

**PREPARATION, CHARACTERIZATION, AND  
COMPUTATIONAL STUDY OF BIMETALLIC  
IRON OXIDE BASED CATALYST FOR  
CATALYTIC OXIDATIVE DESULFURIZATION  
OF MODEL DIESEL**

**NOR ATIQ SYAKILA BINTI MOHD NAZMI**

**UNIVERSITI SAINS MALAYSIA**

**2021**

**PREPARATION, CHARACTERIZATION, AND  
COMPUTATIONAL STUDY OF BIMETALLIC  
IRON OXIDE BASED CATALYST FOR  
CATALYTIC OXIDATIVE DESULFURIZATION  
OF MODEL DIESEL**

by

**NOR ATIQ SYAKILA BINTI MOHD NAZMI**

**Thesis submitted in fulfilment of the requirements  
for the degree of  
Master of Science**

**December 2021**

## ACKNOWLEDGEMENT

First and foremost, praise and thanks to the God, the Almighty, for his showers of blessing throughout my research work to complete the research successfully.

I would like to express my sincere gratitude to my supervisor Dr Wan Nazwanie Wan Abdullah for the continuous support of my master study and research, for her patience, motivation and immense knowledge. Her guidance helps me in all the time of research and writing of this thesis. Not forgotten, special appreciation goes to my co-supervisor, Prof. Farook Adam and Dr Fazira Ilyana Bt Abdul Razak, for their kindness and knowledge regarding on this research.

I thank to my best friend forever (Nurul Syifa') and my fellow friends; especially, final year student batch 2018 for the stimulating discussions, for the sleepless nights we were working together and for all the memories we had in the last two years.

I am extremely grateful to my parents, Mohd Nazmi Bin Ishak and Noorliza Binti Mohd Yusoff for their love, prayers, caring and sacrifices for educating and preparing me for my future. Also I express my thanks to my brother, my aunties, my uncles and my whole big family for theirs support and valuable prayers.

Lastly, my thanks and appreciation also to all staff of School of Chemistry especially department of Inorganic chemistry and people who have willingly help me out with their abilities.

# TABLE OF CONTENTS

<b>ACKNOWLEDGEMENT.....</b>	<b>ii</b>
<b>TABLE OF CONTENT.....</b>	<b>iii</b>
<b>LIST OF TABLES.....</b>	<b>vi</b>
<b>LIST OF FIGURES.....</b>	<b>vii</b>
<b>LIST OF ABBREVIATIONS.....</b>	<b>xi</b>
<b>ABSTRACT.....</b>	<b>xiv</b>
<b>CHAPTER 1 INTRODUCTION.....</b>	<b>1</b>
1.1 Background of study.....	1
1.1.1 Composition of Sulfur in Diesel.....	2
1.1.2 Sulfur Regulations.....	3
1.2 Technologies used in treatment of diesel.....	5
1.3 Oxidative Desulfurization.....	8
1.4 Catalyst.....	9
1.5 Computational Studies.....	10
1.6 Statement of the Problem.....	11
1.7 Significant of Study.....	13
1.8 Objective of Research.....	14
<b>CHAPTER 2 LITERATURE REVIEW.....</b>	<b>16</b>
2.1 Catalytic Oxidation System.....	16
2.1.1 Catalyst for Oxidative Desulfurization.....	16
2.1.2 Oxidant for Oxidative Desulfurization.....	21
2.2 Mechanism of Catalytic Oxidative desulfurization.....	25
2.3 Desulfurization Mechanism by Computational Study.....	30

2.4	Summary.....	31
<b>CHAPTER 3 METHODOLOGY.....</b>		<b>32</b>
3.1	Apparatus.....	32
3.2	Materials.....	32
3.3	Preparation of alumina supported catalyst by IWI method.....	33
3.4	Preparation of Simulated Diesel.....	34
3.5	Catalytic Oxidative Desulfurization Process.....	35
3.6	Sulfur Measurement in Oxidative Desulfurization Reaction .....	36
3.6.1	Gas Chromatography- Flame Ionization Detector (GC-FID) .....	36
3.7	Characterization of Catalyst.....	36
3.7.1	X-ray Diffraction (XRD).....	37
3.7.2	Field Emission Scanning Electron Microscopy – Energy Dispersive X-Ray (FESEM-EDX).....	37
3.7.3	Nitrogen Adsorption-Desorption Analysis.....	38
3.7.4	High-Resolution Transmission Electron Microscopy (HRTEM)....	38
3.8	Mechanistic Study by Density Functional Theory.....	39
<b>CHAPTER 4 RESULT AND DISCUSSIONS.....</b>		<b>40</b>
4.1	Characterization of Co/Fe-Al <sub>2</sub> O <sub>3</sub> catalyst.....	40
4.1.1	Nitrogen Adsorption Analysis (NA).....	40
4.1.2	X-Ray Diffraction (XRD).....	45
4.2	Catalytic Oxidative Desulfurization of Co/Fe-Al <sub>2</sub> O <sub>3</sub> catalyst.....	56
4.2.1	Effect of Oxidation and Extraction.....	56
4.2.2	Effect of reaction time and temperature.....	58
4.2.3	Screening of Catalyst.....	60
4.2.4	Effect of Dopant.....	61

4.2.5	Effect of Dopant Ratio.....	63
4.2.6	Effect of Calcination Temperature.....	64
4.2.7	Effect of Catalyst Dosage.....	65
4.2.8	Repeatability Testing .....	67
4.2.9	Catalyst Recycling Test.....	68
<b>CHAPTER 5 MECHANISTIC STUDY.....</b>		<b>70</b>
5.1	Introduction.....	70
5.1.1	Cat-ODS Reaction Mechanism of DBT by TBHP-Fe/Al <sub>2</sub> O <sub>3</sub> Catalyst.....	70
<b>CHAPTER 6 CONCLUSION AND FUTURE RECOMMENDATION</b>		<b>80</b>
6.1	Conclusion.....	80
6.2	Recommendation.....	82
<b>REFERENCES.....</b>		<b>83</b>
<b>APPENDICES</b>		
<b>PUBLICATION AND PRESENTATION</b>		

## LIST OF TABLES

	<b>Page</b>
Table 3.1	Precursor of catalyst .....34
Table 4.1	Physical properties of Co/Fe-Al <sub>2</sub> O <sub>3</sub> catalyst at different number of loading and calcination temperature.....43
Table 4.2	Peak assingment in XRD patterns of Co/Fe- Al <sub>2</sub> O <sub>3</sub> catalyst with different calcination temperature.....46
Table 4.3	Peak assingment in XRD patterns of Co/Fe- Al <sub>2</sub> O <sub>3</sub> catalyst with different dopant ratio .....48
Table 4.4	EDX analysis of comparison between the elemental composition in the Co/Fe- Al <sub>2</sub> O <sub>3</sub> catalyst with different calcination temperature and dopant ratio.....51
Table 4.5	Concentration of element in Co/Fe- Al <sub>2</sub> O <sub>3</sub> catalyst.....52
Table 4.6	Effect of oxidant and extraction solvent in desulfurization process,58
Table 5.1	Energy of reaction pathway 1 and pathway 2for the oxidation of DBT by TBHP in the presence of Co/Fe- Al <sub>2</sub> O <sub>3</sub> catalyst.....75
Table 5.2	Energy of reaction for the oxidation of DBT and 4,6-DMDBT by TBHP .....76

## LIST OF FIGURES

		<b>Page</b>
Figure 1.1	Sulfur compound in diesel.....	2
Figure 1.2	International Diesel Fuel Quality Standard,2014.....	4
Figure 1.3	International Diesel Fuel Quality Standard,2020.....	4
Figure 1.4	Commonly available sulfur compound in the diesel and order of difficulty in removing different organosulfur compound during HDS .....	6
Figure 1.5	Oxidative desulfurization reaction pathways.....	8
Figure 2.1	Proposed oxidation mechanism for DBT in TBHP-MoO <sub>3</sub> system .....	25
Figure 2.2	Proposed oxidation mechanism for DBT by the W <sub>3</sub> O <sub>3</sub> /MoO <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub> .....	26
Figure 2.3	A proposed cyclic mechanism for the oxidation of DBT by TBHP in the presence of Co/Mn/Al <sub>2</sub> O <sub>3</sub> catalyst.....	27
Figure 2.4	A proposed cyclic mechanism for the oxidation of DBT by TBHP in the presence of Fe/MoO <sub>3</sub> -Po <sub>4</sub> /Al <sub>2</sub> O <sub>3</sub> catalyst.....	28
Figure 2.5	The proposed mechanism in the oxidative desulfurization of DBT in the presence of MoO <sub>3</sub> /V <sub>2</sub> O <sub>5</sub> /MCM-41.....	29
Figure 2.6	Oxidation reaction of DBT, MDBT, and 2-MDBT using HCO <sub>3</sub> H as oxidant.....	30
Figure 3.1	Calibration curve for model diesel.....	35
Figure 3.2	Experimental setup for Catalytic Oxidative Desulfurization reaction .....	38
Figure 4.1	N <sub>2</sub> adsorption/desorption isotherm of (a) Fe-Al <sub>2</sub> O <sub>3</sub> (400°C) (b) Co/Fe-	



	Al <sub>2</sub> O <sub>3</sub> (10:90) 400°C (c) Co/Fe-Al <sub>2</sub> O <sub>3</sub> (10:90) 500°C (d) Co/Fe-Al <sub>2</sub> O <sub>3</sub> (20:80) 400°C (e) Co/Fe-Al <sub>2</sub> O <sub>3</sub> (30:70) 400°C (f) used (10:90) 400°C	41
Figure 4.2	Pore size distribution for (a) Fe-Al <sub>2</sub> O <sub>3</sub> (400°C) (b) Co/Fe- Al <sub>2</sub> O <sub>3</sub> (10:90) 400°C (c) Co/Fe- Al <sub>2</sub> O <sub>3</sub> (10:90) 500°C (d) Co/Fe- Al <sub>2</sub> O <sub>3</sub> (20:80) 400°C (e) Co/Fe- Al <sub>2</sub> O <sub>3</sub> (30:70) 400°C (f) used (10:90)400°	42
Figure 4.3	XRD diffractogram of (a) Co/Fe- Al <sub>2</sub> O <sub>3</sub> (10:90) 400°C (b) Co/Fe- Al <sub>2</sub> O <sub>3</sub> (10:90) 500°C (c) Co/Fe- Al <sub>2</sub> O <sub>3</sub> , (10:90) 700°C	45
Figure 4.4	XRD diffractogram of (a) Co/Fe- Al <sub>2</sub> O <sub>3</sub> (10:90) 400°C (b) Co/Fe- Al <sub>2</sub> O <sub>3</sub> (20:80) 400°C (c) Co/Fe- Al <sub>2</sub> O <sub>3</sub> , (30:70) 400°C	47
Figure 4.5	FESEM micrograph of (a) Co/Fe- Al <sub>2</sub> O <sub>3</sub> , (400°C) (b) Co/Fe- Al <sub>2</sub> O <sub>3</sub> , (500°C) (c) Co/Fe- Al <sub>2</sub> O <sub>3</sub> , (700°C) 10:90	50
Figure 4.6	FESEM micrograph of (a) Co/Fe- Al <sub>2</sub> O <sub>3</sub> , 10:90, (b) Co/Fe- Al <sub>2</sub> O <sub>3</sub> (20:80) (c) Co/Fe- Al <sub>2</sub> O <sub>3</sub> , (30:70) 400°C (d) used catalyst	50
Figure 4.7	HRTEM images of Co/Fe- Al <sub>2</sub> O <sub>3</sub> (10:90) catalyst calcined at (a) 400°C and (b) 500°C	54
Figure 4.8	HRTEM images and particle size distribution curve of Co/Fe- Al <sub>2</sub> O <sub>3</sub> calcined at (a) 400°C and (b) 500°C at 20 nm scale	55
Figure 4.9	Effect of solvent extraction (Reaction conditions: T = 50°C, time= 30 min, solvent = DMF, extraction T = 29°C, mixing time = 30 min, no. of extraction stage = 1)	57
Figure 4.10	Effect of reaction time without the presence of Co/Fe- Al <sub>2</sub> O <sub>3</sub> , 400°C catalyst in Cat-ODS process of model diesel (Reaction conditions: Oxidant = TBHP, T = 50°C, time = 30 min, solvent =DMF, extraction	

	T = 29°C, mixing time = 30 min, no. of extraction stage = 1).....	58
Figure 4.11	Effect of temperature in Cat-ODS process of model diesel (Reaction conditions: Oxidant = TBHP, T = 50°C, time = 30 min, solvent = DMF, extraction T = 29°C, mixing time = 30 min, no. of extraction stage = 1).....	59
Figure 4.12	Catalytic Oxidative desulfurization over the transition metal catalyst (Reaction conditions: Oxidant = TBHP, T = 50°C, time = 30 min, solvent = DMF, extraction T = 29°C, mixing time = 30 min, no. of extraction stage = 1).....	61
Figure 4.13	Effect of dopants towards Fe- Al <sub>2</sub> O <sub>3</sub> (Reaction conditions: Oxidant= TBHP, T = 50°C, time = 30 min, solvent = DMF, extraction T = 29°C, mixing time = 30 min, no. of extraction stage = 1.....	62
Figure 4.14	Effect of cobalt loading (Reaction conditions: Oxidant = TBHP, T= 50°C, time = 30 min, solvent = DMF, extraction T = 29°C, mixing time = 30 min, no. of extraction stage = 1).....	64
Figure 4.15	Effect of calcination temperature of Co/Fe-Al <sub>2</sub> O <sub>3</sub> catalyst on catalytic oxidative desulfurization reaction (Reaction conditions: Oxidant = TBHP, T = 50°C, time = 30 min, solvent = DMF, extraction T = 29°C, mixing time = 30 min, no. of extraction stage= 1).....	66
Figure 4.16	Effect of catalyst dosage (Reaction conditions: Oxidant = TBHP, T = 50°C, time = 30 min, solvent = DMF, extraction T = 29°C, mixing time = 30 min, no. of extraction stage = 1).....	67
Figure 4.17	Repeatability testing over Co/Fe-Al <sub>2</sub> O <sub>3</sub> catalyst calcined at 400°C (Reaction conditions: Oxidant = TBHP, T = 50°C, time = 30 min, solvent = DMF, extraction T = 29°C, mixing time = 30 min, no. of	

	extraction stage = 1).....	68
Figure 4.18	catalyst cycling testing over Co/Fe-Al <sub>2</sub> O <sub>3</sub> catalyst calcined at 400°C for 5h (Reaction conditions: Oxidant = TBHP, T = 50°C, time = 30 min, solvent = DMF, extraction T = 29°C, mixing time = 30 min, no. of extraction stage = 1).....	69
Figure 5.1	A proposed reaction pathway 1 for the oxidation of dibenzothiophene by TBHP in the presence Co/Fe-Al <sub>2</sub> O <sub>3</sub> catalyst.....	71
Figure 5.2	A proposed reaction pathway 2 for the oxidation of Dibenzothiophene by TBHP in the presence Co/Fe-Al <sub>2</sub> O <sub>3</sub> catalyst.....	72
Figure 5.3	Energy Level for Pathway 1 and Pathway 2 of dibenzothiophene with TBHP and Co/Fe-Al <sub>2</sub> O <sub>3</sub> catalyst.....	73
Figure 5.4	Energy level of Pathway 1 and Pathway 2.....	74
Figure 5.5	Energy level diagram for the oxidation of DBT and 4,6-DMDBT by TBHP in the presence of Co/Fe-Al <sub>2</sub> O <sub>3</sub> catalyst.....	77
Figure 5.6	Energy level diagram for the oxidation of 4,6-DMDBT by TBHP in the presence of Co/Fe-Al <sub>2</sub> O <sub>3</sub> catalyst.....	77
Figure 5.7	A proposed reaction for the oxidation of dibenzothiophene by TBHP.....	79

## LIST OF ABBREVIATIONS

4,6- DMDBT	4,6- dimethyl dibenzothiophene
ACN	Acetone Nitrile
ADS	Adsorptive Desulfurization
Al <sub>2</sub> O <sub>3</sub>	Alumina
DBT	Dibenzothiophene
DFT	Density Functional theory
DMF	N, N- dimethylformamide
DMSO	N, N- dimethyl Sulfoxide
EDS	Extractive solvent
FESEM-EDEX	Field Emission Scanning Electron Microscope- Energy Dispersive X-Ray
GC-FID	Gas Chromatography- Flame Ionization Detector
H <sub>2</sub> O <sub>2</sub>	Hydrogen peroxide
HDS	Hydrodesulfurization
HRTEM	High Resolution Transmission Electron Microscope
IL	Ionic Liquid
NA	Nitrogen Adsorption
ODS	Oxidative Desulfurization
TBHP	tert- butyl hydroperoxide
Th	Thiophene
ULSD	Ultra-low sulfur diesel
XRD	X-Ray Diffraction
AAS	Atomic Absorption Spectroscopy

**PENYEDIAN, PENCIRIAN DAN KAJIAN KOMPUTASI MANGKIN  
DWILOGAM FERUM OKSIDA UNTUK PENYAHSULFURAN OKSIDATIF  
MODEL DIESEL**

**ABSTRAK**

Penyahsulfuran oksida bermangkin (Cat-ODS) diperkenalkan sebagai teknik baru dalam mencapai diesel sulfur ultra rendah. Dalam kajian ini, mangkin yang disokong pada alumina menggunakan kaedah impregnasi basah dan dicirikan dengan N<sub>2</sub>-adsorpsi/desorpsi (NA), mikroskopik elektron pengimbas pelepasan medan (FESEM), difraksi sinar-X (XRD) dan Elektron Transmisi Resolusi Tinggi (HRTEM). Model diesel digunakan dalam Cat-ODS bagi mengkaji pretasi mangkin Fe yang disokong pada alumina. Dalam kaedah pengekstrakan, keadaan operasi yang dioptimumkan adalah seperti berikut; N, N- dimetilformamida (DMF) sebagai nisbah pelarut DMF dan diesel terbaik 1.0 pada suhu persekitaran (50°C) selama 30 minit untuk mencapai 63.42% (thiophene), 78.93% (DBT) dan 68.79% (4,6- DMDBT) dalam model diesel. Kajian lebih lanjut dilakukan, di mana mangkin heterogen dan oksidan ditambahkan dalam model diesel semasa reaksi oksidasi. Pelbagai dopan (Co,Cu dan Ni) diperkenalkan kepada mangkin berasaskan ferum dan hasilnya menunjukkan bahawa Co/Fe(10:90)/Al<sub>2</sub>O<sub>3</sub> yang dikalsinasi pada suhu 400°C menyumbang peratusan penukaran sulfur tertinggi dengan thiophene (93%), DBT (100%) dan 4,6-DMDBT (89%). Hasil XRD menunjukkan bahawa mangkin adalah struktur amorfus dengan luas permukaan BET 226.10 m<sup>2</sup>/g. Sementara itu, mikrograf FESEM menggambarkan bahawa mangkin mempunyai zarah agregat homogen. Al<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub> dan Co<sub>3</sub>O<sub>4</sub> sebagai spesies aktif untuk pemangkin Co/Fe (10:90)/Al<sub>2</sub>O<sub>3</sub> disahkan oleh analisis XRD, EDX dan HRTEM. Selain itu, ujian kebolehulangan

menunjukkan bahawa mangkin Co/Fe (10:90)/Al<sub>2</sub>O<sub>3</sub> mempunyai aktiviti pemangkinan yang tinggi dan dapat digunakan berulang kali dengan sedikit perubahan dalam prestasi pemangkin setelah lima kali digunakan kembali. Dalam kajian mekanistik, dua jalur reaksi dicadangkan dan berdasarkan teori ketumpatan fungsional (DFT) pada Co/Fe-Al<sub>2</sub>O<sub>3</sub>, jalur dengan tenaga keseluruhan -40.78 eV disarankan untuk pengoksidaan lengkap DBT. Oleh itu, sistem Cat-ODS menunjukkan teknologi yang menjanjikan pelengkap bagi hidropenyahsulfuran (HDS) untuk menghasilkan diesel sulfur rendah.

**PREPARATION, CHARACTERIZATION, AND COMPUTATIONAL  
STUDY OF BIMETALLIC IRON OXIDE BASED CATALYST FOR  
CATALYTIC OXIDATIVE DESULFURIZATION OF MODEL DIESEL**

**ABSTRACT**

Catalytic oxidative desulfurization (Cat-ODS) has been introduced as a new technique in achieving ultra-low sulfur diesel. In this study, Fe catalyst supported on alumina were prepared by wetness impregnation method and characterized using N<sub>2</sub>-adsorption/desorption (NA), field emission scanning electron microscopic (FESEM), X-ray diffraction (XRD) and High-Resolution Transmission Electron (HRTEM). The performance of the Fe catalyst supported on alumina was investigated in Cat-ODS of model diesel. In extraction method, the optimized operational conditions obtained were as follows; N,N- dimethylformamide (DMF) as the best solvent DMF to diesel ratio of 1.0 at ambient temperature (50°C) for 30 minutes to achieve 63.42% (thiophene), 78.93%(DBT) and 68.79% (4,6-DMDBT) in model diesel. Further studied was continued, where a heterogenous catalyst and oxidant were added in model diesel during oxidation reaction. Various dopants (Co, Cu and Ni) were introduced to the iron based catalysts and the results showed that Co/Fe (10:90)/Al<sub>2</sub>O<sub>3</sub> calcined at 400°C contributed the highest percentage of sulfur conversion with thiophene (93%), DBT (88%) and 4,6-DMDBT (89%) respectively. XRD results showed that the catalyst was amorphous in structure with BET surface area of 226.10 m<sup>2</sup>/g. Meanwhile, FESEM micrographs illustrated that the catalyst has homogeneous aggregated particles. Al<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub> and Co<sub>3</sub>O<sub>4</sub> as active species for Co/Fe (10:90)/Al<sub>2</sub>O<sub>3</sub> catalyst were confirmed by XRD, EDX and HRTEM analysis.

Besides, reproducibility test showed that the Co/Fe (10:90)/Al<sub>2</sub>O<sub>3</sub> catalyst has high catalytic activity and can be repeatedly used with little change in catalytic performance after five reused. In mechanistic study, two reaction pathways were proposed and based on the density functional theory (DFT) on Co/Fe-Al<sub>2</sub>O<sub>3</sub>, the pathway with the overall energy of -40.78 eV was suggested for the complete oxidation of DBT. Therefore, the Cat-ODS system showed the promising technology to be compliment with hydrodesulfurization (HDS) to produce low sulfur diesel.



## CHAPTER 1

### INTRODUCTION

#### 1.1 Background of study

Crude oil is primary supply of energy around the world. It is unrefined petroleum product composed of hydrocarbon deposits and other organic material. In the current area today, crude oil has been refined to produce usable products such as gasoline, diesel, and various other forms of petrochemicals. These mixtures are classified based on the boiling ranges during the acquisition of the different extracts. Diesel fuel is refined from crude oil with a boiling point 160- 380° C (Betiha et al., 2018). Diesel fuel is composed of aliphatic hydrocarbon and aromatic hydrocarbon. It is commonly used as a fuel for heavy transportation (trucks, boats, buses, trains, and machinery). Diesel engines are more efficient than gasoline. Nevertheless, high sulfur compound content, especially in diesel fuel can cause environmental problems. Combustion of high sulfur compound releases harmful sulphur oxide (SO<sub>x</sub>) into Atmosphere and can contribute to air pollution, haze, and acid rain that indirectly affect human health (Zeng et al, 2014) (Guo et al., 2012). In order to have a healthy environment, many efforts have been made by government focusing on green technology that can preserve our environment. Therefore, the control of sulfur content in fuels is becoming increasingly strict around the world. In concern, United State Environmental Protection Agency (USEPA) has assigned that the sulfur content in diesel should to be lower to 10ppm (Bakar, Ali, Kadir, & Mokhtar, 2012)(Abdullah, Bakar, Ali, Mokhtar, & Omar, 2017).

### 1.1.1 Composition of Sulfur in Diesel

Sulfur in diesel fuel exists in various specification. There are more than 60 types of organic sulfur compounds in diesel fuel and can be classified into four main groups which are sulphide, mercaptans, disulfides, and thiophene sulfur in crude oil is mainly present in the form of organosulfur compounds. Organosulfur compounds such as thiophene, dibenzothiophene, and its derivatives are difficult to remove by simple desulfurization process, due to the aromatic structure and steric hindrance. Figure 1.1 show the various type of sulfur compounds in diesel.

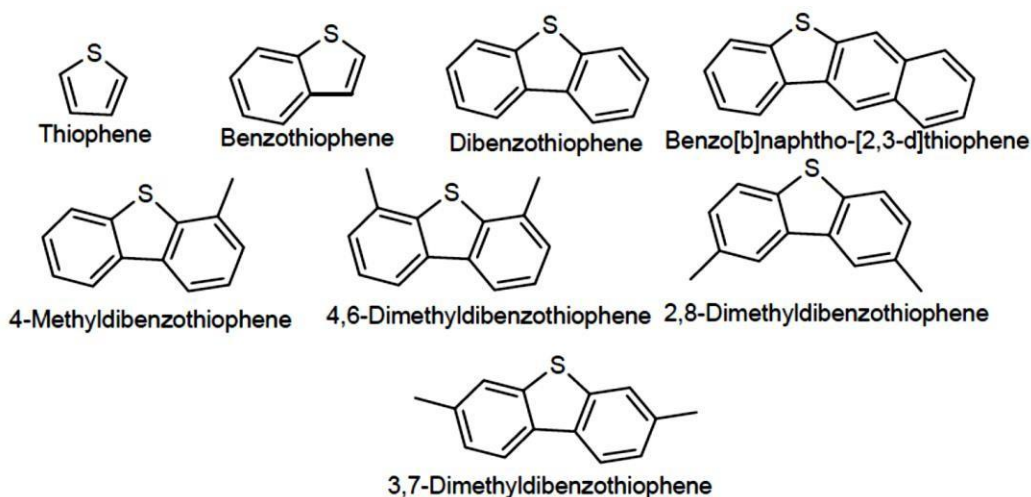


Figure 1.1 Sulfur compound in diesel

### 1.1.2 Sulfur Regulations

In ensuring the sulfur content in diesel meet the regulations set by the government, more stringent regulation of sulfur in diesel has been established to lower the sulfur content in diesel. Since 2006, almost all of the diesel fuel available in Europe and North America are Ultra-Low Sulfur Diesel fuel (ULSD) which the diesel contains 97% less sulfur (<15ppm). In Malaysia, there is little known about the level of sulfur in diesel fuel. Exposure about the level of sulfur in diesel was only adopted in Malaysia in 2009. All oil companies in Malaysia were required to upgrade their fuel quality to comply with the Euro 2 Standards, where the sulfur content in diesel were 500 ppm (Ramalingam and Fuad 2017). Nevertheless, in 2014, sulfur content in diesel reduced to <500 ppm. This has made Malaysia move towards the implementation of Euro 4 Standards (50ppm) by the year 2020 (Advisors, 2018). Figure 1.2 shows international map of sulfur limit by certain countries around the world in 2014 and it shows the sulfur content in diesel for Malaysia are still high compared to other countries. However, the existence of technology has enabled Malaysia to reach the standard of Euro 4 with sulfur content less than 50 ppm by the year 2020. In Figure 1.3 proves that Malaysia has successfully reduce sulfur content to less than 50ppm by the year 2020. However, the current technology used is costly and requires reactor and severe operating condition such as high pressure and temperature. In order to achieve the ultra-low sulfur diesel, it is necessary to modify the HDS process such as reduce the feedstock of fuel in reactor, increase the reactor volume, performing a multi-stage HDS process and increase the temperature of reactor (Abdullah et al., 2017). These are the technical challenges, which from an economical standpoint are difficult to perform.

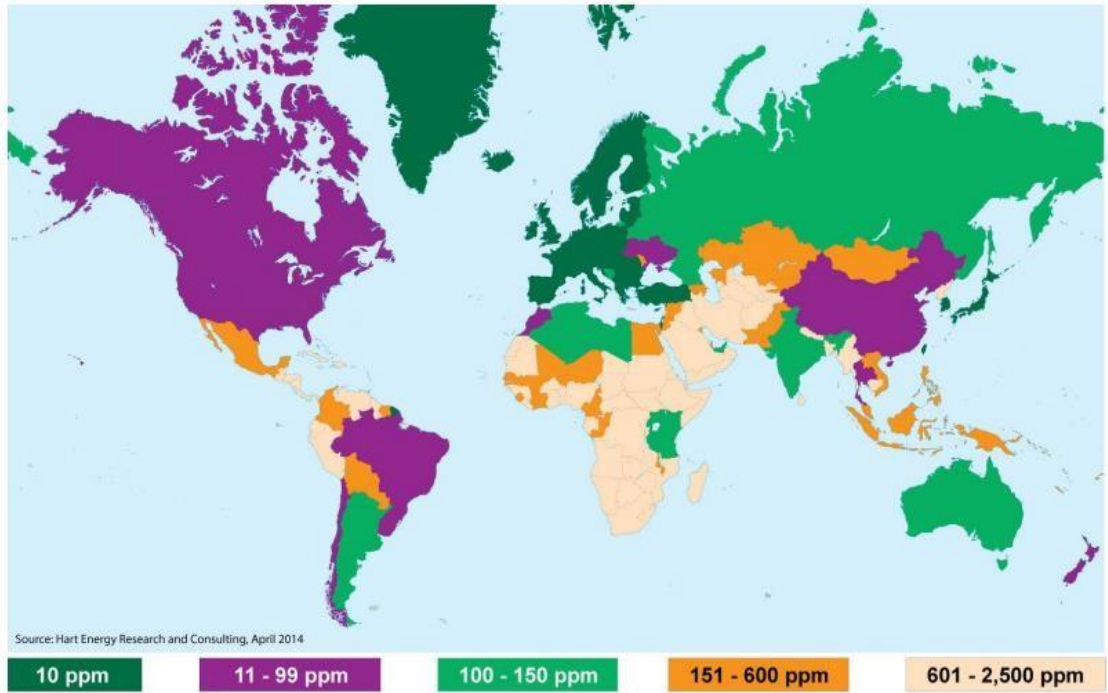


Figure 1.2 International Diesel Fuel Quality Standard, 2014

### Maximum Sulfur Limits in On-Road Diesel, 2020

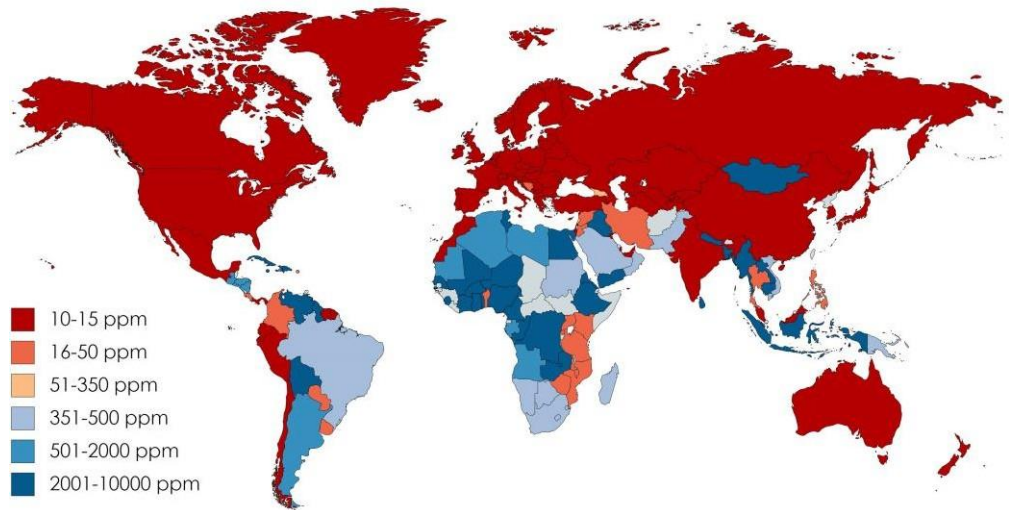


Figure 1.3 International Diesel Fuel Quality Standard, 2020

## 1.2 Technologies used in treatment of diesel

The conventional process in sulfur removal is hydrodesulfurization (HDS) process. HDS is a catalytic hydrogenation process that removes impurities includes nitrogen, metals, oxygen, and sulfur compounds (thiols, mercaptans, and disulfides) from liquid petroleum fractions, but it is less effective in the removal of aromatic sulfur compounds such as dibenzothiophene (DBT) and their alkylated derivatives (4,6- dimethyl dibenzothiophene) (Betiha et al., 2018)(Subhan et al., 2019). The capability of HDS towards the removal of different organosulfur compounds is given in Figure 1.4. Organosulfur compounds have sterically hindered bond energy, which make them difficult to desulfurize by HDS process. Moreover, n-electrons located on the sulfur atom of organosulfur compounds undergo the delocalization with aromatic rings, creating more resonance structures and extra stability (Rajendran et al., 2020). In addition, to the resonance structure, more electron density and steric factor around the sulfur atom also promote stability of organosulfur compounds and as a result, the current HDS has become inefficient to treat organosulfur compounds. Besides, HDS process usually applies Ni, Co, and supported on  $Al_2O_3$  catalysts in the temperature range of 290–455 °C and  $H_2$  pressures of 150–3000 psi (Mokhtari, Akbari, & Omidkhah, 2019). This technology is an expensive process due to high operational cost, and high operational temperature in hydrogen gas atmosphere (Muhammad, Shoukat, Rahman, Rashid, & Ahmad, 2018)(Betiha et al., 2018)

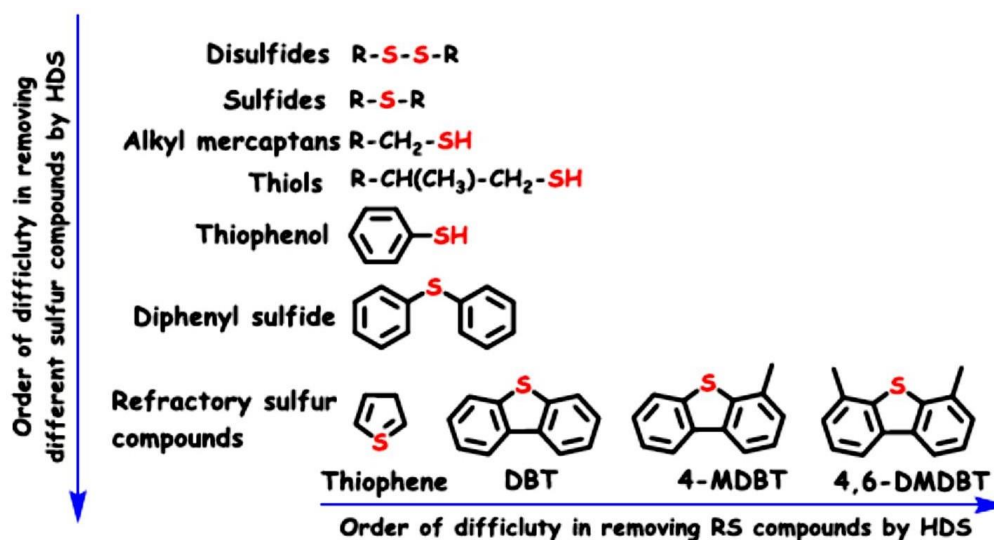


Figure 1.4 Common available sulfur compounds in the diesel feedstocks and the order of difficulty in removing different organosulfur compounds during HDS (Rajendran et al., 2020)

Since HDS is not applicable for removal of aromatic sulfur compound, a new alternative for desulfurization process was introduced which is extraction desulfurization (EDS). This process involves the transferring of sulfur compound in the oil into a solvent and the efficiency depends on the solvent's and sulfur compound's polarity. (Betiha et al., 2018). This process might be challenging in selecting a suitable solvent. The sulfur compound in diesel fuel have an isolated electron pair as Lewis base that can donate a pair of electrons to form a bond. Therefore, strong polar solvent with Lewis acid that rich of electron of acceptor can be used to remove sulphide in EDS (Li et al., 2019). The common extractant solvents included acetonitrile, N,N-dimethylformamide, dimethylsulfoxide and pyrrolidone (Majid et al., 2020). However, these conventional extractants are highly volatile and could give toxicity effect when applying into a large-scale separation (Majid et al., 2020). Extraction stage requires a lot of solvent which makes the process uneconomical. Besides, problem also arise to deal with high volume of used

extraction solvent and it is necessary to regenerate the extraction solvent. Solvent regeneration is necessary in order to prevent wasting a huge amount the solvents, which could otherwise cause environmental problem. However, this process is quite challenging since the performance and efficiency varies depend on the solvent.(Aghaei, Shahhosseini, & Sobati, 2020).

In support of the green technology introduced by the government, most researchers have reduced the use of solvent and focus more on the development of sustainable green chemistry. To begin this issue, ionic liquid (IL) has been tested to study their capability as extractant in EDS. IL is a kind of molten salt that consists of a cation and anion element with negligible vapor pressure and easy to be recycle (Majid et al., 2020). Their negligible vapour pressure allows the extracted product to be separated from the ILs through low pressure distillation with potential energy savings. EDS process utilizing ILs can be complementary for the HDS process, due to its high extraction ratio and selectivity over molecular solvents in removing organosulfur compound. However, this approach has some limitation such as the recovery and recycling of ionic liquid during desulfurization is difficult.

Besides, another approached for desulfurization is by adsorption process. Adsorptive desulfurization (ADS) is an easy operation and green method for desulfurization process. ADS depend on the capacity of a strong sorbent to specifically adsorb organosulfur compound from refinery streams. The common adsorbents used in ADS like activated carbon, clay and metal oxide. This process is an economically promising technique due to their simple operating condition (mild temperature and pressure), availability of cheap, regenerated adsorbent and high selectivity toward

sulfur containing compound. However, application to heavy oil with higher sulfur content, is unpractical due to the poor accessibility of large molecule in the narrow pores and steric hindrance that reduce the effectiveness (Kuwahara, 1973).

### 1.3 Oxidative Desulfurization

In ensuring the sulfur content in diesel meets the regulations set by the government, many efforts have been made in searching a prompt and efficient desulfurization system to overcome the abundance of organosulfur in diesel fuel. Among new technology, Oxidative Desulfurization (ODS) is economically feasible for large scales utilization. It requires lower capital and low operating costs compared to conventional method HDS. ODS technology has attracted much attention it is convenient for producing ultra-low sulfur fuel under mild conditions.

Basically, oxidative desulfurization involves two main steps; oxidation of sulfur containing compound to sulfoxides and sulfone by a selective oxidant and the second step is removal of sulfoxide and sulfone from diesel by extraction, adsorption, and distillation (Moslemi, Najafi, Najafi, & Rezaei, 2019)(L. Wang et al., 2018)(Abdullah et al., 2017). Oxidation reaction process is shown in Figure 1.5

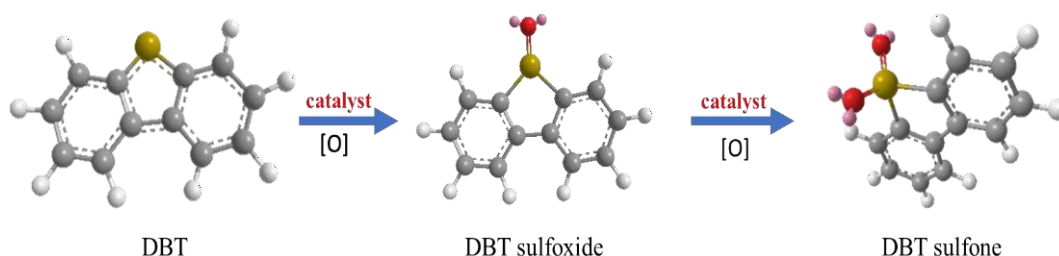


Figure 1.5 Oxidative Desulfurization Reaction Pathway



Numerous oxidants on ODS have been used such as hydrogen peroxide ( $H_2O_2$ ), tert-butyl hydroxide (TBHP), air, and molecular oxygen in different ODS system (Ramos et al., 2020)(Abdullah, Ali, & Bakar, 2016). The oxidation of sulfur containing compound leads to the formation of sulfoxide and sulfone, which are highly polar and can be removed by extraction with polar solvent such as acetonitrile, methanol, dimethylsulfoxide, N,N-dimethylformamide (DMF). ODS has been considered as a new technology for deep desulfurization of transport fuel due to its efficiency in removing organosulfur compound (DBT and its derivatives) in mild condition.

#### **1.4 Catalyst**

Catalyst play an important role in the oxidative desulfurization process. Previous studies on catalyst show significant activity for the oxidation of organosulfur compound (Abdullah et al., 2016)(Abdullah et al., 2017)(Ramos et al., 2018)(Subhan et al., 2019)(Bakar et al., 2012)(Muhammad et al., 2018). The common catalyst used in oxidative desulfurization is homogenous catalyst. However, homogenous catalyst is difficult to separate from the reaction product, and this limits its recyclebility. Due to this deficiency, attention has turned to heterogenous catalyst that is composed of transition metal in high oxidation state dispersed on a support with large surface area. The advantages of heterogenous catalyst is that it is easy to be recovered from the spent solution. Metal oxides have attracted attention as oxidation catalyst in desulfurization. However, most of the previous studies focus on molybdenum (Mo). This might be because of molybdenum oxide supported catalysts give high performance in catalytic oxidative desulfurization activities (Muhammad et al., 2018)(Bakar et al., 2012)(Abdullah et al., 2017)(Subhan et al., 2019). Alumina ( $\gamma-Al_2O_3$ ) is usually used as a support for

heterogeneous catalyst due to its high dispersion to stabilize a small cluster size, has a good texture and cheap (D. Liu, Wang, Liu, & Prins, 2017). Bhutto et al. 2016 found that the Mo catalyst supported on  $\text{Al}_2\text{O}_3$  showed strong catalytic activity compared with Mo catalyst supported on  $\text{TiO}_2$  and  $\text{SiO}_2$  compounds.

## 1.5 Computational Studies

Many experimental studies have been published concerning the oxidative desulfurization mechanism of aromatic sulfur compounds over catalyst. To address this issue, one must figure out how the aromatic sulfur compound interacts with the active centre of the catalyst to form the oxidized products (Bian et al., 2020)( Li et al., 2019).

Density functional theory (DFT) method was extensively employed to investigate the adsorption mechanism of gaseous molecules on solid material (Shen et al., 2018). It is a widely used approach as it has high accuracy and low computational cost (Shen et al., 2018) (Padak & Wilcox, 2009). The Gaussian 09 software was used for all the energy calculation in this work. DFT calculation was carried out to obtain the equilibrium geometries and energies of the intermediates in the proposed mechanism. The B3LYP hybrid functional set is known to produce accurate bond energies and thermodynamic properties of reactions using DFT(Padak & Wilcox, 2009). Therefore, the interaction of sulfur compound with catalyst and TBHP oxidant were studied in detailed by computational study.

## 1.6 Statement of the Problem

Currently, diesel-containing about 500 ppm of total sulfur content contributed to environmental and industrial problems. It is important to remove the impurities in order to meet the new specification of sulfur in diesel. The introduction of the next step up in fuel quality in Malaysia, Euro 4M, has been delayed many times. Its implementation was pushed back from 2012 to 2015. Nevertheless, on November 2014, Boustead Petroleum Marketing Sdn Bhd (BHPetrol) was the first petroleum company that offer Euro 5 (Erwan Norshal, 2015). Euro 5 diesel, contains only 10 ppm of sulfur compared to 500 ppm for Euro 2M. As the first petroleum company in Malaysia to offer the fuel, BHPetrol is targeting the Infiniti Euro 5 diesel facility by the end of September 2015(Sanchit Agarwal, 2015). At present, the Euro 5 diesel is available by Shell, Petronas and BHPetrol, the major players in fuel stations in the country. However, the availability of Euro 5 diesel it is not yet made mandatory by the government. Delays in implementation might be due to the conventional HDS method that need heavy cost in operating and not effective in removing organosulfur compounds in diesel. Besides, for the complete removal of organosulfur compounds, the traditional HDS requires more catalyst (3 times extra), the increased initial temperature by 311 K and increased amount of H<sub>2</sub> gas (50-100% increase). However, these suggestions seem to be practically impractical in light of the modifications that need to be done in the reactor design and economy. Thus, the research on finding new catalysts which could possibly achieve the 100% removal of organosulfur compounds has been promoted through the years. However, none of the alternative catalysts have been industrialized yet. This inspire the researchers to find the different way to accomplish the 100% removal of organosulfur compounds from liquid fuels under

mild conditions with the chance to lower the final fuel price and economize the desulfurization energy consumption. Besides, recent studies reported that iron oxide ( $\text{Fe}_2\text{O}_3$ ) is a potential candidate for desulfurization due to its low cost, easy recyclability and good adsorptive performance. However, the oxidative activity of pure  $\text{Fe}/\text{Al}_2\text{O}_3$  is relatively low. Thus, it is important to further enhance the catalytic performance of Cat-ODS reaction by introducing some modification. These intended modifications can increase the contact area of the catalyst with another metal oxide which is also known as a dopant.

The theoretical efforts in elucidating the related ODS reaction mechanisms based on high-level quantum chemical investigations are relatively scarce. Although many experimental studies have been published concerning the oxidative desulfurization method, there is no conclusion about the ODS activity of aromatic sulfur compounds and oxidant. Thus, with the new approach of computational method, we concentrated on mechanism pathway of oxidative desulfurization of DBT and 4,6-DMDBT. In addition, the presence of a catalyst in ODS reaction was also studied to prove that the catalyst can improve the ODS reaction.

Furthermore, air quality is one of the important criteria for achieving a developed country status. The presence of sulfur in diesel is one of the factors that cause particulate and black soot that reduce air quality. Due to these facts, the initiative to invent in get very optimum sulfur needed in diesel fuel. Oxidative desulfurization (ODS) process has been widely used in removing sulfur compound in diesel. ODS is not replacing the common HDS process but more to complementary the HDS process. Since ODS was introduced, researchers have tried to reduce the sulfur content in diesel; however, the catalysts produced are only suitable for single usage and it might cause a waste of resources in order to treat the diesel in the large

scale. Therefore, some initiatives are needed to improve this method to be very environmentally friendly by using green chemistry approach.

The novelty of this research study are as follows;

- 1) A development of bimetallic based catalyst with the use of alumina ( $\text{Al}_2\text{O}_3$ ) as a support, iron oxide as base and addition of transition metal as a dopant to increase the performance of the catalyst in the catalytic oxidative desulfurization.
- 2) Propose a mechanism between catalyst, oxidant, and sulfur compound (DBT and its derivatives) in catalytic oxidative desulfurization reaction and confirmed with computational studies by DFT calculation method.

### **1.7 Significant of Study**

The major problem of Malaysia diesel fuel is the presence of organosulfur compounds that will result in low quality of Malaysian diesel. Current technology use hydrodesulfurization (HDS) as the main method to reduce the sulfur content in diesel fuel is found to be less effective. In addition, removing the impurities in diesel fuel can increase the price of diesel fuel and this will improve the country's economy. Therefore, in this study it is very important to remove the impurities in diesel fuel for the new specification of the sulfur in diesel.

Besides, reducing the organosulfur in diesel fuel can increase the quality of environment and reduce percentage of air pollution. This Cat-ODS process able to produce green diesel and potential to become green and sustainable technology.

## 1.8 Objective of Research

The objectives of the research are:

1. To synthesize and characterize an active, selective and stable potential iron oxide catalyst with alumina as the support and modify with transition metal as dopant via impregnation method.
2. To test and optimize the prepared catalyst in oxidative desulfurization process of model diesel.
3. To propose mechanism and verify by computational study.

## 1.9 Scope of Study

Three main scopes are focused to achieve the objective of this study. First scope was synthesized of alumina supported iron oxides-based catalysts by incipient wetness impregnation method. The catalytic screening of the prepared catalysts were tested on the model diesel containing a mixture of model sulfur compounds namely thiophene (100 ppmw), dibenzothiophene (150 ppmw) and 4,6-dimethyldibenzothiophene (250 ppmw) with 500 ppm of total sulfur content. The catalyst doped with different dopants of transition metal such as cobalt, copper and nickel. The potential catalyst was further investigated on different dopant ratios and different calcination temperature in the range 400°C-700°C. The most potential catalysts were characterized by nitrogen adsorption/desorption technique, x-ray diffraction (XRD), field emission scanning electron microscope (FESEM), energy dispersive analysis of x-ray (EDX), atomic absorption spectroscopy (AAS) and high-resolution transmission electron microscopy (HRTEM). The second scope was tested and optimized the prepared catalyst in oxidative desulfurization process of model diesel. catalytic oxidative desulfurization was optimized with different oxidants (*tert-*

butyl hydroperoxide and hydrogen peroxide), oxidation reaction (reaction temperature, reaction time) and different extraction solvents. The potential catalysts were investigated under the optimum conditions and tested for reproducibility effect.

The last scope was proposed of mechanism study between the oxidant and catalyst verified by density functional theory (DFT). All calculation along the reaction pathway were performed using Gaussian 09 and Gaussian 16 package programs.

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 Catalytic Oxidation System

Most studies on oxidative desulfurization (ODS) focused on the development of oxidant and catalyst for selective oxidation. In catalytic oxidation approach, together with acetic acid/formic acid, homogenous acid, and ionic liquid have several obstacles which include separation and restoration are quite hard compare to heterogenous catalyst. Previous literatures have reported on the usage of homogenous and heterogenous catalyst within the procedure of liquid phase oxidation of sulfur compound.

##### 2.1.1 Catalyst for Oxidative Desulfurization

In order to achieve low sulfur fuel, many different approaches have been taken. Farshi and Shiralizadeh (2015) have studied the desulfurization reaction in heavy fuel oil by using oxidative desulfurization process (ODS). Hydrogen peroxide ( $H_2O_2$ ) was used as an oxidant and formic acid/acetic acid as catalyst were mixed with the fuel oil. The experiment was carried out in batch reactor. They claimed that mixing of  $H_2O_2$  with acetic acid has better effect in comparison than  $H_2O_2$  with formic acid for desulfurization of heavy fuel. As much as 2.75% of sulfur amount was decreased to 1.14% by using  $H_2O_2$  as oxidant and acetic acid as catalyst. A similar observation was found by (Duarte et al., 2011) who investigated the model sulfur compound of DBT and 4,6-DMDBT by using  $H_2O_2$  as an oxidant and acetic acid as a catalyst followed by extraction with methanol. Sulfur removal up to 99%



of sulfur removal was achieved for the model compounds by using a molar proportion for H<sub>2</sub>O<sub>2</sub>: acetic acid: sulfur of 64:300:1, after 9 min of ultrasound treatment at 90° C which were better than without ultrasound. On the other hand, Mamaghani et al. worked on a model diesel containing benzothiophene, dibenzothiophene and its derivatives, where formic acid was used as a catalyst and H<sub>2</sub>O<sub>2</sub> as an oxidant. Based on the results, it showed that 100% sulfur removal was achieved under optimal condition; O/S (oxidant/sulfur) = 15, formic acid/S = 22 at temperature 65°C in 56 min. The ODS process via H<sub>2</sub>O<sub>2</sub>-CH<sub>3</sub>COOH/HCOOH organic acid system is a mild reaction condition system, wherein the peroxide-organic acid mixture has strong oxidizing ability for achieving high sulfur removal efficiency. However, the use of oil soluble organic acid as a catalyst in the reaction mixture causes separation problems, which greatly affects the fuel properties of diesel oil.

In the past year, there are many research works done on heteropolyacid (POMs) or polymetallic oxide catalysts. Li et al. 2020, studied the Keggin- type POM@MOF- 199@LZSM-5(PMZ) catalyst in oxidative desulfurization process. The catalyst gave high efficiency in the removal of DBT using O<sub>2</sub> as an oxidant. The conversion rate reached 100% in 120 min. This study has been supported by (Ding & Wang, 2016) that found the composite HPW@MOFs combined with oxidant O<sub>2</sub> provides a very effective oxidative desulfurization system for the removal of dibenzothiophene (DBT) from model diesel and real diesel as well. 90% removal of DBT from model diesel can be achieved after 240 min under optimal conditions. Importantly, the catalyst was found to be recyclable and reusable multiple times, with only a slight decline in activity. Tang et al., (2013) also applied the POMs catalyst (HPW-TUD-1) for oxidative desulfurization of model diesel fuel, by using H<sub>2</sub>O<sub>2</sub> as the oxidant. The catalyst was observed to be highly effective in the desulfurization of

benzothiophene derivatives of sulfur compounds. The achieved sulfur reduction was 98% under optimum conditions, and the catalyst could be recycled for three times.

Year after year attention has turned to heterogenous catalyst because of the advantage of separating catalyst with the product. Heterogenous catalyst are mainly composed of active phase dispersed on a support with large specific area. Among transition metal, molybdenum gains more interest as active phase. In 2012, Bakar et al. (2012) studied the effect of transition metal oxide catalyst on the performance of ODS using model diesel. Various transition metal such as iron, manganese, molybdenum, tin, zinc, and cobalt were selected to investigate the catalytic activity performance. The results showed that the catalytic activity decreased in the order of  $\text{Mo} > \text{Mn} > \text{Sn} > \text{Fe} \approx \text{Co} > \text{Zn}$ . A screening of several catalysts showed that  $\text{MoO}_3$  was an active species for the oxidation of DBT compound using dimethylformamide (DMF) as an extraction solvent and TBHP as an oxidant. In the presence of TBHP as an oxidant, the oxidation reactivity of the organosulfur compounds over TBHP– $\text{MoO}_3/\text{Al}_2\text{O}_3$  was decreased in the order:  $\text{DBT} > 4,6\text{-DMDBT} > \text{T}$ . They claimed that, Mo catalyst oxidize organosulfur compound more than other catalyst due to low oxidation potential and high Lewis acidity in its highest oxidation state.

Teimouri et al., (2018) studied the utilization of molybdenum and vanadium oxides supported on MCM-41 for the catalytic oxidative desulfurization of dibenzothiophene. Their catalytic activity in the oxidation of dibenzothiophene was investigated using  $\text{H}_2\text{O}_2$  as an oxidant.  $\text{MoO}_3/\text{V}_2\text{O}_5/\text{MCM-41}$  catalysts were synthesized by incorporating the vanadium and molybdenum oxides on the MCM-41 support by the impregnation method. The results indicated that the catalytic activity of catalysts was improved by enhancing high  $\text{MoO}_3/\text{V}_2\text{O}_5$  content (20% $\text{MoO}_3$ /20%  $\text{V}_2\text{O}_5$ / 60% MCM-41) and could convert 99.06% of dibenzothiophene under optimum conditions.

Mokhtar et al. (2018) investigated the development of bimetallic and trimetallic oxide molybdena based on catalyst supported alumina. Various dopants and co-dopants such as V, Ti and W were used to improve the removal of sulfur compound from diesel. The  $\text{W}/\text{MoO}_3/\text{Al}_2\text{O}_3$  catalyst showed highest conversion of sulfur removal 88.7% (Th), 95.6% (DBT) and 94.2% (4,6-DMDBT) compared to  $\text{V}/\text{MoO}_3/\text{Al}_2\text{O}_3$  catalyst had slightly lower the sulfur removal. However, by using trimetallic catalyst, the  $\text{V}/\text{W}/\text{MoO}_3/\text{Al}_2\text{O}_3$  catalyst performed a complete removal (100%) of DBT and 4,6-DMDBT, and for thiophene, 94.5% was removed. They claimed trimetallic oxide catalyst of molybdena based on alumina support showed a great performance in desulfurization of model diesel and commercial diesel.

Qiu et al. (2015) reported the study on mesoporous  $\text{H}_3\text{PMo}_{12}\text{O}_{40}/\text{SiO}_2$  catalyst and its catalytic performance in oxidative desulfurization of fuel oil. The characterization results show that the preparation conditions of HPMo dosage, type of the template and calcination temperature display important influences on the pore structure and the specific surface area of the catalysts. The specific surface area of the catalyst reached the maximal value of  $1211 \text{ m}^2/\text{g}$  with the average pore diameter of 2.6 nm, when HPMo dosage was 20 wt.%, octadecyltrimethyl ammonium chloride was used as the template and calcination temperature was  $360^\circ\text{C}$ . The HPMo/SiO<sub>2</sub> catalysts were very efficient for the oxidation of DBT and BT in the model fuel oil using H<sub>2</sub>O<sub>2</sub> as the oxidant. Under the optimum condition of catalyst dosage 0.05 g, H<sub>2</sub>O<sub>2</sub> dosage 0.05 mL and reaction temperature  $70^\circ\text{C}$ , the conversion rate of DBT reached 100% only in 60 min and BT achieved 99.2% in 150 min. Recycling of the catalyst indicates the decrease of the activity of the reused catalyst, which is mainly attributed to the slow leaching of the active molybdenum species.

Catalytic oxidative desulfurization of supported ceria-based catalyst was studied by Abdullah et al., 2017. The ceria containing catalysts showed good catalytic activity and gave high sulfur removal with >90% of total sulfur removal at reaction temperature of  $45^\circ\text{C}$ . The effect of transition metal elements dopants over M/Ce (10:90)/Al<sub>2</sub>O<sub>3</sub> catalysts (M= Zr, Mn and Cu) were studied. It was found that, the catalytic activity of Mn/Ce/Al<sub>2</sub>O<sub>3</sub> was higher than the monometallic catalysts, Ce/Al<sub>2</sub>O<sub>3</sub>. Under these optimum conditions: tert-butyl hydroperoxide (TBHP)/sulfur ratio of 3, 5.26% Mn/11.68%Ce/Al<sub>2</sub>O<sub>3</sub>, temperature of  $45^\circ\text{C}$ , 30 min of reaction, complete removal of model organosulfur compounds were obtained. In addition, >90% of sulfur was removed in commercial diesel by using Mn/Ce/Al<sub>2</sub>O<sub>3</sub> catalyst.

### 2.1.2 Oxidant for Oxidative Desulfurization

Oxidant play an important role in oxidative desulfurization process. An oxidant in oxidative desulfurization donate oxygen atom to the S-compounds in sulfides, disulfides, thiols and their derivatives to form sulfones or sulfoxides.  $H_2O_2$  and TBHP were commonly used in oxidative desulfurization process.

In order to understand the role of TBHP in oxidative desulfurization, Wang et al. (2003) studied the oxidation of sulfur compound in kerosene, in the presence of  $Mo/Al_2O_3$  catalyst. They reported that in the presence of catalyst, oxidized DBT peak was observed while in absence of  $Mo/Al_2O_3$  catalyst, no oxidized DBT peak was observed, conforming no oxidation reaction occur in the system without catalyst. They claimed that the catalyst was necessary for oxidation of DBT to DBT sulfone with TBHP.

Sikarwar et al. (2018) studied the catalytic oxidative desulfurization of DBT using  $Mo/MCM-41$  catalyst derived from coal fly ash and TBHP as an oxidant. The Experiments were performed at different O/S ratios in the range of 1:1 to 5:1 using TBHP at 363 K, 3 h reaction time. They claimed that the removal of DBT increased significantly with an increment in the O/S molar ratio, DBT removal was raised from 55% to 94%, when O/S ratio enhanced from 1:1 to 2:1. However, further increase in O/S up to 5:1, the final removal percentage was observed almost constant without appreciable change in final removal percentage.

The effect of the  $H_2O_2$  on the removal of sulfur compound in diesel was studied using graphene analogous hexagonal boron nitride (h-BN) as a metal free catalyst with  $H_2O_2$  as the oxidant by Wu et al., (2020). The obtained h-BN catalyst showed excellent catalytic oxidative desulfurization (ODS) with hydrogen peroxide ( $H_2O_2$ ) as the oxidant. The result showed that when the  $n(O)/n(S)$  was 3, only 55% of sulfur removal was achieved after 180 min of reaction. The sulfur removal increased to 75% when the  $n(O)/n(S)$  raised to 4. With the  $n(O)/n(S)$  further increased to 5, 99.4% of sulfur removal was achieved, illustrating the deep desulfurization. They found that,  $n(O)/n(S)=5$  was achieved as the optimized oxidant amount. Besides, this study found that it is the boron radicals in h-BN activated  $H_2O_2$  to generate OH species, which can readily oxidize sulfides to corresponding sulfones for separation.

On the other hand, Bakar et al. (2012) studied the effects of oxidant on desulfurization. Peracid acid (PAA) and TBHP were selected as oxidants due to their high oxidizability in the ODS. In their study both of oxidants provide free radical in oxidation reaction and contributed to the formation of oxidized sulfur. However, TBHP has higher desulfurization degree than PAA due to the good dissolving ability of TBHP in the diesel oil. Using TBHP, the total sulfur removal achieved were 41.4%, 50.3% and 40.8% of thiophene, DBT and 4,6-DMDBT respectively. In addition, TBHP was also reactive to most organic compounds in the absence of metal catalysts.

The study was continued by Abdullah et al. (2016) on investigation of  $Fe/MoO_3-Po_4/Al_2O_3$  catalyst in ODS of diesel fuel with TBHP-DMF system. They revealed that,  $Fe/MoO_3- PO_4(10:90)/ Al_2O_3$  catalyst calcined at  $500^\circ C$  performed higher catalytic activity. The catalyst reacted with TBHP and formed active species, consequently enhance the oxidation reaction of sulfur to sulfone. The catalyst was able

to reduce sulfur levels in commercial diesel from about 440 ppmw to 17.6 ppmw with 96% of total sulfur removal.

Muhammad et al. (2018) was worked on the enhancing effect of a highly cost effective and efficient metal, Fe, incorporation to Co or Ni based Mo/Al<sub>2</sub>O<sub>3</sub> catalysts in the oxidative desulfurization (ODS) of dibenzothiophene (DBT) using H<sub>2</sub>O<sub>2</sub> and formic acid as oxidants. The result showed that Fe greatly enhanced the oxidative desulfurization process following catalytic activity order as: Fe–Ni–Mo/Al<sub>2</sub>O<sub>3</sub> > Fe–Co–Mo/Al<sub>2</sub>O<sub>3</sub> > Ni–Co–Mo/Al<sub>2</sub>O<sub>3</sub> > Ni–Mo/Al<sub>2</sub>O<sub>3</sub> > Co–Mo/Al<sub>2</sub>O<sub>3</sub> > Mo/Al<sub>2</sub>O<sub>3</sub>. They also investigated the effect of the amount of H<sub>2</sub>O<sub>2</sub> and formic acid in presence of Fe promoted Mo–Al<sub>2</sub>O<sub>3</sub> catalysts. They claimed H<sub>2</sub>O<sub>2</sub> exhibited higher efficiency towards the oxidation process compared to formic acid.

Wang et al. (2018) studied a Lewis acidic ionic liquid (ILs) [ODBU]Cl/nZnCl<sub>2</sub> (n = 1, 2, 3, 4, and 5) for oxidative desulfurization of model and diesel fuel oils, with H<sub>2</sub>O<sub>2</sub> as the oxidant. The effect of H<sub>2</sub>O<sub>2</sub> was investigated and they claimed that H<sub>2</sub>O<sub>2</sub>/S molar ratio had a significant influence on the removal of DBT. The H<sub>2</sub>O<sub>2</sub>/S molar ratio had a significant influence on the removal of DBT. It was observed that unsatisfying results of 63.4% sulfur removal was obtained at H<sub>2</sub>O<sub>2</sub>:S molar ratio of 2:1. However, when the H<sub>2</sub>O<sub>2</sub>:S molar ratio was increased to 4:1, 99.8% of DBT sulfur removal was achieved. Complete sulfur removal was obtained within 1 h using 6:1 of H<sub>2</sub>O<sub>2</sub>:S molar ratio.

In 2019, Liu et al. studied catalytic oxidative desulfurization of model and real diesel. Three oxidants, tert-butyl hydroperoxide 70% in water (TBHP), cumene hydroperoxide (CHP) as well as a hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) solution were tested in the oxidation of DBT over Mo@COMOC-4 at 70 °C with an O/S molar ratio of 5. The

results revealed that TBHP affords the best sulfur removal efficiency of DBT with nearly 70%, which may be due to the less steric hindrance in comparison to CHP (~30%) and H<sub>2</sub>O<sub>2</sub> (only 8%). It was claimed that H<sub>2</sub>O<sub>2</sub> showed low conversion probably due to the poor solubility of the compound in the organic phase. Interestingly, the sulfur removal was enhanced with 92.5% of sulfur removal in catalyst-TBHP system of real diesel using acetonitrile as extraction solvent.