

PREPARATION, CHARACTERIZATION AND MECHANISTIC STUDY OF  
ALUMINA SUPPORTED POLYMOLYBDATE BASED CATALYSTS FOR  
CATALYTIC OXIDATIVE DESULFURIZATION OF DIESEL FUEL

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*Here's a token of love and gratitude.*

*Specially dedicated to my beloved family (Wan Abdullah, Che Residah, Abe, Kza, Kha, Kyah, Kna, Kda, Kmah, Adeq, my brothers and sister in law, my niece and nephews) for the continuous supports, encouragements and prayers.*

*For my dearest husband, Ammar Karim; My source of strength and comfort*

*Thanks for always being there for me.*

*May Allah bless all of you.*

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## ABSTRACT

Existing technique of hydrodesulfurization (HDS) is no longer applicable in achieving Euro IV standard diesel, as for it high operational cost, low efficiency and high operating temperature in the hydrogen gas atmosphere. Due to these drawbacks, the utilization of the oxidative desulfurization catalyst was introduced as an alternative or a complementary to the HDS process. In this study, the performance of the alumina supported polymolybdate based catalyst on the oxidative desulfurization (ODS) of the commercial diesel was investigated using *tert*-butyl hydroperoxide (TBHP) as an oxidizing agent and *N,N*-dimethylformamide as an extraction solvent. The commercial diesel with total of sulfur of 440 ppmw was employed to evaluate the elimination potential of the sulfur compounds.  $M/\text{Al}_2\text{O}_3$  ( $M=\text{Mo}$ ) and  $M_1/M_2/\text{Al}_2\text{O}_3$  ( $M_1 = \text{Fe, Co, Cu, Ca, Ba, Sr, } M_2 = \text{Mo}$ ) were prepared by the wet impregnation method and tested in this reaction. Further investigation on the doped molybdenum revealed that  $\text{Fe}/\text{MoO}_3\text{-PO}_4/\text{Al}_2\text{O}_3$ , calcined at  $500^\circ\text{C}$  was the best catalyst in this study. Utilization of the catalyst was able to reduce the sulfur levels in the commercial diesel of 440 ppmw to Euro IV diesel of less than 18 ppmw, with 96% of total sulfur removal after the second extraction. X-ray diffraction analysis (XRD) results showed that the best catalyst is highly amorphous, while micrograph of the field emission scanning electron microscopy (FESEM) illustrated an inhomogeneous distribution of various particle sizes. The energy dispersive X-ray analysis (EDX) results have confirmed the presence of Mo, P and Fe in all of the prepared catalysts. X-ray photoelectron spectroscopy (XPS) analysis for the surface of  $\text{Fe}/\text{MoO}_3\text{-PO}_4/\text{Al}_2\text{O}_3$  catalyst calcined at  $500^\circ\text{C}$  showed the binding energy for Mo  $3d_{5/2}$  231.7 eV and Mo  $3d_{3/2}$  235.2 eV were corresponded to the formation of  $\text{Mo}^{6+}$ . Temperature programme desorption of ammonia (TPD) analyses showed that the catalysts contribute a strong Lewis acid character. The phosphorus-31 nuclear magnetic resonance ( $^{31}\text{P}$  NMR) analyses indicated the presence of mainly monomeric phosphates in catalyst calcined at  $400^\circ\text{C}$  and  $500^\circ\text{C}$ , whereas mixtures of monomeric and polyphosphates and  $\text{AlPO}_4$  are present in catalyst calcined at  $600^\circ\text{C}$ . Statistical response surface methodology (RSM) by Box-Behnken design suggested that 0.10 g of  $\text{Fe}/\text{MoO}_3\text{-PO}_4$  (10:90)/ $\text{Al}_2\text{O}_3$  with Fe loading of 10 wt.% and calcination temperature of  $530^\circ\text{C}$  have achieved maximum sulfur elimination of 84.8%. Mechanistic study by Fourier transform infra-red (FTIR) showed an agreement with Langmuir-Hinshelwood mechanism with the adsorption of TBHP on the catalyst surface. The reaction mechanisms of peroxy oxygen was identified and proposed as the reaction between peroxide and dibenzothiophene to form dibenzothiophene sulfoxide. Further oxidation process with the presence of polymolybdate alumina supported catalyst has led to the formation of sulfone. The results obtained have proven that  $\text{Fe}/\text{MoO}_3\text{-PO}_4(10:90)/\text{Al}_2\text{O}_3$  can be used as the potential catalyst for the removal of sulfur in the Malaysian diesel towards achieving the 'green diesel' production.

## ABSTRAK

Teknik penyahsulfuran secara hidro (HDS) yang sedia ada tidak lagi sesuai untuk mencapai diesel piawai Euro IV, disebabkan kos operasi yang tinggi, kecekapan yang rendah dan suhu pengoperasian yang tinggi dalam atmosfera gas hydrogen. Disebabkan kelemahan ini, penggunaan mangkin penyahsulfuran oksidatif telah diperkenalkan sebagai alternative atau pelengkap kepada proses HDS. Dalam kajian ini, prestasi mangkin polimolibdat berpenyokong alumina ke atas penyahsulfuran oksidatif diesel komersial telah dikaji menggunakan *tert*-butil hidroperoksida (TBHP) sebagai agen pengoksidaan dan *N,N*-dimetilformamid sebagai pelarut pengekstrakan. Diesel komersial dengan jumlah sulfur sebanyak 440 ppmw telah digunakan untuk menilai keupayaan penyingkiran sebatian sulfur.  $M/Al_2O_3$  ( $M=Mo$ ) dan  $M_1/M_2/Al_2O_3$  ( $M_1 = Fe, Co, Cu, Ca, Ba, Sr, M_2 = Mo$ ) telah disediakan dengan kaedah pengisitepuan basah dan diuji dalam tindak balas ini. Kajian lanjut ke atas molibdenum yang telah didop menunjukkan  $Fe/MoO_3-PO_4/Al_2O_3$  yang dikalsin pada suhu 500°C adalah mangkin terbaik dalam kajian ini. Penggunaan mangkin telah dapat mengurangkan kandungan sulfur di dalam diesel komersial 440 ppmw kepada diesel Euro IV yang kurang daripada 18 ppmw, dengan 96% penyingkiran jumlah sulfur selepas pengekstrakan kedua. Keputusan analisis pembelauan sinar-X (XRD) menunjukkan mangkin terbaik berkeadaan sangat amorfus manakala mikrograf daripada mikroskopi imbasan elektron pancaran medan (FESEM) menggambarkan taburan tidak seragam pelbagai saiz zarah. Keputusan analisis tenaga serakan sinar-X (EDX) telah mengesahkan kehadiran Mo, P dan Fe di dalam semua mangkin yang disediakan. Analisis spektroskopi foto elektron sinar-X (XPS) untuk permukaan mangkin  $Fe/MoO_3-PO_4/Al_2O_3$  yang dikalsin pada suhu 500°C menunjukkan tenaga pengikatan bagi Mo  $3d_{5/2}$  231.7 eV dan Mo  $3d_{3/2}$  235.2 eV adalah  $Mo^{6+}$ . Analisis penyahjerap pengaturcaraan suhu ammonia (TPD) pula menunjukkan bahawa mangkin menyumbangkan ciri asid Lewis yang kuat. Analisis resonans magnet nuclear fosforus-31 ( $^{31}P$  NMR) menunjukkan kehadiran spesies fosfat monomerik pada mangkin yang dikalsin pada suhu 400°C dan 500°C, manakala campuran monomerik dan polifosfat dan  $AlPO_4$  didapati pada mangkin yang dikalsin pada suhu 600°C. Metodologi statistik gerak balas permukaan (RSM) oleh reka bentuk Box-Behnken mencadangkan, bahawa 0.10 g mangkin  $Fe/MoO_3-PO_4$  (10:90)/ $Al_2O_3$  dengan 10 wt.% muatan Fe dan suhu pengkalsinan 530°C dapat mencapai penyingkiran maksimum sulfur sebanyak 84.8%. Kajian mekanisme menggunakan spektroskopi infra-merah transformasi Fourier (FTIR) menunjukkan persetujuan dengan mekanisme Langmuir-Hinshelwood, dengan penyerapan TBHP di atas permukaan mangkin. Mekanisme tindak balas oksigen peroksi telah dikenalpasti dan dicadangkan sebagai tindak balas antara peroksida dan dibenzotiofena untuk membentuk dibenzotiofena sulfoksida. Proses pengoksidaan selanjutnya dengan kehadiran mangkin polimolibdat berpenyokong alumina telah mengarah kepada pembentukan sulfon. Keputusan diperoleh membuktikan bahawa  $Fe/MoO_3-PO_4(10:90)/Al_2O_3$  boleh digunakan sebagai mangkin yang berpotensi untuk penyingkiran sulfur di dalam diesel Malaysia ke arah mencapai penghasilan 'diesel hijau'.

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## LIST OF ABBREVIATIONS

|                                |   |   |
|--------------------------------|---|---|
| 4,6-DMDBT                      | - | 4,6-Dimethyldibenzothiophene  |
| ADS                            | - | Adsorptive Desulfurization  |
| Al <sub>2</sub> O <sub>3</sub> | - | Alumina   |
| ANOVA                          | - | Analysis of Variance  |
| ASTM                           | - | American Society of Testing Materials                                   |
| BBD                            | - | Box-Behnken Design  |
| BDS                            | - | Biodesulfurization  |
| BET                            | - | Brunnauer, Emmet and Teller   |
| BT                             | - | Benzothiophene  |
| Cat-ODS                        | - | Catalytic Oxidative Desulfurization                                     |
| CCD                            | - | Central Composite Design  |
| CHP                            | - | CumeneHydroperoxide   |
| DBT                            | - | Dibenzothiophene  |
| DMF                            | - | <i>N, N</i> -dimethylformamide  |
| DMSO                           | - | <i>N, N</i> -dimethylsulfoxide  |
| EDS                            | - | Extractive Desulfurization  |
| EPA                            | - | Environmental Protection Agency   |
| EtOH                           | - | Ethanol   |
| FESEM-EDX                      | - | Field Emission Scanning Electron Microscope- Energy<br>Dispersive X-Ray |
| FTIR                           | - | Fourier Transform Infrared Spectroscopy                                 |
| GAA                            | - | Glacial Acetic Acid   |
| GC-FPD                         | - | Gas Chromatography- Flame Photometric Detector                          |
| GCMS                           | - | Gas Chromatography –Mass Spectroscopy                                   |
| H <sub>2</sub> O <sub>2</sub>  | - | Hydrogen Peroxide   |
| HC                             | - | Hydrocarbon   |
| HDS                            | - | Hydodesulfurization   |

|                     |   |  |
|---------------------|---|--|
| HPMO                |   | Phosphomolybdic acid   |
| IL                  | - | Ionic Liquid   |
| IUPAC               | - | International Union of Pure and Applied Chemistry                |
| IWI                 | - | Incipient Wetness Impregnation                                   |
| LOF                 | - | Lack-of-fit  |
| NA                  | - | Nitrogen Gas Adsorption  |
| NMP                 |   | 1-methyl-2-pyrrolidone   |
| ODS                 | - | Oxidative Desulfurization  |
| OSC                 | - | Organic Sulfur Compound  |
| PAA                 | - | Peracetic Acid   |
| PDF                 | - | Powder Diffraction File  |
| <sup>31</sup> P NMR | - | <sup>31</sup> Phosphorus Nuclear Magnetic Resonance spectroscopy |
| RSM                 | - | Response Surface Methodology                                     |
| SG                  | - | Sol-Gel  |
| TBHP                | - | <i>Tert</i> -Butyl Hydroperoxide                                 |
| TGA-DTA             | - | Thermogravimetry Analysis-Differential Thermal Analysis          |
| Th                  | - | Thiophene  |
| TPD                 | - | Temperature Programme Desorption                                 |
| UAOD                | - | Ultrasound-Assisted Oxidation Desulfurization                    |
| ULSD                | - | Ultra-Low Sulfur Diesel  |
| USEPA               |   | United State Environmental Protection Agency                     |
| XPS                 | - | X-Ray Photoelectron Spectroscopy                                 |
| XRD                 | - | X-Ray Diffraction  |

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## CHAPTER 1

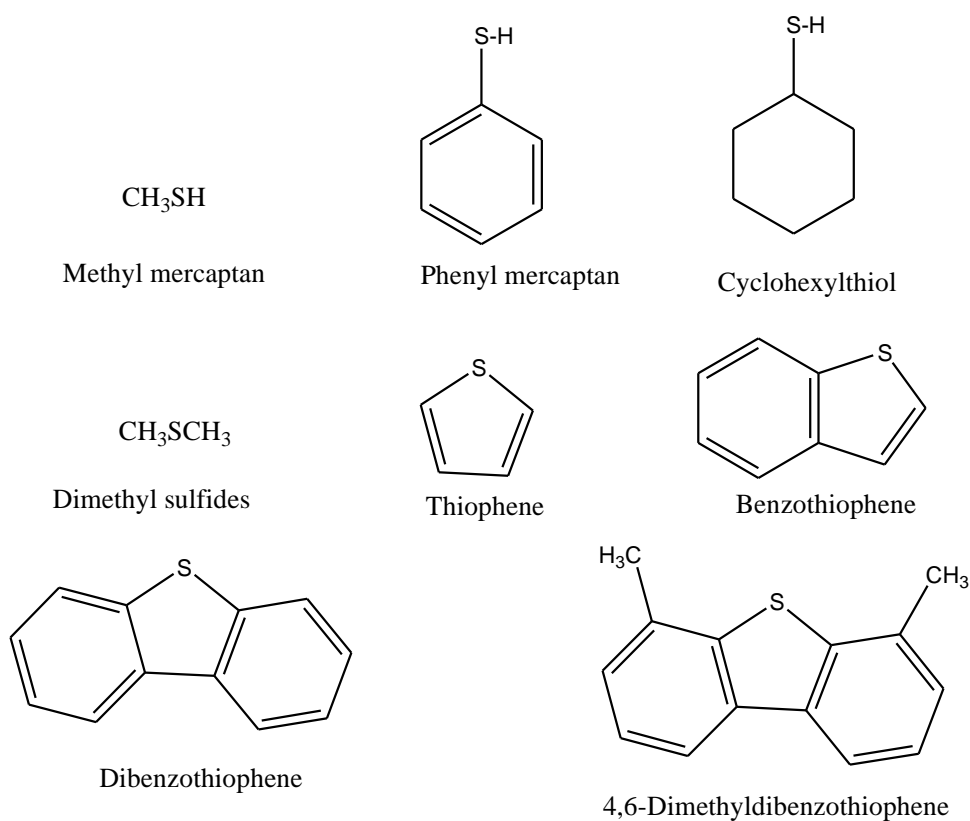
### INTRODUCTION

#### 1.1 Background of Study

Diesel is extensively used as a fuel both in high way transportation vehicles (e.g. cars, buses and trucks) and non-highway transportation systems (e.g. locomotives, marine vessels, farm equipments, etc.). Diesel engines are 25–40% more fuel-efficient than gasoline engines. Nevertheless, they suffer from associated particulate, NO<sub>x</sub> and SO<sub>x</sub> emissions that are harmful to human health and the major cause of acid rain. Sulfur, a natural part of the crude oil from which diesel fuel is derived, is one of the key causes of particulates or soot in diesel. In a petroleum refinery, the desulfurization of petroleum feedstock is important because high levels of organics sulfur in the feed can contaminate the noble metal catalyst during catalytic reforming stage. Besides, the removal of sulfur from feeds can improve the color and stability of products such as gasoline from catalytic cracking unit known as a sweetening process.

Diesel fuel contains more than 60 types of organic sulfur compounds that can be divided into four main groups which are sulfides, mercaptans, disulfides and thiophene (Srivastava 2012). The organic sulfur contains one or more sulfur atoms covalently bonded to the remainder of the molecular structure as thiols, thioethers and sulfides or form as sulfur-bearing heterocycle compounds. The aromatic sulfur containing heterocycle called thiophenes are particular common in diesel fuel. Benzothiophenes (BT) and dibenzothiophenes (DBT) are types of condense thiophene derivative which are considered challenging substrates. Thiophene itself is easier to

hydrogenolyse whereas 4,6-dibenzothiophene is the most difficult substrate. Sulfur in crude oils is mainly present in the form of organosulfur compounds. Examples of some sulfur compounds in crude oils are presented in Figure 1.1.



**Figure 1.1** Sulfur compounds in crude oils (Ogunlaja 2013)



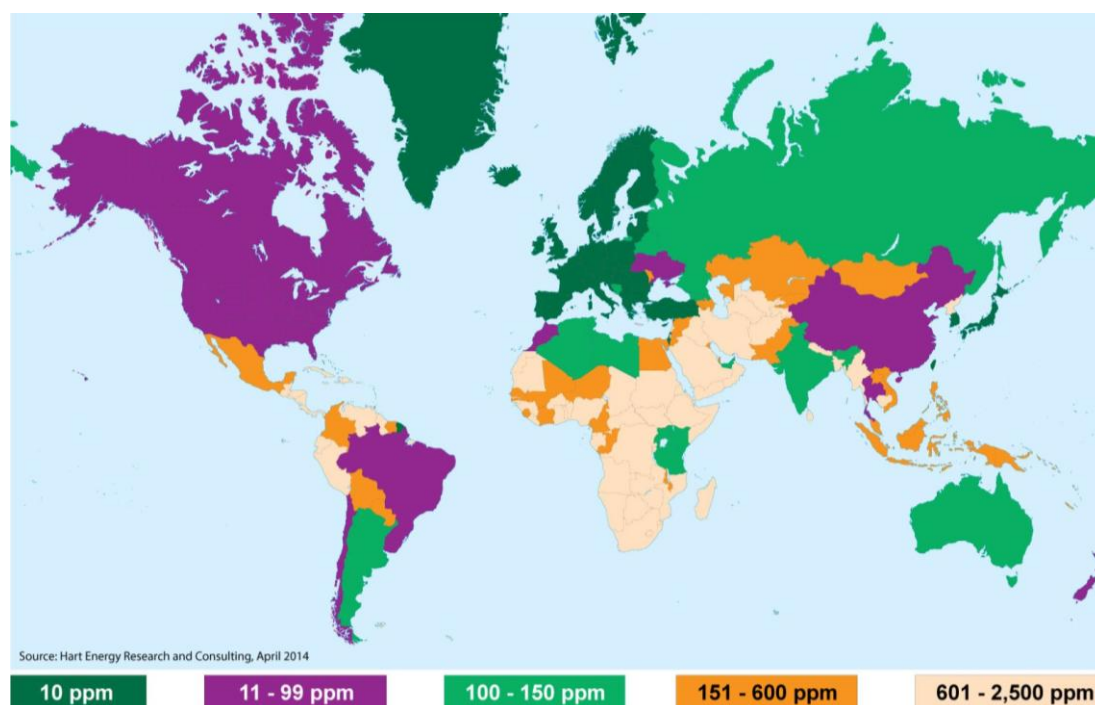
## 1.2 Standards

The specifications and quality changes of transportation fuels represent the most challenging problems for the refiners in the new millennium. New diesel fuel specification, particularly for the industrialized nations, such as Europe, U.S., and Japan, requires drastic reduction in the sulfur contents (Table 1.1). Other countries are following the footsteps of the industrialized nations to increase the fuel quality to meet the stringent specifications.

**Table 1.1** Changes of sulfur specifications of motor diesel fuels in Europe and U.S. over time ( Ismagilov *et al.*, 2011)

| Country/Property        | Europe 2000 | Europe 2009 | U.S. 1993 | U.S. 2009 |
|-------------------------|-------------|-------------|-----------|-----------|
| Sulfur, ppmw            | 350         | 10          | 500       | 15        |
| Cetane number           | 51          | 51          | 40        | 40        |
| ASTM D86 95V% point, °C | 360         |             | 338       |           |
| Aromatics, V%           |             |             | 35        | 35        |
| Poly aromatics, W%      | 11          | 11          |           |           |

Low-sulfur containing crude oils are referred to as sweet oils, while the high-sulfur containing crude oils are referred to as sour crudes and are less desirable due to high cost involved in treating (desulfurizing) the oils. Various crude oils around the world have different sulfur contents (ppmw). In many countries around the world, environmental regulations have been introduced to reduce the sulfur content of diesel fuel and other transportation fuels to ultralow levels (10–15 ppmw) (Zongxuan *et al.*, 2011). The United State Environmental Protection Agency (USEPA) recommended that the sulfur content in diesel should be reduced to 15 ppm by year 2006 (Srivastava 2012). Currently, the maximum allowable sulfur content in diesel in USA and Europe is 10 ppmw. Figure 1.2 shows the roadmap of sulfur limit by certain countries around the world in 2014 and it show the requirement sulfur content in diesel for Malaysia are still high as compared to the other countries.



Source: International Fuel Quality Center, April 2014

**Figure 1.2:** Roadmap of International Diesel Fuel Quality Standard

The environmental regulation of Malaysia for sulfur concentration in diesel fuels is reduced from more than 2000 ppmw to <500 ppmw in 2009 with Euro 2M standard and will be lowered further to 50 ppmw with Euro 4M standard by the year 2020. Table 1.2 shows the sulfur content in different types of diesel. Refineries in Malaysia are facing major challenges to meet the fuel sulfur specification along with the required reduction of aromatics contents. Therefore, oxidative desulfurization (ODS) technique was introduced as an interesting alternative technology to meet the challenges of introducing Euro 4M with sulfur content less than 50 ppmw.

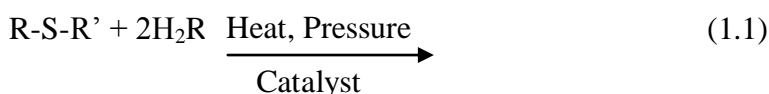
**Table 1.2** Sulfur content in different types of diesel

| Types of Diesel                   | Sulfur Content (ppmw) |
|-----------------------------------|-----------------------|
| Euro II (Low Sulfur Diesel)       | 500                   |
| Euro IV (Ultra Low Sulfur Diesel) | 50                    |
| Euro V (Green Diesel)             | 10                    |
| Euro VI (Very Low Sulfur Diesel)  | < 5                   |

Source: The Malaysian Insider, July 2015.

### 1.3 Current Technologies Used in Treatment of Diesel

Hydrodesulfurization (HDS) is the conventional process for reducing of organosulfur in gasoline, diesel and other intermediate distillates. This process is highly efficient in removing thiols, sulfides, disulfides, and some thiophene derivatives, but it was less effective for dibenzothiophene derivatives with steric hindrance on the sulfur atom (refractory organosulfur compounds), such as 4,6-dimethyldibenzothiophene (4,6-DMDBT). These compounds are sterically hindered in dehydrogenation and also their C-S bond energy is almost equal with the C-H bond energy, which make them hard to desulfurize by hydrotreatment (Attar and Corcoran, 1978). Besides, the current hydrodesulfurization technology requires the use of a higher reaction temperature, a higher reaction pressure, a larger reactor volume or more active catalyst or some combination of these. All of these require high operating expenses. Equation 1.1 shows the general reaction of the hydrodesulfurization.



Since HDS method unable to remove refractory organosulfur compounds, a new alternatives for desulfurization process was introduced which combines the selective adsorption of the sulfur compounds (SARS unit) and the hydrodesulfurization (HDS) This method utilizing a transition metal compound supported in silica gel successfully remove refractory organosulfur compounds at ambient condition (Ma *et al.*, 2002).

Besides, another approached for deep desulfurization is biodesulfurization which can specifically remove sulfur from refractory hydrocarbons under mild conditions and it can be potentially used in industrial desulfurization. Microbial desulfurization is an environmentally friendly method that can remove sulfur without lowering the calorific value of the fuel. Some microorganisms can consume the sulfur in thiophenic compounds such as DBT and reduce the sulfur content in fuel. Desulfurization by microorganism is potentially advantageous as it is carried out in mild conditions, thus it is considered as an energy-saving process. Secondly,

biocatalysts are involved in biological activities, thus the desulfurization would be highly selective (Soleimani *et al.*, 2007). However, biological removal of sulfur has several limitations that prevent it from being applied today. The metabolism of sulfur compounds is typically slow compared to chemical reactions.

Photocatalytic oxidative desulfurization is another method to enhance the ODS process in fuel. Photocatalytic oxidation of the oil desulfurization is combined with photochemical reaction and liquid-liquid extraction. Under normal temperature and pressure, oil and extractant are added at the same time to begin the photocatalytic oxidation, and the oxidant can be oxygen, hydrogen peroxide and titanium dioxide. Photocatalytic oxidation desulfurization can achieve applications in the decomposition of organic compounds with high-pressure mercury lamp of visible light or ultra-violet. Although the photocatalytic desulfurization method has several advantages such as simple process, low cost for oxidation reaction, but it has some limitation such as a slow response and the light required for a long time ( Zhang *et al.*, 2009).

Desulfurization by ionic liquid is based on extraction theories and it is mild process. The purpose of research on ionic liquid is to economize desulfurization energy requirement and to decrease CO<sub>2</sub> production that is associated with other desulfurization processes such as HDS. Ionic liquids are an alternative to replace organic solvents because they have no measurable vapor pressure below their decomposition temperature and can be designed to have different properties depending on their structure. Imidazolium based ionic liquids, such as [BMIM][PF<sub>6</sub>], [EMIM][BF<sub>4</sub>], [BMIM][MeSO<sub>4</sub>], [BMIM][AlCl<sub>4</sub>], [BMIM][O<sub>2</sub>CSO<sub>4</sub>], have demonstrated a high selective partitioning for heterocyclic sulfur-containing molecules such as DBT, single  $\beta$  and di- $\beta$  methylated DBTs.

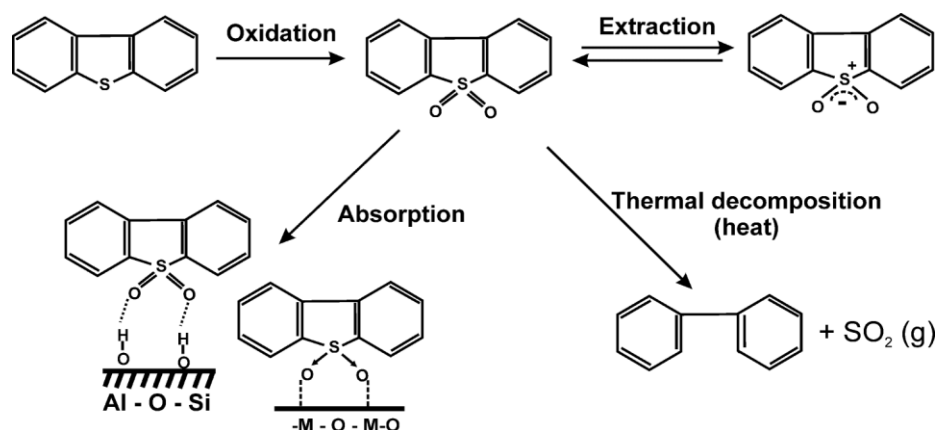
However this approach has some limitation such as the recovery and recycling of ionic liquid during desulfurization is difficult. Organic solvent extraction techniques can be used to recover ionic liquid however loss of solvent during extraction is undesirable. Some chlorometallate ionic liquid shows good selectivity

for sulfur removal however they are sensitive to air and moisture and may cause alkene polymerization in fuel (Soleimani *et al.*, 2007).

#### 1.4 Oxidative Desulfurization

Several new processes as alternatives to current hydrodesulfurization (HDS) technology have been proposed such as selective sulfur adsorption, selective sulfur oxidation, biodesulfurization and oxidative desulfurization (ODS) combined with extraction is considered to be one of the promising process, because it has some potential advantages over HDS. First, the refractory- substituted dibenzothiophenes (DBTs) are easily oxidized at relatively mild conditions so expensive hydrogen gas is not required. Therefore, the capital cost of ODS is significantly less than HDS since this process is more suitable for small and medium size refineries, especially those that are isolated and not located close to hydrogen pipeline. The oxidation of sulfur containing compounds leads to the formation of the corresponding sulfoxides and sulfones, which are highly polar and can be removed by extraction with polar solvents such as acetonitrile, methanol and N,N-dimethylformamide. Oxidative desulfurization (ODS) has been considered as a new technology for the deep desulfurization of transport fuels, which is not a replacement process to HDS but is a complementary process to HDS, because the refractory compounds in HDS, including alkyl dibenzothiophene (DBT) compounds [e.g., 4,6-dimethyl DBT (4,6-DMDBT)], show the highest oxidation rate in ODS and can achieve a sulfur content of <10 ppm (ULSD) (Ceden˜o-Caero and Alvarez-Amparan 2014).

Generally, oxidative desulfurization involves two main steps which first oxidation of sulfur containing compounds to sulfoxides and sulfones by a selective oxidant. The oxidant can be supplied by either peroxy organic acids, hydroperoxides, ozone or peroxy acids. The second step is proceed by removal of sulfoxides and sulfones from diesel by extraction, absorption, adsorption or distillation (Chica *et al.*, 2006). This reaction is shown in Figure 1.3.



**Figure 1.3:** Simplified reaction scheme of sulfone compounds removal after the ODS process ( Ismagilov *et al.*, 2011)

## 1.5 Catalyst

The use of catalysts is vital in the oxidative desulfurization reaction. From previous studies on both oxidants and catalyst, some catalysts show significant activity for the oxidation of DBT, benzothiophene (BT) and other sulfur-containing organic compounds. It was reported in previous study that the use of organic acids, and polyoxometallic acids and their salts in aqueous solution, as catalyst in the oxidation by H<sub>2</sub>O<sub>2</sub>. However, it is known that homogeneous catalyst are difficult to separate from reaction products, and this limit their recycling (García-Gutiérrez *et al.*, 2006). Thus preparation of new supported catalyst constitute the most desirable improvement of the oxidative desulfurization process.

Catalysts that are usually employed for oxidative desulfurization reaction are transition metal in high oxidation state with Lewis acidity such as Mo(IV), Ti(IV), (V) and W(IV) which were prepared by impregnation method. Most of the studies have been concentrated on heterogeneous MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>. Recently, Bakar *et al.*, (2012) reported that MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> was an active catalyst for the oxidation of dibenzothiophenic compounds. It was also reported that the activity of catalysts for the oxidation of thiophene, DBT and 4,6-DMDBT diminished in the order : Mo>Mn>Sn>Fe~Co> Zn. Moreover, the criteria of low oxidation potentials and high Lewis acidity in its highest oxidation state accelerated Mo catalyst to oxidize

organosulfur compounds more than other catalyst. Likewise, the increase in the sulfur elimination can be enhanced by using catalysts containing phosphorus (phosphate) (García-Gutiérrez *et al.*, 2006).

Alumina is often used as support catalyst due to its favorable ability to stabilize a small cluster size. In previous studied, it was reported that, the activity of the catalyst were depended on the type of supports used which was in the following order of  $\text{Al}_2\text{O}_3 > \text{SiO}_2 > \text{TiO}_2 > \text{SiO}_2\text{-Al}_2\text{O}_3$  (Mori *et al.*, 1998). The loading of transition metal oxide may enhance the efficiency of catalyst, it may enhances the dispersion and distribution of molybdenum on support (Bakar *et al.*, 2012) The used of transition metal as dopant will not only reduced the price of the catalyst but will also improve the thermal stability of alumina supported catalyst and promoting the dipersion of metal support.

## **1.6 Response Surface Methodology (RSM)**

Response surface methodology (RSM) is a set of techniques used to develop models from experimental or simulation data and can be used to obtain an optimal response (Dube *et al.*, 2013). Although RSM is typically referred to as the process of identifying and fitting an appropriate response surface model from experimental data, it can be applied to numerical modeling studies, where each run can be regarded as an experiment (White 1987.; Li *et al.*, 2011). Compared to other RSM designs, Box-Behnken design (BBD) is the most frequently employed and offers some advantages; requiring few experimental points and high efficiency (Box *et al.*, 1960).

## **1.7 Statement of the Problem**

Hydrodesulfurization (HDS) is the conventional method for lowering sulfur levels in diesel oil, but this technology requires severe conditions and is expensive. Common available oxidative desulfurization (ODS) methods are now

facing problem for reducing sulfur content in diesel fuel to concentration nearly to 50 ppmw. Currently, the main obstacles for industrial application of ODS are their low oxidation activity and their low selectivity for sulfides, the difficulties in separation and recovery of the catalysts after the reaction, the low utilization efficiency of oxidant and the introduction of other components to the oxidation system.

It appears that catalysts have been used in most investigations to enhance the effectiveness of oxidant in ODS process. However, most research done was limited only to monometallic oxide catalyst and focused on model diesel. Thus, in this research focused will be made on performance of new supported bimetallic oxide and trimetallic catalysts in commercial diesel. Besides, the development of alumina supported catalysts containing molybdenum and their evaluation in the OD process of diesel fuel has been widely investigated in oxidative desulfurization process. However, molybdenum containing phosphorus had not been widely used for its ability as a based catalyst for the oxidative desulfurization. Therefore, in the present study, catalyst prepared from phosphomolybdic acid was selected as based catalyst in Cat-ODS reaction.

Recently, a promising alternative oxidative desulfurization using transition metal catalyst has been developed. The chosen catalyst should be of high efficiency for oxidative desulfurization reaction and able to give high percentage of sulfur removal. Molybdenum phosphate was used as base catalyst doped with transition and alkaline earth metal such as cobalt, copper, ferum, calcium, barium, and strontium. Furthermore, with conventional catalyst system, the percentage of sulfur removal is not as high as desired when it was applied to large scale of commercial diesel. Therefore, a new catalysts system must be studied to see what material can convert sulfur into sulfones in maximum percentage so that it can be applied to the world standard diesel which sulfur content should be below 50 ppmw. This method is an economical method since the catalyst can be recycled, and it is also environmental friendly since it does not emit any toxic gas into air while reaction takes place. Therefore, CAT -ODS approach are expected to produce diesel comply to Euro IV standard, diesel with affordable price and diesel of cost effective and operational production.



## 1.8 Objectives of Research

The objectives of this study are:

1. To synthesize an active, selective and stable potential polymolybdate based catalysts with alumina as the support and modifies with transition metal and alkaline earth metal as dopant via impregnation method.
2. To test and optimized the prepared catalysts in oxidative desulfurization process on commercial diesel.
3. To characterize the potential catalyst with various analytical techniques.
4. To study on the optimization of the catalytic oxidative desulfurization technique by Response Surface Methodology (RSM).
5. To postulate the mechanism study on the desulfurization.

## 1.9 Scope of Research

In the removal of sulfur compound, a series of alumina supported polymolybdate based catalysts will be developed to be tested in the catalytic oxidative desulfurization reaction. The catalysts will be doped with different dopants of transition metal such as cobalt, iron, copper, iron and alkaline earth metal such as calcium, barium and strontium at various dopant ratios and calcinations temperature. The undoped molybdena catalysts are also prepared in order to compare the performance with the bimetallic and trimetallic catalysts. The Cat-ODS process was further optimized with various oxidants namely hydrogen peroxide ( $H_2O_2$ ), tert-butylhydroperoxide (TBHP) and peracetic acid (PAA). The prepared catalysts were applied in oxidative desulfurization process using commercial diesel containing 440 ppmw sulfur, obtained from Petronas, Malaysia. Lastly, the potential catalysts were tested on its reproducibility activity. The characterization of the potential catalysts was conducted by various techniques in order to understand the physical properties of the catalysts such as X-ray diffraction (XRD) for bulk structure, field emission

scanning electron microscope (FESEM) for morphology study, energy dispersive X-ray (EDX) analysis for elemental composition study, nitrogen adsorption (NA) for pore texture and surface area of the catalyst. Thermal gravimetric analysis (TGA) was used to study the mass loss of the catalyst during temperature change and  $^{31}\text{P}$  Phosphorus nuclear magnetic resonance spectroscopy ( $^{31}\text{P}$  NMR) was used to assign structures of phosphorus containing compounds. Temperature programmed desorption (TPD) and X-ray photoelectron spectroscopy (XPS) characterization were tested on the most potential catalyst in this study due to the expensive analysis cost compared to the other characterization analyses. An optimization on the catalytic oxidative desulfurization by using response surface methodology (RSM) was studied to obtain the best experimental condition and parameter. A mechanistic study was divided into two parts which were a study on the catalyst surface and the oil model itself. Thiophene (Thio), dibenzothiophene (DBT) and 4,6 dibenzothiophene (4,6 DBT) were used as the model compound to study the ODS mechanism of commercial diesel using TBHP. The gas chromatography –flame photometric detector (GC-FPD) was used to identify the oxidation products and Fourier transform infrared spectroscopy (FTIR) was used for mechanistic surface study of the catalyst. The flow chart for the research framework is given in Appendix A.

### **1.10 Significance of Study**

The major problem of Malaysia diesel fuel is the presence of organosulfur compounds that will result in low quality of Malaysian diesel. It is important to remove the impurities in order to meet the new specifications for sulfur in diesel and increase the price of diesel fuel. Besides that, the presence of sulfur in diesel is one of the key causes of particulates and soot in diesel. Soot is the main culprit of diesel engine's harmful black exhaust fumes and is among the major source of air pollution. Several studies have shown that the amount of  $\text{SO}_x$  emission and particulate matter emissions are directly proportional to the amount of sulfur contained in fuel. If the proposed oxidative desulfurization system with new formulation catalyst can convert sulfur into sulfones in maximum percentage, thus it will help to reduce the environmental pollution caused by sulfur in diesel.

The transition metal and alkaline earth metal catalyst are easily prepared, environmental friendly and reusable. All the ingredients in the synthesis of the catalyst are easily available, cheap and stable. The catalyst is safe to handle because it can be used at low reaction temperature. It requires minimum modification to the already existing system and offers cost effective operating system.

Different supported catalysts have been used in the oxidation by hydrogen peroxide on the organosulfur compounds such as sulfides and dibenzothiophene (DBT), to sulfone. These catalysts have shown good catalytic activities in the case of model systems but there are just a few reports of the processing of commercial diesel using either hydrogen peroxide or *tert*-butyl hydroperoxide. Therefore, with a new catalytic system proposed using stable polymolybdate based catalyst, it is possible to achieve sulfur concentration in commercial diesel less than 15 ppmw (ultra low sulfur diesel). Cat ODS technique able to produce low price diesel and became green and sustainable technologies because the catalyst and solvent can be recycle.

The problem of deep desulfurization of hydrocarbon fuels can be solved by application of catalytic oxidative desulfurization. The advantages of catalytic ODS processes are summarized as follows:

- 1) It does not require expensive hydrogen for production of ULSD;
- 2) It operated under mild conditions-low pressure and temperature;
- 3) The refractory sulfur species (e.g., 4,6-DMDBT) are desulfurized preferentially in the ODS processes.

This method is very environmental friendly and utilizes a green chemistry concept. The novelty of this research study are as follows:

- (1) A development of polymolybdate based catalysts with the use of alumina beads as a support and addition of transition metal and alkaline earth metal as a dopant to increase the performances of the catalysts in the catalytic oxidative desulfurization.
- (2) Development of a simple and cost effective method (Cat-ODS) for the treatment of commercial diesel.

(3) To deduce mechanistic study on the catalytic oxidative desulfurization techniques for the removal of sulfur in the model diesel sample by using and GC-FPD and FTIR instrument.

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