

CONVERSION OF CYCLOHEXANE TO CYCLOHEXANOL AND CYCLOHEXANONE USING $H_3[PMo_{12}O_{40}] \cdot nH_2O/ZrOCl_2$ AS CATALYST

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ABSTRACT

Synthesis and preparation polyoxometalate compound $H_3[PMo_{12}O_{40}] \cdot nH_2O$ supported with $ZrOCl_2$ at various weights of $ZrOCl_2$ i.e. 0.25 g, 0.50 g, 0.75 g, 1.00 g, 1.25 g, 0.01 g and 0.05 g to form $H_3[PMo_{12}O_{40}] \cdot nH_2O/ZrOCl_2$ have been conducted. These compound than was characterized through functional group analysis using FT-IR spectrophotometer and XRD analysis. The results showed that the optimal preparation was $H_3[PMo_{12}O_{40}] \cdot nH_2O/ZrOCl_2$ with support 0.05 g. FT-IR spectrum of $H_3[PMo_{12}O_{40}] \cdot nH_2O/ZrOCl_2$ show wavenumber at 1033.85 cm^{-1} for vibration P-O, 887.26 cm^{-1} for vibration M=O, 840.96 cm^{-1} and 655.80 cm^{-1} for vibration Mo-O-Mo. The existence of support was identified at wavenumber 1404.18 cm^{-1} for vibration Zr-OH and 478.35 for vibration Zr-O-Zr. XRD powder analysis showed that material $H_3[PMo_{12}O_{40}] \cdot nH_2O/ZrOCl_2$ was amorphous material. Material $H_3[PMo_{12}O_{40}] \cdot nH_2O/ZrOCl_2$ was applied in oxidation of cyclohexane using hydrogen peroxide as oxidant. Oxidation process was optimized through reaction time H_2O_2 amount, temperature and catalyst weight. The results showed that the highest conversion in the using of $H_3[PMo_{12}O_{40}] \cdot nH_2O/ZrOCl_2$ catalyst found at 2 hours reaction time, 3 mL H_2O_2 , 80°C temperature and 0.038 g catalyst with conversion 99.18 %. Selectivity of best reaction was 6.96 % for cyclohexanol and 24.9% for cyclohexanone, which was identified by GC-MS.

Keywords: $H_3[PMo_{12}O_{40}] \cdot nH_2O-ZrO_2$, cyclohexane, cyclohexanol, cyclohexanone.

INTRODUCTION

Synthesis of chemical compounds to obtain novel compounds or unique properties has been developed until this decade. Synthesis and transformation of compounds have been conducted using conventional organic synthesis through several step reactions or using catalyst for simple way (Albero and García, 2016). The advantages of catalysts are to decrease the activation energy and to increase the reaction rate of transformation reactions (Hattori, 2015). Catalysts can be supplied from commercial or can be synthesized in laboratory. The development of catalysts is also increase sharply at this time in order to supply for industrial process. Commercial catalysts are not enough to supply for industrial process and sometime reaction is not selective and not appropriate for many organic reaction transformations. In General, catalyst can be divided into two type i.e. for acid base reactions and for oxidation reduction reactions (Busca, 2014 ; Maruyama and Shinagawa, 2016). Both reactions can be carried out in homogeneous or heterogeneous systems. The heterogeneous catalysts are increase sharply at this time due to reusability of that catalyst, thus can decrease the cost process (Lee et.al, 2015).

Polyoxometalates are metal oxygen clusters which have acid base and oxidation reduction properties (Uchida et.al, 2007). Polyoxometalates are also intensively used as catalysts in industrial process for organic reaction and transformation (Uchida et.al, 2012). The development of polyoxometalates is intriguing due to dual properties of these compound as acid base and redox properties.

The development of polyoxometalate for catalysis of organic reaction has been conducted such as grafting (Yang et.al, 2016), impregnation (Farsani and Yadollahi, 2014), intercalation or pillarization agent (Imron and Said, 2017), or exchange heteroatom-addenda atoms (Putaj and Lafebvre, 2011). The final goal of this modification is to obtain polyoxometalate with high acidity and redox properties for organic transformation reactions. One of the interesting reaction using polyoxometalate is conversion of cyclohexane to cyclohexanol and cyclohexanone (Alshaheri et.al, 2017). Cyclohexanol and cyclohexanone is important starting material for nylon-6 and nylon -6,6 (Lesbani et.al, 2016; Gopi et.al, 2017). Thus research of conversion of cyclohexanone is vital.

Conversion of cyclohexane using polyoxometalates as catalyst has been conducted using Keggin type (Kholdeeva et.al, 2005), support polyoxometalate (Jatupisarnpong and Trakarnpruk, 2012), or metal oxide (Wu et.al, 2016) In this research, polyoxometalate $H_3[PMo_{12}O_{40}] \cdot nH_2O$ has been supported with $ZrOCl_2$ to form $H_3[PMo_{12}O_{40}] \cdot nH_2O/ZrOCl_2$. Material $H_3[PMo_{12}O_{40}] \cdot nH_2O/ZrOCl_2$ was used as catalyst for oxidation of cyclohexane to cyclohexanol and cyclohexanone. Transformation of cyclohexane to

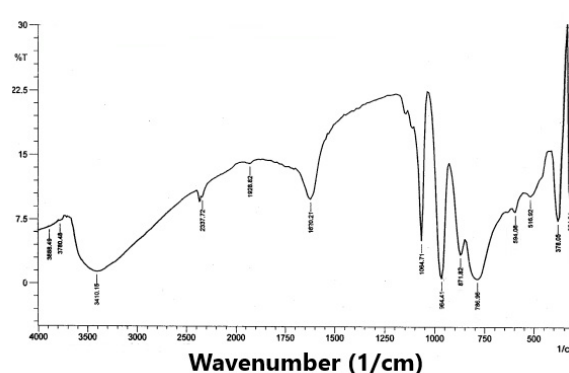


Figure 1. FTIR spectra of $H_3[PMo_{12}O_{40}] \cdot nH_2O$

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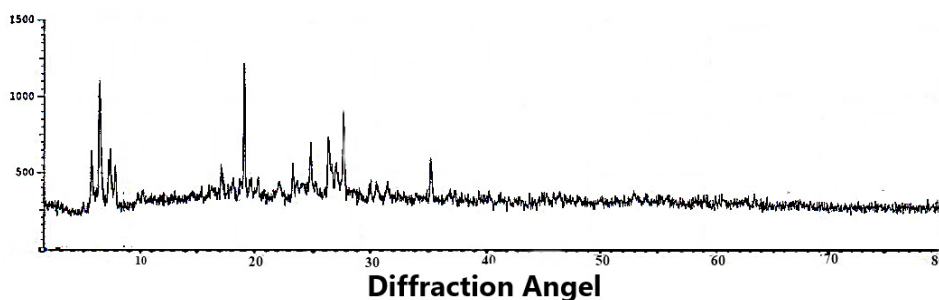
Received: 15 January 2017

Received in revised form: 15 June 2017

Accepted: 17 June 2017

DOI: 10.26554/sti.2017.2.3.59-63

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Figure 2. XRD powder pattern of $H_3[-PMo_{12}O_{40}].nH_2O$

cyclohexanol and cyclohexanone was studied by reaction time, hydrogen peroxide amount, temperature, and catalyst weight.

EXPERIMENTAL SECTION

Chemical and Equipments

Chemicals were supplied from Merck and Sigma Aldrich such as sodium molybdate, hydrochloric acid, diethyl ether, acetone, naphthalene, methanol, ammonia, phosphoric acid, perchloric acid, cyclohexane, and zirconium oxochloride. Water was supplied from Integrated Research Laboratory, Graduate School, Sriwijaya University.

FTIR spectrum were recorded using Shimadzu Prestige-21 FTIR spectrophotometer by KBr method. Spectrum was scanning in the range of wavenumber $300-4000\text{ cm}^{-1}$. XRD powder pattern was obtained from Shimadzu X-Ray Lab X type 6000 diffractometer and sample was scanning at $1^\circ.\text{min}^{-1}$. Monitoring reaction was performed using GC Shimadzu-2010 Plus with combination with GC-MS Agilent-5974 inert.

Synthesis of $H_3[-PMo_{12}O_{40}].nH_2O$

Solution of sodium molybdat 2.85 M (420 mL) was added with 6.8 mL phosphoric acid (85%). The yellow salt of $Na_2H[PMo_{12}O_{40}]$ was formed from warm solution. Dry solid of $Na_2H[PMo_{12}O_{40}]$ (250 g) was dissolved with 200 mL water. The solution was slowly added with 5- mL of hydrochloric acid (36%). The solution was extracted using diethyl ether to form 2 layers. Layer of $H_3[-PMo_{12}O_{40}].nH_2O$ was collected and concentrated using vacuum to produce $H_3[-PMo_{12}O_{40}].nH_2O$. Polyoxometalate $H_3[-PMo_{12}O_{40}].nH_2O$ was characterized using FTIR and XRD powder analyses.

Preparation of $H_3[-PMo_{12}O_{40}].nH_2O/ZrOCl_2$

Preparation of $H_3[PMo_{12}O_{40}].nH_2O/ZrOCl_2$ was conducted according to Devassy et.al (2002) with slightly modification as follow. One gram of polyoxometalate was dissolve with 10 mL methanol (solution A). Solution of zirconia was prepared by dissolved various weights of zirconium oxochloride with 10 mL ammonia (10 M) (solution B). Solution A was mixed with solution B with slowly stirring. Solution was centrifuge at 15000 rpm for 20 minutes to obtain $H_3[PMo_{12}O_{40}].nH_2O/ZrOCl_2$. Material $H_3[PMo_{12}O_{40}].nH_2O/ZrOCl_2$ was washed with acetone and dried at 120°C for overnight. Characterization was conducted using FTIR and XRD analyses.

Catalytic Study of Cyclohexane using $H_3[PMo_{12}O_{40}].nH_2O/ZrOCl_2$ as Catalyst

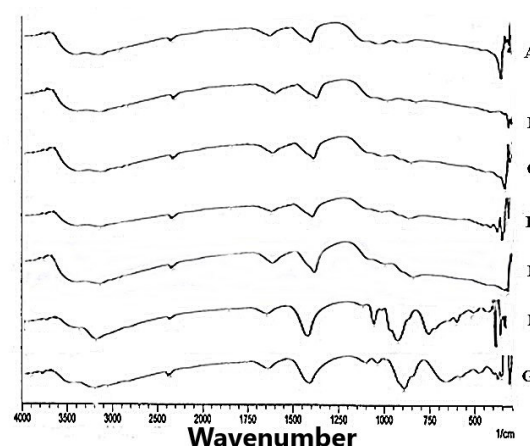
Catalytic study of cyclohexane was adopted from Simões et.al (1999) with slightly modification as follow. Polyoxometalate as catalyst (0.021 mmol) cyclohexane (2 mL), hydrogen peroxide (29.4 mmol) were mixed in Schlenk tube which was equipped with magnetic bar. Naphthalene (12 mg) was added into the solution. The

solution was stirred at various time and reaction was monitored with GC with combination with GC-MS. In order to obtain optimum results, catalytic study conversion of cyclohexane to cyclohexanol and cyclohexanone was conducted using various amount of hydrogen peroxide, various temperature, and various catalyst weights.

RESULTS AND DISCUSSION

FTIR spectra of $H_3[-PMo_{12}O_{40}].nH_2O$ is presented in Figure 1. Polyoxometalate $H_3[-PMo_{12}O_{40}].nH_2O$ is Keggin type and has unique vibration at wavenumber in the range $700-1100\text{ cm}^{-1}$ (Tümer et.al, 2017). Vibration at 1064.7 cm^{-1} is assigned as vibration of P-O, 964.4 cm^{-1} as Mo=O, 871.8 cm^{-1} and 786.9 cm^{-1} as Mo-O-Mo (center and edge). Other vibrations are found at wavenumber 3410.1 cm^{-1} which is attributed from O-H due to water of crystallization in polyoxometalate. Further caharacterization was conducted using XRD as shown in Figure 2.

Figure 2 showed that polyoxometalate $H_3[-PMo_{12}O_{40}].nH_2O$ has diffraction in the range of 2θ at 7-10 deg, 17-20 deg, and 26-30 deg which has characteristic for Keggin type polyoxometalate. The highest intensity was found at 2θ 7-8 deg, 20 deg, and 29 deg. The high intensity of diffraction below 10 deg indicated that polyoxometalate $H_3[-PMo_{12}O_{40}].nH_2O$ has high crystallinity. Thus polyoxometalate $H_3[-PMo_{12}O_{40}].nH_2O$ was supported with zirconium oxochloride with various weight. FTIR spectrum of $H_3[-PMo_{12}O_{40}].nH_2O/ZrOCl_2$ with various weight is shown in Figure 3.

Figure 3. FTIR spectrum of $H_3[-PMo_{12}O_{40}].nH_2O/ZrOCl_2$ with various weight of $ZrOCl_2$; A(0.25 g), B (0.50 g) , C (0.75 g), D (1.0 g), E (1.25 g), F (0.01 g), G (0.05 g)

FTIR spectrum in Figure 3 showed that polyoxometalate $H_3[-PMo_{12}O_{40}].nH_2O$ was appeared at wavenumber in the range $700-1000\text{ cm}^{-1}$ and zirconium as support will appear at wavenumber $400-600\text{ cm}^{-1}$. Figure 3A-E did not show any vibration of polyoxometalate due to overlapping and broad vibration of zirconia as sup-

Table 1. Conversion of cyclohexane using $H_3[-PMo_{12}O_{40}]_n \cdot nH_2O/ZrOCl_2$ as catalyst.

Polyoxometalate (1) : Zirconium (g)	Code	Conversion (%)
0.25	A	50.12
0.50	B	76.13
0.75	C	72.39
1.00	D	41.43
1.25	E	85.70
0.01	F	97.00
0.05	G	99.18
Polyoxometalate only	H	89.21
Zirconium only	I	49.84

port. Figure 3 F-G showed that polyoxometalate $H_3[-PMo_{12}O_{40}]_n \cdot nH_2O$ was appeared in the range 700-1000 cm^{-1} . Vibrations of zirconia as Zr-O and Zr-O-Zr were also appeared and can be distinguished in FTIR spectrum 7F-G. Further characterization was conducted using XRD powder analysis as shown in Figure 4.

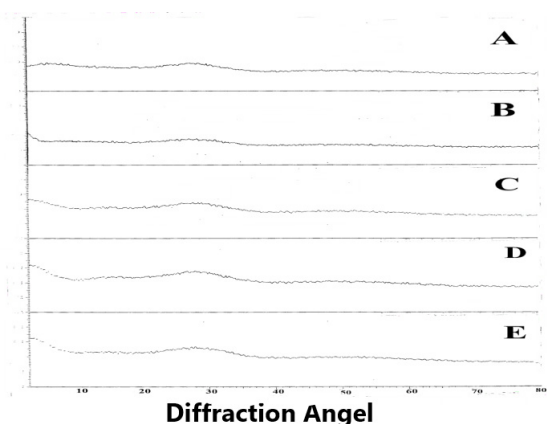


Figure 4. XRD powder patterns of $H_3[-PMo_{12}O_{40}]_n \cdot nH_2O/ZrOCl_2$ with various weight of $ZrOCl_2$; A(0.25 g), B (0.50 g), C (0.75 g), D (1.0 g), E (1.25 g).

Figure 4 showed that material $H_3[-PMo_{12}O_{40}]_n \cdot nH_2O/ZrOCl_2$ has broad patterns. Probably due to water of crystallization can create material with low crystallinity. All various weights of support create material with amorphous properties. Although material $H_3[-PMo_{12}O_{40}]_n \cdot nH_2O/ZrOCl_2$ has amorphous properties but catalytic performance of these material should be investigated deeply. This experiment was convert cyclohexane to cyclohexanol and cyclohexanone using $H_3[-PMo_{12}O_{40}]_n \cdot nH_2O/ZrOCl_2$ as catalyst. The first experiment was screening of catalyst as shown in Table 1.

Table 2. Effect of reaction time for conversion of cyclohexane using $H_3[-PMo_{12}O_{40}]_n \cdot nH_2O/ZrOCl_2$

Reaction time (hour)	Conversion (%)
0.5	35.18
1.0	87.83
1.5	97.28
2.0	99.04
2.5	95.07

Table 1 showed that supporting polyoxometalate can increase conversion of cyclohexane. The use of polyoxometalate without support as catalyst can convert cyclohexane 89.21% and zirconium as catalyst can convert cyclohexane 49.84%. Table 1 also showed

that by decreasing support amount can increase conversion of cyclohexane. Zirconium as support of polyoxometalate can convert cyclohexane up to 18% by using 0.05 g zirconium (code G). Thus catalyst G was used for investigation of catalytic properties of $H_3[-PMo_{12}O_{40}]_n \cdot nH_2O/ZrOCl_2$ for conversion of cyclohexane. The first experiment was conducted by investigation of reaction time. The results are shown in Table 2.

Table 2 shows by increasing reaction time can increase conversion of cyclohexane. The optimum reaction time was 2 hours. Reaction time before 2 hours resulted low to moderate conversion. Reaction at 2.5 hours was inappropriate and decrease the conversion. Probably due to kinetic labile properties of $H_3[-PMo_{12}O_{40}]_n \cdot nH_2O/ZrOCl_2$ than conversion of cyclohexane was decreased. Further was investigation of hydrogen peroxide amount and the results are presented in Table 3.

Table 3. Effect of hydrogen peroxide amount

H_2O_2 (mL)	Conversion (%)
2.0	94.42
2.5	96.86
3.0	99.18
3.5	98.14

Table 3 showed that hydrogen peroxide 3.0 mL was suitable for activation of catalyst. Hydrogen peroxide is green oxidant but low activity. Catalyst is needed to increase activity of hydrogen peroxide as oxidant to supply oxygen atom to the oxidation reaction. Although hydrogen peroxide 3.0 mL is optimal for oxidation of cyclohexane but all results in Table 3 shows high conversion of cyclohexane. Thus the next experiment used 3.0 mL hydrogen peroxide as oxidant.

Table 4. Effect of temperature

Temperature ($^{\circ}C$)	Conversion (%)
60	95.62
70	98.22
80	99.18
85	94.28

Effect of temperature was investigated and the results is presented in Table 4. Table 4 shows temperature 80 $^{\circ}C$ is appropriate for oxidation of cyclohexane and conversion reach 99.18%. Temperature reaction below 80 $^{\circ}C$ is not suitable for conversion of cyclohexane due to low energy activation in catalytic process. The effect of catalyst is also investigated and the results are shown in

Table 5.

Table 5. Effect of catalyst weight

Catalyst weight (g)	Conversion (%)
0.010	98.31
0.038	99.18
0.050	98.80
0.100	98.82

Table 5 showed that catalyst $H_3[-PMo_{12}O_{40}].nH_2O/ZrOCl_2$ can convert cyclohexane up to 99.18% by using 0.038 g of catalyst. These amount is less than 1/10 mmol of starting material. Other amounts in the range 0.010-0,100 g is also suitable for oxidation due to high conversion results.

Oxidation of cyclohexane to cyclohexanol and cyclohexanone using $H_3[-PMo_{12}O_{40}].nH_2O/ZrOCl_2$ as catalyst resulted conversion up to 99%, thus selectivity toward products should be investigated. The experiment used GC-MS for identification and chromatogram of reaction mixtures is presented in Figure 5.

Figure 5 showed that oxidation of cyclohexane formed cyclohexanol and cyclohexanone as main products. Other by products were identified but small starting material was also still remaining. Mass spectrum of cyclohexanol and cyclohexanone are presented in Figure 6 and 7, respectively.

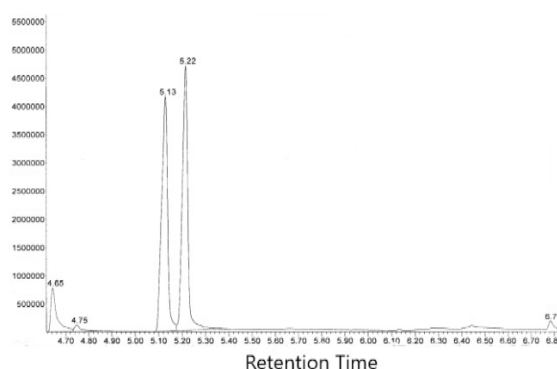


Figure 5. Chromatogram of reaction mixtures

Calculation of cyclohexanol and cyclohexanone as main products resulted selectivity 6.96% for cyclohexanol and 24.90% for cyclohexanone. The total selectivity was 31.86%. This results shows catalyst $H_3[-PMo_{12}O_{40}].nH_2O/ZrOCl_2$ is not selective for oxidation of cyclohexane to cyclohexanol and cyclohexanone.

CONCLUSION

Polyoxometalate $H_3[-PMo_{12}O_{40}].nH_2O$ supported with 0.05 g $ZrOCl_2$ can convert 99.18% cyclohexane. Selectivity of products cyclohexanol and cyclohexanone were 6.96% and 24.9%, respectively.

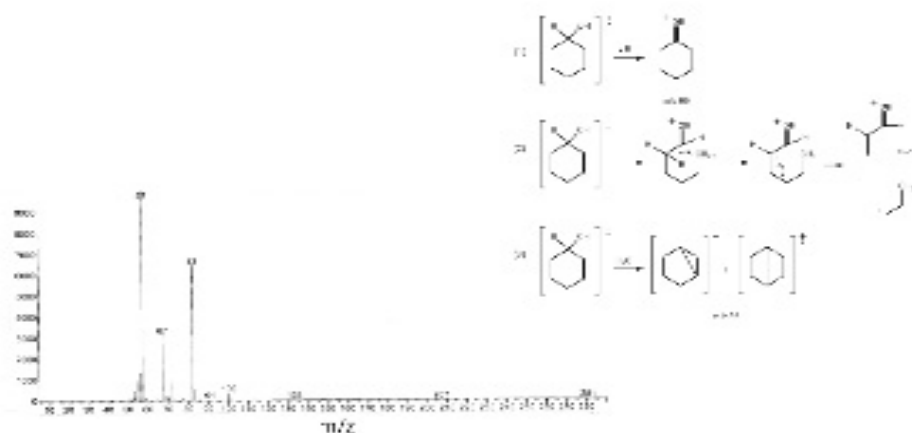


Figure 6. MS spectra and fragmentation of cyclohexanol

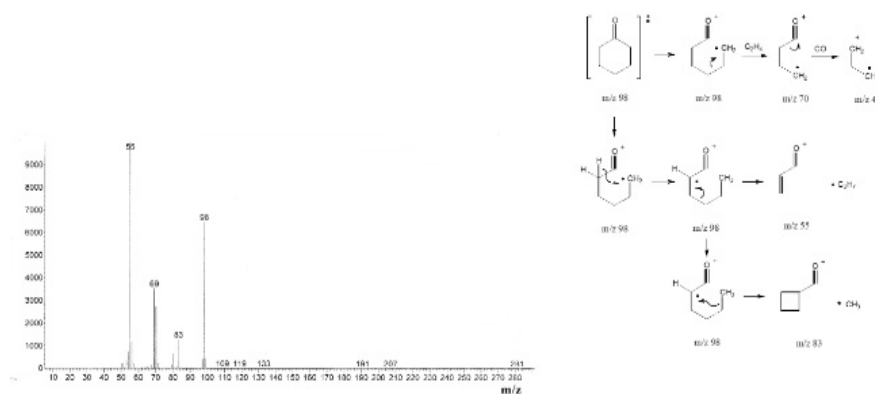


Figure 7. MS spectra and fragmentation of cyclohexanone

ACKNOWLEDGEMENT

AL thank Ministry of Research Technology and Higher Education Republic of Indonesia for support of this research through "Hibah Kompetensi" 2015-2016.

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