours, 12 hours, 24 hours, 36 hours and 48 hours. Next, is measured by X-ray powder diffraction to determine the optimal time of pillarization.

Characterization of Double Layer Hydroxides, Polyoxometalate $H_3[\alpha-PW_{12}O_{40}] \cdot nH_2O$ and Double Layer Hydroxides Pillared with Polyoxometalate $H_3[\alpha-PW_{12}O_{40}] \cdot nH_2O$ Using X-Ray Analysis

The double layer hydroxides material characterized using XRD is presented in Figure 4. Double layer hydroxy has a strong diffraction peak at 2θ value i.e. 11.70 with basal spacing 7.5 . The diffraction angles at 29 deg , 27 deg and 28 deg are typical of the Mg-Al double layer hydroxides. According to Hurma and Kose (2016), the X-ray diffraction pattern showing the layered structure is in the 2θ diffraction of 10 deg and 60 deg . The layered structure allows the anion to reside on the interlayer of the double layer hydroxides material, according to Brandl et al (2017) the peak in the 2θ diffraction pattern of 60 deg indicates that the presence of anions on interlayers may be anion nitrate, carbonate, hydroxy or other anions.

Analysis of the polyoxometalate $H_3[\alpha-PW_{12}O_{40}] \cdot nH_2O$ compound was followed by characterization using X-ray diffraction. This characterization is aimed at determining the optimal pillarization time obtained from the crystallinity of the compound and determining the height of the gallery in the layered structure. The XRD powder pattern of $H_3[\alpha-PW_{12}O_{40}] \cdot nH_2O$ is shown in Figure 5.

Figure 5 shows the X-ray diffraction patterns $H_3[\alpha-PW_{12}O_{40}] \cdot nH_2O$ compounds with the 2θ main regions of $15-20^\circ \text{ deg}$, $24-31^\circ \text{ deg}$, and $40-45^\circ \text{ deg}$ wherein those diffraction are characteristic for crystalline polyoxometalate compounds $H_3[\alpha-PW_{12}O_{40}] \cdot nH_2O$. The result of the measurement analysis is known that the highest peak occurs in the $25-31^\circ \text{ deg}$ and 45° deg . Further, the polyoxometalate compound is pillared with a double layer hydroxides material at various times of pillarization which aims to increase the distance between layers in a double layer hydroxy material. The polyoxometalate $H_3[\alpha-PW_{12}O_{40}] \cdot nH_2O$ compound obtained from the preparation results is further pillarized by double layer hydroxides material. The pillarized material is further characterized by X-ray power diffraction as in Figure 6.

Figure 6a shows the highest peak of 11.5° , 23.11° , dan 34.52° .

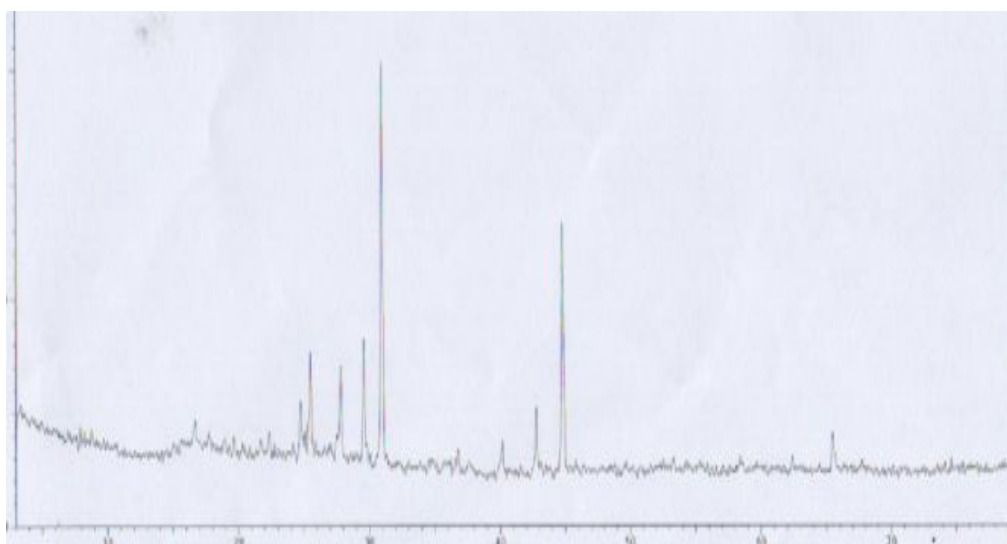


Figure 5. X-ray diffraction pattern of a polyoxometalate $H_3[\alpha-PW_{12}O_{40}] \cdot nH_2O$.

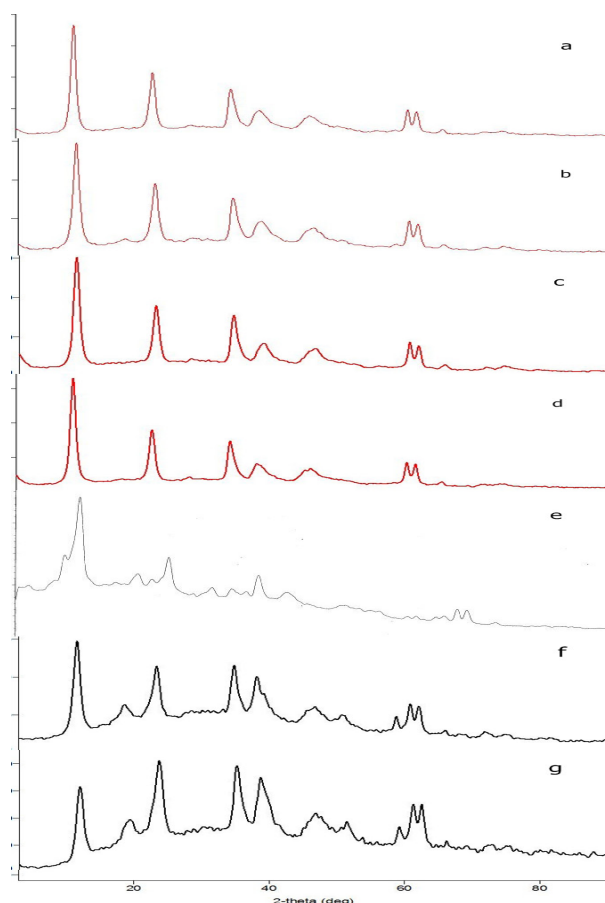


Figure 6. XRD powder patterns of Mg/Al double layer hydroxides pillared with polyoxometalate $H_3[\alpha-PW_{12}O_{40}] \cdot nH_2O$ at various times pillarization : (a) 3 hours, (b) 6 hours, (c) 9 hours, (d) 12 hours, (e) 24 hours, (f) 36 hours and (g) 48 hours.

Figure 5b shows areas comprising regions of 11.56° , 23.23° , and 34.60° having relatively high crystallinity (Matsunaga et al, 2017). These three diffractions denotes the properties of double layer hydroxide materials having a plated structure with a basal spacing of 7.64Å , 3.82Å , and 2.59Å , The area that emerged in 60° - 63° shows an anion adhesion on the interlayer of double layer hydroxide material.

Figure 6c shows an angular difference of the diffraction form showing the presence of a Mg-Al double layer hydroxides material

in region 20 having a peak of 11.47° , 23.22° , and 34.63° indicated the successfully of anions present in a double layer hydroxides material. Diffraction at 62.02° with a basal value the largest spacing compared to the 3 hours and 6 hours pillarization times. Figure 6d has the same diffraction pattern as Figure 6a.

Figure 6e shows a diffraction angle of 11.12° , 22.85° , and 34.5° . Figure 5f shows also the presence of a double layer hydroxides pillared material at 11.691° diffraction angle with a larger basal spacing compared to a double layer hydroxy material of 0.00644Å . Diffraction at 18.30° with a larger basal spacing compared to a double layer hydroxides material 0.06Å . As well as the diffraction angle of 18.33° has a difference of 0.03Å , and the diffraction angle of 4.71° deg has a difference of 0.00466Å . While in Figure 6g has a diffraction angle of 11.98° , and 35.11° with basal spacing 7.38Å and 2.55Å . Therefore, the most success of pillarization is 36 hour time comparison of the other times.

CONCLUSION

Pillarization of Mg/Al double layer hydroxides with polyoxometalate $H_3[\alpha-PW_{12}O_{40}] \cdot nH_2O$ at various times showed that pillarization at 36 hours can optimal pillar double layer hydroxides.

ACKNOWLEDGEMENT

The author would like to thank Prof. Aldes Lesbani, Ph.D for fruitful discussion of this research.

REFERENCES

- Brandl, M., Sayed, M.H., Riedel, I.H., Hocka, R., Gütay, L. (2017). In-situ XRD investigation of selenization of CZTS nanoparticles. *Journal of Alloys and Compounds*, 714, 35-38.
- Delidovich, I. And Palkovits, R. (2015). Structure-performance correlations of Mg-Al hydrotalcite catalysts for the isomerization of glucose into fructose. *Journal of Catalysis*, 327, 1-9.
- Goodarzi, A.R., Fateh, S. N., and Shekary, H. (2016). Impact of Organic Pollutants of The Macro and Micro Structure Responses of Na-Bentonite. *Journal Applied Clay Science*, 121, 17-28.
- Hincapié, G., López, D., Moreno, A. (2017). Infrared analysis of methanol adsorption on mixed oxides derived from Mg/Al hydrotalcite catalysts for transesterification reactions. *Catalysis Today*, In Press. <https://doi.org/10.1016/j.cattod.2017.05.052>
- Hanifah, Y.and Palapa, N.R. (2016). Mg/Al double layer hydroxides: intercalation with $H_3[\alpha-PW_{12}O_{40}] \cdot nH_2O$. *Science & Tech-*

- nology Indonesia, 1, 16-19.
- Han, S.A., Sohn, A., Kim, S.W. (2017). Recent Advanced in Energy Harvesting and Storage Applications with Two-Dimensional Layered Materials. *FlatChem*, In Press. <https://doi.org/10.1016/j.flatc.2017.07.006>
- Hurma, T., Kose, S. (2016). XRD Raman analysis and optical properties of CuS nanostructured film, *Optik. International Journal for Light and Electron Optics*, 127, 6000-6006.
- Kim, H. J., Chu, H. J., Moon, J., Han, S. H., and Shul, G. Y. (2009). Preparation of Heteropoly Acid Entrapped in Nano Silica Matrix. *Molecular Crystals and Liquid Crystals Journal*. 371, 131-134.
- Kwon, T., and Pinnavaia, J. T. (1989). Layered Double Hydroxide Pillared by Polyoxometalate Keggin Ion Structure. *Synthetic Materials*. 1, 381-383.
- Lin, X., Wen, C. H., and Bo, E. W. (1997). Advances in Study of A New Class of Pillared Layered Microporous Materials Polyoxometalate Type Hydrotalcite Catalysis. *Journal of Natural Gas Chemistry*. 6, 155-168.
- Matsunaga, S., Inoue, I., Mihara, K., Nomiya, K. (2017). Synthesis and crystal structure of hexacerium(IV) cluster-containing Keggin polyoxometalate trimer. *Inorganic Chemistry Communications*, 80, 61-64.
- Pinnavaia, T.J. (2016). Pillared Clays. In *Reference Module in Materials Science and Materials Engineering*, 61, 178-194.
- Qin, L., Wang, W., You, S., Dong, J., Zhou, Y., and Wang, J. (2014). In Vitro Antioxidant Activity and In Vivo Antifog Effect of Layered Double Hydroxide Nanoparticles as Delivery Vehicles for Folic Acid. *International Journal of Nanomedicine*, 9, 5701-5710.
- Shimizu, K., Nakamuro, Y., Yamanaka, R., Hatamachi, T., and Kodama, T. (2006). Pillaring of High Charge Density Synthetic Miccas by Intercalation of Oxides Nanoparticles. *Microporous and Mesoporous Materials*, 95, 135-140.
- Zhang, J., Zhang, F., Ren, L., and Duan, X. (2004). Synthesis of Layered Double Hydroxide Anionic Clays Intercalated by Carboxylate Anions. *Material Chemistry and Physics*, 85, 207-214.
- Zhang, Y., Su, J., Pan, Q., and Qu, W. (2012). Polyoxometalate Intercalated MgAl Layered Double Hydroxide and its Photocatalytic Performance. *Journal of Materials Science and Engineering*, 2, 59-63.