

THERMAL STABILITY EFFECT OF $H_4[PVMo_{11}O_{40}]/SiO_2$ Leni Sinaga^{1*}, Aldes Lesbani¹¹Department of Chemistry, Faculty of Mathematics and Natural Science, Srinijaya University*Corresponding Author Email: Leni.sinaga@gmail.com

ABSTRACT

Synthesis and characterization of supported polyoxometalate $H_4[PVMo_{11}O_{40}].nH_2O$ with SiO_2 through sol-gel method have been done. The compound $H_4[PVMo_{11}O_{40}]/SiO_2$ was characterized through FT-IR spectrophotometer, XRD, and SEM-EDX. The results showed that FT-IR spectrum of $H_4[PVMo_{11}O_{40}]/SiO_2$ has the primary vibration on wavenumber at 1064.7 cm^{-1} (P-O); 964.4 cm^{-1} (Mo=O); 864.1 cm^{-1} (Mo-O_c-Mo); 779.2 cm^{-1} (Mo-O_c-Mo); 462.9 cm^{-1} (Si-O); and 1087.9 cm^{-1} (Si-O-Si). The XRD diffraction pattern showed that $H_4[PVMo_{11}O_{40}].nH_2O$ has the highest crystallinity. However, after it's supported with SiO_2 , the properties of crystallinity has decreased due to the excess water during the support process. The result of SEM-EDX showed that $H_4[PVMo_{11}O_{40}]/SiO_2$ material has homogeneous distribution with particle size distribution of 1330 nm (1,33 μm). The acidity test by qualitative and quantitative methods show that $H_4[PVMo_{11}O_{40}]/SiO_2$ more acidic than $H_4[PVMo_{11}O_{40}].H_2O$. The effect temperature on the crystallinity showed that increasing calcination temperature made the crystallinity properties of $H_4[PVMo_{11}O_{40}]/SiO_2$ increased.

Keywords: polyoxometalate, $H_4[PVMo_{11}O_{40}].nH_2O$, SiO_2 .

INTRODUCTION

Polyoxometalates are metal-oxygen cluster compounds which has variation of structures, high Bronsted acidity, and high solubility depending on counter ions. Several structures of polyoxometalates are identified such as Keggin type, Dawson type, Anderson type, Lacunary type, and others. Among these structures, Keggin type has been applied into various applications especially in catalytic transformation of functional organic groups. The research about polyoxometalates is emphasized especially for catalytic reaction both in homogeneous and heterogeneous systems. In heterogeneous system, polyoxometalate as catalyst can be used several times in catalytic process.

The development of polyoxometalates as catalyst recently is still developed in order to increase the acidity of these compounds. Various methods have been used for these aim such as modification structures and supported using other compounds. Supported polyoxometalate with various compounds can be conducted using complex and coordination compounds, metal ions, and metal oxides. Metal oxides are frequently used as polyoxometalate support such as titanium oxide, silica oxide, zirconia oxide, zinc oxide, and alumina oxide. Polyoxometalate supported silica oxide was applied as catalyst for hydration of propene.

High temperature stability of polyoxometalates is also one of the interesting aspects to develop the properties of polyoxometalate and polyoxometalate supported metal oxides. Many chemical reactions are carried out at high temperature to obtain high conversion and selectivity. Polyoxometalate $H_3[PW_{12}O_{40}]$ for example has been applied for dehydrogenation of ethylene to obtain 74% conversion at 510 °C. Thus in this

research, thermal stability of polyoxometalate supported metal ion was reported.

Polyoxometalate $H_4[PVMo_{11}O_{40}].nH_2O$ has been synthesized and supported with silica oxide hydrolysis of tetra ethyl ortho silicate (TEOS). Hydrolysis of TEOS in liquid phase can create facile diffusion to polyoxometalate compound. Another research using metal oxide of silica resulted polyoxometalate supported silica with higher morphology size. By using TEOS as a source of metal oxide, the morphology size of polyoxometalate supported metal oxide can be smaller than the use of metal oxide directly. The polyoxometalate $H_4[PVMo_{11}O_{40}].nH_2O$ supported silica oxide from TEOS was characterized using FTIR spectrophotometer, X-Ray analysis, and SEM for morphology analysis. Furthermore, polyoxometalate supported silica oxide was tested at various temperatures in order to know the thermal stability of this compound.

EXPERIMENTAL SECTION

Chemical was used in this research is directly used after purchased from Merck and Sigma-Aldrich such as disodium hydrogen phosphate, sodium metavanadate, sodium molybdate, sodium bis(2-ethylhexyl succosuccinate), ammonia, cyclohexane, diethyl ether, n-butyl amine, and acetonitrile.

Characterization was conducted using Shimadzu FTIR Pesticide-21 spectrophotometer using KBR disc, X-Ray Shimadzu Lab X type-6000 with scanning 1 deg.min⁻¹, and titration analysis for acidity. Acidity was tested both quantitative using titration and qualitative using ex-situ analysis and ammonia as probe molecule.

Synthesis of $H_4[PVMo_{11}O_{40}].nH_2O$

Sodium hydrogen phosphate (7.1 g) was dissolve with 100 mL water. The solution was mixed with solution of sodium metavanadate (6.1 g in 100 mL hot water). The solution was stirred and kept at room temperature. The solution was added

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slowly with 5 mL of sulfuric acid to form red solution. Into the red solution, 133 g of sodium molybdate (in 200 mL water) was added with slow stirring. Furthermore, 85 mL of sulfuric acid was added and the color of solution to be red light. The red light solution was extracted with diethyl ether and polyoxometalate fraction was collected by vacuum to obtain orange crystal, which was purified with water several times. Characterization was conducted using FTIR, X-Ray and SEM analyses.

Synthesis of $H_4[PVMo_{11}O_{40}].nH_2O/SiO_2$

Compound $H_4[PVMo_{11}O_{40}].nH_2O/SiO_2$ was synthesized as follow: 1.5 g sodium bis(2-ethylhexyl succosuccinate) was dissolved with 1 mL cyclohexane (solution A). Polyoxometalate $H_4[PVMo_{11}O_{40}].nH_2O$ (0.76 g) was dissolved with water (solution B). Solution B was added into solution A with slow stirring for 30 minutes and 11.2 mL TEOS was added step by step during stirring process. The stirring process was continued for 2 hours at 60 °C to form yellow solid bulky material. The solid material was dried overnight under vacuum and characterized using FTIR, X-ray analysis, SEM analysis, and acidity.

RESULTS AND DISCUSSION

Figure 1 shows vibrational peaks of polyoxometalate at wavenumber range 300-4000 cm^{-1} . The main vibration $H_4[PVMo_{11}O_{40}].nH_2O$ was appeared at 1067.7 cm^{-1} ($\nu P-O$), 964.4 cm^{-1} ($\nu Mo=O$), 864.1 cm^{-1} ($\nu Mo-Oe-Mo$) and 779.2 cm^{-1} ($\nu Mo-Oc-Mo$). These vibrations are well known for polyoxometalate $H_4[PVMo_{11}O_{40}].nH_2O$. In that spectrum, another vibration is found due to water vibration. Vibration of O-H is appeared at wavenumber 3410 cm^{-1} . Although FTIR spectrum of $H_4[PVMo_{11}O_{40}].nH_2O$ is appropriate with standard literature but other characterizations were attempted to clearly identified of polyoxometalate $H_4[PVMo_{11}O_{40}].nH_2O$ using X-Ray analysis and morphology analysis by SEM. X-Ray powder analysis of $H_4[PVMo_{11}O_{40}].nH_2O$ is shown in Figure 2.

FTIR spectrum of $H_4[PVMo_{11}O_{40}].nH_2O$ is shown in Figure 1.

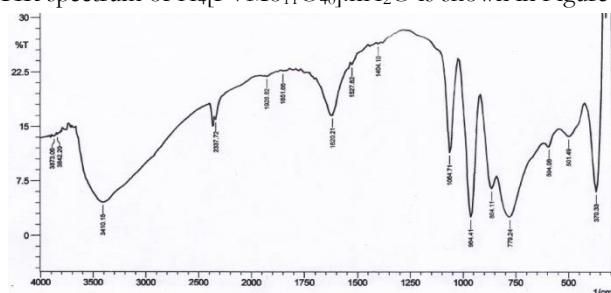


Fig.1. FTIR spectra of $H_4[PVMo_{11}O_{40}].nH_2O$.

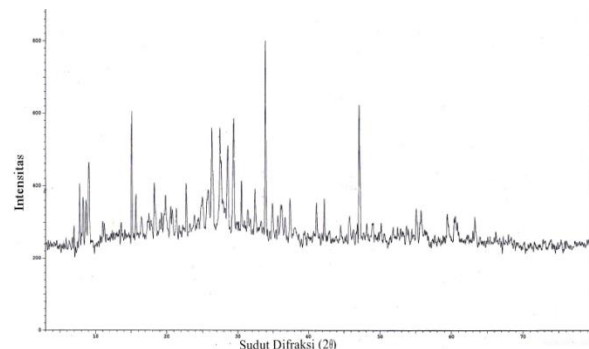


Figure 2. X-Ray powder pattern of $H_4[PVMo_{11}O_{40}].nH_2O$.

Diffraction of $H_4[PVMo_{11}O_{40}].nH_2O$ was appeared mainly at 2θ value 8-10 deg, 21-29 deg, and 33-37 deg. These diffraction pattern is characteristic for crystalline Keggin type polyoxometalate. Compound $H_4[PVMo_{11}O_{40}].nH_2O$ is Keggin type polyoxometalate thus the X-ray pattern is appropriate with standard. From X-ray powder pattern in Fig 2, diffractions at 15 deg, 33.8 deg, and 47 deg have highest diffraction shows high crystallinity of $H_4[PVMo_{11}O_{40}].nH_2O$. Surface morphology analysis is shown in Figure 3.

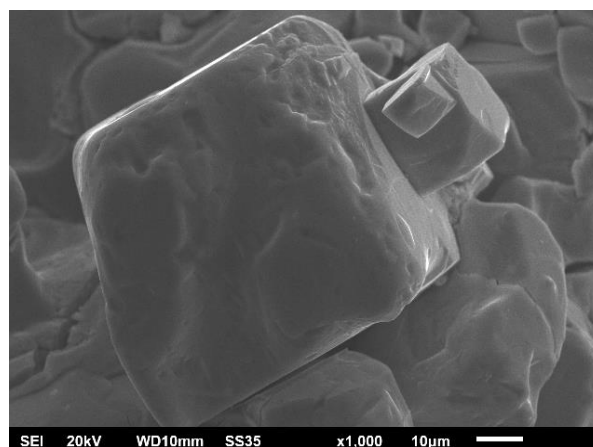


Fig.3 SEM image of $H_4[PVMo_{11}O_{40}].nH_2O$.

Morphology analysis using SEM in Figure 3 showed that $H_4[PVMo_{11}O_{40}].nH_2O$ has large size with ununiformed shape. The calculation of particle size showed that $H_4[PVMo_{11}O_{40}].nH_2O$ has average diameter size 66 μm . These particle size is large and particle size should be reduced by modification using support. The SEM analysis is continued by EDX to identified metal content in the $H_4[PVMo_{11}O_{40}].nH_2O$, as shown Figure 4.

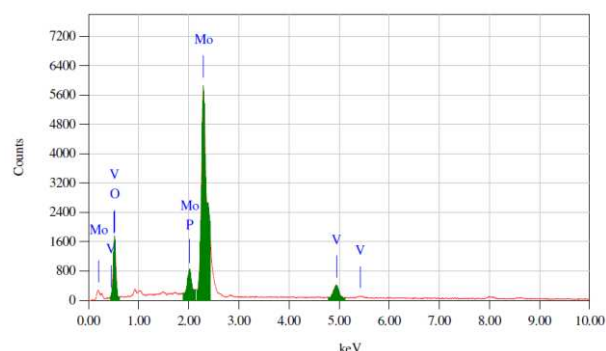
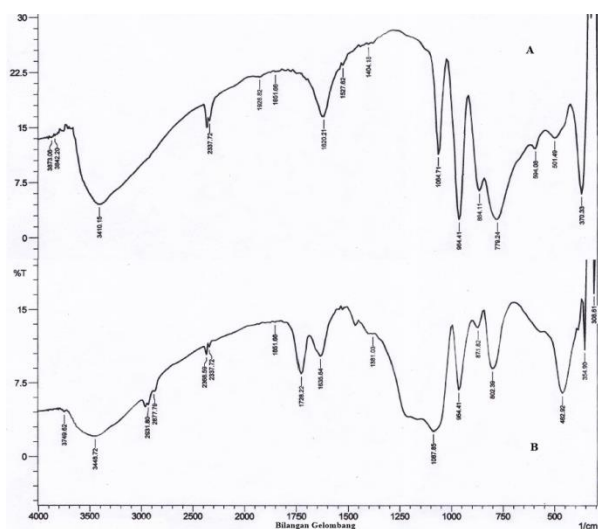
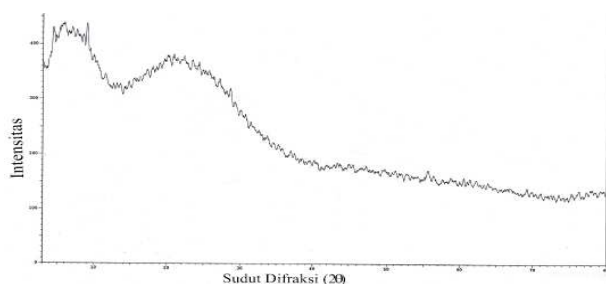


Figure 4. EDX of $H_4[PVMo_{11}O_{40}].nH_2O$.

The main elements in $H_4[PVMo_{11}O_{40}].nH_2O$ was molybdenum, vanadium, and phosphor. Thus polyoxometalate $H_4[PVMo_{11}O_{40}].nH_2O$ was successfully synthesized. Polyoxometalate $H_4[PVMo_{11}O_{40}].nH_2O$ supported SiO_2 was also characterized using FTIR, X-Ray, and SEM analyses. FTIR spectrum of $H_4[PVMo_{11}O_{40}].nH_2O$ and $H_4[PVMo_{11}O_{40}]/SiO_2$ is presented in Figure 5.

A largely different was found in the FTIR spectrum before and after supporting with SiO_2 in the wavenumber 1000-1300 cm^{-1} , which was attributed from silica. Vibration at wavenumber 1087.9 cm^{-1} is assigned as asymmetric stretching of Si-O-Si. This results indicated that polyoxometalate supported silica was probably completed but to know the full information then X-Ray and SEM analyses was conducted. XRD powder pattern of $H_4[PVMo_{11}O_{40}]/SiO_2$ is shown in Figure 6.

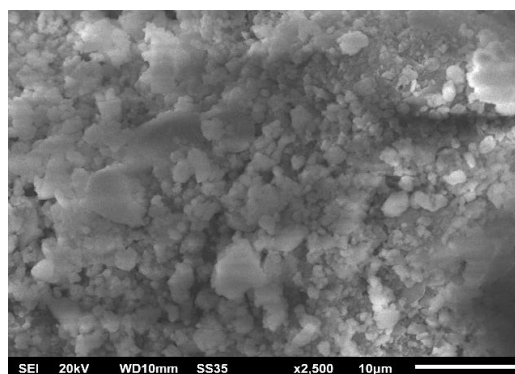
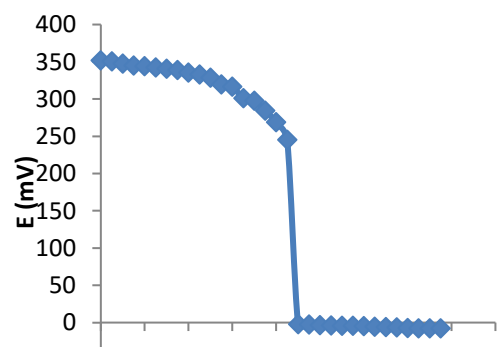
Figure 5. FTIR spectrum of $H_4[PVMo_{11}O_{40}].nH_2O$ (A) and $H_4[PVMo_{11}O_{40}]/SiO_2$ (B).Figure 6. XRD powder pattern of $H_4[PVMo_{11}O_{40}]/SiO_2$.

The XRD powder analysis in Figure 6 showed that polyoxometalate supported silica has low crystallinity to be amorphous. Polyoxometalate supported silica probably has high water content resulted materials with slightly amorphous. This pattern is almost different with XRD pattern of $H_4[PVMo_{11}O_{40}].nH_2O$. SEM analysis data of $H_4[PVMo_{11}O_{40}]/SiO_2$ also has different from $H_4[PVMo_{11}O_{40}].nH_2O$. Particle size of H_4

$[PVMo_{11}O_{40}]/SiO_2$ is almost reduced to be 1.33 μm with uniform shape as shown in Figure 7.

The acidity of $H_4[PVMo_{11}O_{40}].nH_2O$ and $H_4[PVMo_{11}O_{40}]/SiO_2$ was conducted using potentiometric titration and the results is shown in Figure 8. Compound $H_4[PVMo_{11}O_{40}].nH_2O$ has potential 351.6 mV and polyoxometalate supported silica $H_4[PVMo_{11}O_{40}]/SiO_2$ has potential 380 mV. Thus polyoxometalate supported silica has higher acidity than $H_4[PVMo_{11}O_{40}].nH_2O$. In order to investigated the properties of $H_4[PVMo_{11}O_{40}]/SiO_2$, thus compound $H_4[PVMo_{11}O_{40}]/SiO_2$ was tested at various high temperature and characterized using X-Ray analysis as shown in Figure 9.

The XRD pattern in Figure 9 showed that compound $H_4[PVMo_{11}O_{40}]/SiO_2$ has high crystallinity at high temperature. By increasing temperature, crystallinity of material slowly increase to be crystalline. Thus water content is vital factor in the polyoxometalate supported metal oxide material.

Figure 7. SEM image of $H_4[PVMo_{11}O_{40}]/SiO_2$.Figure 8. Potentiometric titration of $H_4[PVMo_{11}O_{40}].nH_2O$ (A) and $H_4[PVMo_{11}O_{40}]/SiO_2$ (B).

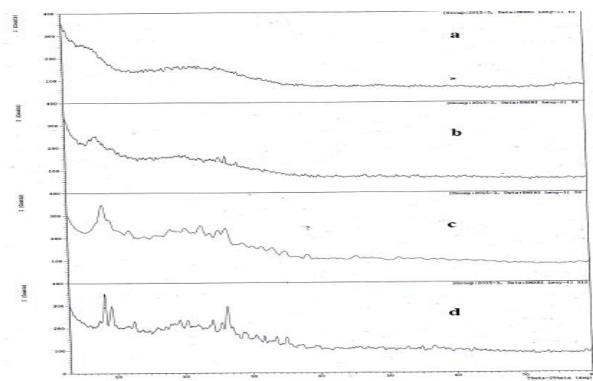


Figure 9. Diffraction patterns of $\text{H}_4[\text{PVMo}_{11}\text{O}_{40}]/\text{SiO}_2$ at various temperatures 300 °C (A), 400 °C (B), 500 °C (C), 600 °C (D).

CONCLUSION

Compound $\text{H}_4[\text{PVMo}_{11}\text{O}_{40}]/\text{SiO}_2$ can be easily synthesized by inorganic synthesis method. This compound has small morphology size and high acidity than starting material. The thermal stability of $\text{H}_4[\text{PVMo}_{11}\text{O}_{40}]/\text{SiO}_2$ showed the stability material by increasing temperature due to decreasing water content.

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