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Mg/Al DOUBLE LAYER HYDROXIDES: INTERCALATION WITH $H_3[\alpha\text{-}PW_{12}O_{40}]\bullet nH_2O$

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ABSTRACT

It has been done the intercalation of polyoxometalate $H_3[\alpha\text{-}PW_{12}O40]\bullet nH_2O$ on Mg-Al double layer hydroxide by comparison weight ratio of double layer hydroxides : polyoxometalate $H_3[\alpha\text{-}PW_{12}O_{40}]\bullet nH_2O$, i.e: 1:1, 1:2, 1:3 and 1: 4. The product of intercalated double layer hydroxide was characterized using FT-IR spectrophotometer, XRD, and TG-DTA analysis. The spectrophotometer results of FT-IR shown the process of intercalation was not optimum for every weight ratio. Characterization using XRD showed the process of intercalation was optimum at a ratio 2:1 that indicated at the area of 11,12°, 22,85° and 34,5° as double layer hydroxide and at the area of 60-63° showed the double layer hydroxide has intercalated with polyoxometalate. The characterization results using TG-DTA analysis at the comparison 2:1 showed loss of OH in the layer at 170 to 220°C and for the decomposition of polyoxometalate $H_3[\alpha\text{-}PW_{12}O_{40}]\bullet nH_2O$ at 300 to 400°C.

Keywords: Double Layer Hydroxide, Intercalation, Polyoxometalate $H_3[\alpha\text{-}PW_{12}O_{40}]\cdot nH_2O$

INTRODUCTION

Layered materials or clay of inorganic minerals are found in nature and can also be synthesized in the laboratory (Abderrazek et al, 2016). Layered material is used as a catalyst, adsorbent, sensor, membrane or ion exchange. As adsorbent, a layered material used for aditive adsorption on vegetable oil (Franchi et al, 1991) as well as its application for the control of contamination of metal ions or organic compounds in the environment.

The advantages of this double layer hydroxide have a great anion exchange properties and can be exchanged for various other anions (Beaudot et al, 2004). The general formula for double layer hydroxide is $[M_{2+(1-x)}M_{3+}x(OH)_2](An-)x/n\bullet nH2O$ which in that positive charges are balanced by the interlayer anions such as Cl^-, NO_3^- and CO_3 (Guo *et al*, 2014). However, The use of these layered materials still has small surface area constraints and narrow layer spacing due to the small exchange ions which are generally alkali and alkaline earth metal ions (Goodarzi et al, 2016). Double layer hydroxide still needs to be modified to increase its surface area and majority modifications made to this research are through intercalation of layered materials with atoms, molecules and complex compounds using ion exchange methods.

The purpose of this intercalation process is expected to produce double layer hydroxide intercalated macro anion that automatically increasing interlayer so it can be used as adsorbent or catalyst. The macro anion is used Polyoxometalate Keggin type $H_3[\alpha\text{-}PW_{12}O_{40}]\cdot nH_2O$. The intercalated macro anion of double layer hydroxide causes the loss of the OH^- anion that located on the layer so it is expected to increase the distance between layers of the double layer hydroxide.

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In this research, synthesis and characterization of double layer hydroxide, polyoxometalate $H_3[\alpha\text{-}PW_{12}O_{40}]\cdot nH_2O$ and double layer hydroxide intercalated polyoxometalate $H_3[\alpha\text{-}PW_{12}O_{40}]\cdot nH_2O$ has been done. Characterization has been conducted using *Fourier Transform Infra Red (FT-IR), X-Ray Diffractometer (XRD) and Thermo Gravimetric-Differential Thermal Analysis (TG-DTA*).

EXPERIMENTAL SECTION

Material and Methods

Double layer hydroxide intercalated with $H_3[\alpha\text{-}PW_{12}O_{40}]\cdot nH_2O$ was performed by ion exchanged method. Characterization of the synthesized compounds was performed by different techniques such as FTIR, X-Ray Diffractometer (XRD). XRD was performed using Shimadzu Lab X-type 6000 to determine the surface area before and after intercalated. The TG-DTA analysis of double layer hydroxide intercalated Polyoxometalate $H_3[\alpha\text{-}PW_{12}O_{40}]\cdot nH_2O$ was evaluated using Shimadzu TG / DTA 60A analyzer from 20°C to 800 °C.

Preparation of Mg-Al LDH and $H_3[\alpha\text{-}PW_{12}O_{40}]\cdot nH_2O$ composite

Preparation of Mg-Al LDH

Mg-Al LDH was synthesized by mixing 64.01 g of $Mg(NO_3)_2.6H_2O$ (2 mol) and 46.64 g of $Al(NO_3)_3.9H_2O$ (1 mol) were dissolved in 150 mL of aquadest (solution A). 10.00 g of NaOH and 26.62 g of $NaCO_3$ was poured into 150 mL aquadest (solution B). Solution A is added to solution B and stirred gradually with the addition of aquadest of 100 mL and a pH adjusted from 9 to 10 to form sediment. The sediment is dried into oven at 80 °C and ready to be characterized using FT-IR spectroscopy and XRD analysis.

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

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. 100 ml of hydrochloric acid is added dropwise to the mixture and stirred using a magnetic stirrer. The stirring process is continuous until all the solid 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 75 mL of diethyl ether cold solution was added and then extracted. After extraction process obtained three layers, the solution separated and taken from the bottom layer. The lowest layer was evaporate using a rotary evaporator to obtain white solid that is $H_3[\alpha\text{-}PW_{12}O_{40}]\cdot nH_2O$. Characterization of $H_3[\alpha\text{-}PW_{12}O_{40}]\cdot nH_2O$ was performed using FT-IR spectrophotometer and XRD analysis.

Intercalation of LDH-POM

Intercalation process of double layer hydroxides by polyoxometalate $H_3[\alpha\text{-}PW_{12}O_{40}]\cdot nH_2O$ by ion exchange method was carried out by preparing 1 g of $H_3[\alpha\text{-}PW_{12}O_{40}]\cdot nH_2O$ (solution A) mixed with 50 mL of distilled water, and 2 g of double layer hydroxide was added with 25 mL NaOH 1 M (solution B). Solution A and solution B are then mixed rapidly under conditions given N_2 gas for 24 hours. Then the suspension is cooled and the product is washed with water and dried at room temperature. Structural analysis, the thermal stability of the inserted product is carried out using XRD, FT-IR and TG-DTA.

RESULTS AND DISCUSSION

Characterization of LDH-POM

Mg-Al LDH and LDH-POM using comparison 1:1, 1:2, 1:3 and 2:1. The characterization of the FT-IR spectra aims to identify the functional groups formed as shown in Figure1.

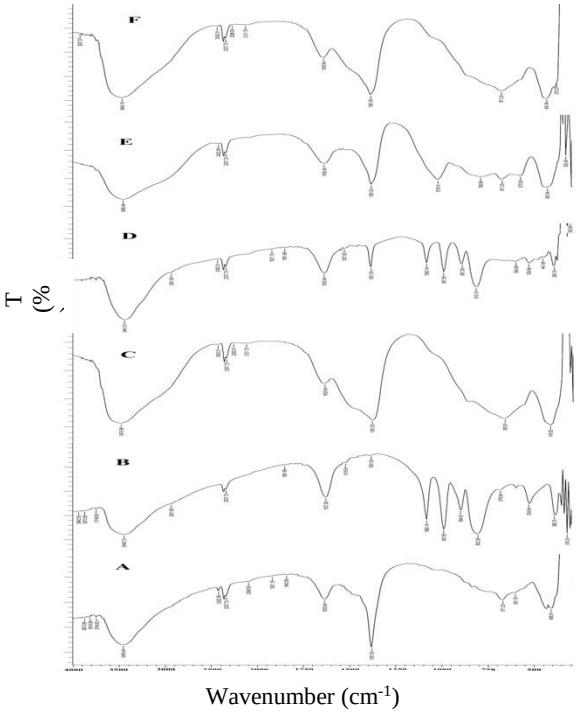

Figure 1. FT-IR spectra of (A) double layer hydroxide (B) Polyoxometalate $H_3[\alpha\text{-}PW_{12}O_{40}]\cdot nH_2O$ (C) Intercalation LDH-POM with a rasio 1: 1 (D) 1: 2 (E) 1: 3 (F) 2: 1.

The FT-IR spectrum of LDH is presented in Figure 1. At 671 and 1381 cm^{-1} which are indicated nitrate bend and the symmetric stretch of nitrate (Handayani, 2013). On the other hand, the characteristic peak of LDH at 601, 408 cm^{-1} which are Al-O and Mg-O vibration. Figure 1B shows the peaks of the functional group of Polyoxometalate$H_3[\alpha\text{-}PW_{12}O_{40}]\cdot nH_2O$. The characteristic of Polyoxometalate is shown at 802, 894, 987 and 1080 cm^{-1} which are related to the W-Oc-W, W-Ob-W, W=O, and P-O. Figure 1C in comparison LDH-POM (1:1) shows the presence of a vibrational peak at 3479.5 cm^{-1} which are related to O-H group vibration. The absorption band at 1635.6 cm^{-1} is indicated buckling of the adsorbed O-H group on interlayer and absorbing bands at 1381 cm^{-1} showing symmetrical nitrate synthesis yield of double layer hydroxide. The three vertices of this vibration are also shown in the FT-IR spectrum of Figure 1D (1:2), 1E (1:3) and 1F (2:1). These three peaks indicate the presence of double layer hydroxide material. The differences presented based on the FT-IR spectrum in Figure 1 are shown by the presence of Polyoxometalate. Figure 1C show a vibration peak for a polyoxometalate at 663 cm^{-1} which is a vibration of W-Oc-W. Figure 1D shows the peak vibration of polyoxometalate at 887-810, 987 and 1080 cm^{-1} which are related to the W-Oc-W, W-O, and P-O vibration. In Figure 1E at 1018 and 786 cm^{-1} are related W-Oc-W and P-O vibration. Whereas in Figure 1 F shows the existence of polyoxometalate at 671 cm^{-1} is W-Oc-W vibration.

Characterization of LDH, Polyoxometalate $H_3[\alpha\text{-}PW_{12}O_{40}]\cdot nH_2O$ and Intercalation Result Using X-Ray Difraction

Polyoxometalate $H_3[\alpha\text{-}PW_{12}O_{40}]\cdot nH_2O$ characterization using XRD. The diffraction is shown in Figure 2.

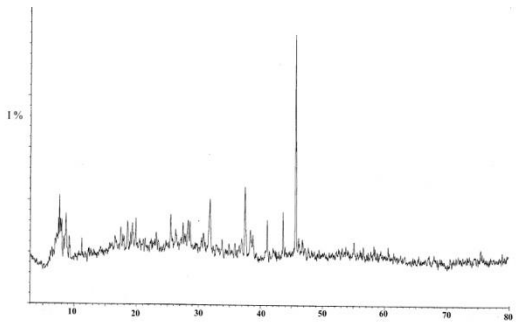

Figure 2. X-ray diffraction of polyoxometalate $H_3[\alpha\text{-}PW_{12}O_{40}]\cdot nH_2O$

Figure 2 shows the X-ray diffraction patterns of $H_3[\alpha\text{-}PW_{12}O_{40}]\cdot nH_2O$ with the principal regions of 2θ ie 6-10°, 15-20°, 22-25° and 35-45° wherein those diffractions are characteristic for crystalline Polyoxometalate $H_3[\alpha\text{-}PW_{12}O_{40}]\cdot nH_2O$ (Zhang *et al*, 2012). The results of the measurement analysis are known to have the largest peaks appear in regions 7° and 37–45°. The presence of diffraction patterns that appear in the 2θ region below 10° denotes the typical peak of the polyoxometalate MO_6 where M is tungsten and has high crystallinity. Polyoxometalate $H_3[\alpha\text{-}PW_{12}O_{40}]\cdot nH_2O$ are subsequently intercalated into a double layer hydroxide material which aims to increase the distance

between the double layer hydroxide layers. The double layer hydroxide material and the intercalated double layer hydroxide are presented in Figure 3.

From the Figure3A, Double layer hydroxide diffraction was showing the highest peak at 27°-29° which is demonstrated double layer hydroxide material. Figure 3B shows the interfraction pattern of double layer hydroxide material intercalated polyoxometalate with the ratio (1: 1) there is the highest diffraction peak that is in the area at 10,8°, 22,4° and 8,9°. Figure 3B shows diffraction peak at 10.8°, 22.4° and 34.1° are having relatively high crystallinity (Kloprogge et al 1999). According, to Wiyantoko (2015), these three diffraction shows the properties of double-layer hydroxide materials, which have layered structures with intensity are 340, 156 and 101. The regions appearing at 60-63° indicate the presence of anions in the interlayer of the layered material. Based on this data can be expressed comparison compared to the ratio in (1: 1), (1: 3) and (2: 1).

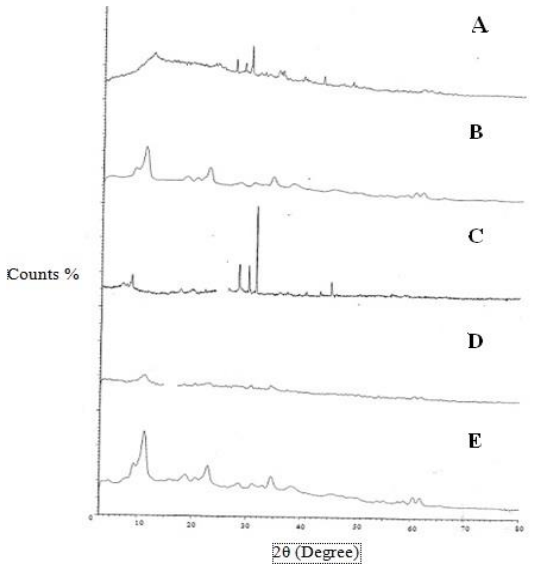

Figure 3. Diffractogram XRD (A) Double layer hydroxide (B) Intercalation of Double Layered Hydroxide with Polyoxometalate with a rasio of 1: 1 (C) 1: 2 (D) 1: 3 (E) 2: 1.

Figure 3C shows the different angles of the diffraction form showing the existence of double layer hydroxide material at 2θ = 10.9°. 22.88° and 34.4° and indicating the diffraction of the success of the anions, which is presented in a double layer hydroxide material at 60.4° and 61.7° with a relatively smaller intensity than the diffraction Fig (1: 1) and (2: 1). Figure 3 D (1:1) is successfully synthesized wherein the polyoxometalate enters the interlayer of the double layer hydroxide material.

Figure 3E also shows the existence of double layer hydroxide material at 2θ = 11.12°, 22.85° and 34.5° which have greater intensity are 518, 192 and 133 than on comparison (1: 1), (1: 2) and (1: 3). The diffraction shows the success of intercalation process of double layer hydroxide material with polyoxometalate at 2θ=60,4° and 61,7° which has greater intensity than on (1: 1), (1: 2) and (1: 3) are 71 and 72.

Characterization of LDH and LDH Intercalated Polyoxometalate $H_3[\alpha\text{-}PW_{12}O_{40}]\cdot nH_2O$ Using TG-DTA

Double layer hydroxide obtain was then characterized using TG-DTA analysis. The purpose of Thermogravimetric Analyzer (TGA) analysis was used to record changes in sample weight as a function of temperature and Differential Thermal Analyzer (DTA) to detect changes in the heat content. The TG-DTA analysis of the double layer hydroxide has a thermogram pattern as shown in Figure 4.

Figure 4 shows the double layer hydroxide decomposed with the loss of water molecules at 77-102°C with weight loss about 23% (Xie, 2006). From the thermogram could be seen a sharp peak DTA at a temperature of 77-102°C.

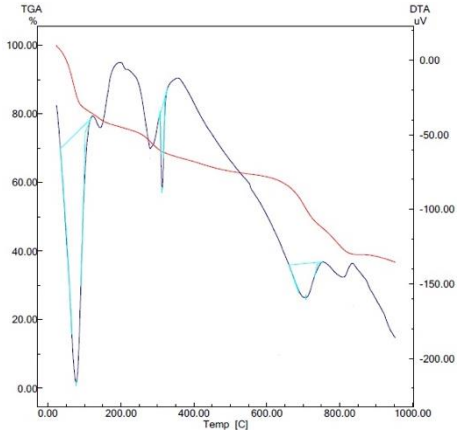

Figure 4. Termogram of Double Layer Hydroxide Material

At 300-320°C, which is the decomposition of the OH group of the interlayer material of the double layer hydroxide material with a loss of weight is 15.22% indicated on the red line ie the weight loss. The endothermic peak at 308 °C indicates loss of carbonate (Li, et al. 2013). According to Yu (2009), dehydroxylation process and loss of Mg/Al-CO_3- ions at the endothermic peak are seen at temperatures around 220°C. The endothermic peak at 650-750°C indicates a double layer hydroxide material decomposition in the presence of an endothermic peak marked by loss of carbonate ions attached to Mg^{2+} dan Al^{3+} with a weight loss about 22.89% (Lin et al, 2001).

The intercalation of double layer hydroxide with polyoxometalate $H_3[\alpha\text{-}PW_{12}O_{40}]\cdot nH_2O$ by weight ratio (2: 1) has a thermogram pattern as in Figure 5.

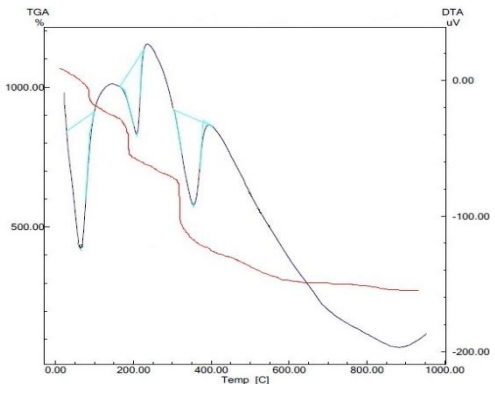

Figure 5. Thermogram Intercalation Result of Double Hydroxy with Polyoxometalate $H_3[\alpha\text{-}PW_{12}O_{40}]\cdot nH_2O$

Figure 5 shows the presence of three endothermic peaks. The first endothermic peak at a temperature of 20-90 ^{o}C is due to the loss of water molecules. At the second endothermic peak at temperatures of 170-220 ^{o}C is demonstrated the decomposition marked by the loss of the OH group present in the interlayer (Zhang et al, 2012).

The third endothermic peak is at a temperature of 300-400 °C which is a decomposition of a polyoxometalate $H_3[\alpha\text{-}PW_{12}O_{40}]\cdot nH_2O$ with loss of hydrogen bonds between $H_3[\alpha\text{-}PW_{12}O_{40}]\cdot nH_2O$ with hydrogen ions (Khozhevnikov, 2012).

CONCLUSION

Intercalation double layer hydroxide with polyoxometalate $H_3[\alpha\text{-}PW_{12}O_{40}]\bullet nH_2O$ in the optimal ratio (2: 1) characterized using FT-IR spectrophotometer has not demonstrated the success of the optimal intercalation process and the characterization using XRD indicates a gallery height of 7.8 Å before The process of intercalation to 7.9 Å after the intercalation process. Further characterization using TG-DTA analysis showed OH loss in the layer at temperature 170-220^{o}C while for decomposition of polyoxometalate $H_3[\alpha\text{-}PW_{12}O_{40}]\bullet nH_2O$ was at 300-400^{o}C.

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