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Desulfurization of 4-Methyl Dibenzothiophene Using Titanium Supported Keggin Type Polyoxometalate

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Abstract. Titanium supported Keggin type polyoxometalate $H_5PV_2Mo_{10}O_{40} \cdot nH_2O$ has been prepared using tetra isopropyl orthotitanate by sol-gel method and microemulsion to form $H_5PV_2Mo_{10}O_{40}/TiO_2$. Compound $H_5PV_2Mo_{10}O_{40} \cdot nH_2O/TiO_2$ was characterized using FTIR spectroscopy, X-Ray analysis, and acidity measurement. FTIR spectrum showed that all vibration of titanium and polyoxometalate were appeared in $H_5PV_2Mo_{10}O_{40} \cdot nH_2O/TiO_2$ with decreasing crystallinity. The acidity of $H_5PV_2Mo_{10}O_{40} \cdot nH_2O/TiO_2$ was higher than $H_5PV_2Mo_{10}O_{40} \cdot nH_2O$. Desulfurization of 4-methyl dibenzothiophene (4-MDBT) using $H_5PV_2Mo_{10}O_{40} \cdot nH_2O/TiO_2$ as catalyst resulted conversion of 4-MDBT was 99% and higher than desulfurization using $H_5PV_2Mo_{10}O_{40} \cdot nH_2O$ under mild conditions.

Keywords: 4-methyldibenzothiophene, tetra isopropyl orthotitanate, desulfurization, polyoxometalate

INTRODUCTION

Sulfur in the environment is mainly caused by transportation fuel. The mainly sulfur compounds in fossil fuel is organosulfur with high refractory index such as benzothiophene (BT), dibenzothiophene (DBT), 4-methyldibenzothiophene (4-MDBT), and 4,6-dimethyldibenzothiophene (4,6-DMDBT) as shown in Fig. 1 [1].

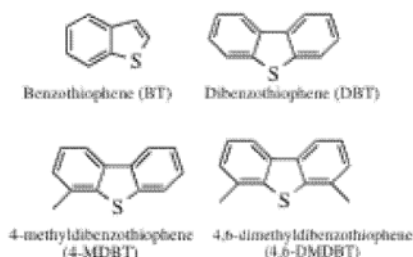


FIGURE 1. Organosulfur with high refractory index in fossil fuel.

Organosulfur content in fossil fuel should be reduced to low sulfur content to eliminate pollution in the environment. Conventionally, sulfur content was industrially removed via hydrodesulfurization (HDS) [2]. In this process, sulfur compounds such as thiophenes, polyaromatic sulfurs, sulfides and disulfides were effectively removed from fuel but not high refractory sulfur compounds such as shown in Fig. 1. High temperature and pressure in HDS process is needed to remove BT and its derivatives. Thus another method such as oxidative desulfurization (OD) is more effective way to remove sulfur compounds containing high refractory index in

mild condition [3]. In the OD system, sulfur compounds were converting to the corresponding polar sulfone which can be easily removed by extraction and physical methods using appropriate catalysts under mild conditions. Oxidation process in OD used oxidant such as molecular oxygen, hydrogen peroxide, nitric acid, ozone, organic peroxide and potassium superoxide [4]. Hydrogen peroxide has been used extensively as oxidant due to produces only water as a by-product. On the other hand, reactivity of hydrogen peroxide is relative low than others thus the role of catalyst in this process is crucial.

Polyoxometalates compounds are metal-oxygen clusters with various shapes, oxidation states, and acidity has been investigated as efficient catalyst for OD under mild conditions[5]. Organosulfurs BT, DBT, 4- MDBT, and 4,6-DMDBT have been successfully carried out via OD using all kinds of polyoxometalates as catalysts[6-7]. The limitation of polyoxometalates as catalyst is due to solubility. Then research to increase heterogeneity of polyoxometalates in wider range of solvents is intensively conducted.

Desulfurization of organosulfurs with high refractory index was carried out by Lesbani et.al (2015) using both Keggin and Dawson Types polyoxometalates and metal oxides supported polyoxometalate [8-9]. Metal oxides are common support in various inorganic materials including polyoxometalates[10]. The role of metal oxides is to increase both catalytic activity and heterogeneity of materials [11].

Herein, titanium oxide which was obtained from reduction of tetraisopropyl ortho titanat was synthesized and characterized to form $H_5PV_2Mo_{10}O_{40} \cdot nH_2O /TiO_2$. In the next step, catalytic properties of $H_5PV_2Mo_{10}O_{40} \cdot nH_2O /TiO_2$ was tested for OD of 4-MDBT as shown in the reaction in Fig. 2.

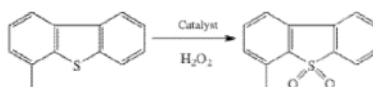


FIGURE 2.OD of 4-MDBT

The effect of reaction times, temperatures, weight of catalysts, and hydrogen peroxide amounts were investigated in OD of 4-MDBT using $H_5PV_2Mo_{10}O_{40} \cdot nH_2O /TiO_2$ as catalyst.

EXPERIMENTAL SECTION

Chemical and Equipment

Chemicals were supplied from Merck and Sigma Aldrich such as sodium molybdate (Merck), sodium hydrogen phosphate (Merck), sodium metavanadate (Aldrich), sulfuric acid (Merck), tetra isopropyl ortho titanate (Aldrich), diethyl ether (Merck), potassium carbonate (Merck), acetone (Sigma-Aldrich), ethanol (Merck), methanol (Merck), hydrogen peroxide (Merck).

FTIR spectrum was recorded using FTIR Shimadzu Prestige-21 spectrophotometer with KBr disc and sample was analyzed in the range of wavenumber area of $300-4000\text{ cm}^{-1}$. XRD powder analysis was conducted using XRD Shimadzu LabX type 6000. Sample was scanning at 1 deg. min^{-1} . Catalytic test reaction was monitored using Shimadzu GC 2010 Plus equipped with RTX-1 capillary column.

Synthesis Polyoxometalate $H_5PV_2Mo_{10}O_{40} \cdot nH_2O$ and characterization

Sodium metavanadate (6.1 g) was dissolved with 25 mL of warm water (solution A). Sodium hydrogen phosphate (1.78 g) was dissolved with 25 mL of water (solution B). Solution B was mixed with solution A at room temperature following with addition of sulfuric acid (1.25 mL) to form red solution (solution C). Sodium molybdate (30.25 g) was dissolved with 50 mL of water (solution D). Solution D was mixed with solution C with slow stirring. Sulfuric acid (21.25 mL) was added slowly during stirring process. Solution was extracted with diethyl ether-sulfuric acid (1:1) about c.a. 40 mL. Fraction in bottom of separation funnel was collected and vacuum evaporated to form red crystal of $H_5PV_2Mo_{10}O_{40} \cdot nH_2O$ [12]. Purification was conducted using water. Characterization of $H_5PV_2Mo_{10}O_{40} \cdot nH_2O$ was carried out using FTIR spectroscopy, powder X-Ray analysis, and acidity measurement.

Preparation of $H_5PV_2Mo_{10}O_{40} \cdot nH_2O/TiO_2$ and characterization

Compound $H_5PV_2Mo_{10}O_{40}/TiO_2$ was prepared according to Kim *et al.*, 2016 with slightly modification. Sodium bis(2-ethylhexyl) sulfosuccinate (5) (0.5 g) was dissolved with 1 mL of cyclohexane (solution A). Compound $H_5PV_2Mo_{10}O_{40} \cdot nH_2O$ (0.76 g) was dissolved with 1 mL of water (solution B). Solution B was added with stirring to solution A for 1 h follow with addition of tetra isopropyl ortho titanate (2 mL). The mixtures were heated at 100 °C for c.a. 30 min to form solid material of $H_5PV_2Mo_{10}O_{40}/TiO_2$ [13]. Characterization of $H_5PV_2Mo_{10}O_{40}/TiO_2$ was performed using FTIR spectroscopy, X-Ray analysis, and acidity measurement.

Oxidation of 4-MDBT

Oxidation of dibenzothiophene was conducted using 250 mL Schlenk flask under oxygen atmospheric condition equipped with magnetic bar and hot plate. In the flask, 0.1 g of catalyst, 0.1 g of dibenzothiophene, 5 mL of hexane, and 0.5 mL hydrogen peroxide were added slowly. The reaction mixtures were stirred for several hours and formation of sulfone was detected using GC at various times. Conversion of dibenzothiophene to sulfone was calculated by comparison chromatogram area of dibenzothiophene after reaction at definite time and initial time. Oxidation of dibenzothiophene was studied through selection of catalysts, reaction times, weight of catalysts, and temperatures reaction.

RESULTS AND DISCUSSION

Characterization using FTIR

IR spectroscopy is extensively used for identification of functional groups in polyoxometalates. Compounds $H_5PV_2Mo_{10}O_{40} \cdot nH_2O$ and $H_5PV_2Mo_{10}O_{40} \cdot nH_2O /TiO_2$ were identified using FTIR as shown in Fig. 3. The characteristic area of polyoxometalates is 700-1100 cm^{-1} . Polyoxometalate $H_5PV_2Mo_{10}O_{40} \cdot nH_2O$ has vibration at wavenumber 1057 cm^{-1} (P-O), 964 cm^{-1} (M=O), 864 cm^{-1} (Mo-Oe-Mo), and 779 cm^{-1} (Mo-Oc-Mo) as shown in Fig. 3A. Titanium supported polyoxometalate $H_5PV_2Mo_{10}O_{40} \cdot nH_2O /TiO_2$ has broad vibration at range 500-1100 cm^{-1} due to facile diffusion of titanium onto polyoxometalate. Although titanium in this research comes from reduction of tetra isopropyl ortho titanate in liquid phase but the phenomena was similar with titanium from titanium(IV) oxide [14]. Therefore identification of $H_5PV_2Mo_{10}O_{40} \cdot nH_2O /TiO_2$ was conducted using X-ray analysis.

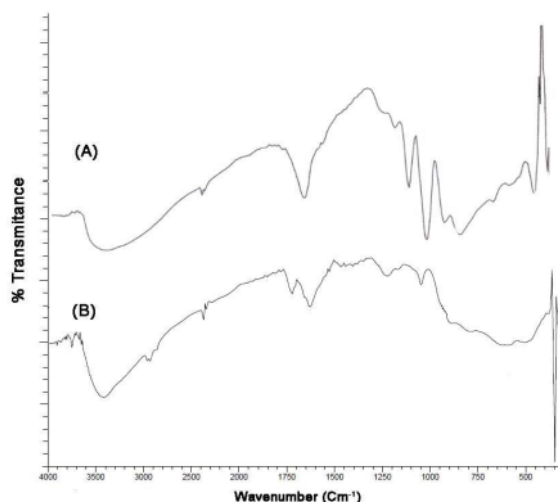


FIGURE 3. FTIR spectra of $H_5PV_2Mo_{10}O_{40} \cdot nH_2O$ (A) and $H_5PV_2Mo_{10}O_{40} \cdot nH_2O/TiO_2$ (B)

Characterization using X-Ray analyses

Polyoxometalate $H_5PV_2Mo_{10}O_{40} \cdot nH_2O$ has strong diffraction peak below 2θ of 10deg indicated these polyoxometalate has high crystallinity as shown in Fig. 4A [15]. On the other hand, supported polyoxometalate with titanium has broad diffraction from 2θ of 5-30deg and material was amorphous properties (Fig. 4B). This

phenomena can be explained due to incomplete support process from titanium to surface of polyoxometalate create a amorphous material of $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}\cdot n\text{H}_2\text{O}/\text{TiO}_2$. Furthermore, acidity measurement was conducted for $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}\cdot n\text{H}_2\text{O}$ and $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}\cdot n\text{H}_2\text{O}/\text{TiO}_2$.

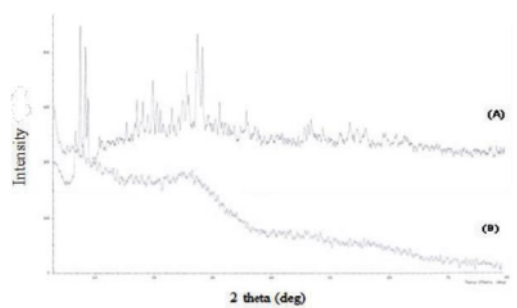


FIGURE 4. XRD powder pattern of $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}\cdot n\text{H}_2\text{O}$ (A) and $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}\cdot n\text{H}_2\text{O}/\text{TiO}_2$ (B).

Qualitative identification of acidity

Acidity of $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}\cdot n\text{H}_2\text{O}$ and $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}\cdot n\text{H}_2\text{O}/\text{TiO}_2$ was identified using ammonia and pyridine adsorption. Ammonia and pyridine are commonly used as a probe for qualitative detection of acid in solid materials [16]. Acidity sites are detected using IR spectrum as shown in Fig. 5 and 6.

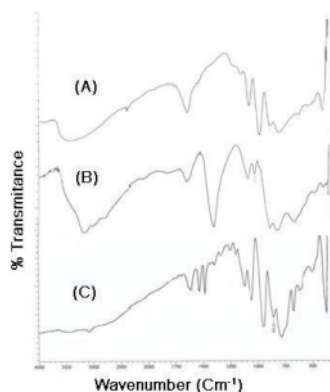


FIGURE 5. FTIR spectra of $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}\cdot n\text{H}_2\text{O}$ (A) exposed with ammonia (B) and pyridine (C).

Polyoxometalate $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}\cdot n\text{H}_2\text{O}$ was exposed with ammonia and pyridine for c.a. 24 h at room temperature. IR spectra showed that vibration at 1400 cm^{-1} for both ammonia and pyridine was obtained. These vibration is assigned as acid sites for both Bronsted and Lewis [17]. These results were found also in titanium supported polyoxometalate $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}\cdot n\text{H}_2\text{O}/\text{TiO}_2$. Therefore the strength of acidity between $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}\cdot n\text{H}_2\text{O}/\text{TiO}_2$ and $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}\cdot n\text{H}_2\text{O}/\text{TiO}_2$ cannot be clearly distinguished. For that reasons, potentiometric titration was conducted using n-butylamine as a titrant[18].

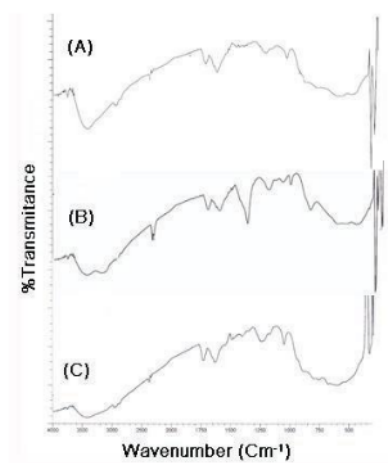


FIGURE 6. FTIR spectra of $H_5PV_2Mo_{10}O_{40} \cdot nH_2O/TiO_2$ exposed with ammonia (A) and pyridine (B).

Potentiometric titration

Titration curve of $H_5PV_2Mo_{10}O_{40} \cdot nH_2O$ and $H_5PV_2Mo_{10}O_{40} \cdot nH_2O/TiO_2$ was shown in Fig. 7. Equivalent point can be clearly seen from that curve while compound $H_5PV_2Mo_{10}O_{40} \cdot nH_2O/TiO_2$ has slope relative with $H_5PV_2Mo_{10}O_{40} \cdot nH_2O$.

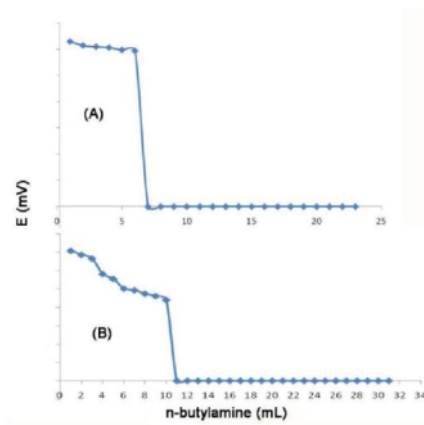


FIGURE 7. Titration curve of $H_5PV_2Mo_{10}O_{40} \cdot nH_2O$ and $H_5PV_2Mo_{10}O_{40} \cdot nH_2O/TiO_2$.

Compounds $H_5PV_2Mo_{10}O_{40} \cdot nH_2O$ and $H_5PV_2Mo_{10}O_{40} \cdot nH_2O/TiO_2$ have potential 314mV and 354 mV, respectively. That results indicated that compound $H_5PV_2Mo_{10}O_{40} \cdot nH_2O/TiO_2$ has higher acidity than compound $H_5PV_2Mo_{10}O_{40} \cdot nH_2O$. Thus reduction of tetra isopropyl ortho titanate to titanium oxide as support agent for polyoxometalate $H_5PV_2Mo_{10}O_{40} \cdot nH_2O$ can increase acidity level of polyoxometalate. The catalytic test for OD of 4-MDBT in this research used $H_5PV_2Mo_{10}O_{40} \cdot nH_2O/TiO_2$ as catalyst.

Catalytic activity

Effect of reaction time

The effect of reaction time in the OD of 4-MDBT using $H_5PV_2Mo_{10}O_{40} \cdot nH_2O/TiO_2$ as catalyst was shown in Table 1. Reaction at 1 h gave 73.3% conversion of 4-MDBT to corresponding sulfone. By increasing

reaction time until 2 h will increase conversion of 4-MDBT to 94.3%. Desulfurization of 4-MDBT was slightly decreased at 3 h and relative stable at 4 h. The next experiment was investigation effect of temperature.

TABLE 1. Effect of reaction time on the oxidation of 4-MDBT

Reaction time (h)	Conversion of 4-MDBT
1	73.4
2	94.3
3	82.0
4	80.3

Effect of temperature

The effect of temperature for desulfurization of 4-MDBT was studied ranging from 40 – 70 °C. Table 2 showed that the optimum temperature for OD of 4-MDBT was 60 °C with 99% conversion. These temperature was relative mild compared with previous reported using other polyoxometalates [19].

TABLE 2. Effect of temperature on the oxidation of 4-MDBT

Temperature (°C)	Conversion of 4-MDBT
40	90.6
50	94.3
60	99.0
70	71.4

Effect of catalyst weight

Catalyst dosage is also important factor for desulfurization process. In this research, catalyst weight from 0.05 g to 0.3 g was investigated for OD of 4-MDBT using $H_5PV_2Mo_{10}O_{40} \cdot nH_2O / TiO_2$ as catalyst.

TABLE 3. Effect of catalyst weight on the oxidation of 4-MDBT

Catalyst weight (g)	Conversion of 4-MDBT
0.05	94.3
0.1	87.0
0.2	68.9
0.3	55.0

The data in Table 3 showed that catalyst weight 0.05 g resulted 94.3% conversion of 4-MDBT to corresponding sulfone. By increasing catalyst weight will decrease conversion of 4-MDBT. This results are opposite with the results of hydrogen peroxide amount as shown in Table 4.

Effect of hydrogen peroxide amount

TABLE 4. Effect of hydrogen amount on the oxidation of 4-MDBT

Hydrogen peroxide (mL)	Conversion of 4-MDBT
1	78.1
3	94.3
4	96.8
5	99.0

Hydrogen peroxide is mild oxidant need activation from catalyst to be active oxygen donor [20]. The results of hydrogen peroxide effect for OD of 4-MDBT showed that 5 mL of hydrogen peroxide was enough for OD of 4-MDBT. Hydrogen peroxide amount less than 5 mL was not optimal for desulfurization of 4-MDBT using $H_5PV_2Mo_{10}O_{40} \cdot nH_2O/TiO_2$ as catalyst.

Regeneration and reuse catalyst

Desulfurization of 4-MDBT using $H_5PV_2Mo_{10}O_{40} \cdot nH_2O$ based catalysts is shown in Table 5. Catalyst $H_5PV_2Mo_{10}O_{40} \cdot nH_2O$ without support material showed 91.6% conversion. By supporting $H_5PV_2Mo_{10}O_{40} \cdot nH_2O$ with titanium can reach conversion 99%. The increasing conversion of 4-MDBT was due to the role of titanium from tetra isopropyl ortho titanate as support material. Reactivity of support catalyst was checked by regeneration catalyst after OD process. Reuse catalyst was washed with water and ethanol (1:1) and dried at 110°C for 3 h. Catalytic activity of 4-MDBT using reuse catalyst showed that slightly decrease conversion of 4-MDBT but catalyst still has activity. In order to check stability of catalyst, IR spectrum of catalyst after regeneration was measured and shown in Fig. 8.

TABLE 5. Catalytic test

Catalyst	Conversion of 4-MDBT
$H_5PV_2Mo_{10}O_{40} \cdot nH_2O$	91.6
$H_5PV_2Mo_{10}O_{40} \cdot nH_2O /TiO_2$	99.0
$H_5PV_2Mo_{10}O_{40} \cdot nH_2O /TiO_2$ 2 nd run	93.1

Vibrations of polyoxometalate and support in the range 500-1100 cm^{-1} were not changed. There is a new peak at 1100-1300 cm^{-1} due to involving of aromatic groups in 4-MDBT into surface of catalyst. These vibration is commonly appeared in catalytic process because of contact of substrate-catalyst [21]. Thus catalyst $H_5PV_2Mo_{10}O_{40} \cdot nH_2O/TiO_2$ has stability under mild conditions.

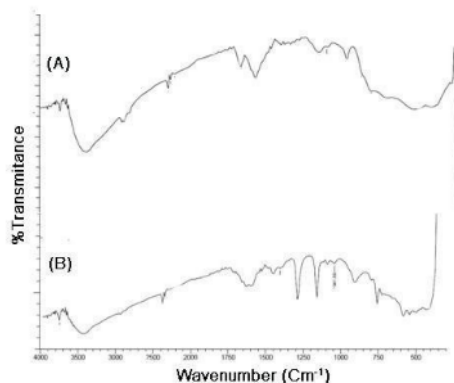


FIGURE 8. FTIR spectra of $H_5PV_2Mo_{10}O_{40} \cdot nH_2O/TiO_2$ before (A) and after (B) OD process.

CONCLUSION

Compound $H_5PV_2Mo_{10}O_{40}/TiO_2$ has higher catalytic activity than $H_5PV_2Mo_{10}O_{40} \cdot nH_2O$ for OD of 4-MDBT under mild condition using hydrogen peroxide as oxidant up to 99% after optimization processes. Regeneration of catalyst $H_5PV_2Mo_{10}O_{40}/TiO_2$ also shows higher catalytic activity than $H_5PV_2Mo_{10}O_{40} \cdot nH_2O$.

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