

CHAPTER III

EXPERIMENTAL

In the present work, ammonium tetrathiomolybdate $(\text{NH}_4)_2\text{MoS}_4$ and tetrabutylammonium thiomolybdate precursor $[(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_4\text{N}]_2\text{MoS}_4$ were used *in situ* to prepared active unsupported MoS_2 catalysts for hydrodesulfurization of a most refractory model compound of dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene(4,6-DMDBT). Hydrodesulfurization of real oil feedstocks, straight run gas oil (SRGO) of 6,100 ppmS and light cycle oil (LCO) of 310 ppmS were also investigated, the experiment was divided into:

1. To synthesize and characterize tetrabutylammonium thiomolybdate (TBATM) precursor.
2. To characterize MoS_2 catalyst generated *in situ* from decomposition of ammonium tetrathiomolybdate (ATM) and tetrabutylammonium thiomolybdate (TBATM) precursors with and without cobalt promoter.
3. To study on various effects for the hydrodesulfurization of DBT and 4,6-DMDBT using *in situ* generated MoS_2 catalyst.
4. To study the hydrodesulfurization of real oil feedstock; straight run gas oil (6100 ppmS) and light cycle oil (310 ppmS).

The detail of the experiments was explained in the following:

3.1 Reagents and solvents

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

Table 3.1 Chemical reagents and suppliers

Chemicals	Suppliers
Ammonium tetrathiomolybdate	Aldrich Chemical Company, Inc., USA.
Benzothiophene	Fluka Chemies A.G., Switzerland
Biphenyl	Fluka Chemies A.G., Switzerland
2-Bromethyl benzene	Fluka Chemies A.G., Switzerland
Cobalt(II) acetate tetrahydrate	Fluka Chemies A.G., Switzerland
Cobalt(II) acetylacetonate	Fluka Chemies A.G., Switzerland
Cobalt(II) chloride	Fluka Chemies A.G., Switzerland
Cobalt(II) nitrate hexahydrate	Fluka Chemies A.G., Switzerland
Cobalt oxide powder	Fluka Chemies A.G., Switzerland
Cyclohexylbenzene	Fluka Chemies A.G., Switzerland
Decahydronaphthalene	Fluka Chemies A.G., Switzerland
Dibenzothiophene	Fluka Chemies A.G., Switzerland
4,6-Dimethyldibenzothiophene	Aldrich Chemical Company, Inc., USA.
1,5-Hexadiene	Fluka Chemies A.G., Switzerland
High purity hydrogen gas (99.99%)	Thai Industrial Gas Co., Ltd., Thailand
High purity nitrogen gas (99.99%)	Thai Industrial Gas Co., Ltd., Thailand
Isopropanol	Lab Scans Co., Ltd., Ireland
Light cycle oil	PTT Plc., Thailand
Molybdenum sulfide	Fluka Chemies A.G., Switzerland
Nickel(II) acetylacetonate	Fluka Chemies A.G., Switzerland
Nickel(II) nitrate hexahydrate	Fluka Chemies A.G., Switzerland
Pyridine	Fluka Chemies A.G., Switzerland
Straight run gas oil	Thai Oil Plc., Thailand
Tetrabutylammonium bromide	Fluka Chemies A.G., Switzerland
Thiophene	Aldrich Chemical Company, Inc., USA.

3.2 Equipments and apparatus

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

3.2.1 Schlenk line

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

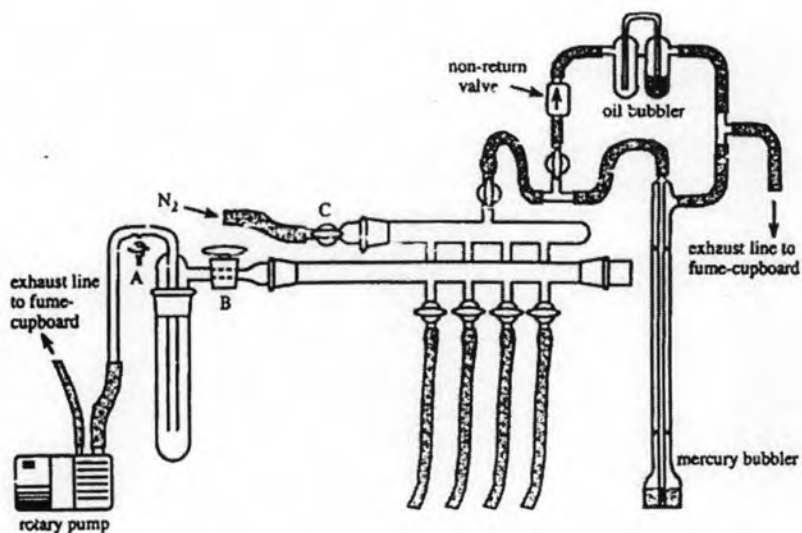


Figure 3.1 Schlenk line.

3.2.2 Schlenk flask

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



Figure 3.2 Round-bottomed Schlenk flask.

3.2.3 Vacuum pump

A pressure of 10^{-3} to 10^{-1} mmHg was adequate for the vacuum supply to the vacuum line in the Schlenk line using Edward RV5 vacuum pump..

3.2.4 Inert gas supply

Ultra high purity nitrogen gas (99.99%) was passed through three column packed with 4 °A molecular sieves, NaOH and P₂O₅, respectively. The inert gas was used to feed in the nitrogen line in Schlenk line.

3.2.5 Syringe and needle

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

3.2.6 Hydrogen gas supply

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

3.2.7 High pressure reactor

3.2.7.1 Reactor

The Parr 4842 reactor was a batch high pressure stirred autoclave model from the Parr Instrument Company, shown in Figure 3.3. The reactor consists of 600 ml stainless steel, cylindrical bomb, bomb head, bomb heater, two stirrers and a cooling coil. The reactor could work at a pressure range of 0 - 2,000 psig and a temperature range of 0 - 350 °C.



Figure 3.3 Parr 4842 high pressure reactor.

3.2.7.2 Reactor fitting

The stirred unit of the reactor was supplied with convenient fittings for hanging the various functions. The parts are indicated with the following letters.

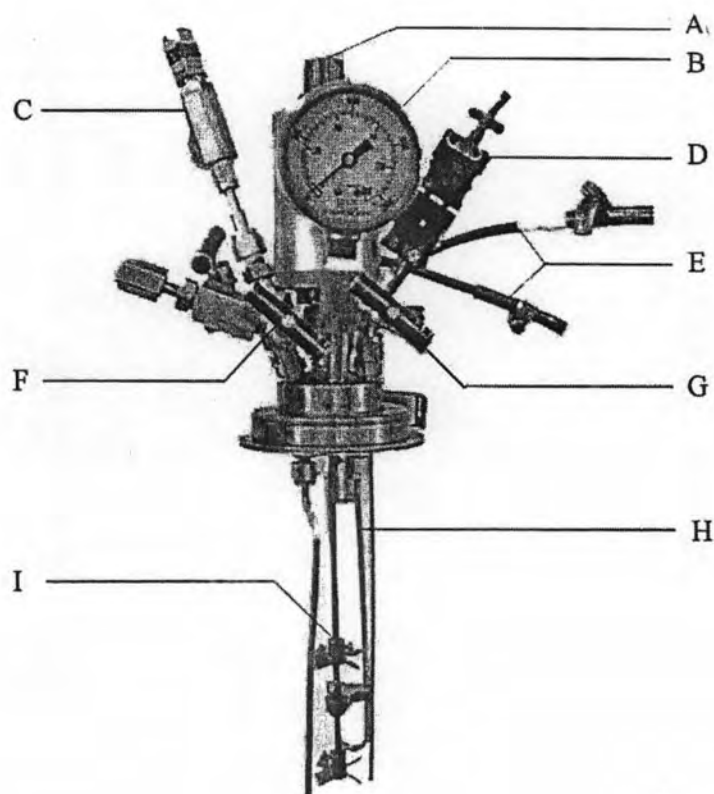


Figure 3.4 Reactor fitting.

- A. A stirrer magnetic drive system
- B. A pressure guage
- C. A safety rupture disc
- D. A dual thermocouple
- E. A water cooling channel
- F. A gas inlet value
- G. A gas release value
- H. A heating rod
- I. A stirring shaft with 6-blade turbine type impeller

3.3 Characterization instruments

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

3.3.1 Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared spectra were recorded on Nicolet FT-IR Impact 410 Spectrophotometer. The solid samples were prepared by pressing the sample with KBr. Infrared spectra were recorded between 400 cm^{-1} to $4,000\text{ cm}^{-1}$ in transmittance mode.

3.3.2 Nuclear magnetic resonance (NMR)

^1H -NMR and ^{13}C -NMR spectra were obtained on Bruker ACF 200 MHz. The NMR spectra were measured in deuterium oxide (D_2O) at room temperature. The center peak of deuterium oxide were used as the internal reference at 4.6 ppm.

3.3.3 Thermogravimetric analyzer (TGA)

TGA involves heating a sample in an inert or oxidizing atmosphere and measuring the weight. The weight change over specific temperature ranges provides indications of the composition of the sample and thermal stability. Measurement of the residue mass of substances according to a controlled temperature program was made using Netzsch STA 409 thermobalance of TA Instruments with an increment of $20^\circ\text{C}/\text{min}$. heating rate under a N_2 flow of $20\text{ cm}^3/\text{min}$.

3.3.4 X-ray diffraction (XRD)

The XRD patterns of catalysts were obtained on Rigaku, DMAX 2002 Ultima Plus X-ray powder diffractometer equipped with a monochromator and a Cu-target

X-ray tube (40 kV, 30 mA) and angles of 2θ ranged from 5 - 80 degree. X-ray diffraction is used to obtain information about the structure and composition.

3.3.5 Nitrogen adsorption (Brunauer-Emmett-Teller method (BET))

BET specific surface area of the catalysts was carried out using a BELSORP-mini. The principle of this method is by adsorption of nitrogen onto the surface. Based upon one adsorbed layer, the quantity of adsorbed material gave directly the total surface area of the sample.

3.3.6 Scanning electron microscope (SEM) and energy dispersive x-ray (EDX)

The SEM photograph, energy dispersive x-ray (EDX) and x-ray mapping were performed using JEOL JSM-5800LV for the surface investigation. A Zygo NewView 5000 white light interferometer (WLI) with a 50 °A objective and 0.4 zoom magnifications provided surface profiles to quantify the surface microroughness.

3.3.7 X-ray fluorescence spectrometry (XRF)

Sulfur content in real oil feedstocks: straight run gas oil (SRGO) and light cycle oil (light cycle oil) was determined using a SISON S X-ray fluorescence spectrometer ARL 8410 (ASTM D4294 method).

3.3.8 Gas chromatography (GC)

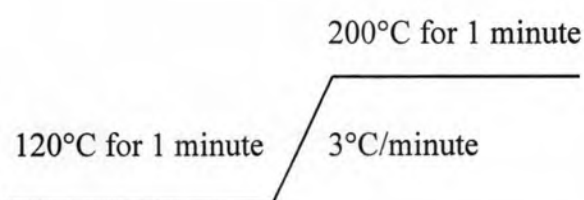
3.3.8.1 Gas chromatography for sulfur model compounds

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

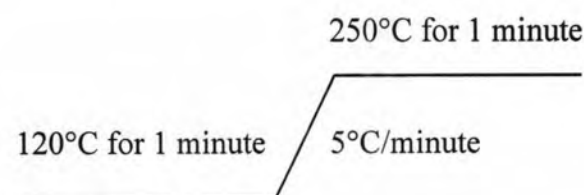
Table 3.2 The GC conditions for sulfur model compounds

Substrate	Carrier gas	Carrier gas pressure (kPa)	Detector Temperature (°C)	Injector Temperature (°C)
DBT	Nitrogen	80	300	250
4,6-DMDBT	Nitrogen	80	300	270

Programmed temperature for DBT :



Programmed temperature for 4,6-DMDBT :



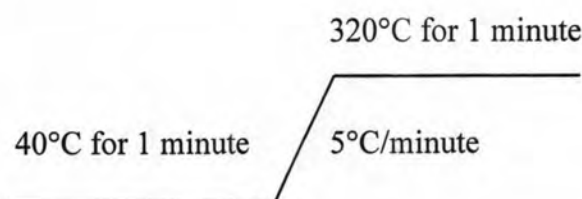
3.3.7.2 Gas chromatography (GC) for real oil feedstocks

Gas chromatography analyses were performed on a Varian CP-3800 gas chromatograph equipped with a flame ionization detector and a 30 m (0.25 mm i.d., 0.25 μm film thickness) CP-5 capillary column. The condition used for the determination of straight run gas oil (SRGO) and light cycle oil (LCO) was set as follows:



Injector : 270 °C
 Detector : 300 °C
 Carrier gas : Helium
 Flow rate : 1.5 ml/min.
 Split ratio : 1:2

Programmed temperature for real oil feedstocks:



3.4 Synthesis of tetrabutylammonium thiomolybdate (TBATM) [32]

Ammonium tetrathiomolybdate $(\text{NH}_4)_2\text{MoS}_4$ (0.6 g, 2.3 mmol) was dissolved in 30 mL of water, and which this solution was stirred at room temperature under nitrogen atmosphere, a solution of tetrabutylammonium bromide $[\text{CH}_3(\text{CH}_2)_3]_4\text{NBr}$ (1.48 g, 4.6 mmol) in 20 mL of water was added, which immediately precipitated $(\text{N}[\text{CH}_3(\text{CH}_2)_3]_4)_2\text{MoS}_4$ as red crystals which were then filtered under vacuum until dry and stored under nitrogen atmosphere.

The compound was characterized by ^1H NMR and ^{13}C NMR.

3.5 Thermal analysis (TGA) of thiomolybdate precursors

Thermogravimetric analysis (TGA) was used to characterize the thermal decomposition of ammonium tetrathiomolybdate (ATM) and tetrabutylammonium thiomolybdate (TBATM) precursors.

3.6 Characterization of *in situ* generated MoS₂ and Co/MoS₂ catalysts

In situ generated MoS₂ catalyst from decomposition of ammonium tetrathiomolybdate (ATM) and tetrabutylammonium thiomolybdate (TBATM) before and after HDS reaction were characterized by the following techniques.

- X-ray diffraction (XRD)
- BET surface area, N₂ adsorption-desorption isotherm and BJH pore size distributions
- Scanning electron microscope (SEM)

3.7 Hydrodesulfurization of sulfur model compounds

Dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) common refractory sulfur compound in the crude oil, were chosen as model substrate for HDS reaction.

3.7.1 Hydrodesulfurization of dibenzothiophene (DBT)

All catalytic reactions of dibenzothiophene were performed in a Parr Model 4842 high-pressure batch reactor at desired conditions. The reactant mixture consisted of dibenzothiophene 0.368 g (2mmol), ammonium tetrathiomolybdate (ATM) precursor 0.052 g (0.2 mmol) or tetrabutylammonium thiomolybdate (TBATM) precursor 0.142 g (0.2 mmol) was added in 50 mL of decalin solvent. The reactor was purged three times with hydrogen gas and then pressurized to the desired pressure. The stirring speed was kept constant at 600 rpm. The reaction time was started when the required temperature was reached. After a measured time interval, the reactor was cooled to room temperature and slowly depressurized. After the reaction, the MoS₂ catalysts were separated from the reaction mixture by filtration, washed with isopropanol to remove residual hydrocarbons and dried at room temperature. *In situ* generated MoS₂ catalysts were characterized by XRD, BET and SEM. The contents of the reaction were analyzed using GC-FID (using 2-bromoethyl benzene as internal

standard). All runs were performed in duplicate. The mean standard deviation for catalytic measurements was about 5%.

Parameters affecting the hydrodesulfurization reaction were studied as follows:

A. Effect of reaction time

The hydrodesulfurization of DBT using MoS_2 *in situ* generated from ATM precursor was investigated by varying reaction time: 0.5, 1.0, 1.5 and 2 h.

B. Effect of hydrogen pressure

The hydrodesulfurization of DBT using MoS_2 *in situ* generated from ATM precursor was investigated by varying hydrogen pressure: 10, 25 and 30 atm.

C. Effect of catalyst precursor amount

The hydrodesulfurization of DBT using MoS_2 *in situ* generated from ATM precursor was investigated by varying molar ratio of DBT/ATM :10/1, 20/1 and 50/1 (based on Mo).

D. Effect of types of catalyst precursor

Ammonium tetrathiomolybdate (ATM) and tetrabutylammonium thiomolybdate (TBATM) precursors were compared with commercial MoS_2 for hydrodesulfurization of DBT.

E. Effect of nitrogen compound

Pyridine was chosen as a representative of inhibiting nitrogen compounds on HDS of DBT using MoS_2 *in situ* generated from ATM by varying amount of pyridine in the range of 10, 40 and 70 ppm.

F. Effect of water addition

The hydrodesulfurization of DBT using MoS₂ *in situ* generated from ATM and TBATM precursor was investigated by adding water at the molar ratio of H₂O/ATM = 450, 600 or mole ratio of H₂O/TBATM = 450, 600. The reaction with H₂O alone was investigated for comparison.

F. Effect of cobalt or nickel promoter

The hydrodesulfurization of DBT using MoS₂ *in situ* generated from ATM and TBATM precursor were investigated by adding promoter. Different types of promoter were investigated: cobalt(II) acetate, cobalt(II) acetylacetonate, cobalt(II) chloride, cobalt(II) nitrate, cobalt oxide powder, nickel(II) acetylacetonate and nickel(II) nitrate.

3.7.2 Hydrodesulfurization of 4,6-dimethyldibenzothiophene

Hydrodesulfurization of 4,6-dimethyldibenzothiophene was carried out in Parr Model 4842 high-pressure batch reactor. The reactant mixture consists of 4,6-DMDBT 0.212 g (1 mmol), ammonium tetrathiomolybdate precursor 0.026 g (0.1 mmol) or tetrabutylammonium thiomolybdate (TBATM) precursor 0.708 g (0.1 mmol) and different amount of water were added in 50 mL of decalin solvent. The reactor was purged three times with hydrogen gas. Finally, it was pressurized to 30 atm hydrogen pressure at room temperature. The reactor was heated to 350 °C. The reaction time was started when the required temperature was reached. After a measured time interval, the reactor was cooled to room temperature and slowly depressurized. The stirring speed was kept constant at 600 rpm. After the reaction, the catalysts were separated from the reaction mixture by filtration, washed with isopropanol to remove residual hydrocarbons and dried at room temperature. *In situ* generated MoS₂ catalysts were characterized by XRD, BET and SEM. The contents of the reaction were analyzed using GC-FID (using 2-bromoethyl benzene as internal standard). All runs were performed in duplicate. The mean standard deviation for catalytic measurements was about 5%.

The hydrodesulfurization of 4,6-DMDBT using MoS_2 *in situ* generated from ATM precursor was investigated by adding different amount of water. The reaction with water alone was also investigated for comparison.

3.8 Hydrodesulfurization of real oil feedstocks

3.8.1 Hydrodesulfurization procedure of real oil feedstocks

The hydrodesulfurization of real feedstocks were carried out in a Parr Model 4842 high-pressure batch reactor at 350 °C under 30 atm H_2 pressure. A prescribed amount of ammonium tetrathiomolybdate (ATM) catalyst precursor and different amount of water were added in 50 mL of straight run gas oil (6100 ppmS; 9.531 mmolS) or 50 ml of light cycle oil (310 ppmS; 0.484 mmolS). The reactor was purged three times with hydrogen gas. Finally, it was pressurized to 30 atm hydrogen pressure. The stirring speed was kept constant at 600 rpm. during all the experiments. The reaction time was started when the required temperature was reached. After a measured time interval, the reactor was cooled to room temperature and slowly depressurized. After the reaction, the catalysts were separated from the reaction mixture by filtration, washed with isopropanol to remove residual hydrocarbons and dried at room temperature. The contents of the reaction were analyzed using XRF and GC-FID. All runs were performed in duplicate. The mean standard deviation for catalytic measurements was about 5%.

Concentration of the remaining sulfur compounds in real oil feedstocks were determined by the XRF method (ASTM D4294). The specified sulfur compounds: thiophene (T), benzothiophene (BT), dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) in real oil feed stocks before and after HDS reaction were checked with GC-FID. The peak area of specified sulfur compounds were used to determine content of each compound.

The effect of water addition on hydrodesulfurization of real oil feedstocks were also investigated.