

## The Role of Molybdenum Oxide Based Catalysts on Oxidative Desulfurization of Diesel Fuel

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### Abstract

The industrial technology, hydrodesulfurization (HDS) is incapable to meet ultra-low sulfur standard due to the limited treatment on organosulfur compound in diesel fuel. In this paper, catalytic oxidative desulfurization of thiophene, dibenzothiophene and 4,6-dimethyldibenzothiophene using molybdenum oxide based catalyst was investigated. A detailed parametric experimental study; number of coating, calcination temperature, addition of dopant was performed on sulfur removal. It was shown that 4.35% WO<sub>3</sub>/16.52% MoO<sub>3</sub>γ-Al<sub>2</sub>O<sub>3</sub>, calcined at 500°C was successfully removed 92.5% of thiophene, 100% of DBT and 100% of 4,6-DMDBT in model diesel at short reaction time and lower temperature.

**Keywords:** Diesel fuel; Catalytic oxidative desulfurization; Molybdenum oxide; Catalyst

### Introduction

It is expected that diesel demand and utilization will increase more in the next few decades in 21<sup>st</sup> century. However, the sulfur compounds present naturally in diesel are the major source of air pollution and health problem [1]. The current technology of reducing sulfur contaminant in diesel fuel is by Hydrodesulfurization (HDS) process, which is carried out under high pressure and temperature and catalyzed by sulfided Co/Mo and/or Ni/Mo catalysts. HDS is the most effective to remove aliphatic sulfur compounds and some thiophene derivatives [2]. Nevertheless, the existing HDS is incapable to meet ultra-low sulfur standard due to the limited treatment on benzothiophenes (BTs) and dibenzothiophenes (DBTs), especially DBTs having alkyl substituents on their 4 and/or 6 positions [3]. A new alternative technology, oxidative desulfurization (ODS) appears as the most promising technique to remove the refractory sulfur-containing in HDS process. ODS process includes two steps: (i) oxidation of sulfur to form sulfoxide/sulfone and (ii) liquid extraction of oxidized diesel. The greatest advantages of applying ODS are mild reaction conditions without the needs of expensive hydrogen and pressure reactor [4]. The ideal system of ODS is using H<sub>2</sub>O<sub>2</sub> and TBHP as oxidants due to their high oxidizability in the presence of heterogeneous catalysts such as activated carbon [5], W/ZrO<sub>2</sub> [6] and V<sub>2</sub>O<sub>5</sub> [7]. Alumina-supported molybdenum oxide-based catalyst has long been widely used as an active catalyst in HDS due to its high stability in severe reactions and high resistance to sulfur poisoning. Therefore, in the present investigation, Mo/Al<sub>2</sub>O<sub>3</sub> catalysts were investigated on calcination temperature, number of coating and various dopants and dopant ratios. The performance of the catalysts was studied in details with accordance to their properties through various characterizations.

### Materials and Methods

#### Materials

All the materials were purchased from QRÉC<sup>®</sup> and used without further treatment. N, N-Dimethylformamide (99%), was used as solvent extraction. Aqueous tert-butyl hydroperoxide (70 wt% TBHP) was used as oxidizing agents. N-octane (99%) was used as solvent for sulfur compounds: thiophene (T, 99%), dibenzothiophenes (DBT, 97%), and 4,6-dimethyl dibenzothiophenes (4,6-DMDBT, 95%). Model diesel for ODS reaction was prepared with 600 ppm comprising thiophene (200 ppm), DBT (200 ppm) and 4,6-DMDBT (200 ppm).

#### Catalyst preparation and characterization

Molybdenum oxide catalysts were prepared by impregnation

to incipient wetness of the support (Al<sub>2</sub>O<sub>3</sub>, Sigma-Adrich, specific surface area 253 m<sup>2</sup>/g and 3-5 mm diameter) with aqueous solution of (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O (QRÉC). The impregnation was carried out in multiple stages with drying in between at ambient temperature for 20 minutes. The amount of added solution was necessary to obtain a molybdenum loading equivalent to one or three or five theoretical monolayers of MoO<sub>x</sub>. Finally, the samples were dried at 80°C overnight and calcined at 500°C, 700°C and 1000°C for 5 h [8]. The molybdenum oxide based catalyst was then doped with various transition metals dopants such as titanium (NH<sub>4</sub>)<sub>2</sub>TiO(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O, vanadium (NH<sub>4</sub>VO<sub>3</sub>) and tungsten ((NH<sub>4</sub>)<sub>6</sub>H<sub>2</sub>W<sub>12</sub>O<sub>40</sub>·H<sub>2</sub>O) using similar method. Thereafter, the potential bimetallic oxide catalyst was investigated in different ratios (90:10, 80:20 and 70:30) and further, calcined at 700°C and 1000°C. Catalysts were characterized by X-Ray Diffraction (XRD) using a Bruker Advance D8 with Siemens 5000 Diffractometer and Cu Kα radiation. Textural properties were obtained by N<sub>2</sub> adsorption/desorption isotherms of the samples, using Micromeritics ASAP 2010 volumetric adsorption analyzer at -196°C. Prior to the measurement, the calcined catalysts were degassed at 200°C for an hour. Meanwhile, elemental composition was determined by energy dispersive X-ray spectroscopy (EDX).

#### Catalytic oxidative desulfurization

All ODS reactions were conducted in a 100 ml round-bottom flask, equipped with a magnetic stirrer and fitted with condenser. In a typical run, the oil bath was first heated and stabilized at the constant temperature (between 60°C-65°C). Then, diesel fuel (10 ml) was added to the flask, followed by the oxidant and catalyst. The mixture was refluxed for 30 minutes under vigorous stirring at atmospheric pressure [5]. The oxidized diesel was extracted with DMF at volume ratio solvent: diesel=1.0. The extraction process was vigorously stirred for 30 minutes followed by phase separation between diesel and solvent. The treated diesel was analyzed by gas chromatography (Agilent 6890N GC) equipped with FPD detector [9].

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## Results and Discussion

### Characterization of catalyst

The BET surface area and elemental composition of the catalysts are summarized in Table 1. The surface area of  $\text{Mo}^{6+}/\text{Al}_2\text{O}_3$  catalyst (231  $\text{m}^2/\text{g}$ ) decreased with the increment of number of loading (209  $\text{m}^2/\text{g}$ ). After the tungsten was added, it can be observed that the surface area of  $\text{W}^{6+}/\text{Mo}^{6+}/\text{Al}_2\text{O}_3$  decreased from 209 to 191  $\text{m}^2/\text{g}$  when tungsten loading was increased. Figure 1 shows the XRD patterns of 16.09%  $\text{Mo}^{6+}/\gamma\text{-Al}_2\text{O}_3$  and 4.35% $\text{W}^{6+}/16.52\%$   $\text{Mo}^{6+}/\gamma\text{-Al}_2\text{O}_3$  catalysts with different calcination temperatures. From XRD, it could be seen that at low calcination temperature, all samples exhibited high noise to signal ratio and very low degree of crystallinity. When calcination was carried out at 700°C, the amorphous phase would transform to the crystalline phase. Those at  $2\theta=34.61, 36.68, 45.56$  and  $67.28^\circ$  were attributed to the orthorhombic phase of alumina, while those at  $2\theta=23.45, 25.50$  and  $27.25^\circ$  were attributed to the  $\text{MoO}_3$  with orthorhombic phase. The reflections due to the spinel compound of  $\text{Al}_2(\text{MoO}_4)_3$  can be seen at  $2\theta=20.84, 22.09$  and  $23.10^\circ$ . According to Imamura et al. [10], when calcination temperature was increased from 500°C to 650°C,  $\text{Al}_2(\text{MoO}_4)_3$  was produced on  $\gamma\text{-Al}_2\text{O}_3$ . However, the tungsten-alumina spinel compound was not present in the sample, possibly due to the formation of bulk  $\text{Al}_2(\text{WO}_4)_3$  is expected to occur at calcination temperatures above 1100°C (Table 1).

### Effect number of coating on alumina supported molybdenum oxide catalysts

Figure 2 shows the sulfur conversion by using  $\text{Mo}^{6+}/\text{Al}_2\text{O}_3$  catalysts with different number of coating. Higher molybdenum loading would enhance sulfur elimination until the loading of  $\text{Mo}^{6+}/\text{Al}_2\text{O}_3$  reached 3x (Th=80%, DBT=90%, 4,6-DMDBT=90%). Beyond this value, a further increase of molybdenum loading would deactivate the activity. It indicated that 16.09 wt. % is the optimum loading of  $\text{Mo}^{6+}/\text{Al}_2\text{O}_3$ . Similar results were obtained by Wang et al. [11], who found that the DBT conversion increase with increasing Mo content up to approximately 16 wt.% and level off beyond this value. The optimal value of molybdenum loading (16.09 wt.%) was then investigated in different calcination temperatures. Based on the results, the catalytic activity of 16.09%  $\text{Mo}^{6+}/\text{Al}_2\text{O}_3$  catalyst was decreased with increase in calcination temperature. The mild calcination temperature at 500°C assured that the surface metal oxide species were fully oxidized and dispersed and that the formation of solid solutions or compounds was avoided [12]. The amorphous property of 16.09%  $\text{Mo}^{6+}/\text{Al}_2\text{O}_3$  contributed to its higher specific surface area (216  $\text{m}^2/\text{g}$ ) and porosity which resulted the highest sulfur removal as compared to that in 700°C and 1000°C.

### Effect of dopant on 16.09% $\text{Mo}^{6+}/\text{Al}_2\text{O}_3$ catalyst

Some efforts have been done to improve the molybdenum catalyst by using other metals such as W, Ti and V in the ODS. Results in figure 3 demonstrate that the alumina supported bimetallic oxide catalysts decreased in the order: W/Mo>Ti/Mo>V/Mo. Complete removal of DBT and 4,6-DMDBT, and 92.5% of thiophene was achieved in the presence of 4.35%  $\text{W}^{6+}/16.52\%$   $\text{Mo}^{6+}/\text{Al}_2\text{O}_3$  catalyst. Results obtained reveal that the addition of tungsten enhances the dispersion and distribution of molybdena on the support, as confirmed by FESEM analysis (not shown). Besides, it can be inferred that the behavior of W was very similar to Mo, meant that the active site structure of W was similar to that of Mo. Therefore, it is better to increase the efficiency of Mo catalyst by doping with tungsten species since Mo species is an active catalyst. It is in agreement with Dieterle et al [13], who stated that

tungsten acts as a promoter and potentially stabilizes the intermediate Mo oxide.

The potential  $\text{W}^{6+}/\text{Mo}^{6+}/\text{Al}_2\text{O}_3$  catalyst was further investigated on different dopant ratios. Table 2 shows that the addition of tungsten (4.35%) to the catalyst increased the conversion of sulfur (thiophene 92.5%, DBT 100% and 4,6-DMDBT 100%) and further increase of tungsten has no additional advantage on the catalytic removal of DBT but deteriorated the conversion of thiophene and 4,6-DMDBT. From FESEM morphology (not shown), an excess of tungsten (more than 4.35%) in the catalyst causes the agglomeration and aggregation of molybdenum oxide on the catalyst surface. Indeed, it lowers the degree of dispersion of molybdenum together with the number of coordinatively unsaturated sites, thus attests weak catalytic activity. For that reason, it proved that optimum tungsten content does not only serve as a structural promoter, but significantly influenced activity and selectivity.

Figure 4 demonstrates that 4.35% $\text{W}^{6+}/16.52\%$  $\text{Mo}^{6+}/\text{Al}_2\text{O}_3$  at 500°C calcination temperature reduced sulfur contents (DBT=100%,

Catalysts	$S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )	Loading <sup>a</sup> (wt. %)	
		W	Mo
$\text{Al}_2\text{O}_3$	253	-	-
$\text{Mo}^{6+}/\text{Al}_2\text{O}_3$	231	-	4.38
3 $\text{Mo}^{6+}/\text{Al}_2\text{O}_3$	216	-	16.09
5 $\text{Mo}^{6+}/\text{Al}_2\text{O}_3$	209	-	22.25
$\text{W}^{6+}/\text{Mo}^{6+}/\text{Al}_2\text{O}_3$	209	4.35	16.52
2 $\text{W}^{6+}/\text{Mo}^{6+}/\text{Al}_2\text{O}_3$	202	6.25	15.63
3 $\text{W}^{6+}/\text{Mo}^{6+}/\text{Al}_2\text{O}_3$	191	8.83	15.12

Table 1: The physical characteristics of molybdenum oxide based catalysts calcined at 500°C.

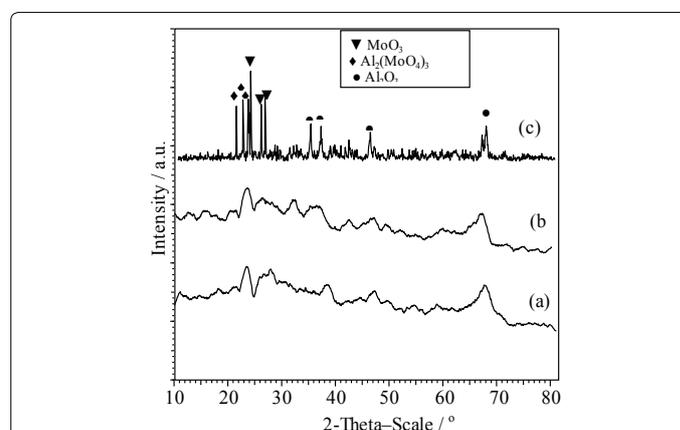


Figure 1: XRD patterns of (a) 16.09%  $\text{Mo}^{6+}/\text{Al}_2\text{O}_3$  (500°C), (b) 4.35% $\text{W}^{6+}/16.52\%$   $\text{Mo}^{6+}/\text{Al}_2\text{O}_3$  (500°C), and (c)  $\text{W}^{6+}/\text{Mo}^{6+}/\text{Al}_2\text{O}_3$ , 10:90 (700°C).

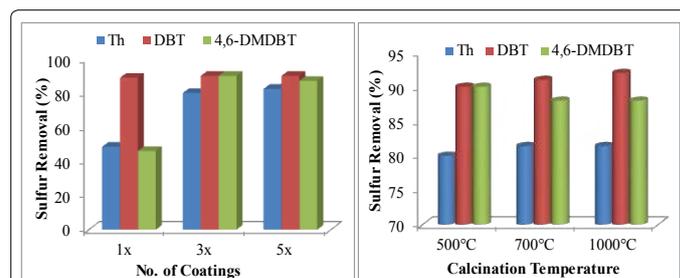


Figure 2: Effect of the number of coatings and calcination temperatures of 16.09%  $\text{Mo}^{6+}/\text{Al}_2\text{O}_3$  catalyst on the performance of sulfur removal in model diesel.

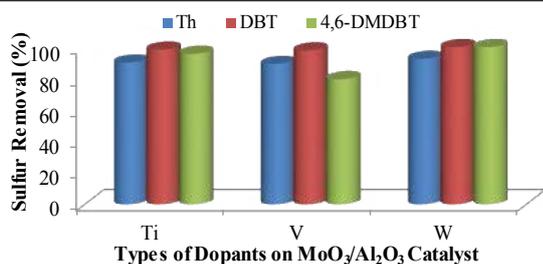


Figure 3: Effect of dopant of  $\text{Mo}^{6+}/\text{Al}_2\text{O}_3$  catalyst on the performance of sulfur removal (%) of thiophene, DBT and 4,6-DMDBT in model diesel.

W:Mo ratio (wt. %)	Sulfur Removal (%)		
	Thiophene	DBT	4,6-DMDBT
10:90	92.5	100	100
20:80	90.6	100	98.5
30:70	87.0	100	96.3

Table 2: Effect of dopant ratios ( $\text{W}^{6+}/\text{Mo}^{6+}/\text{Al}_2\text{O}_3$ ) on the performance of sulfur removal (%) of thiophene, DBT and 4,6-DMDBT in model diesel.

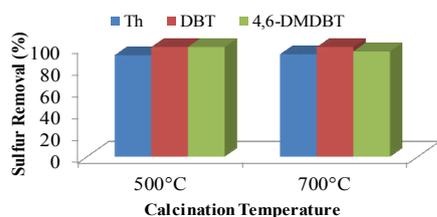


Figure 4: Effect of calcination temperature of 4.35% $\text{W}^{6+}/16.52\% \text{Mo}^{6+}/\text{Al}_2\text{O}_3$  catalyst on the performance of sulfur removal (%) of thiophene, DBT and 4,6-DMDBT in model diesel.

4,6-DMDBT=100%) higher than at 700°C even though its thiophene removal lower than at 700°C calcination temperature. Since the results are quite similar, it implies that increase in calcination temperature, decrease in activity and selectivity. XRD patterns (Figure 1) demonstrated that 4.35%  $\text{W}^{6+}/16.52\% \text{Mo}^{6+}/\text{Al}_2\text{O}_3$  calcined at 500°C possesses amorphous structure while at 700°C, the catalyst forms crystalline structure. The amorphous phase of 4.35%  $\text{W}^{6+}/16.52\% \text{Mo}^{6+}/\text{Al}_2\text{O}_3$  (500°C) catalyst resulted higher catalytic activity as compared to that in 700°C. It is in agreement with Vaudagna et al. [14], who observed that the higher the calcination temperature gave the smaller surface area, thus decrease the catalytic conversion of sulfur compounds.

## Conclusion

It can be concluded that the optimum condition of alumina supported molybdenum oxide catalyst was threefold number of coating (16.09 wt.%) at 500°C. Further improvement on molybdena catalyst indicated that oxidative desulfurization (ODS) for model diesel has been achieved over the 4.35%  $\text{WO}_3/16.52\% \text{MoO}_3/\gamma\text{-Al}_2\text{O}_3$  calcined at 500°C. The most refractory sulfur compounds DBT and 4,6-DMDBT can be removed completely in 30 minutes at ambient pressure and temperature (60°C). Higher calcination temperature (700°C) and tungsten loading of molybdena based catalysts showed deteriorating effect on the catalytic activity.

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