

## Oxidation of Cyclohexane to Cyclohexanol and Cyclohexanone Over $H_4[\alpha\text{-SiW}_{12}\text{O}_{40}]/\text{TiO}_2$ Catalyst

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### ABSTRACT

Oxidation of cyclohexane to cyclohexanol and cyclohexanone was carried out using  $H_4[\alpha\text{-SiW}_{12}\text{O}_{40}]/\text{TiO}_2$  as catalyst. In the first experiment, catalyst  $H_4[\alpha\text{-SiW}_{12}\text{O}_{40}]/\text{TiO}_2$  was synthesized and characterized using FTIR spectroscopy and X-Ray analysis. In the second experiment, catalyst  $H_4[\alpha\text{-SiW}_{12}\text{O}_{40}]/\text{TiO}_2$  was applied for conversion of cyclohexane. The conversion of cyclohexane was monitored using GC and GCMS. The results showed that  $H_4[\alpha\text{-SiW}_{12}\text{O}_{40}]/\text{TiO}_2$  was successfully synthesized using 1 g of  $H_4[\alpha\text{-SiW}_{12}\text{O}_{40}]$  and 0.5 g of  $\text{TiO}_2$ . The FTIR spectrum showed vibration of  $H_4[\alpha\text{-SiW}_{12}\text{O}_{40}]$  appeared at  $771\text{-}979\text{ cm}^{-1}$  and  $\text{TiO}_2$  at  $520\text{-}680\text{ cm}^{-1}$ . The XRD powder pattern analysis indicated that crystallinity of catalyst still remained after impregnation to form  $H_4[\alpha\text{-SiW}_{12}\text{O}_{40}]/\text{TiO}_2$ . The  $H_4[\alpha\text{-SiW}_{12}\text{O}_{40}]/\text{TiO}_2$  catalyst was used for oxidation of cyclohexane in heterogeneous system under mild condition at 2 h,  $70\text{ }^\circ\text{C}$ , 0.038 g catalyst, and 3 mL hydrogen peroxide to give cyclohexanone as major product.

**Keywords:** cyclohexane; cyclohexanol; cyclohexanone; oxidation;  $H_4[\alpha\text{-SiW}_{12}\text{O}_{40}]/\text{TiO}_2$

### ABSTRAK

Oksidasi sikloheksan menjadi sikloheksanol dan sikloheksanon telah dilakukan menggunakan  $H_4[\alpha\text{-SiW}_{12}\text{O}_{40}]/\text{TiO}_2$  sebagai katalis. Pada eksperimen awal, katalis  $H_4[\alpha\text{-SiW}_{12}\text{O}_{40}]/\text{TiO}_2$  disintesis dan dikarakterisasi menggunakan spektroskopi FTIR dan analisis X-Ray. Pada tahap kedua, katalis  $H_4[\alpha\text{-SiW}_{12}\text{O}_{40}]/\text{TiO}_2$  diaplikasikan untuk konversi sikloheksan. Konversi sikloheksan dimonitor dengan menggunakan GC dan GCMS. Hasil penelitian menunjukkan bahwa  $H_4[\alpha\text{-SiW}_{12}\text{O}_{40}]/\text{TiO}_2$  berhasil disintesis menggunakan 1 g  $H_4[\alpha\text{-SiW}_{12}\text{O}_{40}]$  dan 0,5 g  $\text{TiO}_2$ . Spektra FTIR menunjukkan vibrasi  $H_4[\alpha\text{-SiW}_{12}\text{O}_{40}]$  muncul pada  $771\text{-}979\text{ cm}^{-1}$  dan  $\text{TiO}_2$  pada  $520\text{-}680\text{ cm}^{-1}$ . Pola difraksi XRD menunjukkan bahwa kristalinitas katalis masih sama dengan bahan awal setelah proses impregnasi membentuk  $H_4[\alpha\text{-SiW}_{12}\text{O}_{40}]/\text{TiO}_2$ . Katalis  $H_4[\alpha\text{-SiW}_{12}\text{O}_{40}]/\text{TiO}_2$  digunakan untuk oksidasi sikloheksan pada sistem heterogen dengan kondisi ringan yakni waktu reaksi 2 jam, temperatur  $70\text{ }^\circ\text{C}$  dan berat katalis 0,038 g serta 3 mL hidrogen peroksida menghasilkan sikloheksanon sebagai produk utama.

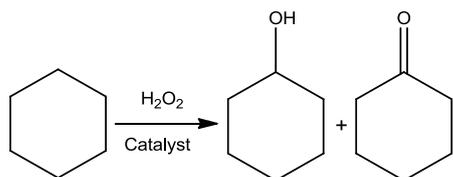
**Kata Kunci:** sikloheksan; sikloheksanol; sikloheksanon; oksidasi;  $H_4[\alpha\text{-SiW}_{12}\text{O}_{40}]/\text{TiO}_2$

### INTRODUCTION

Fine chemical synthesis using heterogeneous catalysts are of growing importance for industrial point of view. Industrial processes are often not selective. Selective reaction is needed to obtain specific products [1]. Selective oxidation cyclohexane to cyclohexanol and cyclohexanone is one of industrially important reaction. Product reaction of cyclohexane is intermediate

materials for adipic acid and caprolactam, which are used for manufacturing nylon-6 and nylon-66 [2]. Recently, industrial process to obtain cyclohexanol and cyclohexanone used oxidation of cyclohexane or hydrogenation of phenol [3]. These processes needed high pressure and temperature. On the other hand, the reaction used soluble copper catalyst resulted homogeneous system with mild operated conditions oxidized cyclohexane [4]. Mesoporous materials such

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**Fig 1.** Oxidation of cyclohexane to cyclohexanol and cyclohexanone [4]

as MCM-41, SBA, and ZMS were efficient catalyst for oxidation of cyclohexane to cyclohexanol in heterogeneous system and catalyst can be regenerated [5-7]. Complex of coordination compounds also shows catalytic activity oxidation of cyclohexane [8]. Hence, the oxidation has been focused on the development of heterogeneous catalyst, which can use at mild conditions. Polyoxometalates are metal oxygen clusters containing various oxidation states, structures, and high acidity reported can be used as catalyst for oxidation of cyclohexane to cyclohexanol and cyclohexanone in homogeneous system [9-10]. Due to small surface area properties of polyoxometalates, this compound is appropriate as catalyst in homogeneous system. Supported polyoxometalates with metal oxide can increase the heterogeneity in the catalytic system [11] and can be used as candidate for oxidation of cyclohexane. The present research used polyoxometalate  $H_4[\alpha-SiW_{12}O_{40}]/TiO_2$  as catalyst which showed high catalytic activity for oxidation of cyclohexane under mild conditions as shown in Fig. 1. The effect of reaction time, temperature reaction, weight of catalyst, and hydrogen peroxide amounts were also studied.

## EXPERIMENTAL SECTION

### Materials

All chemical reagents with analytical grade were used directly without further purification such as sodium metasilicate (Aldrich), sodium tungstate (Merck), hydrochloric acid (Ajax Finechem Pty Ltd), diethyl ether (Merck), titanium oxide (Merck), ethanol (Merck), and acetone (Merck).

### Instrumentation

FTIR spectrum was collected using Shimadzu FTIR-Prestige-21 and samples were prepared as KBr pellets. XRD powder measurement was performed on Shimadzu XRD Lab X type 6000 diffractometer and the data was acquired over  $2\theta$  0-90 deg. Monitoring reaction was performed using gas chromatography (Shimadzu GC-2010 Plus) with RTX-Wax column (30 m x 0.25 mm)

and a FID detector. GC-MS analysis was conducted using GCMS Agilent 5973 inert.

### Procedure

#### Synthesis of polyoxometalate $H_4[\alpha-SiW_{12}O_{40}] \cdot nH_2O$

The acid polyoxometalate  $H_4[\alpha-SiW_{12}O_{40}] \cdot nH_2O$  was synthesized as follows: sodium metasilicate (11 g, 50 mmol) was dissolved into 100 mL of water (solution A). Sodium tungstate (182 g, 0.55 mol) was dissolved into 300 mL of boiling water (solution B). A solution of 4 M HCl (165 mL) was added drop by drop over 5 min with vigorous stirring in order to dissolve the local precipitate of tungstic acid. Then solution A was added quickly to solution B followed by adding 50 mL of 4 M HCl. The pH is around 5 to 6. The solution was kept at 373 K for 1 h. A solution of 1 M sodium tungstate (50 mL, 50 mmol) and immediately thereafter, 80 mL of 4 M HCl were added. The solution was filtered after cooling to room temperature.

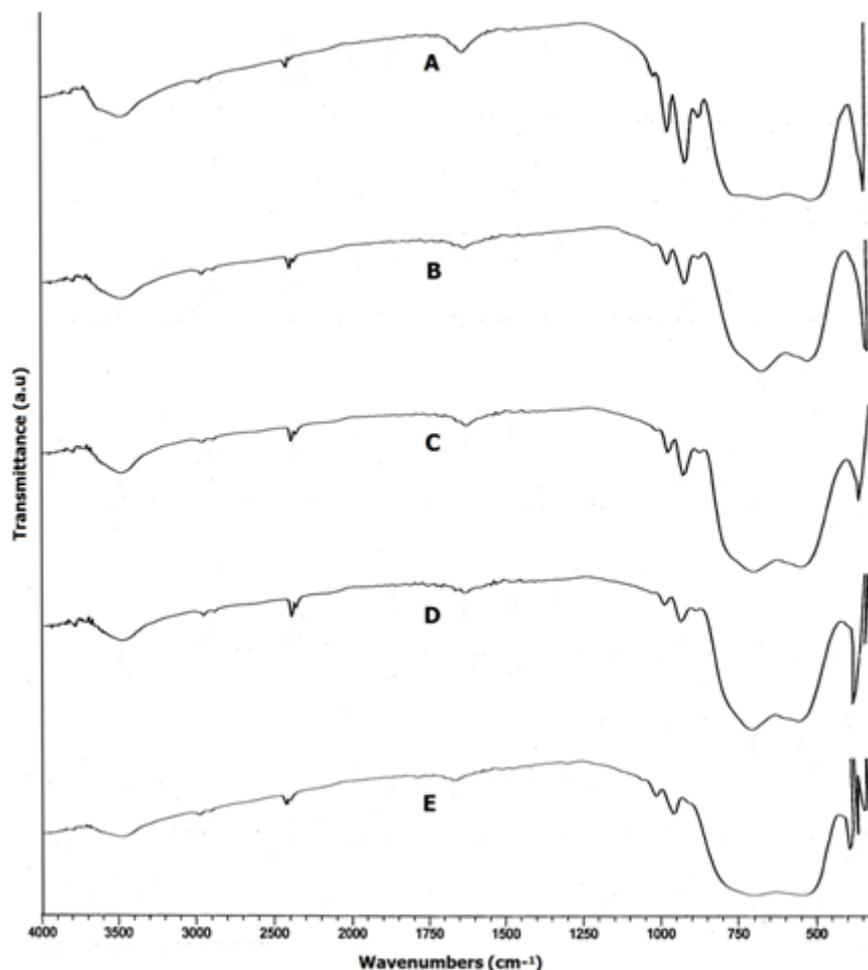
The solution was extracted with 80 mL diethyl ether and 120 mL of a mixture of equal volumes of diethyl ether and concentrated hydrochloric acid chilled to 253 K. The heaviest layer was collected, concentrated to produce white crystal, which was recrystallized from water to obtain acid type polyoxometalate  $H_4[\alpha-SiW_{12}O_{40}]$  [12].

#### Preparation of catalyst $H_4[\alpha-SiW_{12}O_{40}]/TiO_2$

Titanium oxide (0.25 g) was mixed with 5 mL of ethanol in 50 mL of beaker glass. In the mixtures were added 1 g of polyoxometalate  $H_4[\alpha-SiW_{12}O_{40}]$  with slowly stirring at 60 °C. The solution was stirred for 1 h. The mixtures were filtered and white solid material was washed with acetone three times. The solid bulk was kept for 24 h under vacuum [13]. Dry solid bulk material was characterized using FTIR spectroscopy and X-Ray analysis. Similar procedure was repeated using titanium oxide in various weights: 0.5 g; 0.75 g; 1 g; and 1.25 g. All materials were characterized also using FTIR and X-Ray analyses.

#### Catalytic oxidation of cyclohexane to cyclohexanol and cyclohexanone

Catalytic study of cyclohexane to cyclohexanol and cyclohexanone was carried out using 100 mL Schlenk flask equipped with septum and magnetic bar. Polyoxometalate 0.013 mmol, cyclohexane 18.5 mmol, and hydrogen peroxide 29.4 mmol were added into Schlenk flask successively. Naphthalene was added as internal standard. Heterogeneous reaction system was heated at 80 °C and was monitored by gas chromatography at initial and interval times [14]. The conversion of cyclohexane was calculated based on area peak of cyclohexane at initial and interval time



**Fig 2.** FTIR spectrum of  $H_4[\alpha-SiW_{12}O_{40}]/TiO_2$  under various weight of  $TiO_2$  (A: 0.25g; B: 0.50 g; C: 0.75 g; D: 1.00 g; and E: 1.25 g)

with naphthalene as standard. The selectivity (%) was calculated using yield of product divided by mole of cyclohexane converted. Catalytic oxidation was investigated through effect of reaction time, temperature, weight of catalyst, and hydrogen peroxide amount.

## RESULT AND DISCUSSION

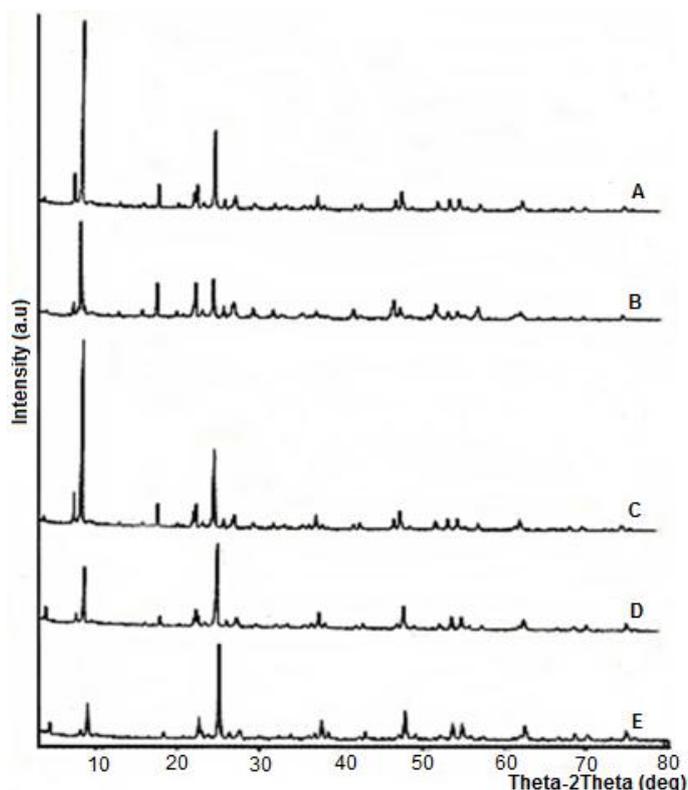
### Catalyst Preparation and Characterization

Polyoxometalates  $H_4[\alpha-SiW_{12}O_{40}] \cdot nH_2O$  and  $H_4[\alpha-SiW_{12}O_{40}]/TiO_2$  were identified using FTIR spectroscopy. FTIR spectrum of  $H_4[\alpha-SiW_{12}O_{40}] \cdot nH_2O$  and  $H_4[\alpha-SiW_{12}O_{40}]/TiO_2$  were shown in Fig. 2.

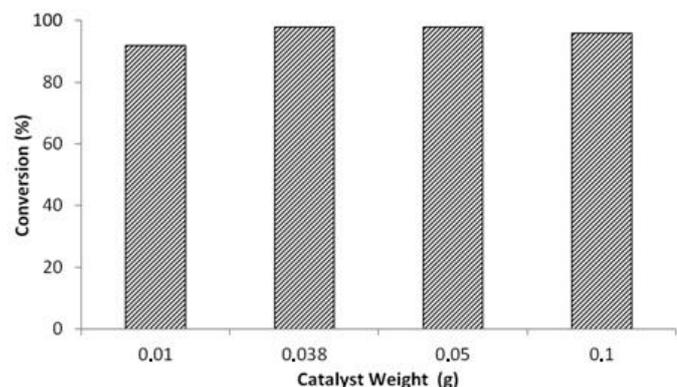
Vibration of polyoxometalate  $H_4[\alpha-SiW_{12}O_{40}] \cdot nH_2O$  was appeared at  $979.8\text{ cm}^{-1}$  ( $\nu W=O$ ),  $925.8\text{ cm}^{-1}$  ( $\nu Si-O$ ),  $879.5\text{ cm}^{-1}$  ( $\nu W-Oe-W$ ), and  $771.5\text{ cm}^{-1}$  ( $\nu W-Oc-W$ ) [15]. Supported polyoxometalate  $H_4[\alpha-SiW_{12}O_{40}] \cdot nH_2O$  with  $TiO_2$  resulted specific vibration for  $TiO_2$  besides

main vibration of polyoxometalate. Main vibration of  $TiO_2$  was identified at  $520-680\text{ cm}^{-1}$  [16]. The FTIR spectrum in Fig. 2 indicated that  $TiO_2$  was impregnated into polyoxometalate  $H_4[\alpha-SiW_{12}O_{40}] \cdot nH_2O$  at various weight of  $TiO_2$ . However, the use of 0.5 g  $TiO_2$  resulted fine impregnation than other weights, which was indicated from vibration of polyoxometalate in the range of  $750-950\text{ cm}^{-1}$ .

The XRD pattern as shown in Fig. 3 is equal with the results from FTIR spectrum which is 0.5 g of  $TiO_2$  resulted both vibration of polyoxometalate and  $TiO_2$  in the range of  $0-30$  deg. The diffraction pattern of  $H_4[\alpha-SiW_{12}O_{40}]/TiO_2$  in the range of  $TiO_2$  from 0.75 g to 1.25 g resulted small pattern at  $18-20$  deg. The XRD pattern of  $H_4[\alpha-SiW_{12}O_{40}]/TiO_2$  in the 0.25 g of  $TiO_2$  as shown in Fig. 3A has largely similarity patterns with  $H_4[\alpha-SiW_{12}O_{40}]/TiO_2$  in the 0.5 g of  $TiO_2$  (Fig. 3B). Otherwise, XRD pattern in the range of  $28-30$  deg in the Figure 3B is almost sharp and clear than in the Fig. 3A. Thus



**Fig 3.** XRD powder pattern of  $H_4[\alpha-SiW_{12}O_{40}]/TiO_2$  under various weight of  $TiO_2$  (A: 0.25 g; B: 0.50 g; C: 0.75 g; D: 1.00 g; and E: 1.25 g)

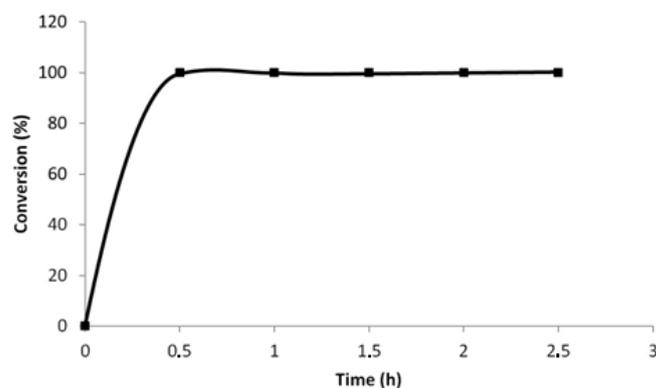


**Fig 6.** Effect of catalyst weight in the oxidation of cyclohexane using  $H_4[\alpha-SiW_{12}O_{40}]/TiO_2$

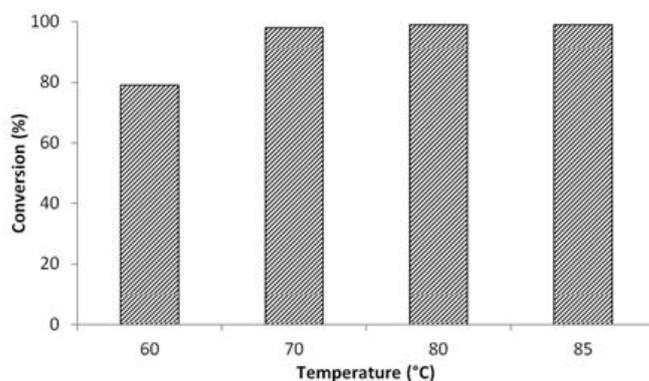
$H_4[\alpha-SiW_{12}O_{40}]/TiO_2$  0.5 g is suggested as successfully impregnated.

### Catalytic Properties

The  $H_4[\alpha-SiW_{12}O_{40}]/TiO_2$  was used as catalyst for oxidation of cyclohexane under atmospheric condition using hydrogen peroxide as green oxidant to form cyclohexanol and cyclohexanone. In the first trial, we



**Fig 4.** Catalytic properties of  $H_4[\alpha-SiW_{12}O_{40}]/TiO_2$  in the oxidation of cyclohexane

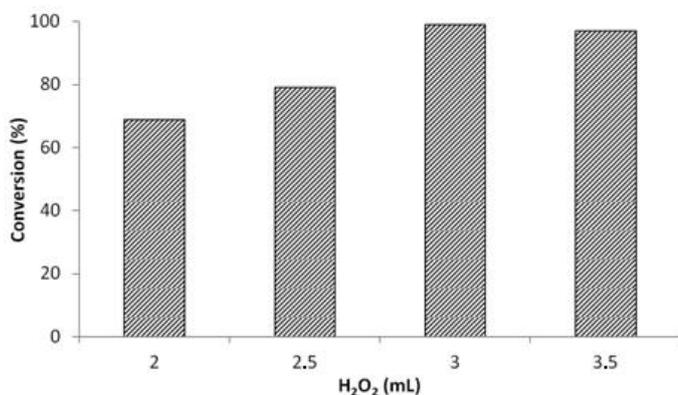


**Fig 5.** Effect of temperature in the oxidation of cyclohexane using  $H_4[\alpha-SiW_{12}O_{40}]/TiO_2$

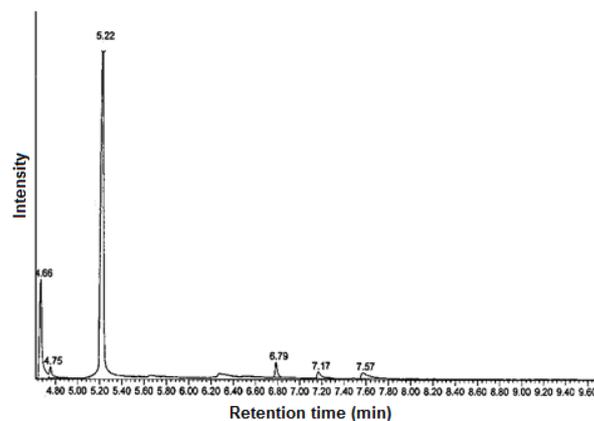
tried the oxidation at various reaction time and the results is presented in Fig. 4.

The catalytic oxidation of cyclohexane to cyclohexanol and cyclohexanone was occurred very fast to achieve almost 100% conversion at 0.5 h. The increasing reaction time did not give any influence to the conversion of cyclohexane. This oxidation reaction is truly heterogeneous which was indicated from solution after filtration process at the end of oxidation. White small particles remain in the filter paper was observed. As we expected that polyoxometalate impregnated with metal oxide can form heterogeneous catalyst for wide range of solvent in the organic reaction and transformation.

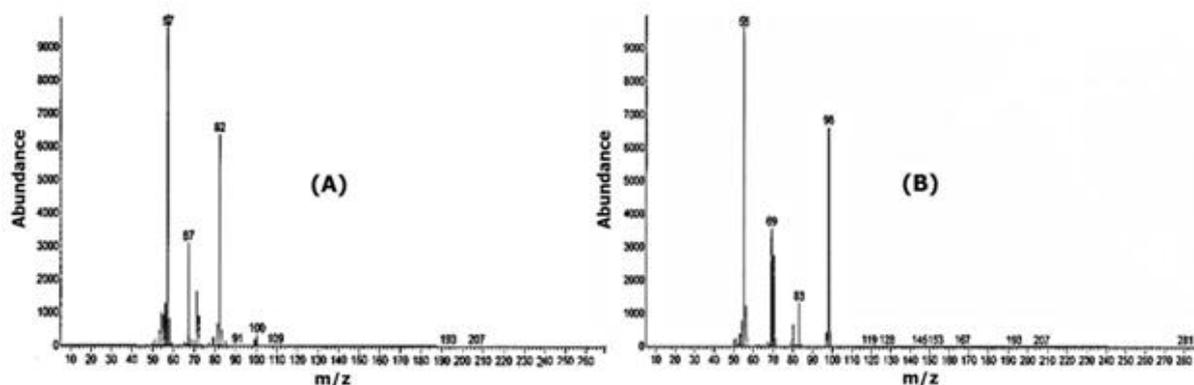
The second experiment of oxidation using  $H_4[\alpha-SiW_{12}O_{40}]/TiO_2$  as catalyst was carried out using various temperatures reaction and the results are shown in Fig. 5. Oxidation Temperature reaction at 60 °C resulted 79% conversion of cyclohexane. Conversion of cyclohexane was increased significantly through adding temperature reaction to 70 °C up to 98%. The conversion is relative equal up to 99% by addition of temperature oxidation to 80 and 85 °C. This phenomenon showed that temperature oxidation was



**Fig 7.** Effect of hydrogen peroxide in the oxidation of cyclohexane using  $H_4[\alpha-SiW_{12}O_{40}]/TiO_2$



**Fig 8.** Chromatogram of GCMS for reaction mixture at 2 h



**Fig 9.** Mass spectrum of cyclohexanol (A) and cyclohexanone (B)

affected to the conversion of cyclohexane. By increasing temperature up to 100 °C resulted similar results with temperature 80-85 °C means relative mild condition is enough for oxidation of cyclohexane using  $H_4[\alpha-SiW_{12}O_{40}]/TiO_2$  as catalyst.

Effect of catalyst weight was investigated in the third stage and the results are shown in Fig. 6. The catalyst weight was selected in the range of 0.01–0.10 g. In the range of 0.01–0.10 g of  $H_4[\alpha-SiW_{12}O_{40}]/TiO_2$  as catalyst for oxidation of cyclohexane to cyclohexanol and cyclohexanone resulted equal conversion of cyclohexane. This results is different from the results effect of temperature, which these parameter affected the conversion of cyclohexane. The results of Fig. 6 indicated that oxidation of cyclohexane was stable with weight of catalyst. Catalyst was needed to active hydrogen peroxide as green oxidant to produce active radical containing oxygen active for oxidation process [17].

Hydrogen peroxide is green oxidant for many organic reactions, which was evaluated deeply in this research. The effect of hydrogen peroxide amount for oxidation of cyclohexane to cyclohexanol and cyclohexanone is shown in Fig. 7. The variation amounts

of hydrogen peroxide were in the range 2–3.5 mL. At initial amount of hydrogen peroxide 2–2.5 mL resulted conversion of cyclohexane less than 80%. By increasing amount of hydrogen peroxide to 3 mL gave 99% conversion of cyclohexane. Oxidation using hydrogen peroxide was commonly occurred in the radical mechanisms, thus formation of radical in this reaction was achieved using 3 mL hydrogen peroxide. The use of hydrogen peroxide 3.5 mL resulted 97% conversion of cyclohexane. Although decreasing of conversion is not significant but the optimum hydrogen peroxide was used in this research was 3 mL.

Conversion of cyclohexane to cyclohexanol and cyclohexanone using  $H_4[\alpha-SiW_{12}O_{40}]/TiO_2$  as catalyst was also checked using GCMS at 2 h reaction times as shown in Fig. 8. There was two peaks identified except cyclohexanol and cyclohexanone means selectivity of reaction is less than 99% for both products. Analysis of mass spectrum showed that butanoic acid and 2-pentanone was formed in the conversion of cyclohexane using  $H_4[\alpha-SiW_{12}O_{40}]/TiO_2$  as catalyst. Calculation of selectivity of cyclohexanol and cyclohexanone in this reaction using 70 °C temperature reaction, 0.038 g of catalyst, 2 h reaction time, and

3 mL of hydrogen peroxide resulted 10% of cyclohexanol and 45% of cyclohexanone.

Two main products were identified using GCMS at retention time less than 6 min is cyclohexanol and cyclohexanone. Fragmentation of both cyclohexanol and cyclohexanone was shown in Fig. 9.

The mechanistic oxidation of cyclohexane to cyclohexanol and cyclohexanone is involving two steps reaction. The first stage is transformation of cyclohexane to cyclohexanol following with further oxidation of cyclohexanol to cyclohexanone in the second stage. All stage of oxidation requested catalyst  $H_4[\alpha\text{-SiW}_{12}\text{O}_{40}]/\text{TiO}_2$  to reduce activation energy of hydrogen peroxide as oxidant. The formation of radical from hydrogen peroxide as oxidant was important step for start the oxidation of cyclohexane.

## CONCLUSION

Catalyst  $H_4[\alpha\text{-SiW}_{12}\text{O}_{40}]/\text{TiO}_2$  can convert cyclohexane to cyclohexanol and cyclohexanone under mild conditions at 2 h reaction time, 70 °C, 0.038 g of catalyst, and 3 mL hydrogen peroxide as oxidant. Conversion of cyclohexane up to 99% with selectivity to cyclohexanol 10% and cyclohexanone 45% with formation of several by products.

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