

PREPARATION OF POLYOXOMETALATE COMPOUND $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})/\text{SiO}_2$ BY SOL-GEL METHOD AND ITS CHARACTERIZATION

Osin R Tambunan^{1*}, Risfidian Mohadi¹

¹Department of Chemistry, Faculty of Mathematic and Natural Science, Univeristas Srinwijaya. Jl. Palembang Prabumulih, Km. 32, Indralaya, Ogan Ilir, Sumatera Selatan

*Corresponding Author E-mail : osintambunan@yahoo.com

ABSTRACT

Preparation of polyoxometalate compound of $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\text{nH}_2\text{O}$ supported with silica derived from the hydrolysis of tetraethyl orthosilicate by sol-gel method has been conducted. The compound was synthesized and characterized using FT-IR spectrophotometer, crystallinity using XRD analysis and the determination of acidity via quantitatively and qualitatively. Qualitative analysis was performed using ammonia and pyridine adsorption and quantitative analysis using potentiometric titration. FT-IR spectrum of $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\text{nH}_2\text{O}$ appeared in wavenumber 786.96 cm^{-1} (W-O_C-W), 918.12 cm^{-1} (W-O_e-W), 964.41 cm^{-1} (W=O), 1087.85 cm^{-1} (P-O), 3572.17 cm^{-1} (O-H), 1404.18 cm^{-1} (N-H) reinforced with wavenumber 1612.49 cm^{-1} with show vibration NH dari NH⁺, and to $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\text{nH}_2\text{O}/\text{SiO}_2$ appears in wavenumbers 794.67 cm^{-1} (W-O_C-W), 918.12 cm^{-1} (W-O_e-W), 1049.28 cm^{-1} (W=O), 1087.85 cm^{-1} (P-O), 3564.15 cm^{-1} (O-H), 470.63 cm^{-1} (Si-O). Diffraction pattern of $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\text{nH}_2\text{O}$ and $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\text{nH}_2\text{O}/\text{SiO}_2$ compound show high cristanility. The acidic properties showed $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\text{nH}_2\text{O}/\text{SiO}_2$ more acidic than $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\text{nH}_2\text{O}$. Analysis of the effect of temperature on the stability of the compounds polyoxometalate $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\text{nH}_2\text{O}/\text{SiO}_2$ show that the temperature of 600°C the shift in wavenumbers of the compounds caused by vibration W=O, W-O_C-W, W-O_e-W has been lost. This shows that at a temperatures of 600°C on heating can cause changes in the structure of polyoxometalate $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\text{nH}_2\text{O}/\text{SiO}_2$.

Keywords : $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\text{nH}_2\text{O}$, Polyoxometalate, SiO_2

INTRODUCTION

Polyoxometalate is a metal-oxygen cluster compound having acid-base properties, has various structural variations and oxidation rates so it is very effective for both acid base and oxidation reaction catalyst. In general, polyoxometalate compounds can be classified into two groups: isopolyoxometalate and heteropolioxometale (Yamase et al, 2002).

Polyoxometalate compounds have many benefits, as a catalyst and basic ingredients of macromolecular synthesis. Its utilization as a catalyst because it has a high acidity that exceeds sulfuric acid and is not toxic (Okuhara et al,1996). Research on polyoxometalate compounds is primarily intended in terms of its superiority as a catalyst which can be performed in homogeneous and heterogeneous system depending on the medium used. In heterogeneous system, polyoxometalate compounds may be used repeatadly of catalytic reaction. Polyoxometalate compounds have attracted attention to continue to be developed due to flexible properties as acid and base as well as an adjustable oxidation rate according to the desired application recruitments (Kozhevnikov, 2002).

Previous research has been done on the development of polyoxometalate compounds using carriers as TiO_2 , ZrOCl_2 , TaCl_5 (Fatimah, 2009). Yang (2011) has also carried on

$(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\text{nH}_2\text{O}$ with SiO_2 sourced from tetraethyl orthosilica (TEOS) and using alcohol as a medium. In his research, TEOS hydrolysis was used as a source of SiO_2 by using microemulsion medium derived from sodium bis(2-ethylhexsil) sulfosuccinate with cyclohexane (Kim *et al*, 2006). According to Eriksson *et al* (2004) microemulsion is a liquid derived from a mixture of water, hydrocarbons, and surfactants. Sari and Situngkir (2016) reported metal oxide from reduction of TEOS (tetra ethyl ortho silicate) supported polyoxometalate. Polyoxometalate compounds embedded with SiO_2 using microemulsions and sol-gel techniques are expected to have characteristics as catalysts having uniform pore sizes and can improve the acidity side of polyoxometalate compounds. In this research, synthesis and characterization of Dawson-type polyoxometalate compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})$ were carried out with SiO_2 . The process of loading is done by sol-gel technique. To know the functional groups of polyoxometalate compound and to know whether or not a SiO_2 carried by polyoxometalate compounds is characterized using FT-IR spectrofotometr and XRD. This characterization is performed both before and after the silica is carried by the polyoxometalate compounds. The acidity of the compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\text{nH}_2\text{O}/\text{SiO}_2$ was studied through quantitative and qualitative studies through potentiometric titration and identification using an FT-IR spectrometer followed by thermal stability test.

EXPERIMENTAL SECTION

The XRD Shimidzu lab X Type 6000, spectofotometer FT-IR Shimidzu prestige 21 were used for characterizatio of the

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polyoxometalate compounds in this research. The materials used in this research were sodium tungsten, ortho phosphoric acid, aquades, ammonia, ammonium chloride, tetraethyl orthosilicates, bis(2-ethylhexyl)sulfosuccinate, n-butylamin, pyridin, cyclohex-ane and acetonitrile.

Synthesis of Dawson-Type Polyoxometalate compounds $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot n\text{H}_2\text{O}$ and its characteritaton.

A total amount of 31.25 g of sodium tungsten was dissolved in water 62.5 mL and added 26.25 mL ortho phosphoric acid while stirred with a magnetic stirrer. The obtained solution was refluxed for 4 hours and obtained a greenish solution. The solution was cooled and added 12.5 g ammonium chloride while stirring for 10 minutes to obtain a pale yellow solid. The obtained solid was filtered, dissolved with 75 mL aquades and the obtain filtrate was added with 12.5 g ammonium chloride to obtain a white solid. The white solid was filtered and dissolved with 31.25 mL of distilled water. The obtained solution was left for 5 days for polyoxometalate compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot n\text{H}_2\text{O}$ according to (Contant, 1990). The polyoxometalate $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot n\text{H}_2\text{O}$ obtained is characterizes by spectrophotometer FT-IR and XRD.

Preparation Polyoxometalate compounds $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot n\text{H}_2\text{O}/\text{SiO}_2$ by Sol-Gel Method (Newman et al, 2006)

Preparation polyoxometalate compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot n\text{H}_2\text{O}/\text{SiO}_2$ was modified from the Kim et al (2006) procedure. The compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot n\text{H}_2\text{O}/\text{SiO}_2$ was synthesized with 0.5 g sodium bis(2-ethylhexyl) sulfosuccinate dissolved with 1 mL siclohexane (Solution A). Compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot n\text{H}_2\text{O}$ of 0.76 g was dissolved with 1 mL of aquadest (Solution B). Solution B was added to solution A while distirer. A total 2 mL tetraethyl ortosilica (TEOS) was added dropwise. Stirred with a magnetic stirrer and heated 60°C. The mixture will form a hydrogel ang heated to 100°C while stirring with a glass spatula. The white solid formed is a compound. $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot n\text{H}_2\text{O}/\text{SiO}_2$. The compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot n\text{H}_2\text{O}/\text{SiO}_2$ was characterized by a FT-IR spectrofotometer, and an XRD diffractometer.

Acidity Test of the Compound $(\text{NH}_4)_6[\beta\text{-P}_2\text{W}_{18}\text{O}_{62}]\cdot n\text{H}_2\text{O}/\text{SiO}_2$ qualitatively

The acidity test was qualitatively modified from the Maksimov et al (2001) procedure by saturation of polyoxometalic compounds using ammonia and also pyridine. For saturation with ammonia as much as 0.5 g of compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot n\text{H}_2\text{O}$ and $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot n\text{H}_2\text{O}/\text{SiO}_2$ inserted into vials and 1 mL of ammonia (NH_3) 25% Into a beaker. A vial bottle is inserted into a beaker containing ammonia and tightly sealed with a plastic kreb. The compound is allowed one day in order to adsorption between ammonia and polyoxometalic compound. For saturation using a pyridine compound, the same work was done. A total of 0.5 g of each compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot n\text{H}_2\text{O}$ and $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot n\text{H}_2\text{O}/\text{SiO}_2$ were inserted into vials and 1 mL of pyridine 25% were fed into beaker. A vial bottle is inserted into a beaker containing ammonia and tightly sealed with a plastic kreb. The compound was allowed for one day to allow adsorption between

pyridine and polyoxometalate compounds. Compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot n\text{H}_2\text{O}$ and $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot n\text{H}_2\text{O}/\text{SiO}_2$ results in saturation with ammonia and pyridine were qualitatively tested by characterization using a FT-IR spectro-photometer.

Acidity Test of the compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot n\text{H}_2\text{O}/\text{SiO}_2$ Quantitatively (Reddy et al, 2006)

A total of 0.1 g of each compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot n\text{H}_2\text{O}$ and $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot n\text{H}_2\text{O}/\text{SiO}_2$ were dissolved in 8 mL acetonitrile and stirred for 6 hours with a magnetic stirrer. The suspension was titrated with 0.05 M n-butylamine which was monitored by glass electrode as a pH sensor. Each droplet of potential titrant pervolume was generated, and recorded and linked potentiometric titration curves between the titrant volume and the resulting potential. The classification of the seams from the acidity side was classified on a scale: $E > 100$ mV (very acidic); $0 > E > 100$ mV (acid side); $-100 < E < 0$ mV (weak acid side); and $E < -100$ mV (acid side is very weak).

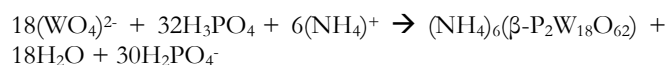
The Impact of Temperature on the Stability of the compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot n\text{H}_2\text{O}/\text{SiO}_2$

The compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot n\text{H}_2\text{O}/\text{SiO}_2$ was heated at various temperature 200°C, 300°C, 400°C, 500°C, and 600°C for 3 hours in he furnance. The combustion compound was cooled and analyzed by using FT-IR spectrofotometer.

RESULTS AND DISCUSSION

Synthesis of Dawson-Type Polyoxometalate compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot n\text{H}_2\text{O}$ and characterization

The synthesis of dawson type polyoxometalate compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot n\text{H}_2\text{O}$ based on the procedure performed by Contant (1990) using sodium tungsten as the base material. The forming polyoxometalate compound were characterized by functional group analysis using a FT-IR spectrophotometer and christanility analysis using XRD analysis. The reaction of polyoxometalate compound formation as follows:



The identification was carried out on a polyoxometalate $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot n\text{H}_2\text{O}$ compound using a FT-IR spectrophotometer in the range of 200-4000 cm^{-1} wave numbers is shown in Figure 1. The spectrum FT-IR polyoxometalate $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot n\text{H}_2\text{O}$ in Figure 1 shows some significant absorption bands located at the wave number of 786 cm^{-1} showing the vibration of the W-Oc-W group (oxygen in the middle of the polyoxometalic compound) And the numbers in 918 cm^{-1} denote the vibration of the W-Oc-W group (the oxygen at the edge of the polyoxometalate compound). The wave number at 964 cm^{-1} shows the vibration of the W = O group, and the wave number at 1087 cm^{-1} denotes the vibration of the P-O group. The wave number at 1404 cm^{-1} denotes the vibration of the N-H group which is amplified by the 1612 cm^{-1} number indicating the NH vibration NH_4^+ (Finke et al, 1987). The compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot n\text{H}_2\text{O}$ was analyzed using

XRD. Diffractogram of compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot n\text{H}_2\text{O}$ presented in figure 2.

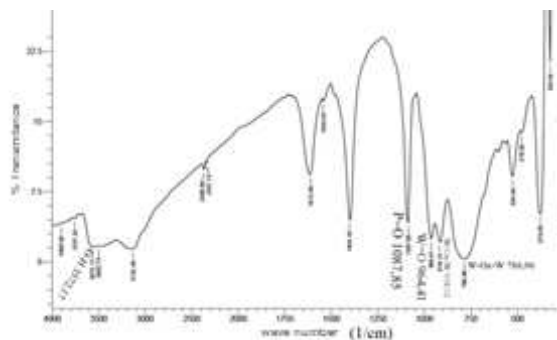


Figure 1. FT-IR spectra polyoxometalate compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot n\text{H}_2\text{O}$

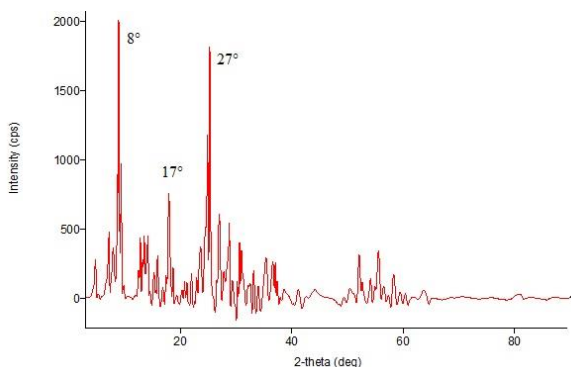


Figure 2. XRD Diffraction pattern of polyoxometalate compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot n\text{H}_2\text{O}$

The diffractogram in figure. 2 shows the diffraction for the highest intensity of the polyoxometalate compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot n\text{H}_2\text{O}$ complexes appearing at the diffraction angles of 8° , 17° , 27° . According to Yang *et al* (2011) the diffraction for polyoxometalate compounds was found in some diffraction regions at $6\text{-}10^\circ$, $15\text{-}20^\circ$, $22\text{-}25^\circ$, and $35\text{-}40^\circ$. The diffraction that appears below 10° in region 2θ shows that the polyoxometalate compound has a very high crystallinity. Diffractogram of polyoxometalate compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot n\text{H}_2\text{O}$ shows the sharp diffraction peaks indicating polyoxometalate $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot n\text{H}_2\text{O}$ compounds have very high crystalline properties in which the atoms of the polyoxometalate compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot n\text{H}_2\text{O}$ is arranged regularly based on the length and angle of the regular bond.

Synthesis of Dawson-Type Polyoxometalate Compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot n\text{H}_2\text{O}/\text{SiO}_2$ And Characteritation.

The preparation of Dawson-Type polyoxometalate compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot n\text{H}_2\text{O}$ with SiO_2 based on the procedure undertaken by Newman *et al*. (2006) in SiO_2 is derived from tetraethyl orthosilicate in the form of a liquid. Identification using spectrophotometer FT-IR compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot n\text{H}_2\text{O}/\text{SiO}_2$ showed the presence of specific vibrations of polyoxometalate and SiO_2 compounds

presented in Figure 3. On FT-IR spectrum of compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot n\text{H}_2\text{O}$ and $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot n\text{H}_2\text{O}/\text{SiO}_2$ noticeable differences before placement and after assuming SiO_2 .

Figure. 3 shows the difference shown by FT-IR spectrum of polyoxometalate $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot n\text{H}_2\text{O}$ compound before being assumed with SiO_2 . According to Derick *et al*, (1999) the asymmetric stretching vibration of Si-O-Si is at the wave number $1130\text{-}1000\text{ cm}^{-1}$. Smith (1999) reported that the Si-O-Si asymmetric stretch vibration was stronger at 1085 cm^{-1} . The FT-IR spectrum of compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot n\text{H}_2\text{O}/\text{SiO}_2$ undergoes a shift of wave numbers for asymmetric Si-O-Si stretching vibration at 1103.28 cm^{-1} . The shift of wave numbers occurs in vibration $\text{W} = \text{O}$. The $\text{W} = \text{O}$ vibrate before embodiment appears at 964.41 cm^{-1} wave numbers and the vibrations after being assumed with SiO_2 appear at 1049.28 cm^{-1} wave numbers. According to Stuart (2004), the vibration -OH vibration in the presence of hydrogen bonding effect is in the range of $3500\text{-}2500\text{ cm}^{-1}$ wavelengths characterized by a widened peak on the FT-IR spectrum. Figure 3B has a shift of wave numbers at the peak 3572.17 cm^{-1} identifies the -OH vibration by the presence of H_2O in the compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot n\text{H}_2\text{O}$ and the wave number at peak 3464.15 cm^{-1} identifies the -OH by the presence of H_2O in the compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot n\text{H}_2\text{O}/\text{SiO}_2$

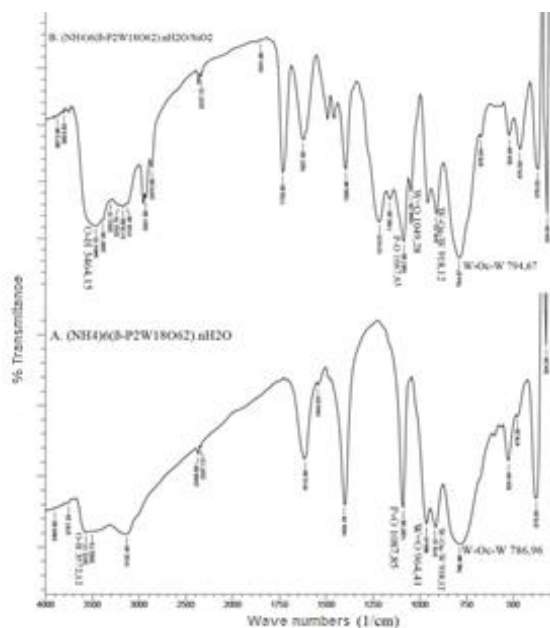


Figure 3. FTIR spectrum of polyoxometalate $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot n\text{H}_2\text{O}$ (A), $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot n\text{H}_2\text{O}/\text{SiO}_2$ (B)

Figure 3A shows the spectra that appear at the wave numbers $786, 918, 964, 1087, 1404\text{ cm}^{-1}$ for vibration of the W-Oc-W group (oxygen in the middle of the polyoxometalate compound), the vibration of the W-Oe-W group (The oxygen at the edges of the polyoxometalate compound), the vibration of the $\text{W} = \text{O}$ group, the vibration of the PO group and the vibration of the NH group reinforced by the 1612 cm^{-1} indicate the NH vibration of NH_4 (Finke *et al*. 1987). In Figure 3B the FT-IR SiO_2 spectrum of the absorption band peak appears at wave number 470 for the vibration of the Si-O group. Figure 3A spectra of FT-IR compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot n\text{H}_2\text{O}/\text{SiO}_2$

have the same absorption bands of both the polyoxometalate $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}$ as well as the SiO_2 absorption bands. This identifies the presence of polyoxometalate $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}$ and SiO_2 forming groups which show the success of SiO_2 baffling process in the polyoxometalate $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}$. Table 1 shows wave numbers of polyoxometalate compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}$ and $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}/\text{SiO}_2$. Further, polyoxometalate $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}$ analysis using XRD. Comparison of the compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}$ and $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}/\text{SiO}_2$ presented in the Figure 4.

Table 1. Wave numbers of polyoxometalate compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}$ and $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}/\text{SiO}_2$

$(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}$	$(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}/\text{SiO}_2$	Vibration Type
964.41	1049.28	W=O
786.96	794.67	W-O _c -W
918.12	918.12	W-O _c -W
1087.85	1087.85	P-O
3572.12	3464.15	O-H

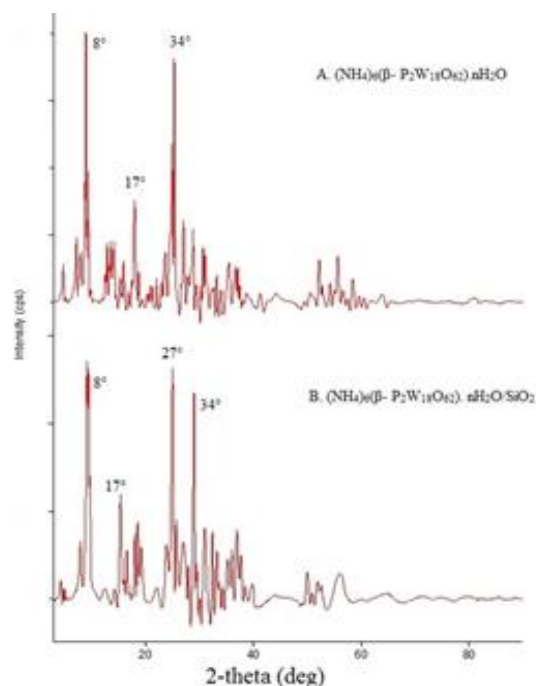


Figure 4. Diffractions of $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}$ (A) and $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}/\text{SiO}_2$ (B)

Polyoxometalate compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}$ which was assumed by SiO_2 was characterized using XRD. Characterization using XRD diffraction angle and crystallinity showed polyoxometalate compounds dengan SiO_2 $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}/\text{SiO}_2$. The comparison of XRD diffraction of the compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}$ with $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}/\text{SiO}_2$ were presented in Figure 4. Figure 4A shows the diffraction of $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}$ that appear at 2θ area under 10° indicates that the compound polyoxometalate $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}$ possess extremely

high crystallinity due atoms $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}$ regularly by Length and angle of bond formed. Figure 4B shows the XRD pattern of compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}/\text{SiO}_2$. The compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}/\text{SiO}_2$ has a high crystallinity by the diffraction angle 2θ 8° , 17° , 27° and 34° , respectively which shows the characteristics of the compound polyoxometalate $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}/\text{SiO}_2$ where atoms polyoxometalate compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}/\text{SiO}_2$ arranged regularly based on the length and angle of a regular bond. In Figure 4B shows the XRD pattern of $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}/\text{SiO}_2$ indicates the diffraction angle changes

Acidity Test Of The compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}$ and $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}/\text{SiO}_2$ Quantitatively

Acidity Test Of The compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}$ Qualitatively

Measurement of acidity in polyoxometalate compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}$ done both qualitatively and quantitatively. Qualitatively, FT-IR spectrophotometer was used in which polyoxometalate $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}$ was saturated with ammonia and with pyridine for one day resulting in adsorption on the surface of the compound adsorpsi $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}$. The saturation result is then compared before or after being saturated with ammonia or pyridine. The spectra of FT-IR compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}$ of saturation result is presented in Figure 5.

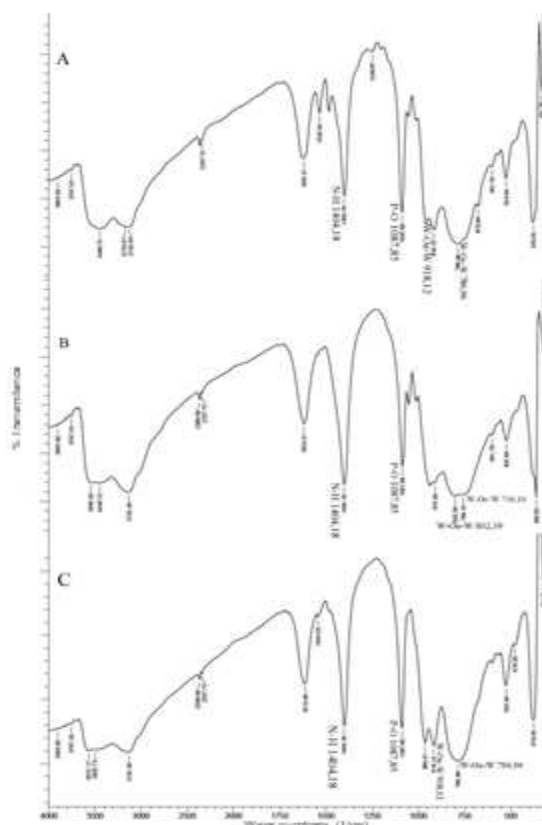


Figure 5. FTIR spectrum of $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}$ saturated with pyridine (A), $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}$ saturated with ammonia (B), $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}$ before saturated (C)

FT-IR spectrum in Figure 5A and B did not find any absorption band at wave number $1400\text{-}1440\text{ cm}^{-1}$ on

polyoxometalate $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}$. According to Dines *et al.* (1991) ammonia forms ammonium ions (NH_4^+) with the observed wave numbers being at $1400\text{-}1440\text{ cm}^{-1}$. In polyoxometalate compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}$ saturated with ammonia and pyridine does not show the ammonium ion vibration (NH_4^+) in the $1400\text{-}1440\text{ cm}^{-1}$ wave numbers range. Ammonia can be adsorbed on the acid side of the heteropoly compound as well as on the metal cations which in this study is not observed as Figure 5A and 5B.

Acidity Test Of Compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}/\text{SiO}_2$ Qualitatively

The compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}/\text{SiO}_2$ is saturated using ammonia and pyridine just as with section 3.3.1. Then the polyoxometalate $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}/\text{SiO}_2$ was characterized using a FT-IR spectrophotometer. The saturated FT-IR $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}/\text{SiO}_2$ spectrum is presented in Figure 6. Figure 6A shows the spectrum of FT-IR polyoxometalate $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}/\text{SiO}_2$ before it is saturated. Figure 6B shows the FT-IR spectrum of polyoxometalate $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}/\text{SiO}_2$ saturated with pyridine. Dines *et al.* (1991) states that ammonia forms an ammonium ion (NH_4^+) with an observed wave number at $1400\text{-}1440\text{ cm}^{-1}$. Seo *et al.* (1988) states that ammonia can be adsorbed on the acid side of the heteropoly compound as well as on the metal cation. The compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}/\text{SiO}_2$ exhibits the ammonium ion vibration $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}/\text{SiO}_2$ the saturation result is shown in the Figure 6.

Polyoxometalate compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}/\text{SiO}_2$ saturated ammonia does not exhibit absorption bands at $1400\text{-}1440\text{ cm}^{-1}$ wave numbers. In this case it is possible that the ammonia is not adsorbed on the polyoxometalate $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}/\text{SiO}_2$. Khalifah and Prasetyoko (2008) explain that pyridine molecules bound to Lewis acid sites are absorbed over the $1400\text{-}1700\text{ cm}^{-1}$ wave range. Figure 6C shows that the pyridine molecule has been adsorbed by the polyoxometalate $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}/\text{SiO}_2$ compound shown in the wave number 1481.33 cm^{-1} . This shows the polyoxometalate compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}/\text{SiO}_2$ having Lewis acid properties.

Acidity Test of the Compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}$ and $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}/\text{SiO}_2$ Quantitatively

Potentiometric titration method is an analytical technique based on the potential measurement of a sensor or electrode. The electrodes used are glass-containing glassy electrode, the liquid having the potential difference properties between the membrane and the electrolyte in contact with the membrane is determined by the activity of the particular ion. The membrane electrode used is a glass electrode. These glass electrodes are said to be ion-selective because they are specific to H^+ ions only.

The acidity measurements of

$(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}$ and $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}/\text{SiO}_2$ were carried out quantitatively by measurement using potentiometric titration with n-butylamine as titrant and acetonitrile as solvent. Acetonitrile is an aprotic solvent as a solvent in compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}$ and $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}/\text{SiO}_2$ so measurable only acidity $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}$ and $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}/\text{SiO}_2$. According to Pecchi *et al.* (1985) the use of benzene, acetonitrile, and iso-octane solvents as solvents in potentiometric titration as a polar solvent to avoid the occurrence of acid or proton adsorption of n-butylamine and acetonitrile as an inert solvent. The measurement by potentiometric method can determine the total acidity and acidity side of a polyoxometallic compound. The initial potential value (E_i) identifies acidity strength from the surface side and classifies the acidity strength based on the span divided into scales: $E_i > 100\text{ mV}$ (acid side is very strong), $0 < E_i < 100\text{ mV}$ (strong acid side), $-100 < E_i < 0\text{ mV}$ (weak acid side), $E_i < -100\text{ mV}$ (acid side is very weak) (Romanelli *et al.*, 2004).

$\text{P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}$ and $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}/\text{SiO}_2$. According to Pecchi *et al.* (1985) the use of benzene, acetonitrile, and iso-octane solvents as solvents in potentiometric titration as a polar solvent to avoid the occurrence of acid or proton adsorption of n-butylamine and acetonitrile as an inert solvent. The measurement by potentiometric method can determine the total acidity and acidity side of a polyoxometallic compound. The initial potential value (E_i) identifies acidity strength from the surface side and classifies the acidity strength based on the span divided into scales: $E_i > 100\text{ mV}$ (acid side is very strong), $0 < E_i < 100\text{ mV}$ (strong acid side), $-100 < E_i < 0\text{ mV}$ (weak acid side), $E_i < -100\text{ mV}$ (acid side is very weak) (Romanelli *et al.*, 2004).

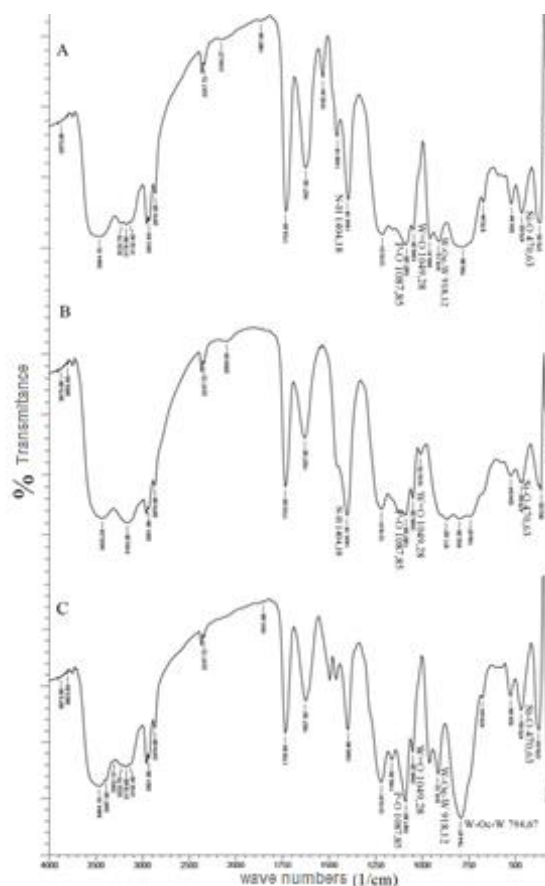


Figure 6. FTIR spectrum of $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}/\text{SiO}_2$ saturated with pyridine (A), $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}/\text{SiO}_2$ saturated with ammonia (B), $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}/\text{SiO}_2$ before saturated (C)

The first and second derivative curves are made to see where the titration equivalent point is shown in Figures 7B and 7C. Equivalent point is performed to see the condition where the base of n-butylamine is added precisely reacts with the compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}$ being titrated. In addition, an equivalence point is performed to determine the amount of base volume of n-butylamine needed to neutralize the $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}/\text{SiO}_2$ compound which is considered to be acidic. Figure 7A shows the result of measurement of compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}$ has an initial potential value of 61.96 mV . Based on the potential value range $0 < E_i < 100$ polyoxometalate $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}$ has a strong acid side. The titration equivalent point is at 0.8 mL of n-

butylamine volume reinforced by the first derivative curve and the second derivative of potentiometric titration data. The titration equivalent point can be observed with sharp potential changes (Mulja and Suharman, 1995). Figures 7B and 7C show the first derivative curves and the second derivative curves of the polyoxometalate $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}$.

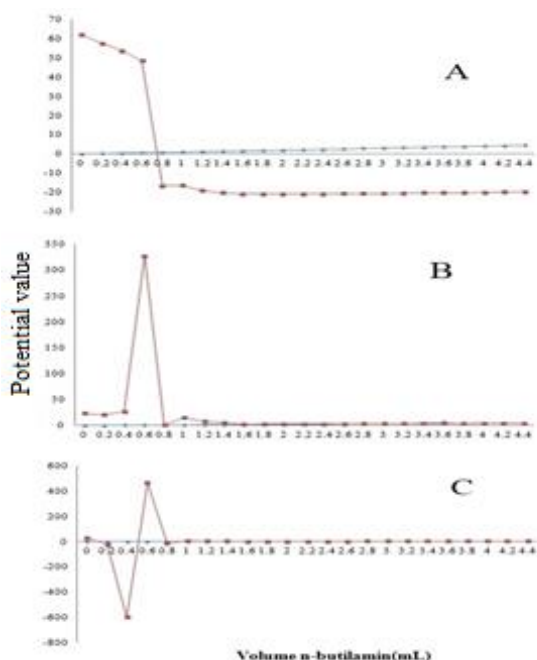


Figure 7. Titration curves of polyoxometalate compound of $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}$ (A), Titration curve first derivate (B), Titration curve second derivate (C)

The measurement of the acidity of the polyoxometalate $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}/\text{SiO}_2$ quantitatively is also carried out through potentiometric titration. From the titration curve presented in Figure 7, the titration equivalent point is obtained when the titration volume is 0.8 mL n-butylamine. Based on equivalence point data, it is found that polyoxometalate $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}/\text{SiO}_2$ compounds require more n-butylamine base volume to neutralize the polyoxometalate compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}/\text{SiO}_2$. This indicates that $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}/\text{SiO}_2$ is more acidic than the polyoxometalate compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}$. This is also supported by looking at the potential initial value comparison. The initial potential value of polyoxometalate compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}/\text{SiO}_2$ is 76.16 mV whereas the initial potential value of polyoxometalate $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}$ amount 61,96 mV. The compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}/\text{SiO}_2$ is included in the acid classification having a strong acid side based on the potential acid strength value range. Increasing the safety of the polyoxometalate $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}/\text{SiO}_2$ compound due to the compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}$ interacts with the carrier SiO_2 derived from tetraethyl orthosilicate. The titration curve of potentiometric compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}/\text{SiO}_2$ can be seen in Figure 8.

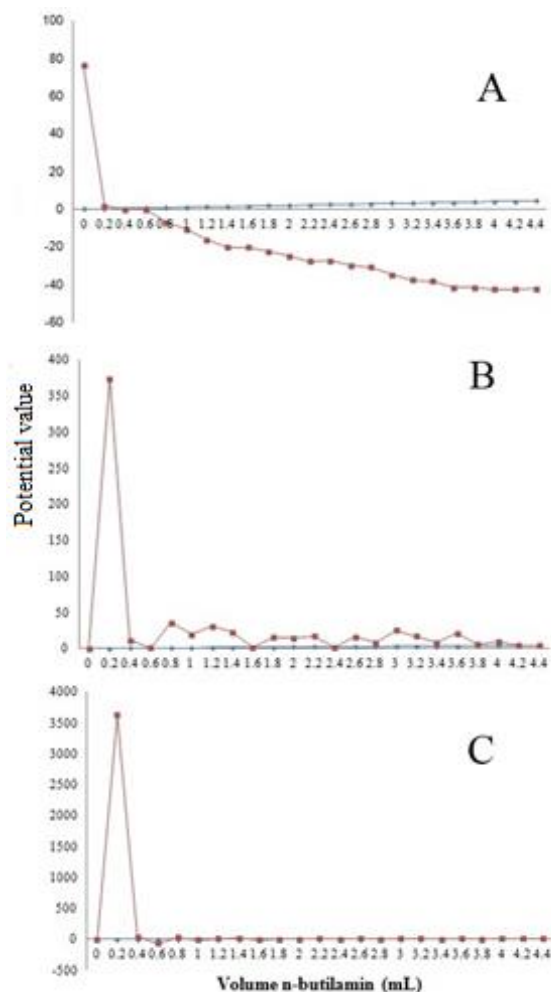


Figure 8. Titration curves of polyoxometalate compound of $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}/\text{SiO}_2$ (A), Titration curve first derivate (B), Titration curve second derivate (C)

The Effect of Temperature on the Stability of the Compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}/\text{SiO}_2$.

The compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}/\text{SiO}_2$ was heated at various temperatures to see the effect of temperature on the stability of the compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}/\text{SiO}_2$. The heating results of the compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}/\text{SiO}_2$ at various temperatures were characterized by an FT-IR spectrophotometer. Figure 9 shows the spectrum of FT-IR polyoxometalate compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}/\text{SiO}_2$ without heating and heated at various temperatures from 200-600°C.

In Figure 9 shows the difference shown by FT-IR spectrum of polyoxometalate $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}/\text{SiO}_2$ before and after heated at the temperature range 200-600°C. Based on the FT-IR spectrum of compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot\text{nH}_2\text{O}/\text{SiO}_2$ which is warmed up the vibrations appear to have shifted wavenumbers.

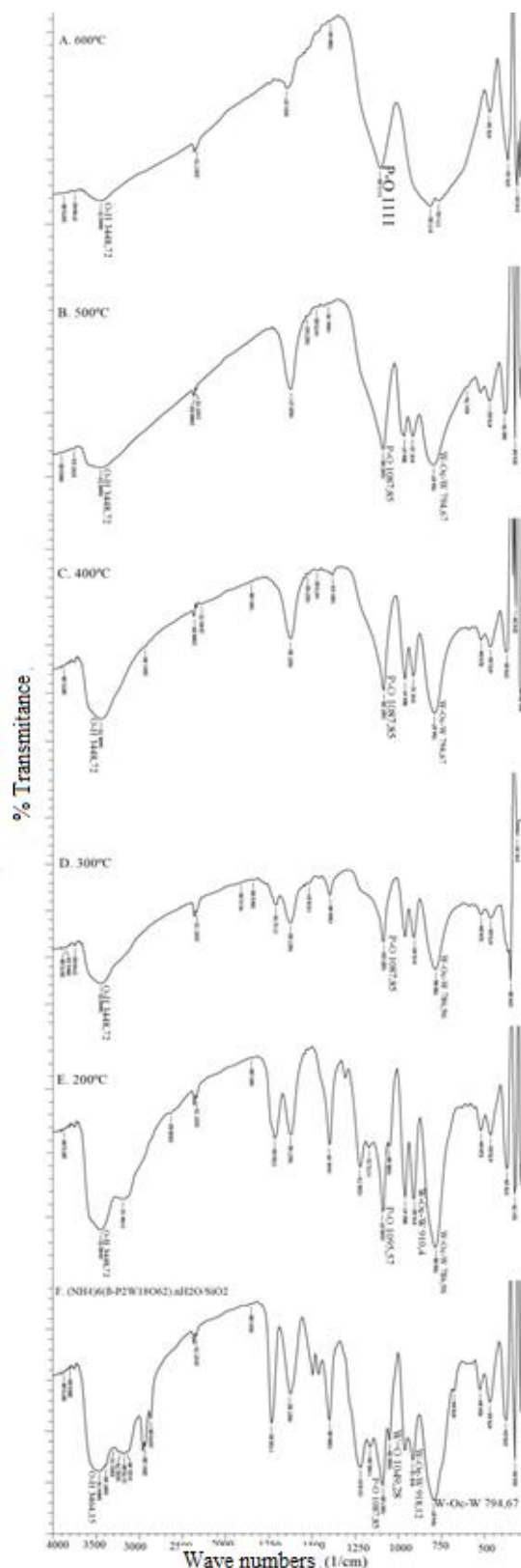


Figure 9. FTIR spectrum of of $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot n\text{H}_2\text{O}/\text{SiO}_2$ at various temperatures (A) 600°C, (B) 500°C, (C) 400°C, (D) 300°C, (E) 200°C, (F) $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot n\text{H}_2\text{O}/\text{SiO}_2$ before heated.

Figure 9 shows the presence of -OH groups in the presence of H_2O observed in the range of 3400-3500 cm^{-1} . Vibration of

polyoxometalate compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot n\text{H}_2\text{O}/\text{SiO}_2$ in the wavenumber 800-1000 cm^{-1} at 600°C indicates a difference caused by vibration $\text{W} = \text{O}$, W-Oe-W vibration and vibration W-Oc-W has been lost. This indicates that on the increase of temperature on heating can cause structure change of polyoxometalate $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot n\text{H}_2\text{O}/\text{SiO}_2$. At a temperature of 200°C shows little difference due to vibration $\text{W} = \text{O}$ that overlap with vibration W-Oe-W and W-Oc-W , whereas with temperature 300°C vibration $\text{W} = \text{O}$ and W-Oe-W was disappeared. This indicates an increase in the heating temperature which may cause changes in the structure of the polyoxometalate $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot n\text{H}_2\text{O}/\text{SiO}_2$.

CONCLUSION

Polyoxometalate compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot n\text{H}_2\text{O}$ and $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot n\text{H}_2\text{O}/\text{SiO}_2$ has been successfully prepared which is characterized by the vibration of the polyoxometalate group as results of the characterization of the FT-IR spectrophotometer. Vibration of the polyoxometalate compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot n\text{H}_2\text{O}$ shows the presence of vibration $\text{W}=\text{O}$ appear on the area 964.41 cm^{-1} , W-Oc-W appear on the area 786.96 cm^{-1} , W-Oe-W appear on the area 918.12 cm^{-1} , P-O appear on the area 1087.85 cm^{-1} , and polyoxometalate compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot n\text{H}_2\text{O}/\text{SiO}_2$ shows the presence of vibration $\text{W}=\text{O}$ appear on the area 1049.28 cm^{-1} , W-Oc-W appear on the area 794.67 cm^{-1} , W-Oe-W appear on the area 918.12 cm^{-1} , P-O appear on the area 1087.85 cm^{-1} , O-H appear on the area 3464.15 cm^{-1} , Si-O appear on the area 470 cm^{-1} . XRD diffraction patterns show polyoxometalate compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot n\text{H}_2\text{O}$ and $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot n\text{H}_2\text{O}/\text{SiO}_2$ has a high crystallinity with an angle of diffraction 2θ each of them 8°-34°. Compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot n\text{H}_2\text{O}/\text{SiO}_2$ has high acidity compared with the compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot n\text{H}_2\text{O}$ acidity test quantitatively. The impact temperature on the stability of the compound $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot n\text{H}_2\text{O}/\text{SiO}_2$ shows of the temperature 600°C there is a shift of compound wavenumbers $(\text{NH}_4)_6(\beta\text{-P}_2\text{W}_{18}\text{O}_{62})\cdot n\text{H}_2\text{O}/\text{SiO}_2$.

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