CHAPTER III
EXPERIMENTAL

3.1 Equipment and Materials

3.1.1 Equipment

1. Packed bed reactor system consists of 2 parts: 1/4" O.D. x 7" long stainless steel reactor with temperature controller and oven and the sample reservoir which is made by 6.5 cm ID x 7.4 cm long stainless steel cylinder.
2. Gas chromatograph (GC)
3. Thermo Finnigan TPDRO 1100
4. X-ray Photoelectron Spectroscopy (XPS)

3.1.2 Chemicals

3.1.2.1 Feedstock and Chemicals

1. 1-Hexyne (97% purity)
2. Alumina (α-Al$_2$O$_3$)
3. Palladium(II) nitrate dihydrate (Pd(NO$_3$)$_2$·2H$_2$O)
4. Manganese(II) acetate tetrahydrate (C$_4$H$_6$MnO$_4$·4H$_2$O)
5. n-Heptane (95% purity, AR grade)

3.1.2.2 Gas

1. Hydrogen (99.99% purity)

3.2 Experimental Procedures

3.2.1 Catalyst Preparation

3.2.1.1 Pd/Al$_2$O$_3$ Catalyst

The α-alumina was impregnated with corresponding amount of palladium (Pd(NO$_3$)$_2$·2H$_2$O) aqueous solution, then dried at 110 °C overnight and subsequently calcined at 500 °C for 3 h.

3.2.1.2 Bimetallic Pd-Mn/Al₂O₃ Catalysts

The Pd-Mn/Al$_2$O$_3$ catalysts were prepared at Pd/Mn atomic ratios of 0.5, 0.75, 1.0, 1.5, 2.0 and 5.0. α-Alumina was first impregnated with corresponding amount of palladium (Pd(NO$_3$)$_2 \cdot$2H$_2$O) aqueous solution, then dried at 110 $^{\circ}$C overnight, and subsequently calcined at 500 $^{\circ}$C for 1 h. After that the manganese (C$_4$H$_6$MnO$_4 \cdot$4H$_2$O) aqueous solution was deposited on the calcined Pd/Al$_2$O$_3$ catalysts and then these catalysts were dried at 110 $^{\circ}$C overnight and calcined again at 500 $^{\circ}$C for 3 h.

3.2.2 Catalyst Characterization

3.2.2.1 Temperature Programmed Reduction (TPR)

Temperature programmed reduction was 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.

3.2.2.2 Hydrogen 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 H$_2$ 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.

3.2.2.3 X-ray Photoelectron Spectroscopy (XPS)

X-ray Photoelectron Spectroscopy were carried out using a AXIS ULTRA^{DLD} to determine the oxidation state of a metal oxide before catalytic testing. The system was equipped with a monochromatic Al X-ray source and a hemispherical analyzer. The spectrometer was operated with the pass energy of 40 eV when recording core level spectra. All peaks were calibrated from referring C 1s spectra located at 284.6 eV.

3.2.3 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 3.1. 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 hydrogen 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.
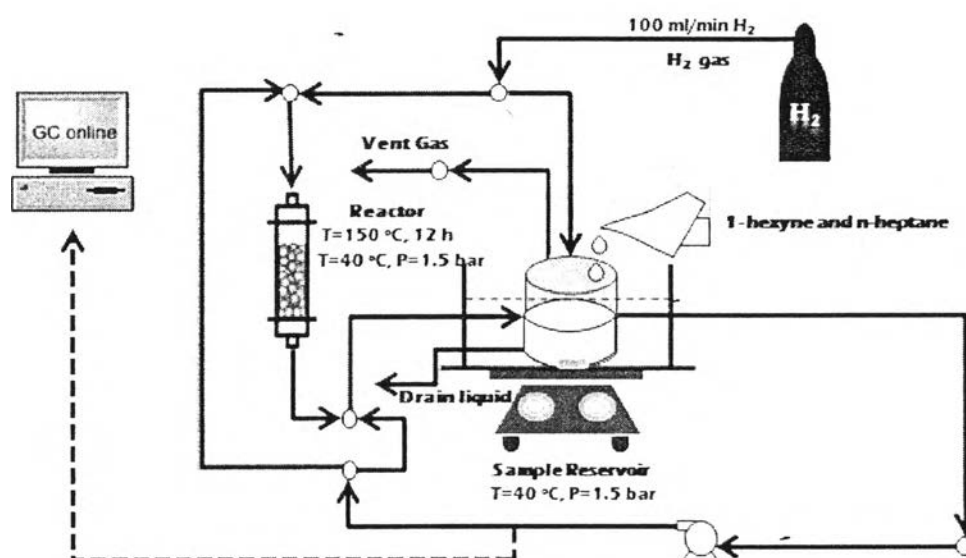

Figure 3.1 The set-up diagram of selective hydrogenation 1-hexyne experiment (Suriyaphaparkorn, 2013).

3.3 Reaction Performance Evaluation

The reaction performance is indicated by conversion of reactant and selectivity of product. From the reaction scheme of the hydrogenation of 1-hexyne in Figure 3.2, 1-hexyne is hydrogenated to 1-hexene, and then 1-hexene is

hydrogenated to *n*-hexane. In this study, the performances of catalyst were indicated by using the conversion of 1-hexyne and the selectivity of 1-hexene and *n*-hexane.

3.3.1 The Conversion of 1-Hexyne

$$1\text{-Hexyne } (\%C_6H_{10_{conv}}) = \frac{\text{moles of } C_6H_{10_{initial}} - \text{moles of } C_6H_{10_{final}}}{\text{moles of } C_6H_{10_{initial}}} \times 100$$

3.3.2 The Selectivity of 1-Hexene and *n*-Hexane

$$1\text{-Hexene selectivity } (\%C_6H_{12_{sel}}) = \frac{\text{moles of } C_6H_{12_{final}} - \text{moles of } C_6H_{12_{initial}}}{\text{moles of } C_6H_{10_{converted}}} \times 100$$

$$n\text{-Hexane selectivity } (\%C_6H_{14_{sel}}) = \frac{\text{moles of } C_6H_{14_{final}} - \text{moles of } C_6H_{14_{initial}}}{\text{moles of } C_6H_{10_{converted}}} \times 100$$

3.3.3 The Yield of 1-Hexene

$$1\text{-Hexene yield } (\%C_6H_{12_{yield}}) = \frac{\text{moles of } C_6H_{12_{final}}}{\text{moles of } C_6H_{10_{initial}}} \times 100$$
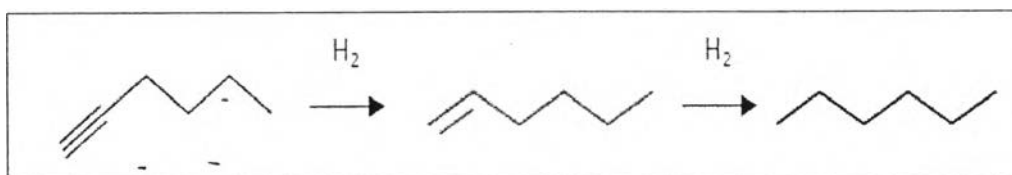

Figure 3.2 The reaction scheme of 1-hexyne hydrogenation.