

การศึกษาปฏิกิริยาไฮโดรดีซัลเฟอไรเซชันและไฮโดรดีไนโตรจิเนชันของไดเบนโซไทโอพีนผสมกับพิ
ริดีนในน้ำมันดีเซลบนตัวเร่งปฏิกิริยาโคบอลต์-โมลิบดีนัมโดยมีอะลูมินา-ไทเทเนียเป็นตัวรองรับ

นางสาวธีราพร เหลืองอ่อน

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต

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HYDRODESULFURIZATION AND HYDRODENITROGENATION OF
DIBENZOTHIOPHENE MIXED WITH PYRIDINE IN DIESEL OIL OVER CoMo
CATALYSTS SUPPORTED ON Al₂O₃-TiO₂

Ms. Teraporn Leungon

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering Program in Chemical Engineering

Department of Chemical Engineering

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HYDRODENITROGENATION OF DIBENZOTHIOPHENE
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อ.ที่ปรึกษาวิทยานิพนธ์หลัก: อ.ดร.อัศวัต ศิริสุข, 86 หน้า.

ในงานวิจัยนี้ได้ทำการศึกษาปฏิกิริยาไฮโดรดีซัลเฟอร์ไรเซชันและปฏิกิริยาไฮโดรดีไนโตรจิเนชันของไดเบนโซไทโอฟีนผสมกับพิริดีนในน้ำมันดีเซลด้วยตัวเร่งปฏิกิริยาโคบอลต์-โมลิบดีนัมบนตัวรองรับโลหะออกไซด์สององค์ประกอบนี้โดยที่ตัวรองรับนี้จะทำการเตรียมโดยใช้เทคนิคโซลเจล ซึ่ง TiO_2 จะเติมลงไปในสัดส่วน 10-50 เปอร์เซ็นต์โดยน้ำหนัก หลังจากนั้นโคบอลต์-โมลิบดีนัมจะถูกตรึงในตัวรองรับโลหะออกไซด์ผสมเหล่านี้โดยตัวเร่งปฏิกิริยาจะทำการวิเคราะห์ด้วยเทคนิค ICP-OES, XRD, N_2 physisorption, H_2 -TPR, NH_3 -TPD และ CO-Chemisorption สำหรับปฏิกิริยาไฮโดรดีซัลเฟอร์ไรเซชันและปฏิกิริยาไฮโดรดีไนโตรจิเนชันจะทำในเครื่องปฏิกรณ์แบบเบดบรรจุที่อุณหภูมิ 350 องศาเซลเซียส และความดัน 80 บาร์ภายใต้ก๊าซไนโตรเจน นอกจากนี้ผลของพิริดีนที่ใช้เป็นตัวแทนของสารประกอบไนโตรเจนซึ่งจะทำการเปลี่ยนความเข้มข้นของไนโตรเจนจำนวน 5 ค่า เพื่อศึกษาผลกระทบที่มีต่อประสิทธิภาพของตัวเร่งปฏิกิริยาก่อนที่จะทำการทดสอบนั้นจะต้องทำตัวเร่งปฏิกิริยาอยู่ในรูปซัลไฟด์ด้วยไดเมทิลไดซัลไฟด์ภายใต้ก๊าซไฮโดรเจนเพื่อกระตุ้นตัวเร่งปฏิกิริยา จากการศึกษาพบว่าการเติม TiO_2 ลงใน Al_2O_3 ช่วยเพิ่มความเป็นกรดของพื้นผิวและช่วยในการรีดิวซ์ของโมลิบดีนัมโดยช่วยลดอันตรกิริยาระหว่างโลหะกับตัวรองรับของตัวเร่งปฏิกิริยา ตัวเร่งปฏิกิริยาโคบอลต์-โมลิบดีนัมบนตัวรองรับ $Al_2O_3-TiO_2$ ที่มี 50 เปอร์เซ็นต์โดยน้ำหนักของ Al_2O_3 แสดงความไวในการเกิดปฏิกิริยาไฮโดรดีซัลเฟอร์ไรเซชันและปฏิกิริยาไฮโดรดีไนโตรจิเนชันสูงที่สุด การเพิ่มความเข้มข้นของพิริดีนที่ใช้เป็นตัวแทนของสารประกอบไนโตรเจนส่งผลให้ความไวในการเกิดปฏิกิริยาไฮโดรดีซัลเฟอร์ไรเซชันลดลงตามลำดับ

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TERAPORN LEAUNGON: HYDRODESULFURIZATION AND
HYDRODENITROGENATION OF DIBENZOTHIOPHENE MIXED WITH
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This research studied the hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) of dibenzothiophene (DBT) mixed with pyridine in diesel oil over CoMo catalysts supported on Al₂O₃-TiO₂ mixed oxides were prepared by sol-gel methods. The amount of TiO₂ that was incorporated into Al₂O₃ was in the range of 10-50 wt. %. Then cobalt and molybdenum were co-deposited on these mixed oxide supports. The catalysts were characterized by ICP-OES, XRD, N₂ physisorption, H₂-TPR, NH₃-TPD, and CO-Chemisorption techniques. HDS and HDN reactions were carried out in a packed bed microreactor at 350°C and 80 bars of H₂ pressure. Five different nitrogen concentrations from pyridine were employed to investigate its effect on the catalytic activity. Prior to each run, the catalyst was sulfided using dimethyldisulfide (DMDS) under hydrogen atmosphere to activate the catalysts. From this study, the addition of TiO₂ to Al₂O₃ increased the surface acidity and led to move reduction of Mo to the lower state by lowering the metal-support interaction of catalysts. The CoMo catalyst on Al₂O₃-TiO₂ supports containing 50 wt. % of Al₂O₃ exhibited the highest activities for both HDS and HDN. Addition of pyridine to the feed lowered the HDS activity of the catalysts. An increase in the concentration of nitrogen compound in the feed led to further reduction in HDS activity of the catalyst.

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CHAPTER I

INTRODUCTION

1.1 Rationale

Petroleum or crude oil is a naturally occurring substance that consists of hydrocarbon as main composition. The contents are mostly alkanes, aromatic hydrocarbon, and impurities such as sulfur compounds, nitrogen compounds, oxygen compounds, metallic compounds, etc. These impurities can lead to pollution to the environment and be harmful to the body. Automobile emission from fossil fuels is an important cause of increased pollution at present. The exhaust gas from motor vehicles contains nitrogen oxides (NO_x) and sulfur oxides (SO_x). When these oxides are exposed to water vapor in the atmosphere, they transform to HNO_3 and H_2SO_4 , which result in the acid rain phenomenon. Moreover, sulfur is also a well-known poison for catalytic converter used in automobile [1].

In recent years, environmental regulations play an important role in the reduction of environmental problems, especially air pollution and global warming. Reduction of sulfur and nitrogen in petroleum can be accomplished by several techniques. Hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) are the processes by which sulfur- and nitrogen-containing impurities are removed from petroleum feedstock and fuels. At present the process is widely used, and is operated at high hydrogen pressure accompanied by hydrogenation of unsaturated and minor cracking of high molecular hydrocarbons.

HDS and HDN catalysts are usually CoMo or NiMo supported on Al_2O_3 . Al_2O_3 is the most common commercial support because of its excellent thermal stability and wide range of chemical, physical and catalytic properties. Nonetheless, Al_2O_3 does not exhibit high catalytic activity for reduction of sulfur in petroleum feedstock when it is used as the supporting material for CoMo or NiMo catalyst.

The preparation of mixed oxide supports containing TiO_2 has attracted attention as support for hydrotreating catalysts because the high hydrodesulfurization (HDS) activity is shown by TiO_2 supported molybdenum catalysts. But disadvantages of TiO_2 as a support is that it was low surface area, low thermal stabilities, and unsuitable mechanical properties therefore, much attention has been spent to the application of mixed oxide containing TiO_2 . It may improve some disadvantages for new support that can be used as industrial catalyst in nowadays [2].

1.2 Objective

The objective of this research is to investigate the effect of addition of TiO_2 to Al_2O_3 support and the effect of nitrogen compound (i.e., of pyridine) on hydrodesulfurization activity of dibenzothiophene over supported CoMo catalysts in the presence of pyridine.

1.3 Research scopes

The scopes of this study are as follows:

1. Mixed Al_2O_3 - TiO_2 supports are prepared by sol-gel methods. The amounts of Al_2O_3 loading are 50, 60, 70, 80, and 90 wt. %.
2. Five different concentrations of nitrogen from pyridine were employed to investigate its effect on the catalytic activity.
3. Cobalt-molybdenum (CoMo) catalysts were prepared by impregnation on those above supports at 2.93 wt. % cobalt and 13.7 wt. % molybdenum.
4. Characterization of CoMo catalyst by the following techniques:
 - Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) to determine elemental composition of the catalyst.
 - X-ray diffraction to determine crystallite size and phase.
 - N_2 physisorption for BET surface area, pore volume, and pore size.
 - Temperature-programmed desorption with ammonia (NH_3 -TPD) to determine the amount of surface acid site.
 - Temperature-programmed reduction with hydrogen (H_2 -TPR) to evaluate the degree of reducibility.

- Carbon monoxide chemisorption (CO-Chemisorption) to determine metal dispersion of the catalysts.

5. Measurement of the catalytic activity of those CoMo catalysts on hydrodesulfurization and hydrodenitrogenation of dibenzothiophene with sulfur content at 2000 ppm and in the presence of pyridine with five different nitrogen concentrations (100, 200, 300, 400, and 500 ppm).

1.4 Research methodology

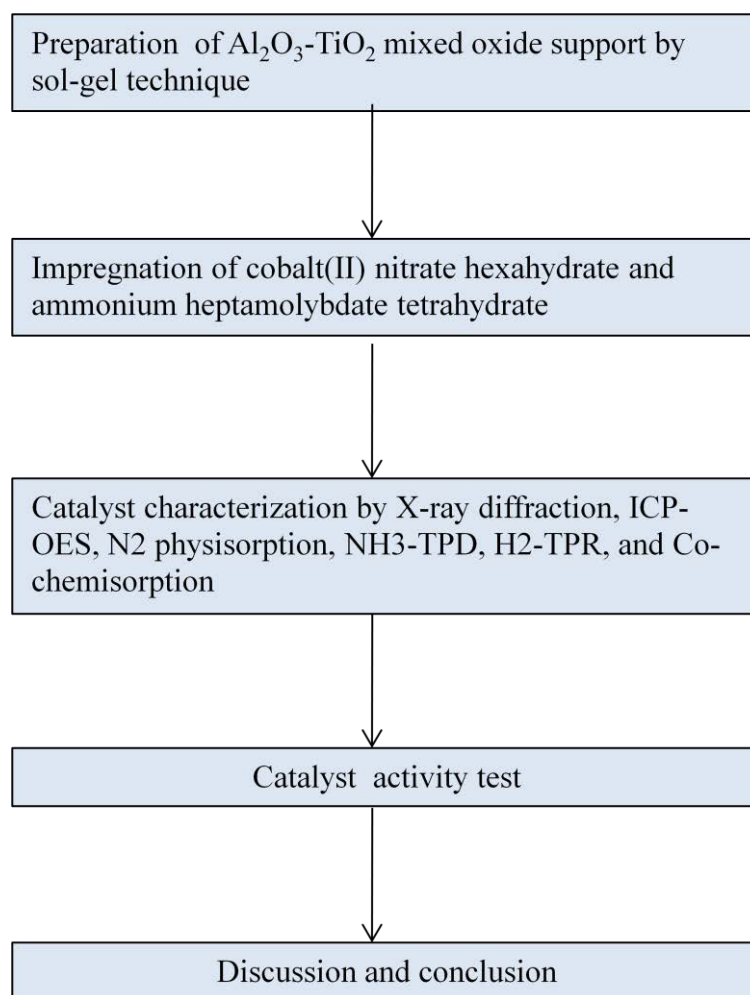


Figure 1.1 Diagram of research methodology

CHAPTER II

THEORY

2.1 Hydrotreating

The objective of the hydrotreating process is remove sulfur, nitrogen, oxygen, and metal atom are hydrogenated using hydrogen as a reactant. These processes use catalysts based on transition metal sulfides. This is attention to improving product quality by hydrogen treatment, mainly consists of hydrodesulfurization (HDS), hydrodenitrogenation (HDN), hydrodeoxygenation (HDO), and hydrodemetalization (HDM). HDS has been the main concern of hydrotreating in industry, due to the increasing use of heavy crude oils which has a high sulfur components and global reductions in the sulfur content allowance of automotive fuels [3]. HDN is problem that has received much attention due to the presence of nitrogen-containing compounds this has resulted in a decrease of HDS process. The presence of nitrogen-containing compounds inhibits HDS and other reactions since their preferred adsorption on catalyst site. HDN is more difficult since nitrogen-containing aromatic rings desire hydrogenation before to nitrogen removal. Hydrogenation of nitrogen-containing aromatic rings is difficult because of steric and thermodynamic limitations [4].

2.1.1 Hydrotreating Catalysts

Catalysts for hydrotreating are alumina supported Mo and W based sulfides with promoters of Ni or Co sulfides. Alumina is the best support in terms of surface area (200-300 m²/g), pore size control, stability of thermal, mechanical strength and cost. Molybdenum (15-20wt %), Co and Ni (1-5wt %) precursor are impregnated to be highly dispersed onto alumina. The impregnated catalyst is calcined and sulfided in the commercial application for the catalytic activity. The Co (Ni) MoS phase, it is believed to active species but the Co (Ni)₉S₈ and Co(Ni)/Al₂O₃ which are not active. The Co (Ni) MoS phase include of small layered crystals of S and Co/Mo as

illustrated in Fig. 2.1 [5]. The Al_2O_3 surface contact with CoMo layer that is in the bottom this is believed difficult to sulfide into the active form, therefore multi-layered stacks of these are believed to be more active on alumina supports. The edge and rim of the Co (Ni) MoS phases are believed particularly active for hydrotreating reactions. However, active sites for hydrogenation and C-X fission are not fully solved.

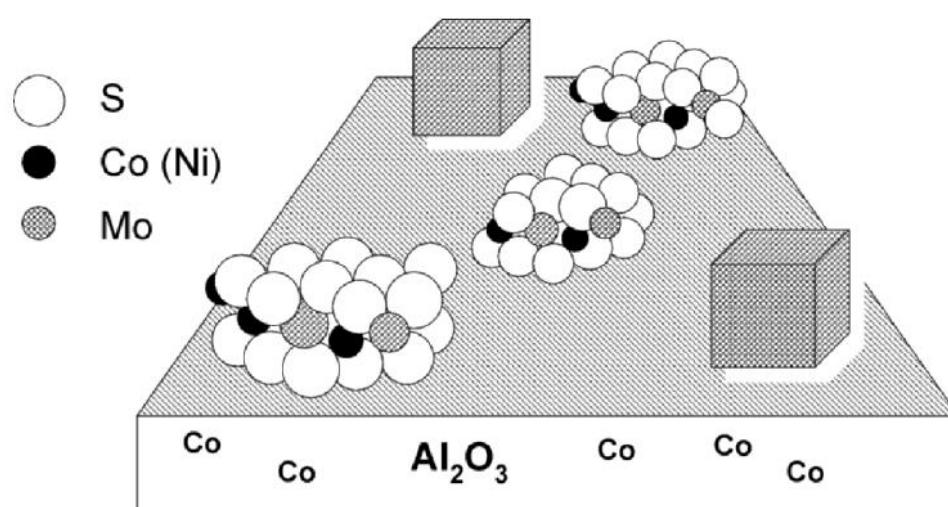


Figure 2.1 The structure of CoMo catalyst [5]

2.1.2 Process flow of hydrotreating

Hydrotreating flow diagram is illustrated in Fig. 2.2, where single stage hydrotreating. The feed oil is pumped up to the required pressure and mixed with make-up and recycle hydrogen-rich gas. The temperature is primarily raised by heat exchange. The feed oil is hydroprocessed over the catalyst in the reactor under a flow of hydrogen-rich gas. The reactor may be increased depend on the condition or throughput rate.

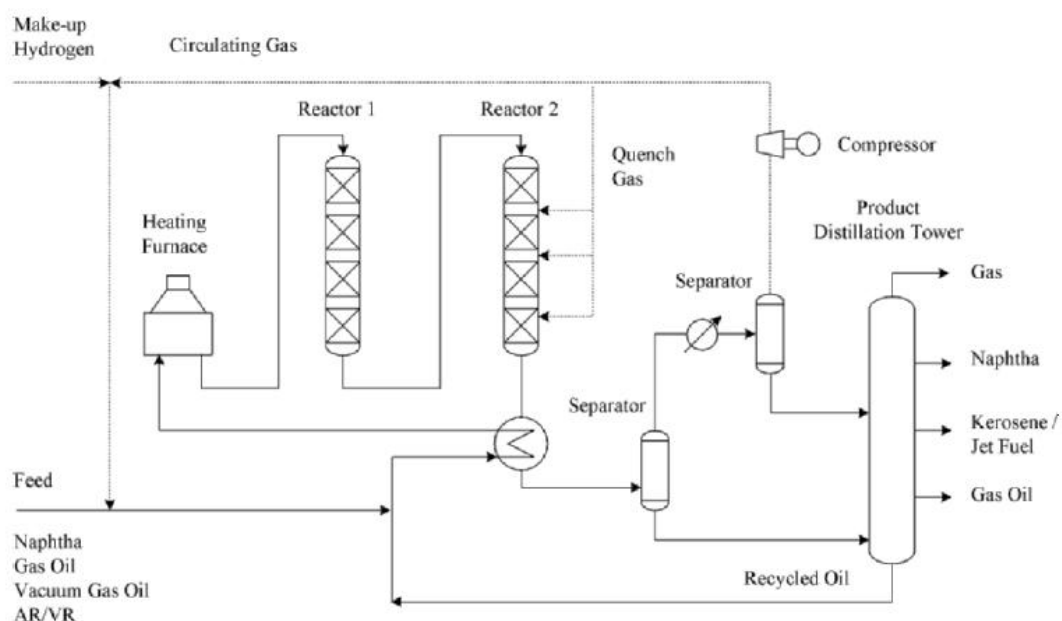


Figure 2.2 Single-Stage Process Flow Diagrams [6]

In general, a fixed bed reactor is used for hydrotreating process. The optimum catalysts are packed in each bed according to the requirements of the bed. The feed oil and hydrogen rich gas are supplied from the top of the reactor. Hydrogen gas is injected at the reactor to control the reaction temperature, due to hydrotreating reactions are exothermic. The reactor is cooled down by feed to the reactor in the heat exchanger. Following heat exchange, the gas and liquid products are separated by a high temperature, high pressure vessel according to boiling points. The gaseous products from the high pressure vessel are fed to an absorbing column for remove H_2S , and the cleaned hydrogen rich gas is recycled to the reactor.

Two types of hydrotreating process are single stage process and multiple stage process. The single stage process has the same process flow as mentioned above. The feed is hydroprocessed continually without obvious separation in between the reactor. However, a single stage process does not mean that only one reactor is used.

In a multi stage process, the unwanted products of the first stage are separated and removed before the second stage. The unwanted products of secondary reaction are poison and inhibitors produced in the first stage are removed before beginning the second stage of the conversion [7]. This reduces the load on the second stage and

increases its reactivity. The multi staged processes have very high conversions, so called deep refining.

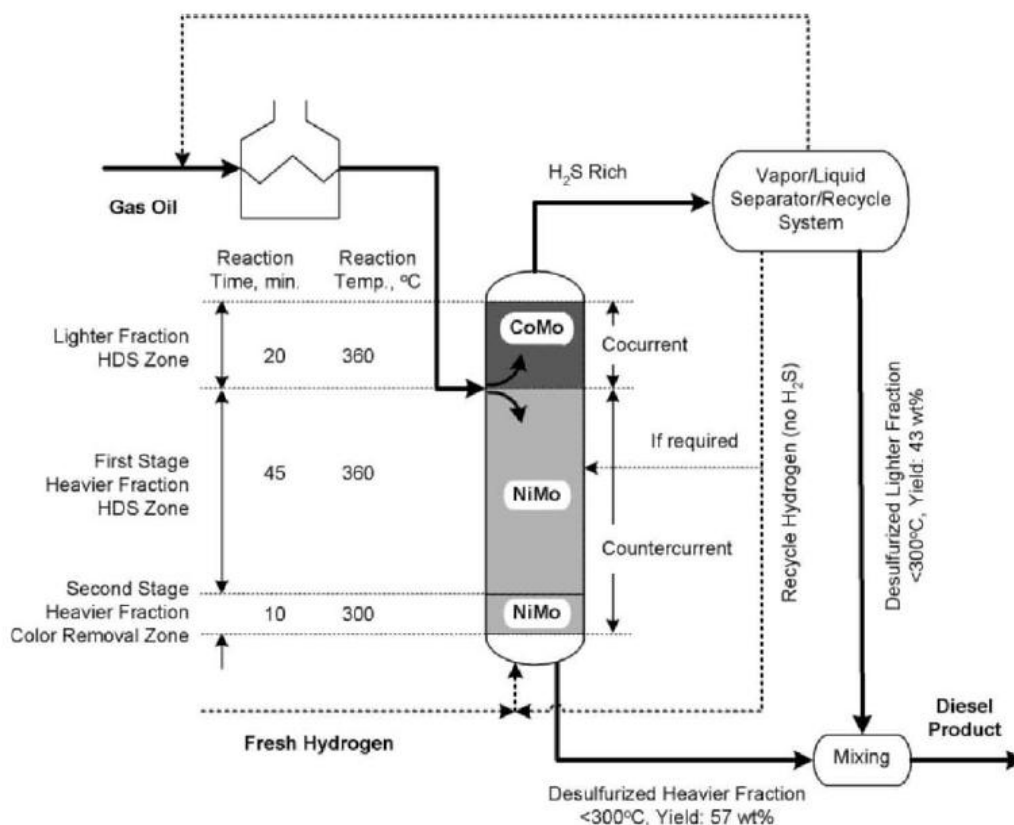


Figure 2.3 Reactor design for deep HDS [8]

The present authors proposed a new type of reactor as shown in Fig. 2.3. The Gas oil was reacted separately in upper and lower parts of the catalyst bed. Hydrogen was charged from the bottom of the reactor. The optimum catalysts can be applied for the respective parts of the bed. Pressure drop may be occurring at the lower part of the reactor, where the hydrogen is up flow while liquid feed is down flow. A honeycomb type catalyst bed is now available for this problem.

Table 2.1 Example of typical hydrotreating processes [9]

Classification and Equation	ΔH^0 at 700 K (kcal/mol)
<i>Hydrodesulfurization</i>	
$C_2H_5SC_2H_5 + 2H_2 \rightarrow 2C_2H_6 + H_2S$	-16.77
$C_2H_5SH + H_2 \rightarrow C_2H_6 + H_2S$	-27.99
	-28.73
	-66.98
<i>Hydrodenitrogenation</i>	
	-93.90
<i>Hydrodeoxygenation</i>	
	-30.51

All reactions and thermodynamic heat of reactions in hydrotreating processes that are important in industrial viewpoints are shown in Table 2.1 in which in the present the sulfur oxides (SO_x) and nitrogen oxides (NO_x) emission affect to the atmosphere both human health and environmental problems. The three reactions in this figure are reaction to remove sulfur, nitrogen, and oxygen atom from organic compounds that contain any one of these atoms in a molecular structure. These reactions require control of many operating conditions such as catalysts, temperature, hydrogen pressure, liquid hourly space velocity (LHSV) of feedstock, gas hourly space velocity (GHSV) of hydrogen gas, etc. Besides all of three reactions that are called hydrogenolysis, hydrogenation of aromatic is also important due to this

addition of hydrogen to unsaturated bonds can contribute to remove of heteroatom from petroleum feedstock.

Hydrogenation reaction is addition of hydrogen molecule to unsaturated bonds of the molecules and to make more saturation degree of the molecules. This reaction is generally exothermic reaction like as hydrogenolysis or hydrotreating that can show in the following reaction:

In these reactions are additions of hydrogen molecules without ring cracking but in more server condition like as high temperature and pressure, hydrocracking can be performed and the obtained molecule may be reformed into long chain without aromatic ring which examples of this hydrocracking reaction are shown in the following reaction:

2.2 Hydrodesulfurization

Hydrodesulfurization (HDS) is the reaction to remove sulfur from petroleum feedstock. This reaction about interaction with hydrogen over solid catalyst under condition of temperature and pressure, according to the generic transformation represented by Equation 2.1




The literature of HDS chemistry and technology has been reviewed by McKinley (1957) and lately by Schuman and Shalit (1970), who included a complete literature compilation.

Many petroleum feedstocks are treated with hydrogen in catalytic processes to eliminate sulfur. HDS processes have had several objectives, among them pretreatment of catalytic reformer feed to protect poisoning of catalyst by sulfur and treatment of gasoline formed catalytic cracking to give sweetened and stabilized products. Desulfurization of heavy petroleum fractions gives products consist of diesel, jet fuels, heating oils, and residual fuel oils. This is the most important studied reaction of the hydrotreating process. HDS process is pretreatment of the feeds for refining step which is carried out over expensive noble metal catalysts readily poisoned by sulfur-containing compounds. Their combustion products create serious environmental hazards such as acid rain.

2.2.1 Sulfur compounds in petroleum and fuels

Petroleum feedstocks is a very complex mixture consisting importantly of hydrocarbons this is containing vary amount of heteroatoms, which depend on source of the crude. Petroleum feedstocks include the sulfur-containing compounds listed in Table 2.2. In general, the compounds listed in the table decreasing reactivity in hydrodesulfurization.

Table 2.2 Typical sulfur compounds in petroleum [10]

Type of sulfur compounds	Structure
Thiols	RSH
Sulfides	RSR'
Disulfides	RSSR'
Thiophene	
Benzothiophene	

Dibenzothiophene

Organic sulfur compounds are widely found in many forms that sulfur atom is chemically bound with carbon and hydrogen atom. In generally, they are usually represented in term of thiols (mercaptans), sulfides, disulfides, thiophene, etc. These sulfur compounds can form oxide compounds such as sulfur dioxide (SO₂), sulfur trioxide (SO₃), etc. when it was burnt with air and its oxide of sulfur can react directly with water or moisture in air to form sulfuric acid (H₃SO₄) that it impacts on environmental in the world [11-14].

2.2.2 Hydrodesulfurization catalysts

The most commonly used catalysts for HDS are derived from alumina support oxides of Co and Mo, which are usually sulfided in operation. The Co-Mo catalysts are perfect for HDS and less active HDN and hydrogenation reactions which are better run over Ni-Mo or the more expensive Ni-W. In contrast to the supported Pt and Pt-alloy catalysts employed in reforming, the HDS catalysts have hydrogenation activity in the presence of high intensity of sulfur compound.

Many other metals have been shown to be active in HDS catalysis, and a number of papers have been published on the study of periodic trends in activities for transition metal sulfides. The metal sulfides and supported sulfides have been considered and experimental studies show that the HDS activities for the desulfurization of dibenzothiophene or of thiophene which related to the position of the metal in the periodic as exemplified in Fig 2.4 [15].

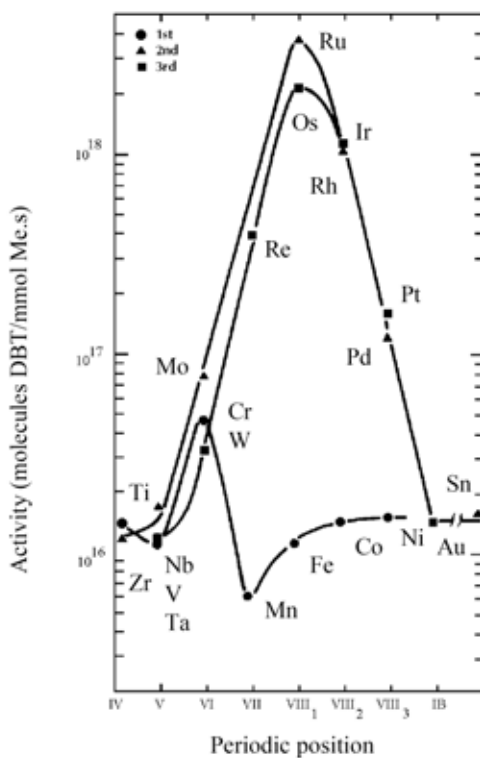


Figure 2.4 Periodic trends of the HDS of DBT at 673 K and 30 bar [16]

Pecoraro and Chianelli [17] studied the activity of the first, second, and third row bulk transition metal sulfide (TMS). They set the HDS experiment by using dibenzothiophene as the feed model in a medium pressure autoclave followed in the Fig. 2.4. The figure shows the activity maximum at the sulfides of Ru and Os for the second and the third row transition metals.

Figure 2.5 Exchange of the labile sulfur on the sulfide Co-Mo/ Al_2O_3 with H_2S [18]

From the Fig. 2.5 and Fig. 2.6 shows the role of labile sulfur in the HDS reaction. In the exchange of sulfur, portion of the sulfur bonded with Co and Mo atoms was considered to be more labile and present as S-H groups in H_2 below 400 °C. When H_2S was liberated from the structure of catalyst, an anion vacancy occurred and the adjacent Mo^{4+} would be partially reduced to Mo^{3+} at the same time. When H_2S was introduced, the adsorbed H_2S dissociated and formed new SH groups which the old anion vacancy disappeared and new vacancy anion appeared by liberating the H_2S molecule.

In order was investigated the relationship between the labile sulfur amount with the HDS activity of the catalyst. Kabe et al. studied and suggested that the amount of labile sulfur can be transformed to anion vacancies (active sites) which this amount can be good relationship with HDS activity.

Figure 2.6 Mechanism of HDS of DBT on sulfide Co-Mo/ Al_2O_3 catalyst [19]

2.2.3 Reaction mechanisms of hydrodesulfurization

A complex of exothermic occurs when hydrotreating petroleum, the main classes of interest here including hydrogenation of aromatics, HDS and HDN. A many of work has been interested to the study of these reaction pathways, their kinetics, product distributions, intermediates, and reaction mechanisms, both on real feeds and mixtures of model compounds. Thermodynamics of the various possible reactions

under standard catalytic conditions are known to control to a large extent the relative rates at which they take place. The various reactants can compete for the active sites, some of them therefore acting as poisons for the degradation of others [20, 21]. The HDS networks are very complex, due to they involve many of primary steps such as adsorption/desorption equilibrium, hydrogenation and hydrogenolysis reactions whose kinetics are strongly dependent on the reaction conditions and the structure of the particular substrate on the substituents present in such molecules. The composition of the catalyst and concentration of active sites are additional key features to be considered for each set of reactions. The literature is available in specialized monographs and reviews, and it continues to be the subject of an interesting. However, a general agreement in detail of mechanism is invoked; some common fundamental steps need to be taken into account, namely:

- The generation and the nature of the active sites
- The dissociative adsorption of hydrogen on the surface of the catalyst
- The chemisorption of the organosulfur compound on the catalytic sites
- The hydrogenation of unsaturated bonds and hydrogenolysis of C-S bonds

2.2.3.1 Hydrodesulfurization of thiophenes

The adsorption of thiophene can occur in two modes. The first mode, one-point (end-on) adsorption of thiophene molecule into coordinately unsaturated sites (CUS) that member of the thiophene ring can be adsorbed which shown in the following equation:



Which this spent catalyst can be refreshed by addition of hydrogen molecule for converting into active form shown in the following equation [22]:

In the second mode, multipoint (side-on) adsorption of the thiophene molecule on CUS shown in the following equation [23]:

For the HDS reactions of thiophene can be envisaged in Fig. 2.7:

(i) The step of hydrogenolysis of both C-S bonds to yield 1, 3-butadiene plus adsorbed sulfur. After hydrogenation of the primary products produce butenes/butane plus H_2S thus regenerating the CUS. The presence of butadiene and the absence of tetrahydrothiophene as products of the mild HDS of thiophene support this pathway. In recently, Startsev proposed the involved idea of a concerted mechanism in the

intermediate butadiene. This is retained in the active site during the reaction in order to the primary products are the butenes [24, 25].

(ii) The direct HDS of H_2S disposal of thiophene to yield 1, 3-butadiyne plus adsorbed H_2S hydrogenation of the diacetylene and desorption of H_2S would lead to the same HDS products [26]. This possibility cannot be applied to alkyl substituted thiophenes which could not possibly generate the corresponding dialkynes, so its relevance is rather limited [27].

(iii) Partial hydrogenation of thiophene leading to the temporary formation of 2,3-dihydrothiophene, which has been proposed on the basis of theoretical as well as experimental and studies [28, 29].

(iv) Complete saturation of thiophene to yield tetrahydrothiophene, followed by hydrogenolysis of the thioether into butane plus H_2S which is thought to occur at elevated pressures where tetrahydrothiophene has been observed as a major intermediate [30].

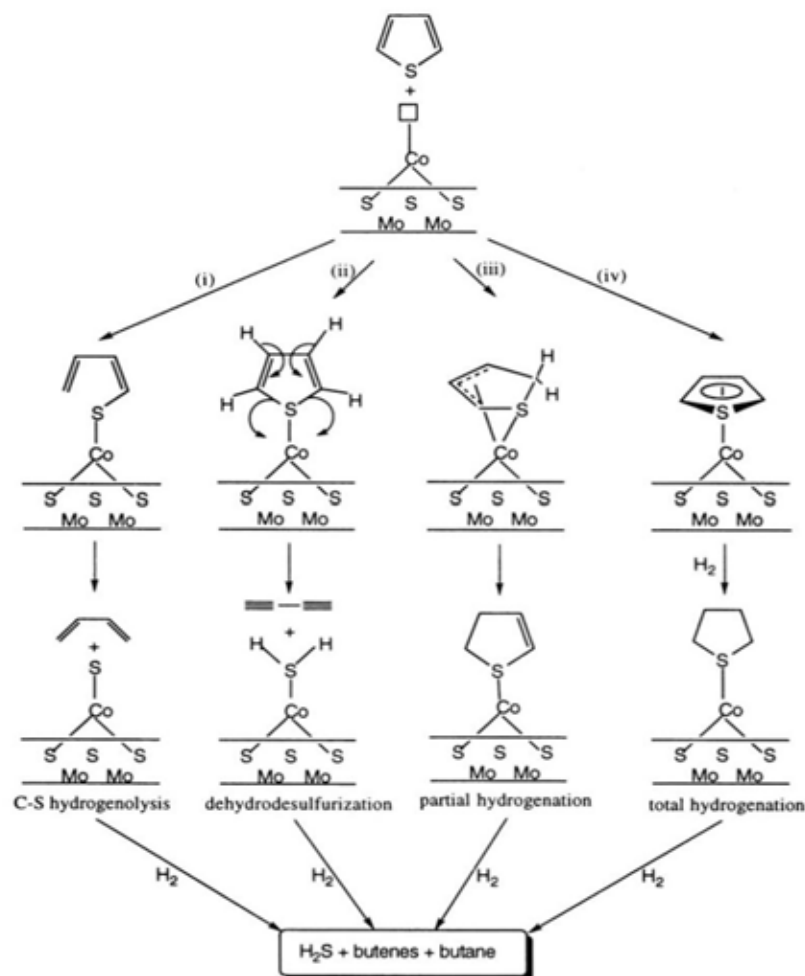


Figure 2.7 Main reaction pathways in HDS of thiophene [31]

2.2.3.2 Hydrodesulfurization of dibenzothiophene

HDS of dibenzothiophenes (DBT) can also via to different pathways. This is shown in a simplified manner in the reaction shown in Fig. 2.8. Two reaction pathways are known to operate in parallel during the HDS of unsubstituted DBT and the preponderance of any one of them depends strongly on the catalyst formulation and on the reaction conditions. Substitution of alkyl in the vicinity of the sulfur atom, as in 4 methyl dibenzothiophene and 4, 6- dimethyl dibenzothiophene, results in a marked decrease in HDS rates. In general, this is associated primarily with a decrease in the rate of the direct sulfur extrusion routes, which is known to be disfavored whenever there is steric congestion around the sulfur atom [12, 13].

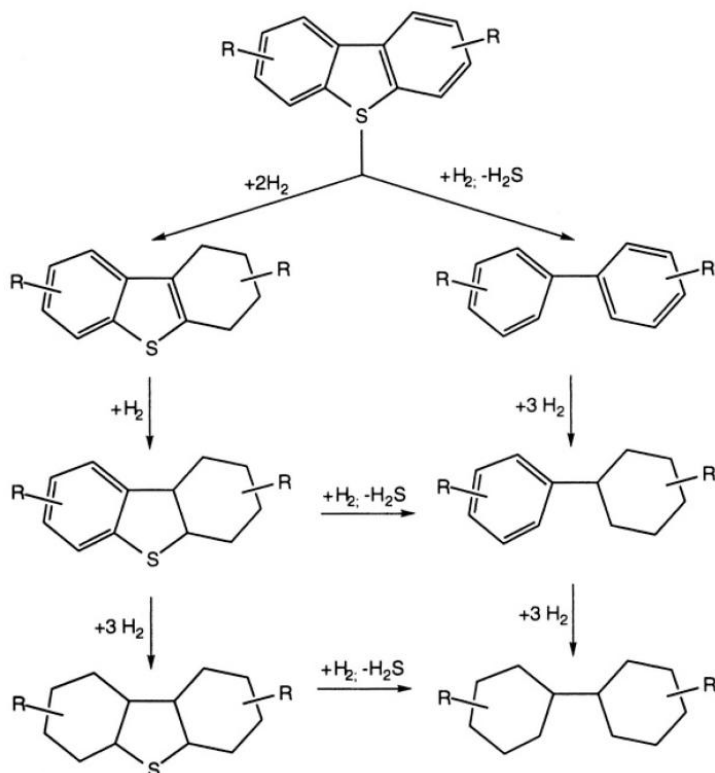


Figure 2.8 Main reaction pathways in HDS of dibenzothiophenes [32].

Egorova, M. et al. [33] have proposed two different reaction pathways. The first reaction pathway, DBT is direct-desulfurized to give biphenyl (BP). The second reaction pathway, DBT is hydrogenated prior to desulfurization to give the 1,2,3,4-tetrahydrodibenzothiophene (THDBT) or to give the 1,2,3,4,10,11 hexahydrodibenzothiophene (HHDBT) which is desulfurized to cyclohexylbenzene (CHB) and the pseudo-first-order rate constants are showed in Fig 2.9.

Figure 2.9 Proposed reaction pathways for dibenzothiophene [34, 35]

The figure shows that direct-desulfurization (DDS) pathway. DBT is desulfurized to BP is much faster than hydrogenation (HYD) pathway, in which DBT is hydrogenated prior to desulfurization over Co-Mo catalysts supported Al_2O_3 (Co-Mo/ Al_2O_3). It was also reported that the selectivity for CHB did not exceed 15% in HDS of DBT catalyzed by Co-Mo/ Al_2O_3 catalysts at 340 °C and 50 atm [34]. The kinetic studies of DBT have been reported by many authors. Broderick and Gates performed the reaction of DBT in n-hexadecane over Co-Mo/ Al_2O_3 at the range of 548-598 K, and 34-160 atm and the rate equation is showed in the following equation:

$$r_{\text{HDS}} = k_{\text{HDS}}K_{\text{DBT}}P_{\text{DBT}}K_{\text{H}}P_{\text{H}}/[(1 + K_{\text{DBT}}P_{\text{DBT}} + K_{\text{H}_2\text{S}}P_{\text{H}_2\text{S}})^2(1 + K_{\text{H}}P_{\text{H}})]$$

Where K_{DBT} = adsorption equilibrium constants of DBT, P_{DBT} = partial pressure of DBT. The rate expression implies that the surface reaction between DBT and H_2 is the rate-determining step and the retarding effects of the reaction come from DBT, H_2 , and H_2S . Furthermore, DBT and H_2 are adsorbed at the separate adsorption sites.

Nagai, M. [35] reported the kinetic studies of DBT for HDS in a vapor phase over Co-Mo/ Al_2O_3 at the range of 473-520 K and 5-50 atm that rate law is consistent with Langmuir-Hinshelwood mechanism without competitive adsorption between DBT, H_2 , and H_2S . The expressions are showed in the following equation:

$$r_{\text{HDS}} = k_{\text{HDS}}K_{\text{DBT}}P_{\text{DBT}}K_{\text{H}}P_{\text{H}}/[(1 + K_{\text{DBT}}P_{\text{DBT}} + K_{\text{H}_2\text{S}}P_{\text{H}_2\text{S}})(1 + K_{\text{H}}P_{\text{H}})]$$


In this study, the activation energy of DBT HDS and the heat of adsorption of H₂ were 23 and 4.5 kcal/mol, respectively.

Singhal et al. [36] reported the kinetic studies of DBT HDS over the range of 558-623 K, 7-26 atm, Co-Mo/Al₂O₃, tetralin solvent. They proposed the rate equation as:

$$r_{\text{HDS}} = k_{\text{HDS}}K_{\text{DBT}}P_{\text{DBT}}K_{\text{H}}P_{\text{H}}/[(1 + K_{\text{DBT}}P_{\text{DBT}} + K_{\text{prod}}P_{\text{prod}})(1 + K_{\text{H}}P_{\text{H}})]$$

Where K_{prod} and P_{prod} are the adsorption equilibrium constant and partial pressure of the products from HDS of DBT such as BP, CHB, and H₂S. The equation shows that products other than H₂S also contributed to the competitive adsorption with DBT.

Table 2.3 Reactivities of several heterocyclic sulfur compounds [37]

Reactant	Structure	Pseudo first order rate constants (L/s.g-cat)
Thiophene		1.38×10^{-3}
Benzothiophene		8.11×10^{-4}
Dibenzothiophene		6.11×10^{-5}
Benzo[<i>b</i>]naphtho-[2,3- <i>d</i>]thiophene		1.61×10^{-4}

7,8,9,10-

Tetrahydrobenzo[*b*]naphtha-
[2,3-*d*]thiophene

Batch reactor, Reaction temperature 300 °C, 71 atm, *n*-hexadecane solvent, concentration of reactant: 0.25 mol%, Co-Mo/Al₂O₃

From this table shows the pseudo first order rate constants of several sulfur compounds which it seems that HDS reactivity depends on the molecular size and the structure of the feed molecules.

2.2.4 The active site of hydrodesulfurization

The most widely accepted model for the structure of promoted HDS catalysts is nowadays the one advanced by Topsøe in terms of a Co-Mo-S phase. This proposal was initially based on very elegant work involving in situ Mössbauer emission spectroscopy, EXAFS and infrared spectroscopy studies of working catalysts. The catalyst is imagine to be consisted of single-sheet crystallites supported on the alumina surface and “decorated” by the promoter atoms (Co, Ni) at the edge planes, as can be seen from the schematic representation shown in Fig. 2.10.

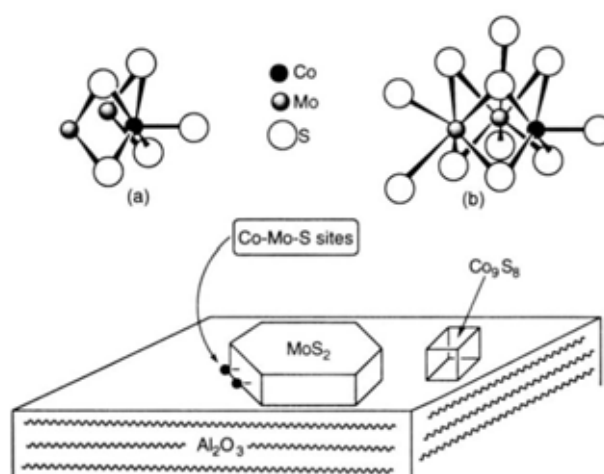


Figure 2.10 Schematic representation of Topsøe's Co-Mo-S model, showing perspective views of: (a) the coordination around the Co site and (b) a Mo₂CoS₁₁ unit at the edge Co-Mo-S site [5]

From EXAFS measurements it appears that each Co is pentacoordinated in an approximately square-base pyramidal arrangement of sulfur ligands in structure (a) in Fig 2.10 with two neighboring Mo atoms, while each Mo is in turn hexacoordinated by a trigonal prismatic array of sulfur atoms with three neighboring Mo atoms and one Co atom shown in (b) in Fig 2.10 [6].

2.2.5 Inhibition of hydrodesulfurization

The active sites for HDS are all commonly or selectively subject to occupancy by the inhibitors. A several species in the feed and product are inhibitors for HDS. Reactive sulfur species appear to be less inhibited than the refractory species. This is because the S atom in the reactive species can easily go through metal insertion to break the C-S bond via the direct HDS route. The major S-compounds present and can compete effectively with inhibitors for the active sites on catalysts. On the contrary, when proceeding by the direct HDS route, the sulfur atom in refractory sulfur species may be sterically hindered. Therefore, their desulfurization must be performed after hydrogenation. Also, their concentrations become very low while H₂S and NH₃ inhibitors increase their. Some processes have been developed which remove H₂S and NH₃ between stages to minimize this problem as described above.

Other feed impurities such as N-compounds are severe inhibitors for the hydrogenative HDS route. They are strong π -bonding species and they inhibit the interaction of the refractory S-compounds with the active hydrogenation site. The overall HDS processes perform better when the N-compound inhibitors are removed prior to hydrotreating. Aromatic species are inhibitors for HDS of refractory sulfur compound as described above because refractory sulfur compound are desulfurized through the hydrogenation route. Aromatic species can be highly concentrated and can inhibit the last stages of HDS. That it is difficult to achieve.

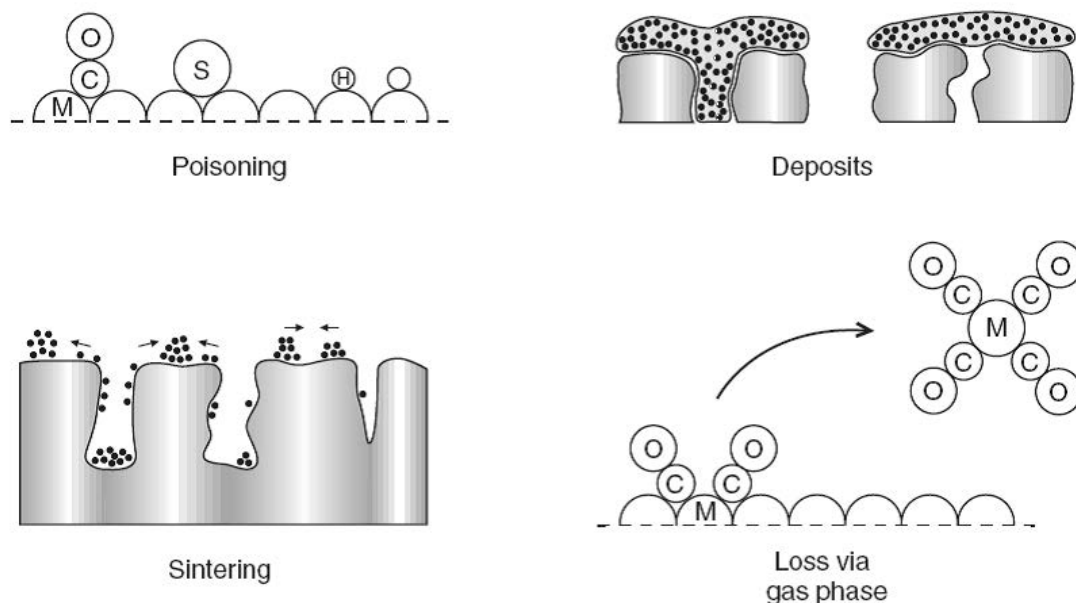


Figure 2.11 Mechanisms of catalyst deactivation [38]

A sulfur compound will be adsorbed on surface of the catalysts by strong chemical interaction and effects on catalytic activity can be illustrated in view of sulfur poisoning during CO hydrogenation on metal surface shown in Fig. 2.11, because sulfur atom blocks the reaction site of the catalyst which the adsorption abilities of metal atom can be changed. Besides these reasons, sulfur effect may be the restructuring of the surface which can cause in dramatic reactivity change. The designation of catalyst and operation of large scale processes for protection of catalyst deactivation or decomposition. The mechanisms of this deactivation issue can be divided into three main categories, e.g. chemical, mechanical, and thermal mechanisms. The poisoning is one of chemical deactivation that have important role to reduce the performance of the catalysts and it is a strong chemisorptions of poison reactants on active sites of the catalysts. The effect of catalytic activities depended on adsorption strength of poison species, sulfur species as a strong poison species like as chloride, oxygen, etc [39].

2.3 Hydrodenitrogenation

Hydrodenitrogenation is to the removal of nitrogen from organonitrogen compounds by reaction with hydrogen over a catalyst, this product is ammonia plus a hydrocarbon, according to the generic transformation represented by Eq. 2.2



This is the most important reaction within of hydrotreating after HDS, due to nitrogen is generally the second most polluting heteroatom in crude oils [40, 41]. The importances of this reaction occur from similar considerations to the ones invoked for the need for HDS, namely:

- Environmental regulations and concerns, since combustion of nitrogen-containing fuels leads to the emission of highly polluting nitrogen oxides, responsible for acid rain.

- Possible poisoning effects due to the basic organonitrogen compounds that adsorb strongly on acid catalysts used in refining steps, such as fluid catalytic cracking (FCC) or hydrocracking (HCK).

- Improving product quality since N-compounds are thought to be responsible for many of the problems related to coloring and gum formation during storage[12].

The nitrogen content of crude oils, in general considerably lower than the sulfur content. The acceptable amounts according to present and future regulations are of the order of less than 0.001 wt. % in fuels and of less than 0.5 wt. % for FCC feeds. This type of nitrogen is present in the heavier fractions and in cracked fractions, the non aromatic N-compounds, mainly amines and nitriles. The most highly refractory molecules that are relevant for HDN-modeling purposes are represented by the families depicted in table 2.4.

Table 2.4 Typical nitrogen compounds in petroleum[42]

Type of nitrogen compounds	Structure
Aniline	
Pyridine	
Quinoline	
Acridine	
Indole	
Carbazole	

The organic compounds of nitrogen are in crude oils such as aniline, pyridine, quinoline, acridine, indole, carbazole, etc. These compounds can be oxidized to form oxides of nitrogen such as nitrogen monoxide (NO), nitrogen dioxide (NO₂), nitrous oxide (N₂O), dinitrogen trioxide (N₂O₃), dinitrogen tetroxide (N₂O₄), dinitrogen pentaoxide (N₂O₅), etc. These oxides can form with moisture in air to nitric acid (HNO₃) that can cause to acid rain the same as sulfuric acid. While compounds of oxygen and metal were found very few amounts in petroleum beneath the surface on the earth that it effects on any problem about environmental pollutions or poisoning of

catalytic processes so these impurities have to remove before the petroleum are fed to any chemical process.

In recent years, the environmental legislations are important role about global and public problems more than in the past because its effect of these problem such as acid rain, global warming, flooding, polar ice melting, ozone depletion, etc. Therefore, these issues have led to the need to manage the quality of the products and service systems that can cause in more serious situation.

2.3.1 Main reaction pathways and mechanisms in hydrodenitrogenation

The reactions are in different combinations of three major types of reactions that take place once the organonitrogen compound has been adsorbed:

- Hydrogenation of N-heterocycles
- Hydrogenation of arene rings
- Hydrogenolysis and cleavage of C-N bonds

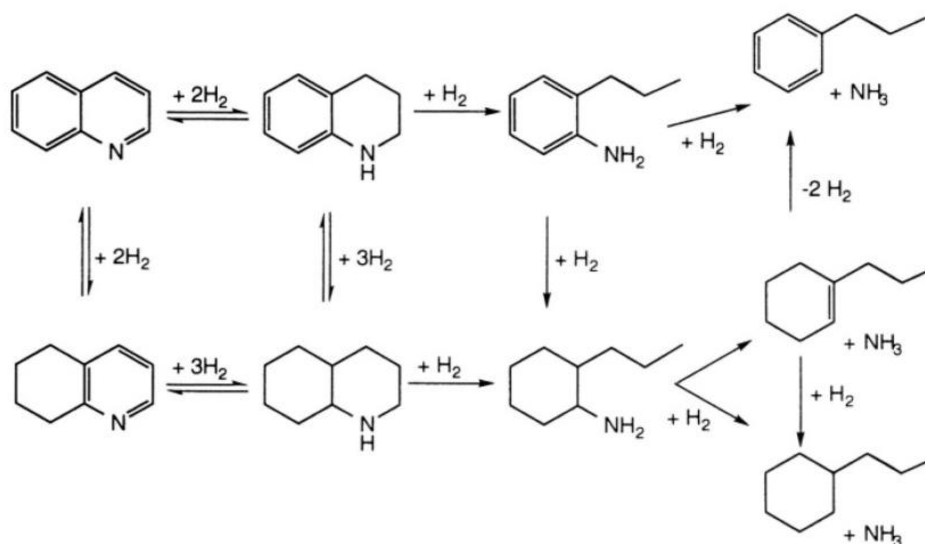


Figure 2.12 Main reaction pathways in HDN of quinoline [43]

This is shown in Fig. 2.12 for quinoline, one of the most frequently used model substrates for HDN mechanistic studies. The prehydrogenation of at least the

N-heterocycle is mandatory for C-N bond breaking. The case of HDS, where prehydrogenation of the S-ring is a possible pathway but not a prerequisite for C-S bond scission. The overall HDN rates are dictated by a hydrogenation rate more than by the C-N bond breakage rate and therefore HDN kinetics must always be thoroughly analyzed in order to avoid misleading conclusions. High pressures of hydrogen are needed in order to increase the equilibrium concentrations of saturated amines. The reaction pathway in Fig. 2.12 would be involve pre-saturation of only the heterocyclic ring, prior to denitrogenation to yield n-propylbenzene. Nevertheless, denitrogenation without prehydrogenation has also been reported, while some authors consider that both rings are necessarily hydrogenated before any C-N bond is broken [44-49].

2.4 Catalyst supports

Some oxide systems are complex by the possibility of phase transition under operating conditions. A number of oxides can be formed in several different phase modifications. Example, TiO_2 can be synthesis in three different forms: anatase, rutile and brookite. Anatase can have areas up to $80 \text{ m}^2 \text{ g}^{-1}$, while rutile, which forms at temperatures above about $550 \text{ }^\circ\text{C}$, has a much lower area. Each material used as a catalyst support must be examined that it does not sinter or suffer from phase transitions under the conditions. Another important parameter in determining which materials (oxides or other compounds) are used as supports is the texture of the solid. The surface area is important because the material to be supported also must have a high surface area to give it acceptable catalytic activities [50].

2.4.1 Alumina (Al_2O_3)

Alumina is one of the supports most commonly used in the preparation of heterogeneous catalysts. This is because it is inexpensive and can be prepared easily in forms that have high surface areas, coupled with readily accessible pore structures. The raw material used for alumina preparation is bauxite. The oxide or oxyhydroxide is calcined to bring about dehydration and to form an alumina. The conditions used for the drying and calcination steps can be important in determining the structure of the resultant alumina. The temperature of calcination has a very significant effect on

surface area. The sequence for the production of the various transition aluminas and ultimately α - Al_2O_3 are as shown in the scheme of Fig. 2.13.

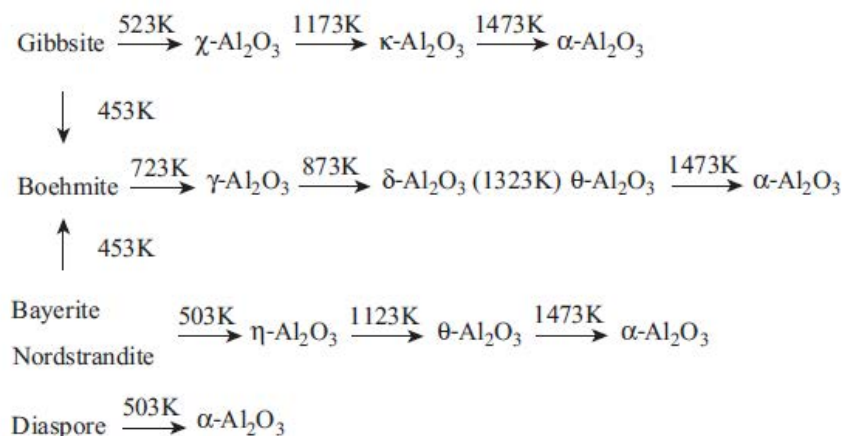


Figure 2.13 The preparation of the transition aluminas [51]

The hydroxide or oxyhydroxide precursors is formed is very dependent on the preparation conditions. However, if the desired product is γ - Al_2O_3 , boehmite is first formed by hydrothermal treatment of one of the trihydrates and this is calcined at about 723 K. which is the most commonly used as a catalyst support. The transition aluminas changes into other modifications at temperatures higher than about 873 K. The transition aluminas are transformed into α - Al_2O_3 (corundum) at temperatures around 1473 K. The forms of alumina, γ -, χ - and η - Al_2O_3 are seldom used as catalyst supports as their surface areas are generally much lower than those of the transition aluminas[52].

2.4.2 Titania (TiO_2)

TiO_2 supported systems exhibited higher activities compared to Al_2O_3 supported over Mo and CoMo catalysts, but it is thermal instability, low surface area and poor mechanical properties. TiO_2 occurs naturally in three crystalline forms:

(i) Rutile, which tends to more stable at high temperatures. The application of almost rutile type is used in industrial products such as paints, cosmetics and foodstuffs.

(ii) Anatase, which tends to be more stable at lower temperatures. This type generally shows a higher photoactivity than other of crystalline forms.

(iii) Brookite, which is usually found only in minerals and has a structure belonging to orthorhombic crystal system. Both of rutile and anatase type have a structure belonging to tetragonal crystal system are as shown in the scheme of Fig. 2.14. The two tetragonal crystal types are more common due to easy to synthesis. Anatase occurs usually in near-regular octahedral, and rutile forms slender prismatic crystal, which are frequently twinned. Rutile is the thermally stable form and is one of the two most important ores of titanium.

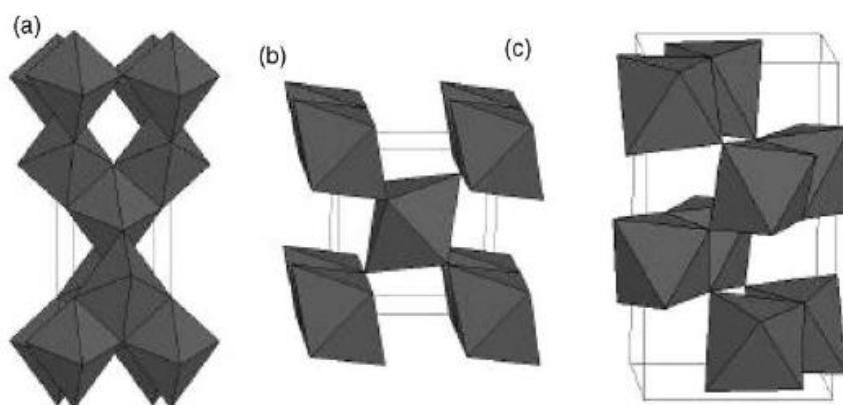


Figure 2.14 Crystal structures of anatase (a), rutile (b), and brookite (c) TiO_2 [51]

The three allotropic forms of TiO_2 have been prepared artificially but only rutile, the thermally stable form, has been obtained in the form of transparent large single crystal. The transformation from anatase to rutile is accompanied by the evolution of ca. 12.6 kJ/mol (3.01 kcal/mol), but the rate of transformation is greatly affected by temperature and by the presence of other substance which may either catalyze or inhibit the reaction. The lowest temperature at which conversion of anatase to rutile takes place at a measurable rate is ca. 700 °C, but this is not a transition temperature. The change is not reversible; ΔG for the change from anatase to rutile is always negative.

CHAPTER III

LITERATURE REVIEW

This chapter contains the reviews of hydrodesulfurization (HDS) that have been investigated by many researchers in the past. The research review for useful knowledge such as catalyst selection, support selection, and operating condition. Some of the highlight researches are summarized in the following sections.

3.1 Hydrodesulfurization of dibenzothiophene (DBT)

In 2000, Chan Kwak et al. [53] presented effect of fluorine have been tested for the hydrodesulfurization (HDS) of 4-methyldibenzothiophene (4-MDBT), and 4,6-dimethyldibenzothiophene (4,6-DMDBT). Fluorine addition to the catalyst promotes for enhancement of metal dispersion and the catalyst acidity. The HDS rates are improved by fluorine addition increase in the order of DBT<4-MDBT<4,6-DMDBT. Products of DBT HDS are obtained by the ring saturation is CHB more than BP produced by the direct desulfurization, while the opposite trend is observed in 4-MDBT HDS. The catalyst acidity reduces the steric hindrance to the C–S bond, which respon for the characteristic trends in the product distribution observed with the individual reactants.

In 2004, Marina Egorova et al. [33] studied over sulfided NiMo/ γ -Al₂O₃, CoMo/ γ -Al₂O₃, and Mo/ γ -Al₂O₃ catalysts. The Ni and Co promoters strongly enhanced the activity of the Mo catalyst in the direct desulfurization pathway of the HDS of DBT and 4,6-DMDBT. H₂S had effect on the HDS of DBT and 4,6-DMDBT, which was negative for the direct desulfurization pathway than for the hydrogenation pathway. The conversion of 4, 6-DMDBT was less affected by H₂S than the conversion of DBT. H₂S had affected to sulfur removal via the direct desulfurization pathway and the ultimate sulfur removal in the hydrogenation pathway, it is same extent over all the catalysts. The CoMo catalyst performed better than the NiMo catalyst in the final desulfurization via the hydrogenation pathway in the HDS of 4, 6-DMDBT at all partial pressures of H₂S.

In 2010, Yinyong Sun et al. [54] studied the HDS of DBT, tetrahydrodibenzothiophene (THDBT) and hexahydrodibenzothiophene (HHDBT) over Co-MoS₂/ γ -Al₂O₃ and Ni-MoS₂/ γ -Al₂O₃. The Co-MoS₂/ γ -Al₂O₃ and Ni-MoS₂/ γ -Al₂O₃ catalysts for desulfurization of DBT at 300 °C were faster than that of THDBT and HHDBT. Pt-Pd/mesoporous NaH-ZSM-5 was much more active than Pt-Pd/ γ -Al₂O₃, Pt-Pd/NaH-ZSM-5 and single metal Pt and Pd catalysts in the HDS of 4,6-DMDBT. Noble metals on mesoporous zeolites are very active HDS catalysts and might be considered as catalysts in the second stage of a deep HDS process.

In 2010, Ara Cho and Sang Heup Moon [55] studied of Co or Ni-promoted Mo sulfide catalysts were prepared by combining three methods, the first method is sonochemical synthesis of Mo sulfides, the second method is chemical vapor deposition (CVD) of promoter addition and the last is fluorination of alumina support, to improve their performance in the HDS process. Sonochemically synthesized Mo sulfides exhibited higher HDS activity for the hydrogenation (HYD) of DBT compounds than in the case of the catalysts prepared by impregnation due to the improved dispersion of the Mo species. The addition of Co or Ni to the catalyst by a CVD method allowed the selective decoration of the Mo-sulfide surface in order to active site for HDS, which had forms the Co-Mo-S and Ni-Mo-S phases. The efficiency of catalysts prepared by combining sonochemical and CVD methods was further improved by the addition of fluorine, which generated Bronsted acid sites that were responsible for the HYD route.

In 2011, Khaja W. Ahmed et al. [56] examined the catalytic activities of CoMo/ γ -Al₂O₃ catalysts was prepared with [Co/(Co + Mo)] ratios of 0.3, 0.4 and 0.5 while containing a total metal content of 19 wt%. These catalysts were tested in a batch autoclave reactor after presulfiding. The objective of Co/ (Co + Mo) ratio was studied on the HDS pathways of BT and DBT. The results of the Co/(Co + Mo) ratio has a significant influence on the overall HDS of BT and DBT as well on the direct desulfurization (DDS) pathway, but no influence on the hydrogenation pathway. A Co/ (Co + Mo) ratio of 0.4 was found to be optimum for the HDS by DDS pathway.

3.2 Hydrodesulfurization over HDS catalysts on mixed oxied supports

In 1996, R. Narvarro et al. [57] studied the hydrodesulfurization of DBT over unpromoted and Pt, Pd, Ni and Ru-promoted molybdenum catalysts supported on amorphous silica-alumina (ASA). Their activities were compared with a commercial Pt/ASA catalyst. The catalytic activity was found to increase in the following order: commercial Pt/ASA \gg PtMo \approx NiMo \approx RuMo $>$ PdMo \approx Mo \approx ASA. Characterization of the catalysts by XPS, TPR, and FTIR spectroscopy and pyridine confirmed that integration of 16.1 wt. % Mo, reduced the interaction between metal with support, and decreased the acidity of the catalysts. The incorporation of promoters enhanced molybdenum surface exposure and decreased the reduction temperature of MoO₃. The Ni-promoted catalyst increased the amount of sulfidable Ni species. Pd-promoted was not very effective due to its poor dispersion, because its low percentage of active sites in the PdMo catalyst.

In 1997, E. Olguin et al. [58] studied molybdenum (Mo), cobalt-molybdenum (CoMo) and nickel-molybdenum (NiMo) catalysts were prepared over mixed TiO₂-Al₂O₃ oxides containing between 0 and 100% TiO₂. The results provided evidence for a support effect on the catalytic activities of the sulfided catalysts. Catalytic activity is reduced when low TiO₂ content in the support, a loss of cobalt in the Al₂O₃ (compared to the pure Al₂O₃ supported samples), but for $x = \text{TiO}_2 / [\text{TiO}_2 + \text{Al}_2\text{O}_3]$ higher than 0.8, the support effect improved the HDS activity. Moreover, the activity depended on the nature of the model molecule used in the catalytic test on the experimental conditions (H₂ or H₂S partial pressure).

In 2003, V.L. Barrio et al. [59] studied the catalytic activities of Pd catalysts with a second metal such as Cu, Ru or Pt over mixed SiO₂-Al₂O₃ oxides (ASA) have been prepared (nominal content: 1 wt%) and tested in the naphthalene hydrogenation (HYD) and dibenzothiophene hydrodesulfurization (HDS) model reactions. The combined use of all these techniques revealed that only in the case of PtPd system a rather uniform distribution of the metals across the pore network is achieved, that the PtPd system exhibited strong Bronsted acid sites. The highest HYD and HDS activities of the PtPd catalyst can be related to a high dispersion of the metals,

uniform distribution and strong Bronsted acidity. The PtPd catalysts presented the highest DBT conversion (83.1%) and the lowest S-containing products (21.9 wt %) as compared with the much higher S-containing products (54.8 wt %) obtained with the Pd/ASA catalyst under the same experimental conditions.

In 2004, Naoyuki Kunisada et al. [60] examined to investigate activities in hydrotreating of straight run gas oil (SRGO) and its conventionally hydrodesulfurized oil (HSRGO) were used NiMoS supported on a series of alumina–silica with variable silica contents of up to 70%. Silica contents of 50 and 27% provided the highest activities in the hydrodesulfurization (HDS) of SRGO and HSRGO, respectively. The highest activity in HDN of SRGO and HDS of SRGO was obtained with the particular silica content of 50%. Silica contents of 27 and 50% provided the largest surface area, pore volume, and NH₃ desorption amount.

In 2007, Mohan S. Rana et al. [61] studied hydrodesulfurization (HDS) of dibenzothiophene (DBT) was carried out in a batch reactor at 3.3 MPa and 340 °C. The activity variation of sulfided catalysts showed as a function of support composition, which established that sulfided active phases strongly depend on the nature and composition of support. The incorporation of MgO, SiO₂, TiO₂ and ZrO₂ with γ -Al₂O₃, which active phase interactions on the support surface. Different preparation methods of catalysts were carried out by using different additives during the impregnation, that co-impregnation method found better activity than sequential impregnation. The mixed oxide supported catalyst showed rapid deactivation with time-on-stream than the alumina supported catalyst that may be due to an enhancement in acidic sites. The activity results depended on catalytic sites is a combination of support composition, additive, impregnation pH, drying and calcinations of catalysts.

In 2007, Jolanta R. Grzechowiak et al. [62] studied alumina–titania supports containing 5–50 wt. % of TiO₂ were prepared by coprecipitation method using inorganic precursors (sodium aluminate and titanium chloride). The results shows that the promoting effect of nickel with molybdenum catalysts supported on Al₂O₃-TiO₂ is significantly lower than that for molybdenum catalyst supported on Al₂O₃ on the HDS

activity, and depends on the TiO_2 content. The SEM results show that 80 wt. % Al support (20 wt. % of TiO_2) molybdenum was aggregated on the external surface of the catalyst, whereas it was uniformly dispersed on the external surface of alumina. Modification of Al_2O_3 - TiO_2 oxides increases the HDN activity of nickel–molybdenum catalysts. The highest HDN activity was obtained for the $\text{NiMo}/\text{Al}_2\text{O}_3$ - TiO_2 catalyst containing 50 wt. % of TiO_2 . The HDN activity was found to depend on protonic acidity and anatase content.

In 2012, Fernando Trejo et al. [63] studied pure and mixed oxides (Al_2O_3 , ZrO_2 , Al_2O_3 - MgO , Al_2O_3 - SiO_2 , Al_2O_3 - TiO_2 , and Al_2O_3 - ZrO_2) were prepared by homogeneous delayed precipitation. CoMo catalysts were impregnated by incipient wetness method to mixed oxide supports. The catalysts were characterized by N_2 physisorption, X-ray diffraction, among other techniques. Acid-base properties were studied with isopropyl alcohol and cumene decomposition. Conversion of isopropyl alcohol leads to the dehydration products. The $\text{CoMo}/\text{Al}_2\text{O}_3$ - SiO_2 catalyst exhibited the highest conversion during cumene cracking. $\text{CoMo}/\text{Al}_2\text{O}_3$ - SiO_2 catalyst was the higher activity during thiophene hydrodesulfurization than $\text{CoMo}/\text{Al}_2\text{O}_3$ - TiO_2 catalyst.

3.3 Effects of nitrogen compounds in hydrodesulfurization

In 2001, Chan Kwak et al. [53] studied the poisoning effect of carbazole and quinoline, this is nitrogen compound on the performance of sulfided $\text{CoMo}/\text{Al}_2\text{O}_3$ in the HDS of dibenzothiophene (DBT), 4-methyldibenzothiophene (4-MDBT), and 4,6-dimethyldibenzothiophene (4,6-DMDBT). The nitrogen compounds inhibit the ring-hydrogenation step (HYD) more than the direct desulfurization step (DDS) in the HDS of DBT. The nitrogen compounds poison acidic sites on the catalyst, due to confirmed by the reduced amounts of pyridine adsorbed and by the inhibited isomerization of 2, 2'-dimethylbiphenyl on the poisoned catalyst. Quinoline exhibits a stronger poisoning effect than carbazole. The HDS activity of the three DBT compounds are suppressed to different extents by the nitrogen compounds because the extent of steric hindrance to the C-S-C bond by methyl groups attached to the ring structure is different depending on the DBT compounds.

In 2001, Georgina C. Laredo et al. [64] studied the inhibiting effect of basic and non-basic nitrogen compounds on the hydrodesulfurization (HDS) of dibenzothiophene (DBT). Nitrogen compounds studied herein are quinoline, indole, carbazole and a quinoline. The inhibiting effect of the non-basic nitrogen compounds was indole and carbazole, it is found to be comparable to that of the basic compound, quinoline. The inhibition behavior of these compounds is highly non-linear, which showed strong inhibition at concentrations of nitrogen as low as 5 ppm.

In 2004, Hong yang et al. [65] studied the effect of nitrogen compounds on the hydrodesulfurization (HDS) activities of dibenzothiophenes in light cycle oil (LCO) was studied over a NiMo/Al₂O₃ commercial catalyst. The inhibition effects of nitrogen compounds on the HDS reactivity of the three sulfur groups total sulfur, hard sulfur, easy sulfur and 14 specific mono-, di- and tri-alkyl substituted dibenzothiophenes were studied. The results showed that the HDS rate significantly increased using ultra-low nitrogen LCO. The HDS rates could be classified into three groups based on the position of the substituents. It was found that 4 and 6 substituted dibenzothiophenes had the lowest HDS rates. On the contrary, the HDS rate of the 14 substituted dibenzothiophenes were increased when the ultra-low nitrogen feed was used. The hydrogenation route is more strongly inhibited than hydrogenolysis route by nitrogen compounds because the hydrogenation route is believed to be the outstanding reaction pathway for 4 and 6 alkyl-substituted dibenzothiophenes.

In 2005, Hiroshi Mizutani et al. [66] studied the inhibition effects of nitrogen compounds on CoMoP/Al₂O₃ catalysts due to doping with Li or USY-zeolite in the hydrodesulfurization (HDS) of dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT). Quinoline was selected as the model nitrogen compound. Conversion and selectivity of the HDS rate were investigated. The HDS of DBT as a reference probe molecule is thought to precede first through direct desulfurization pathways, then to hydrogenolysis. An important amount of benzene was detected in the case of CoMoP/zeolite-Al₂O₃. In the presence of quinoline, a strong inhibition effect was observed for all the catalysts. The inhibition effects of quinoline on CoMoP/Al₂O₃-Li were smaller than the other catalysts, because this resulted in the enhancement of HDS activity. Furthermore, from the XPS

investigations we can conclude that CoMoP/Al₂O₃-Li showed a relatively higher sulfidation degree for both Mo and Co. Thus, it seems to have a relatively higher catalytic activity.

CHAPTER IV

EXPERIMENTAL

This chapter describes the preparation of the Al₂O₃-TiO₂ mixed oxide supports for the CoMo catalysts. The catalyst characterization and the catalytic activity test are also explained in this chapter. The chemicals needed and preparation method of CoMo catalyst are explained in sections 4.1 and 4.2. The details on characterization of catalyst are described in section 4.3. Finally, the procedure for testing catalytic activity in hydrodesulfurization of dibenzothiophene is given in section 4.4.

4.1 Chemicals used in the study

The chemicals used in the preparation of Al₂O₃-TiO₂ mixed oxide supports, the preparation of CoMo catalysts, and the catalytic activity test are listed in Table 4.1.

Table 4.1 Chemicals used in the study

Chemicals	Formulas	Suppliers
Aluminium triisopropoxide, > 98 %	C ₉ H ₂₁ AlO ₃	Sigma-Aldrich
Ammonium heptamolybdate tetrahydrate, 99.98 %	(NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O	Sigma-Aldrich
Cobalt (II) nitrate hexahydrate, 99.999 %	Co(NO ₃) ₂ ·6H ₂ O	Sigma-Aldrich
Dibenzothiophene, 98 %	C ₁₂ H ₈ S	Sigma-Aldrich
Diesel oil	-	Thaioil Public Company Limited, Thailand

Table 4.1 (continued) Chemicals, formulas, and suppliers

Chemicals	Formulas	Suppliers
Dimethyl disulfide, > 99 %	(CH ₃) ₂ S ₂	Sigma-Aldrich
Nitric acid, 65 %	HNO ₃	Merck
Pyridine, 99.8 %	C ₅ H ₅ N	Sigma-Aldrich
Titanium (IV) isopropoxide, 97 %	Ti[OCH(CH ₃) ₂] ₄	Sigma-Aldrich

4.2 Catalyst preparation

4.2.1 Preparation of Al₂O₃-TiO₂ mixed oxide supports

The Al₂O₃-TiO₂ mixed oxide supports were synthesized by the sol-gel method, using aluminum isopropoxide and titanium (IV) isopropoxide as precursor for Al₂O₃ and TiO₂, respectively. The mixed oxide supports at various composition of Al₂O₃ in TiO₂ can be made by separately synthesis of TiO₂ sol and Al₂O₃ sol. The resulting solid was dried at 110 °C overnight and calcined at 450 °C for 4 h. The Al₂O₃-TiO₂ mixed oxide supports with five different molar ratios are listed in Table 4.2.

Table 4.2 Symbols and composition of the Al₂O₃-TiO₂ mixed oxide supports

Symbols	Amount (wt.%)	
	Al ₂ O ₃	TiO ₂
50Al-50Ti	50	50
60Al-40Ti	60	40
70Al-30Ti	70	30
80Al-20Ti	80	20
90Al-10Ti	90	10

4.2.2 Preparation of CoMo catalyst

The CoMo catalysts were synthesized using the co-impregnation method with cobalt (II) nitrate hexahydrate (as a precursor for Co) and ammonium heptamolybdate tetrahydrate (as a precursor for Mo) at 2.93 wt.% of Co and 13.7 wt.% of Mo. These precursor were dissolved in water and then added to the support by impregnation. After that, the CoMo catalysts was dried at 120 °C for 2 h, then calcined at 450 °C for 3 h under air flow. The impregnated sample are listed in Table 4.3.

Table 4.3 Symbols and composition of the CoMo catalysts

Symbols	Amount (wt.%)	
	Co	Mo
CoMo/50Al-50Ti		
CoMo/60Al-40Ti		
CoMo/70Al-30Ti	2.93	13.7
CoMo/80Al-20Ti		
CoMo/90Al-10Ti		

4.3 Characterization of catalyst

4.3.1 Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES)

The metal content was determined using inductively coupled plasma-optical emission spectroscopy (ICP-OES). The amount of metal on the surface was measured with an inductively coupled plasma-optical emission spectrometer (ICP-AES) Perkin Elmer 20 model PLASMA-1000. Approximately 0.03 g of the catalyst was digested in 5 ml of 49 % hydrofluoric acid. The catalyst was stirred at 60 °C until solid catalyst was completely digested. After that, the solution was dilute to 100 ml in volumetric flask by using deionized water.

4.3.2 X-ray diffraction (XRD)

XRD patterns of the catalysts were determined by diffraction of an X-ray beam as a function of the angle of the incident beam. The XRD spectrum of the catalyst was measured by using D8 Advance of Bruker AXS, equipped with a long fine focus ceramic Cu K α X-ray source. The pattern was recorded in the 2θ range between 20° to 80° with a resolution of 0.5° . The XRD spectra were used to identify the crystal structure of the mixed oxide supports and the catalysts.

4.3.3 N₂ physisorption

The BET specific surface area, pore volume, and pore size distribution of the catalysts were determined by N₂ physisorption technique. Approximately 0.2 g of catalyst was loaded in BEL sorp-max to perform nitrogen adsorption measurement at 77 K. The catalyst was degassed at 200 °C for 2 hours by BELPREP-VAC II prior to each measurement. Finally, specific surface area, pore volume and pore size distribution were calculated according to Brunauer-Emmett-Teller (BET) and Barret-Joyner-Halenda (BJH) methods.

4.3.4 Temperature- programmed reduction with hydrogen (H₂-TPR)

The reducibility of the catalysts was assessed using temperature-programmed reduction with hydrogen (H₂-TPR) by using 10 % H₂/Ar as reducing gas. Approximately 0.1 g of catalyst was loaded to Micromeritic ChemiSorb 2750 instrument equipped with a TCD detector. Prior to starting the reduction step, the catalyst was heated up from room temperature to 200 °C with a heating rate of 10 °C/min under nitrogen gas flow with a flow rate of 25 ml/min and the temperature was held for 2 hours. After that, the catalyst was cooled down to room temperature and then 10 % H₂/Ar was introduced to the system at a flow rate 25 ml/min and the temperature was raised from room temperature to 800 °C at a rate of 10 °C/min.

4.3.5 Temperature-programmed desorption with ammonia (NH₃-TPD)

The surface acidity of the catalyst was determined by temperature-programmed desorption (NH₃-TPD) by using NH₃ gas as a probe molecule NH₃-TPD.

Approximately 0.05 g of catalyst was placed in a quartz tube and then in a temperature-controlled furnace of BELCAT-A instrument. Helium gas with a flow rate of 50 ml/min was fed through the tube and the catalyst was then heated up from room temperature to 500 °C with a heating rate of 10 °C/min and was held for one hour to remove moisture and impurities on the surface. After that, the catalyst was cooled down to 100 °C. Then 10 % NH₃ in helium gas was fed through the tube and was held for 30 minutes. Subsequently, helium gas was flowed through the catalyst at a flow rate of 50 ml/min for 45 minutes. Finally, the catalyst was heated to 800 °C with a heating rate of 10 °C/min and the adsorbed NH₃ that it was removed from the surface of the catalyst was detected by a TCD detector.

4.3.6 Chemisorption using carbon monoxide as a probe molecule (CO-Chemisorption)

The active sites on CoMo catalysts were determined by chemisorption of carbon monoxide as a probe molecule. The CoMo catalysts were sulfided by using 5 % H₂S/H₂ gas as a sulfiding agent. Approximately 0.1 g of the catalyst was placed in a quartz reactor in a BELCAT-A. Then helium was fed through the reactor at a flow rate of 30 ml/min. Subsequently, the reactor was heated to 400 °C with a heating rate of 10 °C/min. After that, helium gas was replaced by 5 % H₂S/H₂ mixture at a flow rate of 50 ml/min for two hours. Finally, the catalyst was cooled down to room temperature by helium gas.

To perform chemisorption, approximately 0.1 g of the sulfided CoMo catalyst was placed in a sample tube and was introduced to BELCAT-A instrument. Helium gas was fed through the tube at a flow rate 50 ml/min for 15 minutes at 30 °C. Then hydrogen gas was fed to the catalyst at a flow rate a 50 ml/min and the temperature was raised to 500 °C with a heating rate of 10 °C/min for 30 minutes. Subsequently, helium was introduced again to cool down the catalyst to 50 °C for 10 minutes. In the final step, carbon monoxide gas was injected to the catalyst pulsewise and was repeated until saturation was obtained.

4.4 Catalytic activity test

Hydrodesulfurization of dibenzothiophene was carried out concurrently in two fixed-bed microreactors. Approximately 0.5 g of the catalyst was loaded in each reactor according to diagram of packing in the reactor is shown in Figure 4.1. The catalyst bed was diluted with silicon carbide and ceramic ball in order to reduce the dispersion effect and create a more homogeneous thermal distribution in the reactor.

The study of hydrodesulfurization of dibenzothiophene was conducted in a three-phase fixed-bed microreactor as shown in Figure 4.2. This system was located at PTT Research and Technology Institute (PTT-RTI)

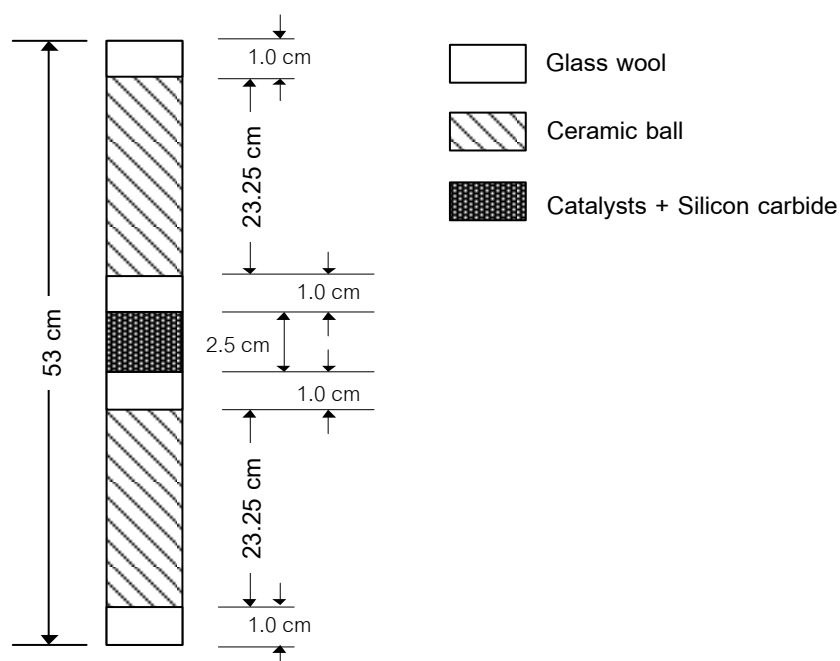


Figure 4.1 Schematic diagram for catalyst packing inside the reactor

The two reactors were introduced to HDS unit. Prior to the activity test, the catalyst was sulfided using dimethyl disulfide (DMDS) in diesel oil at a sulfur content of 2.35 % (w/v). The temperature program for the sulfidation step was shown in Figure 4.3. The presulfided catalyst was first activated in hydrogen at a flow rate of

10.8 nl/h, pressure 60 bars. The temperature was raised from 160 °C to 350 °C and remained at that temperature for 4 hour.

After the presulfide catalyst step was finished, the diesel feed containing DMDS for sulfidation step was replaced by the diesel feed containing dibenzothiophene (DBT) feed with 2000 ppm of S at a flow rate of 0.36 ml/min. Prior to the HDS reaction, the temperature and the hydrogen pressure in the reactor system were adjusted to 350 °C and 80 bar, respectively. The time for the sampling step of the liquid products was shown in Figure 4.4. After 12 hours, the first sample was taken and subsequent samples were taken every 6 hours. Approximate 1 microliter of samples was diluted with isooctane (ratio of sample: isooctane is 1:10). The samples were then analyzed for total sulfur content using Analytik Jena Multi EA5000.

Further experiments involved diesel feed that contained dibenzothiophene with a sulfur content of 2000 ppm and pyridine with various nitrogen content. Five different nitrogen concentrations (100, 200, 300, 400, and 500 ppm) were employed to investigate the effect of nitrogen content on HDS activity of the catalyst. The testing procedure were similar to the procedure without pyridine mentioned above. Approximate 1 microliter of samples was diluted with isooctane (ratio of sample: isooctane is 1:10). The sample were analyzed for both total sulfur and nitrogen contents by using Analytik Jena Multi EA5000.

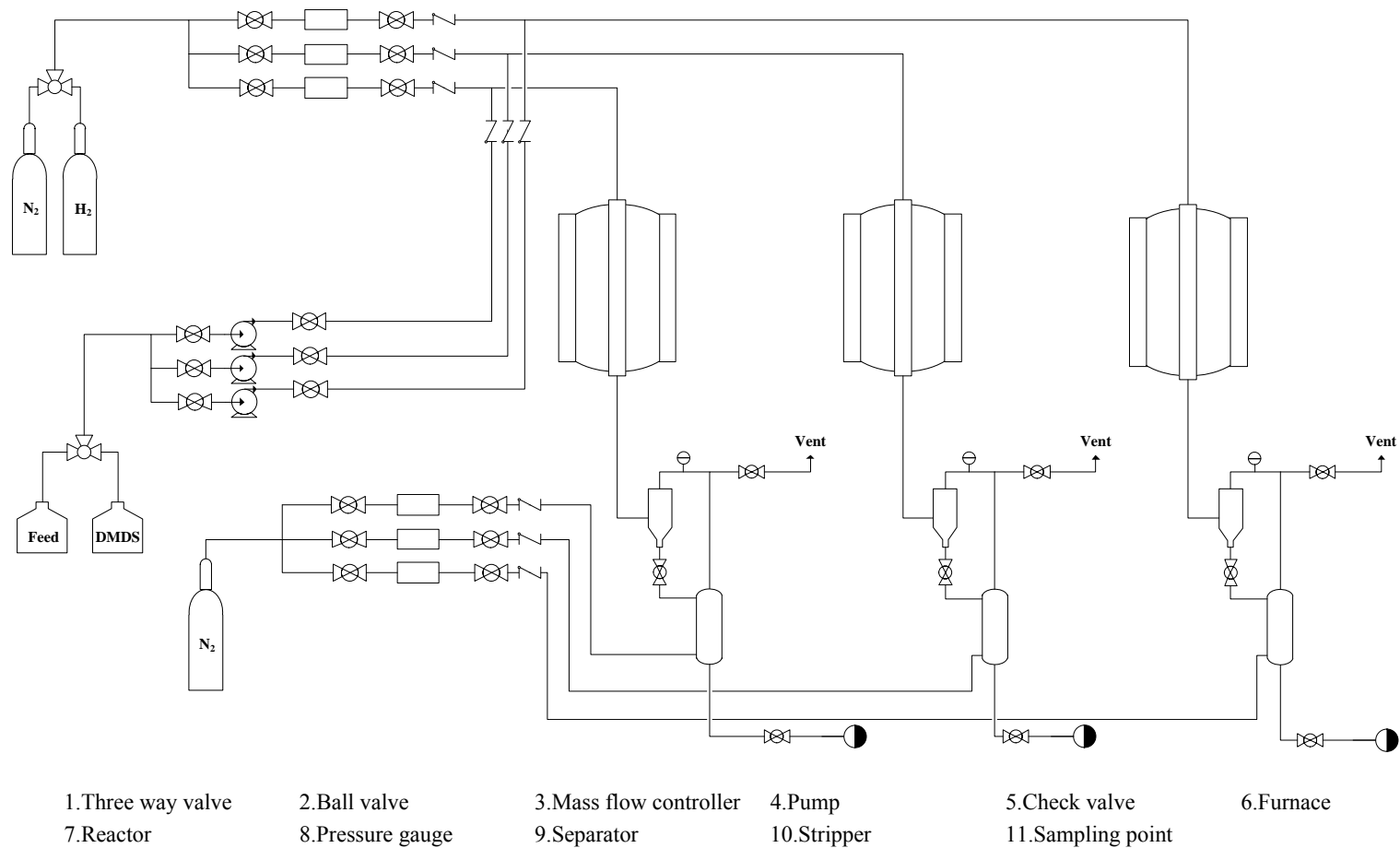


Figure 4.2 Schematic diagram of the HDS unit

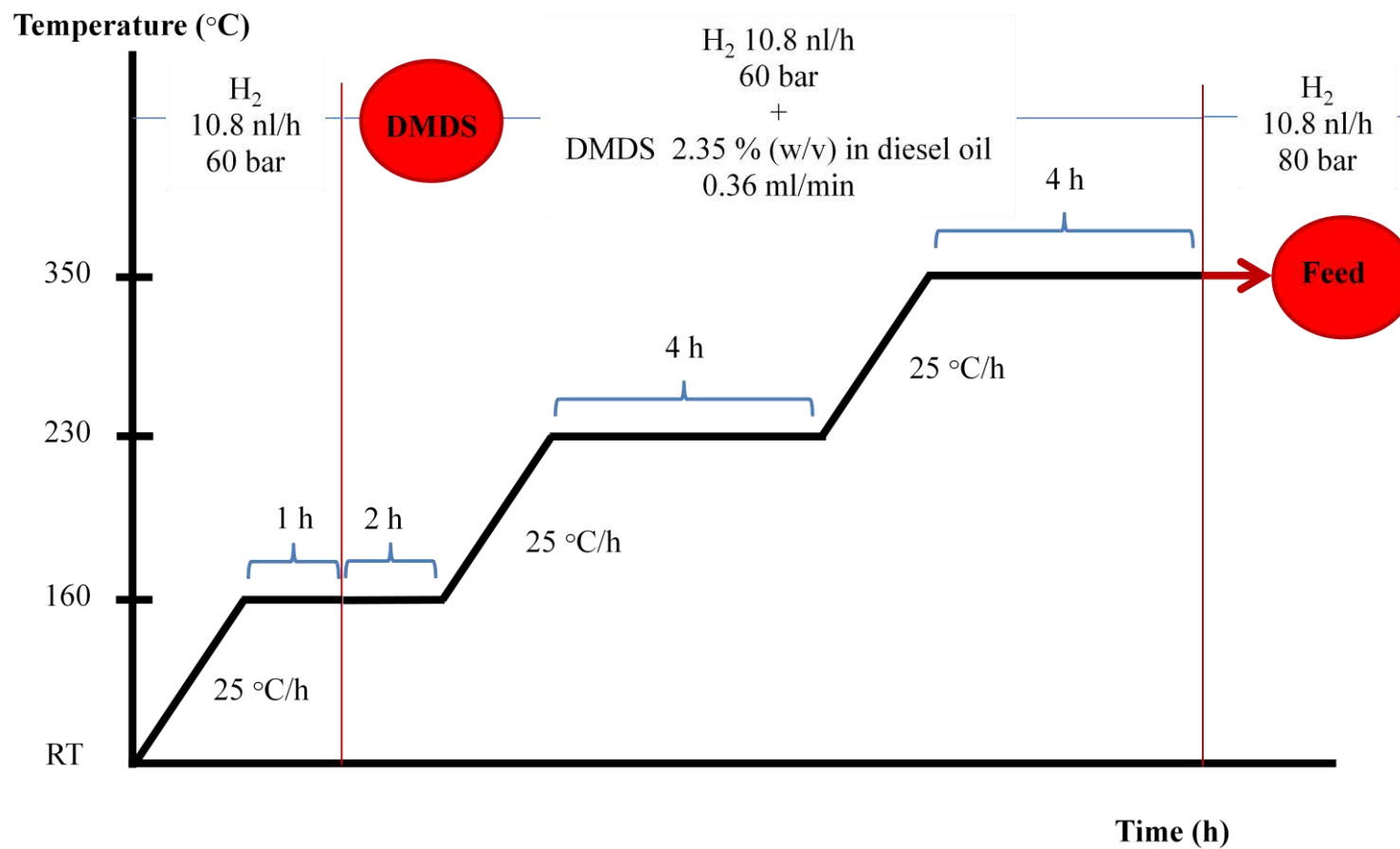


Figure 4.3 Temperature program for the sulfidation step of the catalysts before catalytic activity tests

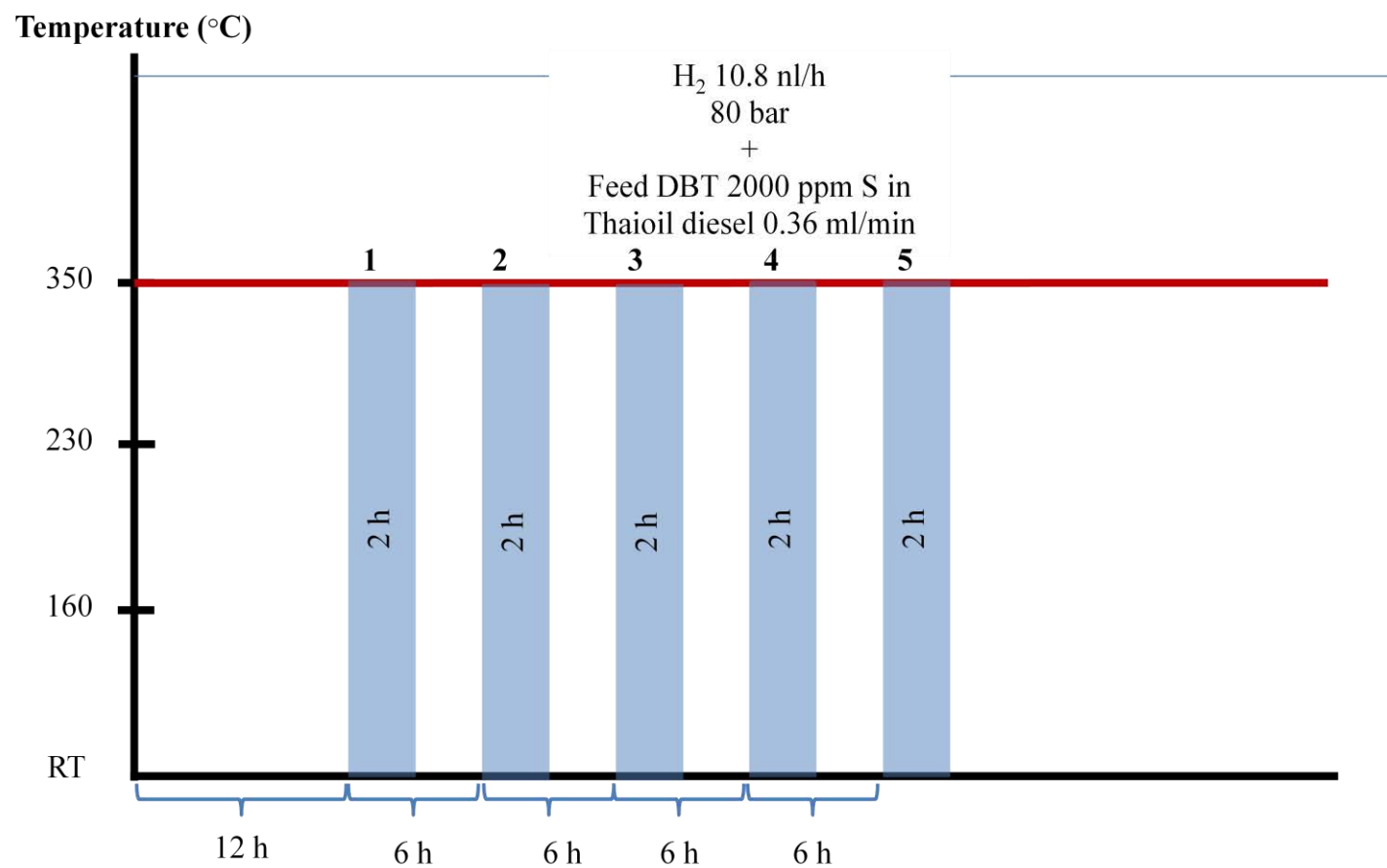


Figure 4.4 The time for the sampling step of the liquid products

CHAPTER V

RESULTS AND DISCUSSION

This chapter presents the physical, chemical, and catalytic properties of the Al_2O_3 - TiO_2 supports and the CoMo catalysts in the hydrodesulfurization (HDS) activity of dibenzothiophene in the presence of nitrogen compound. In addition, hydrodenitrogenation (HDN) activities of five different nitrogen concentrations from pyridine were measured to investigate its effect on the catalytic activity.

5.1 Characterization of the Al_2O_3 - TiO_2 mixed oxide supports and the CoMo catalysts

Al_2O_3 - TiO_2 supports were characterized for specific surface area, pore volume, and pore size by N_2 physisorption. Elemental analysis by inductively coupled plasma optical emission spectroscopy (ICP-OES) was used to confirm the composition of Al_2O_3 and TiO_2 in their supports. X-ray diffraction (XRD) was also used to detect crystal phases of Al_2O_3 and TiO_2 in the supports.

The CoMo catalysts were characterized using several techniques such as ICP-OES, XRD, N_2 physisorption, temperature-programmed desorption with ammonia (NH_3 -TPD), temperature programmed reduction with hydrogen (TPR) and chemisorption using carbon monoxide as a probe molecule (Co-Chemisorption).

5.1.1 Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES)

The elemental compositions of catalysts were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES). The compositions of the mixed oxide supports and catalysts are listed in Tables 5.1 and 5.2, respectively. The result obtained from ICP-OES was close to the intended content of the catalyst.

The composition of various mixed oxide supports in form of percentage are compared with those obtained from ICP-OES. The intended compositions of Al_2O_3 in the mixed oxide support are 50, 60, 70, 80, and 90 wt%, while the result from ICP-

OES are 52.46, 63.50, 72.85, 82.35 and 90.88 wt% of Al₂O₃, respectively. From this results, the compositions of all supports that were prepared by a sol-gel method were close to the intended values.

Table 5.1 Compositions of the Al₂O₃-TiO₂ mixed oxide supports as determined by ICP-OES

Supports	Composition (wt. %)	
	Al ₂ O ₃	TiO ₂
50Al-50Ti	52.46	47.54
60Al-40Ti	63.50	36.50
70Al-30Ti	72.85	27.15
80Al-20Ti	82.35	17.65
90Al-10Ti	90.88	9.12

The CoMo catalysts were characterized with ICP-OES to determine the amount of the active metal component. From Table 5.2, the amounts of cobalt (Co) was in the range of 2.75-3.34 wt.% and molybdenum (Mo) was in the range of 11.72-14.48 wt.%, while the intended amount of Co and Mo are 2.93 and 13.7 wt.%, respectively (in elemental form).

Table 5.2 Compositions of the CoMo catalysts as determined by ICP-OES

Catalysts	Composition (wt.%)	
	Co	Mo
CoMo/50Al-50Ti	3.34	14.48
CoMo/60Al-40Ti	3.34	14.09
CoMo/70Al-30Ti	3.12	13.43
CoMo/80Al-20Ti	2.75	11.72
CoMo/90Al-10Ti	2.84	11.79

5.1.2 N₂ physisorption

N₂ physisorption was used to determine the specific surface area, pore volume and average pore size of the Al₂O₃-TiO₂ mixed oxide supports and the CoMo catalysts and the results from this measurement are shown in Tables 5.3 and 5.4.

Table 5.3 Specific surface area, pore volume, and pore diameter of the Al₂O₃-TiO₂ mixed oxide supports as determined by N₂ physisorption

Supports	Surface area (m ² /g)	Pore volume (cm ³ /g)	Pore diameter (nm)
50Al-50Ti	272.9	0.30	4.38
60Al-40Ti	267.0	0.29	4.27
70Al-30Ti	270.5	0.29	4.33
80Al-20Ti	263.5	0.29	4.37
90Al-10Ti	240.4	0.28	4.67

The specific surface area and pore volume of the supports increased with increasing TiO₂ content. The 50Al-50Ti possessed the largest specific surface area (272.9 m²/g) and the largest pore volume (0.3 cm³/g). On the other hand, pore diameter increased with increasing Al₂O₃ content. The specific surface area and pore volume of the catalyst were reduced after the impregnation of metal. These results are presented Table 5.4.

Table 5.4 indicates that after the Al₂O₃-TiO₂ mixed oxide supports were impregnated with cobalt (Co) and molybdenum (Mo), the surface area and pore volume decreased. This may be because of the second calcination after metal impregnation.

Table 5.4 Specific surface area, pore volume, and pore size of the CoMo catalysts as determined by N₂ physisorption

Catalysts	Surface area (m ² /g)	Pore volume (cm ³ /g)	Pore diameter (nm)
CoMo/50Al-50Ti	200.0	0.20	4.0
CoMo/60Al-40Ti	169.6	0.16	4.4
CoMo/70Al-30Ti	124.8	0.15	4.7
CoMo/80Al-20Ti	144.1	0.16	4.5
CoMo/90Al-10Ti	134.0	0.15	4.6

In addition to three properties (specific surface area, pore volume, and pore diameter), pore size distribution of these supports as determined from BJH method is also shown in Figures 5.1 and 5.2.

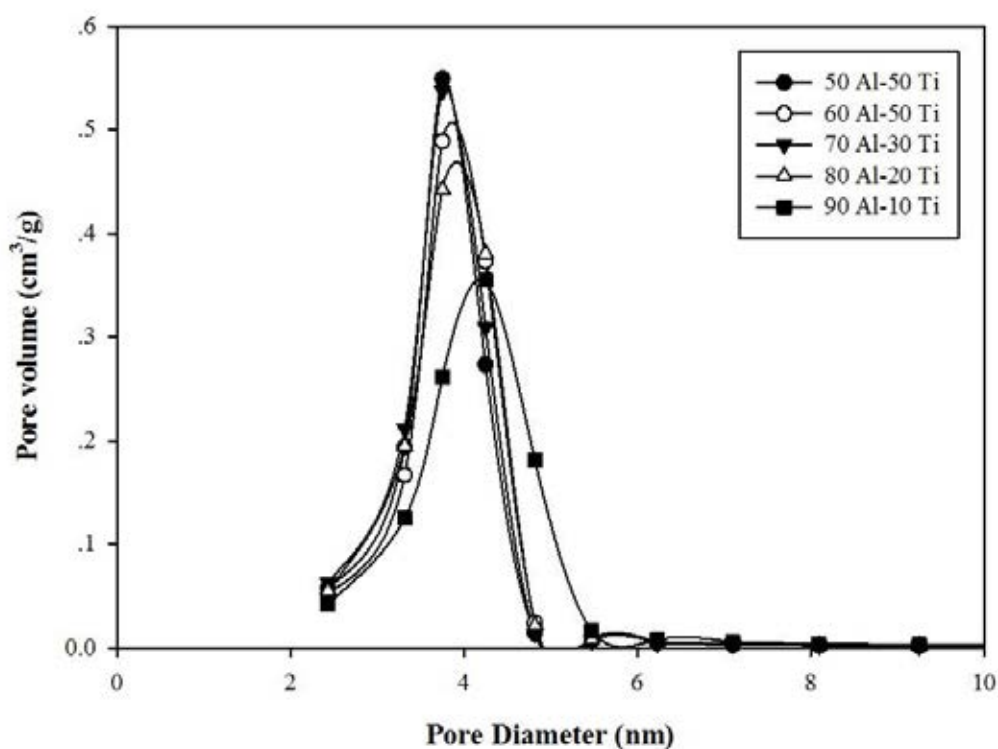


Figure 5.1 Pore size distribution of the Al₂O₃-TiO₂ mixed oxide supports by BJH plo

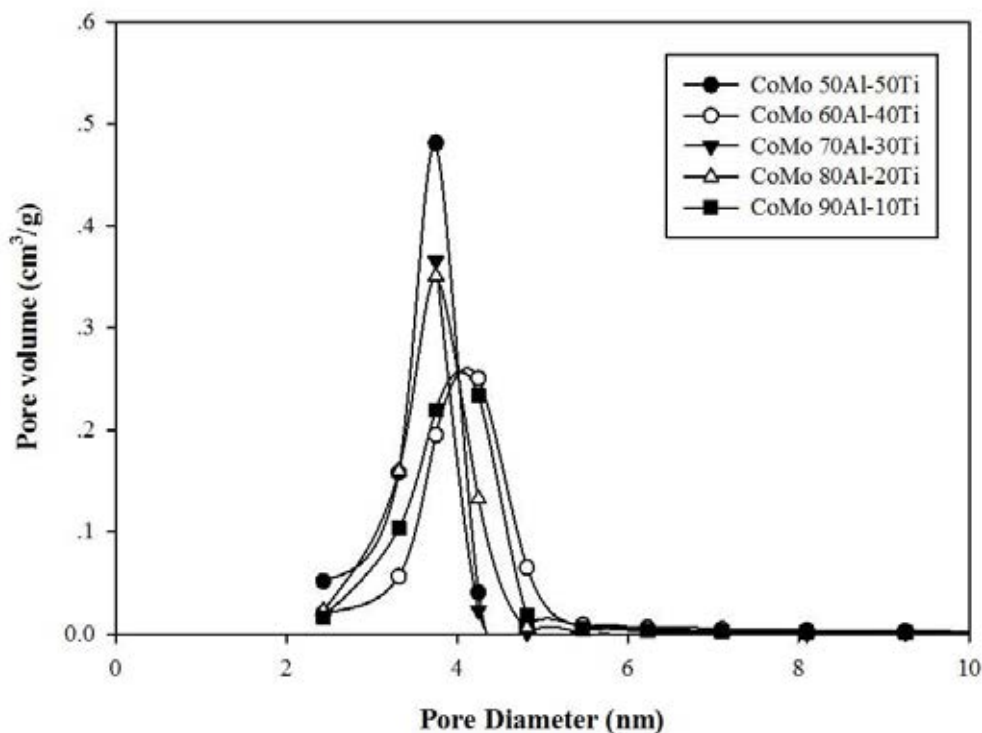


Figure 5.2 Pore size distribution of the CoMo catalysts by BJH plot

Pore size distribution of the Al_2O_3 - TiO_2 mixed oxide supports and the CoMo catalysts by BJH plot are given in Figures 5.1 and 5.2, respectively. Both figures display similar shape in the distribution of pore diameter. The distribution appears to be unimodal with an average about 4 nm.

5.1.3 X-ray diffraction (XRD)

The XRD technique was used to investigate the crystal structure of support. XRD was scanned in the range of 2θ between 20° and 80° . The XRD patterns of the Al_2O_3 - TiO_2 mixed oxide supports and the CoMo catalysts are shown in Figures 5.3 and 5.4, respectively.

Figure 5.3 shows the XRD patterns of the Al_2O_3 - TiO_2 mixed oxide supports with different Al_2O_3 contents. The peaks corresponding to the γ - Al_2O_3 structure were observed, particularly at the 2θ of 38.5° , 46.3° and 66.7° [67]. As the amount of Al_2O_3 in the support increase, the peaks were more pronounced. The typical peak of anatase

TiO₂ were also observed at the 2 Θ of 25.3°, 39.0°, 48.1°, 55.1° and 62.9°. The presence of small amount of brookite phase was observed at 30.9° [68].

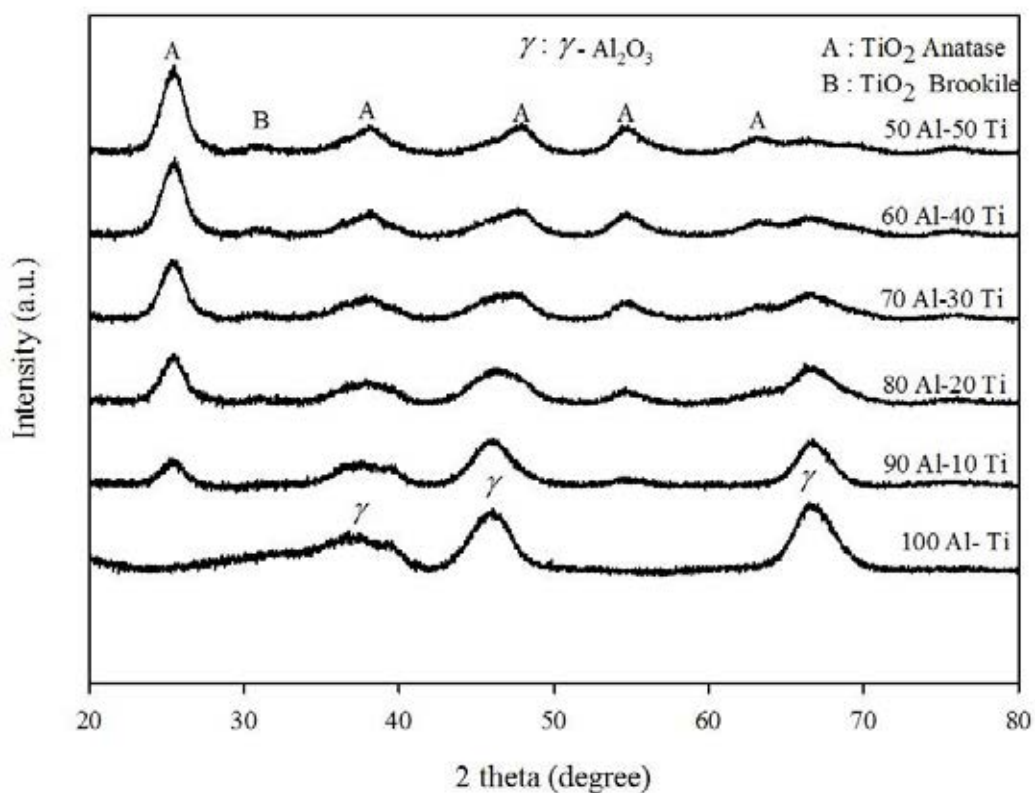


Figure 5.3 XRD patterns of the Al₂O₃-TiO₂ mixed oxide supports

The XRD patterns of the CoMo catalysts supported on Al₂O₃-TiO₂ mixed oxide are presented in Figure 5.4. After cobalt and molybdenum were impregnated into the Al₂O₃-TiO₂ mixed oxide supports, the signals of crystalline CoMoO₄ were observed at the 2 Θ of 22°, 25° and 27° in the XRD patterns for all catalysts [69]. The formation of CoMoO₄ phase in the CoMo catalysts that were prepared by co-impregnation was reported by other investigators [70]. Moreover, the peak of crystalline rutile phase of TiO₂ could be observed at the 2 Θ of 28.5°, 33.7°, 36.7° and 40.3°. In addition, the weak signals of brookite phase were present at the 2 Θ of 46.2° and 49.3°. These peaks occurred because the support underwent the second calcination after metal impregnation, thereby leading to the transformation of the TiO₂ phase from anatase to rutile phase.

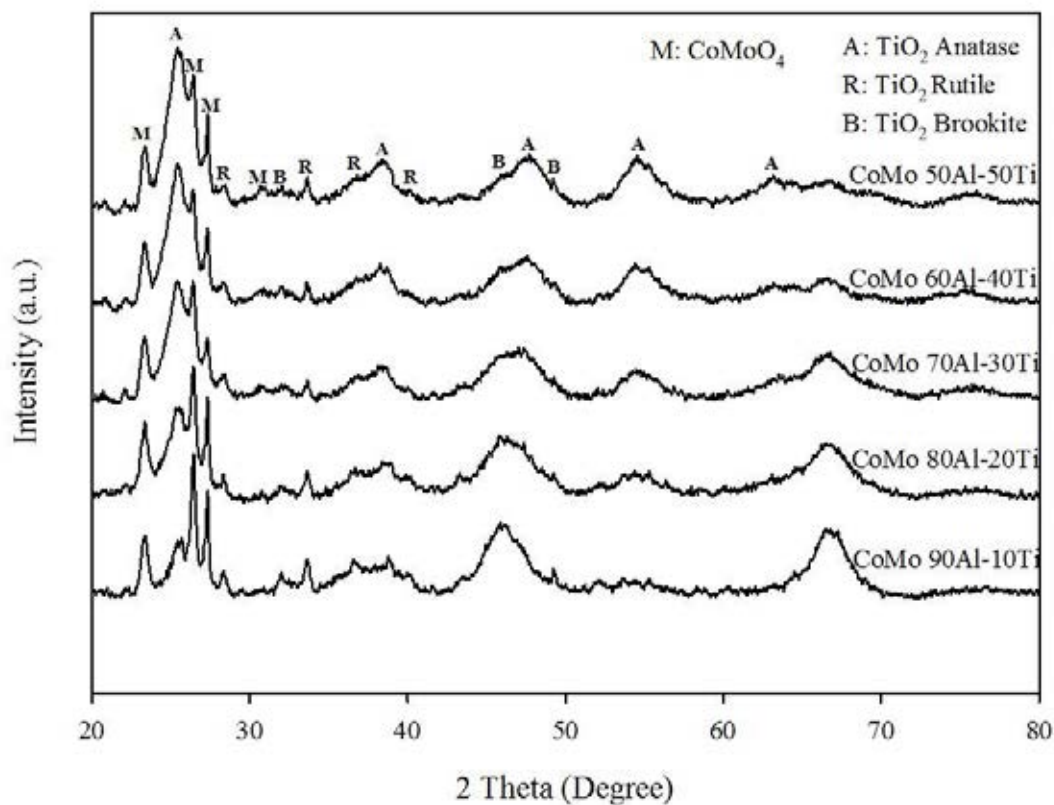


Figure 5.4 XRD patterns of the CoMo catalysts

5.1.4 Temperature-programmed reduction with hydrogen (H₂-TPR)

Temperature-programmed reduction with hydrogen (H₂-TPR) was used to determine the type and reducibility of the cobalt and molybdenum species present in the catalysts. The CoMo catalysts in form of metal oxides such as CoO and MoO₃ were characterized by reducing from these oxide forms to metal forms such as Co and Mo. The H₂-TPR experiment was used to measure the reducibility of the catalysts that assessed the ability to reform the form of metal oxide to metal. The reduction of catalyst is an important step in sulfidation during which the catalyst was reduced and was subsequently sulfided to activate the catalyst before hydrotreatment.

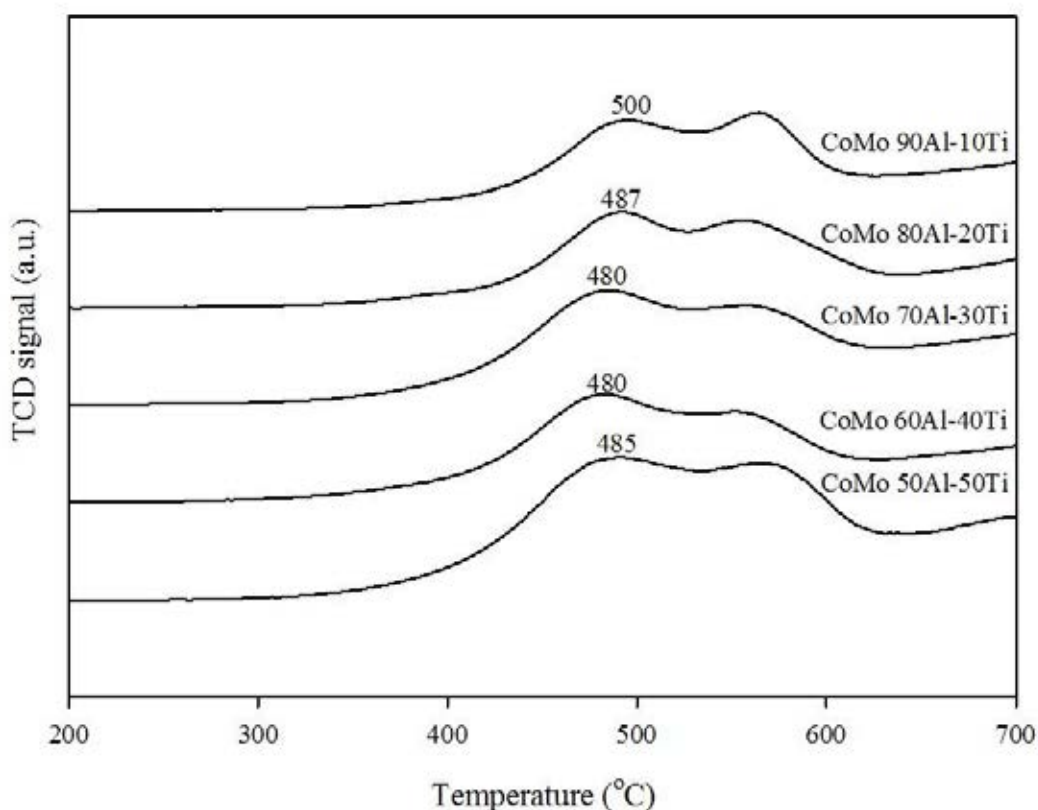


Figure 5.5 TPR profiles of the CoMo catalysts

H₂-TPR results are presented in Figure 5.5. Two reduction peaks were observed at the temperature ranges of 480-500 °C and 550-590 °C. The first reduction peak around 480 to 500 °C was indicative of the reduction of Mo⁶⁺ (MoO₃) to Mo⁴⁺ (MoO₂) [71]. The second reduction peak detected around 550 to 590 °C may correspond to the interaction between Co and Mo species due to the CoMoO₄ phase, that was in agreement with the XRD results [72, 73]. From Figure 5.5, the CoMo catalysts supported on 60Al-40Ti mixed oxide shows the lowest reduction temperature at 480 °C. When TiO₂ was incorporated into supports at 10, 20, 30, 40, and 50 wt%, reduction peaks were observed at 500, 487, 480, 480 and 485 °C, respectively. This result suggests that the presence of TiO₂ in the supports shifted the reduction peak to lower temperature.

In addition, the quantitative evaluation of the CoMo catalysts are represented in Table 5.5. H₂ consumption for reduction of the CoMo was determined from area under the curve.

Table 5.5 Amount of hydrogen consumption for reduction of the CoMo catalysts

Catalysts	H ₂ consumption (mmol/g)
CoMo/50Al-50Ti	2.974
CoMo/60Al-40Ti	2.760
CoMo/70Al-30Ti	3.072
CoMo/80Al-20Ti	1.983
CoMo/90Al-10Ti	1.924

Table 5.5 shows that H₂ consumption in the reduction of CoMo/70Al-30Ti and CoMo/50Al-50Ti were higher than that of the other catalyst as a result of higher TiO₂ content in the support of catalyst. An increase in the amount of TiO₂ in the support gave rise to larger amount of reducible Mo in the catalyst by reducing the metal-support interaction.

5.1.5 Chemisorption using carbon monoxide as a probe molecule (CO-Chemisorption)

This section represents the determination of active sites on the catalysts using chemisorption with carbon monoxide (CO) pulse injection until surface of the catalysts was saturated with CO gas. Prior to each measurement, the catalyst must be pre-sulfided with mixture of H₂S and H₂ in which composition of H₂S in H₂ is 5 % (v/v). Sulfided CoMo catalysts were reduced with H₂. Anion vacancies that were generated were active sites of the catalysts.

CO probe molecules were injected over surface of the catalysts at which the molecule can be adsorbed. We employed this concept to explain the relationship between catalytic activities and amount of active sites of the catalysts

For details about this measurement, the sulfided CoMo catalysts was placed into the apparatus. Firstly, sulfided CoMo catalysts were reduced by hydrogen gas to create anion vacancies (active sites of the catalyst). Secondly, CO gas was injected pulse wise after the first step was finished which CO gas can be adsorbed efficiently on these anion vacancies. After these two steps have been finished, a computer program (Chem Master™) automatically provided CO uptake of the catalyst. Then the metal dispersion of the catalyst can be calculated (see Appendix D) and the result is summarized into Table 5.6.

Table 5.6 CO-Chemisorption results of the CoMo catalysts

Catalysts	CO uptake (cm ³ STP/g)	Metal dispersion (%)
CoMo/50Al-50Ti	0.3840	18.42
CoMo/60Al-40Ti	0.3790	18.18
CoMo/70Al-30Ti	0.3125	15.02
CoMo/80Al-20Ti	0.2535	12.19
CoMo/90Al-10Ti	0.1751	8.40

CO-Chemisorption results are shown in Table 5.6. CoMo/50Al-50Ti has the highest CO uptake and metal dispersion (0.3840 cm³ STP/g and 18.42 %, respectively). In contrast, CoMo/90Al-10Ti has the lowest CO uptake and metal dispersion (0.1751 cm³ STP/g and 8.40 %, respectively). In addition, CO uptake and metal dispersion became lower when more TiO₂ were present in the support. The amount of active site of the catalyst was in agreement with the results of H₂-TPR. The TPR data was indicated that CoMo catalyst supported on TiO₂-rich support (CoMo/50Al-50Ti) is more reducible and sulfidable compared to the other catalysts. Therefore, CoMo/50Al-50Ti contained the highest amount of active site.

5.1.6 Temperature-programmed desorption with ammonia (NH₃-TPD)

The surface acidity of the CoMo catalyst was determined by the temperature programmed desorption with ammonia (NH₃-TPD). This technique was used to determine the acidity on surface of the catalysts in qualitative and quantitative forms. The temperature range in which the ammonia was desorbed was an indicator of the strength of the acid sites. The results from this measurement are presented in Figure 5.6 and Table 5.7.

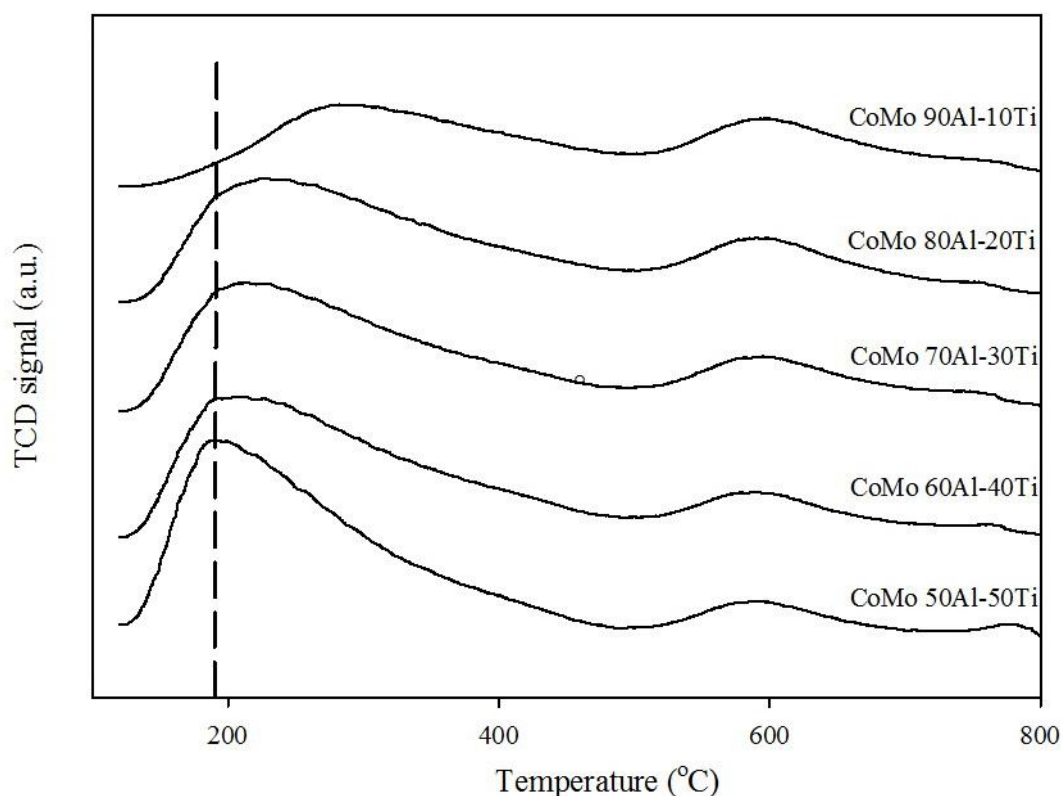


Figure 5.6 NH₃-TPD profiles of the CoMo catalysts

From NH₃-TPD experiments, the strength of the acid site can be evaluated by the temperature at which the adsorbed NH₃ desorbs as seen in Figure 5.6. Three peaks were observed at temperature ranges of 120-500 °C, 500-700 °C and 700-800 °C, which will be named weak, medium and strong acid sites, respectively [74]. The increase in Al₂O₃ in the support shifted the peak associated with weak acid site to higher temperature. It can be explained that Al₂O₃ increased the interaction between NH₃ and the catalyst.

In addition to qualitative view point, quantitative data were presented in Table 5.7. The data in this table was calculated from the integration of the three peaks of TCD signal versus time using a computer program, Chem Master™.

Table 5.7 Quantitative results from NH₃-TPD of the CoMo catalysts

Catalysts	Acid amount (mmol NH ₃ /g)	Weak acid amount (mmol NH ₃ /g)	Medium acid amount (mmol NH ₃ /g)	Strong acid amount (mmol NH ₃ /g)
CoMo/50Al-50Ti	0.947	0.733	0.155	0.059
CoMo/60Al-40Ti	0.810	0.632	0.157	0.021
CoMo/70Al-30Ti	0.815	0.602	0.189	0.024
CoMo/80Al-20Ti	0.808	0.582	0.204	0.022
CoMo/90Al-10Ti	0.610	0.370	0.240	-

The total acidities of the CoMo catalysts were determined by NH₃-TPD as amounts of NH₃ desorbed per mass of the catalysts (see Table 5.7). The result from NH₃-TPD shows that the total acidity of CoMo/50Al-50Ti catalysts was higher than that of other catalysts, which can be attributed to the higher content of TiO₂ in catalyst support. Moreover, The total acidity was also separated according to weak, medium and strong acidities. The weak and strong acid sites on the CoMo catalysts increased with increasing TiO₂ content. However, amount of medium acid sites decreased with increasing in the TiO₂ content. Moreover, the amount of weak acid site is greater than the other two acid sites, i.e., medium and strong acid sites. The activities of the catalysts was believed to depend on the weak acidity. The high surface acidity of the catalyst can improves the cracking ability. Moreover, the acidity of TiO₂ could increase the catalytic activity by facilitating hydrogenolysis of C-S bond [61].

5.2 Catalytic activity test

The experiment for catalytic activity test involved three stages of the investigation. Firstly, the effect of sulfur compound on the hydrodesulfurization activity was investigated. Secondly, the effect of the presence of nitrogen compound on the HDS activity was investigated. Finally, the effect of the concentration nitrogen compound on hydrodesulfurization and hydrodenitrogenation activities were investigated by varying the nitrogen compound content in the feed. So the feeds were divided into three groups. The first feed consisted of dibenzothiophene (DBT) with a sulfur content of 2000 ppm in diesel oil. The second feed was mixture of DBT and pyridine in diesel oil with 2000 ppm of sulfur and 500 ppm of nitrogen, respectively. Finally, the third feed consisted of DBT with a sulfur content of 2000 ppm and pyridine with various nitrogen contents (100, 200, 300, 400, and 500 ppm) in diesel oil. Hydrodesulfurization and hydrodenitrogenation activities were measured. These samples were analyzed for total sulfur and nitrogen contents, which then were used to calculate HDS and HDN activities as followed.

$$\text{HDS activity (\%)} = \frac{S_1 - S_2}{S_1} \times 100 \%$$

$$\text{HDN activity (\%)} = \frac{N_1 - N_2}{N_1} \times 100 \%$$

Where

S_1	is sulfur content in feed
S_2	is sulfur content in product
N_1	is nitrogen content in feed
N_2	is nitrogen content in product

The average activities of CoMo catalysts are presented in Figure 5.7. In details, the first bar on the left is the average HDS activities of the catalysts in case of the feed containing only DBT. The second bar, in the middle was the average HDS activities of the catalysts for the feeds containing both DBT and pyridine. Finally, the third bar on the right is the average HDN activities of the catalysts for the feeds

containing both DBT and pyridine. In addition to the bar chart, numerical results are also listed in Table 5.8.

5.2.1 Catalytic activities CoMo catalyst

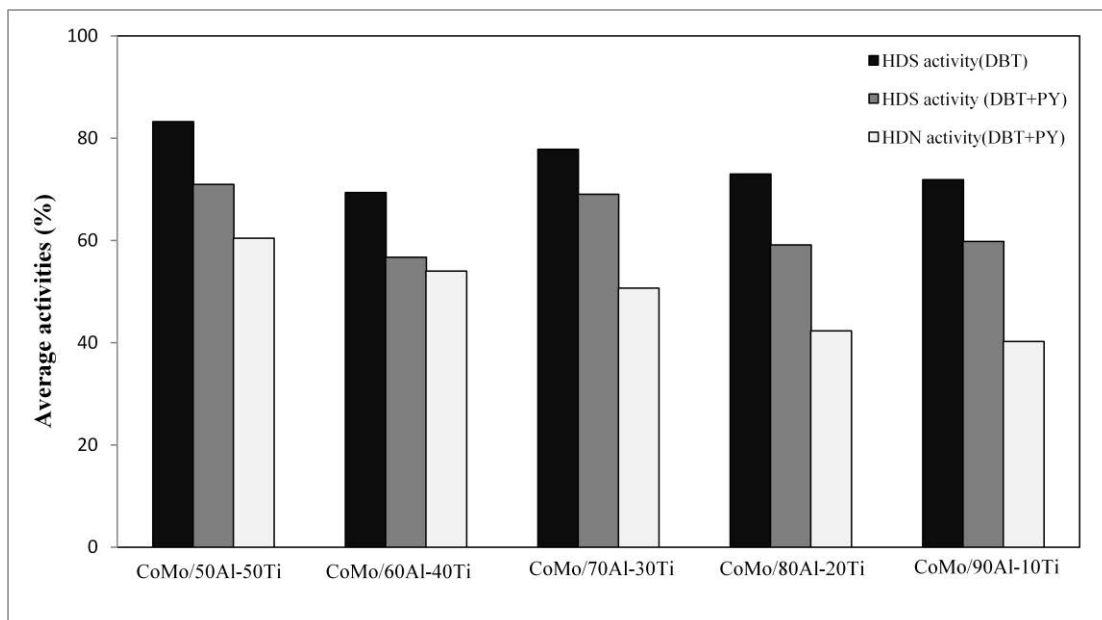


Figure 5.7 Catalytic activities of the CoMo catalysts

From Figure 5.7, in case of the feed that contained only DBT, The CoMo catalyst supported on 50Al-50Ti showed the highest HDS activities (83.22%). HDS activities of these catalysts appeared to decrease with increasing Al_2O_3 content in the support.

When the feeds contained both DBT and pyridine the highest HDS activities was observed for CoMo/50Al-50Ti (70.95%). Similar trend of decreasing HDS activity was observed in this case, too.

When the feeds contained both DBT and pyridine the highest HDS activities was observed for CoMo/50Al-50Ti (60.44%). HDN activities of these catalysts appeared to decrease with increasing Al_2O_3 content in the support.

Table 5.8 Catalytic activities of the CoMo catalysts

Catalysts	HDS activities (%)		HDN activities (%)*
	DBT	DBT + pyridine	
CoMo/50Al-50Ti	83.22	70.95	60.44
CoMo/60Al-40Ti	69.35	56.72	54.00
CoMo/70Al-30Ti	77.84	69.05	50.67
CoMo/80Al-20Ti	73.00	59.14	42.34
CoMo/90Al-10Ti	71.80	59.83	40.26

* Feed is mixture of DBT and pyridine

5.2.2 Effect of nitrogen compound for HDS and HDN on CoMo catalyst

The inhibition of HDS activity has been studied extensively. The inhibitors investigated included aromatics, nitrogen compound, sulfur compound, type of reactor and operating conditions. Of these, nitrogen compounds have been identified as the one with the most detrimental effect. The study found that the presence of nitrogen compounds in feed stream greatly reduced HDS activity of the catalyst. Knudsen et al. said that the nitrogen compounds present in the feed were the strong inhibitors for the HDS reaction through both hydrogenation and hydrogenolysis pathways [75]. The HDS of DBT occurred less frequently through the hydrogenation pathway because of the nitrogen compounds poisoning of the acidic sites of the catalyst, as confirmed by Nagai et al [35].

Only two catalysts (i.e., CoMo/50Al-50Ti and CoMo/60Al-40Ti) were selected to investigate the effect of nitrogen compound. The results are illustrated in Figures 5.8 and 5.9. Clearly, CoMo/50Al-50Ti catalyst gave the higher activity than CoMo/60Al-40Ti catalyst for all concentrations of nitrogen. HDS and HDN activities of two catalysts were lower when the concentration of pyridine became greater probably because nitrogen compounds were the strong inhibitors for both HDS and HDN reactions. So active site on the catalyst for hydrotreatment was hindered by the presence of nitrogen in pyridine [76].

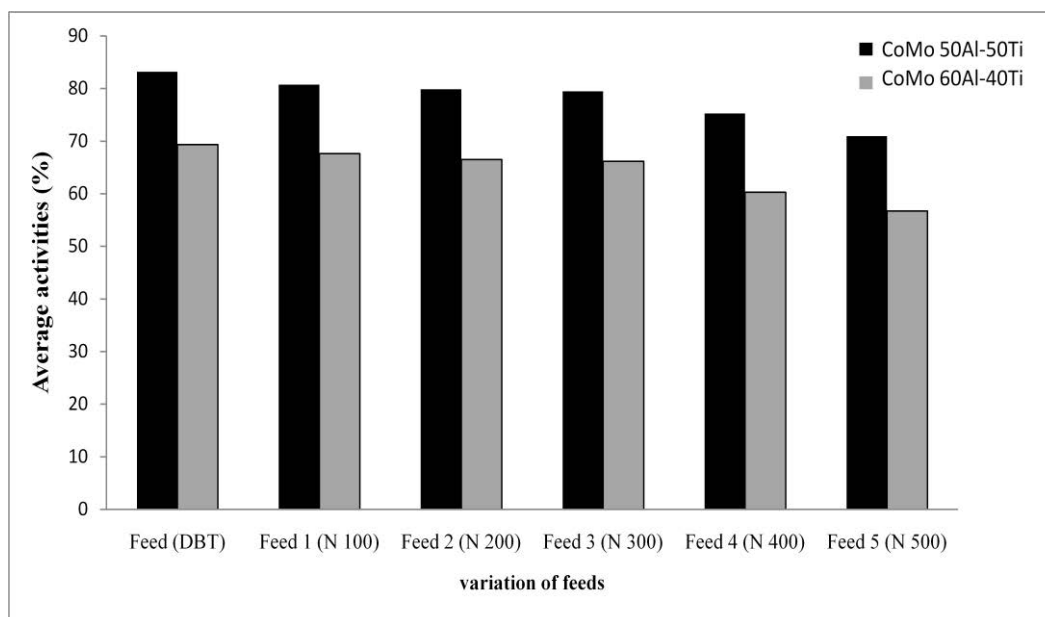


Figure 5.8 HDS activity with feed that contained various amount of nitrogen of the CoMo catalysts

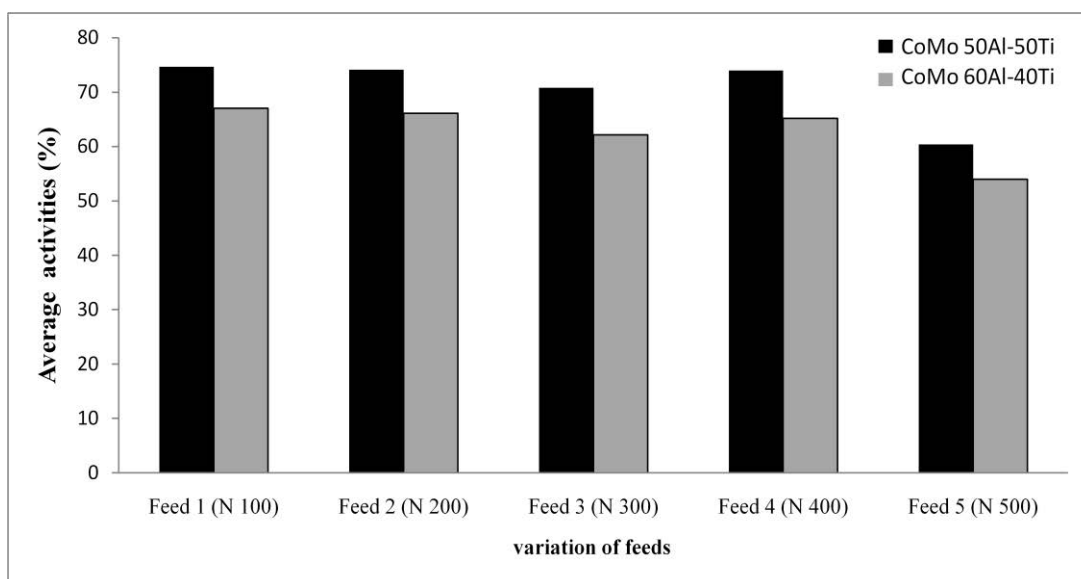


Figure 5.9 HDN activity with feed that contained various amount of nitrogen of the CoMo catalysts

Both HDS and HDN activities for CoMo/50Al-50Ti that contained more TiO₂ in the support were higher probably because TiO₂ could facilitate the reduction of metal, as seen from H₂-TPR results (see Figure 5.5 and Table 5.5). In addition, TiO₂ in the support increased the surface acidity of the catalyst as seen from NH₃-TPD results (see Table 5.7). Moreover, TiO₂ in the support increased amount of active site and metal dispersion as seen from (see Table 5.6), leading to higher catalytic activ

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

In this chapter, section 6.1 provides the conclusions of this study on the catalytic activities of the CoMo catalysts for hydrodesulfurization and hydrodenitrogenation. Additionally, recommendations of this research for future study are given section 6.2.

6.1 Conclusions

1. Al_2O_3 - TiO_2 mixed oxide supports were synthesized by a sol-gel method. The amount of TiO_2 that was incorporated into Al_2O_3 increased the surface acidity of catalysts.
2. Considering the reduction behaviors, addition of TiO_2 in mixed oxide supports led to greater reduction of Mo to the lower state by lowering the metal-support interaction of catalyst.
3. HDS and HDN activities for CoMo/50Al-50Ti catalyst were the highest due to larger TiO_2 content in the other catalysts.
4. The presence of pyridine in diesel oil decreased both HDS and HDN activities. Higher concentration of pyridine led to further reduction in HDS and HDN activities.

6.2 Recommendations

1. The support containing other oxide could be studied for the effect of oxide support on the activity of hydrodesulfurization.
2. Active species on the catalysts should be varied for study the effect of metal components on the Al_2O_3 - TiO_2 mixed oxide supports.
3. The effect of nitrogen compounds should be investigated for other nitrogen compound

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APPENDICES

APPENDIX A

CALCULATION FOR CATALYST PREPARATION

Preparation of CoMo catalysts was shown as follow:

1. Cobalt (II) nitrate hexahydrate

Formula: $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$

Molecular weight: 291.04 g/mol

Purity: 99.999 wt.% metal

2. Ammonium heptamolybdate tetrahydrate

Formula: $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$

Molecular weight: 1235.88 g/mol

Purity: 99.98 wt.% metal

The catalysts contained composition of cobalt and molybdenum at 2.93 and 13.7 wt.% based on metal, respectively.

Example: For 5 g of the catalyst

$$\text{Co} = 0.0293 \times 5 = 0.1465 \text{ g}$$

$$\text{Mo} = 0.137 \times 5 = 0.6850 \text{ g}$$

$$\text{Support} = 5 - 0.293 - 1.37 = 3.337 \text{ g}$$

For Co 0.293 g (molecular weight of cobalt is 58.93 g/mol) required was prepared from $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$:

$$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} = \frac{\text{Mw of } \text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}}{\text{Mw of Co} \times 0.99999} \times \text{weight of Co required}$$

$$= \frac{291.04}{58.93 \times 0.99999} \times 0.293$$

$$= 1.4471 \text{ g}$$

For Mo 1.37 g (molecular weight of molybdenum is 95.94 g/mol) required was prepared from $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$:

$$(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O} = \frac{\text{Mw of } (\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}}{\text{Mw of Mo} \times 7 \times 0.9998} \times \text{weight of Mo required}$$

$$= \frac{1235.88}{95.94 \times 7 \times 0.9998} \times 1.37$$

$$= 2.5217 \text{ g}$$

APPENDIX B

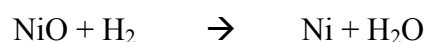
CALCULATION FOR HYDROGEN CONSUMPTION

For determining the amount of H₂ consumption for H₂-TPR in each catalyst, it can be assumed that phase of CoO and MoO₃ were reduced with H₂ to Co and Mo, respectively.

Assumption

For the CoMo catalysts, it can be assumed that the major species of calcined the CoMo catalysts is NiO. We used standard NiO for calibration in calculation of H₂ consumption. When 0.1 g of NiO has integral area between TCD signal versus time equal to 220.26 units for complete reduction.

For NiO reduction:



From this equation:

$$\text{Mole of H}_2 \text{ for complete reduction} = \text{Mole of NiO used}$$

Calculation of the calibration of H₂ consumption using NiO (has 220.26 area units for complete reduction)

$$\begin{aligned} \text{Mole of H}_2 \text{ consumption} &= \text{mole of NiO} \\ &= 1.3389 \times 10^{-3} \text{ mol} \\ &= 6.0787 \times 10^{-6} \text{ mol/area unit} \end{aligned}$$

$$\text{Integral area of the calcined catalyst} = X \text{ unit}$$

$$\text{The amount of H}_2 \text{ consumption} = 6.0787 \times 10^{-6} \times X \text{ unit}$$

APPENDIX C

ADSORPTION-DESORPTION DATA

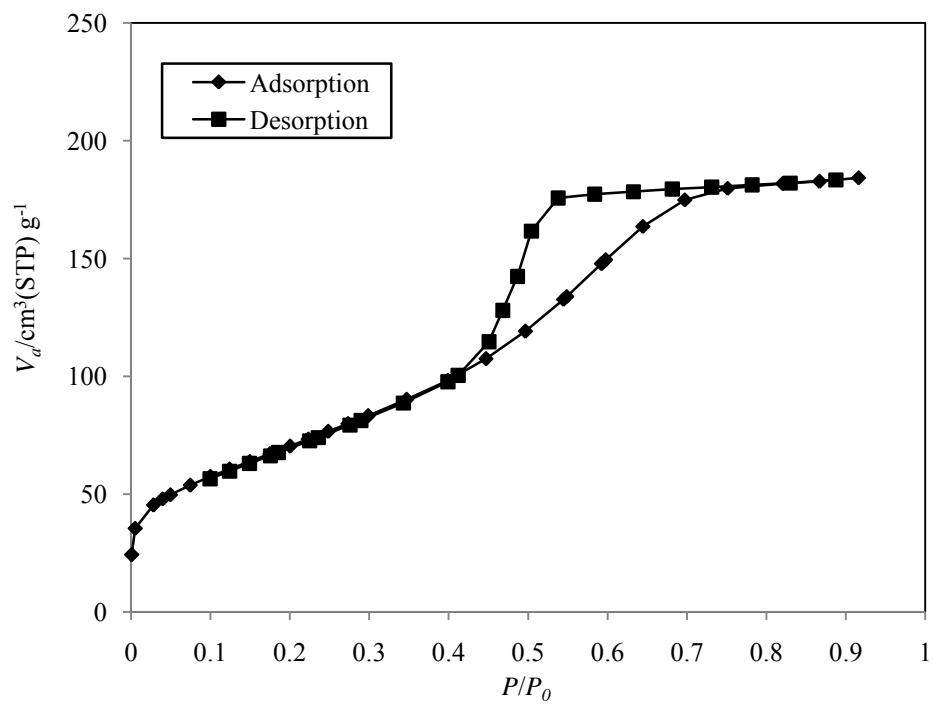


Figure C.1 Adsorption-desorption isotherm of 50Al-50Ti support

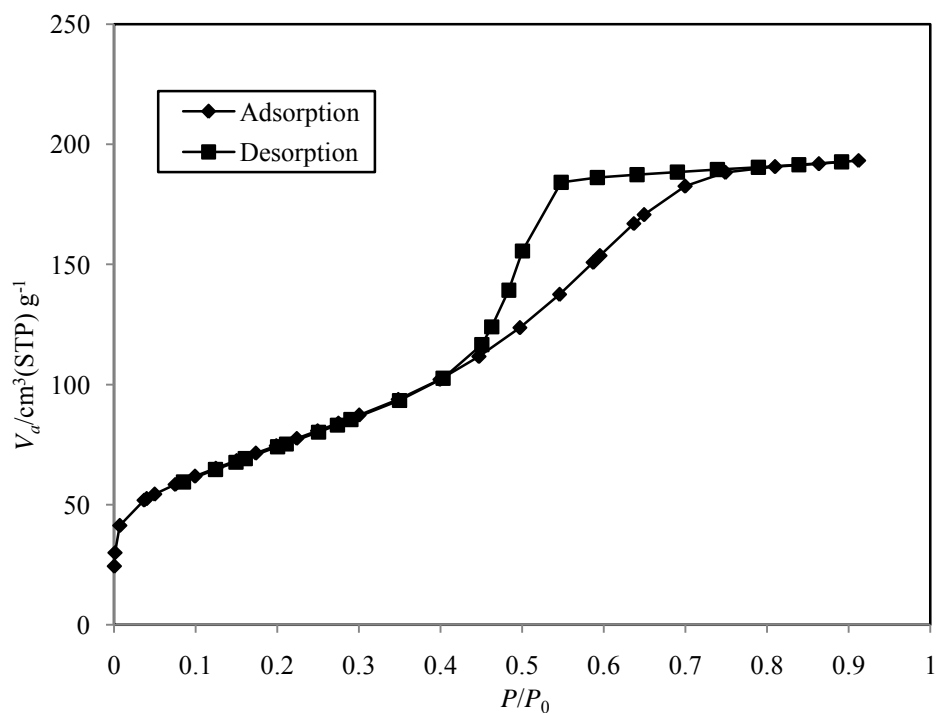


Figure C.2 Adsorption-desorption isotherm of 60Al-40Ti support

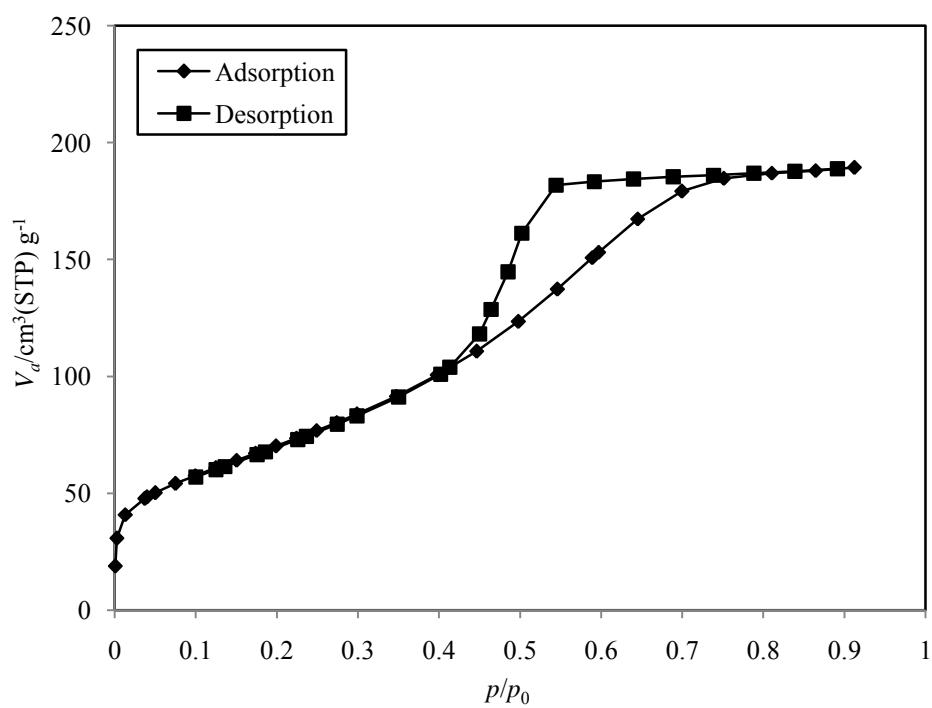


Figure C.3 Adsorption-desorption isotherm of 70Al-30Ti support

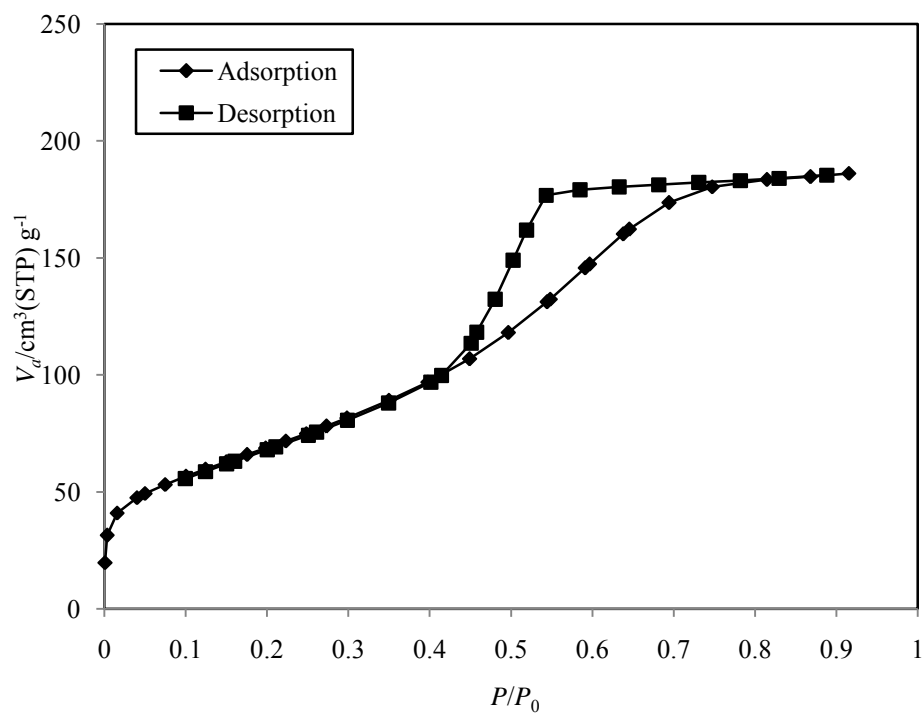


Figure C.4 Adsorption-desorption isotherm of 80Al-20Ti support

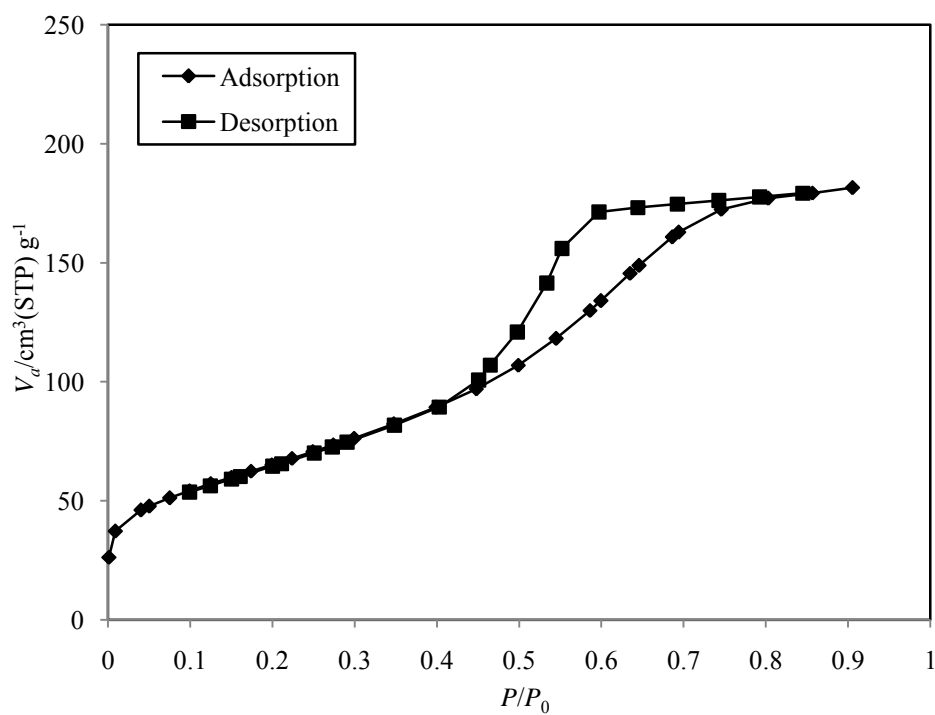


Figure C.5 Adsorption-desorption isotherm of 90Al-10Ti support

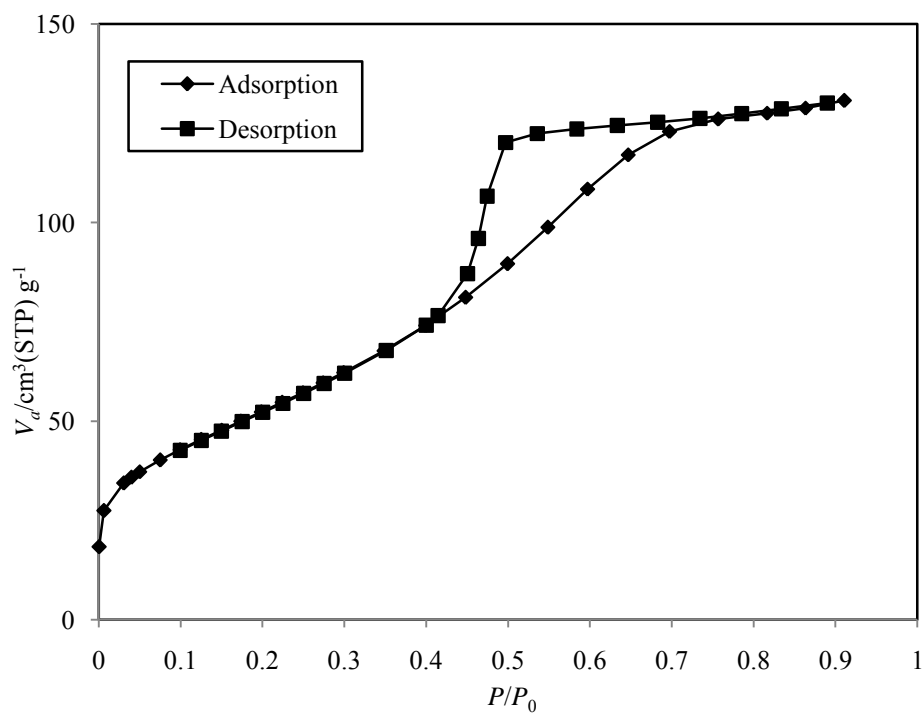


Figure C.6 Adsorption-desorption isotherm of CoMo/50Al-50Ti catalyst

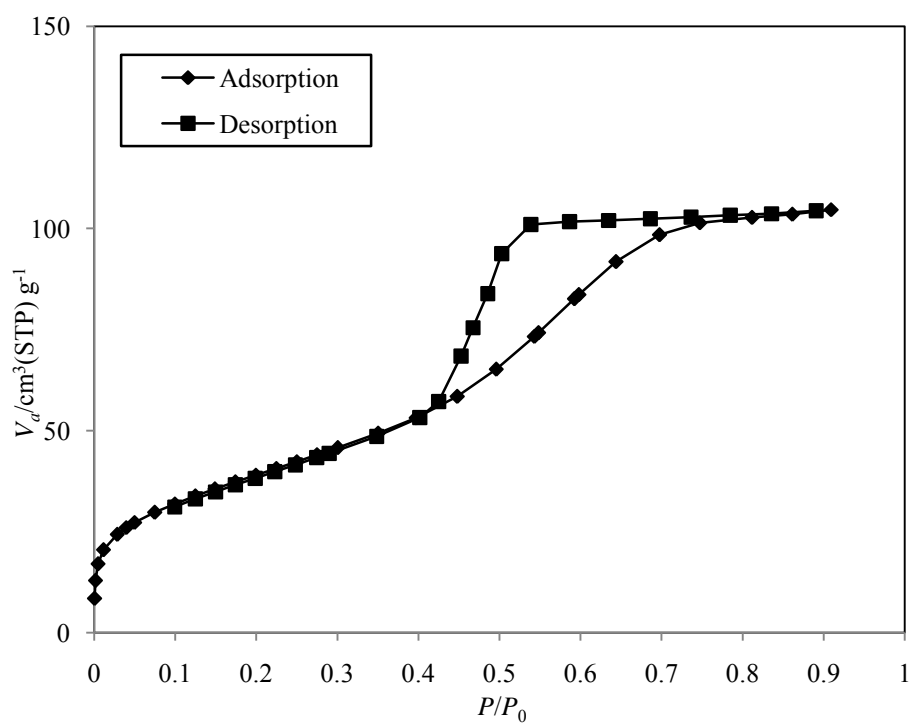


Figure C.7 Adsorption-desorption isotherm of CoMo/60Al-40Ti catalyst

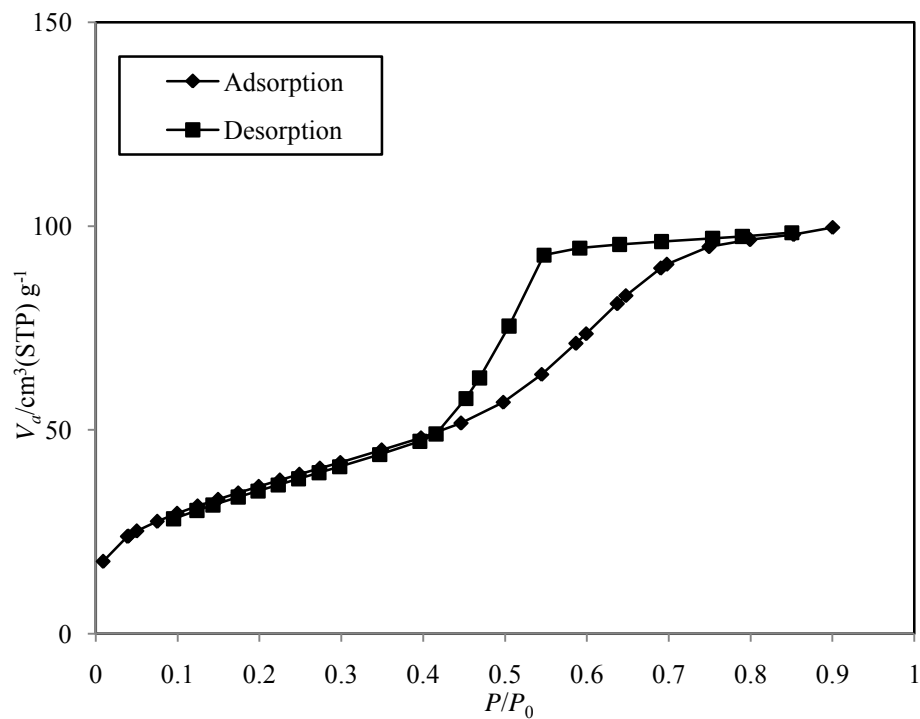


Figure C.8 Adsorption-desorption isotherm of CoMo/70Al-30Ti catalyst

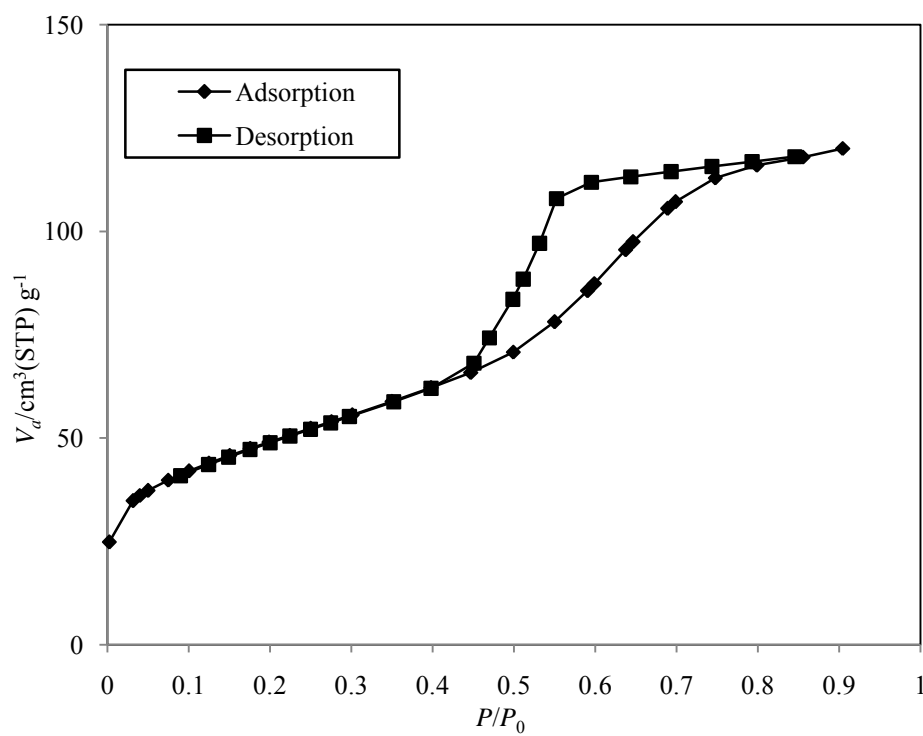


Figure C.9 Adsorption-desorption isotherm of CoMo/80Al-20Ti catalyst

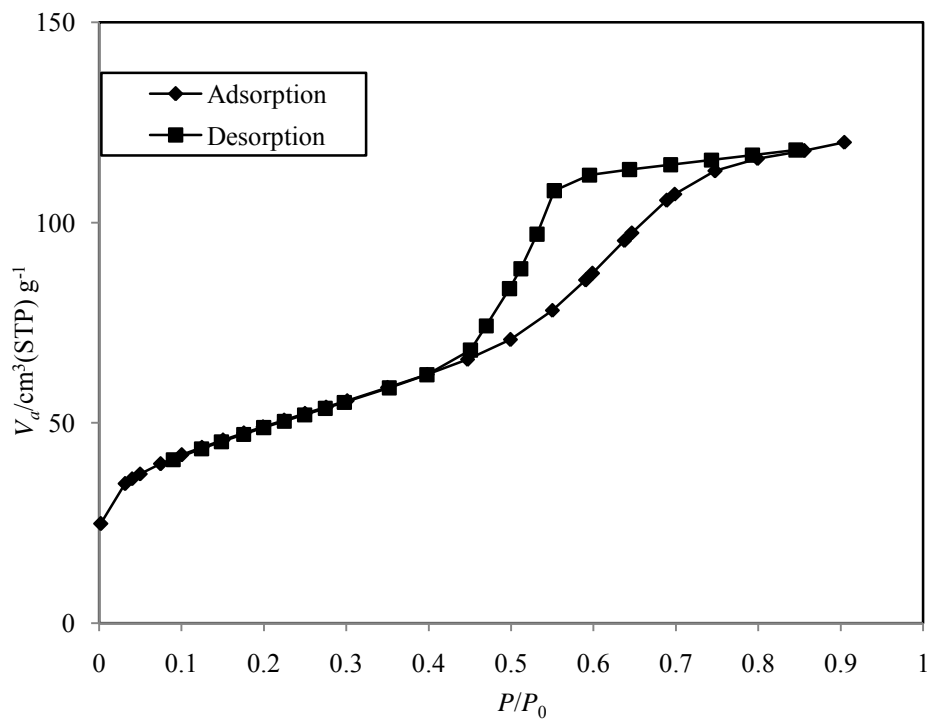


Figure C.10 Adsorption-desorption isotherm of CoMo/90Al-10Ti catalyst

APPENDIX D

CALCULATION FOR METAL DISPERSION

Carbon monoxide (CO) chemisorption is a technique for determining active sites of the catalysts.

For calculation a metal dispersion of the CoMo catalysts (2.93 wt.% Co and 13.7 wt.% Mo):

$$\begin{aligned}
 \text{Mw average} &= (\text{wt.\% of Co} \times \text{Mw of Co} + \\
 &\quad \text{wt.\% of Mo} \times \text{Mw of Mo}) / (\text{wt.\% of Co} + \text{wt.\% of Mo}) \\
 &= (0.0293 \times 58.93 + 0.137 \times 95.94) / (0.0293 + 0.137) \\
 &= 89.42 \text{ g/mol}
 \end{aligned}$$

Example: For 0.05 g of the Catalyst that it has CO uptake 0.384 cm³ STP/g

$$\begin{aligned}
 \text{Co} &= 0.05 \times 0.0293 \\
 &= 1.47 \text{ mg} \\
 \text{Mo} &= 0.05 \times 0.137 \\
 &= 6.85 \text{ mg} \\
 \text{Metal amount} &= 1.47 + 6.85 \text{ mg} \\
 &= 8.32 \text{ mg}
 \end{aligned}$$

Assume one CO molecule will chemisorb with one molecule of metals (Co or Mo)

$$\begin{aligned}
 \text{Mole of metals} &= \text{Mole of CO} \\
 &= 0.384 / 22400 \text{ mol} \\
 &= 0.017 \text{ mmol}
 \end{aligned}$$

$$\text{Amount of metals} = 0.017 \times \text{Mw average}$$

$$= 0.017 \times 89.42$$

$$= 1.533 \text{ mg}$$

$$\text{Metal dispersion (\%)} = \frac{\text{Amount of metal by CO uptake}}{\text{Amount of metal by the catalyst}} \times 100$$

$$= \frac{1.533 \text{ mg}}{8.32 \text{ mg}} \times 100$$

$$= 18.42$$

VITA

Miss Teraporn Leungon was born on October 6th, 1987 in Chanthaburi, Thailand. She finished high school from Princess Chulabhorn's College Chonburi in 2006. She graduated bachelor degree in Chemical Engineering from Faculty of Engineering and Industrial Technology, Silpakorn University. She continued her master's study at Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University in June 2011.

PUBLICATION

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