THERMAL STABILITY OF POLYOXOMETALATE COMPOUND OF KEGGIN K$_8$[β$_2$-SiW$_{11}$O$_{39}$]·nH$_2$O SUPPORTED WITH SiO$_2$

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ABSTRACT

Synthesis through sol-gel method and characterization of polyoxometalate compound of K$_8$[β$_2$-SiW$_{11}$O$_{39}$]·nH$_2$O supported with SiO$_2$ have been done. The functional groups of polyoxometalate compound was characterized by FT-IR spectrophotometer for the functional groups and the degree’s of crystalinity using XRD. The acidity of K$_8$[β$_2$-SiW$_{11}$O$_{39}$]·nH$_2$O/SiO$_2$ was determined qualitative analysis using ammonia and pyridine adsorption and the quantitative analysis using potentiometric titration method. The results of FT-IR spectrum of K$_8$[β$_2$-SiW$_{11}$O$_{39}$]·nH$_2$O appeared at wavenumber 987.55 cm$^{-1}$ (W=O), 864.11 cm$^{-1}$ (W-Oe-W), 756.1 cm$^{-1}$ (W-Oe-W), 3425.58 cm$^{-1}$ (O-H), respectively and spectrum of K$_8$[β$_2$-SiW$_{11}$O$_{39}$]SiO$_2$ appeared at wavenumber 956.69 cm$^{-1}$ (W=O), 864.11 cm$^{-1}$ (W-Oe-W), 3448.72 cm$^{-1}$ (O-H), respectively. The diffraction of XRD pattern of K$_8$[β$_2$-SiW$_{11}$O$_{39}$]·nH$_2$O and K$_8$[β$_2$-SiW$_{11}$O$_{39}$]·nH$_2$O/SiO$_2$ compounds show high crystalinity. The acidic properties showed K$_8$[β$_2$-SiW$_{11}$O$_{39}$]·nH$_2$O/SiO$_2$ more acidic compared to K$_8$[β$_2$-The SiW$_{11}$O$_{39}$]·nH$_2$O. The qualitative analysis showed pyridine compound adsorbed more of polyoxometalate the temperature, surface area, and acidity of the catalyst. The temperature affects collisions between molecules and certain chemical reactions require heating at high temperatures to obtain maximum results. As an example the hydroxylation reaction of n-hexane requires the temperatures above 400 ° C and requires the Bronsted acid side in the reaction to obtain a high percent conversion (Eid et al, 2013).

The synthesis of H$_4$[γ-H$_2$SiV$_2$W$_6$O$_{36}$] has been carried out with various variations of embedding SiO$_2$, TiO$_2$, ZrOCl$_2$ and TaCl$_5$ by Karim (2014), which the product material has not been tested for its qualitative and quantitative acidity. Meanwhile Marci (et al 2013) has carried out the research by embedding Keggin H$_3$PW$_{12}$O$_{40}$ type polyoxometalate compounds with various metal oxides such TiO$_2$, SiO$_2$, ZrO$_2$, ZnO, and Al$_2$O$_3$. From the many several metal oxides which has been used, polyoxometalate compounds which are embedded with SiO$_2$ have higher catalytic character which applied to the propene hydration reaction.

In this research, the synthesis of Keggin K$_8$[β$_2$-SiW$_{11}$O$_{39}$]·nH$_2$O polyoxometalate compound which is embedded by SiO$_2$ metal oxide. The metal oxide of SiO$_2$ was obtained from reaction of tetraethyl orthosilical hydrolysis (TEOS) known as the sol gel method. The embedded result of synthesized polyoxometalate compounds were characterized by a Fourier Transform Infra Red (FT-IR) spectrophotometer and X-Ray Diffractometer (XRD). Polyoxometalate compounds K$_8$[β$_2$-SiW$_{11}$O$_{39}$]·nH$_2$O was soaked on the acid compounds before and after embedded qualitatively and quantitatively. The thermal stability character of K$_8$[β$_2$-SiW$_{11}$O$_{39}$]·nH$_2$O and K$_8$[β$_2$-SiW$_{11}$O$_{39}$]·nH$_2$O/SiO$_2$ were tested by heating it at various temperature using furnace and the heating results were catalytic properties increase. The catalytic activity is affected by the temperature, surface area, and acidity of the catalyst. The temperature affects collisions between molecules and certain chemical reactions require heating at high temperatures to obtain maximum results. As an example the hydroxylation reaction of n-hexane requires the temperatures above 400 ° C and requires the Bronsted acid side in the reaction to obtain a high percent conversion (Eid et al, 2013).

Keywords : K$_8$[β$_2$-SiW$_{11}$O$_{39}$]·nH$_2$O, polyoxometalate, SiO$_2$.

INTRODUCTION

Polyoxometalate compound is the cluster compound of metal-oxygen which acid-base properties, it has various structural and oxidation rates, so it is very effective for both acid-base reaction and reduction oxidation reaction catalyst (Yamase dkk, 2002). Polyoxometallic compounds are effective as catalysts because they have higher acidity than sulfuric acid and not toxic (Okuhara et al, 1996). This compound has been applied as a catalyst in industrial processes in developed countries such as Japan (Nakagawa and Mizuno, 2007).

The research of polyoxometalate compounds are primarily intended in terms of its superiority as a catalyst which can be performed either in homogeneous or heterogeneous systems depending on the medium are used. In a heterogeneous system, the polyoxometalate compound can be used repeatedly in catalytic reaction.

The polyoxometalate compound has a low surface area and high solubility in a polar solvent (Kim et al, 2006). The Catalyst which have a small surface area is suitable for homogeneous catalysts while the homogeneous catalysts can not be recycled. To designed the polyoxometalate compound as a heterogeneous catalyst, modification should carried out by embedding. Modification of polyoxometalate compounds can be embedding by inclusion using both metal oxide and non-oxide metals (Newman et al, 2006). The embedding is carried out to have a large surface area which can be used as heterogeneous catalysis and can increase the acidity of the compound, so that the...
characterized by a FT-IR spectrophotometer. The acidity and thermal stability character of polyoxometalate compounds were tested perior to be used as catalysts in chemical reactions that require heating at high temperatures.

**EXPERIMENTAL SECTION**

The instruments which used in this research X-Ray diffractometer (XRD) Rigaku MiniFlex 600 and FT-IR Shimadzu Prestige-21 Spectrophotometer. The substances used in this research were sodium metasilicate (Na$_2$SiO$_3$), sodium tungstate (Na$_2$WO$_4$), hydrochloric acid (HCl), potassium chloride (KCl), potassium carbonate (K$_2$CO$_3$), tetraethyl orthosilicate (TEOS), Sodium bis (2-Ethylhexyl) sulfosuccinate of 1.5 g was dissolved with 1 mL of acetonitrile and K$_3$CO$_3$, potassium carbonate (K$_2$CO$_3$) and KCl, potassium carbonate (K$_2$CO$_3$), sodium metasilicate (Na$_2$SiO$_3$) in this research were sodium metasilicate (Na$_2$SiO$_3$), cyclohexane, pyridine, ammonia (NH$_3$), n-butylamine, acetonitrile and aquades (H$_2$O).

**Synthesis of Polyoxometalate Compounds K$_8[\beta_2$-SiW$_{11}$O$_{39}]$·nH$_2$O and Its Characterization**

The 11 g (50 mmol) Na$_2$SiO$_3$ compound was dissolved in aquades (100 mL) and 4M HCl depleted slowly to a pH range of 5-6 and stirred. The solvent was mixed with Na$_2$WO$_4$ of 182 g (0.55 mmol) which was dissolved with aquades (100 mL). The mixture was added with KCl of 80 g. With the addition of the mixture to be white and formed of sediment. After that, the mixture was filtered using filter paper, then the solid was dried by vacuum. The compounds K$_8[\beta_2$-SiW$_{11}$O$_{39}]$·nH$_2$O/SiO$_2$ was heated at 200 ° C, 300 ° C, 400 ° C and 500 ° C for 2 hours in the furnace. The heating compound was cooled and characterized by an FTIR spectrophotometer.

**RESULTS AND DISCUSSION**

**Synthesis and Characterization of Keggin type Polyoxometalate Compounds K$_8[\beta_2$-SiW$_{11}$O$_{39}]$·nH$_2$O**

The synthesis of compound K$_8[\beta_2$-SiW$_{11}$O$_{39}]$·nH$_2$O was performed by addition of potassium chloride (KCl) to the compound [B$_2$SiW$_{11}$O$_{39}]$·nH$_2$O acting as a K$^+$ ion donator. At the end of the synthesis process there was obtained a white solid which was a compound K$_8[\beta_2$-SiW$_{11}$O$_{39}]$·nH$_2$O. The result of synthesis in the form of white solid was then characterized using FT-IR spectrophotometer which aims to identify the functional group formed as shown in Figure 1.
vibration of W-O-W group 878 cm$^{-1}$, and vibration of W-O-W 779 cm$^{-1}$. The compound K$_2$[β$_2$-SiW$_{11}$O$_{39}$]∙nH$_2$O synthesis results in this study is in accordance with vibrations according to Okuhara (et al 2001). In addition to the 3425.58 cm$^{-1}$ wave numbers indicating the vibration -OH which indicates the presence of H$_2$O in the polyoxometalate compound K$_2$[β$_2$-SiW$_{11}$O$_{39}$]∙nH$_2$O. The presence of a hydrogen bonding effect is characterized by a widened peak in the FT-IR spectrum of Stuart (2004). K$_2$[β$_2$-SiW$_{11}$O$_{39}$]∙nH$_2$O.

After the compound K$_2$[β$_2$-SiW$_{11}$O$_{39}$]∙nH$_2$O was characterized using FT-IR spectrophotometer, then the polyoxometalate compound K$_2$[β$_2$-SiW$_{11}$O$_{39}$]∙nH$_2$O was analyzed by XRD. Diffraction of K$_2$[β$_2$-SiW$_{11}$O$_{39}$]∙nH$_2$O polyoxometalate compound - nH$_2$O is presented in Figure 2.

Figure 2. XRD Diffraction Patterns Polyoxometalate Compound K$_2$[β$_2$-SiW$_{11}$O$_{39}$]∙nH$_2$O

Figure 3 shows the difference shown by the FT-IR spectrum of the polyoxometalate compound K$_2$[β$_2$-SiW$_{11}$O$_{39}$]∙nH$_2$O before being carried out with SiO$_2$. According to Derrick (et al 1999) the symmetric vibration of Si-O-Si is at the wave number 1130-1000 cm$^{-1}$. Smith (1999) reported that the vibration of Si-O-Si symmetric stretching was stronger at 1085 cm$^{-1}$. The FTIR spectra of compound K$_2$[β$_2$-SiW$_{11}$O$_{39}$]∙nH$_2$O/SiO$_2$ undergo a shift of wave numbers for asymmetric Si-O-Si stretch vibration at 1103.28 cm$^{-1}$. The shift of wave numbers occurs in vibration W=O. The W=O vib before it is presented appears at the wave number 987.55 cm$^{-1}$ and the vibration after carrying with SiO$_2$ appears at the wave number 956.69 cm$^{-1}$. According to Stuart (2004) vibration -OH vibration in the presence of hydrogen bonding effect is in the range of 3500-2500 cm$^{-1}$ wavelength characterized by a widened peak on the FT-IR spectra. Figure 3 (B) experiences a shift in the number of waves at the peak of 3448.72 cm$^{-1}$ identifies the -OH vibration by the presence of H$_2$O on the K$_2$[β$_2$-SiW$_{11}$O$_{39}$]∙nH$_2$O/SiO$_2$ and the wave number at peak 3425.58 cm$^{-1}$ identifies vibration -OH by the presence of H$_2$O in the compound K$_2$[β$_2$-SiW$_{11}$O$_{39}$]∙nH$_2$O/SiO$_2$. The primary wave numbers of K$_2$[β$_2$-SiW$_{11}$O$_{39}$]∙nH$_2$O and K$_2$[β$_2$-SiW$_{11}$O$_{39}$]∙nH$_2$O/SiO$_2$ are presented in Table 1.

Table 1. Wave number K$_2$[β$_2$-SiW$_{11}$O$_{39}$]∙nH$_2$O and K$_2$[β$_2$-SiW$_{11}$O$_{39}$]∙nH$_2$O/SiO$_2$

| Vibration K$_2$[β$_2$-SiW$_{11}$O$_{39}$]∙nH$_2$O | Vibration K$_2$[β$_2$-SiW$_{11}$O$_{39}$]∙nH$_2$O/SiO$_2$ |
|---------------------------------------------|---------------------------------------------|
| 987.55 cm$^{-1}$ | 956.69 cm$^{-1}$ |
| 864.11 cm$^{-1}$ | 864.11 cm$^{-1}$ |
| 756.1 cm$^{-1}$ | 756.1 cm$^{-1}$ |
| 3425.58 cm$^{-1}$ | 3448.72 cm$^{-1}$ |
| - | 1103.28 cm$^{-1}$ |

The polyoxometalate compound - K$_2$[β$_2$-SiW$_{11}$O$_{39}$]∙nH$_2$O which was supported with SiO$_2$ then characterized using XRD. The diffraction and crystallinity of polyoxometalate compounds K$_2$[β$_2$-SiW$_{11}$O$_{39}$]∙nH$_2$O/SiO$_2$. Comparison of XRD of compound K$_2$[β$_2$-SiW$_{11}$O$_{39}$]∙nH$_2$O with K$_2$[β$_2$-
SiW$_{11}$O$_{39}$$\cdot$nH$_2$O/SiO$_2$ are presented in Figure 4. (A) Ka[β₂-SiW$_{11}$O$_{39}$]$\cdot$nH$_2$O diffraction emerging below 10° in region 2θ indicates that the polyoxometalate compound Ka[β₂-SiW$_{11}$O$_{39}$]$\cdot$nH$_2$O has very high crystalline properties due to the atom of the polyoxometalate compound Ka[β₂-SiW$_{11}$O$_{39}$]$\cdot$nH$_2$O is arranged regularly based on the length and angle of bond formed. Figure 4 (B) shows the XRD pattern of Ka[β₂-SiW$_{11}$O$_{39}$]$\cdot$nH$_2$O/SiO$_2$. The compound Ka[β₂-SiW$_{11}$O$_{39}$]$\cdot$nH$_2$O/SiO$_2$ has a high crystallinity with a diffraction angle of 2θ each at 8°, 18°, 27°, and 34° indicating the characteristics of the polyoxometalate compound Ka[β₂-SiW$_{11}$O$_{39}$]$\cdot$nH$_2$O/SiO$_2$ in which the atoms of the polyoxometalate compound Ka[β₂-SiW$_{11}$O$_{39}$]$\cdot$nH$_2$O/SiO$_2$ were arranged regularly on the basis and length of the regular bonding. Figure 4 (B) shows the pattern of XRD Ka[β₂-SiW$_{11}$O$_{39}$]$\cdot$nH$_2$O/SiO$_2$ indicating a change in the diffraction angle.

The acidity test of compound Ka[β₂-SiW$_{11}$O$_{39}$]$\cdot$nH$_2$O and Ka[β₂-SiW$_{11}$O$_{39}$]$\cdot$nH$_2$O/SiO$_2$ in qualitatively

**The Acidity test of Ka[β₂-SiW$_{11}$O$_{39}$]$\cdot$nH$_2$O**

The acidity measurement of the polyoxometalate compound · Ka[β₂-SiW$_{11}$O$_{39}$]$\cdot$nH$_2$O is carried out both qualitatively and quantitatively. The FT-IR spectrophotometer method was performed for qualitatively, where Ka[β₂-SiW$_{11}$O$_{39}$]$\cdot$nH$_2$O polyoxometalate compound was saturated with ammonia and with pyridine for 2 days resulting in saturation on the surface of Ka[β₂-SiW$_{11}$O$_{39}$]$\cdot$nH$_2$O. The saturation result were compared before or after being saturated with ammonia or pyridine. The saturation result was measured by a FTIR spectrophotometer. The FTIR spectra Ka[β₂-SiW$_{11}$O$_{39}$]$\cdot$nH$_2$O saturation result shown in Figure 5.

Polyoxometalate compound Ka[β₂-SiW$_{11}$O$_{39}$]$\cdot$nH$_2$O of the FT-IR spectra of Figure 5 shows no absorption bands at 1400-1440 cm$^{-1}$ wavelengths on a Ka[β₂-SiW$_{11}$O$_{39}$]$\cdot$nH$_2$O polyoxometalate compound with or without saturation Pyridine. According to Dines (et al, 1991) ammonia forms ammonium ions (NH$_4^+$) with the observed wave numbers at 1400-1440 cm$^{-1}$, but in the polyoxometalate compound Ka[β₂-SiW$_{11}$O$_{39}$]$\cdot$nH$_2$O not exhibit ammonium ion vibrations (NH$_4^+$) at wave number 1400-1440 cm$^{-1}$. Ammonia can be adsorbed on the acid side of the heteropoly compound and in the metal cation (Seo et al, 1988). Ammonia was not adsorbed on the polyoxometalate compound Ka[β₂-SiW$_{11}$O$_{39}$]$\cdot$nH$_2$O. It was possible that the polyoxometalate compound Ka[β₂-SiW$_{11}$O$_{39}$]$\cdot$nH$_2$O does not exhibit ammonium ion vibration (NH$_4^+$) at wave numbers 1400-1440 cm$^{-1}$. Figure 5 (B) shows a vibration of -OH at a wave number of 3448.72 cm$^{-1}$ which identifies the presence of H$_2$O in a polyoxometalate compound Ka[β₂-SiW$_{11}$O$_{39}$]$\cdot$nH$_2$O. According to Stuart (2004), vibration -OH vibration, with the effect of hydrogen bonds in the range of 3500-2500 cm$^{-1}$ wavelengths characterized by wider peaks in the FT-IR spectra.

Figure 5. FTIR spectrum of polyoxometalate compound Ka[β₂-SiW$_{11}$O$_{39}$]$\cdot$nH$_2$O (A), FTIR spectra of polyoxometalate compound Ka[β₂-SiW$_{11}$O$_{39}$]$\cdot$nH$_2$O. Saturation with ammonia (B), FT-IR spectra of polyoxometalate compound Ka[β₂-SiW$_{11}$O$_{39}$]$\cdot$nH$_2$O saturation with pyridine (C)

Polyoxometalate compound Ka[β₂-SiW$_{11}$O$_{39}$]$\cdot$nH$_2$O compounds with saturation with pyridine in Figure 5 (C) exhibit an -OH shift vibration appearing at a 3425.58 cm$^{-1}$ wave number identifying H$_2$O in a polyoxometalate compound Ka[β₂-SiW$_{11}$O$_{39}$]$\cdot$nH$_2$O. According to Khalifah and Prasetyo (2008) pyridine molecules bound to Lewis acid sites absorbed at wave numbers 1400-1700 cm$^{-1}$. Figure 5 (C) FT-IR spectra does not show the wave number. In this case, pyridine was unsorbed in the polyoxometalate compound Ka[β₂-SiW$_{11}$O$_{39}$]$\cdot$nH$_2$O. FT-IR digital specimen data of Ka[β₂-SiW$_{11}$O$_{39}$]$\cdot$nH$_2$O compounds with saturation with ammonia and pyridine.

**The Acidity Test of Ka[β₂-SiW$_{11}$O$_{39}$]$\cdot$nH$_2$O/SiO$_2**

The compound Ka[β₂-SiW$_{11}$O$_{39}$]$\cdot$nH$_2$O/SiO$_2$ was saturated using ammonia and pyridine. Then the material was characterized by an FT-IR spectrophotometer. The saturation result was measured by an FTIR. The FT-IR spectra of Ka[β₂-SiW$_{11}$O$_{39}$]$\cdot$nH$_2$O/SiO$_2$ of the saturation results are shown in Figure 6.

Figure 6 (A) shows the FTIR spectra of a polyoxometalate compound Ka[β₂-SiW$_{11}$O$_{39}$]$\cdot$nH$_2$O/SiO$_2$ before being saturated. Figure 6 (B) shows the FTIR spectra of a polyoxometalate compound Ka[β₂-SiW$_{11}$O$_{39}$]$\cdot$nH$_2$O/SiO$_2$ with saturation using
ammonia. Dennis (et al 1991) states that ammonia forms an ammonium ion (NH₄⁺) 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 and in the metal cation. The compound K₈[β₂-SiW₁₁O₃₉]·nH₂O/SiO₂ exhibits the vibration of the NH₄⁺ ammonium ion appearing at the wave number 1404.18 cm⁻¹.

Figure 6. FTIR spectra of polyoxometalate compounds K₈[β₂-SiW₁₁O₃₉]·nH₂O/SiO₂ (A), FT-IR spectra of polyoxometalate compounds K₈[β₂-SiW₁₁O₃₉]·nH₂O/SiO₂. Saturation with ammonia (B), FT-IR spectra of polyhydroxide compound K₈[β₂-SiW₁₁O₃₉]·nH₂O/SiO₂ saturation with pyridine (C).

Polyoxometalate compounds K₈[β₂-SiW₁₁O₃₉]·nH₂O/SiO₂ saturated with ammonia absorbance bands not found at wavelength 1400-1440 cm⁻¹. In this case it is possible that the ammonia was not adsorbed on the polyoxometalate compound K₈[β₂-SiW₁₁O₃₉]·nH₂O/SiO₂. Stuart (2004) states that vibration -OH vibration in the presence of hydrogen bonding effect is in the range of 3500-2500 cm⁻¹ wavelengths characterized by a widened peak on the FTIR spectra. Polyoxometalate compounds K₈[β₂-SiW₁₁O₃₉]·nH₂O/SiO₂ exhibit a -OH loop vibration at 3425.58 cm⁻¹ wave numbers identifying the presence of H₂O in the polyoxometalate compound K₈[β₂-SiW₁₁O₃₉]·nH₂O/SiO₂.

Figure 6 (C) shows the spectra of K₈[β₂-SiW₁₁O₃₉]·nH₂O/SiO₂ compounds with saturation using ammonia also exhibiting a -OH looping vibration at a 3425.58 cm⁻¹ wave number that identifies the presence of H₂O in the polyoxometalate compound K₈[β₂-SiW₁₁O₃₉]·nH₂O/SiO₂. The Caliph and Prasetyoko (2008) explain that pyridine molecules bound to Lewis acid sites are absorbed at wave numbers 1400-1700 cm⁻¹. Picture no. 10 (C) shows that the pyridine molecule has been adsorbed by the polyoxometalate compound K₈[β₂-SiW₁₁O₃₉]·nH₂O/SiO₂ has Lewis acid character.

Based on the FTIR spectrum of Figure 5 and 6, it can be seen that the wave number 1404.18 cm⁻¹ is a vibration of the ammonium ion NH₄⁺. The compound K₈[β₂-SiW₁₁O₃₉]·nH₂O/SiO₂ saturated with ammonia (Figure 6 B) does not show the uptake of ammonia molecules at the 1404.18 cm⁻¹ wave number as well as the compound K₈[β₂-SiW₁₁O₃₉]·nH₂O (Figure 5 B). In this case the ammonia is not adsorbed on the compound K₈[β₂-SiW₁₁O₃₉]·nH₂O and the compound K₈[β₂-SiW₁₁O₃₉]·nH₂O/SiO₂. The FT-IR spectra at Figure 5 (C) does not show the uptake of pyridine molecules at the 1404.18 cm⁻¹ wave number while the FT-IR spectra of Figure 6 (C) of K₈[β₂-SiW₁₁O₃₉]·nH₂O/SiO₂ see the wave number 1481.33 cm⁻¹ but does not show sharp spectra. It can be concluded that qualitatively pyridine adsorbed more on the polyoxometalate compound K₈[β₂-SiW₁₁O₃₉]·nH₂O/SiO₂.

The acidity test of compound K₈[β₂-SiW₁₁O₃₉]·nH₂O and K₈[β₂-SiW₁₁O₃₉]·nH₂O/SiO₂ in Quantitative

The acidity measurements of the K₈[β₂-SiW₁₁O₃₉]·nH₂O and K₈[β₂-SiW₁₁O₃₉]·nH₂O/SiO₂ compounds were quantitatively measured by titration of potentiometric potassium using n-butylamine as titrant and acetonitrile as solvent. Acetonitrile is an aprotic solvent as a solvent on the compound K₈[β₂-SiW₁₁O₃₉]·nH₂O and K₈[β₂-SiW₁₁O₃₉]·nH₂O/SiO₂ so that only the acidity of K₈[β₂-SiW₁₁O₃₉]·nH₂O and K₈[β₂-SiW₁₁O₃₉]·nH₂O/SiO₂. According to Pecchi (et al 1985) using benzene solvent, acetonitrile and iso-octane as solvents in potentiometric titration and selected acetonitrile as a polar solvent to avoid the adsorption of n-butylamine and acetonitrile as an inert solvent.

The measurement by potentiometric method can determine the total acidity and acidity strengths of a polyoxometalate compound. The initial potential value (Eᵢ) identifies acidity strength from the surface side and classifies the acidity strength based on the range that classifies in scale: Eᵢ > 100 mV (acidity is very strong), 0 < Eᵢ < 100 mV (strong acidity), -100 < Eᵢ < 0 mV (weak acidity), Eᵢ < -100 mV (acidity is very weak) (Romanelli et al, 2004). The first derivative curve and the second derivative are made to be able to see where the titration equivalent point is shown in Figure. 11 The equivalent point was performed to see the condition in which the base of n-butylamine is added precisely reacts with the acidic K₈[β₂-SiW₁₁O₃₉]·nH₂O nH₂O which was titrated. In addition, an equivalence point is performed to determine the amount of base volume of n-butylamine required to neutralize K₈[β₂-SiW₁₁O₃₉]·nH₂O/SiO₂ acid.

Figure 7 shows the results of measurement of the compound K₈[β₂-SiW₁₁O₃₉]·nH₂O has an initial potential value of 54.4 mV. Based on the potential value range of 0 < Eᵢ < 100 the polyoxometalate compound K₈[β₂-SiW₁₁O₃₉]·nH₂O has a strong acid side. The titration equivalent point is at 0.2 mL of n-butylamine volume reinforced by the first derivative curve and the second derivative of potentiometric titration. The titration equivalent point can be observed with sharp potential changes (Mulja and Suharman, 1995). Figure 8 and 9 show the first derivative curves and the second derivative curves of the polyoxometalate compound K₈[β₂-SiW₁₁O₃₉]·nH₂O.

The measurement of the acidity level of the polyoxometalate compound K₈[β₂-SiW₁₁O₃₉]·nH₂O/SiO₂ is also carried out through potentiometric titration. From the titration curve presented in Figure 10, the titration equivalent point was obtained at the time of titration volume of 0.4 mL n-butylamin. Based on the data of the equivalence point it is found that the
polyoxometalate \( \text{K}_8[\beta_2-\text{SiW}_{11}O_{39}]\cdot n\text{H}_2\text{O}/\text{SiO}_2 \) compound requires more base volume of n-butylamine to neutralize the polyoxometalate compound \( \text{K}_8[\beta_2-\text{SiW}_{11}O_{39}]\cdot n\text{H}_2\text{O}/\text{SiO}_2 \). This indicates that \( \text{K}_8[\beta_2-\text{SiW}_{11}O_{39}]\cdot n\text{H}_2\text{O}/\text{SiO}_2 \) is more acidic than a polyoxometalate compound \( \text{K}_8[\beta_2-\text{SiW}_{11}O_{39}]\cdot n\text{H}_2\text{O} \). This is also supported by looking at the potential initial value comparison. The initial potential value of \( \text{K}_8[\beta_2-\text{SiW}_{11}O_{39}]\cdot n\text{H}_2\text{O}/\text{SiO}_2 \) ions is 76.6 mV whereas the initial potential value of \( \text{K}_8[\beta_2-\text{SiW}_{11}O_{39}]\cdot n\text{H}_2\text{O} \) compounds is 54.4 mV. The compound \( \text{K}_8[\beta_2-\text{SiW}_{11}O_{39}]\cdot n\text{H}_2\text{O}/\text{SiO}_2 \) is included in the acidic acid classification strong based on the potential value range of acid strength.

Increased density of polyoxometalate compounds \( \text{K}_8[\beta_2-\text{SiW}_{11}O_{39}]\cdot n\text{H}_2\text{O}/\text{SiO}_2 \) because the compound \( \text{K}_8[\beta_2-\text{SiW}_{11}O_{39}]\cdot n\text{H}_2\text{O} \) interacts with the carrier \( \text{SiO}_2 \).

**Figure 7.** Potentiometric titration curve of compound \( \text{K}_8[\beta_2-\text{SiW}_{11}O_{39}]\cdot n\text{H}_2\text{O} \)

**Figure 8.** The first titular titration curve of potentiometric titration of compound \( \text{K}_8[\beta_2-\text{SiW}_{11}O_{39}]\cdot n\text{H}_2\text{O} \)

**Figure 9.** The second titular titration curve of potentiometric titration of compound \( \text{K}_8[\beta_2-\text{SiW}_{11}O_{39}]\cdot n\text{H}_2\text{O} \)

**Figure 10.** Potentiometric potentiometric curve of compound \( \text{K}_8[\beta_2-\text{SiW}_{11}O_{39}]\cdot n\text{H}_2\text{O}/\text{SiO}_2 \)

**Figure 11.** The first derivative titration curve, potentiometric titration of compound \( \text{K}_8[\beta_2-\text{SiW}_{11}O_{39}]\cdot n\text{H}_2\text{O}/\text{SiO}_2 \)

**Figure 12.** The second derivative titration curve, potentiometric titration of compound \( \text{K}_8[\beta_2-\text{SiW}_{11}O_{39}]\cdot n\text{H}_2\text{O}/\text{SiO}_2 \)

Potentiometric titration method is an analytical technique based on the potential measurement of a sensor or electrode. The electrodes used are glass-containing glassed 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 only to \( \text{H}^+ \) ions. Potential measurements of polyoxometalate compound \( \text{K}_8[\beta_2-\text{SiW}_{11}O_{39}]\cdot n\text{H}_2\text{O}/\text{SiO}_2 \) can be performed with potentiometric titration because the compound \( \text{K}_8[\beta_2-\text{SiW}_{11}O_{39}]\cdot n\text{H}_2\text{O}/\text{SiO}_2 \) has \( \text{H}^+ \) ions. Potentiometric titration curve of \( \text{K}_8[\beta_2-\text{SiW}_{11}O_{39}]\cdot n\text{H}_2\text{O}/\text{SiO}_2 \) can be seen in Figure 10.

**The thermal Stability Compound of \( \text{K}_8[\beta_2-\text{SiW}_{11}O_{39}]\cdot n\text{H}_2\text{O}/\text{SiO}_2 \)**

The compound \( \text{K}_8[\beta_2-\text{SiW}_{11}O_{39}]\cdot n\text{H}_2\text{O}/\text{SiO}_2 \) of results the preparation was heated at various temperatures to see the thermal stability of \( \text{K}_8[\beta_2-\text{SiW}_{11}O_{39}]\cdot n\text{H}_2\text{O}/\text{SiO}_2 \). The heating results at various temperatures were characterized by FTIR.
Table 2 shows the vibrations of the IR spectra of W-O cm⁻¹ and -1 cm⁻¹. Figure 13 (A) and (B) show the wave numbers 3425.58 cm⁻¹ and 3448.72 cm⁻¹, respectively. Figure 13 (C), (D), (E) and (F) indicate wave numbers 3433.29 cm⁻¹, 3441.01 cm⁻¹, 3425.58 cm⁻¹, and 3402.43 cm⁻¹, respectively. These wave numbers are identified as OH groups in the presence of H₂O with a slight amount seen from percent transmittance. Figure 13 (F) shows excellent thermal stability properties in the presence of small amount of H₂O which was characterized by a shift in the wavelength number of the OH group. The vibration of polyoxometalate compound K₈[β₂-SiW₁₁O₃₉]-nH₂O/SiO₂ in the 800-1000 cm⁻¹ wave range at 500°C shows slight differences due to vibration W=O overlapping with vibrations W-O-W and W-O-H. This suggests that on increasing the heating temperature may cause changes in the structure of polyoxometalate compounds. Table 2 shows the vibrations of the K₈[β₂-SiW₁₁O₃₉]-nH₂O, K₈[β₂-SiW₁₁O₃₉]-nH₂O/SiO₂ without heating and after heating at a temperature of 200°C - 500°C.

Table 2. Wave number of compound K₈[β₂-SiW₁₁O₃₉]-nH₂O, K₈[β₂-SiW₁₁O₃₉]-nH₂O/SiO₂ without heating and heating at a temperature of 200°C-500°C.

| Wave number | 200°C | 300°C | 400°C | 500°C |
|-------------|-------|-------|-------|-------|
| C           | C     | C     | C     | C     |
| 987.55      | 987   | 987.69| 979   | W     |
| 864.11      | 864.11| 887   | 887   | 5     | 8     | W=O   |
| 756.1       | 2     | 2     | 864   | 858   | W     | W     |
| 3425.5      | 3448.72| 794   | 740   | 1     | 3     | O₈-W |
| 8           | 6     | 6     | 732   | 748   | WW-W  |
| 3433        | 3441  | 9     | 3     | O₈-W  | .2    | .0    | 3425  | 3402  |
| SiO₂        |       |       |       |       |       | Si-O- | A     | H     |

CONCLUSION

Polyoxometalate compounds K₈[β₂-SiW₁₁O₃₉]-nH₂O and K₈[β₂-SiW₁₁O₃₉]-nH₂O/SiO₂ were synthesized. The main vibration of the IR spectra of K₈[β₂-SiW₁₁O₃₉]-nH₂O/SiO₂ shows the presence of vibration W=O appearing in the area of 987.55 cm⁻¹. W-O-W appears in the area of 864.11 cm⁻¹, W-O-H appears in the area of 756.1 cm⁻¹, O-H, OH appears in the area of 3425.58 cm⁻¹ and for the compound K₈[β₂-SiW₁₁O₃₉]-nH₂O/SiO₂ vibration W=O appears in the region 956.69 cm⁻¹. W-O-H appears at 864.11 cm⁻¹ and OH area appears at 3448.72 cm⁻¹. The XRD diffraction pattern for K₈[β₂-SiW₁₁O₃₉]-nH₂O/SiO₂ differs at the diffraction angles of 8°, 9°, 17°, 24°, 35° and for the compound K₈[β₂-SiW₁₁O₃₉]-nH₂O/SiO₂ appears at the angle of diffraction of 2θ each of 8°, 18°, 27°, and 34°. Polyoxometalate compound K₈[β₂-SiW₁₁O₃₉]-nH₂O/SiO₂ with a potential value of 76.6 mV has a higher acidity value than the compound K₈[β₂-SiW₁₁O₃₉]-nH₂O having a potential value of 54.3 mV. Qualitative analysis by using ammonia and pyridine to compound K₈[β₂-SiW₁₁O₃₉]-nH₂O and K₈[β₂-SiW₁₁O₃₉]-nH₂O/SiO₂ it was found that the pyridine compound adsorbed more on the polyoxometalate compound K₈[β₂-SiW₁₁O₃₉]-nH₂O/SiO₂. The thermal stability test of the compound K₈[β₂-SiW₁₁O₃₉]-nH₂O/SiO₂ shows at a temperature of 500°C of K₈[β₂-SiW₁₁O₃₉]-nH₂O/SiO₂ compound slightly altered the structure of the polyoxometalate compound characterized by overlapping of vibrations in the range of 800-1000 cm⁻¹.

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