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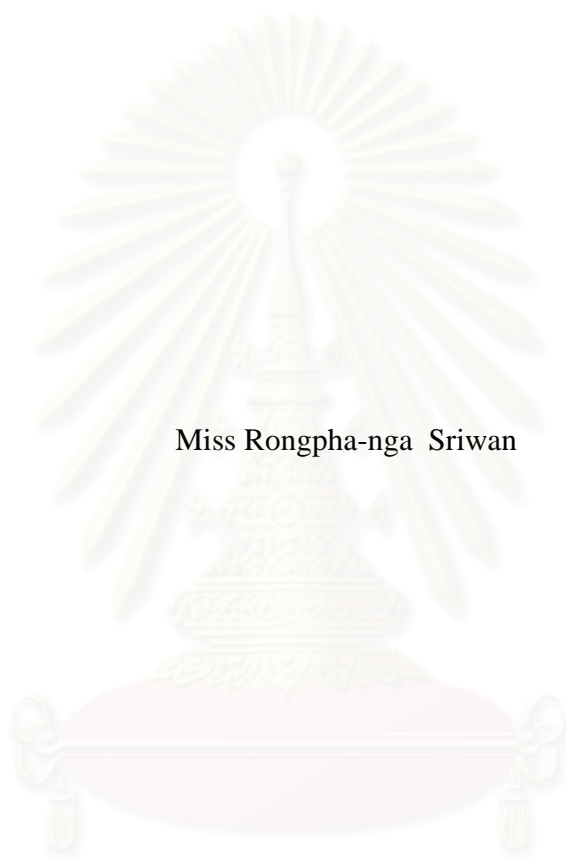
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HYDRODESULFURIZATION OF BENZOTHIOPHENES CATALYZED BY
MOLYBDENUM/COBALT/RUTHENIUM



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รงค์พะงา ศรีววรรณ: ไฮโดรดีซัลเฟอร์ไรเซชันของสารกลุ่มเบนโซไทโอฟีนเร่งปฏิกิริยาด้วย โมลิบดีนัม/โคบอลต์/รูทีเนียม (HYDRODESULFURIZATION OF BENZOTHIOPHENES CATALYZED BY MOLYBDENUM/COBALT/RUTHENIUM) อ.ที่ปรึกษา:รศ.ดร.วิมลรัตน์ ตระการพุกภัย; จำนวนหน้า 66 หน้า. ISBN 974-17-3506-5.

งานวิจัยนี้ศึกษาปฏิกิริยาไฮโดรดีซัลเฟอร์ไรเซชันของเบนโซไทโอฟีนด้วยตัวเร่งปฏิกิริยาที่เป็น โลหะชนิดเดียวและโลหะหลายชนิด โดยได้สังเคราะห์ตัวเร่งปฏิกิริยาขึ้นได้แก่ $[Cp^*RuCl_2]_2$, $Cp^*RuCl(PPh_3)_2$, $[CpMo(CO)_3]_2$ และ $CpMo(CO)_3H$ อุณหภูมิ ความดันแก๊สไฮโดรเจน และอัตรา ส่วนโดยโมลของเบนโซไทโอฟีนและรูทีเนียมมีผลต่อแอกติวิตีการเร่งปฏิกิริยา สำหรับตัวเร่งปฏิกิริยา แบบโลหะชนิดเดียวที่ประกอบด้วยรูทีเนียม ผลการทดลองชี้ให้เห็นว่า $[Cp^*RuCl_2]_2$ เป็นตัวเร่งปฏิกิริยา ที่ไม่ว่องไว สารเชิงซ้อน $Cp^*RuCl(PPh_3)_2$ ในระบบของเหลวสองวัฏภาคสามารถเร่งปฏิกิริยาไฮโดรดี ซัลเฟอร์ไรเซชันของเบนโซไทโอฟีนได้ เกิดผลิตภัณฑ์คือไดไฮโดรเบนโซไทโอฟีน (ผลิตภัณฑ์จากการ เกิดปฏิกิริยาไฮโดรจิเนชัน) และเอทิลเบนซีน (ผลิตภัณฑ์จากการเกิดปฏิกิริยาไฮโดรจิโนไลซิส) ตัวเร่ง ปฏิกิริยานี้แสดงเปอร์เซ็นต์การเปลี่ยนรูปสูงกว่าการใช้ตัวเร่งปฏิกิริยา $Ru(PPh_3)_3Cl_2$ ซึ่งเกิดผลิตภัณฑ์ เฉพาะไดไฮโดรเบนโซไทโอฟีน สำหรับสารเชิงซ้อนโมลิบดีนัม ปฏิกิริยาที่ใช้ $[CpMo(CO)_3]_2$ ในโทลู อีนให้เปอร์เซ็นต์การเปลี่ยนรูปสูงกว่าในระบบของเหลวสองวัฏภาค การใช้ $CpMo(CO)_3H$ ให้ผลได้ ของผลิตภัณฑ์ที่น้อยกว่า เมื่อเปรียบเทียบระหว่างสารเชิงซ้อนรูทีเนียมและ โมลิบดีนัมพบว่ารูทีเนียม เป็นตัวเร่งปฏิกิริยาที่มีประสิทธิภาพมากกว่า ทั้งนี้อาจเนื่องจากความสามารถในการเร่งปฏิกิริยาไฮโดรจิ เนชันของรูทีเนียม และความสามารถในการสลายพันธะของ Cp^* อย่างไรก็ตาม ปฏิกิริยาที่เร่งปฏิกิริยา ด้วยตัวเร่งปฏิกิริยาโมลิบดีนัมเกิดปฏิกิริยาไฮโดรจิโนไลซิส ได้ผลิตภัณฑ์เป็นเอทิลเบนซีน ได้ทำการ ศึกษาตัวเร่งปฏิกิริยาที่ประกอบด้วยโลหะมากกว่า 1 ชนิด โดยใช้ตัวเร่งปฏิกิริยาที่มีโลหะสองชนิดได้ แก่ $Cp^*RuCl(PPh_3)_2 + Mo(CO)_6$ หรือ $[CpMo(CO)_3]_2$ หรือ $Co_2(CO)_8$ และตัวเร่งปฏิกิริยาที่มีโลหะสาม ชนิดได้แก่ $Cp^*RuCl(PPh_3)_2 + [CpMo(CO)_3]_2 + Co_2(CO)_8$ ผลการทดลองพบว่าให้เปอร์เซ็นต์การ เปลี่ยนรูปที่ต่ำกว่าการใช้ตัวเร่งปฏิกิริยาที่มีโลหะชนิดเดียว

สาขาวิชา.....ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์.....ลายมือชื่อนิสิต.....

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RONGPHA-NGA SRIWAN: HYDRODESULFURIZATION OF
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In this work, hydrodesulfurization of benzothiophenes using monometallic and multimetallic catalysts were studied. $[\text{Cp}^*\text{RuCl}_2]_2$, $\text{Cp}^*\text{RuCl}(\text{PPh}_3)_2$, $[\text{CpMo}(\text{CO})_3]_2$ and $\text{CpMo}(\text{CO})_3\text{H}$ were prepared. The temperature, hydrogen pressure and BT/Ru mole ratio affected the catalytic activity. For the monometallic catalysts containing ruthenium: the results indicated that $[\text{Cp}^*\text{RuCl}_2]_2$ was inactive catalyst. The hydride complex, $\text{Cp}^*\text{RuH}_3(\text{PPh}_3)$ showed catalytic activity. The $\text{Cp}^*\text{RuCl}(\text{PPh}_3)_2$ in liquid-biphasic system can catalyze the hydrodesulfurization of benzothiophene to give dihydrobenzothiophene (product from hydrogenation) and ethylbenzene (product from hydrogenolysis), this catalyst showed higher %conversion than $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$ which gave only dihydrobenzothiophene. For molybdenum complexes, the reaction using $[\text{CpMo}(\text{Co})_3]_2$ in toluene resulted in higher %conversion than in liquid-biphasic system. Using $\text{CpMo}(\text{CO})_3\text{H}$, yielded lower amount of product. Comparing between ruthenium and molybdenum complexes, the former is more effective catalyst. It might be due to the hydrogenation ability of ruthenium and the bond cleavage ability of Cp^* . However, the reaction catalyzed by the molybdenum catalyst occurred *via* hydrogenolysis, yielding ethylbenzene as product. Catalysts containing more than one metal were also investigated for the catalytic activity, bimetallic catalysts, $\text{Cp}^*\text{RuCl}(\text{PPh}_3)_2 + \text{Mo}(\text{CO})_6$ or $[\text{CpMo}(\text{CO})_3]_2$ or $\text{Co}_2(\text{CO})_8$ and trimetallic catalyst, $\text{Cp}^*\text{RuCl}(\text{PPh}_3)_2 + [\text{CpMo}(\text{CO})_3]_2 + \text{Co}_2(\text{CO})_8$ were used. The results indicated lower %conversion than those of monometallic catalysts.

Field of study Petrochemistry and Polymer Science Student's signature

Academic year 2003 Advisor's signature

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สถาบันวิทยบริการ
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CONTENTS

	Page
ABSTRACT (IN THAI).....	iv
ABSTRACT (IN ENGLISH).....	v
ACKNOWLEDGEMENTS.....	vi
CONTENTS.....	vii
LIST OF TABLES.....	xi
LIST OF FIGURES.....	xii
LIST OF ABBREVIATIONS.....	xiv
CHAPTER I INTRODUCTION.....	1
1.1 The objectives of research.....	3
1.2 The scope of research.....	3
CHAPTER II THEORY AND LITERATURE REVIEWS.....	4
2.1 Sulfur compounds.....	4
2.2 Hydrotreating.....	5
2.3 Hydrodesulfurization.....	7
2.3.1 Hydrogenation.....	10
2.3.2 Hydrogenolysis.....	11
2.4 Hydrodesulfurization catalyst.....	11
2.4.1 Heterogeneous catalyst.....	15
2.4.2 Homogeneous catalyst.....	17
2.4.2.1 Mononuclear metal system.....	18
2.4.2.2 Polynuclear metal system.....	22
CHAPTER III EXPERIMENTAL.....	26
3.1 Chemicals.....	26
3.2 Equipments.....	27
3.2.1 Schlenk line.....	27
3.2.2 Schlenk flask.....	28
3.2.3 Heating bath.....	29

CONTENTS (CONTINUED)

	Page
3.2.4 Vacuum pump.....	29
3.2.5 Inert gas supply... ..	29
3.2.6 Syring and needle.....	29
3.2.7 Hydrogen gas supply.....	29
3.2.8 Parr reactor.....	29
3.3 Characterization instruments.....	31
3.3.1 Gas chromatography (GC).....	31
3.3.2 Gas chromatography-mass spectrometry (GC-MS).....	31
3.3.3 Fourier transform infrared spectrometry (FT-IR).....	31
3.3.4 Nuclear magnetic resonance spectroscopy (NMR).....	32
3.4 Catalysts preparation.....	32
3.4.1 Preparation of pentamethylcyclopentadienyl ruthenium chloride, $[\text{Cp}^* \text{RuCl}_2]_2$	32
3.4.2 Preparation of pentamethylcyclopentadienyl ruthenium dichloride triphenylphosphine $[\text{Cp}^* \text{RuCl}_2(\text{PPh}_3)]$ stock solution ($0.01 \times 10^{-3} \text{ M}$).....	32
3.4.3 Preparation of cyclopentadienylmolybdenum tricarbonyl dimer, $[\text{CpMo}(\text{CO})_3]_2$	33
3.4.4 Preparation of cyclopentadienylmolybdenum tricarbonyl hydride $\text{CpMo}(\text{CO})_3\text{H}$ (<i>in situ</i>).....	34
3.5 Hydrodesulfurization procedure.....	34
3.5.1 Hydrodesulfurization of benzothiophene using monometallic catalysts.....	34
3.5.1.1 $[\text{Cp}^* \text{RuCl}_2]_2$	34
A. Effect of triphenylphosphine.....	34
B. Effect of reducing agent.....	35
C. Comparison of catalysts.....	35
D. Effect of temperature.....	35
3.5.1.2 $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$	35
3.5.1.3 $[\text{Cp}^* \text{RuCl}_2]_2$ in liquid-biphase.....	35

CONTENTS (CONTINUED)

	Page
3.5.1.4 Hydrodesulfurization of dibenzothiophene using [Cp*RuCl ₂] ₂	35
3.5.1.5 [CpMo(CO) ₃] ₂	36
3.5.2 Hydrodesulfurization of benzothiophene using multimetallc catalysts.....	36
A. [Cp*RuCl ₂] ₂ + molybdenum complexes.....	36
B. [Cp*RuCl ₂] ₂ + Co ₂ (CO) ₈	37
C. [Cp*RuCl ₂] ₂ + [CpMo(CO) ₃] ₂ + Co ₂ (CO) ₈	37
CHAPTER IV RESULTS AND DISCUSSION.....	38
4.1 Preparation of pentamethylcyclopentadienyl ruthenium chloride, [Cp*RuCl ₂] ₂	38
4.2 Preparation of pentamethylcyclopentadienyl ruthenium dichloride triphenylphosphine, Cp*RuCl ₂ (PPh ₃).....	39
4.3 Preparation of cyclopentadienylmolybdenum tricarbonyl dimer, [CpMo(CO) ₃] ₂	41
4.4 Hydrodesulfurization of benzothiophene using monometallic catalysts.....	43
4.4.1 [Cp*RuCl ₂] ₂	43
A. Effect of triphenylphosphine.....	43
B. Effect of reducing agent.....	44
C. Comparison of catalysts.....	44
D. Effect of temperature.....	44
4.4.2 Ru(PPh ₃) ₃ Cl ₂	45
4.4.3 [Cp*RuCl ₂] ₂ in liquid-biphase system.....	45
4.4.4 Hydrodesulfurization of dibenzothiophene using [Cp*RuCl ₂] ₂ ..	48
4.4.5 [CpMo(CO) ₃] ₂	48
4.5 Hydrodesulfurization of benzothiophene using multimetallic catalysts.....	50
4.6 Characterization of products.....	51
4.6.1 Gas chromatography.....	51

CONTENTS (CONTINUED)

	Page
4.6.2 Mass spectrometry.....	52
4.6.2.1 Hydrodesulfurization of benzothiophene.....	52
4.6.2.2 Hydrodesulfurization of dibenzothiophene.....	54
CHAPTER V CONCLUSION AND SUGGESTION.....	56
REFERENCES.....	58
APPENDICES.....	63
VITA.....	66



สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

LIST OF TABLES

	Page
Table 1.1 Elementary composition of crude oil.....	1
Table 2.1 Examples of the sulfur compounds found in petroleum.....	5
Table 2.2 Comparison of homogeneous and heterogeneous catalysts.....	15
Table 4.1 %Conversion of BT using $[\text{Cp}^*\text{RuCl}_2]_2$ catalyst.....	43
Table 4.2 %Conversion of BT using $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$ catalyst.....	45
Table 4.3 %Conversion of BT using $[\text{Cp}^*\text{RuCl}_2]_2$ in liquid-biphase system....	46
Table 4.4 %Conversion of DBT using $\text{Cp}^*\text{RuCl}(\text{PPh}_3)_2$	48
Table 4.5 %Conversion of BT using $[\text{CpMo}(\text{CO})_3]_2$	48
Table 4.6 %Conversion of BT using multimetallic catalysts.....	50


 สถาบันวิทยบริการ
 จุฬาลงกรณ์มหาวิทยาลัย

LIST OF FIGURES

	Page
Figure 2.1 Hydrotreating unit.....	6
Figure 2.2 Reaction pathways for benzothiophene hydrodesulfurization.....	10
Figure 2.3 Layer structure of MoS ₂	13
Figure 2.4 Structure model of a sulfided CoMo/Al ₂ O ₃ catalyst.....	13
Figure 2.5 Top and side views of a square-pyramidal CoMoS structure.....	14
Figure 2.6 The mechanism for the reaction between benzothiophene and hydrogen catalyzed by (triphos)Rh{η ³ -S(C ₆ H ₄)CH=CH ₂ }.....	19
Figure 2.7 The reaction of tris(triethylphosphine)platinum(0) with dibenzothiophene, benzothiophene and thiophene.....	20
Figure 2.8 Hydrodesulfurization of benzothiophene using [(triphos)RuH(BH ₄)].....	21
Figure 2.9 The photochemical reaction of [Me ₂ Si(C ₅ Me ₄) ₂]Mo(Ph)H towards thiophenes.....	22
Figure 2.10 Desulfurization of thiophene on a bimetallic cluster Cp ₂ *Mo ₂ Co ₂ S ₃ (CO) ₄	23
Figure 2.11 Syntheses of ruthenium complexes (15), (16) and (17).....	23
Figure 2.12 Hydrodesulfurization of benzothiophene by binuclear iridium complex.....	24
Figure 2.13 Hydrodesulfurization of benzothiophene and dibenzothiophene with the trimetallic hydride cluster.....	25
Figure 2.14 The bridging 2-methylthiophene complexes.....	25
Figure 3.1 Schlenk line.....	28
Figure 3.2 Round-bottomed and tube Schlenk flasks.....	28
Figure 3.3 Parr reactor, Parr 4842.....	30
Figure 3.4 Reactor fitting.....	30
Figure 4.1 ¹ H-NMR spectrum of [Cp* ₂ RuCl ₂] ₂	38
Figure 4.2 FT-IR spectrum of [Cp* ₂ RuCl ₂] ₂	39
Figure 4.3 ¹ H-NMR spectrum of Cp* ₂ RuCl ₂ (PPh ₃).....	40

LIST OF FIGURES (CONTINUED)

	Page
Figure 4.4 FT-IR spectrum of Cp* RuCl ₂ (PPh ₃).....	40
Figure 4.5 ¹ H-NMR spectrum of [CpMo(CO) ₃] ₂	41
Figure 4.6 FT-IR spectrum of [CpMo(CO) ₃] ₂	42
Figure 4.7 Hydrogenolysis reaction of benzothiophene catalyzed by rhodium catalyst. Dependence of the rate on the (a) hydrogen pressure; (b) catalyst concentration.....	47
Figure 4.8 GC chromatogram from hydrodesulfurization of BT.....	51
Figure 4.9 GC chromatogram from hydrodesulfurization of DBT.....	52
Figure 4.10 Mass spectrum of benzothiophene.....	53
Figure 4.11 Mass spectrum of dihydrobenzothiophene.....	53
Figure 4.12 Mass spectrum of ethylbenzene.....	54
Figure 4.13 Mass spectrum of dibenzothiophene.....	55
Figure 4.14 Mass spectrum of tetrahydrodibenzothiophene.....	55

LIST OF ABBREVIATIONS

b	broad (NMR)	hex.	hexane
BT	Benzothiophene	hr	hour (s)
Bu	Butyl	m	medium (IR)
cm ⁻¹	unit of wavenumber	Me	methyl
Cp	C ₅ H ₅	ppm	part per million
Cp [*]	C ₅ Me ₅	Ph	phenyl
°C	degree Celsius	s	singlet (NMR)
d	doublet (NMR)	s	strong (IR)
DBT	Dibenzothiophene	sulphos	-O ₃ S(C ₆ H ₄)CH ₂ C(CH ₂ PPh ₂) ₃
DHBT	Dihydrobenzothiophene	TH-DBT	tetrahydrodibenzothiophene
EB	Ethylbenzene	triphos	MeC(CH ₂ PPh ₂) ₃
Et	Ethyl	w	weak (IR)
equi	equivalent (s)	δ	chemical shift
HDS	Hydrodesulfurization		

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CHAPTER I

INTRODUCTION

Petroleum crudes are a complex mixture of various organic compounds, and the major components are hydrocarbon. Large amounts of heteroatoms are also included and their concentrations change depending on their origin. In addition to hydrocarbons, other compounds containing small amounts of sulfur, oxygen, and nitrogen are also present and their physical characteristics vary widely. The elementary composition of crude oil usually falls within the following range in Table 1.1.

Table 1.1 Elementary composition of crude oil¹

Element	% By weight
Carbon	84 – 87
Hydrogen	11 – 14
Sulfur	0 – 3
Nitrogen	0 – 0.6

The chemical operation, such as treating and filtering, are governed by the presence of sulfur, oxygen, and nitrogen compounds and, to some extent, by the small amounts of reactive hydrocarbons that may be present.² The oxygen is often combined in the form of naphthenic acids. Nitrogen is most often found in naphthene base oils and is generally supposed to be in the form of basic compounds similar to the alkyl quinolines. Sulfur may be present as dissolved free sulfur, hydrogen sulfide, or as organic compounds, such as the thiophenes, sulfonic acids, mercaptans, alkyl sulfates, and alkyl sulfides. Some of these sulfur compounds are not found in crude petroleum, but they are produced from other compounds during distillation and refining.

Sulfur reduction in gasoline is prompted by several factors. First, metal catalysts used in subsequent reformer units, Pt-based reforming catalysts, are sensitive to the amount of sulfur in the feedstock. In fact, some bimetallic reforming catalysts require the sulfur content to be limited to the vicinity of 1 ppm or less. Second, air pollution control standards require the reduction of the sulfur in automotive diesel fuels to limited sulfur contents. Since the 1970's, the US federal government has enacted regulations aimed at producing cleaner burning fuels with the goal of reducing air pollution. Federal regulations have resulted in the introduction of lead-free gasoline, lower evaporative emissions, addition of oxygenates during winter months, and significantly lower levels of sulfur in fuels. One of the biggest movements in recent legislation for reduction of sulfur in gasoline products was started by a speech by Bill Clinton on May 1, 1999. He announced a new United States Environmental Protection Agency regulation calling for a reduction of sulfur content of diesel fuels dramatically, from the current maximum allowable value of 500 ppm for automotive diesel fuels down to 50 ppm (or as low as 30 ppm) by the year 2004. Similar efforts are underway around the world. Third, some of the sulfur in gas oil fed to a catalytic cracker is in the form of coke, which is then hydrogenated and released as sulfur dioxide and sulfur trioxide. These oxides combine with the water formed by combustion to give sulfurous and sulfuric acid, which may cause serious corrosion in the colder parts of engines or furnaces. Fourth, the organosulfur content of the feed to the hydrocracker must be reduced to avoid poisoning of the hydrocracking catalyst. Last, the reduction of sulfur reduces the amount of corrosion in the refining process, improves the odor of the product, and reduces the amount of sulfur that can poison the catalytic converter of an automobile.³⁻⁵

Because of its enormous industrial and environmental importance, the removal of sulfur is accomplished by catalytic hydrodesulfurization. Consequently, the focus for much hydrodesulfurization research has moved to the very most refractory sulfur compounds, benzothiophene. Hydrodesulfurization is routinely carried out in oil refineries using commercial catalyst, CoMo/Al₂O₃ which is prepared by coimpregnation of Mo salt on alumina support, followed by sulfidation with H₂S/H₂. Typically severe condition is needed (T = 300-500 °C, P = 70-170 atm). It was found that efficiency is increased by introduction of late transition metals, Co or Ru, Rh as promoters. The role of the metal promoter in the activation of thiophene or

benzothiophene has been supported by several homogeneous modeling studies which clearly show that C-S bond scission is brought about by promoter complexes. Therefore, the information obtained from homogeneous catalysis enables us to understand and better improve the efficiency of the catalysts as well as an attempt to find a catalyst which can be used under milder condition.

1.1 The objectives of research

1. To prepare catalysts containing ruthenium, molybdenum, cobalt and combination between them.
2. To perform hydrodesulfurization of benzothiophenes using the prepared catalysts.
3. To characterize the products obtained.

1.2 The scope of research

Catalysts containing ruthenium, molybdenum, cobalt and combination between them, $[\text{Cp}^*\text{RuCl}_2]_2$, $\text{Cp}^*\text{RuCl}_2\text{PPh}_3$ and $[\text{CpMo}(\text{CO})_3]_2$ were prepared. The hydrodesulfurization of benzothiophenes was studied by using either the prepared catalyst or other metal compounds and varying parameters affecting the reaction. The reaction products were characterized by gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS) for the determination of % conversion and % product yield.

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CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Sulfur compounds

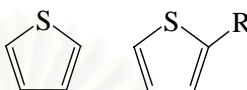
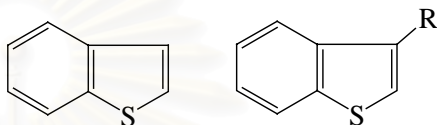
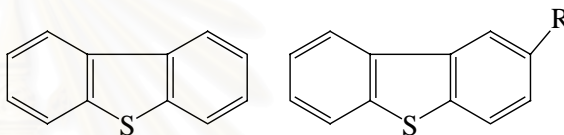
Sulfur is the heteroatom most frequently formed in crude oils. Sulfur concentrations can range from 0.1 to more than 3 weight percent, moreover, this content is correlated with the gravity of the crude oil, its quality (light or heavy) and its sources.

The sulfur compounds found in petroleum or synthetic oils are generally classified into one of two types: nonheterocycles and heterocycles. The former compounds comprise with thiols, sulfides, and disulfides. The heterocycle compounds are composed of thiophenes, benzothiophenes, and dibenzothiophenes.

Hydrogen sulfide, H_2S , is found with the reservoir gas and dissolved in the crude (<50 ppm by weight). If one of the hydrogen atoms is replaced by a hydrocarbon group, the compound is called a mercaptan or thiol. They are formed during the distillation of crude oils; they may cause severe corrosion of the processing units, and addition of chemicals, proper temperature control and the application of special alloys in plant equipment are required to control them.⁶

The non-corrosive sulfur compounds, although not directly corrosive, may cause corrosion on decomposition at higher temperatures, are sulfides, disulfides, and thiophenes. If both of the two hydrogen atom in hydrogen sulfide are replaced by hydrocarbon groups, the compound is called a sulfide or thioether. The disulfides are formed either from mercaptans by oxidation or from sulfides and sulfur. Thiophenes are sulfur compounds with one to several rings structure and their alkyl or aryl substituents. Examples of sulfur compounds are shown in Table 2.1.

Table 2.1 Examples of the sulfur compounds found in petroleum

Compound class	Structure
<i>Nonheterocycles</i>	
Thiols (mercaptan)	RSH
Sulfides	RSR'
Disulfides	RSSR'
<i>Heterocycles</i>	
Thiophenes	
Benzothiophenes	
Dibenzothiophenes	

Crude oil is passed through several operations designed to separate it into fractions, to convert the certain fractions from the primary distillation (usually material of high molecular weight) to products of greater market and to purify the products, especially to remove the sulfur compounds. Many of the products made by the process of separation and conversion need further treatment by hydrotreating, before they can be distributed for use. Not only is good technical performance in an appliance needed but color, smell, stability on storage are all important and the removal, or limitation, of constituents harmful in use is also desirable.⁷

2.2 Hydrotreating

The hydrotreating of petroleum represents one of the largest scale chemical processes carried out by industry in the world today. It included hydrodesulfurization, hydrodenitrogenation, and hydrogenation. In hydrodesulfurization and hydrocracking, cracking and desulfurization operations occur simultaneously and it is relative as to which predominates of feed.⁸ All the reactions are exothermic, so the control of temperature in the reactor, especially the catalyst bed, is very important. The methods

of treatment range from involving a controlled chemical reaction to an extension of the physical separations already applied.

Thus, hydrotreating is a process to catalytically stabilize petroleum products and/or remove objectionable elements from products of feedstocks by reacting them with hydrogen at high pressure over a hot heterogeneous catalyst.⁹ Stabilization usually involves converting unsaturated hydrocarbons such as olefins and gum-forming unstable diolefins to paraffins. Objectionable elements removed by hydrotreating include sulfur, nitrogen, oxygen, halides, and residual metals prior to further processing. These contaminants can affect on the equipment, the catalysts, and the quality of the finished product. Typically, hydrotreating done prior to processes such as catalytic reforming so that the catalyst is not contaminated by feedstock. Hydrotreating is also used prior to catalytic cracking to reduce sulfur and improve product and to upgrade middle-distillate petroleum fractions into finished kerosene and diesel fuel.

There are about 30 hydrotreating processes available. A typical hydrotreating unit is shown in Figure 2.1.¹⁰

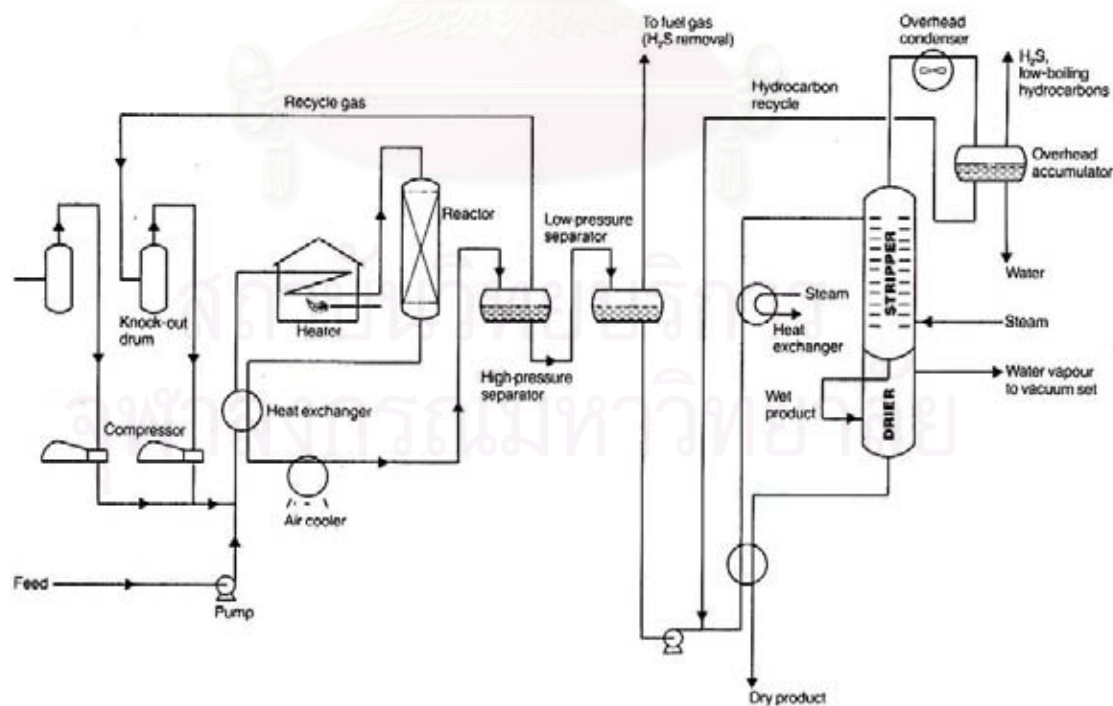


Figure 2.1 Hydrotreating unit.

The oil feed is mixed with hydrogen-rich gas either before or after it is preheated to the proper reactor inlet temperature by heat exchange with reactor effluent and by a furnace. Most hydrotreating reactions are carried out below 427 °C to minimize cracking and the feed is usually heated to between 260-427 °C. The oil feed combined with the hydrogen-rich gas enters the top of the fixed-bed reactor loaded with catalyst. In the reactor, the sulfur and nitrogen compounds present in oil feed to produce hydrogen sulfide and ammonia, respectively, the olefins present are saturated with hydrogen and the oil feed will be free from metals. The metals remain on the surface of the catalyst and the reaction products leave the reactor with the oil-hydrogen stream. The reactor effluent is cooled, typically 40-50 °C, before separating the oil from the hydrogen-rich gas. The hydrogen-rich gas from the high-pressure separation is recycled to combine with the feed, and the low-pressure off-gas stream rich in hydrogen sulfide is sent to a gas-treating unit, where hydrogen sulfide is removed. The clean gas is then suitable as fuel for the refiner furnaces. The liquid stream, the product from hydrotreating, is stripped off any remaining hydrogen sulfide and other undesirable components in a stripping column.^{6, 10}

Hydrotreating is applied to a wide range of feedstocks from naphtha to reduced crude. When the process is employed specifically for sulfur removal it is usually called hydrodesulfurization or HDS. To meet environmental objectives it also may be necessary to hydrogenate aromatic rings to reduce aromatic content by converting aromatics to paraffins.

2.3 Hydrodesulfurization

Feedstocks, either petroleum or coal-derived liquids, usually contain impurities such as nitrogen, sulfur, oxygen, and metal compounds. The sulfur compounds are removed for one of the following reasons:

- (1) To prevent poisoning of sulfur-sensitive metal catalysts used in subsequent reactions and the catalytic converter in an automobile.
- (2) To remove the unpleasant odor.
- (3) To minimize the amounts of sulfur oxides introduced into the atmosphere (contribution to acid rain) by combustion of petroleum-based fuels in catalytic cracking to meet environmental restrictions.

- (4) To reduce the amount of corrosion in the refining process.

In recent years, the air pollution by diesel exhaust gas in large city area has become a serious problem, and it is important to reduce the sulfur content in light gas oil. The problem has been caused by the rapid increase in petroleum product demand throughout the world.

Sulfur in petroleum feedstocks is contained in a variety of organic compounds, such as mercaptans(thiols), sulfides, disulfides, and the more refractory thiophenes, benzothiophenes, and dibenzothiophenes.¹¹

There are three major ways of sulfur removal process:⁷

- (1) *Oxidation process*. This process converts mercaptans to the alkyl disulfides, which are much less offensive in smell, by copper chloride and hypochlorite. The copper chloride can be used either as a fixed bed or can be mixed as powder with the oil.
- (2) *Mercaptan dissolving process*. This process involves washing the gasoline with sodium, calcium, or magnesium hydroxides for the removal of low concentrations of hydrogen sulfide and mercaptans but it is not economical when they are present in high concentrations because the alkali solution is usually discarded and replaced when exhausted.
- (3) *Hydrodesulfurization process*. This process removes other sulfur compounds along with mercaptans, hydrogen sulfide, and sulfide. The thiophenes, benzothiophenes, and dibenzothiophenes are the most difficult to remove in those simple ways and have been the focus of most hydrodesulfurization studies.

Hydrodesulfurization (HDS), which first came into practice during World War II in the production of petroleum, is a catalytic hydrogenation process used to remove sulfur in petroleum-based feedstocks and primarily constitutes hydroprocessing or hydrotreating. The organosulfur compounds in feedstocks are reacted with hydrogen to give hydrogen sulfide and hydrocarbon, to make hydrocarbon feeds suitable for catalytic reformers with their sulfur-sensitive Re-Pt/Al₂O₃ catalysts.¹² A general reaction pathway for the HDS of sulfur compound is presented in Eq. 2.1:



The hydrogen sulfide is then removed in the stabilizing tower of the fractioning system. The remaining traces are easily removed by washing with aqueous alkali.

Alkyl sulfur compounds react quite easily, but the heterocyclic compounds are more stable. Thiophene and its derivatives are therefore often used as model reactants for HDS since they represent the most difficult compounds in fuel feedstocks to desulfurize. Major source of aromatic sulfur compounds in gasoline are coking and cracking naphthas. In the latter, the content of sulfur may be as high as 1300 ppm with a 2:1 predominance of benzothiophenes over thiophenes.

The hydrodesulfurization reaction generally proceeds through two parallel pathways. The first assumes that hydrogenation of the unsaturated heterocycle to a saturated (or partially saturated) species is followed by hydrogenolysis, while the second postulates that hydrogenolysis occurs first and that the product moieties are hydrogenated in subsequent steps. The principal mechanisms proposed for the hydrodesulfurization of benzothiophene are summerized in Figure 2.2. Two major reaction pathways for the hydrodesulfurization of benzothiophene have been occurred:¹³

- (1) Benzothiophene is desulfurized prior to partial hydrogenation to dihydrobenzothiophene to give styrene, which is hydrogenated to ethylbenzene.
- (2) Benzothiophene is hydrogenated prior to desulfurization to give dihydrobenzothiophene, which is desulfurized to ethylbenzene.

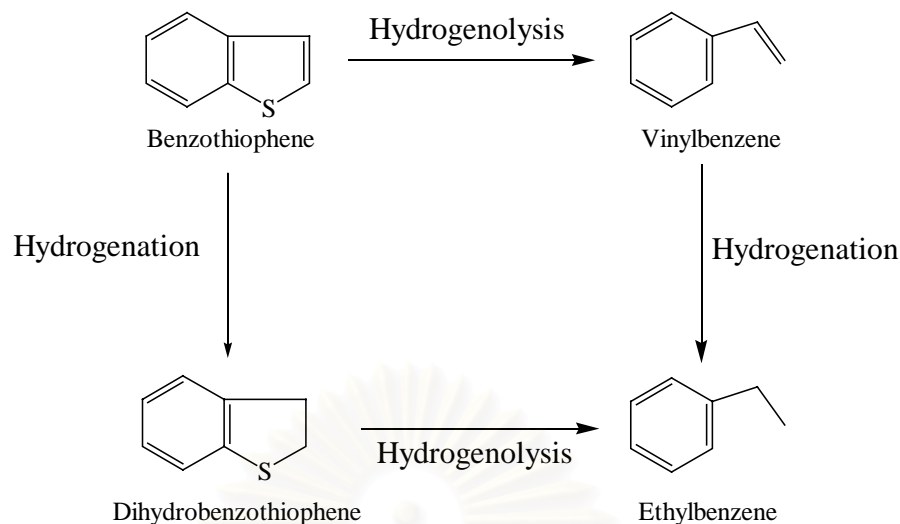
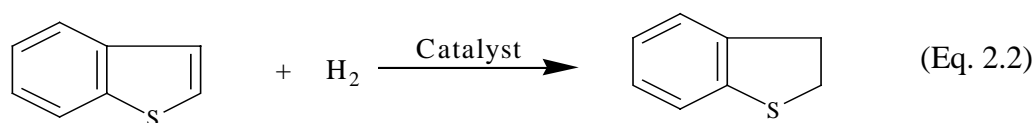


Figure 2.2 Reaction pathways for benzothiophene hydrodesulfurization.

2.3.1 Hydrogenation

The development of efficient catalysts for the hydrogenation of thiophenes remains an important goal in hydrodesulfurization chemistry.¹⁴ In fact, the cyclic thioether products can subsequently be desulfurized over conventional hydrodesulfurization catalysts under milder reaction conditions than those necessary to accomplish the hydrodesulfurization of the thiophene precursors. This aspect is particularly important for the benzothiophene and dibenzothiophene because the conventional catalysts can desulfurize the corresponding cyclic thioethers, dihydrobenzothiophene and hexahydrodibenzothiophene, without affecting the benzene rings, necessary to preserve a high octane number.

Several homogeneous hydrogenation reactions of the model substrate benzothiophene to dihydrobenzothiophene have been studied, in the presence of metal catalysts.¹⁵ (Eq. 2.2)



Benzothiophene is a particularly interesting substrate since it represents one of the most abundant and refractory compounds in heavy oils. It is believed that hydrodesulfurization of benzothiophene over solid catalysts involves the selective hydrogenation to dihydrobenzothiophene prior to desulfurization to give ethylbenzene.

2.3.2 Hydrogenolysis

Hydrogenolysis reactions mean those metal-mediated transformations of thiophenes that result in the opening and hydrogenation of the substrates to give the corresponding unsaturated thiols, which eventually are reduced to the saturated derivatives (Eq. 2.3). Hydrogenolysis reactions of thiophenes are of great relevance in the hydrodesulfurization process as the aromatic thiols can be desulfurized by conventional heterogeneous catalysts under milder conditions than those required to desulfurize the thiophenes.



2.4 Hydrodesulfurization catalyst

Hydrodesulfurization is conducted by treating the fuel with hydrogen at approximately 350-400 °C with 100 bar hydrogen pressure. This process has been cited as the largest volume and most important industrial catalytic application of transition metals. The first hydrodesulfurization catalysts, unsupported metal sulfides used to liquefy coal, were developed in the 1920s. During the 1970s it was discovered that the active metal, usually molybdenum, formed small disulfide particles, which were located in the pores of the alumina support. A fair understanding of the structure and role of the promoter metal was not established until the 1980s.¹⁶

Catalysts developed for hydrodesulfurization are derived from oxides of transition metals supported on different compounds, although the most commonly used is alumina. These catalysts are converted, at least partially, to sulfides during operation. Some commercial catalysts are presulfided, that is, already converted to sulfide form before being used. Sulfiding the catalyst involves both replacement of some oxide anions by sulfide and partial reduction of the metal. The two elements

which are constituents of hydrodesulfurization catalysts are molybdenum or tungsten. Combinations of either of these elements with cobalt or nickel make especially effective hydrodesulfurization catalysts. The molybdenum oxide supported on alumina and promoted by cobalt is the most general use today because it has proven to be highly selective for sulfur removal, easy to regenerate and resistant to poisons. The ratio of molybdenum to cobalt is always considerably greater than 1. However, neither cobalt nor nickel is, by itself, a good catalyst. Substances which have little or no catalytic activity themselves but which enhance the effectiveness of other catalytically active materials, are called promoters.^{17,18}

The conventional CoMo/Al₂O₃ catalyst is prepared by impregnation of γ -Al₂O₃ with an aqueous solution of molybdenum and cobalt salts. This precursor is dried and calcined. Enough molybdenum is used to give about one monolayer on the surface. In acidic solutions, the molybdate is present almost exclusively in the form of heptamers, [Mo₇O₂₄]⁶⁻, and the resulting surface species are believed to be present in islands containing presumably seven Mo ions, with Mo-O-Al bonds. There are also patches of uncovered support. The promoter Co is usually added simultaneously. Some of the promoter ions are present on the surface, but some occupy octahedral and tetrahedral sites in the bulk of the alumina support.

Before use, the Mo and some fractions of the Co in the catalyst are converted into the sulfide form, for example, by treatment with H₂S and H₂ or sulfur compounds easy to decompose at lower temperatures such as carbon disulfides and dimethyl disulfides in an atmosphere of H₂ to give MoS₂ in which small amounts of Co²⁺ ions are incorporated.¹⁹ The surface structures formed in the sulfiding step have been characterized. They resemble rafts of MoS₂ on the support surface, with a thickness of only a few layers. Bulk MoS₂ has a layer structure represented schematically in Figure 2.3. There are alternating layers of sulfur anions interspersed with layers of molybdenum cations, and there are empty layers between some of the sulfur layers. The planar surface of sulfur atoms is relatively unreactive, but the edges, with exposed Mo²⁺ ions, are reactive.¹²

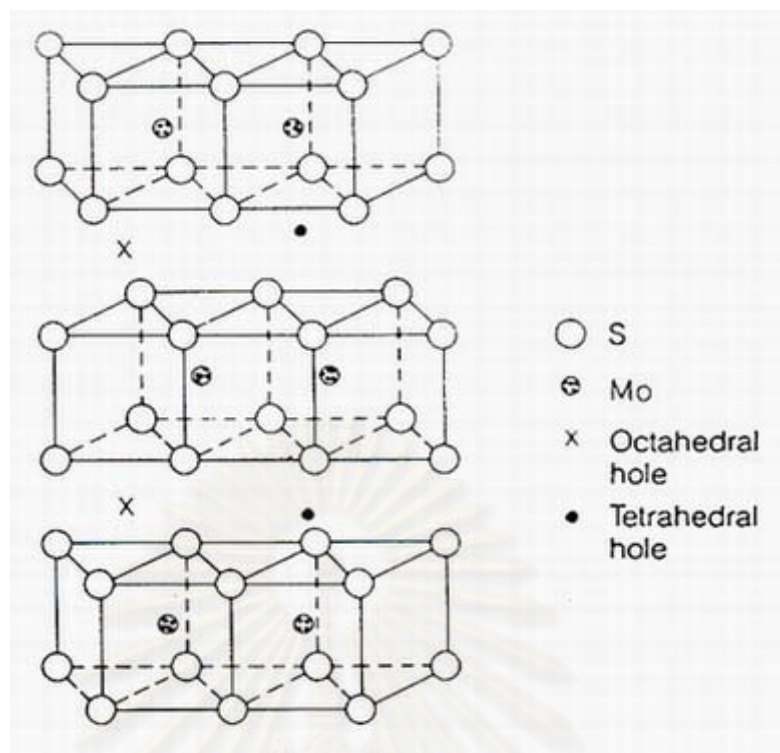


Figure 2.3 Layer structure of MoS_2 .

The cobalt promoter ions are believed to be present at the edges. A surface model of alumina supported Co-Mo binary catalysts is presented in Figure 2.4. Mo is present as microcrystalline MoS_2 and Co as Co_9S_8 , Co^{2+} in the alumina phase and Co species interacting with the MoS_2 phase. The active species are proposed to be a so called CoMoS phase in which atomically dispersed Co sulfides are believed to be anchored on the edge surface of MoS_2 particles.²⁰ A Co atom is connected to MoS_2 by four sulfur atoms. An additional sulfur atom is attached to a Co atom.²¹ The CoMoS structures is shown in Figure 2.5.

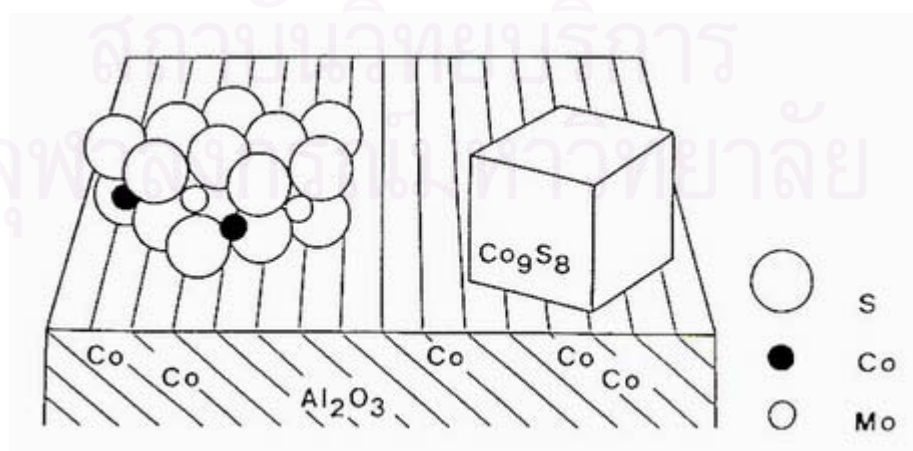


Figure 2.4 Structure model of a sulfided CoMo/ Al_2O_3 catalyst.

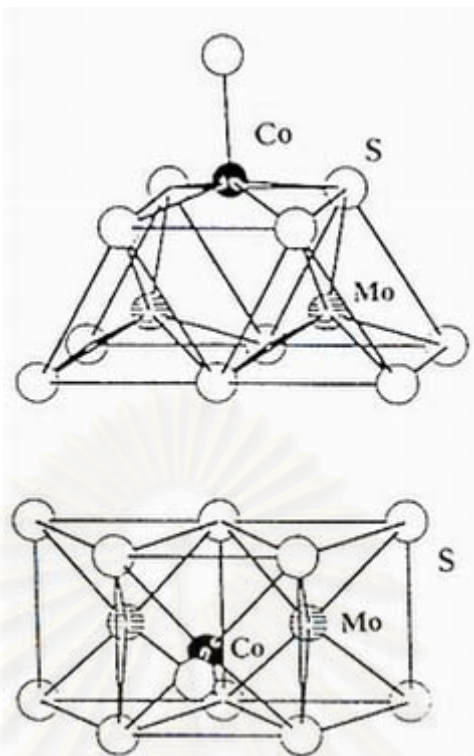


Figure 2.5 Top and side views of a square-pyramidal CoMoS structure.

The numerous catalysts known today can be classified according to various criteria: structure, composition, area of application, or state of aggregation. The catalysts shall classify according to the state of aggregation in which they act. There are two large groups: heterogeneous catalysts (solid-state catalysts) and homogeneous catalysts.

In industrial use, both types of catalyst are subjected to deactivation as a result of chemical or physical processes. Table 2.2 summarizes the advantages and disadvantages of the two classes of catalyst.

Table 2.2 Comparison of homogeneous and heterogeneous catalysts

	Homogeneous	Heterogeneous
<i>Effectivity</i>		
Active centers	All metal atoms	Only surface atoms
Concentration	Low	High
Selectivity	High	Lower
Diffusion problems	Practically absent	Present (mass-transfer controlled reaction)
Reaction conditions	Mild (50-200 °C)	Severe (often >250 °C)
Applicability	Limited	Wide
Activity loss	Irreversible reaction with products (cluster formation); poisoning	Sintering of the metal crystallites; poisoning
<i>Catalyst properties</i>		
Structure/stoichiometry	Defined	Undefined
Modification possibilities	High	Low
Thermal stability	Low	High
<i>Catalyst separation</i>	Sometimes laborious(chemical decomposition, distillation, extraction)	Fixed-bed: unnecessary Suspension: filtration
<i>Catalyst recycling</i>	Possible	Unnecessary (fixed-bed) or easy (suspension)
<i>Cost of catalyst losses</i>	High	Low

2.4.1 Heterogeneous catalyst

Heterogeneous catalysis takes place between several phases. Generally the catalysts are metals or metal compounds, and the reactants are gases or liquids. The catalyst surface exposed to fluid reactants is responsible for the catalytic effect. It is natural then that the catalyst be made to have a high exposed surface area per unit weight.²²

Alumina-supported CoMo and NiMo, heterogeneous catalyst, have been conventional catalysts of petroleum hydrotreatment for a long time. However, the development of novel catalysts with high catalytic activity is needed in order to achieve clean fuel production.

Ishihara, A. *et al.*²³ investigated the catalysts for hydrodesulfurization of dibenzothiophene. They found that the catalysts prepared from silica-alumina supported molybdenum compounds showed higher yields of biphenyl, cyclohexylbenzene and bicyclohexyl than conventional sulfided molybdena-alumina. Specifically, the catalysts derived from silica-alumina supported anionic molybdenum carbonyls gave the highest yields among silica-alumina supported ones.

Lee, D. K. *et al.*²⁴ investigated the effects of transition metal addition to a commercial CoMo/ γ -Al₂O₃ catalyst on the hydrotreatment of atmospheric residual oil. Among the transition metals added to CoMo/ γ -Al₂O₃ catalyst, nickel and tungsten improved the performance of the catalyst, while ruthenium showed no effects. NiCoMo/ γ -Al₂O₃ and WCoMo/ γ -Al₂O₃ showed higher activities and more improved maintenance in all hydrotreating reactions than did a commercial CoMo/ γ -Al₂O₃ catalyst, which was due mainly to the increase in the hydrodesulfurization catalytic activity.

Isoda, T. *et al.*²⁵ examined the catalytic activities of sulfided Ru-CoMo/Al₂O₃ for the desulfurization of 4,6-dimethyldibenzothiophene (4,6-DMDBT) in decane and decane with naphthalene to find selective catalysts which desulfurize 4,6-DMDBT in the presence of naphthalene through preferential hydrogenation of its phenyl ring. Addition of Ru to CoMo catalyst exhibited an excellent activity for hydrodesulfurization of 4,6-DMDBT and suffered less inhibition by coexisting naphthalene, whereas significant retardation was observed over NiMo/Al₂O₃ and Ru-NiMo/Al₂O₃. RuS₂ is suggested as the site for the selective hydrogenation of 4,6-DMDBT, the hydrogenated product of which is transferred immediately to the Co-Mo-S active site to be desulfurized.

Isoda, T. *et al.*²⁶ also studied the hydrodesulfurization of 4,6-DMDBT over a zeolite-Y containing CoMo/Al₂O₃, conventional CoMo/Al₂O₃ and NiMo/Al₂O₃. Isomerization and considerable transalkylation of 4,6-DMDBT into 3,6-DMDBT and into tri- or tetramethyldibenzothiophenes, respectively, were observed characteristically over CoMo/Al₂O₃-zeolite catalyst. Migration of methyl groups enhances the hydrodesulfurization reactivity of the sulfur species by diminishing the steric hindrance. From the result, they found that CoMo/Al₂O₃-zeolite exhibited the best activity for hydrodesulfurization of the sulfur species through the effective desulfurization of refractory alkyldibenzothiophene.

Farag, H. *et al.*²⁷ synthesized several series of Co-Mo-based carbon catalysts series using three methods, successive impregnation, successive impregnation with sulfidation in between, and equilibrium adsorption methods. The activities of sulfided catalysts for hydrodesulfurization of dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) as models of sulfur-containing compounds found in petroleum oil were studied using an autoclave reactor operating at 2.9 MPa hydrogen pressure. The activity results were found to be highly dependent on the method of preparation. Sulfidation of the Mo precursor before cobalt (promoter) addition was found to greatly enhance the activity, which is nearly 2-fold as active as the commercial Co-Mo/Al₂O₃ catalyst. Furthermore, the highest synergetic effect between Co and Mo for hydrodesulfurization activity was observed at a Co/Mo atomic ratio of 0.325.

2.4.2 Homogeneous catalyst

Catalytic processes that take place in a uniform gas or liquid phase are classified as homogeneous catalysis. Homogeneous catalysts are generally well-defined chemical compounds or coordination complexes, which together with the reactants, are molecularly dispersed in the reaction medium. Due to their high degree of dispersion, homogeneous catalysts exhibit a higher activity per unit mass of metal than heterogeneous catalysts. The high mobility of the molecules in the reaction mixture results in more collisions with substrate molecules. The reactants can approach the catalytically active center from any direction, and a reaction at an active center does not block the neighboring centers. This allows the use of lower catalyst concentrations and milder reaction conditions.

The hydrodesulfurization process has attracted a great deal of interest of a number of inorganic and organometallic chemists. Most of the investigations in this field have been directed toward understanding how organosulfur compounds interact with transition metal sites on catalyst surfaces and are activated in ways that result in desulfurization.

2.4.2.1 Mononuclear metal system

Hydrodesulfurization reactions of thiophenes have been observed by using mononuclear metal species. In general, an external source of hydrogen atom is required to bring about the hydrodesulfurization step.

Bianchini, C. *et al.*²⁸ studied the reaction between benzothiophene and hydrogen (15-60 atm) catalyzed by (triphos)Rh{ η^3 -S(C₆H₄)CH=CH₂} (1) in the temperature range from 120-180 °C. The mechanism was shown in Figure 2.6. Under catalytic conditions, the 2-vinylthiophenolate ligand in complex (1) was hydrogenated to 2-ethylthiophenolate (step a). Reaction of this unsaturated Rh(I) fragment with hydrogen then gave the dihydride, (triphos)Rh(H)₂[μ -o-S(C₆H₄)C₂H₅] (2), which could reductively eliminate either hydrogen or 2-ethylthiophenol. The reductive elimination of hydrogen resulted in the formation of an equilibrium concentration of the dimer, [(η^2 -triphos)Rh{ μ -o-S(C₆H₄)C₂H₅}]₂ (3), which was inactive toward benzothiophene. The dihydride complex (2), in fact, was the species which, upon reductive elimination of 2-ethylthiophenol, might interact with benzothiophene (step c). The elimination of 2-ethylthiophenol from complex (2) was greatly accelerated by increasing the temperature and also by interaction with benzothiophene which stabilized the unsaturated Rh(I) fragment through the formation of an η^1 -S adduct (step c). It was generally agreed that adducts of this type play a crucial role in the C-S bond cleavage of thiophenic molecules by metal species. Step d illustrated this process, which led to the formation of a rhodabenzothiabenzene hydride intermediate. This intermediate was unstable and rapidly converts to complex (1) *via* a simple reductive coupling reaction so that a new catalysis cycle for the opening and hydrogenation of benzothiophene could begin.

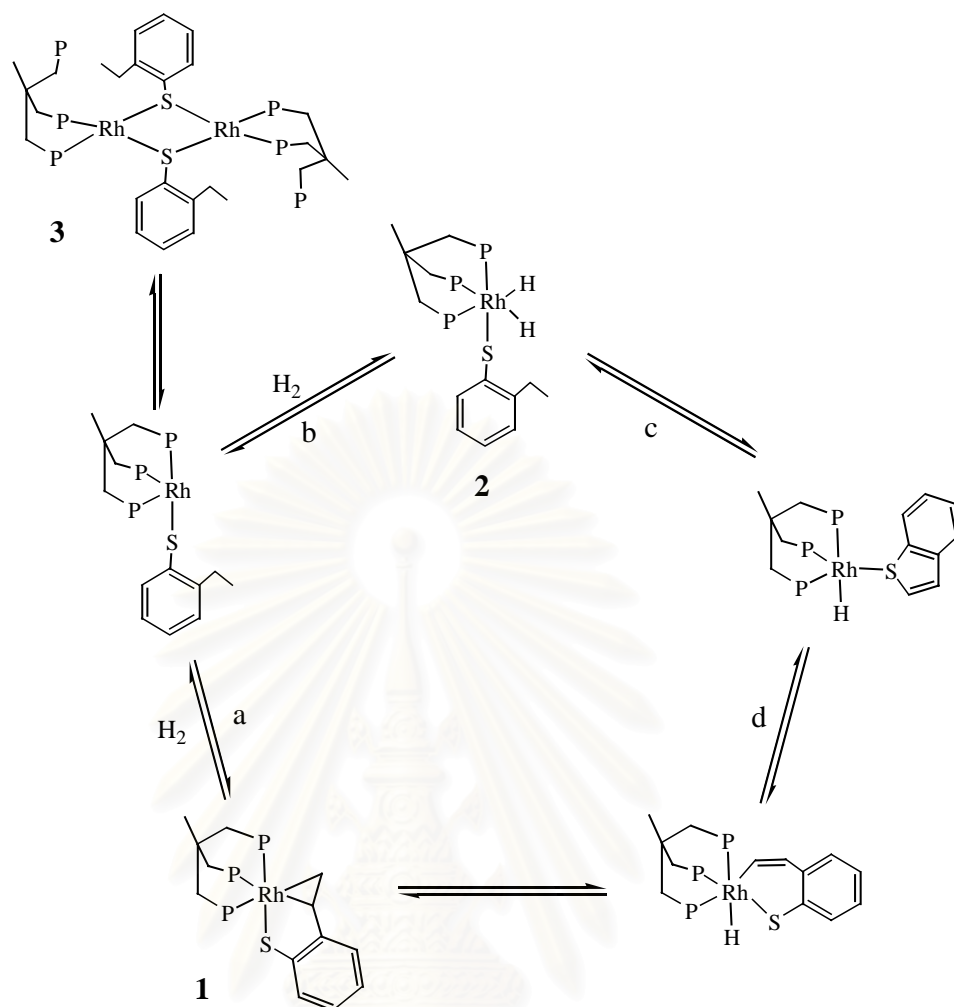


Figure 2.6 The mechanism for the reaction between benzothiophene and hydrogen catalyzed by $(\text{triphos})\text{Rh}\{\eta^3\text{-S}(\text{C}_6\text{H}_4)\text{CH}=\text{CH}_2\}$.

Garcia, J.J. *et al.*²⁹ discovered the insertion of $\text{Pt}(\text{PEt}_3)_2$ into one C-S bond of dibenzothiophene, benzothiophene and thiophene. The thiaplatinacycles, $[(\text{PtSC}_{12}\text{H}_8(\text{PEt}_3)_2)]$ (4), $[(\text{PtSC}_8\text{H}_6(\text{PEt}_3)_2)]$ (5), and $[(\text{PtSC}_4\text{H}_4(\text{PEt}_3)_2)]$ (6), respectively, are formed by the reversible reaction of tris(triethylphosphine)platinum(0) with the thiophene, as shown in Figure 2.7. All three complexes were degraded by hydride reagents to give the completely desulfurized hydrocarbons: biphenyl from complex (4), styrene and ethylbenzene from complex (5), and butadiene and butenes from complex (6). The thiaplatinacycles (4) and (5) were very efficiently hydrodesulfurized on reaction with hydrides (for example; Et_3SiH) to give biphenyl and styrene, respectively, and a platinum-thiol complex, $\text{Pt}(\text{Et}_3\text{P})(\text{H})(\text{SH})$; complex (5) also gave some ethylbenzene.

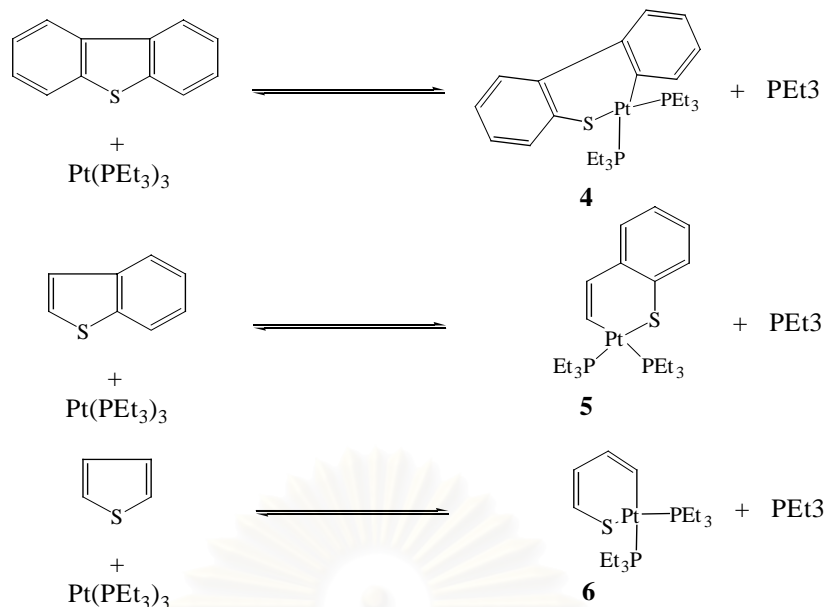


Figure 2.7 The reaction of tris(triethylphosphine)platinum(0) with dibenzothiophene, benzothiophene and thiophene.

Cooke, W.S. *et al.*³⁰ examined the catalytic reactions of dibenzothiophene (DBT) with 6.9 MPa hydrogen pressure at 400 °C for 30 min by using molybdenum hexacarbonyl, $\text{Mo}(\text{CO})_6$. A metal loading of 36 mol% resulted in high conversion, hydrodesulfurization, and hydrocracking. The use of a higher boiling solvent (octadecane vs tridecane) was beneficial in providing increasing conversion, hydrodesulfurization, and hydrogenation. $\text{Mo}(\text{CO})_6$ at 36 mol% loading, with added sulfur at 6:1 ratio and octadecane solvent, gave 100% conversion of dibenzothiophene.

Bianchini, C. *et al.*³¹ studied the catalytic activity of zwitterionic Rh(I) complex [(sulphos)Rh(cod)] for the hydrogenolysis reactions of benzothiophene in liquid-biphase systems. In the presence of sodium hydroxide or other strong bases, the fast and selective hydrogenolysis of benzothiophene to 2-ethylthiophenol sodium salt occurred. In a typical liquid-biphase hydrogenolysis reaction [0.035 mmol of catalyst, 3.5 mmol of benzothiophene, 4.5 mmol of sodium hydroxide, 5 ml of methanol, 5 ml of H_2O , 10 ml of n-heptane, 30 bar of hydrogen, 160 °C], all the substrate was practically consumed in 5 hours to give the 2-ethylthiophenolate product. The 2-ethylthiophenolate was converted to 2-ethylthiophenol by acidification step with hydrochloric acid. The strong base plays a dual role in the hydrogenolysis reaction: it promoted the formation of the Rh-H species (which was necessary for the C-S

insertion step) by heterolytic splitting of hydrogen and accelerated the conversion of benzothiophene by aiding the reductive elimination of the hydrogenolysis product.

Bianchini, C. *et al.*³² also reported the ruthenium (II) (tetrahydroborate)hydride complex [(triphos)RuH(BH₄)] (7), which reacted with benzothiophene in THF at 40 °C yielding, after 3 hours, a mixture of four different compounds: [(triphos)RuH{BH₃(O-S(C₆H₄)CH₂CH₃)}] (8), [(triphos)Ru{η⁴-S(C₆H₄)CH(CH₃)}] (9), [(triphos)RuH(μ-S(C₆H₄CH₂CH₃)₂HRu(triphos))] (10) and [(triphos)RuH(μ-BH₄)HRu(triphos)]⁺ (11⁺). The reaction was shown in Figure 2.8. After two further hours of reaction, complex (9) disappeared and was completely converted to complex (10). Further heating at 40 °C did not change the product composition (complexes (8), (10), and (11⁺) in a 4:1.3:3 ratio). A variety of independent reactions with isolated compounds had been performed with the aim of elucidating the mechanism of the C-S insertion/hydrogenation of benzothiophene to the 2-ethylthiophenolate ligand. The μ-thiolate complex (10) reacted in THF with dihydrogen (≥ 160 °C, 30 bar H₂) or with HBF₄·OEt₂ (20 °C) yielding ethylbenzene and 2-ethylthiophenol, respectively. No reaction occurred with LiHBet₃.

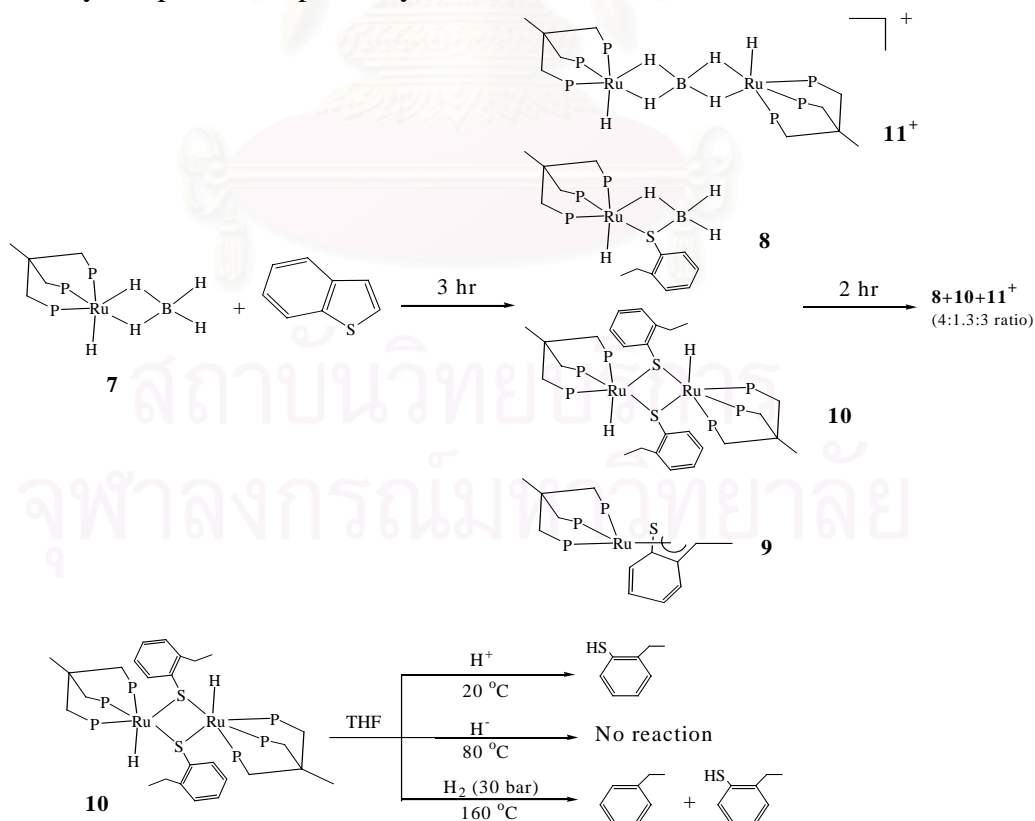


Figure 2.8 Hydrodesulfurization of benzothiophene using [(triphos)RuH(BH₄)].

Churchill, D.G. *et al.*³³ performed the photochemical reaction of *ansa* molybdenocene complexes, $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{MoH}_2$ and $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{Mo}(\text{Ph})\text{H}$ towards thiophenes and found C-S bond cleavage by molybdenum (Figure 2.9). The $[\text{Me}_2\text{Si}]$ *ansa* bridge plays a role in achieving the C-S bond cleavage. In the absence of a bridge the permethyl molybdenocene counterpart, Cp^*MoH_5 , was unreactive toward thiophene. The constraints imposed by the *ansa* bridge inhibited the $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]$ ligand from undergoing an intramolecular deactivation reaction and thereby promoted intermolecular C-S bond activation. This markedly different reactivity of thiophene toward $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{MoH}_2$ and Cp^*MoH_2 represented a notable example of an “*ansa* effect”.

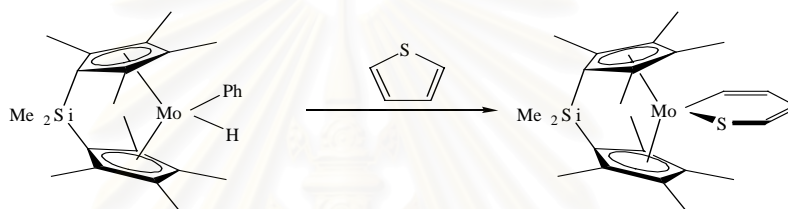


Figure 2.9 The photochemical reaction of $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{Mo}(\text{Ph})\text{H}$ towards thiophenes.

2.4.2.2 Polynuclear metal system

For hydrodesulfurization of thiophenic molecules, multimetallic homogeneous systems, especially when both component and promoter metals are present, are much more effective.

Curtis, M.D. *et al.*³⁴ reported desulfurization of thiophene on a soluble hetero bimetallic cluster $\text{Cp}_2^*\text{Mo}_2\text{Co}_2\text{S}_3(\text{CO})_4$ (12). The complex reacted with thiophene at 150 °C under 15 atm of hydrogen to produce alkanes with the carbon numbers of C_2 - C_4 and $\text{Cp}_2^*\text{Mo}_2\text{Co}_2\text{S}_4(\text{CO})_2$ (13), which included sulfur from thiophene. This new cluster can be converted to the original cluster through the reaction with carbon monoxide. (Figure 2.10)

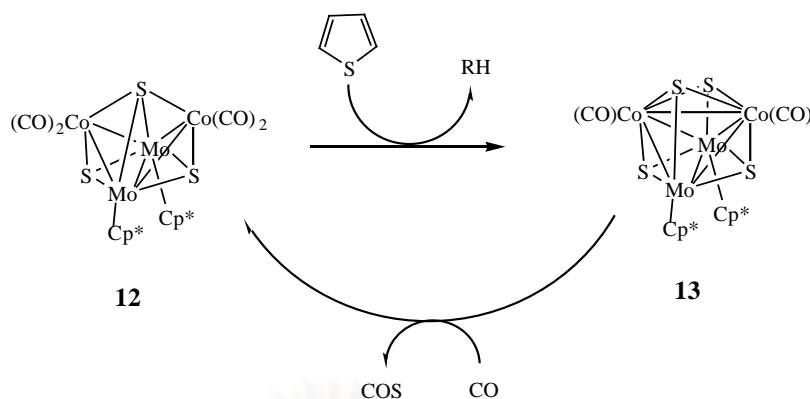


Figure 2.10 Desulfurization of thiophene on a bimetallic cluster $\text{Cp}_2^* \text{Mo}_2 \text{Co}_2 \text{S}_3 (\text{CO})_4$.

Arce, A.J. *et al.*³⁵ reported that the reaction of $[\text{Ru}_3(\text{CO})_{12}]$ with benzothiophene (14) under reflux in THF gave complexes $[\text{Ru}_3(\text{C}_8\text{H}_6)(\text{CO})_8]$ (15), $[\text{Ru}_2(\text{C}_8\text{H}_6\text{S})(\text{CO})_6]$ (16), and $[\text{Ru}_2(\text{C}_8\text{H}_6)(\text{CO})_6]$ (17) in 28, 17, and 10% yield, respectively, as shown in Figure 2.11. Complexes (15) and (17) were formed by C-S bond cleavage and extrusion of the sulfur atom. The dinuclear complex (16) was isolated and heated in cyclohexane for 20 min to afford an insoluble black by-product, which suggested the formation of RuS_2 and the sulfur-free complex (17). Although complex (17) was obtained in low yield (10%), this could be increased if the reaction was carried out under 1 atm of carbon monoxide at room temperature over a period of 24 hours.

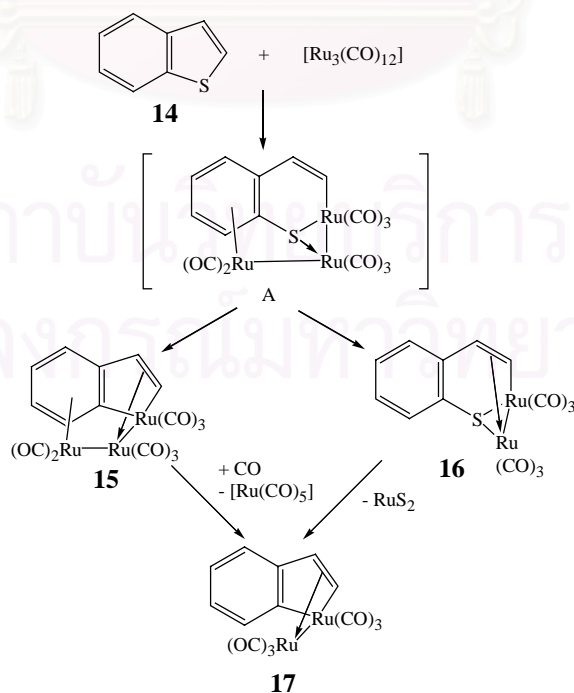


Figure 2.11 Syntheses of ruthenium complexes (15), (16) and (17).

Vicic, D.A. *et al.*³⁶ studied the reaction of the dimer $[\text{Cp}^*\text{IrHCl}]_2$ in benzene solution with either thiophene or benzothiophene at 90 °C in the presence of H_2 , which gave the hydrogenolysis products, $[\text{Cp}^*\text{IrCl}]_2(\mu\text{-H})(\mu\text{-SC}_4\text{H}_9)$ (18) and $[\text{Cp}^*\text{IrCl}]_2(\mu\text{-H})(\mu\text{-S}(\text{C}_6\text{H}_4)\text{CH}_2\text{CH}_3)$ (19), respectively, in high yields (Figure 2.12). Upon further thermolysis under H_2 , the completely desulfurized products, and ethylbenzene, could be made. In the absence of H_2 , reaction of $[\text{Cp}^*\text{IrHCl}]_2$ with thiophene gave an additional trinuclear product $[\text{Cp}^*\text{IrCl}]_3(\text{H})(\text{SC}_4\text{H}_6)$.

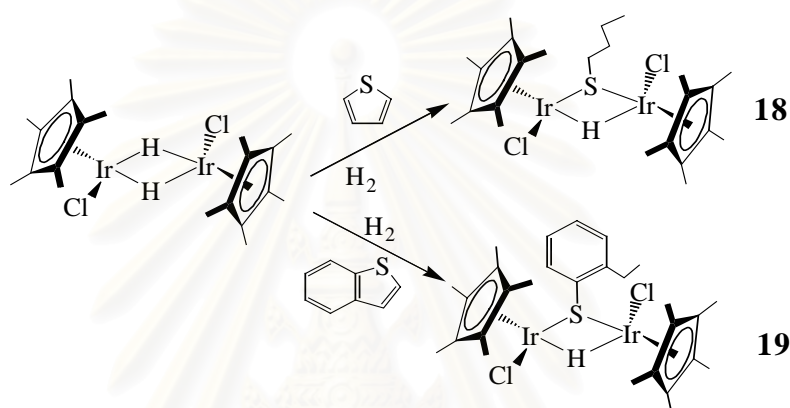


Figure 2.12 Hydrodesulfurization of benzothiophene by binuclear iridium complex.

Matsubara, K. *et al.*³⁷ reported a new approach to hydrodesulfurization of benzothiophene and dibenzothiophene giving ethylbenzene and biphenyl, respectively, with the aid of the trimetallic hydride cluster (20). Treatment of complex (20) with 3 equivalents of benzothiophene in toluene at 50 °C for 12 hours afforded μ_3 -sulfido- μ_3 -alkylidyne complex $(\text{Cp}'\text{Ru})_3(\mu\text{-H})_2(\mu_3\text{-S})(\mu_3\text{-CCH}_2\text{C}_6\text{H}_5)$ (22) as a result of the successive cleavage of two carbon-sulfur bonds. The complex (22) underwent hydrogenolysis by treating with H_2 (7.2 atm) in THF to produce ethylbenzene and the μ_3 -sulfido complex (11) in 96% and 84% yields, respectively. Complex (20) showed activity for the cleavage of the carbon-sulfur bonds in dibenzothiophene as well as benzothiophene. The reaction of complex (20) with dibenzothiophene proceeded at 110 °C for 8 days to form complex (23) and biphenyl in yields of 67% and 64%, respectively. (Figure 2.13)

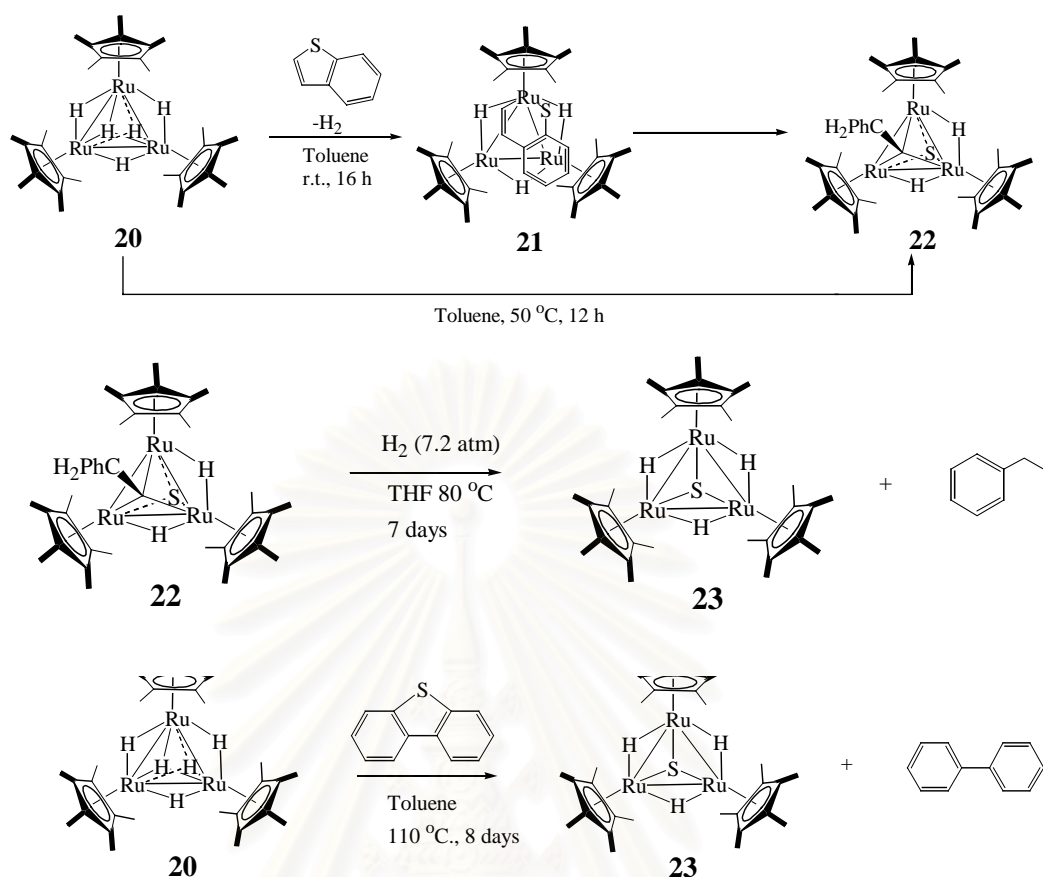


Figure 2.13 Hydrodesulfurization of benzothiophene and dibenzothiophene with the trimetallic hydride cluster.

Jones, W.D. *et al.*³⁸ studied the reaction of thiophene and 2-methylthiophene with the dinuclear polyhydride $[\text{Cp}^*\text{RuH}_2]_2$ at ambient temperature for 48-60 hours to give a C-S ring-opened “flyover” complex (Figure 2.14). No incorporation of hydrogen was observed. The C-S cleavage occurred away from the methyl group in 2-methylthiophene. An unusual η^3, η^4 -coordination was seen in which each atom of the thiophene was bound to one of the metal centers.

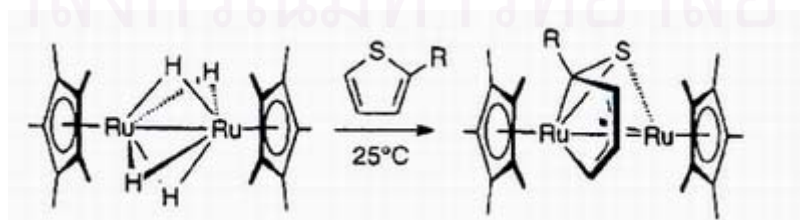


Figure 2.14 The bridging 2-methylthiophene complexes.

CHAPTER III

EXPERIMENTAL

In the present study of the hydrodesulfurization of benzothiophenes catalyzed by molybdenum/cobalt/ruthenium, the experiments were divided into:

1. Catalysts preparation
2. Hydrodesulfurization of benzothiophenes with the prepared catalysts

The details of the experiments were explained in the following.

3.1 Chemicals

All analytical grade of chemicals used in this experiment were obtained as follows :

Chemicals	Suppliers
High purity hydrogen gas (99.99%)	Thai Industrial Gas Co., Ltd., Thailand
High purity nitrogen gas (99.99%)	Thai Industrial Gas Co., Ltd., Thailand
Toluene	Lab Scans Co., Ltd., Ireland
Benzothiophene	Fluka Chemie A.G., Switzerland
Dibenzothiophene	Fluka Chemie A.G., Switzerland
Ruthenium trichloride hydrate, $\text{RuCl}_3 \cdot \text{H}_2\text{O}$	Aldrich Chemical Company, Inc., USA.
Tris-triphenylphosphine ruthenium (II) dichloride, $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$	Fluka Chemie A.G., Switzerland
Ethanol	Merck, Germany
Absolute ethanol	Carlo Erba, Italy

Chemicals	Suppliers
Cyclohexanol	Ajax Chemicals, Australia
Tetrahydrofuran	Lab Scans Co., Ltd., Ireland
Pentamethylcyclopentadiene, C ₅ Me ₅ H	Aldrich Chemical Company, Inc., USA.
Lithium aluminium hydride, LiAlH ₄	Fluka Chemie A.G., Switzerland
Sodium borohydride, NaBH ₄	Fluka Chemie A.G., Switzerland
Potassium tri-sec butyl borohydride, KBu ₃ BH	Fluka Chemie A.G., Switzerland
Acetonitrile, CH ₃ CN	Merck, Germany
Chloroform	Lab Scans Co., Ltd., Ireland
Nitric acid	Merck, Germany
Sodium hydroxide	Carlo Erba, Italy
Sulfur	Fisher Scientific Company, USA.
Molybdenum hexacarbonyl, Mo(CO) ₆	Fluka Chemie A.G., Switzerland
Dicobalt octacarbonyl, Co ₂ (CO) ₈	Johnson Matthey, USA.
Triphenylphosphine, PPh ₃	Fluka Chemie A.G., Switzerland
Dicyclopentadiene	Fluka Chemie A.G., Switzerland
Glacial acetic acid	BDH Laboratory Supplies, England

3.2 Equipments

All equipments used in the catalyst preparation and hydrodesulfurization, were listed as follows:

3.2.1 Schlenk line

Schlenk line consists of nitrogen and vacuum line. The vacuum line was equipped with the solvent trap and pump, respectively. The nitrogen line was connected to the moisture trap and the oil bubbler to provide a seal from the atmosphere when nitrogen line was evacuated. The Schlenk line was shown in Figure 3.1.

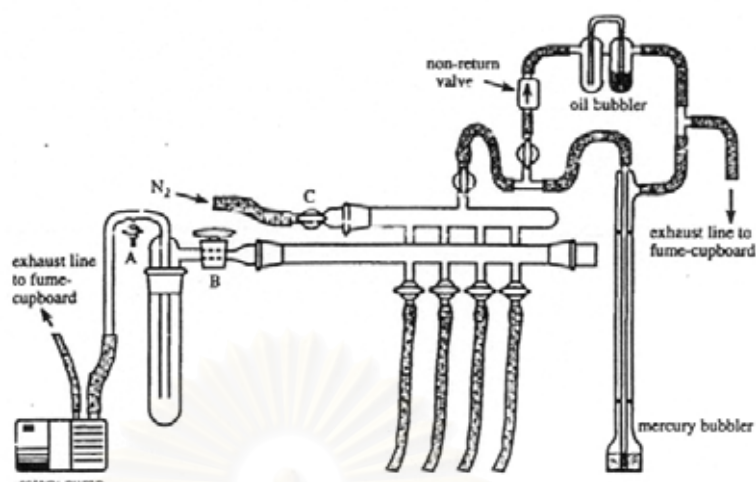


Figure 3.1 Schlenk line.

3.2.2 Schlenk flask

A flask with a side-arm for connection to the manifold is used. Some typical examples are shown in Figure 3.2.

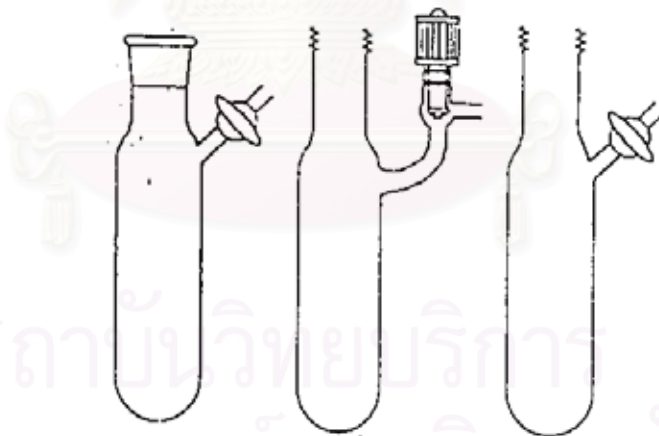


Figure 3.2 Round-bottomed and tube Schlenk flasks.

3.2.3 Heating bath

The heating oil bath with thermometer was used to control the temperature of reaction.

3.2.4 Vacuum pump

A pressure of 10^{-3} to 10^{-1} mmHg was adequate for the vacuum supply to the vacuum line in the Schlenk line.

3.2.5 Inert gas supply

The nitrogen gas was passed through three columns packed with 4 °A molecular sieves, NaOH and P₂O₅, respectively. The inert gas was used to feed in the nitrogen line of Schlenk line.

3.2.6 Syringe and needle

The syringes with volume of 50, 10, 5 ml, needles No. 19, 20 were used.

3.2.7 Hydrogen gas supply

The hydrogen gas was used to feed in hydrodesulfurization reaction in Parr reactor.

3.2.8 Parr Reactor

A Parr 4842 reactor, 600 ml, stainless-steel pressure reactor was used for hydrodesulfurization reaction, shown in Figure 3.3. The reactor consists of stainless steel cylindrical bomb, reactor fitting, bomb heater, cooling coil and temperature controller. The stirring unit of the reactor was supplied with convenient fittings for hanging the various functions. The reactor fitting is shown in Figure 3.4.



Figure 3.3 Parr reactor, Parr 4842.

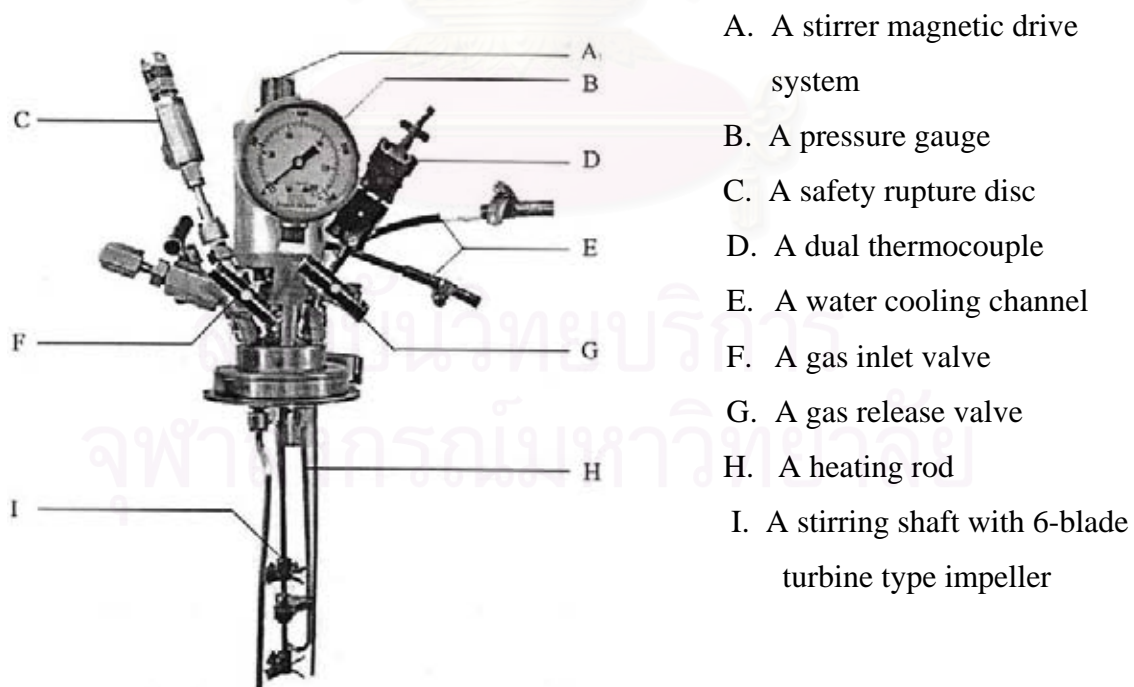


Figure 3.4 Reactor fitting.

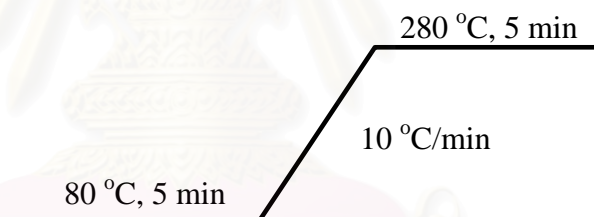
3.3 Characterization instruments

The instruments used to characterize catalyst and hydrodesulfurization products were specified in the following:

3.3.1 Gas chromatography (GC)

Gas chromatography analyses were performed on a Shimadzu GC-14B gas chromatograph equipped with a flame ionization detector and a 30 m (0.25 mm i.d., 0.25 μ m film thickness) DB-1 capillary column. The condition used for the determination of %conversion of substrate and %yield of products were set as follows:

Carrier gas	: Nitrogen
Carrier gas pressure	: 80 kPa
Detector temperature	: 290 °C
Injection temperature	: 220 °C
Programmed temperature	



3.3.2 Gas chromatography -mass spectrometry (GC-MS)

Gas chromatography was carried out on Varian, Star 3400CX and mass spectrometry was carried out on Varian, Saturn 4D by Department of Chemistry, Chulalongkorn University.

3.3.3 Fourier transform infrared spectrometry (FT-IR)

Fourier transform infrared spectra of the catalysts were recorded on Nicolet FT-IR Impact 410 Spectrophotometer at Department of Chemistry, Chulalongkorn University. The solid samples were prepared by pressing the sample with KBr. Infrared spectra were recorded between 400 cm^{-1} to 4000 cm^{-1} in transmittance mode.

3.3.4 Nuclear magnetic resonance spectroscopy (NMR)

$^1\text{H-NMR}$ spectra were obtained on Bruker ACF 200 MHz at Department of Chemistry, Chulalongkorn University. The NMR spectra were measured in chloroform-d at room temperature. The center peak of chloroform was used as the internal reference ($^1\text{H-NMR}$ at 7.2 ppm).

3.4 Catalysts preparation

Reactions were performed using standard Schlenk technique.

3.4.1 Preparation of pentamethylcyclopentadienyl ruthenium chloride, $[\text{Cp}^*\text{RuCl}_2]_2$ ³⁹

$[\text{Cp}^*\text{RuCl}_2]_2$ was prepared by the reaction of ruthenium trichloride hydrate (1.00 g, 4.82 mmol) with pentamethylcyclopentadiene (1.7 ml, 10.96 mmol) in 15 ml of ethanol. The mixture was refluxed at 85 °C for 3 hr. After cooling to room temperature, the dark brown precipitate (0.92 g, 91.71 %yield) was filtered on a fine frit, washed with ethanol/hexane and dried under reduced pressure.

$^1\text{H-NMR}$ (CDCl_3), $\delta(\text{ppm})$: 4.3 (b, 30H)

ref.³⁹ (CDCl_3), $\delta(\text{ppm})$: 4.9 (b, 30H)

FT-IR (KBr): ν (cm^{-1}): 2898(m), 1470(s), 1372(s), 438(m)

ref.³⁹ (KBr): 2983, 2906, 1478, 1375, 440

3.4.2 Preparation of pentamethylcyclopentadienyl ruthenium dichloride triphenylphosphine $[\text{Cp}^*\text{RuCl}_2(\text{PPh}_3)]$ stock solution ($0.01 \times 10^{-3} \text{ M}$)⁴⁰

$\text{Cp}^*\text{RuCl}_2(\text{PPh}_3)$ was prepared by the reaction of $[\text{Cp}^*\text{RuCl}_2]_2$ (0.1224 g, 0.20 mmol) with one equivalent of triphenylphosphine in 20 ml absolute ethanol. The mixture was refluxed at 85 °C for 30 hr and stirred at room temperature for another day to obtain orange-brown solution which was used further. To characterize the complex spectroscopically, the $\text{Cp}^*\text{RuCl}_2(\text{PPh}_3)$ stock solution was pumped off solvent under vacuum, leaving brown solid.

$^1\text{H-NMR}$ (CDCl_3), $\delta(\text{ppm})$: 1.8 (d, 15H), 7.3-7.7 (b, 15H)

FT-IR (KBr): ν (cm^{-1}): 3010(m), 2950(m), 1629(w), 1427(w), 1260(w), 532(m)

3.4.3 Preparation of cyclopentadienylmolybdenum tricarbonyl dimer, $[\text{CpMo}(\text{CO})_3]_2$ ⁴¹

Sodium sand: it was first prepared under nitrogen in three-necked flask. Sodium (0.28 g, 12 mmol) cut into pieces, washed with hexane was vigorously stirred in xylene under reflux temperature until all sodium was dispersed to become sodium sand. After cooling to room temperature, xylene was removed with syringe.

Cyclopentadienyl sodium (CpNa): it was prepared by suspending sodium sand (0.28 g, 12 mmol) in 20 ml distilled dry tetrahydrofuran. The dicyclopentadiene which was cracked to cyclopentadiene (1.3 ml, 16 mmol) was then added dropwise.

$\text{CpMo}(\text{CO})_3\text{Na}$: CpNa solution was treated with molybdenum hexacarbonyl ($\text{Mo}(\text{CO})_6$) (2.64 g, 10 mmol) and the mixture was refluxed at the boiling point for 24 hr with stirring, producing a yellow-brown solution of $\text{CpMo}(\text{CO})_3\text{Na}$.

$\text{CpMo}(\text{CO})_3\text{H}$: it was prepared by adding excess (3 times the stoichiometric amount) of glacial acetic acid to $\text{CpMo}(\text{CO})_3\text{Na}$ solution at room temperature and stirring about an hour.

$[\text{CpMo}(\text{CO})_3]_2$: it was prepared by oxidation of the $\text{CpMo}(\text{CO})_3\text{H}$ solution by air. The mixture became dark red. After about an hour of stirring, the solvent was removed and the product was extracted with hot toluene. The combined toluene extracts were filtered, and the filtrate was evaporated under vacuum, leaving dark-red precipitate (1.88 g, 71.21 % yield).

$^1\text{H-NMR}$ (CDCl_3), $\delta(\text{ppm})$: 5.2 (s, 10H)

FT-IR (KBr): $\nu(\text{cm}^{-1})$: 2954(m), 1952(m), 1886(m), 1701(m), 1618(w), 1097(m)

3.4.4 Preparation of cyclopentadienylmolybdenum tricarbonyl hydride

$\text{CpMo}(\text{CO})_3\text{H}$ (*in situ*)⁴¹

$\text{CpMo}(\text{CO})_3\text{H}$ (*in situ*) was prepared from the reaction of $[\text{CpMo}(\text{CO})_3]_2$ with acid. So its preparation was followed in the same way of $[\text{CpMo}(\text{CO})_3]_2$ (section 3.4.3), except that after cooling $\text{CpMo}(\text{CO})_3\text{Na}$ solution (0.1 M) to room temperature, the desired amount of solution was transferred to the reactor and then excess (3 times the stoichiometric amount) of glacial acetic acid was added.

3.5 Hydrodesulfurization procedure

All catalytic reactions of benzothiophenes were performed in a Parr reactor at desired conditions. A prescribed amount of benzothiophenes, precursor catalyst and other substances were added in 50 ml of solvent. The reactor was purged three times with hydrogen gas and then pressurized to the desired pressure. The stirring speed was kept constant at 500 rpm. The reaction time was started when the required temperature was reached. After a measured time interval, the reactor was cooled to room temperature and slowly depressurized. The contents of the reactor were extracted by chloroform and treated with nitric acid and sodium hydroxide solution, respectively, to remove catalyst. Sampling (1 ml) was taken, added cyclohexanol (internal standard) and analyzed by GC and GC-MS.

3.5.1 Hydrodesulfurization of benzothiophene using monometallic catalysts

3.5.1.1 $[\text{Cp}^*\text{RuCl}_2]_2$

Reactions were performed using $[\text{Cp}^*\text{RuCl}_2]_2$ (0.05 mmol) prepared in section 3.4.1, benzothiophene (2 mmol) in ethanol, using varied triphenylphosphine and reducing agent. The mixture was stirred for 24 hr with 20 atm of hydrogen pressure.

A. Effect of triphenylphosphine

The addition of excess of triphenylphosphine to $[\text{Cp}^*\text{RuCl}_2]_2$ in ethanol and refluxing for at least 24 hr converted the complex to $\text{Cp}^*\text{RuCl}(\text{PPh}_3)_2$.⁴² This phosphine complex was used for the hydrodesulfurization. The $\text{Cp}^*\text{RuCl}(\text{PPh}_3)_2$ complex was prepared *in situ* in the reactor by mixing $[\text{Cp}^*\text{RuCl}_2]_2$ with 2.5 equivalents of triphenylphosphine.

B. Effect of reducing agent

In order to convert $\text{Cp}^*\text{RuCl}(\text{PPh}_3)_2$ to $\text{Cp}^*\text{RuH}_3(\text{PPh}_3)^{45}$, the reducing agent (7.2-fold amount of catalyst) was added in the solution. To compare the activity, three reducing agents were used, sodium borohydride (NaBH_4), lithium aluminium hydride (LiAlH_4) and potassium tri-sec butyl borohydride (KBu_3BH).

C. Comparison of catalysts

The $\text{Cp}^*\text{RuCl}_2(\text{PPh}_3)$ stock solution (0.05 mmol) prepared in section 3.4.2 was employed as a catalyst in the hydrodesulfurization of benzothiophene at 85 °C. This catalyst was compared with $\text{Cp}^*\text{RuCl}(\text{PPh}_3)_2$ (*in situ*), prepared as described in section 3.5.1.1A.

D. Effect of temperature

The hydrodesulfurization of benzothiophene using $\text{Cp}^*\text{RuCl}(\text{PPh}_3)_2$ (*in situ*) was investigated by varying temperature: 85 and 110 °C.

3.5.1.2 $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$

The reactions were carried out using $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$ (0.04 mmol) and one equivalent of triphenylphosphine in toluene at 110 °C for 24 hr with 20 atm of hydrogen pressure. The BT/Ru mole ratio was varied: 100/1, 57/1 and 20/1.

3.5.1.3 $[\text{Cp}^*\text{RuCl}_2]_2$ in liquid-biphase

In these experiments, the basic co-reagent: NaOH or $\text{Ca}(\text{OH})_2$ (25 equivalents) and triphenylphosphine (2.5 equivalents) were added into liquid-biphase system, $\text{MeOH}/\text{hexane}$ (1:1). $[\text{Cp}^*\text{RuCl}_2]_2$ was used as starting material to prepare $\text{Cp}^*\text{RuCl}(\text{PPh}_3)_2$ (*in situ*) as mentioned in section 3.5.1.1A. BT/Ru mole ratio was varied from 20/1 to 10/1. The reactions were carried out at 160 °C for 24 hr with different hydrogen pressure (10, 20 and 30 atm).

3.5.1.4 Hydrodesulfurization of dibenzothiophene using $[\text{Cp}^*\text{RuCl}_2]_2$

The hydrodesulfurization of dibenzothiophene was performed using $[\text{Cp}^*\text{RuCl}_2]_2$ catalysts. $[\text{Cp}^*\text{RuCl}_2]_2$ (0.05 mmol) in ethanol, LiAlH_4 (0.36 mmol) and 2.5 equivalents of triphenylphosphine were charged in the reactor. The reaction

condition was at 85 °C for 48 hr with 20 atm of hydrogen pressure and DBT/Ru mole ratio was 20/1.

To perform the reaction at higher temperature (200 °C), solvent was changed to toluene and DBT/Ru mole ratio was 5/1.

3.5.1.5 [CpMo(CO)₃]₂

The hydrodesulfurization experiments were carried out using [CpMo(CO)₃]₂ prepared in section 3.4.3 and CpMo(CO)₃H (*in situ*) prepared in section 3.4.4 in various conditions.

The hydrodesulfurization reaction using [CpMo(CO)₃]₂ was performed in either toluene or liquid-biphase system. In the former solvent, BT/Mo mole ratio was varied from 20/1 to 10/1 and the reaction was carried out at 200 °C for 24 hr with 20 atm of hydrogen pressure. In liquid-biphase system, the same condition was used, except that BT/Mo mole ratio was fixed at 20/1 and 2.5 equivalents of triphenylphosphine in the presence of base (NaOH) were introduced.

In another experiment, 0.2 mmol of CpMo(CO)₃Na solution prepared in section 3.4.4 was transferred to reactor and then excess (3 times the stoichiometric amount) of glacial acetic acid was added. Mole ratio of BT/Mo was 10/1 and tetrahydrofuran was also added in reactor to make volume equal 50 ml. The reactor pressurized with hydrogen to 20 atm and then heated to 160 °C with stirring for 24 hr.

3.5.2 Hydrodesulfurization of benzothiophene using multimetallic catalysts

The hydrodesulfurization was also investigated using multimetallic catalysts: ruthenium with molybdenum and/or cobalt.

A. [Cp***RuCl**]₂ + molybdenum complexes

The procedure described above in section 3.5.1.3 for the hydrodesulfurization of benzothiophene using [Cp***RuCl**]₂ (0.05 mmol) as starting material to form Cp***RuCl**(PPh₃)₂ in liquid-biphase was followed. Molybdenum compound was added as listed below. The reactions were performed at 160 °C for 24 hr with 20 atm of hydrogen pressure.

Catalysts	BT/Ru/Mo mole ratio
$\text{Cp}^*\text{RuCl}(\text{PPh}_3)_2 + \text{Mo}(\text{CO})_6$	20/1/1
$\text{Cp}^*\text{RuCl}(\text{PPh}_3)_2 + [\text{CpMo}(\text{CO})_3]_2$	20/1/1
$\text{Cp}^*\text{RuCl}(\text{PPh}_3)_2 + [\text{CpMo}(\text{CO})_3]_2$	20/1/3

B. $[\text{Cp}^*\text{RuCl}_2]_2 + \text{Co}_2(\text{CO})_8$

$[\text{Cp}^*\text{RuCl}_2]_2$ (0.05 mmol), $\text{Co}_2(\text{CO})_8$ (0.05 mmol) and LiAlH_4 (0.36 mmol) were stirred for one day in the reactor at room temperature with 5 atm of hydrogen pressure. After releasing pressure, benzothiophene (2 mmol) was added. The reaction was performed for 24 hr at 160 °C with 20 atm of hydrogen pressure.

C. $[\text{Cp}^*\text{RuCl}_2]_2 + [\text{CpMo}(\text{CO})_3]_2 + \text{Co}_2(\text{CO})_8$

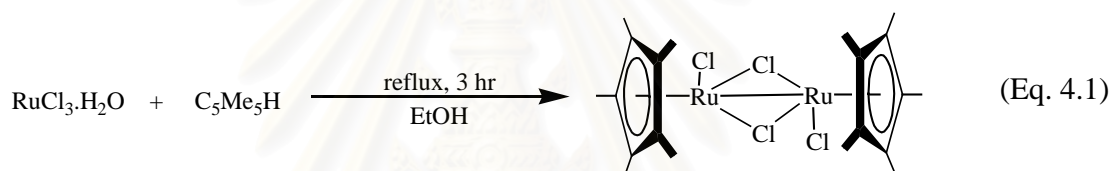
The procedure in section 3.5.1.3A was followed for the hydrodesulfurization, but $\text{Co}_2(\text{CO})_8$ was also introduced as a third metal. Mole ratio of BT/Ru/Mo/Co was 20/1/3/1.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Preparation of pentamethylcyclopentadienyl ruthenium chloride, $[\text{Cp}^* \text{RuCl}_2]_2$

$[\text{Cp}^* \text{RuCl}_2]_2$ was prepared by the reaction of $\text{RuCl}_3 \cdot \text{H}_2\text{O}$ with pentamethylcyclopentadiene in refluxing ethanol for 3 hours to produce dark brown precipitate (92 %) (Eq. 4.1).³⁹



$[\text{Cp}^* \text{RuCl}_2]_2$ was characterized by $^1\text{H-NMR}$ (in CDCl_3) and FT-IR, shown in Figures 4.1- 4.2, respectively. The $^1\text{H-NMR}$ spectrum appeared a broad signal of methyl protons at δ 4.3 ppm.

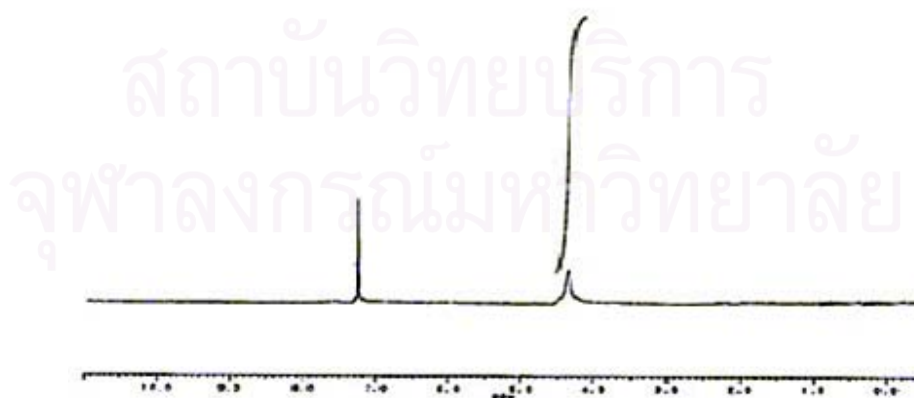


Figure 4.1 $^1\text{H-NMR}$ spectrum of $[\text{Cp}^* \text{RuCl}_2]_2$.

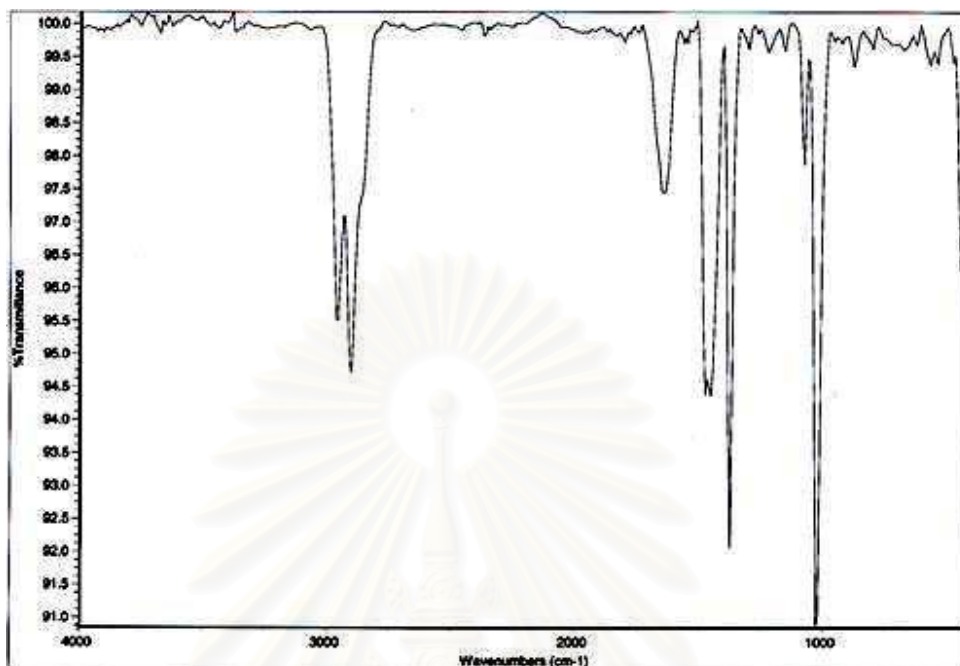
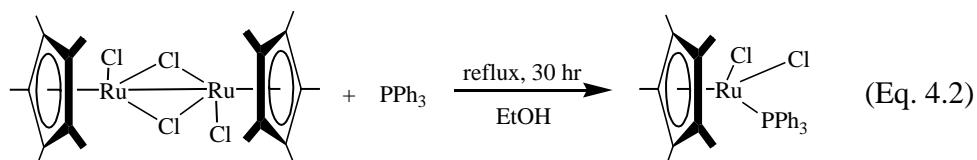


Figure 4.2 FT-IR spectrum of $[\text{Cp}^* \text{RuCl}_2]_2$.

The FT-IR spectrum showed the following characteristic absorption bands at 2898 cm^{-1} (CH_3 stretching), 1694 cm^{-1} ($\text{C}=\text{C}$ stretching), 1470 and 1372 cm^{-1} (CH_3 bending) and Ru-Cl stretching vibration at 438 cm^{-1} .

4.2 Preparation of pentamethylcyclopentadienyl ruthenium dichloride triphenylphosphine, $\text{Cp}^* \text{RuCl}_2(\text{PPh}_3)$

$\text{Cp}^* \text{RuCl}_2(\text{PPh}_3)$ was prepared by the reaction of $[\text{Cp}^* \text{RuCl}_2]_2$ with one equivalent of triphenylphosphine in absolute ethanol (Eq. 4.2).⁴⁰ The orange-brown solution was obtained.



$\text{Cp}^*\text{RuCl}_2(\text{PPh}_3)$ was characterized by $^1\text{H-NMR}$ (in CDCl_3) and FT-IR, shown in Figures 4.3- 4.4, respectively. The $^1\text{H-NMR}$ spectrum exhibited a signal of methyl protons at δ 1.8 ppm and aromatic protons could be detected around δ 7.3-7.7 ppm.

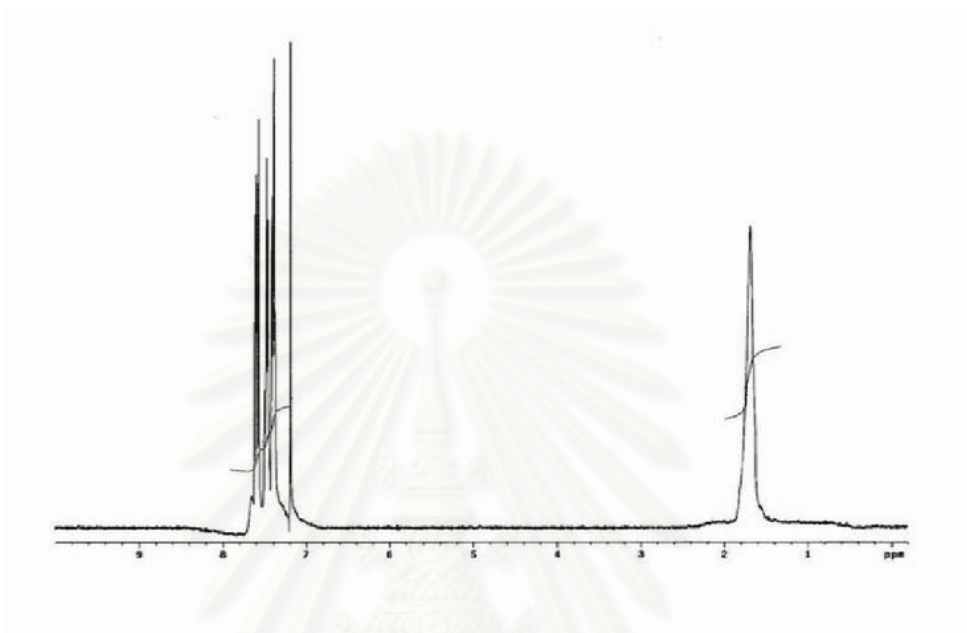


Figure 4.3 $^1\text{H-NMR}$ spectrum of $\text{Cp}^*\text{RuCl}_2(\text{PPh}_3)$.

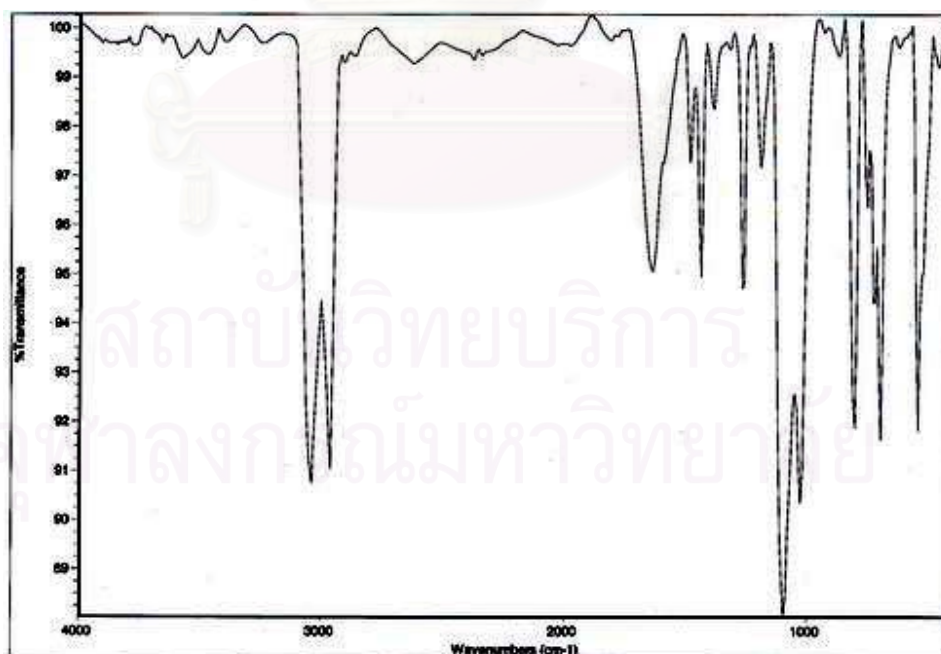
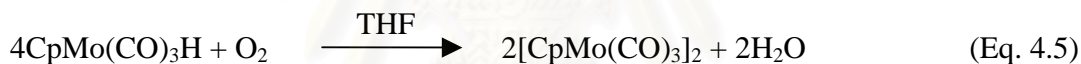
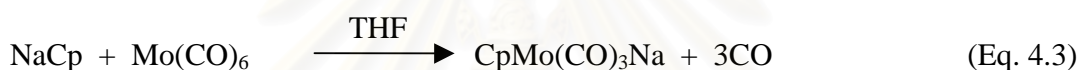


Figure 4.4 FT-IR spectrum of $\text{Cp}^*\text{RuCl}_2(\text{PPh}_3)$.

The FT-IR spectrum revealed the absorption bands: 3010 cm^{-1} (=C-H stretching), 2950 cm^{-1} (CH_3 stretching), 1629 cm^{-1} (C=C stretching), 1427 cm^{-1} (P-Ar stretching), 1260 cm^{-1} (CH_3 bending) and Ru-Cl stretching vibration at 532 cm^{-1} .

4.3 Preparation of cyclopentadienylmolybdenum tricarbonyl dimer, $[\text{CpMo}(\text{CO})_3]_2$

$[\text{CpMo}(\text{CO})_3]_2$ was prepared by the reaction of $\text{Mo}(\text{CO})_6$ with cyclopentadienyl sodium (NaCp) in THF. The mixture was refluxed for 24 hours, producing a yellow-brown solution of the sodium compound, $\text{CpMo}(\text{CO})_3\text{Na}$. The excess of glacial acetic acid was added. After about an hour of stirring, $\text{CpMo}(\text{CO})_3\text{H}$ was obtained. The oxidation of $\text{CpMo}(\text{CO})_3\text{H}$ gave $[\text{CpMo}(\text{CO})_3]_2$ (Eq. 4.3-4.5).⁴¹



$[\text{CpMo}(\text{CO})_3]_2$ was characterized by $^1\text{H-NMR}$ (in CDCl_3) and FT-IR, shown in Figures 4.5- 4.6, respectively. The $^1\text{H-NMR}$ spectrum appeared a signal of Cp ligand at δ 5.2 ppm.

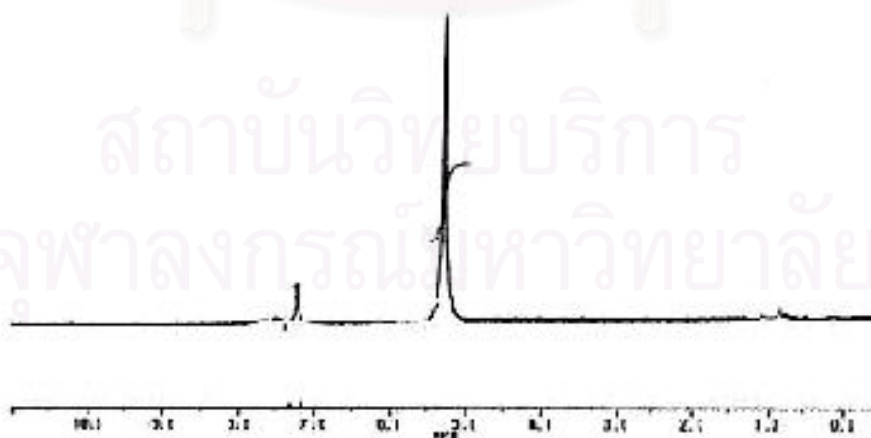


Figure 4.5 $^1\text{H-NMR}$ spectrum of $[\text{CpMo}(\text{CO})_3]_2$.

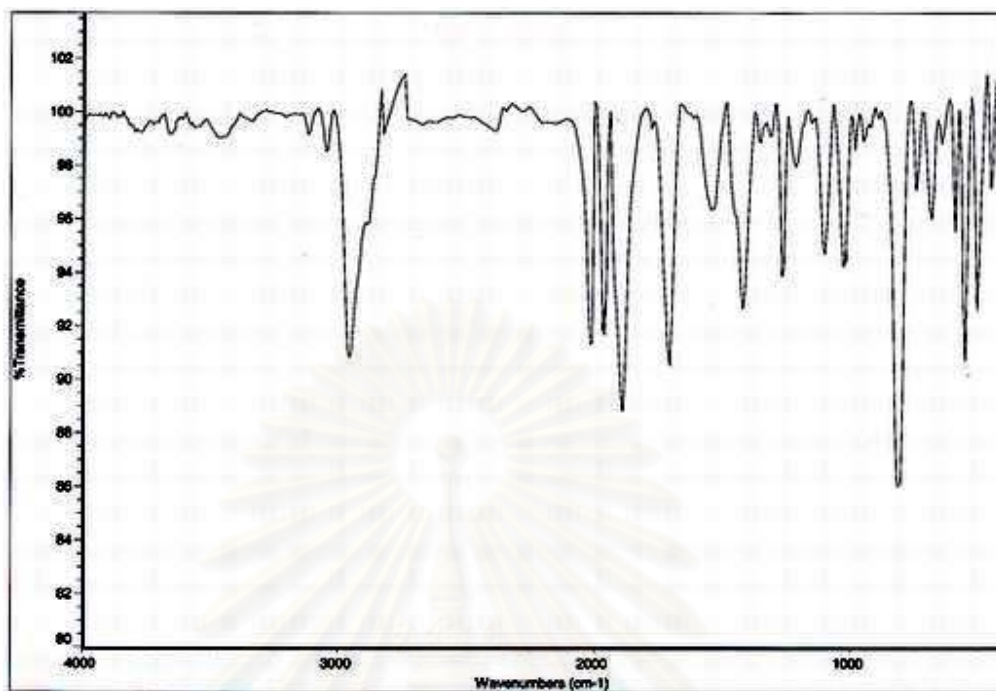


Figure 4.6 FT-IR spectrum of $[\text{CpMo}(\text{CO})_3]_2$.

The FT-IR spectrum displayed the adsorption bands at 2954 cm^{-1} (CH stretching), 1952 , 1886 and 1701 cm^{-1} (CO stretching), 1618 cm^{-1} (C=C stretching) and 1097 cm^{-1} (CH bending).

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4.4 Hydrodesulfurization of benzothiophene using monometallic catalysts

4.4.1 $[\text{Cp}^*\text{RuCl}_2]_2$

%Conversions of benzothiophene from hydrodesulfurization reaction catalyzed by $[\text{Cp}^*\text{RuCl}_2]_2$ were shown in Table 4.1.

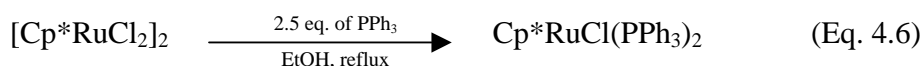
Table 4.1 %Conversion of BT using $[\text{Cp}^*\text{RuCl}_2]_2$ catalyst

Entry	Catalyst	Reducing Agent	T (°C)	%Conv BT 24 h	%DHBT 24 h
1	$[\text{Cp}^*\text{RuCl}_2]_2$	-	85	-	-
2	$\text{Cp}^*\text{RuCl}(\text{PPh}_3)_2$	-	85	7.0	5.0
3	$\text{Cp}^*\text{RuCl}(\text{PPh}_3)_2$	LiAlH_4	85	21.6	18.4
4	$\text{Cp}^*\text{RuCl}(\text{PPh}_3)_2$	NaBH_4	85	9.9	7.6
5	$\text{Cp}^*\text{RuCl}(\text{PPh}_3)_2$	KBu_3BH	85	7.0	6.0
6	$\text{Cp}^*\text{RuCl}_2(\text{PPh}_3)$	LiAlH_4	85	16.5	15.0
7	$\text{Cp}^*\text{RuCl}(\text{PPh}_3)_2$	LiAlH_4	110	25.0	22.5

$[\text{Cp}^*\text{RuCl}_2]_2$ 0.05 mmol; BT 2 mmol; solvent EtOH; reducing agent/Ru mole ratio 3.6/1
Condition: 24 hr; PH_2 20 atm

A. Effect of triphenylphosphine

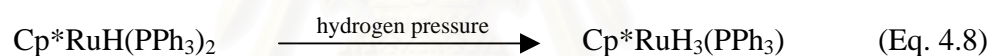
Entries 1 and 2 in Table 4.1 indicated that $[\text{Cp}^*\text{RuCl}_2]_2$ was an inactive catalyst for hydrodesulfurization, since no product was occurred. However, the addition of triphenylphosphine results in the higher %conversion, giving dihydrobenzothiophene (DHBT) as product. This can be explained that in the presence of excess triphenylphosphine, $[\text{Cp}^*\text{RuCl}_2]_2$ was reacted to form $\text{Cp}^*\text{RuCl}(\text{PPh}_3)_2$ (Eq.4.6), which is an active catalyst for hydrogenation.⁴²



B. Effect of reducing agent

Three types of reducing agent were investigated; lithium aluminium hydride (LiAlH_4), sodium borohydride (NaBH_4) and potassium tertiary butyl borohydride (KBu_3BH).

From Table 4.1 (entries 3-5), the %conversion of BT increased in the order: $\text{KBu}_3\text{BH} < \text{NaBH}_4 < \text{LiAlH}_4$, because LiAlH_4 has more reducing power than the others thus it could easily reduce catalyst. The hydride ion reduced $\text{Cp}^*\text{RuCl}(\text{PPh}_3)_2$ to $\text{Cp}^*\text{RuH}(\text{PPh}_3)_2$ in ethanol (Eq. 4.7). The treatment of $\text{Cp}^*\text{RuH}(\text{PPh}_3)_2$ with H_2 resulted in $\text{Cp}^*\text{RuH}_3(\text{PPh}_3)$ (Eq. 4.8), an active catalyst for activation of the carbon-hydrogen bonds. This result is in good agreement with that reported, the reaction of $[\text{Cp}^*\text{RuCl}_2]_2$ with NaBH_4 afforded ruthenium hydride complex in lower yield than LiAlH_4 .⁴³



C. Comparison of catalysts

The reaction of $[\text{Cp}^*\text{RuCl}_2]_2$ with one equivalent of triphenylphosphine yielded $\text{Cp}^*\text{RuCl}_2(\text{PPh}_3)$, while in the presence of 2.5 equivalents of triphenylphosphine, $\text{Cp}^*\text{RuCl}(\text{PPh}_3)_2$ was obtained. The latter species was easily reduced by LiAlH_4 to form the ruthenium hydride complex which is an active catalyst. Thus, the results from entries 3 and 6 showed that %conversion was slightly decreased when using $\text{Cp}^*\text{RuCl}_2(\text{PPh}_3)$ in stead of $\text{Cp}^*\text{RuCl}(\text{PPh}_3)_2$ as catalyst.

D. Effect of temperature

The influence of temperature was investigated by varying temperature: 85 and 110 °C. The results (entries 3 and 7) showed that higher temperature gave higher %conversion of benzothiophene and %yield of DHBT than those at the lower temperature. It can be remarked that the collisions between benzothiophene and catalyst

increase with increasing temperature as the rate of reaction is directly proportional to the frequency of molecular collisions.⁴⁴

4.4.2 Ru(PPh₃)₃Cl₂

The %conversions of benzothiophene from hydrodesulfurization reaction catalyzed by Ru(PPh₃)₃Cl₂ were presented in Table 4.2.

Table 4.2 % Conversion of BT using Ru(PPh₃)₃Cl₂ catalyst

Entry	BT/Ru mole ratio	%Conv BT 24 h	%DHBT 24 h
1	100/1	11.3	10.0
2	57/1	15.0	11.5
3	20/1	17.5	15.0

Ru(PPh₃)₃Cl₂ 0.05 mmol; solvent toluene

Condition: 110 °C; 24 hr; PH₂ 20 atm

From Table 4.2, it was shown that DHBT product trended to enhance with decreasing BT/Ru mole ratio (increasing catalyst concentration). The possible explanation may be because there were more active sites for the hydrogenation of benzothiophene. These results corresponded to previous research, reported that the rate of hydrogenation of poly(styrene-co butadiene) using Ru(PPh₃)₃Cl₂ increased with respect to catalyst concentration.⁴⁵

4.4.3 [Cp*₂RuCl₂]₂ in liquid-biphase system

The effect of hydrogen pressure, base and BT/Ru mole ratio was investigated. The %conversions of benzothiophene from hydrodesulfurization reaction catalyzed by Cp*₂RuCl(PPh₃)₂ prepared *in situ* from [Cp*₂RuCl₂]₂, in liquid-biphase system, were illustrated in Table 4.3.

Table 4.3 %Conversion of BT using $[\text{Cp}^*\text{RuCl}_2]_2$ in liquid-biphase system

Entry	Catalyst	BT/Ru mole Ratio	Base	H ₂ (atm)	%Conv BT 24 h	%DHBT 24 h	%EB 24 h
1	$\text{Cp}^*\text{RuCl}(\text{PPh}_3)_2$	20/1	NaOH	30	41.5	37.0	2.5
2	$\text{Cp}^*\text{RuCl}(\text{PPh}_3)_2$	20/1	NaOH	20	30.0	27.0	1.5
3	$\text{Cp}^*\text{RuCl}(\text{PPh}_3)_2$	20/1	NaOH	10	19.0	14.5	1.0
4	$\text{Cp}^*\text{RuCl}(\text{PPh}_3)_2$	20/1	$\text{Ca}(\text{OH})_2$	20	28.5	24.5	1.5
5	$\text{Cp}^*\text{RuCl}(\text{PPh}_3)_2$	10/1	NaOH	20	39.5	32.5	3.0

$[\text{Cp}^*\text{RuCl}_2]_2$ 0.05 mmol; solvent MeOH/hexane(1:1); base/Ru mole ratio 25/1

Condition: 160 °C; 24 hr

Under hydrogen pressure, in combination with a strong base, $\text{Cp}^*\text{RuCl}(\text{PPh}_3)_2$ formed $\text{Cp}^*\text{RuH}(\text{PPh}_3)_2$ (Eq. 4.9) which can react further to form $\text{Cp}^*\text{RuH}_3(\text{PPh}_3)$ (Eq. 4.10) which was reported to be an efficient catalyst for the hydrodesulfurization.^{40, 46}



The effect of hydrogen pressure was studied by varying hydrogen pressure from 10 to 30 atm. As shown in Table 4.3 (entries 1-3), %conversion of benzothiophene and %yield of products increased with the hydrogen pressure. The major product was DHBT, hydrogenated product, moreover, ethylbenzene (EB), hydrogenolysis product, occurred. This result was supported by an experiment of the hydrogenolysis of benzothiophene by rhodium catalyst in the range of 5-30 atm, the rate increased with the hydrogen pressure (Figure 4.7, (a)). The highest conversion is observed at 30 atm.³¹

A comparison between entries 2 and 4 from Table 4.3 showed that NaOH gave insignificant difference in %conversion than $\text{Ca}(\text{OH})_2$ when both of them were added excess. As already reported for other related hydrogenolysis reactions of benzothiophene

in the homogeneous phase, the use of excess strong bases such as KOC_4H_9 or KOH affects neither the selectivity nor the activity.³¹

Considering mole ratio of BT/Ru, the results from entries 2 and 5 (Table 4.3) indicated that the highest %conversion was obtained at 10/1 mole ratio of BT/Ru. It could be reasonably assumed that there were more active sites to react with benzothiophene. It was usually reported that the hydrogenolysis reaction is the first-order with respect to the concentrations of the catalyst precursor (Figure 4.7, (b)).³¹

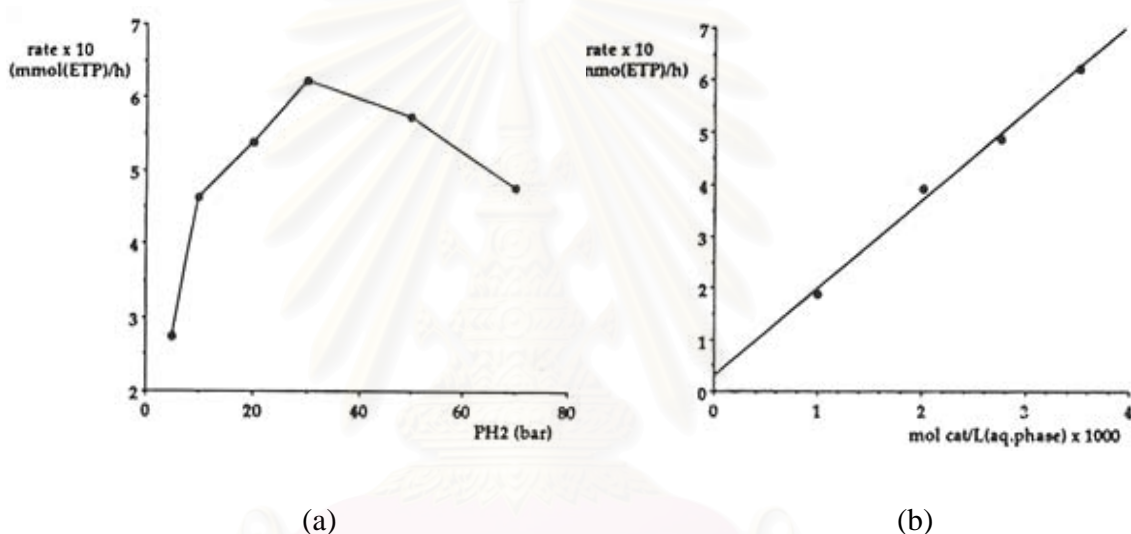


Figure 4.7 Hydrogenolysis reaction of benzothiophene catalyzed by rhodium catalyst. Dependence of the rate on the

(a) hydrogen pressure

(b) catalyst concentration

4.4.4 Hydrodesulfurization of dibenzothiophene using $[\text{Cp}^*\text{RuCl}_2]$

The %conversions of hydrodesulfurization of dibenzothiophene were ascribed in Table 4.4.

Table 4.4 % Conversion of DBT using $\text{Cp}^*\text{RuCl}(\text{PPh}_3)_2$

Entry	Catalyst	DBT/Ru mole ratio	Reducing Agent	T (°C)	H ₂ (atm)	%Conv DBT 48 h	%TH- DBT 48 h
1	$\text{Cp}^*\text{RuCl}(\text{PPh}_3)_2$	20/1	LiAlH_4	85	20	8.0	7.0
2	$\text{Cp}^*\text{RuCl}(\text{PPh}_3)_2^*$	5/1	LiAlH_4	200	20	16.0	10.3

$\text{Cp}^*\text{RuCl}(\text{PPh}_3)_2$ 0.1 mmol based on Ru; solvent EtOH; reducing agent/Ru mole ratio 3.6/1

*toluene solvent

From Table 4.4, hydrodesulfurization of dibenzothiophene gave low %conversion and %yield of TH-DBT, this result can be explained by the higher stability of dibenzothiophene due to the presence of benzene rings which resulted in conjugation.⁴⁷ It is known that dibenzothiophene was one of the most unreactive sulfur compounds in higher boiling fractions of fuels.

4.4.5 $[\text{CpMo}(\text{CO})_3]_2$

The %conversions of benzothiophene from hydrodesulfurization reaction catalyzed by $[\text{CpMo}(\text{CO})_3]_2$ were shown in Table 4.5.

Table 4.5 % Conversion of BT using $[\text{CpMo}(\text{CO})_3]_2$

Entry	Catalyst	BT/Mo mole ratio	Solvent	PPh_3 (equi)	NaOH (mmol)	T (°C)	H ₂ (atm)	%Conv BT 24 h	%EB 24 h
1	$[\text{CpMo}(\text{CO})_3]_2$	20/1	toluene	-	-	200	20	8.0	4.0
2	$[\text{CpMo}(\text{CO})_3]_2$	10/1	toluene	-	-	200	20	13.5	9.0
3	$[\text{CpMo}(\text{CO})_3]_2$	20/1	MeOH/hex.	2.5	2.57	200	20	0	0
4	$\text{CpMo}(\text{CO})_3\text{H}$	10/1	THF	-	-	160	20	5.0	3.5

$[\text{CpMo}(\text{CO})_3]_2$ 0.05 mmol; $\text{CpMo}(\text{CO})_3\text{H}$ 0.1 mmol; Condition: 24 hr

The hydrodesulfurization reaction using $[\text{CpMo}(\text{CO})_3]_2$ was performed in either toluene or liquid-biphase system. In entries 1 and 2 from Table 4.5, toluene was used as solvent, the results showed that the highest %conversion was obtained at BT/Mo mole ratio = 10/1. Decreasing the ratio (increasing catalyst concentration) caused the increasing in the active sites, similar to the results of ruthenium complexes, but the obtained product was EB, hydrogenolysis product. Therefore, $[\text{CpMo}(\text{CO})_3]_2$ was active for hydrogenolysis reaction.

When the reaction was performed in liquid-biphase system (entry 3 from Table 4.5), no product occurred. It was probably because the NaOH would shield active molybdenum species or reduce the reactivity of active sites.¹³

In entry 4 from Table 4.5, $\text{CpMo}(\text{CO})_3\text{H}$ reacted with benzothiophene to give low %yield of ethylbenzene, this might be due to the instability of molybdenum hydride complex.

4.5 Hydrodesulfurization of benzothiophene using multimetallic catalysts

The %conversions of benzothiophene from hydrodesulfurization reaction catalyzed by multimetallic catalysts (in section 3.5.2) were illustrated in Table 4.6.

Table 4.6 %Conversion of BT using multimetallic catalysts

Entry	Catalyst	Base	H ₂ (atm)	%Conv BT 24 h	%DHBT 24 h	%EB 24 h
1	Cp*RuCl(PPh ₃) ₂ + Mo(CO) ₆ (1:1)	NaOH	20	4.0	1.0	0.7
2	Cp*RuCl(PPh ₃) ₂ + [CpMo(CO) ₃] ₂ (1:1)	NaOH	20	12.0	9.0	2.5
3	Cp*RuCl(PPh ₃) ₂ + [CpMo(CO) ₃] ₂ (1:3)	NaOH	20	9.0	5.0	1.0
4	[Cp*RuCl ₂] ₂ + Co ₂ (CO) ₈ * (1:1)	-	20	5.0	2.0	0
5	Cp*RuCl(PPh ₃) ₂ + [CpMo(CO) ₃] ₂ + Co ₂ (CO) ₈ (1:3:1)	NaOH	20	6.0	4.5	1.0

[Cp*RuCl₂]₂ 0.05 mmol; BT 2 mmol; solvent entries 1-3, 5=MeOH/hexane(1:1), entry 4=THF

Condition: 24 hr

*LiAlH₄ 0.36 mmol was added.

In bimetallic catalysts which resulted from the reaction between Cp*RuCl(PPh₃)₂, prepared *in situ* and molybdenum compound (Mo(CO)₆ or [CpMo(CO)₃]₂), entries 1-3 (Table 4.6), it was observed that %conversion was lower than using Cp*RuCl(PPh₃)₂ in liquid-biphase (30.0 %conversion in Table 4.3). As shown in previous experiment that [CpMo(CO)₃]₂ was inactive in the presence of NaOH. The result pointed out that molybdenum compound demonstrated a negative effect on catalyzation, it may react with Cp*RuCl(PPh₃)₂ to form new catalyst species that showed the low catalytic activity.

In entry 3 from Table 4.6, the reaction between $[\text{Cp}^*\text{RuCl}_2]_2$ and $\text{Co}_2(\text{CO})_8$ with LiAlH_4 in THF was expected to form Ru-Co complex⁴⁸, but it was inactive for hydrodesulfurization. It gave low %conversion of benzothiophene and the only product was hydrogenated product, DHBT.

In entry 5 from Table 4.6, the trimetallic catalyst system, also showed the lower %conversion, similar to bimetallic catalysts, $\text{Cp}^*\text{RuCl}(\text{PPh}_3)_2$ and $[\text{CpMo}(\text{CO})_3]_2$ (entry 24). This indicated that $\text{Co}_2(\text{CO})_8$ did not involve in the reaction.

4.6 Characterization of products

4.6.1 Gas chromatography

The GC chromatograms of hydrodesulfurization of benzothiophene and dibenzothiophene were shown in Figures 4.8- 4.9.

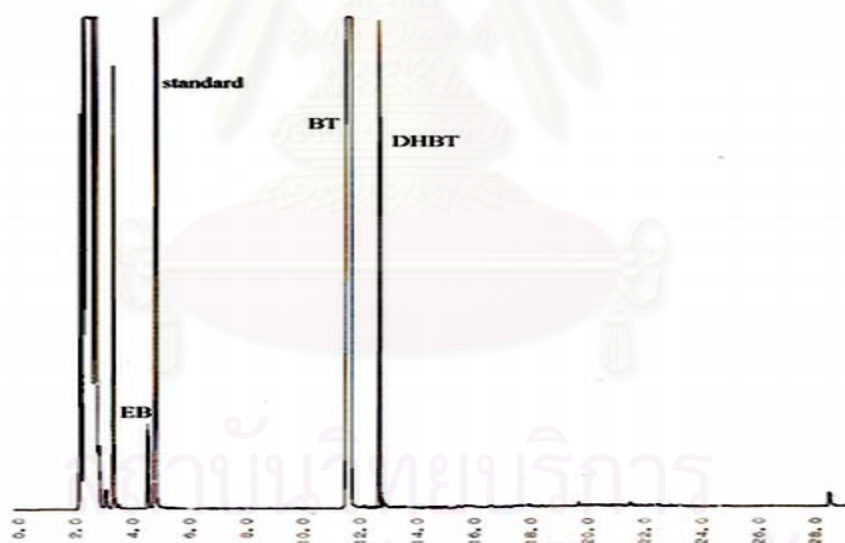


Figure 4.8 GC chromatogram from hydrodesulfurization of BT.

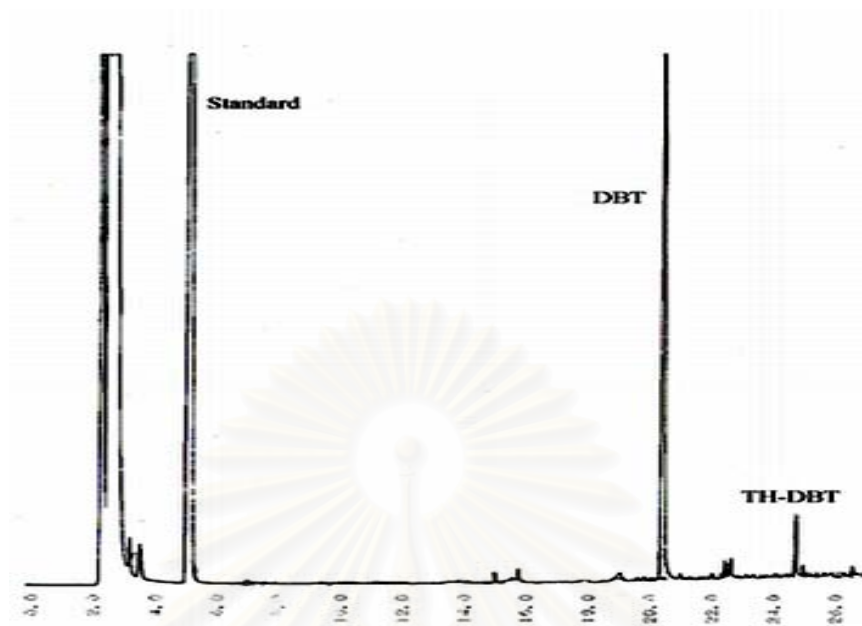


Figure 4.9 GC chromatogram from hydrodesulfurization of DBT.

4.6.2 Mass spectrometry

4.6.2.1 Hydrodesulfurization of benzothiophene

The sample obtained from the hydrodesulfurization of benzothiophene was determined by GC-MS to detect the mass spectrum of each GC peak on GC chromatogram that included substrate and products. All of mass spectra for hydrodesulfurization of benzothiophene were shown as follows:

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The substrate of hydrodesulfurization was benzothiophene, which showed mass spectrum at $m/z = 134$.

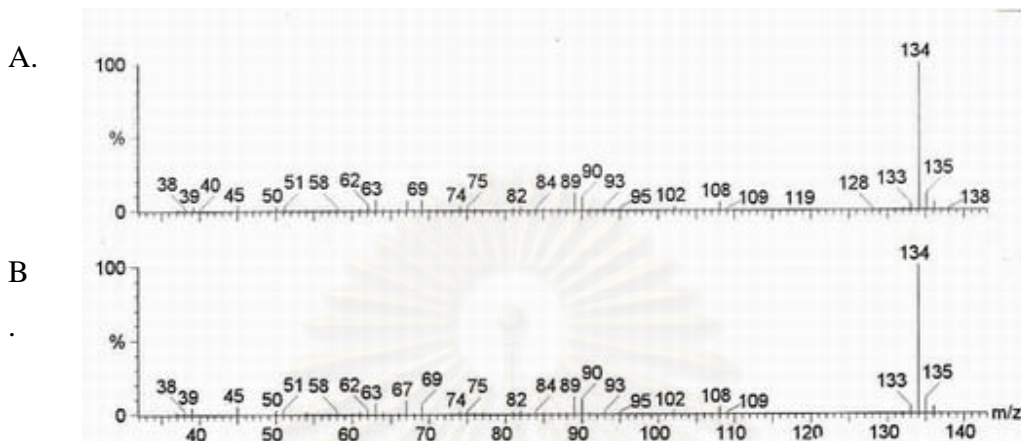


Figure 4.10 Mass spectrum of benzothiophene.

A. Sample

B. Benzothiophene reference

The hydrogenation product of benzothiophene was dihydrobenzothiophene (DHBT), which gave $m/z = 136$.

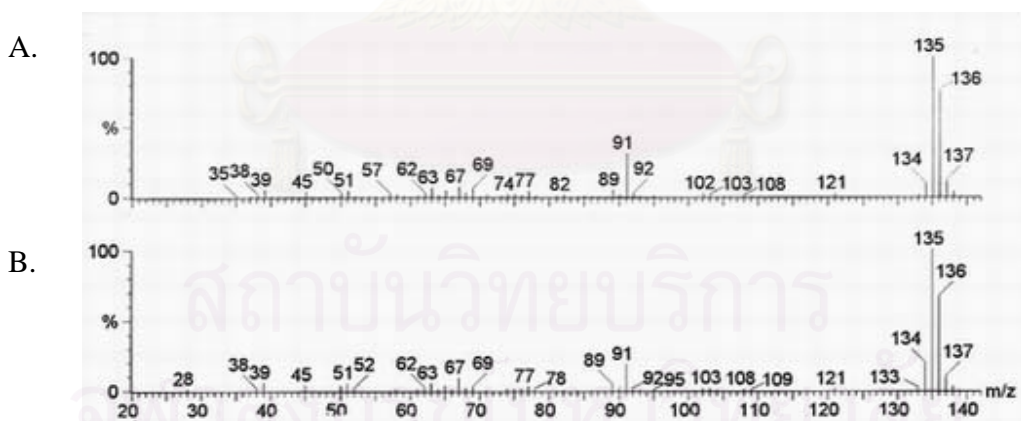


Figure 4.11 Mass spectrum of dihydrobenzothiophene.

A. Sample

B. Dihydrobenzothiophene reference

The hydrogenolysis product of benzothiophene was ethylbenzene (EB), which showed $m/z = 106$.

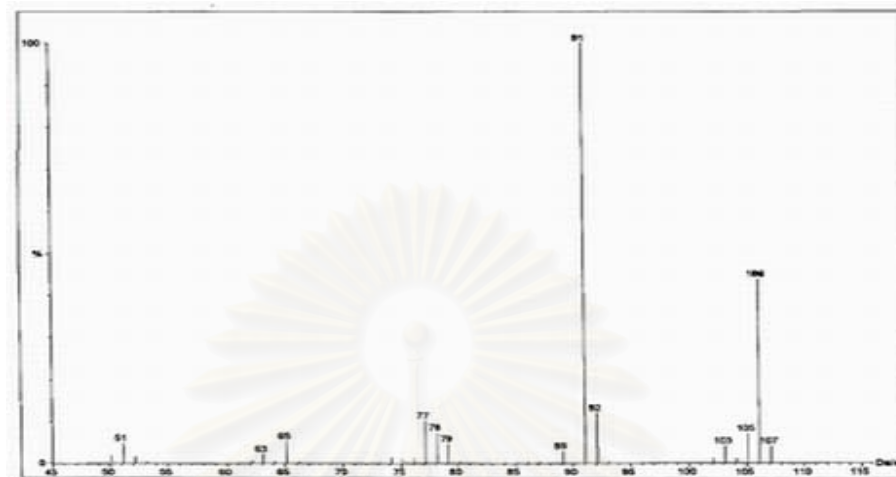


Figure 4.12 Mass spectrum of ethylbenzene.

4.6.2.2 Hydrodesulfurization of dibenzothiophene

The sample obtained from the hydrodesulfurization of dibenzothiophene was also determined by GC-MS. The mass spectra of each GC peak on GC chromatogram were shown as follows:

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Dibenzothiophene was also the hydrodesulfurization substrate, which gave mass spectrum at $m/z = 184$.

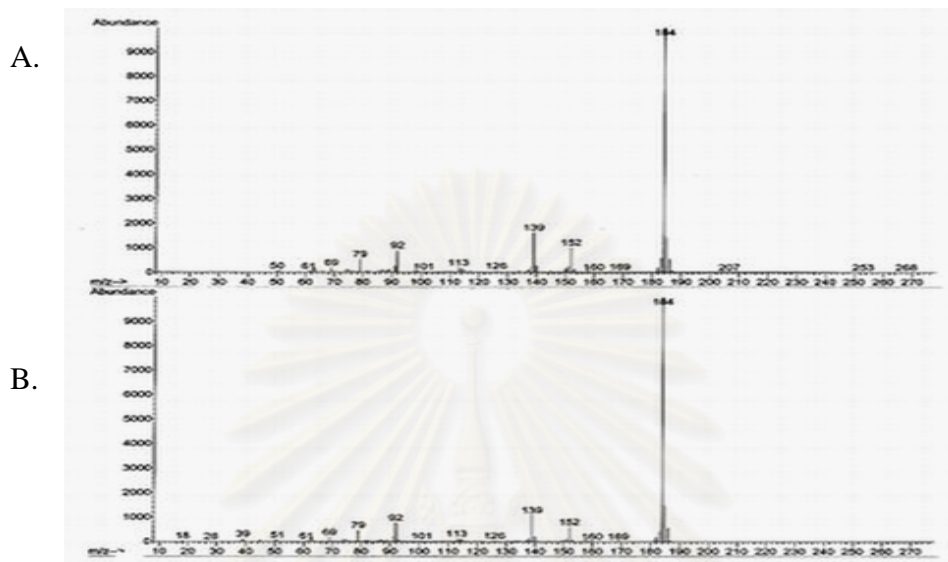


Figure 4.13 Mass spectrum of dibenzothiophene.

A. Sample

B. Dibenzothiophene reference

The hydrogenation product of dibenzothiophene was tetrahydrodibenzothiophene, which showed $m/z = 188$.

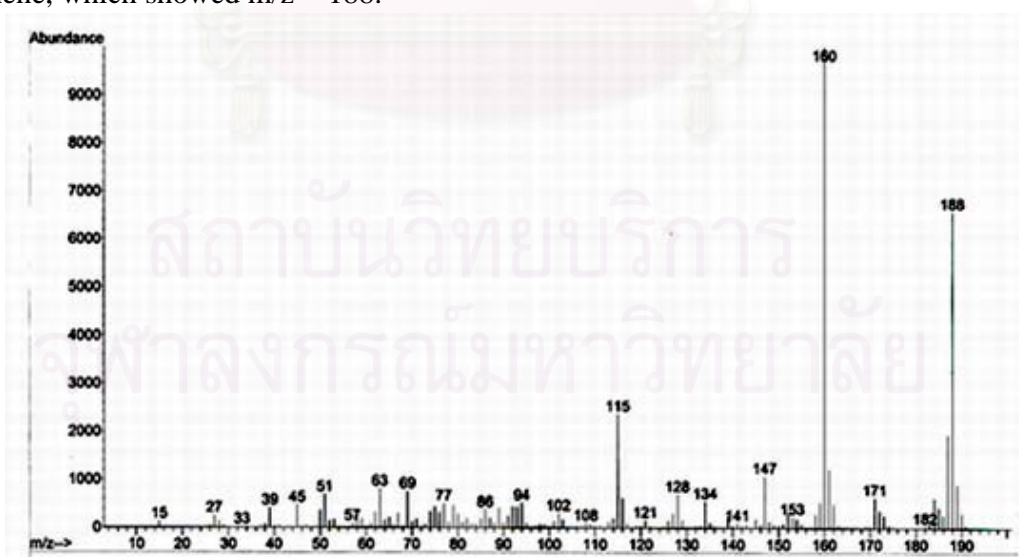


Figure 4.14 Mass spectrum of tetrahydrodibenzothiophene.

CHAPTER V

CONCLUSION AND SUGGESTION

Several catalysts were prepared: $[\text{Cp}^*\text{RuCl}_2]_2$, $\text{Cp}^*\text{RuCl}(\text{PPh}_3)_2$, $[\text{CpMo}(\text{CO})_3]_2$ and $\text{CpMo}(\text{CO})_3\text{H}$ and used for hydrodesulfurization of benzothiophenes, the reactions were studied in the homogeneous catalytic system using monometallic and multimetallic catalysts.

For the hydrodesulfurization of benzothiophenes, it was found that temperature, hydrogen pressure and BT/Ru mole ratio affected the catalytic activity. For the reactions using monometallic catalysts containing ruthenium: $[\text{Cp}^*\text{RuCl}_2]_2$ was found to be an inactive catalyst except that it reacted with 2.5 equivalents of PPh_3 to form $\text{Cp}^*\text{RuCl}(\text{PPh}_3)_2$ (*in situ*) which in the presence of excess reducing agent and hydrogen pressure it was further converted to hydride complex, $\text{Cp}^*\text{RuH}_3(\text{PPh}_3)$, this complex is an efficient catalyst, this might be due to the ability of Cp^* ligand in C-S cleavage as well as the hydrogenation ability of Ru. Comparing many types of reducing agent, the result revealed that LiAlH_4 is a better reducing agent than NaBH_4 and KBu_3BH . The reaction product catalyzed by $\text{Cp}^*\text{RuH}_3(\text{PPh}_3)$ was proved to be dihydrobenzothiophene (DHBT), hydrogenated product. The similar result was obtained when using $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$ as catalyst. For liquid-biphase system, (methanol/hexane), using $\text{Cp}^*\text{RuH}_3(\text{PPh}_3)$ which formed by the reaction between $[\text{Cp}^*\text{RuCl}_2]_2$ in basic condition (NaOH) and hydrogen pressure showed high conversion (42%), yielding dihydrobenzothiophene (37%) as well as ethylbenzene (3%) as a second product (from the hydrogenolysis reaction). For comparison, it was reported that hydrogenation of benzothiophene catalyzed by $[(\text{sulphos})\text{Rh}(\text{cod})]$ at 200 °C for 17 hr, no C-S bond scission of benzothiophene occurs, resulted in dihydrobenzothiophene (30%). When the reaction lasted for 70 hr, the conversion was 50% with ethylbenzene (7%). Under biphasic conditions at 175 °C, dihydrobenzothiophene (24%) occurs. The addition of NaOH to the catalytic system dramatically increases %conversion and %yield of product. Although, this work using

ruthenium catalysts resulted in lower %conversion, rhodium catalyst is more expensive than ruthenium.

For monometallic catalyst systems containing molybdenum: $[\text{CpMo}(\text{CO})_3]_2$ and $\text{CpMo}(\text{CO})_3\text{H}$ were used. The reaction using $[\text{CpMo}(\text{CO})_3]_2$ in toluene gave the 14% conversion whereas using $[\text{CpMo}(\text{CO})_3]_2$ in liquid-biphase gave no conversion. For $\text{CpMo}(\text{CO})_3\text{H}$ (*in situ*), it gave low conversion (5%), this might be due to the instability of molybdenum hydride complex. At the same BT/metal mole ratio (20/1), %conversion from molybdenum catalyst was lower (8%) than ruthenium catalyst (30%), however, the reaction catalyzed by the molybdenum catalyst occurred *via* hydrogenolysis, yielding ethylbenzene as product.

Typically, dibenzothiophene (DBT) is more difficult to hydrodesulfurize. However, it was also studied using $\text{Cp}^*\text{RuCl}(\text{PPh}_3)_2$ (*in situ*) and reducing by LiAlH_4 . It gave 8 %conversion which is lower than benzothiophene and TH-DBT was hydrogenated product.

In multimetallic catalysts, bimetallic catalysts, $\text{Cp}^*\text{RuCl}(\text{PPh}_3)_2$ (*in situ*) + $\text{Mo}(\text{CO})_6$ or $[\text{CpMo}(\text{CO})_3]_2$ or $\text{Co}_2(\text{CO})_8$ and trimetallic catalyst, $\text{Cp}^*\text{RuCl}(\text{PPh}_3)_2$ (*in situ*) + $[\text{CpMo}(\text{CO})_3]_2$ + $\text{Co}_2(\text{CO})_8$ were used. The experimental results indicated that using multimetallic catalyst gave lower %conversion than monometallic catalysts, it pointed out that molybdenum and cobalt compounds demonstrated a negative effect on catalyzation, it may inhibit the active site of $\text{Cp}^*\text{RuCl}(\text{PPh}_3)_2$.

Suggestion for further work

Hydrodesulfurization of dibenzothiophene should be developed using liquid-biphase system.

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APPENDICES

สถาบันวิทยบริการ
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Calculation of the correction factor

The correction factor was calculated based upon the results obtained from gas chromatographic analysis (see also the experimental section). The substrate used was 2 mmol, whereas the internal standard, cyclohexanol, 0.05 mmol was added.

Example

A : exact amount of desired product prepared (mmol)

B : total volume of the reaction (ml)

C : peak area of the desired product

D : peak area of the internal standard

The calculation of the correction factor can be described as follows:

The amount of the desired product from the reaction mixture

$$= (0.05 \times C / D) = F \text{ mmol}$$

The amount of the desired product in B ml (total volume of the reaction)

$$= (F) \times (B) = G \text{ mmol}$$

Thus, the correction factor of the desired product

$$= (A)/(G) = H$$

The calculation of % yield of the desired product can be calculated as:

$$\% \text{Yield of product} = [(G) \times (H) / 2] \times 100$$

The correction factor of chemicals are listed as follows:

Benzothiophene = 0.64

Dibenzothiophene = 0.64

Ethylbenzene = 0.98

Calculation of %conversion of benzothiophene from peak area of GC

Using peak areas obtained from GC analysis

$$\% \text{conv.} = [(A_{\text{in}} - A_{\text{out}}) / A_{\text{in}}] \times 100$$

Where A_{in} = Peak area of benzothiophene at the inlet of the reaction

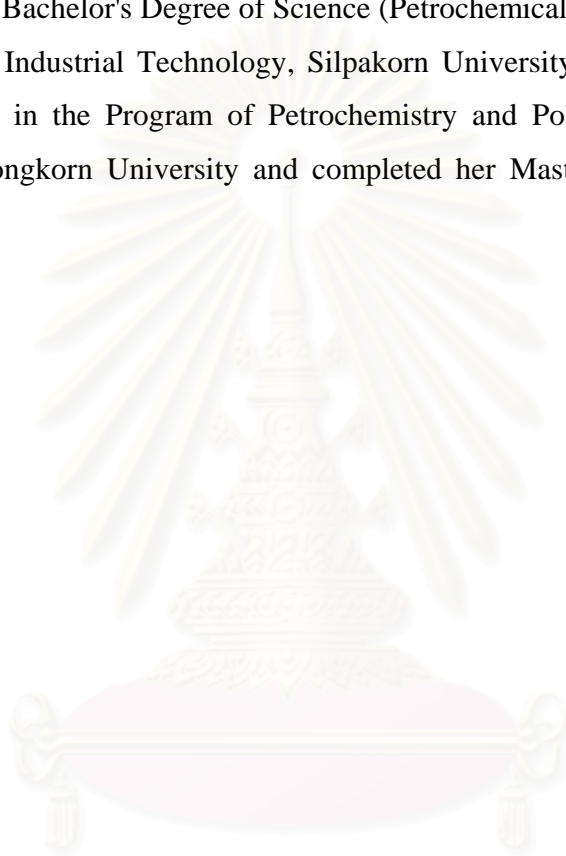
A_{out} = Peak area of benzothiophene at the outlet of the reaction



สถาบันวิทยบริการ
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