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Research Article

Facile Oxidative Desulfurisation of Benzothiophene Using Polyoxometalate $H_4[\alpha-SiW_{12}O_{40}]/Zr$ Catalyst

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Abstract

A highly active catalyst $H_4[\alpha-SiW_{12}O_{40}]/Zr$ based polyoxometalate Keggin type was prepared by wet impregnation method and was characterized by FTIR spectroscopy, X-ray diffractometer, surface textural property by SEM, and analysis of porosity by BET method. $H_4[\alpha-SiW_{12}O_{40}]/Zr$ was successfully synthesized and showed uniform properties with block solid structure which was applied as heterogeneous stable catalyst for oxidative desulfurization of benzothiophene under simple and mild condition using H_2O_2 as oxidant. Facile conversion of benzothiophene to sulfone by using heterogeneous $H_4[\alpha-SiW_{12}O_{40}]/Zr$ catalyst up to 99% was observed to show the active catalytically. Keggin $H_4[\alpha-SiW_{12}O_{40}]/Zr$ cage structure after reaction was different from fresh catalyst which was indicated by the instability of $H_4[\alpha-SiW_{12}O_{40}]/Zr$ under reaction condition. © 2015 BCREC UNDIP. All rights reserved

Keywords: polyoxometalate; desulfurization; benzothiophene; Keggin type; $H_4[\alpha-SiW_{12}O_{40}]/Zr$

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1. Introduction

Sulfur compound is well known being present in fuel and also contribute as the source of air pollution. Sulfur gas, SO_x , is generated from combustion of various activities that use oil fuel such as vehicle engines and factories. Thus, the low content of sulfur in the oil fuel is needed, and the sulfur content has been agreed worldwide have to be less than 10 ppm [1]. Tra-

ditional method to decrease sulfur content in oil fuel is hydrodesulfurization process [2]. In this method, high hydrogen pressure, high temperature reaction, and molybdenum based catalysts are used [3]. These conditions are used in refinery petroleum companies until this time but reaction under mild condition is preferred due to safety conditions. Recently, oxidative desulfurization is still developed in order to decrease sulfur content in fuel. By using oxidative desulfurization process, reaction condition could easily be controlled not only in factory but also in the laboratory under mild condition

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with no hydrogen requirement [4]. In the oxidative desulfurization, sulfur removed by two steps. First step is oxidation of sulfur to sulfone and the next step is removal of these compounds by extraction, adsorption, distillation, or decomposition [5]. Catalyst in the oxidative desulfurization is playing a key role, studies in depth for exploring the roles still under investigation until now.

Polyoxometalates are metal-oxygen cluster with various structures. They have unique acid properties and redox activities. Catalytic using Keggin and Dawson types polyoxometalates as catalyst has been reported in various organic reactions including oxidative desulfurization [2]. Keggin type of polyoxometalates $H_3PW_xMo_{12-x}O_{40}$ ($x=1, 3, 6$) and $H_3PW_{12}O_{40}$ have high catalytic activity for oxidative desulfurization with desulfurization efficiency of 99.79% under hydrogen peroxide [7]. In order to improve the catalytic activity in heterogeneous system and stability of the Keggin type polyoxometalate $H_4[a-SiW_{12}O_{40}]$ which has indicated from specific surface area and porosity, we support $H_4[a-SiW_{12}O_{40}]$ with zirconium by wet impregnation, thus these material is applied for oxidative desulfurization of benzothiophene as sulfur compound model under mild conditions. Zirconium was selected as the support due to its acid properties and unique physico-chemical properties for organic reactions and transformations [8]. Furthermore, this article presented the gradual characterization of $H_4[a-SiW_{12}O_{40}]/Zr$ catalyst, application of $H_4[a-SiW_{12}O_{40}]/Zr$ as desulfurization catalyst of benzothiophene.

2. Materials and Methods

2.1. Materials

All materials were analytical grade from Merck and Aldrich such as sodium metasilicate (Merck), sodium tungsten (Merck), zirconium oxo chloride octahydrate (Merck), and benzothiophene (Aldrich).

2.2. Synthesis and Characterization of $H_4[a-SiW_{12}O_{40}]/Zr$

Polyoxometalate $H_4[a-SiW_{12}O_{40}]$ was synthesized and characterized according to the litera-

ture [9]. Material $H_4[a-SiW_{12}O_{40}]/Zr$ was prepared according to Devassy *et al.* with a slight modification [10]. Zirconium(IV) oxide chloride octahydrate was dissolved in ammonia solution and was mixed with $H_4[a-SiW_{12}O_{40}]$ solution, the solution was prepared in methanol. Solution mixtures were stirred overnight and then were followed by centrifugation at 15,000 rpm. White solid material of $H_4[a-SiW_{12}O_{40}]/Zr$ was collected and washed with acetone and dried at 100 °C for 1 d. Material $H_4[a-SiW_{12}O_{40}]/Zr$ was characterized using Shimadzu 8201 PC Shimadzu FTIR spectrophotometer on KBr disc. X-ray diffraction was performed using Shimadzu Lab X Type 6000 diffractometer and data were collected over 2θ range of 0-90° at scanning speed of 1° min⁻¹. SEM surface photo was analyzed using JED-2300 SEM analysis station.

2.3. Catalytic Oxidative Desulfurization

The catalytic oxidative desulfurization of benzothiophene was carried out in 100 ml Schlenk flask equipped with magnetic bar as follow: 0.1 g of benzothiophene was dissolved in 5 ml of hexane and 0.1 g catalyst and 0.5 ml of H_2O_2 were added slowly in a flask. The mixture was stirred for 3 h at 40 °C using stirring speed at 100 rpm. The catalytic oxidative desulfurization was monitored using GC with RTX-1 column equipped with FID detector at initial and final reaction. Oxidative desulfurization of benzothiophene was studied deeply through investigation of reaction time, weight of catalyst, and temperature reaction.

Conversion of BT was calculated to evaluate the catalytic activity of $H_4[a-SiW_{12}O_{40}]/Zr$ by using Equation (1):

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

in which C_o is initial concentration of BT, and C_t is final concentration of BT.

3. Results and Discussion

FTIR spectrums of $H_4[a-SiW_{12}O_{40}]$ and $H_4[a-SiW_{12}O_{40}]/Zr$ are presented in Figure 1 with selected unique vibration shown in Table 1. FTIR spectrum of $H_4[a-SiW_{12}O_{40}]$ contains bands at 1620 cm⁻¹ (uOCO), 979 cm⁻¹ (uW=O), 786 cm⁻¹ (uW-Oe-W), 925 cm⁻¹ (uSi-O), and 880

Table 1. FTIR data of $H_4[a-SiW_{12}O_{40}]$ (A) and $H_4[a-SiW_{12}O_{40}]/Zr$

Material	W=O (cm ⁻¹)	W-Oe-W (cm ⁻¹)	W-Oc-W (cm ⁻¹)	Si-O (cm ⁻¹)	Zr-O (cm ⁻¹)
$H_4[a-SiW_{12}O_{40}]$	979	925	786	1020	-
$H_4[a-SiW_{12}O_{40}]/Zr$	955	848 (br)	770 (br)	1010 (br)	462

cm⁻¹ (uW-Oc-W) [11]. After supported with zirconium, all specific vibration of H₄[α-SiW₁₂O₄₀] was changed to broad spectrum in lower wavelength at 694-955 cm⁻¹ due to zirconium but bands at 462 cm⁻¹ is still appeared. In general, Keggin structure was maintained after supported with zirconium.

XRD powder pattern of H₄[α-SiW₁₂O₄₀] and H₄[α-SiW₁₂O₄₀] supported with zirconium is shown in Figure 2. Polyoxometalate H₄[α-SiW₁₂O₄₀] has diffraction peaks at low range angle at 2θ = 6-8 ° and high range angle at 2θ = 24-29 °. These diffraction are usually observed in the Keggin type polyoxometalate with formula [X_M12O₄₀]ⁿ⁻ [12]. Polyoxometalate H₄[α-SiW₁₂O₄₀] after supported with zirconium showed low intensity peaks at 2θ = 6-8 ° and

broad peaks at 2θ = 24-29 °. Diffraction peaks of zirconium at 2θ = 14-20 ° almost disappeared. Formation of material H₄[α-SiW₁₂O₄₀]/Zr was indicated from diffraction peaks at 2θ = 32°. Diffraction of H₄[α-SiW₁₂O₄₀]/Zr with broad peaks indicated that material contain some water of crystallizations, which can be eliminated from Keggin structure by heating material at temperature above 120 °C. We further investigate the formation of material H₄[α-SiW₁₂O₄₀]/Zr by SEM analysis and found that morphology of H₄[α-SiW₁₂O₄₀]/Zr is different from H₄[α-SiW₁₂O₄₀] show H₄[α-SiW₁₂O₄₀] supported with zirconium.

Polyoxometalate H₄[α-SiW₁₂O₄₀] shows a homogeneous morphology with size tube. On the

Table 2. Porosity analysis of H₄[α-SiW₁₂O₄₀] and H₄[α-SiW₁₂O₄₀]/Zr

No	Catalyst	Surface Area (m ² /g)	Pore Volume (m ³ /g)	Pore Size (nm)
1	H ₄ [α-SiW ₁₂ O ₄₀]	27.89	0.035	2.561
2	H ₄ [α-SiW ₁₂ O ₄₀]/Zr	72.96	0.080	1.318

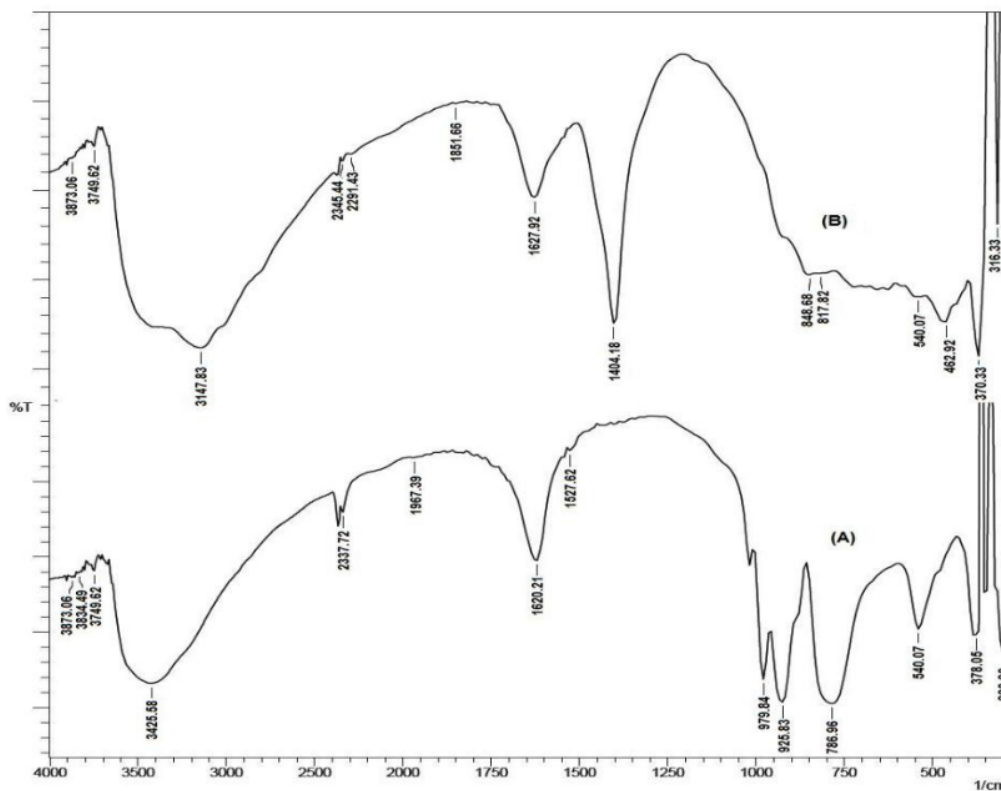


Figure 1. FTIR spectrum of H₄[α-SiW₁₂O₄₀] (A) and H₄[α-SiW₁₂O₄₀]/Zr (B)

other hand, material $H_4[\alpha-SiW_{12}O_{40}]/Zr$ showed heterogeneous shape with small aggregate formation. Although size and shape are heterogeneous but analysis of textural properties as shown in Table 2 indicated material $H_4[\alpha-SiW_{12}O_{40}]/Zr$ has higher specific surface and pore volume area about two times than that of $H_4[\alpha-SiW_{12}O_{40}]$. Through this data, we expected that catalytic activity of $H_4[\alpha-SiW_{12}O_{40}]/Zr$ is higher than $H_4[\alpha-SiW_{12}O_{40}]$.

Oxidative desulfurization of benzothiophene using $H_4[\alpha-SiW_{12}O_{40}]$ and $H_4[\alpha-SiW_{12}O_{40}]/Zr$ as catalysts under H_2O_2 as oxidant showed a slight different % conversion values of which for $H_4[\alpha-SiW_{12}O_{40}]$ it was 99% and 99.90% for $H_4[\alpha-SiW_{12}O_{40}]/Zr$. Although % conversion of

benzothiophene to sulfone using $H_4[\alpha-SiW_{12}O_{40}]$ only reaching up to 99% but the reaction is almost 100% by $H_4[\alpha-SiW_{12}O_{40}]/Zr$ as catalyst. We deeply investigate oxidative desulfurization of benzothiophene especially for the effect of temperature time, catalyst weight, and temperature reaction.

Effect of reaction time for desulfurization of benzothiophene showed conversion up to 100% was reached at 3 h reaction time. Reaction at initial time converts benzothiophene to sulfone with low conversion. By increasing time reaction to 3 h, it can convert all the benzothiophene to sulfone. In relation to that, if the reaction time was extended for one or more hours, it will no further benefit for the process. This is because 3 h reaction has achieved 99 % conver-

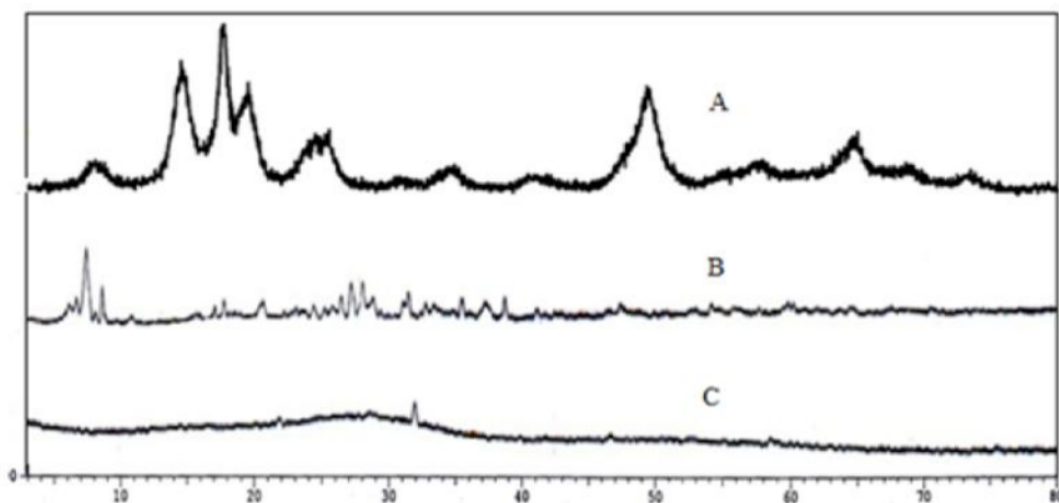


Figure 2. XRD powder pattern of $ZrOCl_2$ (A), $H_4[\alpha-SiW_{12}O_{40}]$ (B) and $H_4[\alpha-SiW_{12}O_{40}]/Zr$ (C)

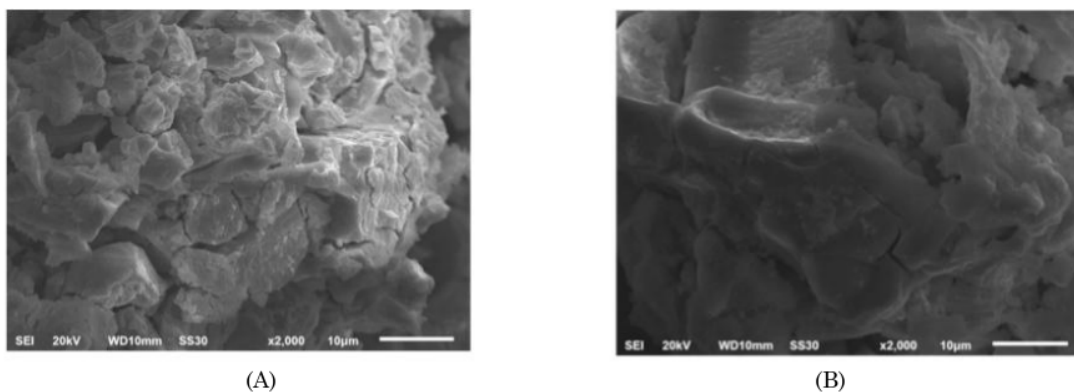


Figure 3. Surface morphology of $H_4[\alpha-SiW_{12}O_{40}]$ (A) and $H_4[\alpha-SiW_{12}O_{40}]/Zr$ (B)

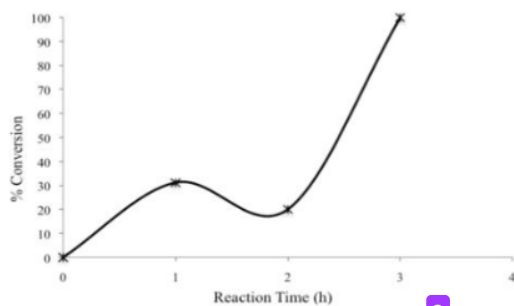


Figure 4. Effect of reaction time to oxidative desulfurization of benzothiophene using $H_4[\alpha-SiW_{12}O_{40}]/Zr$ catalyst

tion. If the reaction time was extended, H_2O_2 will be exhausted.

Long *et al.* [13] reported that oxidative desulfurization of dibenzothiophene achieved its optimum condition while using 0.3 g catalyst. In our research, we found 0.1 g catalyst of $H_4[\alpha-SiW_{12}O_{40}]/Zr$ is effective for conversion of benzothiophene as shown in Figure 5. This results showed some similarity with $C_{16}PMo(O_{22})/agarose$ catalyst, which use 0.1 g catalyst for desulfurization of dibenzothiophene [14]. Catalyst weight of 0.1 g is already met the 1/10 mmol reactant standard which is sufficient for catalyzing desulfurization. Catalyst

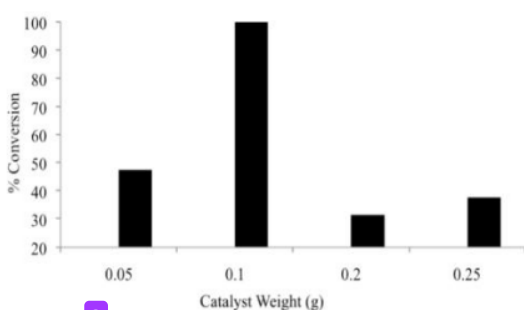


Figure 5. Effect of catalyst weight

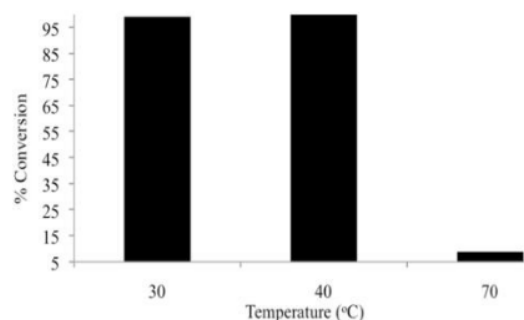


Figure 6. Effect of temperature reaction

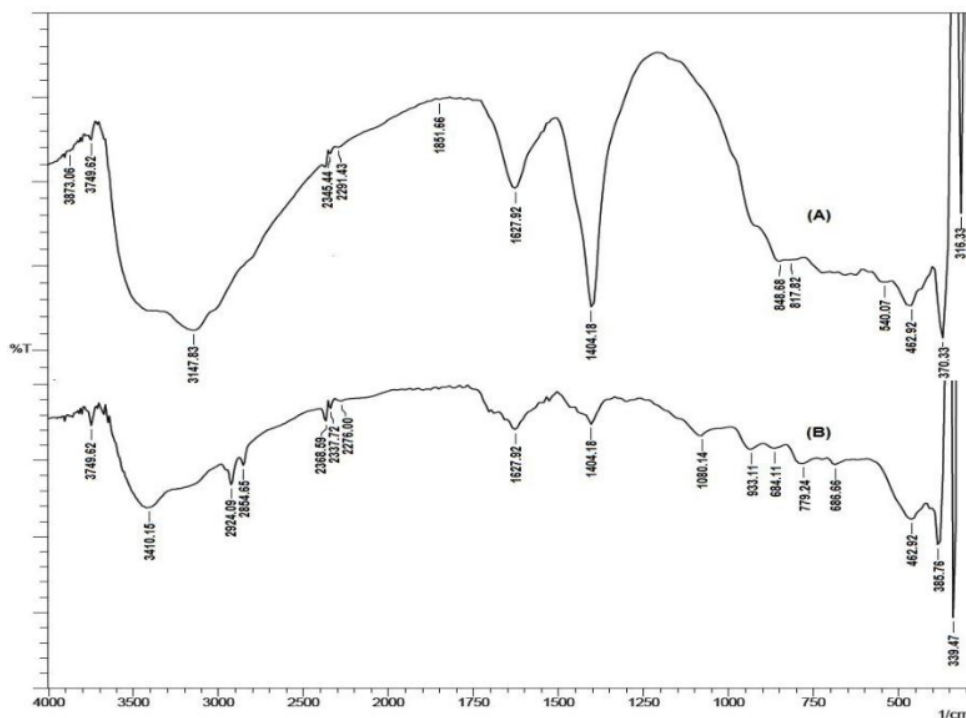


Figure 7. FTIR spectrum of $H_4[\alpha-SiW_{12}O_{40}]/Zr$ before (A) and after reaction (B)

weight under that value (e.g. 0.5 g) is not enough to activate H_2O_2 while above that value (e.g. more than 0.5 g) is useless (e.g. no longer efficient for the process). In the condition of H_2O_2 is not active, the catalyst will not facyle. Thus catalyst weight should be on the precise value. Our result is similar to desulfuration of dibenzothiophene using catalyst $C_{16}PMo(O_2)_2/agarose$, this is due to the mol ratio of the catalyst which is at least 1/10 mol or mmol catalyst being used in the catalytic system was in accordance with condition of this experiment.

One of oxidative desulfurization advantages if it is compared to hydrodesulfurization is its reaction only require a mild operating condition, this was indicated by the reaction at low temperature. This research showed temperature at 40 °C is enough to convert benzothiophene to sulfone. Reaction at higher temperature can decrease the % conversion of benzothiophene. Figures 4 and 5 indicated a desulfurization reaction system where 3 h reaction time and 0.1 g catalyst $H_4[\alpha-SiW_{12}O_{40}]/Zr$ weight resulted 99% conversion of dibenzothiophene in which H_2O_2 was optimum to activate the catalyst.

On the other hand, desulfurization of dibenzothiophene using anatase sandwich type polyoxometalate $(Bu_4N)_7H_3[P_2W_{18}Cd_4(Br)_2O_{68}-TiO_2]$ was successfully carried out at 60 °C with conversion up to 99% [15]. This is probably related to the stability of H_2O_2 as oxidant. The effect of temperature desulfurization of benzothiophene is shown in Figure 6.

Catalyst of $H_4[\alpha-SiW_{12}O_{40}]/Zr$ is catalytically active for oxidative desulfurization of benzothiophene due to the supporting of zirconium atom. In this study we observed that Keggin structure of $H_4[\alpha-SiW_{12}O_{40}]$ was almost collapse after reaction. Afterwards, FTIR spectrum in Figure 7 show the unique and specific vibration of $H_4[\alpha-SiW_{12}O_{40}]/Zr$ at wavelength 700-1100 cm^{-1} , it is altered and caused the appearance of an organic component at 2900 cm^{-1} of which was believed caused by reaction of benzothiophene. These results indicated that the reuse catalyst could not be performed. Although the heterogeneous catalytic using $H_4[\alpha-SiW_{12}O_{40}]/Zr$ catalyst is a limited cycle but the facile desulfurization still can be obtained by using $H_4[\alpha-SiW_{12}O_{40}]/Zr$.

4. Conclusions

In this article we dem²strated that $H_4[\alpha-SiW_{12}O_{40}]/Zr$ catalyst has a high catalytic activity for oxidative desulfurization of ben-

²zothiophene under mild condition. A complete benzothiophene conversion (99%) was achieved after 3 h reaction at 40 °C. Catalyst of $H_4[\alpha-SiW_{12}O_{40}]/Zr$ could be recycled after catalysis cycle with a loss of polyoxometalate $H_4[\alpha-SiW_{12}O_{40}]/Zr$ cage. Despite the catalyst lost its structure after the catalysis but it still have a better application compare to the industrial catalyst such as Co/Mo catalysts due to its mild catalyst reaction condition requirement.

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