

Catalytic Desulfurization of Benzothiophene Using Keggin Type Polyoxometalates as Catalyst

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ABSTRACT

Performance of catalytic desulfurization of benzothiophene (BT) was studied using polyoxometalates as catalyst. Polyoxometalates $H_3[\alpha-PW_{12}O_{40}]$ and $H_4[\alpha-SiW_{12}O_{40}]$, have different heteroatom in Keggin structure and catalytic activities. Polyoxometalates $H_3[\alpha-PW_{12}O_{40}]$ and $H_4[\alpha-SiW_{12}O_{40}]$ have high crystallinity with homogeneous distribution particles. Desulfurization of BT using polyoxometalates $H_3[\alpha-PW_{12}O_{40}]$ and $H_4[\alpha-SiW_{12}O_{40}]$ resulted % conversion up to 99% for 3 h reaction time and at temperature 40 °C. Application of polyoxometalates $H_3[\alpha-PW_{12}O_{40}]$ and $H_4[\alpha-SiW_{12}O_{40}]$ for crude oil desulfurization showed % conversion of 4.19-88.38%. The main functional groups of polyoxometalates still retained after catalytic desulfurization indicated the stability of polyoxometalate compounds.

Key word: desulfurization, benzothiophene, Keggin type polyoxometalate, oxidation, catalytic reaction

INTRODUCTION

Desulfurization of fuel oil has become an increasingly important research due to environmental problem [1]. Sulfur compound in environment is derived from fuel oil containing sulfur compounds such as polysulfides, mercaptans, disulphides, thiophenes, and benzothiophenes [2]. Nowadays, sulfur level in the fuel oil is limited until 10 ppm [3]. Hydrodesulfurization is a traditional method, recently is used for petroleum refinery industry [4]. This reaction is operated at high temperature reaction and high hydrogen pressure using molybdenum-based catalysts, which is very expensive. Thus, alternative desulfurization processes are still developed until now for lowering the operational cost [5]. Oxidative desulfurization is being considered to be one of the most promising processes, which is mostly operated at mild condition. Xu et.al (2014) reported ultra-deep desulfurization was achieved using peroxophosphomolybdate catalysts with regeneration of catalysts [6]. A similar phenomenon was conducted by Chamack et.al (2014), they used tungsten-substituted molybdophosphoric acid as efficient catalyst for desulfurization [7]. On the other hand, mesoporous silica such as MCM-41, MCM-48, and SBA-15 was applied as catalyst for desulfurization of dibenzothiophene and 4,6-dimethyl dibenzothiophene using t-butyl hydroperoxide as oxidant [8]. However, catalyst still plays a key role for desulfurization of fuel oil. Catalyst based on polyoxometalate compounds has been investigated deeply for fuel

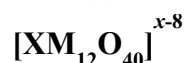
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oil desulfurization due to its beneficiary's characteristics such as acidity, oxygen transfer ability, various structures, and redox properties [9-14]. Keggin type polyoxometalate $[XM_{12}O_{40}]^{x-8}$ possess a heteroatom X and addenda atom M, it is well known for its polyoxometalate structure.

In this report, we synthesized and characterized Keggin type polyoxometalates $H_3[\alpha-PW_{12}O_{40}]$ and $H_4[\alpha-SiW_{12}O_{40}]$ to evaluate performance of these polyoxometalate for desulfurization of benzothiophene using H_2O_2 as green oxidant. Our study also reported the resistance structure of polyoxometalate after reaction, which is one of the beneficial outcomes, resulted from our work.

Figure 1. Keggin type Polyoxometalate (right). X = heteroatom, X = oxidation state, and M = addenda atom



EXPERIMENT

Chemicals

Chemical reagents were used after purchased such as benzothiophene (BT) (Aldrich), hydrogen peroxide (Merck), sodium tungsten (Merck), sodium meta silicate (Aldrich), sodium metavanadate (Aldrich), hydrochloric acid (Fluka) and hexane (Merck). Crude fuel oil was obtained from Banyuasin district area of South Sumatera, Indonesia.

Physical measurements

FTIR spectra were recorded in KBr disc on a Shimadzu 8201PC spectrophotometer in the range $300-4000\text{ cm}^{-1}$. The XRD pattern was collected from Shimadzu Lab X type 6000 diffractometer and the data were collected over 2θ range of $0-90^\circ$ at scanning speed of $^\circ\text{ min}^{-1}$. SEM photo analysis was performed using JED-2300 SEM analysis station. GC was performed using Shimadzu 2010 plus equipped with Restex RTX-1 Column and FID detector.

Polyoxometalates (POM) preparation

Polyoxometalates $H_3[\alpha-PW_{12}O_{40}]$ and $H_4[\alpha-SiW_{12}O_{40}]$ were synthesized and characterized according to literatures [15-16].

Catalyst characterization

Polyoxometalates catalysts were characterized using FTIR spectroscopy in KBr disc, X-Ray powder diffractometer, and surface photo profile using SEM analysis

Oxidative desulfurization test

The model fuel oil containing sulfur compound (BT) 0.1 g was place into 100 mL Schlenk flask equipped with magnetic bar. Thus 5 mL hexane, 0,5 mL H_2O_2 30% wt, and 0.05 g catalyst were dropped into a flask. The mixture was stirred for 3 h at 70°C . Desulfurization process was monitored using GC with RTX-1 column equipped with FID detector. The conversion of DBT was calculated to see performance of polyoxometalates

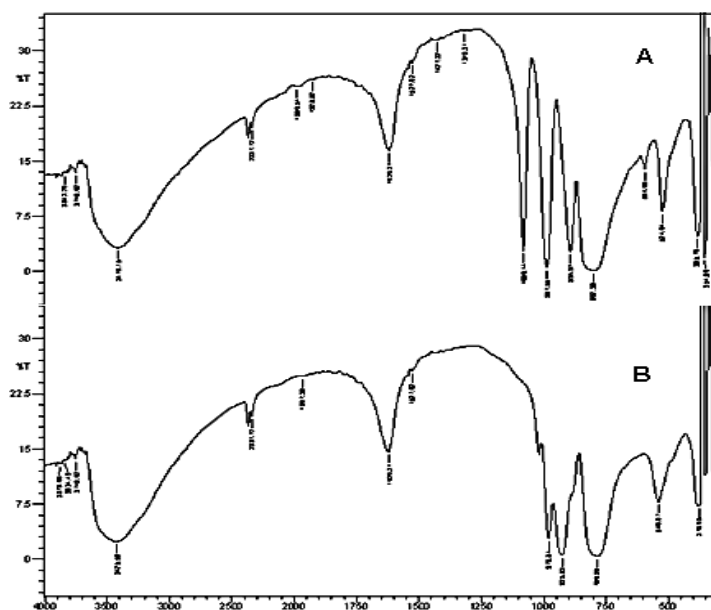
catalysts using equation 1, in which Co is initial concentration of BT, and Ct is final concentration of BT.

$$\% \text{ Conversion} = [(Co-Ct)/Co] \times 100\% \quad (1)$$

RESULT AND DISCUSSION

The FTIR spectrum of polyoxometalates $H_3[\alpha-PW_{12}O_{40}]$ and $H_4[\alpha-SiW_{12}O_{40}]$ is shown in Figure 2.

Figure 2. FTIR spectrum of $H_3[\alpha-PW_{12}O_{40}]$ (A) and $H_4[\alpha-SiW_{12}O_{40}]$ (B)



The FTIR spectrum of $H_3[\alpha-PW_{12}O_{40}]$ shows bands at 1620 cm^{-1} (νOCO), 987 cm^{-1} ($\nu\text{W=O}$), 894 cm^{-1} ($\nu\text{W-Oe-W}$), 802 cm^{-1} ($\nu\text{W-Oc-W}$), 1080 cm^{-1} ($\nu\text{P-O}$). These vibration bands are similar with polyoxometalate $H_4[\alpha-SiW_{12}O_{40}]$, which has vibration at 1620 cm^{-1} (νOCO), 979 cm^{-1} ($\nu\text{W=O}$), 786 cm^{-1} ($\nu\text{W-Oe-W}$), 925 cm^{-1} ($\nu\text{Si-O}$), and 880 cm^{-1} ($\nu\text{W-Oc-W}$). These polyoxometalates are Keggin type which have similar bands, they only different on heteroatom species. These Keggin type polyoxometalate have specific vibration bands according to literatures [17].

XRD powder patterns of polyoxometalates $H_3[\alpha-PW_{12}O_{40}]$ and $H_4[\alpha-SiW_{12}O_{40}]$ are shown in Figure 3.

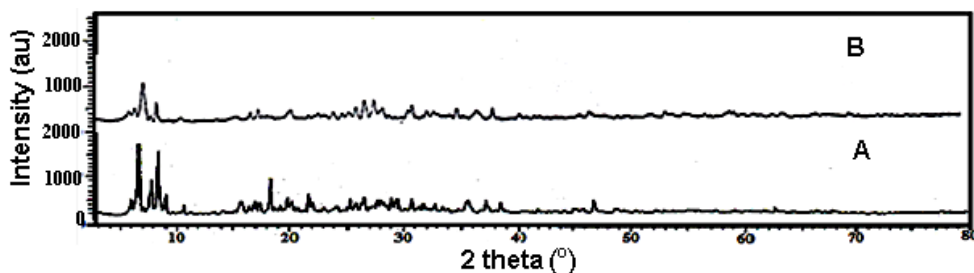


Figure 3. XRD powder pattern of $H_3[\alpha-PW_{12}O_{40}]$ (A) and $H_4[\alpha-SiW_{12}O_{40}]$ (B)

Both Keggin type and Dawson type of polyoxometalates have intense diffraction peaks at small angle, which corresponds to the crystal structure of high crystallinity polyoxometalate. The XRD patterns, which are shown in Figure 2 also revealed that both Keggin type and Dawson type polyoxometalates have a different number of water molecules.

The difference is indicated by the diffraction at angle above 10 deg. There is no water molecules effect is found the crystallization system of polyoxometalates, but it gave a small effect to the cell unit dimension for both the Keggin type polyoxometalate. For further future application of polyoxometalates as catalyst, the water of crystallization will not have an effect on the catalytic system.

Figure 4 shows SEM images of polyoxometalate $H_3[\alpha-PW_{12}O_{40}]$ and $H_4[\alpha-SiW_{12}O_{40}]$. The SEM images indicate some stick homogeneous morphology were found in polyoxometalate $H_3[\alpha-PW_{12}O_{40}]$. While the $H_4[\alpha-SiW_{12}O_{40}]$ particle is seen as a block shape with small particles appeared in the surface. In this study, we found that all morphology of these polyoxometalates is affected by the synthetic technique. Other than that, we also found all of them have particle size distribution above 100 nm.

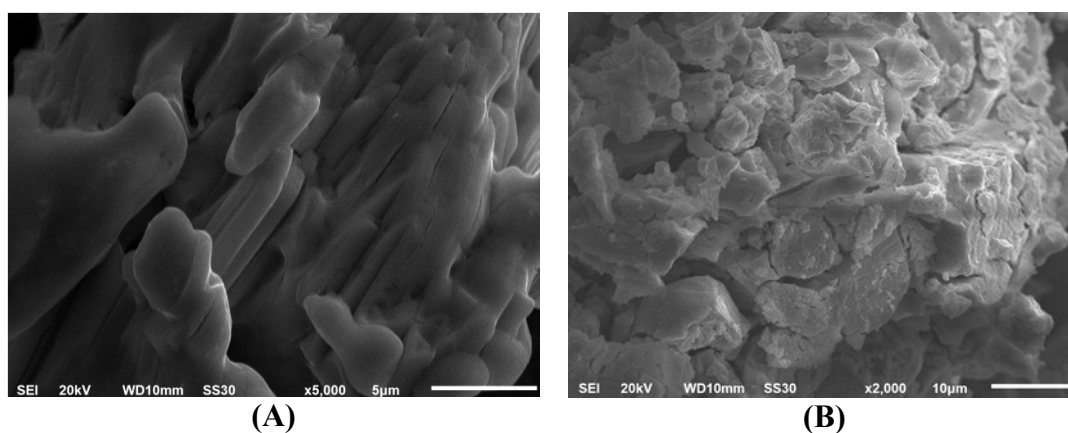


Figure 4. SEM profile of $H_3[\alpha-PW_{12}O_{40}]$ (A) and $H_4[\alpha-SiW_{12}O_{40}]$ (B)

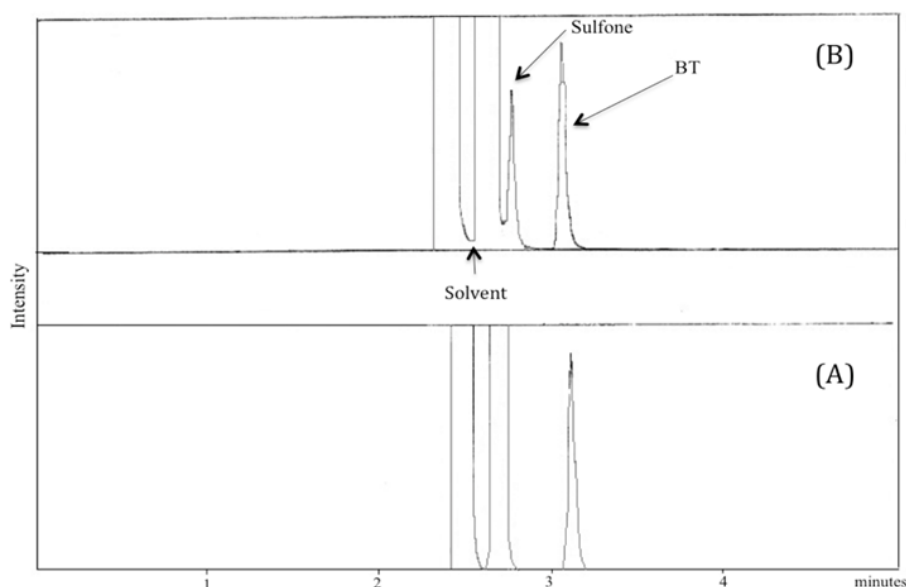
Polyoxometalates $H_3[\alpha-PW_{12}O_{40}]$ and $H_4[\alpha-SiW_{12}O_{40}]$ are used as oxidative desulfurization catalysts for processing benzothiophene to sulfone under mild conditions. The conversion percentages are shown in Table 1 and show a yield conversion up to 99%.

Table 1. Conversion of benzothiophene using polyoxometalates as catalysts

No	Polyoxometalate	% Conversion
1	$H_3[\alpha-PW_{12}O_{40}]$	91.75
2	$H_4[\alpha-SiW_{12}O_{40}]$	99.67

Wang et.al (2014) reported that desulfurization of benzothiophene can be carried out easily at mild condition in range of temperature of 60-80 °C. Regarding the temperature being used, this report has some slight similar finding to our work [8]. Moreover, chromatogram of oxidative desulfurization of benzothiophene using catalyst $H_3[\alpha-PW_{12}O_{40}]$ is shown in Figure 5. This result indicate that selective desulfurization was found in our work. The desulfurization process affords only sulfone as the main product.

Figure 5.
Chromatogram
desulfurization of
benzothiophene
using catalyst
 $H_3[\alpha-PW_{12}O_{40}]$
(A) at 0 h and (B)
after reaction for
1 h.



Similar condition was applied for oxidative desulfurization of benzothiophene in crude fuel oil. Crude fuel oil used in this study was obtained from traditional exploration in Banyuasin, South Sumatera, Indonesia. Analysis using GC showed that crude fuel oil contains benzothiophene, dibenzothiophene, and 4,6-dimethyl dibenzothiophene. We decided to focus on the reduction of dibenzothiophene in the real fuel oil sample using polyoxometalates catalyst. The results are presented in Table 2.

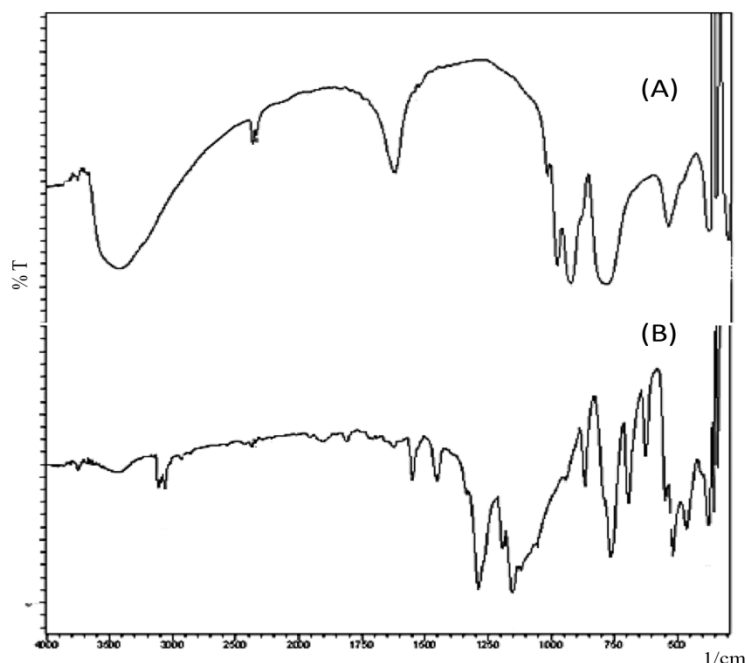
Table 2. Desulfurization of crude fuel oil

No	Polyoxometalate	% Conversion
1	$H_3[\alpha-PW_{12}O_{40}]$	88.38
2	$H_4[\alpha-SiW_{12}O_{40}]$	4.190

The result (Table 2) shows that polyoxometalate $H_3[\alpha-PW_{12}O_{40}]$ can convert benzothiophene in real sample in 88.38%, while polyoxometalate $H_4[\alpha-SiW_{12}O_{40}]$ convert dibenzothiophene up to 4%. A possible reasoning for these difference results is more likely due to the steric hindrance in the real crude fuel sample. Additionally, it has been reported as well that the acidity of polyoxometalate $H_3[\alpha-PW_{12}O_{40}]$ in acetone at 298 K is 1.6 (pK1), 3.0 (pK2), and 3.98 (pK3) while $H_4[\alpha-SiW_{12}O_{40}]$ has acidity 2.0 (pK1), 3.61 (pK2), and 5.3 (pK3) [18]. Thus polyoxometalate $H_3[\alpha-PW_{12}O_{40}]$ has higher acidity than $H_4[\alpha-SiW_{12}O_{40}]$. Therefore, considering the acidity of catalysts, then the Keggin structure of polyoxometalate after oxidative desulfurization of benzothiophene is investigated deeply using FTIR spectrophotometer and the results is shown in Figure 6.

FTIR spectrum in Figure 5 showed that polyoxometalate $H_3[\alpha-PW_{12}O_{40}]$ has all vibration similarity to the fresh catalyst. Only a small shift specific vibration of $H_3[\alpha-PW_{12}O_{40}]$ was detected. Some new vibrations appeared in the sample which indicated aromatic and C-H organic moiety that were detected at wave numbers of 1550, 1450, and 2924 cm^{-1} . Thus, we believe that the reuse heterogeneous catalytic system can be performed using polyoxometalate $H_3[\alpha-PW_{12}O_{40}]$ and $H_4[\alpha-SiW_{12}O_{40}]$.

Figure 6. FTIR spectrum of polyoxometalate $H_3[\alpha-PW_{12}O_{40}]$ before desulfurization (A) and after desulfurization of benzo thiophene (B).



CONCLUSION

Polyoxometalates $H_3[\alpha-PW_{12}O_{40}]$ and $H_4[\alpha-SiW_{12}O_{40}]$ were successfully synthesized and characterized. The use of polyoxometalates $H_3[\alpha-PW_{12}O_{40}]$ and $H_4[\alpha-SiW_{12}O_{40}]$ as catalysts for desulfurization of benzo thiophene can superficially convert benzo thiophene up to 99% under mild condition. Desulfurization of crude fuel oil using $H_3[\alpha-PW_{12}O_{40}]$ and $H_4[\alpha-SiW_{12}O_{40}]$ resulted % conversion up to 88%. This results show the high activity of polyoxometalates $H_3[\alpha-PW_{12}O_{40}]$ and $H_4[\alpha-SiW_{12}O_{40}]$ as catalysts for desulfurization of sulfur in fuel oil.

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