

## 12-Tungstophosphoric Acid/Silica Catalyst for Oxidation of Benzothiophene

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12-Tungstophosphoric acid  $H_3[\alpha-PW_{12}O_{40}]$  was impregnated with silica to form 12-tungstophosphoric acid/silica catalyst. Structural properties of catalyst were characterized using Fourier transform infrared spectroscopy, X-ray diffraction, scanning electron microscopy, and nitrogen adsorption desorption. The results showed that silica was impregnated into  $H_3[\alpha-PW_{12}O_{40}]$  with increasing surface area properties. The catalytic activity under mild condition from  $H_3[\alpha-PW_{12}O_{40}]$  after impregnation with silica slightly increased compared to original catalyst. The structure of catalyst after reaction was stable, which indicate the possibility of reusing the catalyst.

**Keywords:** 12-Tungstophosphoric acid, Silica, Benzothiophene, Oxidation.

### INTRODUCTION

Sulfur compounds especially organic sulfur is naturally available in fossil fuel. This compound contributed into air pollution that is a major source of SO<sub>x</sub> [1]. In 2010, the international regulation such as in Japan and Europe make a limitation of sulfur content in diesel up to 10 ppmw [2]. The long and stable regulation in the future probably implements a standard of zero content for sulfur in transportation fuel. Consequently, sulfur content in fossil fuel should be fully reduced with clean and efficient technologies.

Industrial process to reduce sulfur content in the fossil fuel was using hydrodesulfurization (HDS). Hydrodesulfurization required harsh conditions such as high temperature and high pressure [3]. Hydrodesulfurization is recommended for removing thiols, sulfides, disulfides aliphatic and acyclic sulfur compounds. This process is effective for sulfur with less steric hindrance [4]. Other organosulfurs with more steric hindrance and refractory index such as benzothiophene and its derivatives could not be fully reduced by hydrodesulfurization. Therefore, it is desirable to carry out desulfurization with relatively mild conditions which could reduce all organosulfur compounds in the fuel. Other alternative processes for desulfurization has been used, such as biodesulfurization, selective adsorption and oxidative desulfurization (ODS) [5]. Oxidative desulfurization is a well known desulfurization method which can reduce benzothiophene and its derivatives. The advantages

of oxidative desulfurization compared with hydrodesulfurization can be explained such as no consumption of H<sub>2</sub> and operational under mild conditions in the presence of catalysts [6]. However, for academical and industrial application, oxidative desulfurization still provides a challenge to be developed especially for catalyst. The reaction system of oxidative desulfurization is conducted in non-acidic media and transition metals catalyst based on Mo, W or V. These catalysts are also used as monocatalyst or supported with various supports [7].

Polyoxometalates (POMs) are metal-oxygen clusters with various shapes, oxidation states, acid-base properties and redox activities. Polyoxometalates have sustainable use for both acid-base and oxidation-reduction catalysts. These various advantages properties are due to design and tune of structure at molecular or atomic level. Polyoxometalates are used intensively as acid base or reduction oxidation catalysts in wide range of organic synthesis [8,9]. Several polyoxometalates are reported for oxidative desulfurization of dibenzothiophenes such as  $H_3PW_xMo_{12-x}O_{40}$  ( $x = 1, 3, 6$ ),  $C_{8.25}H_{0.5}PW_{12}O_{40}$  and  $H_3PW_{12}O_{40}$  with reusable and catalytic activity similar with fresh catalyst [10]. Anderson type of polyoxometalate  $[(C_{18}H_{37})_2N(CH_3)_2]_3Co(OH)_6Mo^{(V,VI)}_6O_{18}$  shows higher catalytic activity in aerobic oxidative desulfurization with high turnover number. The order of desulfurization decreases in the order of 4,6-dimethyl dibenzothiophene > dibenzothiophene > benzothiophene [11]. Polyoxometalate encapsulated with metal organic framework

that called "PW<sub>12</sub>MIL-101" was also effective for desulfurization of organosulfur such as dibenzothiophene and 4,6-dimethyl dibenzothiophene with three times recycled catalyst [12]. On the other hand, tungsten, which has been used as starting material for polyoxometalate synthesis also shows catalytic activity after depositing tungsten on resin D152. These catalysts showed catalytic ability until 7 times reused for desulfurization of dibenzothiophene. However, tungsten-containing catalyst could also be used as potential metal for desulfurization of various organosulfur compounds.

Herein, polyoxometalate H<sub>3</sub>[α-PW<sub>12</sub>O<sub>40</sub>] containing tungsten as addenda atom was used for desulfurization of benzothiophene after supported with silica to form H<sub>3</sub>[α-PW<sub>12</sub>O<sub>40</sub>]/Si solid catalyst. Our group also reported desulfurization of benzothiophene using polyoxometalate [13] and polyoxometalate supported zirconia as efficient catalysts [14]. Silica oxide is a relatively inert oxides which can support other materials after impregnation, encapsulation, or sintering processes [15]. H<sub>3</sub>[α-PW<sub>12</sub>O<sub>40</sub>]/Si solid catalyst was prepared easily through wet impregnation process following characterization using FTIR analysis, SEM measurement, X-ray diffraction and porosity analysis using N<sub>2</sub> adsorption desorption. Catalyst H<sub>3</sub>[α-PW<sub>12</sub>O<sub>40</sub>]/Si exhibit high catalytic activity toward benzothiophene under mild reaction conditions.

## EXPERIMENTAL

Chemicals which were used are purchased, such as benzothiophene (Sigma Aldrich), sodium tungsten (Merck), sodium hydrogen phosphate (Merck), hydrochloric acid (Merck), diethyl ether (Merck) and methanol (Merck).

Infrared spectra was recorded in KBr disc on FT-IR Shimadzu Pestic-21 Spectrophotometer at 4000-300 cm<sup>-1</sup>. X-ray powder pattern was collected from Shimadzu Lab X Type 6000 diffractometer. Data was acquired over 2θ range of 0-90° at scanning speed of 1° min<sup>-1</sup>. The surface morphology of catalyst was performed using JEOL JED-2300 SEM analysis station. Porosity analysis was carried out using Autosorb iQ automated gas sorption analyzer Quantachrome. Gas chromatography (GC) equipped with a RTX-1 capillary column using FID detector was used for reaction monitoring.

**Synthesis of H<sub>3</sub>[α-PW<sub>12</sub>O<sub>40</sub>] and characterization:** A sodium tungstate (125 g) and 20 g of disodium phosphate were dissolved in 187.5 mL of boiling water. A concentrated hydrochloric acid (100 mL) was added dropwise with constant stirring. Phosphotungstic acid begins to separate when about half of acid is added. When the solution has cooled, diethyl ether (75 mL) was added. After shaking, three layers remain and a little amount of water was added to dissolve the remaining of sodium chloride. The acid-ether complex in the lower layer was collected following the evaporation and recrystallization using water to produce H<sub>3</sub>[α-PW<sub>12</sub>O<sub>40</sub>] [16]. Polyoxometalate was characterized using FT-IR spectroscopy and X-ray powder analysis.

**Synthesis of H<sub>3</sub>[α-PW<sub>12</sub>O<sub>40</sub>]/Si and characterization:** Synthesis of H<sub>3</sub>[α-PW<sub>12</sub>O<sub>40</sub>]/Si was carried out according to Newman *et al.* [17] with slight modification as follows: 1 g of H<sub>3</sub>[α-PW<sub>12</sub>O<sub>40</sub>] was dissolved in 50 mL of methanol to be clear solution. Silica powder (2.5 g) was added in the solution with

slow stirring for 0.5 h. The resulting mixture was kept overnight followed by evaporation using rotary evaporator. White powder crystal was collected and dried at 120 °C. Characterization of catalyst was performed using FT-IR, X-ray powder analysis, morphology analysis by SEM and porosity analysis.

**Oxidation of benzothiophene:** Oxidation of benzothiophene was carried out according to Yu *et al.* [18] with slight modification as follows: in 100 mL of Schlenk flask, 0.1 g of benzothiophene was dissolved in 5 mL of hexane and 0.1 g catalyst along with 0.5 mL of H<sub>2</sub>O<sub>2</sub> were added slowly into a flask. The mixture was stirred for 3 h at 40 °C. Reaction was monitored using GC with RTX-1 capillary column equipped with FID detector. Oxidation of benzothiophene was investigated deeply through reaction time, weigh of catalyst and temperature oxidation.

## RESULTS AND DISCUSSION

**Catalysts preparation and characterization:** Oxidation of benzothiophene using hydrogen peroxide catalyzed by H<sub>3</sub>[α-PW<sub>12</sub>O<sub>40</sub>]/Si is presented in Fig. 1.

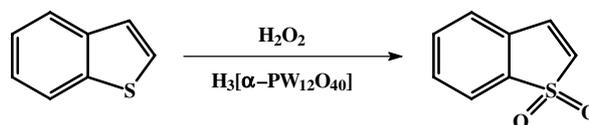


Fig. 1. Oxidation of benzothiophene using H<sub>2</sub>O<sub>2</sub> as green oxidant

Hydrogen peroxide was selected as green oxidant in this research due to formation of water as green by-product in the reaction. Hydrogen peroxide is a relatively mild oxidant compared to several other oxidant agents such as potassium permanganate, potassium dichromate or nitric acid, thus oxidation process using hydrogen peroxide should be activated by catalyst. In industrial process, oxidation of benzothiophene was carried out under high pressure and temperature [19]. In order to obtain mild conditions, the role of catalyst is the main object to explore. We applied catalyst based on tungsten such as polyoxometalate compound H<sub>3</sub>[α-PW<sub>12</sub>O<sub>40</sub>] and polyoxometalate supported metal ion H<sub>3</sub>[α-PW<sub>12</sub>O<sub>40</sub>]/Si for desulfurization of benzothiophene. Polyoxometalates H<sub>3</sub>[α-PW<sub>12</sub>O<sub>40</sub>] and H<sub>3</sub>[α-PW<sub>12</sub>O<sub>40</sub>]/Si were characterized firstly using FTIR spectroscopy and the spectrum is presented in Fig. 2.

Specific vibration of polyoxometalate H<sub>3</sub>[α-PW<sub>12</sub>O<sub>40</sub>] was observed in wavelength 1080 cm<sup>-1</sup> ν(P-O), 987 cm<sup>-1</sup> (W=O), 895 cm<sup>-1</sup> (W-Oc-W) and 802 cm<sup>-1</sup> (W-Oe-W) [20]. Supported polyoxometalate H<sub>3</sub>[α-PW<sub>12</sub>O<sub>40</sub>]/Si also indicated the same vibration, with parent additional vibration of Si-O which appeared at wavelength 463 cm<sup>-1</sup>. All these vibrations are summarized in Table-1.

Polyoxometalates are metal-oxygen crystal, which was easily identified using X-ray powder analysis. In this research, we attempt to analyze diffraction pattern of polyoxometalate and supported polyoxometalate. The X-ray diffraction pattern of H<sub>3</sub>[α-PW<sub>12</sub>O<sub>40</sub>], SiO<sub>2</sub> and H<sub>3</sub>[α-PW<sub>12</sub>O<sub>40</sub>]/Si is shown in Fig. 3.

Diffraction pattern in Fig. 3 shows the high crystallinity of both polyoxometalate H<sub>3</sub>[α-PW<sub>12</sub>O<sub>40</sub>] (Fig. 3A) and H<sub>3</sub>[α-PW<sub>12</sub>O<sub>40</sub>]/Si (Fig. 3C), in contrast with silica which has sharp peak around 30°. The X-ray powder diffraction of supported

TABLE-1  
VIBRATION OF POLYOXOMETALATE  $H_3[\alpha-PW_{12}O_{40}]$  AND  $H_3[\alpha-PW_{12}O_{40}]/Si$

Catalyst	$\nu(P-O)$ ( $cm^{-1}$ )	$W=O$ ( $cm^{-1}$ )	$W-Oc-W$ ( $cm^{-1}$ )	$W-Oe-W$ ( $cm^{-1}$ )	$Si-O$ ( $cm^{-1}$ )
$H_3[\alpha-PW_{12}O_{40}]$	1080	987	895	802	–
$H_3[\alpha-PW_{12}O_{40}]/Si$	1080	987	895	802	463

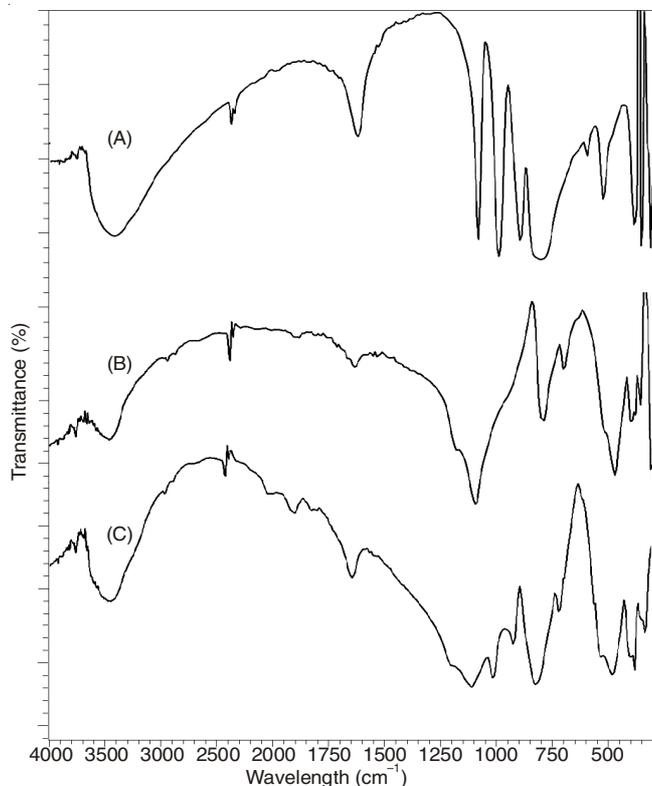


Fig. 2. FTIR spectrum of  $H_3[\alpha-PW_{12}O_{40}]$  (A),  $SiO_2$  (B) and  $H_3[\alpha-PW_{12}O_{40}]/Si$  (C)

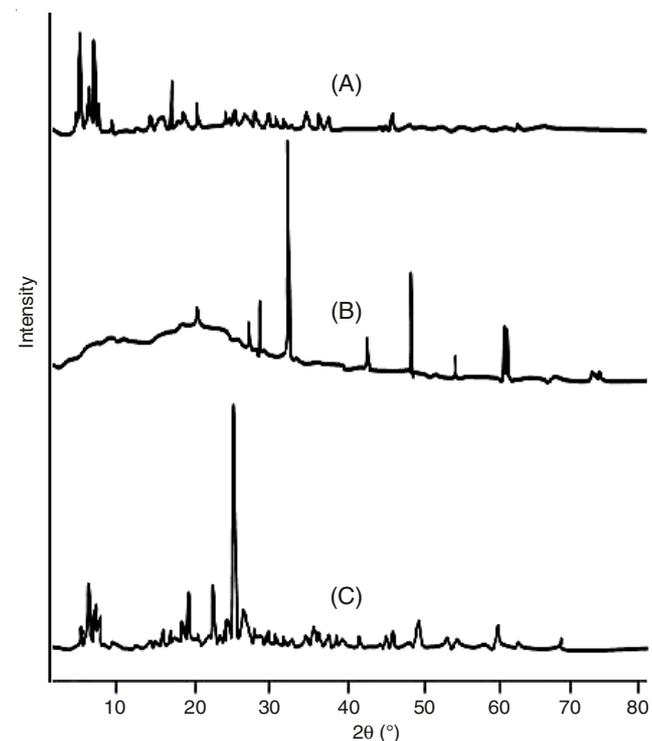


Fig. 3. XRD powder pattern of  $H_3[\alpha-PW_{12}O_{40}]$  (A),  $SiO_2$  (B) and  $H_3[\alpha-PW_{12}O_{40}]/Si$  (C)

polyoxometalate  $H_3[\alpha-PW_{12}O_{40}]/Si$  indicated sharp peak at  $2\theta$  less than  $10^\circ$ , which has polyoxometalate species and several sharp peaks around  $2\theta$   $20-30^\circ$ , which has oxide species. These peaks can be acceptable for polyoxometalate supported metal ion [21]. Polyoxometalate  $H_3[\alpha-PW_{12}O_{40}]$  was successfully supported with silica according to this powder pattern. Thus catalyst  $H_3[\alpha-PW_{12}O_{40}]/Si$  can be applied for desulfurization of benzothiophene in this research.

To emphasize the characterization data, we measure morphology of  $H_3[\alpha-PW_{12}O_{40}]$  and  $H_3[\alpha-PW_{12}O_{40}]/Si$  using SEM and porosity using BET analysis. The SEM photo of  $H_3[\alpha-PW_{12}O_{40}]$ ,  $H_3[\alpha-PW_{12}O_{40}]/Si$  and porosity data was presented in Fig. 4 and Table-2, respectively.

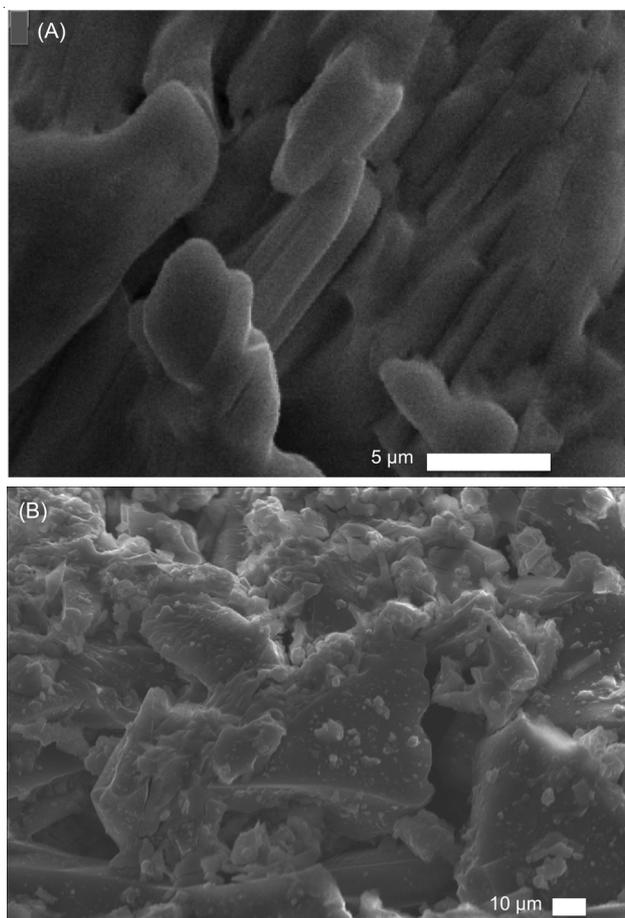


Fig. 4. Morphology of  $H_3[\alpha-PW_{12}O_{40}]$  (A) and  $H_3[\alpha-PW_{12}O_{40}]/Si$  (B)

TABLE-2  
TEXTURAL PROPERTIES OF CATALYST  
( $N_2$  PHYSISORPTION DATA)

Catalyst	Surface area ( $S_{BET}$ , $m^2/g$ )	Pore volume ( $V_{BJH}$ , $cm^3/g$ )	Pore diameter ( $\phi_{BJH}$ , nm)
$H_3[\alpha-PW_{12}O_{40}]$	1.82	0.009	6.29
$H_3[\alpha-PW_{12}O_{40}]/Si$	11.76	0.017	2.70

Morphology of catalyst as shown in Fig. 4 indicated the changes of morphology structure and particle size distribution of catalyst after supported silica was observed. Smaller particles indicated supported silica with agglomeration process and the irregular shapes are formed. The photo of catalysts in Fig. 4 is related with nitrogen adsorption desorption data in in Table-2.

The textural properties of  $H_3[\alpha-PW_{12}O_{40}]$  and  $H_3[\alpha-PW_{12}O_{40}]/Si$  such as surface area, pore volume and pore diameter are shown in Table-2. The results showed that surface area and pore volume of catalysts after supported silica was increasing in the same order suggest the successful of supported process. These results were also familiar with morphology of catalyst after support with silica with morphologies changes of catalyst.

**Catalytic properties:** We investigated the catalytic reaction properties of  $H_3[\alpha-PW_{12}O_{40}]$  and  $H_3[\alpha-PW_{12}O_{40}]/Si$  toward oxidation of benzothiophene using  $H_2O_2$  as green oxidant. In the beginning results using 0.1 g of benzothiophene, 0.1 g catalyst and 0.5 mL  $H_2O_2$  resulted both  $H_3[\alpha-PW_{12}O_{40}]$  and  $H_3[\alpha-PW_{12}O_{40}]/Si$  to have catalytic activity. Per cent conversion of benzothiophene using  $H_3[\alpha-PW_{12}O_{40}]$  and  $H_3[\alpha-PW_{12}O_{40}]/Si$  was 91.8 and 99.7 %, respectively. The oxidation reaction profile of benzothiophene using  $H_3[\alpha-PW_{12}O_{40}]/Si$  as catalyst is shown in Fig. 5.

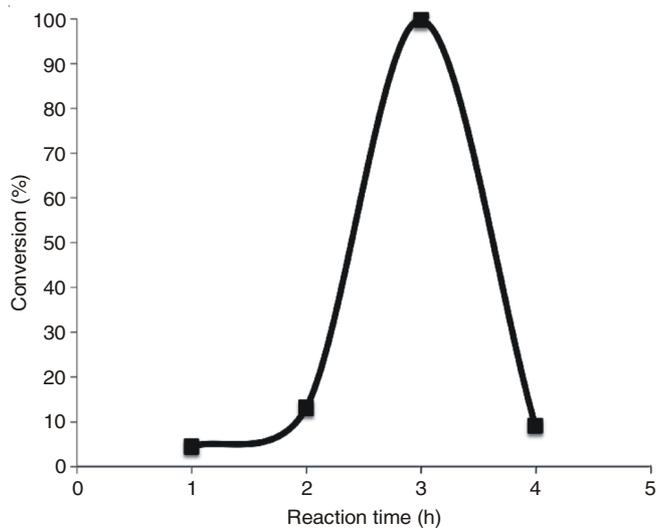


Fig. 5. Oxidation of benzothiophene using  $H_2O_2$  and  $H_3[\alpha-PW_{12}O_{40}]/Si$  catalyst

Oxidation of benzothiophene at initial time was relatively low and increase slowly by increasing reaction time (Fig. 5). Reaction sharply increased after more than 2 h of reaction time and up to 99 % at 3 h. By increasing reaction time to 4 h, reaction has decreased to initial reaction time. This could be attributed to the further oxidation of product into formation of several by-products. We analyzed the chromatogram of reaction after 4 h oxidation and found other peaks. This oxidation reaction was truly heterogeneous when we stop the reaction at 2 h and obtained white solid catalyst in the reaction mixture. The white solid catalyst of  $H_3[\alpha-PW_{12}O_{40}]/Si$  after 2 h reaction was identified using FTIR spectroscopy as shown in Fig. 6.

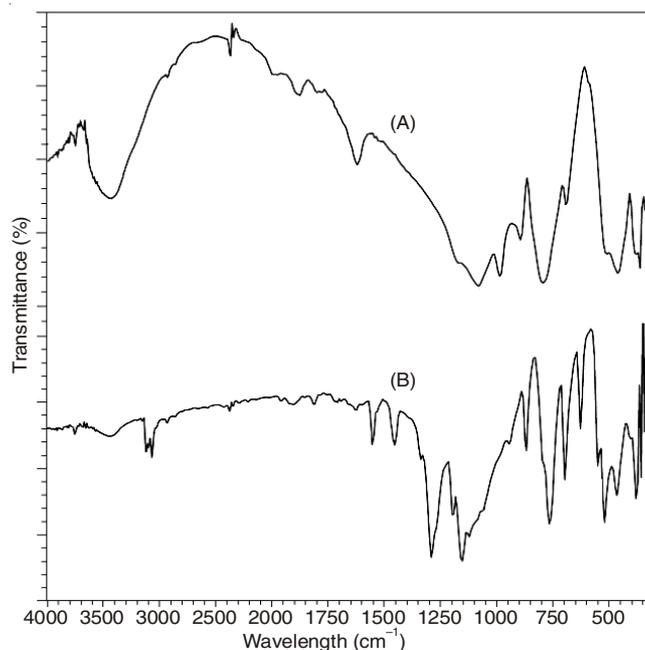


Fig. 6. FTIR spectrum of fresh catalyst (A) and after reaction 2 h (B)

Characteristic peaks were observed for  $H_3[\alpha-PW_{12}O_{40}]/Si$  after oxidation of benzothiophene for 2 h. Other vibrations appeared, which were related to vibration of benzothiophene. According to FTIR data, the frame structure of polyoxometalate  $H_3[\alpha-PW_{12}O_{40}]$  was well kept and stable under the oxidation reaction condition. The above results indicated the possibility of catalyst to be used again.

Several parameters affecting oxidation of benzothiophene such as weight of catalyst and temperature were investigated as follows.

The oxidation of benzothiophene was carried out under various weight of fresh catalyst  $H_3[\alpha-PW_{12}O_{40}]/Si$  in the range of 0.05 to 0.25 g. The weight result of catalyst effect on the benzothiophene conversion is shown in Fig. 7. In general, conversion of benzothiophene decreased by increased weight of catalyst. When the amount of catalyst increased from 0.05 to 0.1 g, the conversion of benzothiophene decreased sharply from 99 to 12 %. The linear phenomenon was observed in the increasing of catalyst until 0.25 g but with slight changes. Therefore, the catalyst weight 0.05 g was preferable for oxidation of benzothiophene using  $H_3[\alpha-PW_{12}O_{40}]/Si$ .

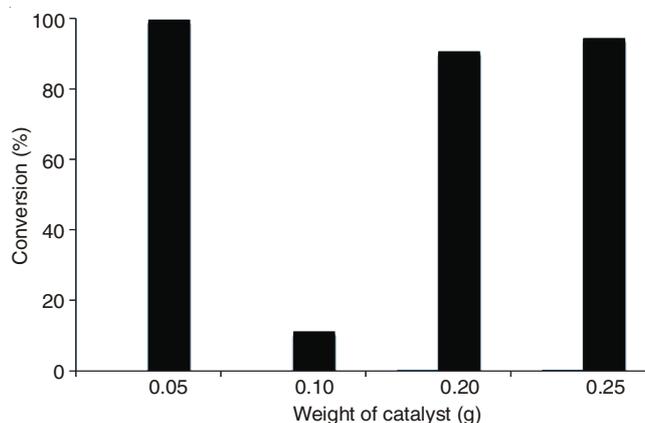


Fig. 7. Oxidation of benzothiophene under various weights of catalyst

The oxidation of benzothiophene was investigated on temperature effect. Fig. 8 shows effect of temperature on oxidation of benzothiophene under given conditions.

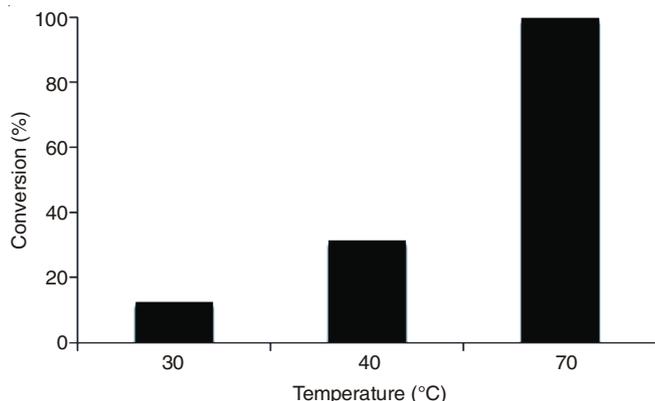


Fig. 8. Oxidation of benzothiophene using  $H_3[\alpha-PW_{12}O_{40}]/Si$  at various temperatures

When reaction was carried out at 30 and 40 °C, conversion of benzothiophene was relatively low (13-32 %). It can be explained that oxidation should be carried out at higher temperature to achieve enough activation energy for oxidation. We found that temperature at 70 °C could convert benzothiophene up to 99 % and benzothiophene oxidized totally. Thus the optimal oxidation of benzothiophene using catalyst  $H_3[\alpha-PW_{12}O_{40}]/Si$  was found at 70 °C.

### Conclusion

Catalyst  $H_3[\alpha-PW_{12}O_{40}]/Si$  was successfully prepared and characterized. Catalytic test of  $H_3[\alpha-PW_{12}O_{40}]/Si$  into oxidation of benzothiophene showed that  $H_3[\alpha-PW_{12}O_{40}]/Si$  has higher catalytic activity than  $H_3[\alpha-PW_{12}O_{40}]$ . Oxidation process toward benzothiophene under mild reaction conditions was optimal at temperature 70 °C. Weight of catalyst was 0.05 g using  $H_2O_2$  as green oxidant results conversion of benzothiophene to corresponding sulfone up to 99%.

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