

OXIDATION OF CYCLOHEXANE TO CYCLOHEXANOL AND CYCLOHEXANONE USING $H_4[\alpha-SiW_{12}O_{40}]/Zr$ AS CATALYST

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**OXIDATION OF CYCLOHEXANE TO CYCLOHEXANOL AND
CYCLOHEXANONE USING $H_4[\alpha-SiW_{12}O_{40}]/Zr$ AS CATALYST**

**OKSIDASI SIKLOHEKSAN MENJADI SIKLOHEKSANOL DAN
SIKLOHEKSANON MENGGUNAKAN $H_4[\alpha-SiW_{12}O_{40}]/Zr$ SEBAGAI KATALIS**

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ABSTRACT

Synthesis and preparation of polyoxometalate $H_4[\alpha-SiW_{12}O_{40}]_nH_2O$ with Zr as support at various weights of Zr 0.01g; 0.05 g; 0.25 g; 0.5 g; 0.75 g; 1 g and 1.25 g to form $H_4[\alpha-SiW_{12}O_{40}]/Zr$ was conducted. The compounds from preparation were characterized using FTIR spectroscopy and crystallinity analysis using X-Ray diffraction. Thus $H_4[\alpha-SiW_{12}O_{40}]/Zr$ was applied as catalyst for oxidation of cyclohexane to cyclohexanol and cyclohexanone. Oxidation process was studied through reaction time, hydrogen peroxide amount, temperature, and weight of catalyst. FTIR spectrum of $H_4[\alpha-SiW_{12}O_{40}]/Zr$ was appeared at wavenumber 771.53-979.84 cm^{-1} and Zr at 486.06-1481.33 cm^{-1} . Diffraction pattern of $H_4[\alpha-SiW_{12}O_{40}]/Zr$ showed that high crystallinity was identified at 2θ 8°-10° and 28.3°. Based on FTIR spectrum and XRD powder pattern, the optimum preparation of $H_4[\alpha-SiW_{12}O_{40}]/Zr$ was obtained using 0.5 g of Zr. The catalytic study of cyclohexane using $H_4[\alpha-SiW_{12}O_{40}]/Zr$ at 0.5 g of Zr resulted conversion about 99.73%. Catalyst can convert cyclohexane with the highest conversion, then used for further deep catalytic investigation. Optimization of oxidation process resulted optimum reaction time at 2 h, 3 mL of hydrogen peroxide amount, 80 °C of temperature, and 0.038 g of catalyst. The GCMS analysis indicated the oxidation of cyclohexane using $H_4[\alpha-SiW_{12}O_{40}]/Zr$ at 0.5 g of Zr formed cyclohexanol and cyclohexanone with selectivity 18.77 and 23.57, respectively.

Keywords: cyclohexane, cyclohexanol, cyclohexanone, $H_4[\alpha-SiW_{12}O_{40}]/Zr$

ABSTRAK

Sintesis dan preparasi senyawa polioksometalat $H_4[\alpha-SiW_{12}O_{40}]_nH_2O$ dengan Zr sebagai pendukung pada berbagai variasi berat Zr yakni 0,01 g; 0,05 g; 0,25 g; 0,5 g; 0,75 g; 1 g dan 1,25 g membentuk $H_4[\alpha-SiW_{12}O_{40}]/Zr$ telah berhasil dilakukan. Senyawa hasil preparasi dikarakterisasi menggunakan spektrofotometer FTIR dan analisis kristalinitas menggunakan difraksi sinar X. Selanjutnya senyawa $H_4[\alpha-SiW_{12}O_{40}]/Zr$ diaplikasikan sebagai katalis untuk oksidasi sikloheksan menjadi sikloheksanol dan sikloheksanon. Proses oksidasi dipelajari melalui waktu reaksi, jumlah hidrogen peroksida, suhu, dan berat katalis. Spektra FTIR dari $H_4[\alpha-SiW_{12}O_{40}]/Zr$ terlihat pada bilangan gelombang 771,53-979,84 cm^{-1} dan Zr pada 486,06-1481,33 cm^{-1} . Pola difraksi $H_4[\alpha-SiW_{12}O_{40}]/Zr$ menunjukkan bahwa kristalinitas yang tinggi ditemukan pada daerah 2θ 8°-10° dan 28,3°. Berdasarkan data spektrum FTIR dan pola difraksi padatan XRD, kondisi optimum

preparasi $H_4[\alpha\text{-SiW}_{12}\text{O}_{40}]/\text{Zr}$ diperoleh menggunakan 0,5 g Zr. Studi katalitik sikloheksan menggunakan $H_4[\alpha\text{-SiW}_{12}\text{O}_{40}]/\text{Zr}$ pada 0,5 g Zr menghasilkan konversi sebesar 99,73%. Katalis dapat mengkonversi sikloheksan dengan konversi tertinggi selanjutnya digunakan untuk meneliti secara mendalam proses katalitik. Optimasi proses oksidasi menghasilkan waktu reaksi optimum pada 2 jam, 3 mL jumlah hidrogen peroksida, suhu 80 °C, dan 0,038 g katalis. Hasil analisis GCMS menunjukkan oksidasi sikloheksan menggunakan $H_4[\alpha\text{-SiW}_{12}\text{O}_{40}]/\text{Zr}$ pada 0,5 g Zr menghasilkan selektivitas sikloheksanol sebesar 18,77% dan sikloheksanon sebesar 23,57%.

Kata kunci: sikloheksan, sikloheksanol, sikloheksanon, $H_4[\alpha\text{-SiW}_{12}\text{O}_{40}]/\text{Zr}$

INTRODUCTION

Oxidation is one of the useful reactions to produce novel compounds, which has various advantages for our life. The development of oxidation reaction at this decade is focuses on catalytic oxidation both in homogeneous and heterogeneous system. The oxidation in heterogeneous system is interesting especially due to reusability of catalyst although the catalytic cycle is not large compare with homogeneous system. One of the crucial oxidation is cyclohexane oxidation to form cyclohexanol and cyclohexanone (Feng, Xie, Hao, Liu, & Luo, 2015). This oxidation is very useful industrially due to production of nylon-6 and nylon-6,6 especially in textile industry. Industrial process of cyclohexane oxidation was used cobalt or manganese as catalysts resulted mixtures of cyclohexanol and cyclohexanone that called KA oils (Liu et al., 2010). These industrial process was conducted in homogeneous system thus separation of catalyst was difficult.

Research to obtain suitable catalyst for cyclohexane oxidation in heterogeneous system has been developed until this decade. Hao et al. (2007) was carried out oxidation of cyclohexane using $\text{Ti}_{45}\text{Zr}_{35}\text{Ni}_{17}\text{Cu}_3$ as catalyst in heterogeneous system for oxidation of cyclohexane in steel reactor. Maksimchuk et al. (2012) used metal organic framework (MOF) as catalyst for oxidation of cyclohexane together with oxygen as oxidator and tertier butyl hydroperoxide under mild conditions. Oxidation in heterogeneous system also

was carried out by Lu et al. (2012) using Co_3O_4 as catalyst and also Zhou et al. (2014), which used various kinds of zeolites and titanium-zeolite to obtain cyclohexanol and cyclohexanone.

Recently, the oxidation of cyclohexane to cyclohexanol and cyclohexanol is still developed especially in heterogeneous system. The important key to carry out this reaction is suitable heterogeneous catalyst for oxidation (Xiao et al., 2016). Inorganic materials such as polyoxometalates compounds have been used widely for many organic reactions and transformations including oxidation of many organic substrates. Polyoxometalates have advantages due to various oxidation states, various structures, and high acidity properties (Uchida, et al., 2012). Lesbani et al. (2014) used Keggin type of polyoxometalate $H_4[\alpha\text{-SiW}_{12}\text{O}_{40}]$ as acid catalyst for pinacol rearrangement due to Brönsted acid properties. On the other hand, Keggin type of polyoxometalates $H_5[\text{BW}_{12}\text{O}_{40}]$ also used as catalyst for oxidation of cyclohexanone to adipic acid (Lesbani et al., 2015). All these polyoxometalates have been used in homogeneous system. In order to increase heterogeneity of polyoxometalates, these materials should be supported with other elements such as metal oxides or metal compounds.

Herein, preparation $H_4[\alpha\text{-SiW}_{12}\text{O}_{40}]/\text{Zr}$ was conducted using various weight of zirconium and thus $H_4[\alpha\text{-SiW}_{12}\text{O}_{40}]/\text{Zr}$ was used as catalyst in heterogeneous system to oxidize cyclohexane to cyclohexanol and

cyclohexanone using hydrogen peroxide as green oxidant. The important factor to obtain high conversion in this reaction was studied such as reaction times, reaction temperatures, hydrogen peroxide amounts, and weights of catalyst.

EXPERIMENTAL SETION

Chemicals and Equipment

All chemicals were used directly after purchased from Merck without further purification such as sodium metasilicate, sodium tungstate, potassium chloride, zirconium oxo chloride, acetone, nitric acid, diethyl ether, ammonia, methanol, cyclohexane, naphthalene, and hydrogen peroxide.

Characterization was conducted using FTIR Shimadzu Prestige-21 using KBr disk, gas chromatography Shimadzu GC-2010 Plus equipped with capillary column RTX-1 and FID detector. Powder XRD analysis was performed using XRD Shimadzu Lab X type-6000. Gas chromatography-mass spectrometry was also used for monitoring reaction using GCMS Agilent-5973 inert.

Synthesis of $H_4[\alpha-SiW_{12}O_{40}].nH_2O$ and Characterization

Polyoxometalate of $H_4[\alpha-SiW_{12}O_{40}].nH_2O$ was synthesized by extraction method using nitric acid from $K_4[\alpha-SiW_{12}O_{40}].nH_2O$. Polyoxo-metalate of $K_4[\alpha-SiW_{12}O_{40}].nH_2O$ was synthesized as follow: 44 g of sodium metasilicate was dissolved with 400 mL of water in 250 mL of Beaker glass (solution A). Sodium tungstate (728 g) was dissolved with 1200 mL of hot water (solution B). In the solution of B was added slowly 4 M hydrochloric acid (660 mL) following with vigorous stirring to remove solid white precipitate of tungstic acid. The mixtures were stirred for 1 h and solution B was added in the reaction mixtures. pH of mixtures were controlled 5-6. During this process, the solution was heated for 1 h. Polyoxometalate of $K_4[\alpha-SiW_{12}O_{40}].nH_2O$ was obtained by addition

of potassium chloride (200 g) into the solution. White crystals of $K_4[\alpha-SiW_{12}O_{40}].nH_2O$ was filtered and dried under vacuum (Lesbani, et al., 2008).

Polyoxometalate of $H_4[\alpha-SiW_{12}O_{40}].nH_2O$ was obtained by dissolving $K_4[\alpha-SiW_{12}O_{40}].nH_2O$ (250 g) with 200 mL of water followed with addition of nitric acid-diethyl ether (50 mL-400 mL). The mixtures were extracted to form three layers. White solid crystals of polyoxometalate $H_4[\alpha-SiW_{12}O_{40}].nH_2O$ were obtained after evaporation of bottom layer. Characterization of $H_4[\alpha-SiW_{12}O_{40}].nH_2O$ was conducted using FTIR spectrophotometer and XRD powder analysis.

Preparation of $H_4[\alpha-SiW_{12}O_{40}]/Zr$ and Characterization

Synthesis of $H_4[\alpha-SiW_{12}O_{40}]/Zr$ was adopted from Devassy et al. (2002) with slightly modification as follow: 0.5 g of polyoxometalate was dissolved with 10 mL of methanol (solution A). The zirconium solution was prepared by dissolved zirconium oxo chloride at various weights; 0.01 g; 0.05 g; 0.25 g; 0.5 g; 0.75 g; 1 g; and 1.25 g with 10 M of ammonia (solution B). Solution A was mixed with solution B and stirred for 30 min. The mixtures were centrifuge 4000 rpm for 15 min to obtain solid material $H_4[\alpha-SiW_{12}O_{40}]/Zr$. $H_4[\alpha-SiW_{12}O_{40}]/Zr$ was collected and washed with acetone. Characterization of $H_4[\alpha-SiW_{12}O_{40}]/Zr$ was carried out through FTIR spectrophotometer and XRD powder analysis.

Oxidation of Cyclohexane to Cyclohexanol and Cyclohexanone Using $H_4[\alpha-SiW_{12}O_{40}]/Zr$ as Catalyst

Conversion of cyclohexane to cyclohexanol and cyclohexanone using $H_4[\alpha-SiW_{12}O_{40}]/Zr$ as catalyst and $H_4[\alpha-SiW_{12}O_{40}]$ as control was conducted in 50 mL of Schlenk flask equipped with magnetic bar. This procedure was adopted from Simões et al (1999). Catalyst (0.043

mmol), cyclohexane (18.5 mmol), and 29.4 mmol of hydrogen peroxide was mixed in Schlenk flask. In the flask, naphthalene as internal standard was added (0.0013 g). The reaction was carried out at 80 °C and reaction progress was monitored using GC and GC-MS. The oxidation reaction was conducted using $H_4[\alpha-SiW_{12}O_{40}]/Zr$ as catalyst in various weights of Zr in order to obtain the highest conversion. Furthermore, oxidation reaction was investigated deeply through optimization of reaction time, hydrogen peroxide amount, temperature reaction, and weight of catalyst.

RESULTS AND DISCUSSION

Polyoxometalate $H_4[\alpha-SiW_{12}O_{40}].nH_2O$ from synthesis was obtained in 85% yield (based on tungsten) and was characterized using FTIR spectrophotometer. FTIR spectrum of $H_4[\alpha-SiW_{12}O_{40}].nH_2O$ was shown in Figure 1. Vibrations of $H_4[\alpha-SiW_{12}O_{40}].nH_2O$ were appeared at wavenumber 981 cm^{-1} which was indicated W=O. Vibration of Si-O was indicated at wavenumber 928 cm^{-1} . The existence vibrations of W-Oc-W (oxygen center) and W-Oe-W (oxygen edge) were appeared at wavenumber 880 cm^{-1} and 785 cm^{-1} (Misono et al., 2001). There was wide stretching vibration of O-H from H_2O appeared at wavenumber 3425 cm^{-1} . All specific vibrations in

Figure 1 is appropriate with Keggin structure. Polyoxometalate $H_4[\alpha-SiW_{12}O_{40}].nH_2O$ was also characterized using XRD powder analysis and the XRD powder pattern was shown in Figure 2.

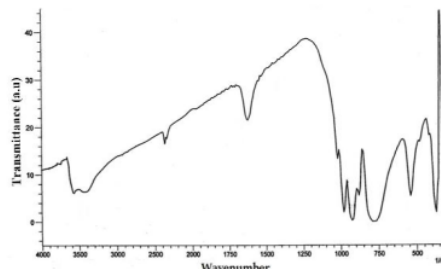


Figure 1. FTIR spectrum of $H_4[\alpha-SiW_{12}O_{40}]$

The XRD powder pattern in Figure 2 has high crystallinity in the diffraction 3-10 deg, 20-30 deg, and 31-37 deg. The range crystallinity of these area has related with polyoxometalate especially Keggin structure such as $H_4[\alpha-SiW_{12}O_{40}].nH_2O$. The FTIR spectrum and XRD powder pattern indicated that polyoxometalate $H_4[\alpha-SiW_{12}O_{40}].nH_2O$ was successfully synthesized and characterized and can be supported with zirconium to form $H_4[\alpha-SiW_{12}O_{40}]/Zr$ on various weight of zirconium. The $H_4[\alpha-SiW_{12}O_{40}]/Zr$ on various weight of zirconium was characterized using FTIR spectrophotometer and XRD powder pattern as shown in Figure 3 and 4, respectively.

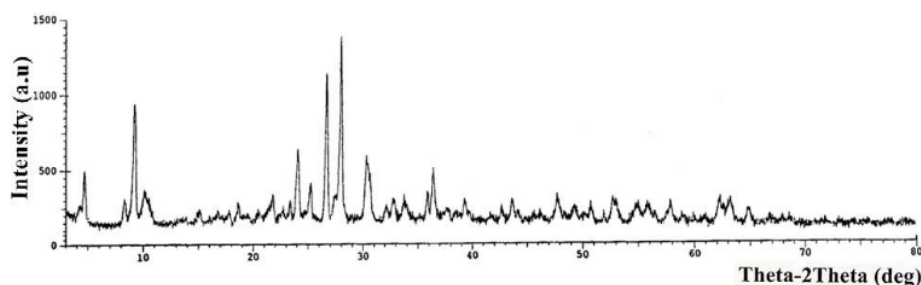


Figure 2. XRD powder pattern of $H_4[\alpha-SiW_{12}O_{40}]$

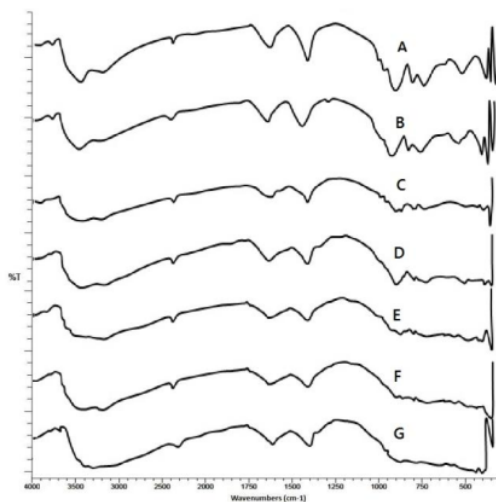


Figure 3. FTIR spectrum of $H_4[\alpha-SiW_{12}O_{40}]/Zr$ on various weight of Zr (A=0.01g; B=0.05g; C=0.25g; D=0.5g; E=0.75g; F=1g; and G=1.25g)

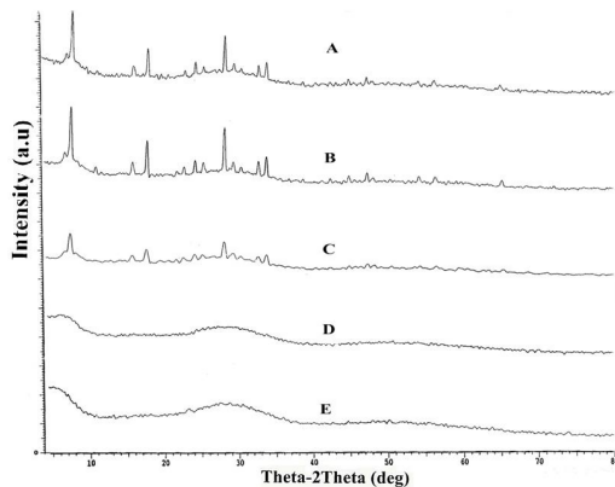


Figure 4. XRD powder pattern of $H_4[\alpha-SiW_{12}O_{40}]/Zr$ on various weight of Zr (A=0.25g; B=0.5g; C=0.75g; D=1g; and E=1.25g)

FTIR spectrum in **Figure 3** showed that by increasing weight of zirconium will decrease the main vibrations of polyoxometalate. Vibration of zirconium such as Zr-O-Zr and Zr-O appeared in the wavenumber $480-500\text{ cm}^{-1}$, while polyoxometalate appeared in the wavenumber $700-1000\text{ cm}^{-1}$. The FTIR spectrum in **Figure 3** also indicated by using zirconium 0.01-0.05 g for supporting polyoxometalate resulted FTIR

spectrum better than other weights of zirconium due to existence vibration of polyoxometalate.

Identification of $H_4[\alpha-SiW_{12}O_{40}]/Zr$ was also carried out using XRD powder analysis as shown in **Figure 4**. The XRD pattern in **Figure 4** has equivalency results with FTIR spectrum in **Figure 3**. In this case, by increasing weight of zirconium will decrease the crystallinity of $H_4[\alpha-SiW_{12}O_{40}]$. This results indicated

that zirconium weight 0.01-0.05 g was suitable to support polyoxometalate to form $H_4[\alpha-SiW_{12}O_{40}]/Zr$.

Supported polyoxometalate $H_4[\alpha-SiW_{12}O_{40}]/Zr$ with weight of zirconium 0.5 g was applied as catalyst for oxidation of cyclohexane to cyclohexanol and cyclohexanone as mayor products. At the beginning of experiment, the oxidation process was studied through reaction time of oxidation and the reaction was monitored using GC and GCMS. Hydrogen peroxide was used as green oxidant. The oxidation of cyclohexane profiles was shown in Figure 5.

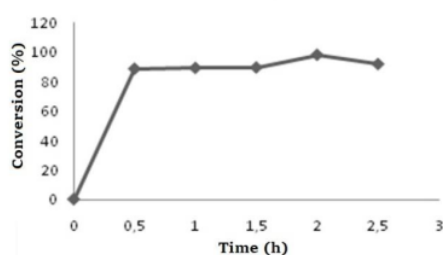


Figure 5. The influence oxidation of cyclohexane using $H_4[\alpha-SiW_{12}O_{40}]/Zr$ as catalyst

Oxidation process as shown in Figure 5 indicated the reaction was proceeding with fast until 82% conversion. The increasing reaction time resulted increasing conversion of cyclohexane. The highest conversion of cyclohexane was achieved for 2 h reaction time. By increasing reaction time until 2.5 h did not give any significant results for conversion of cyclohexane. For further investigation oxidation process, reaction was conducted at 2 h. The effect of temperature in the oxidation cyclohexane was investigated deeply form 60-85 °C and the results are shown in Figure 6.

The optimum temperature for oxidation of cyclohexane was achieved at 80 °C to give highest conversion. Temperature oxidation below 80 °C did not give optimal oxidation because activation energy did not enough to support oxidant. Temperature oxidation higher than 80 °C was not suitable for

oxidation, which was indicated from lower conversion results. Thus temperature oxidation 80 °C was used for optimization of hydrogen peroxide.

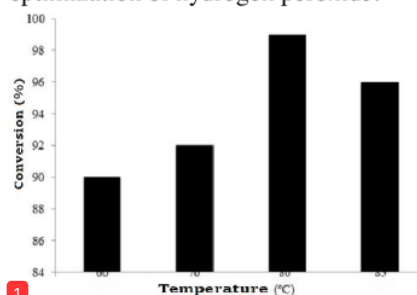


Figure 6. The influence of temperature in the oxidation of cyclohexane

The results of hydrogen peroxide effect into cyclohexane oxidation should be optimized due to oxygen needed for reaction was depends on type of reactions. Hydrogen peroxide with low oxygen contents resulted low conversion reaction. On the other hand, hydrogen peroxide with high oxygen contents gave several by-products in the reaction. Thus in this research, the hydrogen peroxide 3 mL was optimum amount to oxidize cyclohexane. This optimization results in the Figure 7 should be followed with investigation of weight of catalyst.

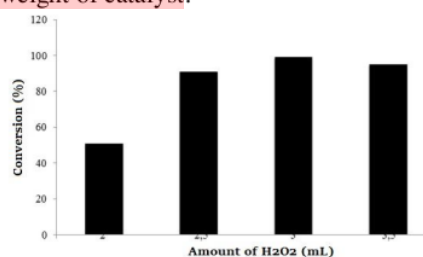


Figure 7. The influence of hydrogen peroxide to the oxidation of cyclohexane

The results of weight of catalyst for oxidation of cyclohexane were presented in Figure 8. The data in Figure 8 showed that $H_4[\alpha-SiW_{12}O_{40}]/Zr$ as catalyst for oxidation of cyclohexane was used optimum at 0.038 g. In the catalytic process, the use of catalyst was recommended less than 1/10 mmol of

reactant and the amount of catalyst 0.038 g in this research was suitable for the oxidation. The weight of $H_4[\alpha-SiW_{12}O_{40}]/Zr$ was optimized because hydrogen peroxide is mild oxidant and need activation to produce radical oxygen for substitution into reactant (Lesbani et al., 2015b).

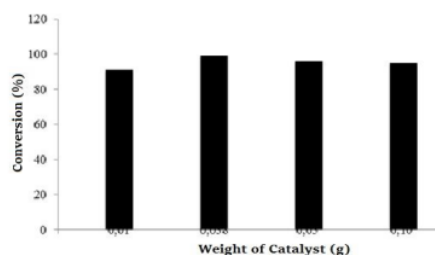


Figure 8. The influence of catalyst weight to the oxidation of cyclohexane

The oxidation of cyclohexane in this research was conducted in heterogeneous system and $H_4[\alpha-SiW_{12}O_{40}]/Zr$ was not dissolved into reaction medium. The conversion after optimization of several parameters was 80-90%. Other products were formed in this reaction system and was identified using GC-MS. The main product of this oxidation was cyclohexanol and cyclohexanone. Other products as by-products were found such as 2-pentanone and cyclopentanone. These by-products were probably formed due to active oxygen from hydrogen peroxide in the reaction mixtures. The structures of main and by-products were illustrated in **Figure 9**.

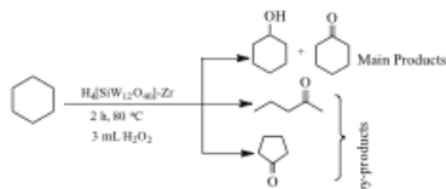


Figure 9. Identification of oxidation reaction mixtures using GC-MS

To complete the results of this research, selectivity of main product was also calculated based on GC measurement

at optimum condition i.e. 2 h reaction time, 80 °C temperature reaction, 3 mL of hydrogen peroxide, and 0.038 g $H_4[\alpha-SiW_{12}O_{40}]/Zr$. The results showed that formation of cyclohexanol was 18.8% and cyclohexanone 23.6%. Thus cyclohexanone was main product in this research.

CONCLUSION

Supported polyoxometalate $H_4[\alpha-SiW_{12}O_{40}]$ with Zr was successfully synthesized using 0.05 g of $ZrOCl_2$ to form $H_4[\alpha-SiW_{12}O_{40}]/Zr$ in 70% yield (based on tungsten). FTIR spectrum and XRD pattern of $H_4[\alpha-SiW_{12}O_{40}]/Zr$ indicated all fraction existed in the supported polyoxometalate. Catalytic oxidation of cyclohexane to cyclohexanol and cyclohexanone using $H_4[\alpha-SiW_{12}O_{40}]/Zr$ as catalyst resulted optimum reaction time at 2 h, 3 mL of hydrogen peroxide, temperature reaction at 80 °C, and catalyst weight 0.038 g to give highest selectivity product to cyclohexanone in 23.6% yield.

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