



## CHAPTER III EXPERIMENTAL

### 3.1 Equipment and Chemical

#### Equipment:

1. Pack bed reactor system mainly consist of 2 parts:  $\frac{1}{2}$ " O.D.x5.9" long stainless steel reactor with temperature controller and heating tape ,and the feed sample reservoir which is made by 8 cm ID x 15cm long stainless steel cylinder.
2. Gas chromatograph (HP 5890 II Plus equipped with FID)
3. Micromeritic TPR 2900 equipped with thermal conductivity detector
4. Atomic Absorption Spectroscopy (Varian/SpectrAA 300)

#### Chemical:

##### Feedstock and Chemicals

1. Highly concentrated vinylacetylene mixed C4 (Bangkok Synthetics Co., Ltd.)
2. Gamma Alumina ( $\text{Al}_2\text{O}_3$ ,Aldrich)
3. Palladium nitrate dihydrate ( $\text{PdN}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$ ,Aldrich)
4. Copper nitrate trihydrate ( $\text{CuN}_2\text{O}_6 \cdot 3\text{H}_2\text{O}$ ,Aldrich)
5. Hexane (AR grade, Fisher Chemical)

##### Gas

1. Nitrogen gas (99.99% purity)
2. Hydrogen gas (99.99% purity)

## 3.2 Experiment Procedure

### 3.2.1 Catalyst Preparation

Pd/Al<sub>2</sub>O<sub>3</sub> catalysts were prepared using Al<sub>2</sub>O<sub>3</sub> as supports. The Pd was deposited on alumina by impregnating with aqueous solution of PdN<sub>2</sub>O<sub>6</sub>•2H<sub>2</sub>O. The catalysts were dried at 110 °C overnight and subsequently calcined at 500 °C for 3 h.

For preparation of Pd-Cu catalysts, alumina was impregnated with PdN<sub>2</sub>O<sub>6</sub>•2H<sub>2</sub>O aqueous solution and then this catalyst was dried at 110 °C overnight and subsequently calcined at 500 °C for 1 h. The CuN<sub>2</sub>O<sub>6</sub>•3H<sub>2</sub>O aqueous solution was used for adding Cu by impregnation method to Pd/Al<sub>2</sub>O<sub>3</sub> which was calcined at 500 °C for 1 h. And then the Pd-Cu catalysts were dried at 110 °C overnight and subsequently calcined at 500 °C for 3 h.

All of prepared catalysts were reduced in a 100 ml/min flow of hydrogen at 300 °C for 1 hr.

### 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 *Atomic Absorption Spectroscopy (AAS)*

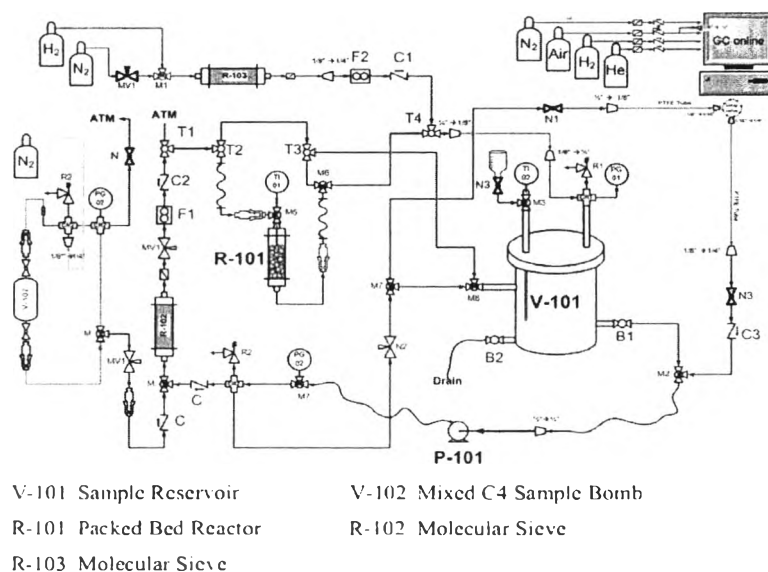
Varian/SpectrAA 300 was used to identify and measure the metal content in the prepared catalysts. A sample was solubilized in a mixture of HF and HNO<sub>3</sub>:HCl (3:1) with ratio of 4:1 at 50 °C and then the mixture were diluted to 50 ml with deionized water. The concentrations of solutions were 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 could be calculated from a stored set of calibration curves.

#### 3.2.2.4 $H_2$ Chemisorption

The catalyst samples were pretreated in a 10 ml/min flow of hydrogen at 300 °C for 1h. 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  $\mu$ l 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.

#### 3.2.3 Catalytic Activity Measurement

The experiment was carried out in a packed bed reactor system as shown in Figure 3.1. Before the reaction test, 0.5 g of catalysts were packed in the reactor and treated at 150 °C for 12 h. In the first step for reaction testing, hexane was filled into the sample reservoir and then the sample reservoir was purged with nitrogen gas by pressurizing and depressurizing. The high concentrated vinylacetylene mixed C4 contained in sample bomb was fed to sample reservoir.



**Figure 3.1** The detail of piping and equipment diagram in the packed bed reactor system.

The temperature of the reactor and sample reservoir were set at desire temperature by the temperature controller. The constant pressure hydrogen was continuously fed to sample reservoir. The sample in the sample reservoir was stirred and circulated through the molecular sieve packed bed and back to sample reservoir by using liquid transfer pump (by-pass the reactor). Some of the circulated liquid was injected to the GC online to measure the composition of liquid. Then the circulated liquid was circulated through the packed bed reactor and the reaction time was started and the composition of circulated liquid was measured every hour by GC online analyzer.

### Reaction Performance Evaluation

The reaction performance is often indicated by conversion of reactant and product selectivity. In this study, the performance of catalysts were indicated by using the conversion of vinylacetylene and ethyl acetylene and the selectivity of 1,3-butadiene and 1-butene.

The conversion of vinylacetylene and ethylacetylene can be written as followed.

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

$$\text{Ethyl acetylene conversion (\%EA}_{\text{conv}}) = \frac{(\text{moles of EA}_{\text{initial}} - \text{moles of EA}_{\text{final}})}{\text{moles of EA}_{\text{initial}}} \times 100$$

The selectivity of 1,3-butadiene and 1-butene can be written as followed.

$$\text{1,3-Butadiene selectivity (\%13BD}_{\text{scl}}) = \frac{(\text{moles of 13BD}_{\text{final}} - \text{moles of 13BD}_{\text{initial}})}{\text{moles of VA converted}} \times 100$$

$$\text{1-Butene selectivity (\%B1}_{\text{scl}}) = \frac{(\text{moles of B1}_{\text{final}} - \text{moles of B1}_{\text{initial}})}{\text{moles of VA + 13BD + 12BD + EA + c2C4 + c2C4 converted}} \times 100$$