

CHAPTER III EXPERIMENTAL

3.1 Materials and Equipment

Equipment:

The experimental system consists of 4 main parts: a 1/4" O.D.x7" long stainless steel packed bed reactor equipped with furnace and temperature controller, a sample reservoir made by 6.5 cm ID x 7.4cm height stainless steel, a hydrogen gas supply cylinder, and a peristaltic pump as shown in Figure 3.1. Inductively Coupled Plasma Spectrometer (ICP), Thermo Finnigan TPDRO 1100 equipped with flame ionization detector and Atomic Absorption Spectroscopy (Varian) are utilized for study the characteristic properties of the catalysts.

Chemical:

1-Hexyne 97%, alumina (α -Al₂O₃), Tetraammine palladium (II) chloride monohydrate (N₂O₆Pd.2H₂O), copper (II) nitrate (Cu(NO₃)₂.3H₂O) and phosphotungstic acid solution (H₃PO₄.12WO₃) were obtained from Aldrich and the solvent, n-heptane, 95% (AR grade) was purchased from Fisher Chemical. Hydrogen (99% purity) was obtained from Thai Industrial Gas.

3.2 Experiment Procedure

3.2.1 Catalyst Preparation

3.2.1.1 *Low loaded Pd/Al₂O₃ catalyst*

The Alpha alumina was impregnated with corresponding amount of palladium (N₂O₆Pd.2H₂O) aqueous solution, then dried at 110 °C overnight and subsequently calcined at 500 °C for 3 h.

3.2.1.2 *Bimetallic Pd-Cu/Al₂O₃ and Pd-W/Al₂O₃ catalysts*

The Pd-Cu/Al₂O₃ catalysts were prepared at Pd/Cu atomic ratios of 0.25, 0.5, 1.0, 1.5 and 2.0. Alpha alumina was first impregnated with corresponding amount of palladium (N₂O₆Pd.2H₂O) aqueous solution, then dried at 110 °C overnight, and subsequently calcined at 500 °C for 1 h. After that the second

metal copper (II) nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) aqueous solution was deposited on the calcined $\text{Pd}/\text{Al}_2\text{O}_3$ catalysts and then these catalysts were dried at 110 °C overnight and calcined again at 500 °C for 3 h. The $\text{Pd-W}/\text{Al}_2\text{O}_3$ catalysts were prepared on similar manner except aqueous solution prepared from $\text{H}_3\text{PO}_4 \cdot 12\text{WO}_3$ was used instead of the copper nitrate solution.

3.3 Catalyst Characterization

3.3.1 Temperature Programmed Reduction (TPR)

Temperature programmed reduction will be employed for evaluating the number and quantity of the reducible species present in the prepared catalyst and the temperature, at which the reduction itself takes place as a function of temperature.

3.3.2 Atomic Absorption Spectroscopy (AAS)

Varian/SpectrAA 300 was used to identify and measure the metal content in the prepared catalysts. A sample will be solubilized in a mixture of HF and $\text{HNO}_3:\text{HCl}$ (3:1) with ratio of 4:1 at 50°C and then the mixture were diluted to 50 ml with deionized water. The concentrations of solutions were determined base on the absorption intensity. Each element can emit the specific wavelengths. The wavelengths generated from cathode lamp were absorbed by the considered element in sample. The concentration of each element which is proportional to the absorbed intensity can be calculated from a stored set of calibration curves.

3.3.3 H₂ Chemisorption

The catalyst samples were pretreated in a 10 ml/min flow of hydrogen at 300 °C for 1 h. Then catalyst samples were purged in nitrogen at 300 °C for 1 h to decompose any Pd-hydride and remove chemisorbed hydrogen. Then catalyst sample were cooled down to 110 °C in 10 ml/min flow of nitrogen. The H₂ chemisorption was performed at 110 °C to prevent Pd-hydride formation. At the beginning of measurement, a pulse of 20 µl hydrogen was introduced to catalyst samples. The hydrogen was detected by Thermal conductivity detector. The hydrogen-signals were lower as hydrogen was chemisorbed on the catalyst sample. If the catalyst sample

takes up the maximum amount of hydrogen, then all following signals would have the same peak area.

3.4 Reaction testing

Before the reaction, catalysts were treated in the reactor at 150 °C for 12 h. After treating the catalysts, the liquid phase selective hydrogenation of 1-hexyne was carried out in the same reactor under 1.5 bar and 40 °C as shown in Figure 19. The 0.5 g of catalyst was packed in the reactor and then 1-hexyne and n-heptane, the feed and solvent respectively were mixed and filled into the sample reservoir. Liquid in the system was circulated by using peristaltic pump. Subsequently constant pressure of H₂ gas was applied to the system and the liquid mixture was passed through the fixed bed reactor. The liquid was analyzed for its composition for every hour by a gas chromatography.

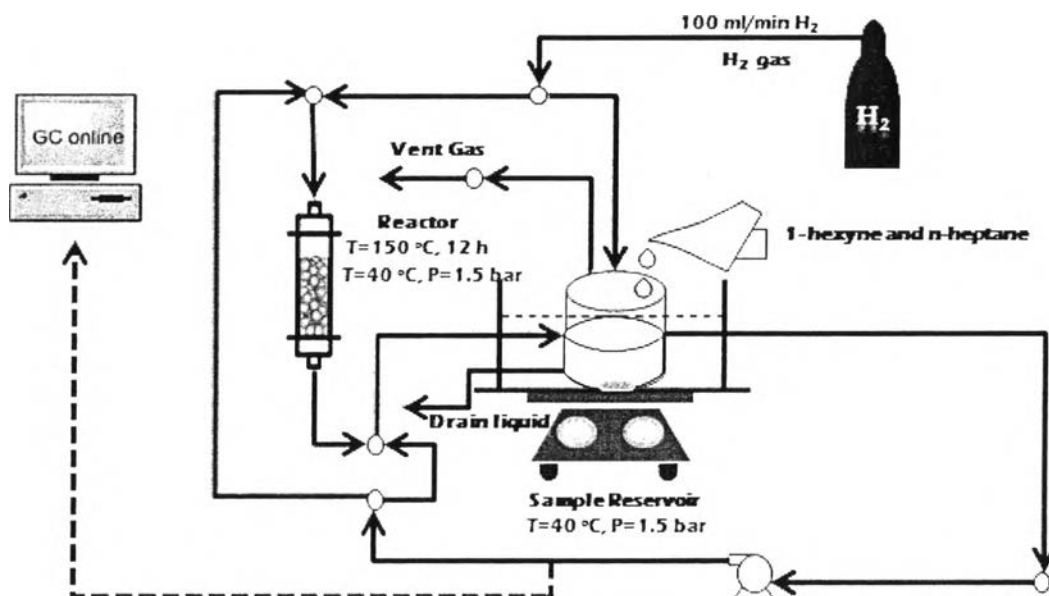


Figure 3.1: The process flow diagram of 1-Hexyne selective hydrogenation reaction.

3.4.1 Reaction Performance Evaluation

Catalytic reaction tests were carried out in a stainless steel packed bed reactor system under 1.5 bar and 40 °C. Throughout the reaction, the temperature and pressure were controlled at the desired values. In this reaction, the conversion and selectivity were calculated to obtain conversion and selectivity.

The conversion of 1-Hexyne can be written as followed

$$\text{1-Hexyne conversion (\%1-Hy}_{\text{conv}}) = \frac{(\text{moles of 1-Hy}_{\text{initial}} - \text{moles of 1-Hy}_{\text{final}})}{\text{moles of 1-Hy}_{\text{initial}}} \times 100$$

The selectivity of 1-Hexene and n-Hexane can be written as followed

$$\text{1-Hexene selectivity (\%1-Hexene}_{\text{sel}}) = \frac{(\text{moles of 1-He}_{\text{final}} - \text{moles of 1-He}_{\text{initial}})}{\text{moles of 1-Hy converted}} \times 100$$

$$\text{n-Hexane selectivity (\%n-Hexane}_{\text{sel}}) = \frac{(\text{moles of n-Ha}_{\text{final}} - \text{moles of n-Ha}_{\text{initial}})}{\text{moles of 1-Hy converted}} \times 100$$