

## CHAPTER III

### EXPERIMENTAL

In the present study of oxidation of benzothiophene and dibenzothiophenes with polyoxometalate catalysts, the experiment is divided into three steps.

1. Preparation and characterization of polyoxometalate catalysts.
2. Study of the optimum conditions for oxidation using polyoxometalate catalysts.
3. Oxidation of sulfur compounds contained in diesel fuels with the suitable catalysts.

#### 3.1 Reagents and Solvents

The reagents and solvents in this experiment are analytical grade.

**Table 3.1** Chemical reagents and suppliers

Reagents and Solvents	Supplier
Acetic acid glacial 100%	Merck, Germany
Acetonitrile	Merck, Germany
Ammonium (meta) vanadate	Fluka Chemie A.G., Switzerland
Benzothiophene	Fluka Chemie A.G., Switzerland
Benzothiophene sulfone	Fluka Chemie A.G., Switzerland
Celite	Fluka Chemie A.G., Switzerland
Dibenzothiophene	Fluka Chemie A.G., Switzerland
Dibenzothiophene sulfone	Fluka Chemie A.G., Switzerland
Diethyl ether	Merck, Germany
4,6-Dimethyldibenzothiophene	Aldrich Chemical Co., Inc., USA

**Table 3.1** Chemicals reagents and suppliers (continued)

Reagents and Solvents	Supplier
Disodium hydrogen orthophosphate	APS Chemicals, Ltd., Australia
Ethanol	Merck, Germany
Ethylbenzene	Merck, Germany
Hexane	Lab Scans Co., Ltd., Ireland
Hydrochloric acid fuming 37%	Merck, Germany
30% Hydrogen peroxide	Merck, Germany
Methanol	Merck, Germany
Ortho-phosphoric acid 85%	Merck, Germany
Perchloric acid 70%	Merck, Germany
Sodium sulfate anhydrous	Merck, Germany
Sodium dihydrogen orthophosphate	APS Chemicals, Ltd., Australia
Sodium (meta) vanadate	Fluka Chemie A.G., Switzerland
Sodium hydroxide	Merck, Germany
Sodium (meta) vanadate	Fluka Chemie A.G., Switzerland
Sodium molybdate dihydrate	Fluka Chemie A.G., Switzerland
Sodium tungstate dihydrate	Fluka Chemie A.G., Switzerland
Tetrabutyl ammonium bromide	Fluka Chemie A.G., Switzerland
Toluene	Lab Scans Co., Ltd., Ireland

## 3.2 Equipments

Gas chromatography (GC) Varian CP-3800 equipped with a flame ionization detector (GC-FID) and CP-Sil. (30 m x 0.25 mm) column was used for identify the products of the oxidation of model sulfur compounds. Inductive couple plasma emission (ICP-AES) Perkin Elmer model PLASMA-1000 was used for determination of %vanadium (V) content in catalyst. Atomic absorption spectrophotometry (AAS) Varian Spectra-AA300 was used for determination of %sodium (Na) content in catalyst. Powder X-ray diffraction patterns were measured on a Rigaku, DMAX 2002/Ultima X-ray diffractometer with nickel filtered  $\text{CuK}_\alpha$  radiation. A Nicolet FT-IR Impact 410 Spectrophotometer was used for determination of functional groups in catalyst. The absorption of metal in catalysts were determined by UV-Visible spectroscopy (UV-Vis) Perkin Elmer Lambda 3000. The reduction temperature of catalysts were measured by temperature programmed reduction (TPR) by a TPR MODEL BEL-CAT equipped with a quartz U-tube and connected to a thermal conductivity detector (TCD). Mass spectroscopy (MS) Micromass Quattro micro<sup>TM</sup> API, ESI technique was used for determination of molecular weight of 4,6-dimethyldibenzothiophene sulfone product. X-ray fluorescence spectrometer (XRF) ARL 8410 (ASTM D4294 method) was used for determination of sulfur content in diesel fuels.

## 3.3 Characterization of catalysts

### 3.3.1 %Na content in catalysts

%Na content in catalyst was determined using atomic absorption spectrophotometry (AAS) Varian Spectra-AA300 at Scientific and Technological Research Equipment Center, Chulalongkorn University.

The catalyst (0.03 g) was dissolved in deionized water and transfer to a 50 ml volumetric flask and made up volume with deionized water.

### 3.3.2 %V content in catalysts

%V content in catalysts was determined using inductive couple plasma emission (ICP-AES) Perkin Elmer model PLASMA-1000 at Scientific and Technological Research Equipment Center, Chulalongkorn University.

The catalyst containing tetrabutylammonium cation could not be dissolved in water. Thus, the catalyst (0.03 g) were calcined in muffle furnace at 500 °C overnight. Concentrated nitric acid was added in the residue. The mixture was heated until dryness on the hot plate three times. After that the residue was dissolved and transferred to a 100 ml volumetric flask and made up volume with deionized water.

For the (VO)H[PW<sub>12</sub>O<sub>40</sub>] and (VO)H[PMo<sub>12</sub>O<sub>40</sub>] catalyst. The catalyst (0.03 g) was dissolved in deionized water and transfer to a 100 ml volumetric flask and made up volume with deionized water.

### 3.3.3 Phase analysis of catalysts

The phase analysis of catalysts were determined by X-ray diffraction spectrometer (XRD). The XRD patterns of the catalyst were obtained using Rigaku, DMAX 2002/Ultima Plus power X-ray diffractometer using CuK<sub>α</sub> radiation, over a  $2\theta$  range of 5-40 degree.

### 3.3.4 Functional groups of catalysts

The functional groups of catalyst were determined by Fourier-transform infrared spectra (FT-IR). The FT-IR spectra were recorded on a Nicolet FT-IR Impact 410 Spectrophotometer at the Department of Chemistry, Chulalongkorn University. The samples were made into a KBr pellet. Infrared spectra were recorded between 400-2000 cm<sup>-1</sup> in transmittance mode.

### 3.3.5 Absorption of metal in catalysts

Absorption of metal in catalysts were recorded on Perkin Elmer Lambda 3000 in the wavelength between 200 nm to 400 nm. The catalysts are soluble in acetonitrile.

### 3.3.6 Reduction temperature of metal in catalysts

The reduction temperature of catalysts were measured by temperature programmed reduction (TPR) by a TPR MODEL BEL-CAT equipped with a quartz U-tube and connected to a thermal conductivity detector (TCD). TPR experiments in a conventional flow system with a moisture trap.

The catalyst (0.15 g) was pretreated at 300 °C in O<sub>2</sub> flow for 2 h and then mixed H<sub>2</sub>-Ar containing 5% (v/v) was flowed with a temperature rate of 10 °C min<sup>-1</sup>. The final temperature was 700 °C [26].

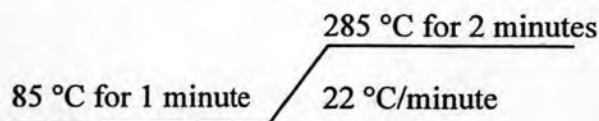
## 3.4 Determination of products

The products of oxidation of model sulfur compounds were analyzed by gas chromatography, Varian CP-3800 GC equipped with a flame ionization detector (GC-FID) and CP-Sil. (30 m x 0.25 mm) column. The condition was used for determination the %yield of products were set as follows:

**Table 3.2** The GC condition for substrates

Substrate	Carrier gas	Detector temperature (°C)	Injection Temperature (°C)
BT	Nitrogen	280	250
DBT	Nitrogen	280	250
4,6-DMDBT	Nitrogen	280	250

Temperature programmed for DBT, BT and 4,6-DMDBT



### 3.5 Determination of molecular weight of 4,6-dimethyldibenzothiophene sulfone product

Determination of molecular weight of 4,6-dimethyldibenzothiophene sulfone products from the oxidation of 4,6-dimethyldibenzothiophene was performed with Mass spectroscopy (MS) with Micromass Quattro micro<sup>TM</sup> API, ESI technique.

### 3.6 Determination of sulfur content in diesel fuel

Sulfur content in diesel fuels was determined using a SISON S X-ray fluorescence spectrometer ARL 8410 (ASTM D4294 method).

### 3.7 Synthesis of catalysts

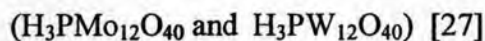
The synthesis of catalysts were carried out according to the procedure in the literatures.

#### 3.7.1 Disodium acidic salts of molybdophosphoric and tungstophosphoric acids: (Na<sub>2</sub>H[PMo<sub>12</sub>O<sub>40</sub>] and Na<sub>2</sub>H[PW<sub>12</sub>O<sub>40</sub>]) [27]

An aqueous solution (20 ml) of sodium molybdate dihydrate: Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O 14.46 g or the solution of sodium tungstate dihydrate: Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O 19.46 g in water was added successively 0.40 ml of 85% H<sub>3</sub>PO<sub>4</sub> and 15 ml of 70% HClO<sub>4</sub>. The precipitate was formed from the yellow solution (for Mo catalyst) or white solution (for W catalyst). After the mixture was cooled to room temperature, the microcrystalline crystals were filtered and dried in vacuum at 50 °C, greenish for Mo

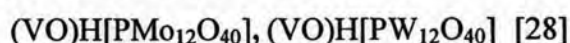
catalyst, 10 g and white for W catalyst, 14 g. They were purified by recrystallization from acetonitrile.

### 3.7.2 Molybdophosphoric and tungstophosphoric acids:



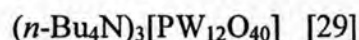
An aqueous solution (10 ml) of  $\text{Na}_2\text{HPMo}_{12}\text{O}_{40}$  7 g or  $\text{Na}_2\text{HPW}_{12}\text{O}_{40}$  10 g was acidified with 12 M HCl to pH = 1 and extracted by diethyl ether 20 ml. The filtrate was concentrated, the precipitate formed was filtered and dried in vacuum at 50 °C gave yellow (for Mo catalyst, 5 g) and white (for W catalyst, 8 g) crystals, respectively. They were purified by recrystallization from acetonitrile.

### 3.7.3 Vanadyl acidic salts of molybdophosphoric acid and tungstophosphoric acid:



$\text{H}_3\text{PMo}_{12}\text{O}_{40}$  1.5 mmol or  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  1.5 mmol was added to 100 ml of a solution of vanadyl acetylacetonate ( $\text{C}_{10}\text{H}_{14}\text{VO}_5$ ) in toluene (0.15 g/100 ml) at room temperature. The mixture is stirred for 5 h. The resulting precipitate was filtered off, washed with water and dried in vacuum at 50 °C to give light green crystals, 1.5 g for  $(\text{VO})\text{H}[\text{PMo}_{12}\text{O}_{40}]$  or dark green crystals, 2.3 g for  $(\text{VO})\text{H}[\text{PW}_{12}\text{O}_{40}]$ . The compounds were recrystallized from acetonitrile.

### 3.7.4 Tetrabutylammonium salts of tungstophosphate:



1 g  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  was dissolved in 20 ml of water, 0.4 ml of 85% aqueous  $\text{H}_3\text{PO}_4$  and 1 ml of concentrated sulfuric acid were then added, and the resulting suspension was stirred at room temperature for 12 h. Addition of 6 ml of water, yielded a clear solution to which 0.28 g of  $n\text{-Bu}_4\text{NBr}$  was added. After 15 min of stirring, the resulting precipitate was filtered off, washed with water, ethanol, and ether, and dried in vacuum at 50 °C gave white crystals 0.7 g. The catalysts were recrystallized from acetonitrile.

### 3.7.5 Tetrabutylammonium salts of tungsto vanadophosphate:

11-Tungsto-1-vanadophosphate:  $(n\text{-Bu}_4\text{N})_4[\text{PVW}_{11}\text{O}_{40}]$

10-Tungsto-2-vanadophosphate:  $(n\text{-Bu}_4\text{N})_5[\text{PV}_2\text{W}_{10}\text{O}_{40}]$

9-Tungsto-3-vanadophosphate:  $(n\text{-Bu}_4\text{N})_6[\text{PV}_3\text{W}_9\text{O}_{40}]$  [30]

First, a stock solution of V(V) was prepared by dissolving 6 g  $\text{NH}_4\text{VO}_3$  and 4 g NaOH in 100 ml of water.

$\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$  0.195 g was added to a solution of 4.125 g of  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  in 150 ml of water, followed by addition of 22 ml of concentrated HCl. After stirring, 5 ml, 20 ml and 80 ml stock solution of V(V) was added for  $V_1$  (yellow solution),  $V_2$  (orange solution) and  $V_3$  catalysts (dark orange solution), respectively.  $n\text{-Bu}_4\text{NBr}$  was added to the solution after heating at 70 °C for 24 h. The precipitates were filtered off, washed with water and EtOH and dried in vacuum at 50 °C. The catalysts were recrystallized from acetonitrile gave yellow crystals 4 g, 4.1 g and 4.5 g for  $V_1$ ,  $V_2$  and  $V_3$ , respectively.

### 3.8 Oxidation of sulfur model compounds

In a round bottom flask, connected with a condenser, model sulfur compound, hexane, catalyst, hydrogen peroxide and acetic acid were mixed. The reaction mixture was stirred for the desired time and temperature. After the reaction finished, acetonitrile (as an extraction solvent) was added to the mixture and stirred for 10 minutes. The biphasic mixture was separated by funnel separation, upper layer (organic phase) and bottom layer (aqueous phase). The aqueous phase was dried over anhydrous sodium sulfate ( $\text{Na}_2\text{SO}_4$ ), 1 ml of aqueous phase was passed through a capillary column containing celite to remove the catalyst. Products were quantified by GC. % Product yield was calculated from peak areas in GC.

Various parameters were evaluated to affect the oxidation of model sulfur compound. The parameters studied in this reaction are type of catalyst, effect of phase transfer catalyst, effect of vanadium (V) substitution and amount of oxidant.



### 3.9 Synthesis of authentic sulfone product

4,6-dimethyldibenzothiophene sulfone was synthesized under the same oxidation reaction in section 3.4. and then the sulfone product was characterized by Mass spectroscopy (MS).

### 3.10 Oxidation of diesel fuel

In a round bottom flask, connected with condenser, diesel oil (10 ml), catalyst, hydrogen peroxide and acetic acid were mixed. The reaction mixture was stirred at 70 °C for 5 h. After the completion of the reaction, the resulting oil was extracted with acetonitrile (10 ml). After that the volume of oxidized oil was measured and then calculated the recovery oil as follows:  $(\text{volume of initial oil} \times 100) / (\text{volume of oxidized oil})$ . The oxidized oil was passed through a glass column containing alumina adsorbent to remove oxidized sulfur. Amount of the remaining sulfur compounds was determined by XRF (ASTM D4294).