

CHAPTER III EXPERIMENTAL

3.1 Catalyst Preparation

Commercial gamma-alumina support ($\gamma\text{-Al}_2\text{O}_3$, Saint-Gobian NorPro Corp, surface area $274\text{ m}^2/\text{g}$, pore volume 1.11 ml/g and pore diameter 104 \AA) was ground and sieved to 40-70 mesh to avoid internal mass transfer limitation. Pt and Pd metals were loaded on gamma-alumina using conventional incipient wetness impregnation technique (IWI) of hydrogen hexachloroplatinate hydrate ($\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$, Acros, 40% Pt) and palladium chloride (PdCl_2 , Carlo, 59.5% Pd), dissolved by distilled 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 1.6 wt% Pt, 0.8 wt% Pd for monometallic, and 0.4 wt% Pt - 0.6 wt% Pd co-impregnation for bimetallic catalysts on gamma-alumina with and without 3 wt% F-promoter ($\text{NH}_4\text{F} \cdot \text{HF}$, Unilab) were prepared by varying calcination 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 $110\text{ }^\circ\text{C}$ overnight, and finally calcined in furnace with different calcination temperature at 250, 300 and $350\text{ }^\circ\text{C}$ with a heating rate of $10\text{ }^\circ\text{C}/\text{min}$ for 2 h. The list of prepared catalysts is shown in Table 4.1.

3.2 Catalyst Characterization

In this work, catalysts were characterized by Thermal Gravimetric Analysis (TGA), Temperature Programmed Reduction (TPR), Hydrogen Chemisorption, and Transmission Electron Microscopy (TEM). The procedure to characterize catalysts in each technique was demonstrated as following.

3.2.1 Thermal Gravimetric Analysis (TGA)

Thermal gravimetric analysis was carried out by Thermal gravimetric analyzer 2950, Dupont instrument with the flowing of air at an ambient temperature to 800°C with a heating rate of 10°C by using aluminum pan.

3.2.2 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 down 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 wait until the signal is 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). Schematic flow diagram of Temperature Programmed Reduction is shown in Figure 3.1.

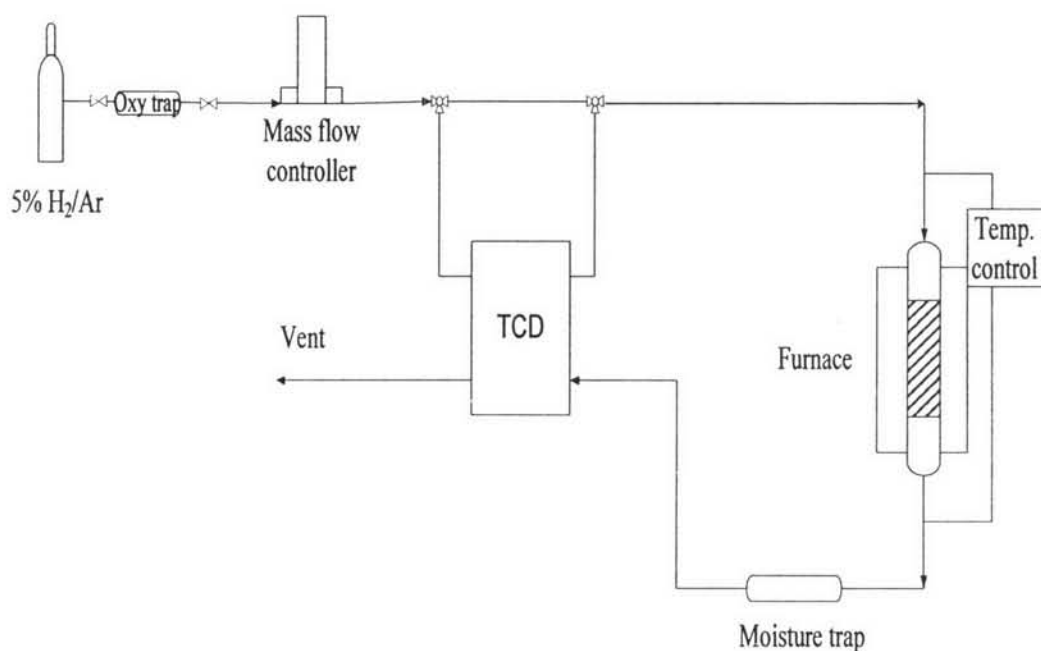


Figure 3.1 Schematic flow diagram of temperature programmed reduction.

3.2.3 Hydrogen Chemisorption

Hydrogen chemisorption was performed in the same apparatus as TPR with the pulse loop of 10 μ l. Prior to the experiment, 50 mg of catalyst was reduced with hydrogen at 300°C for 1.5 h, to convert metal oxide into metallic metal, and then purged by nitrogen at 300°C for 0.5 h and cooled down to room temperature, after that pulse the hydrogen gas to adsorb hydrogen on the surface of the catalyst. Volumetric hydrogen chemisorption was measured at 25°C and detected by thermal conductivity detector (TCD). The dispersion, hydrogen to metal molar ratio (H/metal), was calculated based on the mole of hydrogen chemisorbed on the catalyst. Schematic flow diagram of hydrogen chemisorption is shown in Figure 3.2.

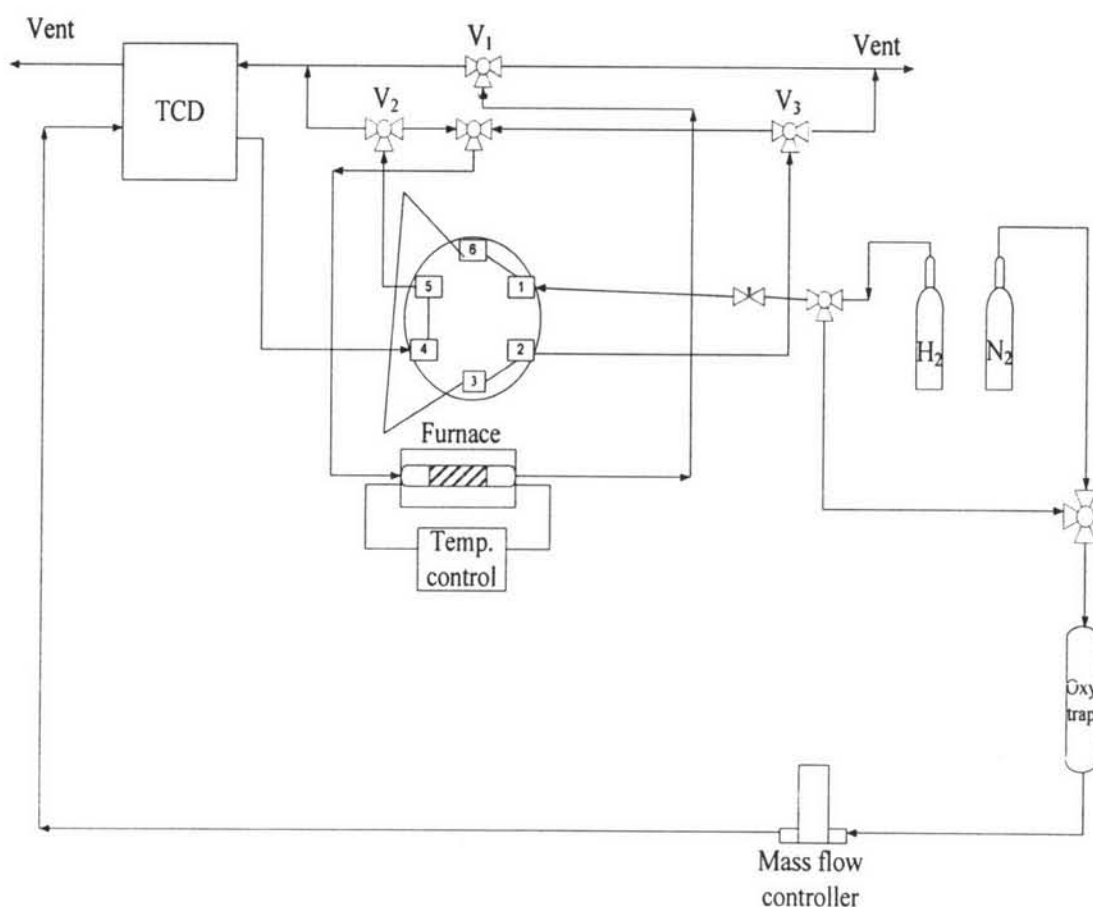


Figure 3.2 Schematic flow diagram of hydrogen chemisorption.

3.2.4 Transmission Electron Microscopy (TEM)

The catalyst was ground and suspended in methanol. The mixture was vibrated by ultrasound for 5 min. A few drops of the resulting suspension were deposited on a TEM grid and subsequently dried and evacuated before the analysis. The TEM images were obtained with a JEOL JEM-2010 TEM.

3.3 **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 the temperature of 275°C with a total pressure of 300 psig and H₂/HC molar ratio of 25. 30 mg of catalyst was used in each test. The catalyst was first reduced under flowing of H₂ at 300 psig for 2 h. After the pretreatment, the reactor was cooled down in H₂ to 275°C. Then, liquid feed was introduced to the reactor using a high-pressure pump. 1,2,3,4-Tetrahydronaphthalene (tetralin, TL, Across, 97+%) was used in this work. The products were online analyzed by a HP6890 gas chromatograph with FID using HP-5 column. The column of gas chromatograph was heated to 250°C from 60°C, an oven temperature to 110°C from 50°C, and the FID detector temperature to 250°C from 60°C with a heating rate of 10°C/min. Experimental apparatus and schematic flow diagram of hydrogenation reaction are shown in Figures 3.3 and 3.4, respectively.

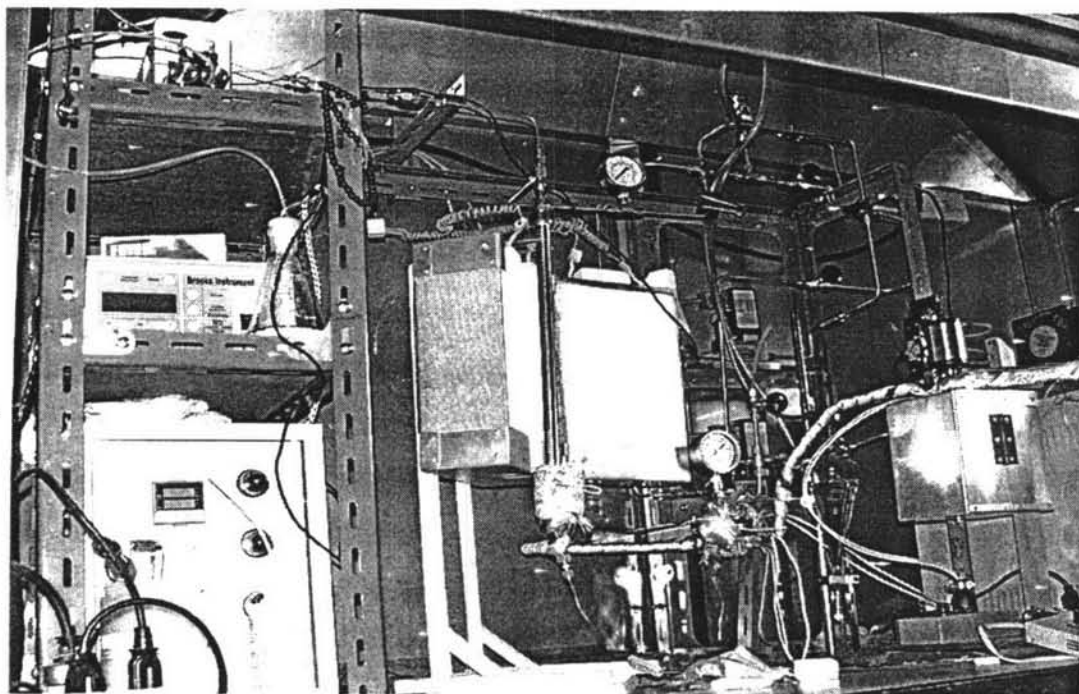


Figure 3.3 Experimental apparatus for hydrogenation reaction.

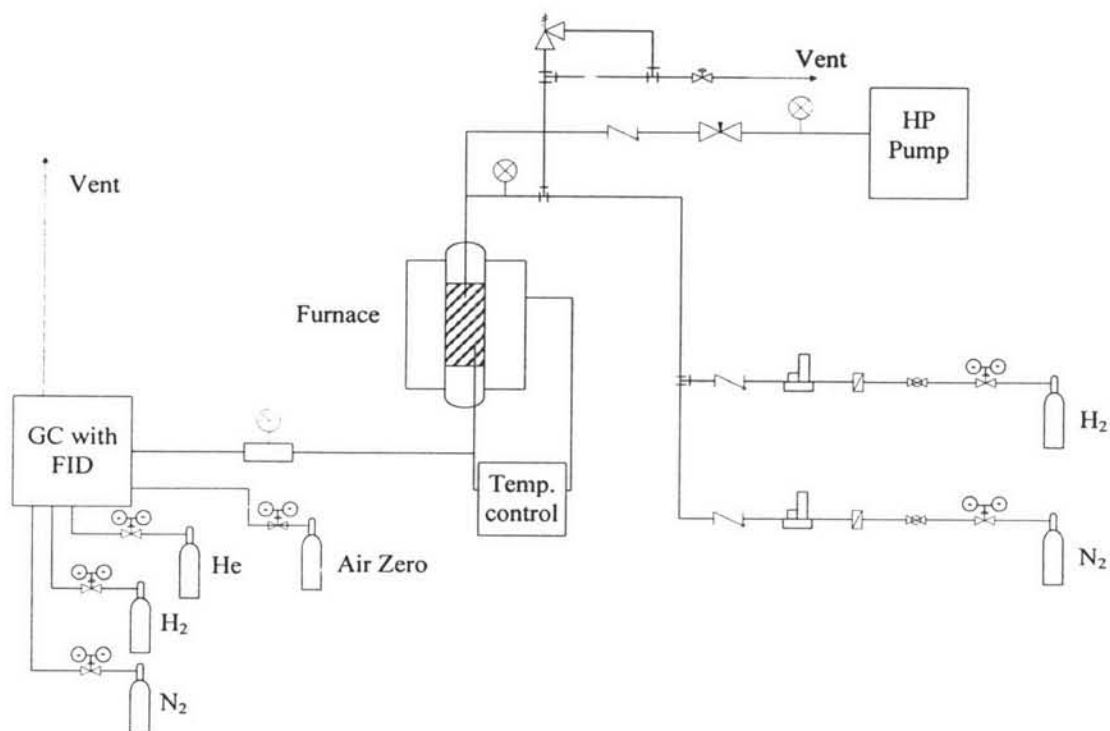


Figure 3.4 Schematic flow diagram of hydrogenation reaction.