

CHAPTER III

EXPERIMENTAL SECTION

3.1 Materials

Catalyst preparation materials:

- Degussa P-25 nonporous titania (TiO_2) with BET area of $50 \pm 5 \text{ m}^2/\text{g}$ was used as the catalyst support.
- Ammonium heptamolybdate, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ was analytical research grade (AR grade) and obtained from J.T. Baker company.
- Nitric acid (HNO_3) of 65% concentration used for adjusting pH was obtained from Merck company.
- Ammonium hydroxide (NH_4OH) of 28% concentration used for adjusting pH was obtained from AJAX Chemical company.

Reaction materials:

- Thiophene ($\text{C}_4\text{H}_4\text{S}$) of 99% purity was from Merck company.

All of gases were used without any further purification:

- Nitrogen (N_2) of 99.999% purity used for flushing and dilution of standard gas was obtained from Thai Industrial Gas Co., Ltd (TIG).
- Hydrogen (H_2) of 99.999% purity used as a reactant gas was obtained from Thai Industrial Gas Co., Ltd (TIG).
- The mixture of 5.5% of n-butene, 1.5% of cis-2-butene, 2.0% of tran-2-butene, 0.5% of n-butane, 0.5% of 1,3-butadiene in nitrogen used as a standard gas was obtained from Thai Industrial Gas Co., Ltd (TIG).

3.2 Catalyst Preparation

The molybdenum on titania catalysts were prepared by impregnation technique and equilibrium adsorption technique. Titania was dried at 100 °C for 12 hours to eliminate volatile water.

3.2.1 Impregnation Technique

This technique was used to prepare 5% loading of molybdenum on titania. 1.3564 grams of ammonium heptamolybdate was dissolved in 4.8 ml distilled water. The solution is so-called “precursor” which is clear in color.

Two grams of dried titania was put into a crucible. The precursor was added dropwise to the titania. The resulting catalyst was dried at 110 °C for 24 hours, and calcined in air at 500 °C for 24 hours.

3.2.2 Equilibrium Adsorption Technique

This technique was used to prepare catalysts at less than a monolayer (4% Mo). Ammonium heptamolybdate solution was prepared at a pH of 2. The pH was adjusted by using nitric acid and ammonium hydroxide. The solution was diluted with distilled water until the concentration of the solution reached 0.007 M. Two grams titania was equilibrated with 250 ml of the solution for 100 hours. Then, the catalyst was filtered from the excess solution. The catalyst was dried at 110 °C for 24 hours and calcined in air at 500 °C for 24 hours.

3.3 Catalyst Characterization

3.3.1 Elemental Analyzer (CHNS)

The elemental analyzer is the equipment used to evaluate the basic elements in the sample which are carbon, hydrogen, nitrogen and sulfur. The sample is burnt in an oxidizing atmosphere and the products are then separated by a column and detected with the TCD detector.

The elemental analyzer was used to determine the sulfidation level of the sulfided catalyst. It was a Perkin-Elmer Series II CHNS/O Analyzer 2400.

The operation conditions were :

combustion furnace temperature = 975 °C

reduction furnace temperature = 501 °C

detector oven temperature = 82.6 °C

3.3.2 Fourier Transform Infrared Spectrometer (FT-IR)

Infrared Spectroscopy is one of the techniques used to determine the functional groups of the substances by taking the advantage of the infrared absorption. The absorbance peaks of oxide and sulfide catalysts were detected with BIO-RAD FTS-45A SPC 3200 using KBr as a background. It was operated at the region of 4400-400 cm^{-1} with a resolution of 8.

3.3.3 Raman Spectroscopy

Raman spectroscopy is a technique which uses the inelastic light scattering to determine the functional groups of substances. Some functional groups which do not appear in FT-IR spectra, may be detected by the raman spectroscopy. The raman spectra of oxide and sulfided catalysts were obtained with a Spex Triplemate spectrograph coupled with a Jobin Yvon Spex cooled CCD detector. The 488-nm line of a Lexel Model No. 95 Ar⁺ laser was used as the excitation source. Typical power at the pellet surface was on the order of 200-300 milliwatt. The spectra were measured in the range of 416 to 1104 cm⁻¹.

3.4 Apparatus

The apparatus for the experiment is schematically shown in Figure 3.1. It consists of four sections; the gas blending system, the thiophene bubbling bottle, the differential flow reactor and the analytical instrumentation.

3.4.1 Gas Controlling System

The mass flow transducers and controller model 840 obtained from Sierra Instrument were used to control the flow rate of reactant gases.

The gases used in this work consisted of hydrogen, nitrogen and mixed standard gases. Nitrogen was used to dilute the standard gas and to

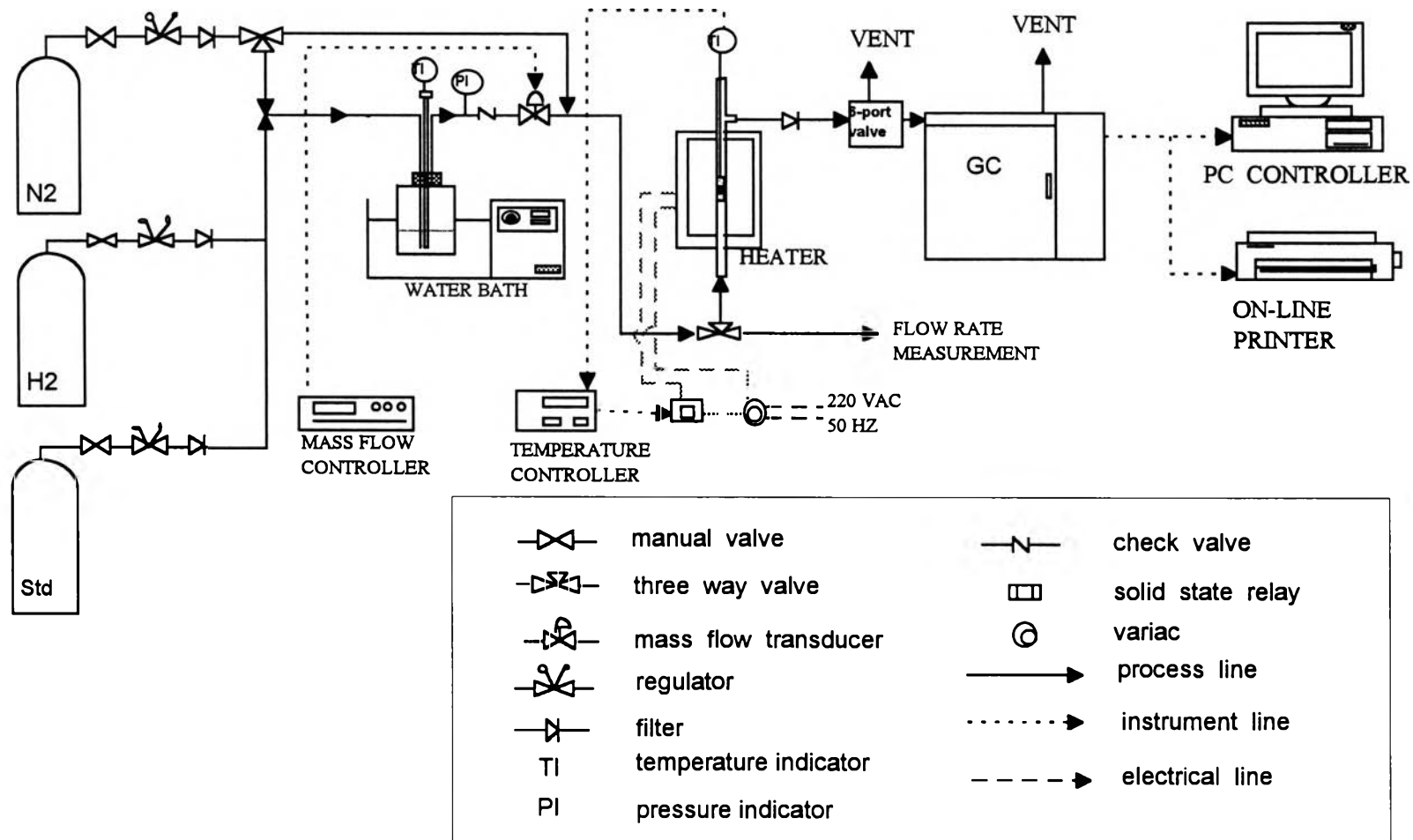


Figure 3.1 Schematic diagram of apparatus for experiment.

flush the system. All of gases passed through micron filters and flowed through the mass flow transducers, check valves were installed to prevent back flow.

3.4.2 Thiophene Bubbling Bottle

Hydrogen was passed through this section to bubble the liquid thiophene at various temperatures. The temperature was adjusted by using a Polyscience water bath model 9501. The thiophene vapor and hydrogen were then flowed through a check valve and a mass flow controller at a constant flow rate of 40 ml/min. The pressure in bubbling bottle was adjusted by using the mass flow controller at upstream of the bubbling bottle.

3.4.3 Differential Flow Reactor

The hydrodesulfurization was carried out in a 1/4 inch in diameter quartz reactor at atmospheric pressure. Fifty milligrams of catalyst was placed in the middle of the reactor. Fifty milligrams quartz wool was packed above the catalyst to prevent a catalyst loss due to entrainment in the gas and was placed at the bottom of the catalyst for support. The reactor was heated by an electrical heater and its temperature was controlled by a PID controller. The temperature of the reaction was measured using a type K thermocouple made of chromel-alumel and located at the top of quartz wool plug. The thermocouple was connected to a model UT37 temperature controller by Yokogawa Instrument. The controller was automatically self-tuned to set up the best proportional, integral and derivative control parameters. At steady temperature, the variation of temperature was ± 0.1 °C.

3.4.4 Analytical Instrumental

A model 8340 Gas Chromatograph (GC) by Fisons with a flame ionization detector (FID) was used to measure the product distribution qualitatively. The oven of GC was maintained at 30 °C. The separation of products was achieved with a 5-foot-long, 1/8-inch-diameter Teflon column packed with n-octane-Porasil C. The carrier gas was nitrogen with a flow rate of 25 ml/min. The injector and detector temperature were 150 °C and 200 °C respectively. The signal from the detector was analyzed by the Chrom-Card program.

Qualitative analysis was obtained by comparison of the product gas retention times with those of standard gases. Quantitative analysis was obtained using the calibration factors obtained with known concentration gases. The calibration was performed using the external standard technique. The cycle of each measurement was 15 minutes. The product gases included hydrogen sulfide, n-butane, n-butene, trans- and cis- butene. The C₄ products were used for calculating the thiophene conversion. Only trace amount of butadiene could be observed.

3.5 Activity and Selectivity Studies

The hydrodesulfurization reaction of thiophene over Mo/TiO₂ catalysts was studied at atmospheric pressure. After the catalyst was heated to the desired reaction temperature of 350 °C, the catalyst was pretreated under reducing conditions using a hydrogen flow rate of 40 ml/min for 12 hours. The pretreated catalyst was contacted with the reactant gas mixtures which were hydrogen and thiophene, at a constant total flow rate of 40 ml/min. The conversion was calculated every 15 minutes by measuring the amount of

C₄ products produced. The activity is defined as a conversion of thiophene per mg of molybdenum. The selectivity is the ratio of the rate constant of hydrogenation reaction (k_{HG}) to the rate constant of hydrodesulfurization reaction (k_{HDS}). The selectivity was measured using the amount of butane and total C₄ products as defined by Okamoto, et al. (1980):

$$\frac{k_{HG}}{k_{HDS}} = \left(\frac{X_B}{1 - X_B} \right) \left(\frac{1 - X_T}{X_T} \right)$$

where X_T = converted thiophene / initial thiophene

X_B = butane / C₄ products

The composition of thiophene in feed stream was adjusted to regulate the sulfur on the surface of the catalysts. The activity and selectivity of catalyst prepared by equilibrium adsorption technique with low molybdenum loading and impregnation technique with high molybdenum loading were compared at various concentrations of thiophene.