

CHAPTER III

EXPERIMENTAL

3.1 Material and Equipment

3.1.1 Chemicals

- Concentrated hydrochloric acid (HCl) was obtained from Mallinckrodt Chemicals
- Dibenzothiophene (C₁₂H₈S) was obtained from Acros Organics
- 1,2,3,4-Tetrahydronaphthalene (tetralin, C₁₀H₁₂) was obtained from Acros Organics
- Ammonium hydrogen difluoride ((NH₄)HF₂) was obtained from Unilab Corporation
- Hydrogen hexachloroplatinate (IV) hydrate (H₂PtCl₆.6H₂O) was obtained from Acros Organics
- Palladium (II) chloride (PdCl₂) was obtained from Carlo Erba
- γ -Alumina (Al₂O₃) was obtained from Saint-Gobian NorPro Corporation
- Acetone ((CH₃)₂CO) was obtained from Labscan Co. Ltd.
- Dodecane (C₁₂H₂₆) was obtained from Fluka Chemical

3.1.2 Gas

- Hydrogen (H₂, HP Grade) was obtained from Thai Industrial Gas Public Co.
- Helium (He, HP Grade) was obtained from Thai Industrial Gas Public Co.
- Nitrogen (N₂, HP Grade) was obtained from Thai Industrial Gas Public Co.

- Air (HP Grade) was obtained from Thai Industrial Gas Public Co.

3.1.3 Equipment

- Reaction system including high pressure liquid pump, mass flow controllers, stainless steel reactor, gas chromatograph, back pressure regulator, etc.
- Temperature programmed reduction (TPR)
- Hydrogen chemisorption
- X-ray photoelectron spectroscopy (XPS)
- Atomic adsorption spectroscopy (AAS)
- Magnetic plate
- Heater
- Oven
- Furnace
- Condenser
- Circulated water

3.2 Catalyst Preparation

The support used was a commercial gamma-alumina ($\gamma\text{-Al}_2\text{O}_3$, Saint-Gobian NorPro Corp) with a surface area of $274\text{ m}^2/\text{g}$, a pore volume of 1.11 ml/g and a pore diameter of 104 \AA . It was ground and sieved to 40-70 mesh to avoid the internal mass transfer limitation. Pt and Pd metals were loaded on gamma-alumina using the conventional incipient wetness impregnation technique (IWI) of hydrogen hexachloroplatinate hydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, Acros, 40% Pt) and palladium chloride (PdCl_2 , Carlo, 59.5% Pd), dissolved by deionized water and concentrated hydrochloric acid, respectively. The metal weight loadings were adjusted in order to have the same total metal molar fraction in all catalysts. In this study 1.8 wt% Pt, 0.8 wt% Pd for monometallic, and 0.7 wt% Pt - 0.6 wt% Pd co-impregnation for bimetallic catalysts on gamma-alumina with and without 3 wt% F were prepared by

varying calcinations temperatures and orders of impregnating between metal and F. After the impregnation, the catalyst was dried under an ambient temperature for 4 h, then dried in an oven at 110°C overnight, and finally calcined in a furnace at 500°C with a heating rate of 10°C/min for 2 h. The addition of ammonium hydrogen difluoride was conducted in the same manner as the metal, using deionized water as a solvent. The list of catalysts prepared and their abbreviation names are shown in Table 4.1.

3.3 Catalyst Characterization

In this work, catalysts were characterized by temperature programmed reduction (TPR), H₂ pulse chemisorption, X-ray photoelectron spectroscopy (XPS) and atomic adsorption spectroscopy (AAS). The procedure to characterize catalysts in each technique was demonstrated as follows:

3.3.1 Temperature Programmed Reduction (TPR)

Temperature programmed reduction was carried out in a 1/4" O.D. quartz reactor. Prior to the test, 50 mg of catalyst was packed in the reactor. For Pd and PtPd catalysts, dry ice was used to cool the sample to 10°C since PdO is an easily reducible oxide, even at room temperature. The TPR profiles were obtained by passing 5.0% H₂/Ar through the sample and waiting until the signal was stable for 20 min before heating the catalyst. The TPR runs were performed with a heating rate of 10°C/min to 700°C. The effluent gas was passed through a moisture trap to remove water and detected by thermal conductivity detector (TCD). A schematic flow diagram of Temperature programmed reduction is shown in Figure 3.1.

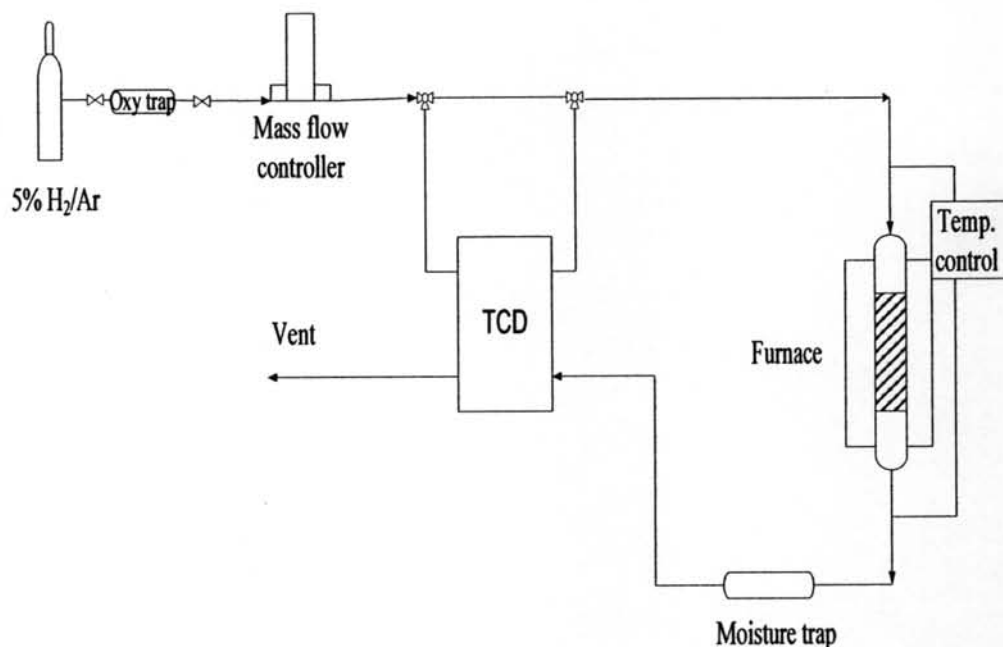


Figure 3.1 Schematic flow diagram of temperature programmed reduction.

3.3.2 H₂ Pulse Chemisorption

H₂ pulse chemisorption measurements were also done by a Thermoquest TPD/R/O 1100 instrument which determines percent metal dispersion on the surface of catalyst. Prior to the experiment, 100 mg of catalyst was reduced with hydrogen at 300°C for 1.5 h, to convert metal oxide into metallic metal, and then pretreated with nitrogen at 500°C for 1 h and cooled to room temperature. The effluent stream was monitored online by TCD detector.

3.3.3 X-ray Photoelectron Spectroscopy (XPS)

The atomic surface composition of the calcined catalysts was analyzed by XPS technique. X-ray photoelectron spectra were acquired with an Alpha 110 Thermo electron corporation with a hemispherical digital electronics analyzer model 8017 with monochromatic Mg K α ($h\nu = 1253.6$ eV) X-ray source. The binding energies (BEs) of Pd 3d, O 1s, F 1s, Al 2p and Cl 2p were referenced to the C 1s peak at 290 eV. This reference gave BE values with a precision of ± 5 eV. Atomic

surface contents were estimated from the areas of the peak, corrected using the corresponding sensitivity factors.

3.3.4 Atomic Adsorption Spectroscopy (AAS)

The actual contents of platinum (Pt) and palladium (Pd) loadings in the prepared catalysts were determined by an atomic absorption spectroscopy. The standard solutions of 1,000 ppm of Pt and Pd used in this work are manufactured by Merck. Firstly, a known weight around 0.15 g of a catalyst were digested in freshly mixing concentrated nitric acid and concentrated hydrochloric acid, usually in a volumetric ratio of one to three (aqua regia) for overnight. The solution was then diluted to the measuring range. The concentration of Pt and Pd were obtained by comparing its absorbance with the calibration curve of the standard solution. A Varian Spectra AA-300 was employed to determine the compositions of Pt and Pd in the catalysts prepared.

3.4 Catalytic Activity Testing

The catalytic activity measurements were carried out in a continuous fixed-bed stainless steel 3/4" O.D. reactor equipped with a thermowell to insert the thermocouple into the center of the catalyst bed. The catalytic activity was measured at a temperature of 300°C with a total pressure of 500 psig and H₂/HC molar ratio of 11. In each test, 40 mg of catalyst was used. The catalyst was reduced under a flow of H₂ at 500 psig for 2 h. After pretreatment, liquid feed was introduced to the reactor using a high-pressure pump. 1, 2, 3, 4-Tetrahydronaphthalene (tetralin, TL, Acros, 97+%) was used in this work. In the case of sulfur-containing feed, calculated amounts of dibenzothiophene (DBT; Aldrich, 99%) as a sulfur compound (350 ppm wt% for normal sulfur poisoning test) and dodecane as a diluent (dodecane: tetralin = 75:25) were added to the feed mixture. The products were online analyzed by a HP6890 gas chromatograph with FID using HP-5 column (diameter, 0.318 mm: length, 30 m). The schematic flow diagram and the experimental apparatus of hydrogenation reaction are shown in Figures 3.3 and 3.4, respectively.

The GC conditions were summarized as follows:

Injection temperature:	250°C
Oven temperature:	50 to 220°C (heating rate 10°C/min)
Carrier gas:	High purity helium
Carrier gas flow rate:	11.4 ml/min
Carrier gas velocity:	76 cm/sec
Column type:	Capillary column (HP-5)
Detector temperature:	250°C

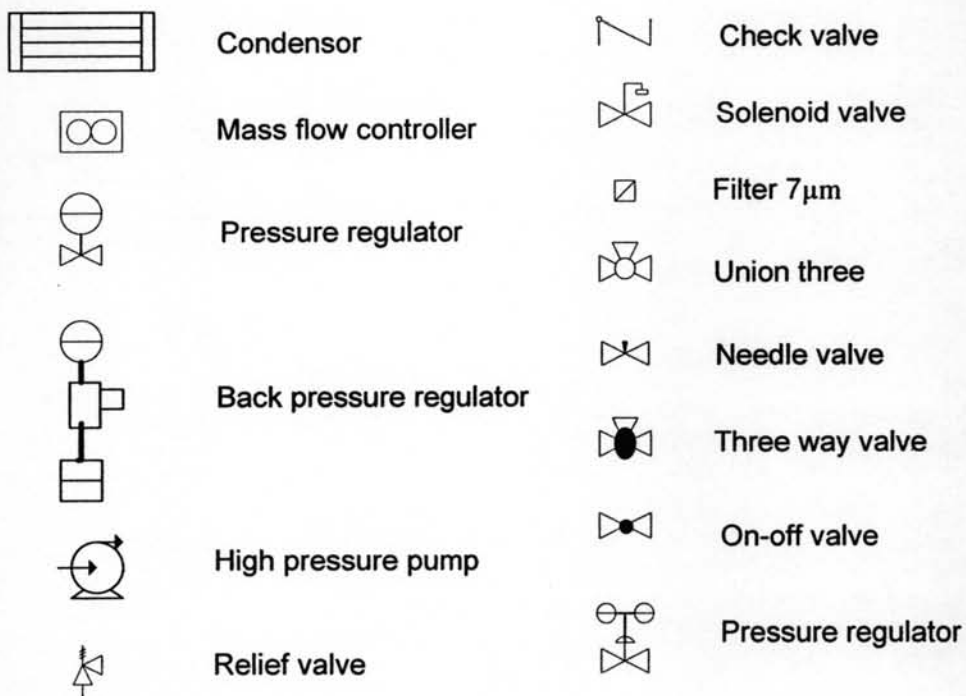
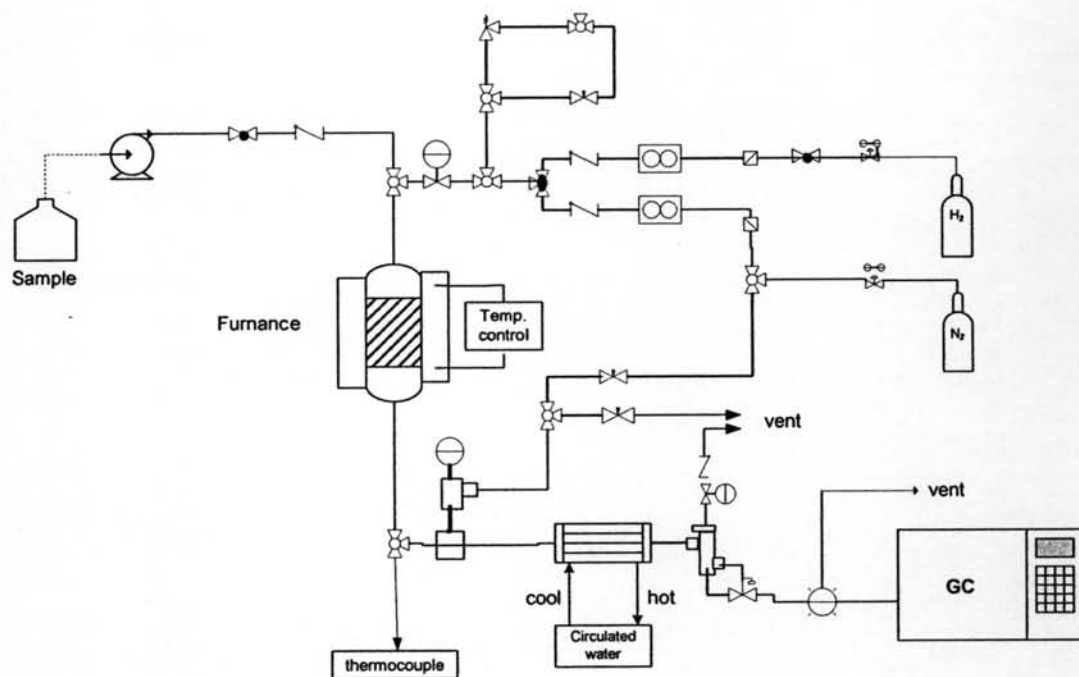


Figure 3.2 Schematic flow diagram of hydrogenation reaction.

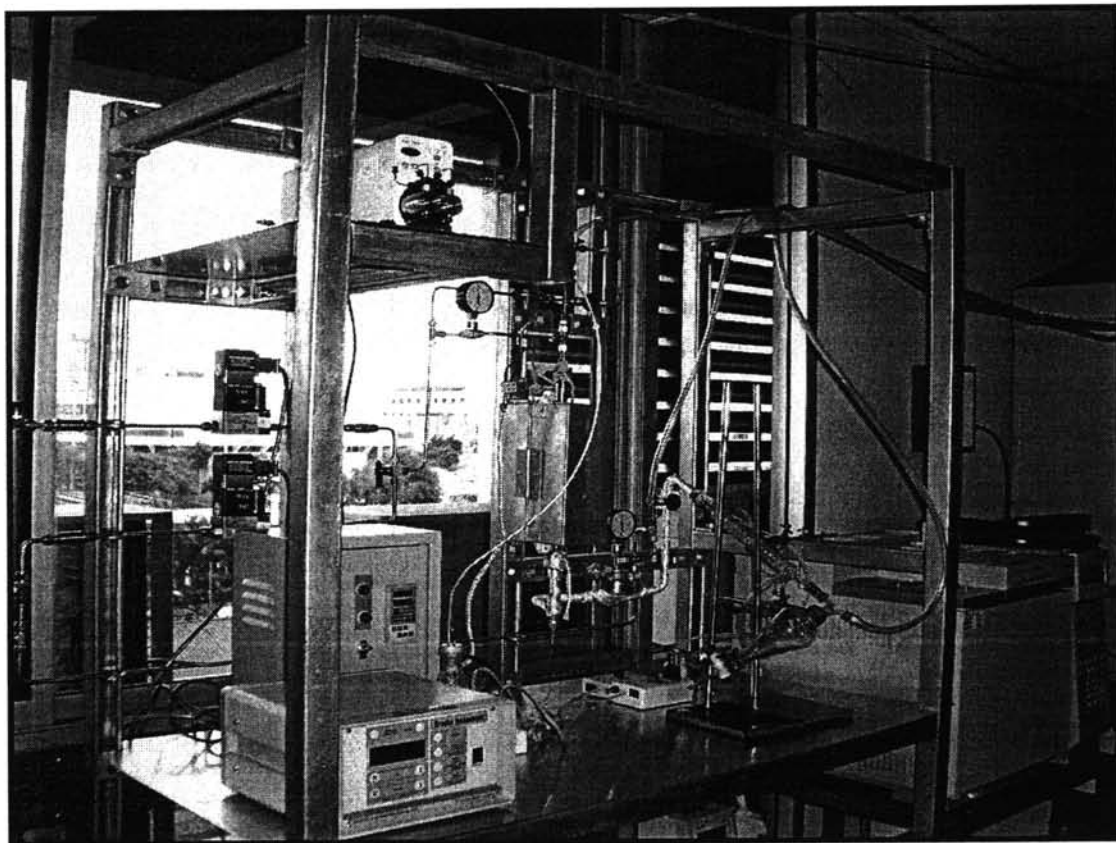


Figure 3.3 Experimental apparatus of hydrogenation reaction.