PREPARATION OF POLYOXOMETALATE COMPOUND (NH₄)₆(β-P₂W₁₈O₆₄)·nH₂O BY SOL-GEL METHOD AND ITS CHARACTERIZATION

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ABSTRACT

Preparation of polyoxometalate compound of (NH₄)₆(β-P₂W₁₈O₆₄)·nH₂O 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 (NH₄)₆(β-P₂W₁₈O₆₄)·nH₂O appeared in wavenumber 786.96 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 (NH₄)₆(β-P₂W₁₈O₆₄)·nH₂O/SiO₂ appears in wavenumbers 794.67 cm⁻¹ (W=O), 918.12 cm⁻¹ (W=O-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 (NH₄)₆(β-P₂W₁₈O₆₄)·nH₂O and (NH₄)₆(β-P₂W₁₈O₆₄)·nH₂O/SiO₂ compound show high crystallinity. The acidic properties showed (NH₄)₆(β-P₂W₁₈O₆₄)·nH₂O/SiO₂ more acidic than (NH₄)₆(β-P₂W₁₈O₆₄)·nH₂O. Analysis of the effect of temperature on the stability of the compounds polyoxometalate (NH₄)₆(β-P₂W₁₈O₆₄)·nH₂O/SiO₂ show that the temperature of 600°C the shift in wavenumbers of the compounds caused by vibration W=O, W-O=, W-O-W has been lost. This shows that at a temperatures of 600°C on heating can cause changes in the structure of polyoxometalate (NH₄)₆(β-P₂W₁₈O₆₄)·nH₂O/SiO₂.

Keywords : (NH₄)₆(β-P₂W₁₈O₆₄)·nH₂O, Polyoxometalate, SiO₂

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 heteropolyoxometalate (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 repeatedly 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 TiO₂, ZrOCl₂, TaCl₅ (Fatimah, 2009). Yang (2011) has also carried on (NH₄)₆(β-P₂W₁₈O₆₄)·nH₂O with SiO₂ sourced from tetraethyl orthosilicic acid (TEOS) and using alcohol as a medium. In his research, TEOS hydrolys was used as a source of SiO₂ by using microemulsion medium derived from sodium bis(2-ethylhexyl) 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 SiO₂ 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 (NH₄)₆(β-P₂W₁₈O₆₄) were carried out with SiO₂. 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 SiO₂ carried by polyoxometalate compounds is characterized using FT-IR spectrometer and XRD. This characterization is performed both before and after the silica is carried by the polyoxometalate compounds. The acidity of the compound (NH₄)₆(β-P₂W₁₈O₆₄)·nH₂O/SiO₂ 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, spectrophotometer FT-IR Shimidzu prestige 21 were used for characterizatio of the
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)sulfosuccinates, n-butylamine, pyridin, cyclohexane, and acetonitrile.

Synthesis of Dawson-Type Polyoxometalate compounds (NH₄)₆[β-P₂W₁₈O₆₂]·nH₂O and its characterization.

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 obtained 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 (NH₄)₆[β-P₂W₁₈O₆₂]·nH₂O according to (Contant, 1990). The polyoxometalate (NH₄)₆[β-P₂W₁₈O₆₂]·nH₂O obtained is characterized by spectrophotometer FT-IR and XRD.

Preparation Polyoxometalate compounds (NH₄)₆[β-P₂W₁₈O₆₂]·nH₂O/SiO₂ by Sol-Gel Method (Newman et al, 2006)

Preparation polyoxometalate compound (NH₄)₆[β-P₂W₁₈O₆₂]·nH₂O/SiO₂ was modified from the Kim et al (2006) procedure. The compound (NH₄)₆[β-P₂W₁₈O₆₂]·nH₂O/SiO₂ was synthesized with 0.5 g sodium bis(2-ethylhexyl) sulfosuccinate dissolved with 1 ml of sicioloxane (Solution A). Compound (NH₄)₆[β-P₂W₁₈O₆₂]·nH₂O of 0.76 g was dissolved with 1 mL of aquades (Solution B). Solution B was added to solution A while stirrer. A total 2 mL tetraethyl ortosilicate (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 spatra. The white solid formed is a compound (NH₄)₆[β-P₂W₁₈O₆₂]·nH₂O/SiO₂. The compound (NH₄)₆[β-P₂W₁₈O₆₂]·nH₂O/SiO₂ was characterized by a FT-IR spectrophotometer, and an XRD diffractometer.

Acidity Test of the Compound (NH₄)₆[β-P₂W₁₈O₆₂]·nH₂O/SiO₂ qualitatively

The acidity test was qualitatively modified from the Maksimov et al (2001) procedure by saturation of polyoxometalicate compounds using ammonia and also pyridine. For saturation with ammonia as much as 0.5 g of compound (NH₄)₆[β-P₂W₁₈O₆₂]·nH₂O and (NH₄)₆[β-P₂W₁₈O₆₂]·nH₂O/SiO₂ inserted into vials and 1 mL of ammonia (NH₃) 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 polyoxometalate compound. For saturation using a pyridine compound, the same work was done. A total of 0.5 g of each compound (NH₄)₆[β-P₂W₁₈O₆₂]·nH₂O and (NH₄)₆[β-P₂W₁₈O₆₂].nH₂O/SiO₂ 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 (NH₄)₆[β-P₂W₁₈O₆₂]·nH₂O and (NH₄)₆[β-P₂W₁₈O₆₂]·nH₂O/SiO₂ results in saturation with ammonia and pyridine were qualitatively tested by characterization using a FT-IR spectrophotometer.

Acidity Test of the compound (NH₄)₆[β-P₂W₁₈O₆₂]·nH₂O/SiO₂ Quantitatively (Reddy et al, 2006)

A total of 0.1 g of each compound (NH₄)₆[β-P₂W₁₈O₆₂]·nH₂O and (NH₄)₆[β-P₂W₁₈O₆₂]·nH₂O/SiO₂ 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 perovls 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 (NH₄)₆[β-P₂W₁₈O₆₂]·nH₂O/SiO₂

The compound (NH₄)₆[β-P₂W₁₈O₆₂]·nH₂O/SiO₂ was heated at various temperature 200°C, 300°C, 400°C, 500°C, and 600°C for 3 hours in he furnace. The combustion compound was cooled and analyzed by using FT-IR spectrofotometer.

RESULTS AND DISCUSSION

Synthesis of Dawson-Type Polyoxometalate compound (NH₄)₆[β-P₂W₁₈O₆₂]·nH₂O and characterization

The synthesis of dawson type polyoxometalate compound (NH₄)₆[β-P₂W₁₈O₆₂]·nH₂O 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 cristallinity analysis using XRD analysis. The reaction of polyoxometalate compound formation as follows:

\[18(WO₄)²⁻ + 32HPO₄ + 6(NH₄)²⁺ → (NH₄)₆[β-P₂W₁₈O₆₂] + 18H₂O + 32HPO₄⁻\]

The identification was carried out on a polyoxometalate (NH₄)₆[β-P₂W₁₈O₆₂]·nH₂O 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 (NH₄)₆[β-P₂W₁₈O₆₂]·nH₂O 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 polyoxometalate 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⁺ (Finke et al, 1987). The compound (NH₄)₆[β-P₂W₁₈O₆₂]·nH₂O was analyzed using
XRD. Diffractogram of compound (NH₄)₆[β-P₂W₁₈O₆²₋₄]·nH₂O. presented in figure 2.

![FT-IR spectra polyoxometalate compound (NH₄)₆(β-P₂W₁₈O₆²₋₄)·nH₂O](image1)

**Figure 1.** FT-IR spectra polyoxometalate compound (NH₄)₆(β-P₂W₁₈O₆²₋₄)·nH₂O

![XRD Diffraction pattern of polyoxometalate compound (NH₄)₆(β-P₂W₁₈O₆²₋₄)·nH₂O](image2)

**Figure 2.** XRD Diffraction pattern of polyoxometalate compound (NH₄)₆(β-P₂W₁₈O₆²₋₄)·nH₂O

The diffractogram in figure 2 shows the diffraction for the highest intensity of the polyoxometalate compound (NH₄)₆(β-P₂W₁₈O₆²₋₄)·nH₂O 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°-10°, 15-20°, 22-25°, and 35-40°. The diffraction that appears below 10° in region 20 shows that the polyoxometalate compound has a very high crystallinity. Diffractogram of polyoxometalate compound (NH₄)₆(β-P₂W₁₈O₆²₋₄)·nH₂O shows the sharp diffraction peaks indicating polyoxometalate (NH₄)₆(β-P₂W₁₈O₆²₋₄)·nH₂O compounds have very high crystalline properties in which the atoms of the polyoxometal compound (NH₄)₆(β-P₂W₁₈O₆²₋₄)·nH₂O is arranged regularly based on the length and angle of the regular bond.

![Synthesis of Dawson-Type Polyoxometalate Compound (NH₄)₆(β-P₂W₁₈O₆²₋₄)·nH₂O/SiO₂ And Characterization](image3)

**Figure 3.** FTIR spectrum of polyoxometalate (NH₄)₆(β-P₂W₁₈O₆²₋₄)·nH₂O (A), (NH₄)₆(β-P₂W₁₈O₆²₋₄)·nH₂O/SiO₂ (B)

Figure 3 shows the difference shown by FT-IR spectrum of polyoxometalate (NH₄)₆(β-P₂W₁₈O₆²₋₄)·nH₂O compound before being assumed with SiO₂. According to Derick et al. (1999) the asymmetric stretching vibration of Si-O-Si is at the wave number 1130-1000 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 (NH₄)₆(β-P₂W₁₈O₆²₋₄)·nH₂O/SiO₂ 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 W = O. The W = O vibration before embodiment appears at 964.41 cm⁻¹ wave numbers and the vibrations after being assumed with SiO₂ 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 3500-3500 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 H₂O in the compound (NH₄)₆(β-P₂W₁₈O₆²₋₄)·nH₂O and the wave number at peak 3464.15 cm⁻¹ identifies the -OH by the presence of H₂O in the compound (NH₄)₆(β-P₂W₁₈O₆²₋₄)·nH₂O/SiO₂

The preparation of Dawson- Type polyoxometalate compound (NH₄)₆(β-P₂W₁₈O₆²₋₄)·nH₂O with SiO₂ based on the procedure undertaken by Newman et al. (2006) in SiO₂ is derived from tetraethyl orthosilicate in the form of a liquid. Identification using spectrophotometer FT-IR compound (NH₄)₆(β-P₂W₁₈O₆²₋₄)·nH₂O/SiO₂ showed the presence of specific vibrations of polyoxometalate and SiO₂ compounds presented in Figure 3. On FT-IR spectrum of compound (NH₄)₆(β-P₂W₁₈O₆²₋₄)·nH₂O and (NH₄)₆(β-P₂W₁₈O₆²₋₄)·nH₂O/SiO₂ noticeable differences before placement and after assuming SiO₂.
have the same absorption bands of both the polyoxometalate (NH$_4$)$_4$[β-P$_2$W$_{18}$O$_{62}$]·nH$_2$O as well as the SiO$_2$ absorption bands. This identifies the presence of polyoxometalate (NH$_4$)$_4$[β-P$_2$W$_{18}$O$_{62}$]·nH$_2$O and SiO$_2$ forming groups which show the success of SiO$_2$ baffling process in the polyoxometalate (NH$_4$)$_4$[β-P$_2$W$_{18}$O$_{62}$]·nH$_2$O. Table 1 shows wave numbers of polyoxometalate compound (NH$_4$)$_4$[β-P$_2$W$_{18}$O$_{62}$]·nH$_2$O and (NH$_4$)$_4$[β-P$_2$W$_{18}$O$_{62}$]·nH$_2$O/SiO$_2$. Further, polyoxometalate (NH$_4$)$_4$[β-P$_2$W$_{18}$O$_{62}$]·nH$_2$O analysis using XRD. Comparison of the compound (NH$_4$)$_4$[β-P$_2$W$_{18}$O$_{62}$]·nH$_2$O and (NH$_4$)$_4$[β-P$_2$W$_{18}$O$_{62}$]·nH$_2$O/SiO$_2$ presented in the Figure 4.

Table 1. Wave numbers of polyoxometalate compound (NH$_4$)$_4$[β-P$_2$W$_{18}$O$_{62}$]·nH$_2$O and (NH$_4$)$_4$[β-P$_2$W$_{18}$O$_{62}$]·nH$_2$O/SiO$_2$

<table>
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<th>Compound</th>
<th>Vibration</th>
<th>Type</th>
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<tr>
<td>(NH$_4$)$<em>4$[β-P$<em>2$W$</em>{18}$O$</em>{62}$]·nH$_2$O</td>
<td>964.41</td>
<td>W=O</td>
</tr>
<tr>
<td>(NH$_4$)$<em>4$[β-P$<em>2$W$</em>{18}$O$</em>{62}$]·nH$_2$O/SiO$_2$</td>
<td>1049.28</td>
<td>W-O-W</td>
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<tr>
<td></td>
<td>786.96</td>
<td>W-O-W</td>
</tr>
<tr>
<td></td>
<td>918.12</td>
<td>W-O-W</td>
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<tr>
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<td>1087.85</td>
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<td>3572.12</td>
<td>O-H</td>
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Figure 4. Diffractions of (NH$_4$)$_4$[β-P$_2$W$_{18}$O$_{62}$]·nH$_2$O (A) and (NH$_4$)$_4$[β-P$_2$W$_{18}$O$_{62}$]·nH$_2$O/SiO$_2$ (B)

Polyoxometalate compound (NH$_4$)$_4$[β-P$_2$W$_{18}$O$_{62}$]·nH$_2$O which was assumed by SiO$_2$ was characterized using XRD. Characterization using XRD diffraction angle and crystallinity showed polioksmetalate compounds with SiO$_2$. (NH$_4$)$_4$[β-P$_2$W$_{18}$O$_{62}$]·nH$_2$O. The comparison of XRD diffraction of the compound (NH$_4$)$_4$[β-P$_2$W$_{18}$O$_{62}$]·nH$_2$O with (NH$_4$)$_4$[β-P$_2$W$_{18}$O$_{62}$]·nH$_2$O/SiO$_2$ were presented in Figure 4. Figure 4A shows the diffraction of (NH$_4$)$_4$[β-P$_2$W$_{18}$O$_{62}$]·nH$_2$O that appear at 2θ area under 10° indicates that the compound polioksmetalate (NH$_4$)$_4$[β-P$_2$W$_{18}$O$_{62}$]·nH$_2$O possess extremely high crystallinity due atoms (NH$_4$)$_4$[β-P$_2$W$_{18}$O$_{62}$]·nH$_2$O regularly by Length and angle of bond formed. Figure 4B shows the XRD pattern of compound (NH$_4$)$_4$[β-P$_2$W$_{18}$O$_{62}$]·nH$_2$O/SiO$_2$. The compound (NH$_4$)$_4$[β-P$_2$W$_{18}$O$_{62}$]·nH$_2$O/SiO$_2$ has a high crystallinity by the diffraction angle 20 8°, 18°, 27° and 34°, respectively which shows the characteristics of the compound polyoxometalate (NH$_4$)$_4$[β-P$_2$W$_{18}$O$_{62}$]·nH$_2$O/SiO$_2$ where atoms polyoxometalate compound (NH$_4$)$_4$[β-P$_2$W$_{18}$O$_{62}$]·nH$_2$O/SiO$_2$ arranged regularly based on the length and angle of a regular bond. In Figure 4B shows the XRD pattern of (NH$_4$)$_4$[β-P$_2$W$_{18}$O$_{62}$]·nH$_2$O/SiO$_2$ indicates the diffraction angle changes.

Acidity Test Of The compound (NH$_4$)$_4$[β-P$_2$W$_{18}$O$_{62}$]·nH$_2$O and (NH$_4$)$_4$[β-P$_2$W$_{18}$O$_{62}$]·nH$_2$O/SiO$_2$ Qualitatively

Acidity Test Of The compound (NH$_4$)$_4$[β-P$_2$W$_{18}$O$_{62}$]·nH$_2$O

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

Figure 5. FTIR spectrum of (NH$_4$)$_4$[β-P$_2$W$_{18}$O$_{62}$]·nH$_2$O saturated with ammonia (A), (NH$_4$)$_4$[β-P$_2$W$_{18}$O$_{62}$]·nH$_2$O saturated with ammonia (B), (NH$_4$)$_4$[β-P$_2$W$_{18}$O$_{62}$]·nH$_2$O before saturated (C)

FT-IR spectrum in Figure 5A and B did not find any absorption band at wave number 1400-1440 cm$^{-1}$ on
polyoxometalate \((\text{NH}_4)_6(\beta-P_2W_{18}O_{62})\).nH_2O. According to Dines et al. (1991) ammonia forms ammonium ions \((\text{NH}_4^+)\) with the observed wave numbers being at 1400-1440 cm\(^{-1}\). In polyoxometalate compound \((\text{NH}_4)_6(\beta-P_2W_{18}O_{62})\).nH_2O saturated with ammonia and pyridine does not show the ammonium ion vibration \((\text{NH}_4^+)\) in the 1400-1440 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 \((\text{NH}_4)_6(\beta-P_2W_{18}O_{62})\).nH_2O/\text{SiO}_2 Qualitatively**

The compound \((\text{NH}_4)_6(\beta-P_2W_{18}O_{62})\).nH_2O/\text{SiO}_2 is saturated using ammonia and pyridine just as with section 3.3.1. Then the polyoxometalate \((\text{NH}_4)_6(\beta-P_2W_{18}O_{62})\).nH_2O/\text{SiO}_2 was characterized using a FT-IR spectrophotometer. The saturated FT-IR \((\text{NH}_4)_6(\beta-P_2W_{18}O_{62})\).nH_2O/\text{SiO}_2 spectrum is presented in Figure 6. Figure 6A shows the spectrum of FT-IR polyoxometalate \((\text{NH}_4)_6(\beta-P_2W_{18}O_{62})\).nH_2O/\text{SiO}_2 before it is saturated. Figure 6B shows the FT-IR spectrum of polyoxometalate \((\text{NH}_4)_6(\beta-P_2W_{18}O_{62})\).nH_2O/\text{SiO}_2 saturated with pyridine. Dines et al. (1991) states that ammonia forms an ammonium ion \((\text{NH}_4^+)\) with an observed wave number at 1400-1440 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 \((\text{NH}_4)_6(\beta-P_2W_{18}O_{62})\).nH_2O/\text{SiO}_2 exhibits the ammonium ion vibration \((\text{NH}_4)_6(\beta-P_2W_{18}O_{62})\).nH_2O/\text{SiO}_2 the saturation result is shown in the Figure 6.

Polyoxometalate compound \((\text{NH}_4)_6(\beta-P_2W_{18}O_{62})\).nH_2O/\text{SiO}_2 saturated ammonia does not exhibit absorption bands at 1400-1440 cm\(^{-1}\) wave numbers. In this case it is possible that the ammonia is not adsorbed on the polyoxometalate \((\text{NH}_4)_6(\beta-P_2W_{18}O_{62})\).nH_2O/\text{SiO}_2. Khalifah and Prasetyoko (2008) explain that pyridine molecules bond to Lewis acid sites are absorbed over the 1400-1700 cm\(^{-1}\) wave range. Figure 6C shows that the pyridine molecule has been adsorbed by the polyoxometalate \((\text{NH}_4)_6(\beta-P_2W_{18}O_{62})\).nH_2O/\text{SiO}_2 compound shown in the wave number 1481.33 cm\(^{-1}\). This shows the polyoxometalate compound \((\text{NH}_4)_6(\beta-P_2W_{18}O_{62})\).nH_2O/\text{SiO}_2 having Lewis acid properties.

**Acidity Test of the Compound \((\text{NH}_4)_6(\beta-P_2W_{18}O_{62})\).nH_2O and \((\text{NH}_4)_6(\beta-P_2W_{18}O_{62})\).nH_2O/\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 electrodes, 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 \((\text{NH}_4)_6(\beta-P_2W_{18}O_{62})\).nH_2O and \((\text{NH}_4)_6(\beta-P_2W_{18}O_{62})\).nH_2O/\text{SiO}_2 were carried out quantitatively by measurement using potentiometric titration with n-butylamine as titrant and acetanilide as solvent. Acetanilide is an aprotic solvent as a solvent in compound \((\text{NH}_4)_6(\beta-P_2W_{18}O_{62})\).nH_2O and \((\text{NH}_4)_6(\beta-P_2W_{18}O_{62})\).nH_2O/\text{SiO}_2 so measurable only acidity \((\text{NH}_4)_6(\beta-P_2W_{18}O_{62})\).nH_2O and \((\text{NH}_4)_6(\beta-P_2W_{18}O_{62})\).nH_2O/\text{SiO}_2. According to Pecchi et al. (1985) the use of benzene, acetanilide, 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 acetanilide as an inert solvent. The measurement by potentiometric method can determine the total acidity and acidity side of a polyoxometalate compound. The initial potential value (Ei) identifies acidity strength from the surface side and classifies the acidity strength based on the span divided into scales: Ei > 100 mV (acid side is very strong), 0 < Ei < 100 mV (strong acid side), -100 < Ei < 0 mV (weak acid side), Ei < -100 mV (acid side is very weak) (Romanelli et al., 2004).

Figure 6. FTIR spectrum of \((\text{NH}_4)_6(\beta-P_2W_{18}O_{62})\).nH_2O/\text{SiO}_2 saturated with pyridine (A), \((\text{NH}_4)_6(\beta-P_2W_{18}O_{62})\).nH_2O/\text{SiO}_2 saturated with ammonia (B), \((\text{NH}_4)_6(\beta-P_2W_{18}O_{62})\).nH_2O/\text{SiO}_2 before saturated (C).
butylamime 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 \((\text{NH}_4)_{4}^{}\beta-P_2\text{W}_{18}\text{O}_{62}\).nH\(_2\)O.

The measurement of the acidity of the polyoxometalate \((\text{NH}_4)_{4}^{}\beta-P_2\text{W}_{18}\text{O}_{62}\).nH\(_2\)O 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 \((\text{NH}_4)_{4}^{}\beta-P_2\text{W}_{18}\text{O}_{62}\).nH\(_2\)O/Si\(_2\)O quantifies require more n-butylamine base volume to neutralize the polyoxometalate compound \((\text{NH}_4)_{4}^{}\beta-P_2\text{W}_{18}\text{O}_{62}\).nH\(_2\)O/Si\(_2\)O. This indicates that \((\text{NH}_4)_{4}^{}\beta-P_2\text{W}_{18}\text{O}_{62}\).nH\(_2\)O/Si\(_2\)O is more acidic than the polyoxometalate compound \((\text{NH}_4)_{4}^{}\beta-P_2\text{W}_{18}\text{O}_{62}\).nH\(_2\)O. This is also supported by looking at the potential initial value comparison. The initial potential value of polyoxometalate compound \((\text{NH}_4)_{4}^{}\beta-P_2\text{W}_{18}\text{O}_{62}\).nH\(_2\)O/Si\(_2\)O amount 61.96 mV whereas the initial potential value of polyoxometalate \((\text{NH}_4)_{4}^{}\beta-P_2\text{W}_{18}\text{O}_{62}\).nH\(_2\)O is 76.16 mV. The compound \((\text{NH}_4)_{4}^{}\beta-P_2\text{W}_{18}\text{O}_{62}\).nH\(_2\)O/Si\(_2\)O 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 \((\text{NH}_4)_{4}^{}\beta-P_2\text{W}_{18}\text{O}_{62}\).nH\(_2\)O/Si\(_2\)O compound due to the compound \((\text{NH}_4)_{4}^{}\beta-P_2\text{W}_{18}\text{O}_{62}\).nH\(_2\)O interacts with the carrier SiO\(_2\) derived from tetraethyl orthosilicate. The titration curve of potentiometric compound \((\text{NH}_4)_{4}^{}\beta-P_2\text{W}_{18}\text{O}_{62}\).nH\(_2\)O/Si\(_2\)O can be seen in Figure 8.

The Effect of Temperature on the Stability of the Compound \((\text{NH}_4)_{4}^{}\beta-P_2\text{W}_{18}\text{O}_{62}\).nH\(_2\)O/Si\(_2\)O

The compound \((\text{NH}_4)_{4}^{}\beta-P_2\text{W}_{18}\text{O}_{62}\).nH\(_2\)O/Si\(_2\)O was heated at various temperatures to see the effect of temperature on the stability of the compound \((\text{NH}_4)_{4}^{}\beta-P_2\text{W}_{18}\text{O}_{62}\).nH\(_2\)O/Si\(_2\)O. The heating results of the compound \((\text{NH}_4)_{4}^{}\beta-P_2\text{W}_{18}\text{O}_{62}\).nH\(_2\)O/Si\(_2\)O at various temperatures were characterized by an FT-IR spectrophotometer. Figure 9 shows the spectrum of FT-IR polyoxometalate compound \((\text{NH}_4)_{4}^{}\beta-P_2\text{W}_{18}\text{O}_{62}\).nH\(_2\)O/Si\(_2\)O without heating and heated at various temperatures from 200-600ºC.

In Figure 9 shows the difference shown by FT-IR spectrum of polyoxometalate \((\text{NH}_4)_{4}^{}\beta-P_2\text{W}_{18}\text{O}_{62}\).nH\(_2\)O/Si\(_2\)O before and after heated at the temperature range 200-600ºC. Based on the FT-IR spectrum of compound \((\text{NH}_4)_{4}^{}\beta-P_2\text{W}_{18}\text{O}_{62}\).nH\(_2\)O/Si\(_2\)O which is warmed up the vibrations appear to have shifted wavenumbers.
polyoxometalate compound \((\text{NH}_4)_6(\beta_2\text{P}_2\text{W}_{18}\text{O}_{62})_2\cdot n\text{H}_2\text{O}/\text{SiO}_2\) in the wavenumber 800-1000 cm\(^{-1}\) at 600°C indicates a difference caused by vibration \(W = O\), \(W\text{-Oe-W}\) vibration and vibration \(W\text{-Oe-W}\) has been lost. This indicates that on the increase of temperature on heating can cause structure change of polyoxometalate \((\text{NH}_4)_6(\beta_2\text{P}_2\text{W}_{18}\text{O}_{62})_2\cdot n\text{H}_2\text{O}/\text{SiO}_2\). At a temperature of 200°C shows little difference due to vibration \(W = O\) that overlap with vibration \(W\text{-Oe-W}\) and \(W\text{-Oe-W}\), whereas with temperature 300°C vibration \(W = O\) and \(W\text{-Oe-W}\) was disappeared. This indicates an increase in the heating temperature which may cause changes in the structure of the polyoxometalate \((\text{NH}_4)_6(\beta_2\text{P}_2\text{W}_{18}\text{O}_{62})_2\cdot n\text{H}_2\text{O}/\text{SiO}_2\).

**CONCLUSION**

Polyoxometalate compound \((\text{NH}_4)_6(\beta_2\text{P}_2\text{W}_{18}\text{O}_{62})_2\cdot n\text{H}_2\text{O}\) and \((\text{NH}_4)_6(\beta_2\text{P}_2\text{W}_{18}\text{O}_{62})_2\cdot n\text{H}_2\text{O}/\text{SiO}_2\) has been successfully prepared which is characterized by the vibration of the polyoxometalate group as results of the characterization of the FT-IR spectrofotometer. Vibration of the polyoxometalate compound \((\text{NH}_4)_6(\beta_2\text{P}_2\text{W}_{18}\text{O}_{62})_2\cdot n\text{H}_2\text{O}\) shows the presence of vibration \(W = O\) appear on the area 964.41 cm\(^{-1}\), \(W\text{-O\text{-W}}\) appear on the area 786.96 cm\(^{-1}\), \(W\text{-Oe-W}\) appear on the area 918.12 cm\(^{-1}\), \(P\text{-O}\) appear on the area 1087.85 cm\(^{-1}\), and polyoxometalate compound \((\text{NH}_4)_6(\beta_2\text{P}_2\text{W}_{18}\text{O}_{62})_2\cdot n\text{H}_2\text{O}/\text{SiO}_2\) shows the presence of vibration \(W = O\) appear on the area 1049.28 cm\(^{-1}\), \(W\text{-O\text{-W}}\) appear on the area 794.67 cm\(^{-1}\), \(W\text{-Oe-W}\) appear on the area 918.12 cm\(^{-1}\), \(P\text{-O}\) appear on the area 1087.85 cm\(^{-1}\), \(O\text{-H}\) appear on the area 3464.15 cm\(^{-1}\), \(Si\text{-O}\) appear on the area 470 cm\(^{-1}\). XRD diffraction patterns show polyoxometalate compound \((\text{NH}_4)_6(\beta_2\text{P}_2\text{W}_{18}\text{O}_{62})_2\cdot n\text{H}_2\text{O}\) and \((\text{NH}_4)_6(\beta_2\text{P}_2\text{W}_{18}\text{O}_{62})_2\cdot n\text{H}_2\text{O}/\text{SiO}_2\) has a high crystallinity with an angle of diffraction 2θ each of them 8°-34°. Compound \((\text{NH}_4)_6(\beta_2\text{P}_2\text{W}_{18}\text{O}_{62})_2\cdot n\text{H}_2\text{O}/\text{SiO}_2\) has high acidity compared with the compound \((\text{NH}_4)_6(\beta_2\text{P}_2\text{W}_{18}\text{O}_{62})_2\cdot n\text{H}_2\text{O}\) acidity test quantitatively. The impact temperature on the stability of the compound \((\text{NH}_4)_6(\beta_2\text{P}_2\text{W}_{18}\text{O}_{62})_2\cdot n\text{H}_2\text{O}/\text{SiO}_2\) shows of the temperature 600°C there is a shift of compound wavenumbers \((\text{NH}_4)_6(\beta_2\text{P}_2\text{W}_{18}\text{O}_{62})_2\cdot n\text{H}_2\text{O}/\text{SiO}_2\).

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