

CHAPTER III

EXPERIMENTAL SECTION

The experimental work is divided into 3 parts: (I) Catalyst Preparation, (II) Catalyst Characterization, and (III) Reaction Testing.

3.1 Catalyst Preparation

A series of Pt/KL catalysts were prepared by two impregnation methods, which are Incipient Wetness Impregnation (IWI) and Vapor Phase Impregnation (VPI). The details of each method are described as follows:

3.1.1 Incipient Wetness Impregnation (IWI) Method

3.1.1.1 *Chemicals*

- Tetraamineplatinum (II) nitrate, $\text{Pt}(\text{NH}_3)(\text{NO}_3)_2$
- Cerium (III) nitrate hexahydrate, $\text{CeN}_3\text{O}_9 \cdot 6\text{H}_2\text{O}$
- Erbium (III) nitrate pentahydrate
- Ytterbium (III) nitrate pentahydrate
- Silica HI-Sil 233 from PPG-Siam Silica Co., Ltd. (Precipitated silica)
- K-LTL zeolite (HSZ-500, $\text{SiO}_2/\text{Al}_2\text{O}_3 = 6$, Surface Area = $280 \text{ m}^2/\text{g}$, supplied by Tosoh (Tokyo, Japan))

3.1.1.2 *Devices & Equipments*

- Tubular reactor 0.4" ID
- Quartz wool
- Carbolite furnace maximum temperature 1500°C

- Field-Cal 570 bubble flow meter
- High purity air zero

3.1.1.3 Procedure

Tetraamineplatinum (II) nitrate was weighed with 0.0199 of platinum precursor per zeolite ratio (See Appendix C) and was dissolved in deionized water using liquid/solid ratio of $0.69 \text{ cm}^3/\text{g}^*$. This step is called dissolving step. Dissolving step was carried out after calcining KL zeolite in air zero at 400°C for 5 hours and followed by impregnation step. The impregnation step was carried out in the closed system of glove box. Firstly, the platinum solution was dropped into the calcined KL zeolite dispersely. After that, the wet sample was left on the lab bench for 4 hours, dried in oven at 110°C for 8 hours, and calcined in air at 350°C for 2 hours respectively. Finally, the Pt/KL catalyst was obtained in oxide form.

For Pt/SiO₂ catalyst, Silica HI-Sil 233 was used instead of K-LTL zeolite, and the procedure remained the same. In case of promoted catalysts, rare earth precursors per zeolite ratio are as follows:

- ❖ 0.0047 gram of Cerium (III) nitrate hexahydrate per gram of zeolite
(See Appendix C)
- ❖ 0.0040 gram of Erbium (III) nitrate pentahydrate per gram of zeolite
(See Appendix C)
- ❖ 0.0039 gram of Ytterbium (III) nitrate pentahydrate per gram of zeolite
(See Appendix C)

In this case, the impregnation of promoter was done before platinum. The procedure of promoted catalyst preparation was done step

* Since pore volume of KL zeolite is typically around $0.69 \text{ cm}^3/\text{g}$, the appropriate volume of deionized water is 0.69 cm^3 for one gram of zeolite.

by step as follows: KL zeolite calcination, dissolving step of promoter, promoter impregnation, lab bench leaving, drying, the calcination of promoter-impregnated sample were done respectively. After these steps, platinum impregnation was done as described above. All air flow rates for calcination and pretreatment step are 100 cc/min· g catalyst.

3.1.2 Vapor Phase Impregnation (VPI) Method

3.1.2.1 *Chemicals*

- Platinum (II) acetyl-acetonate, Pt(AcAc)₂
- Cerium (III) acetyl-acetonate, Ce(AcAc)₃
- Erbium (III) acetyl-acetonate, Er(AcAc)₃
- Ytterbium (III) acetyl-acetonate, Yb(AcAc)₃
- K-LTL zeolite (HSZ-500, SiO₂/Al₂O₃ = 6, Surface Area = 280 m²/g, supplied by Tosoh (Tokyo, Japan)

3.1.2.2 *Devices & Equipments*

- Tubular reactor 0.4" ID
- Quartz wool & glass wool
- Carbolite furnace maximum temperature 1500 °C
- Field-Cal 570 bubble flow meter
- Yamatake – Honeywell SDC10 temperature controller
- High purity air zero
- High purity helium gas

3.1.2.3 *Procedure*

0.0202 gram of Platinum (II) acetyl-acetonate was weighed per gram of zeolite (See Appendix C) and was mixed directly with zeolite powder. This mixing step was done after KL-zeolite had been calcined in

air zero at 400°C for 5 hours, and then followed by impregnation step. In impregnation step, the mixed catalyst was packed in a tubular reactor and the temperature was increased gradually in helium flow step by step as follows:

- Hold at 40°C for 3 hours
- Hold at 60°C for 1 hour
- Hold at 80°C for 1 hour
- Hold at 100°C for 1 hour
- Hold at 130°C for 15 minute
- Cool down to room temperature

Finally, pretreat the catalyst in the flow of air zero at 350°C for 2 hours, then restore the Pt/KL catalyst in a desiccator.

For promoted catalysts, the platinum precursor was impregnated after the rare earth precursor had been impregnated. Both impregnations followed the same procedure as described above. The amounts of rare earth precursor required for the impregnation are shown below:

- ❖ 0.0047 gram of Cerium (III) acetyl acetonate per gram of zeolite
(See Appendix C)
- ❖ 0.0042 gram of Erbium (III) acetyl acetonate per gram of zeolite
(See Appendix C)
- ❖ 0.0041 gram of Ytterbium (III) acetyl acetonate per gram of zeolite
(See Appendix C)

All air flow rates for calcination and pretreatment steps were maintained at 100 cc/min·g catalyst. Helium flow rates were fixed at approximately 4 cc/min.

3.2 Catalyst Characterization

Pt/KL catalysts were characterized by two different methods, BET Surface Area Analysis and Atomic Absorption Spectroscopy (AAS).

3.2.1 BET Surface Area Analysis

Prior to the analyzing process, the samples were outgased for roughly 1-2 hour. The analyzing step was mainly in computer program and was not described in detail here.

3.2.2 Atomic Absorption Spectroscopy (AAS)

3.2.2.1 *Chemicals*

- Concentrated HCl (38%)
- Concentrated HNO₃ (65%)
- Whatman filter papers No.42, 125 mm diameter
- H₂PtCl₆ 540.97 ppm
- Deionized water
- Mivaris heater
- Glassware

3.2.2.2 *Procedure*

Approximately 0.15 gram of catalysts was weighed and dissolved with 5 ml of aqua regia (the mixing solution of concentrated HCl at 82ml and HNO₃ at 18ml). In order to minimize the error caused by humidity, this step was proceeded after drying the glassware overnight. Then the samples were digested by heating and stirring alternately for 2 hours and followed by filtering using filter paper No. 42. The deionized water was added to the filtered solution until the total volume was 50 ml.

For standard Pt solutions, the concentrations of 10 ppm, 20 ppm, 30 ppm, 40 ppm, and 50 ppm were chosen. Each concentration consisted of different amounts of Pt solution as described below:

- ❖ 0.9242 ml of Pt solution for 10 ppm,
- ❖ 1.8485 ml of Pt solution for 20 ppm,
- ❖ 2.7727 ml of Pt solution for 30 ppm,
- ❖ 3.6970 ml of Pt solution for 40 ppm, and
- ❖ 4.6213 ml of Pt solution for 50 ppm.

540.97 ppm of H_2PtCl_6 was used as Pt solution and each concentration was added with 5 ml of aqua regia and was made up to a volume of 50 ml with deionized water.

After all the samples and standard Pt solutions were prepared, they were tested by Atomic Absorption Spectroscopy to find out the exactly percent of metal loading. The results were reported in chapter IV.

3.3 Reaction Testing

n-Butane hydrogenolysis in hydrogen was used to explore the Pt/KL functions. To carry out the reaction, 0.15 gram of sample was packed between two plugs of quartz wool in a Pyrex glass tube reactor. The reactor was located inside an electrical furnace controlled by a thermocouple and a PID controller. The hydrogenolysis system was shown in Figure 3.1.

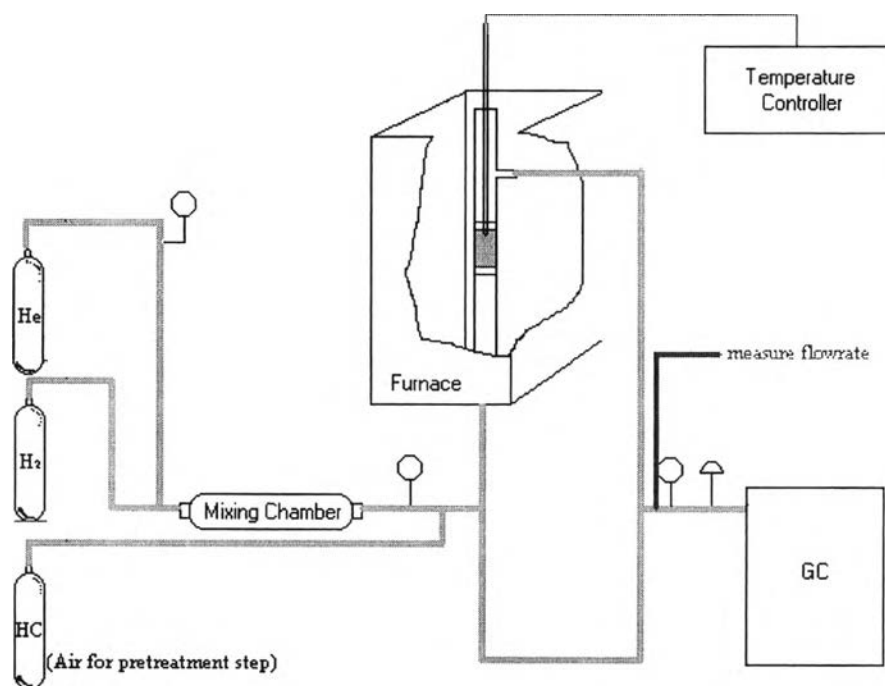


Figure 3.1 n-Butane hydrogenolysis system controlled by a PID temperature controller.

Prior to the reaction, the sample was pretreated in order to assure that the catalyst was ready for the tested reaction. The catalyst was first calcined in air flow of approximately $30 \text{ cm}^3/\text{min}$ at 350°C and was held at this condition for 2 hour to achieve clean & clear pore volume. In order to activate the catalyst, hydrogen was introduced into the system at $30 \text{ cm}^3/\text{min}$ simultaneously with raising the temperature to 450°C . The catalyst was held at this condition for one hour. Finally hydrogen was switched to helium with the same flow rate and the temperature was decreased to the reaction temperature (See Figure 3.2). Before starting up the reactions, n-butane, hydrogen, and helium were mixed and controlled at a designed ratio. Since the obtained results was expected to help us better understand the functions of Pt/KL catalysts, a variety of variables were

examined in the thesis. Pt/SiO₂ in the amorphous form was used as the reference material to compare with Pt/KL prepared by both IWI and VPI methods. The unpromoted catalysts were also compared with the catalysts promoted with Cerium, Erbium, and Ytterbium. The hydrogenolysis experiments were carried out isothermally at different temperatures of 250, 300, 350, and 400 °C. Kinetic study of n-butane hydrogenolysis was carried out at 350, 375, and 400 °C, and the study was conducted on two systems: (i) 3 and 4.5 cm³/min of butane flow rates in 30 cm³/min fixed system of hydrogen, and (ii) 17.5 and 30 cm³/min of hydrogen flow rates in 3 cm³/min fixed system of n-butane. These two systems were also balanced by helium so that the total flow rates were fixed. After completing each 10 hour reaction running^{*}, all the gas flow rates were measured again many times by a bubble flow meter. Standard deviations were evaluated to assure the accuracy of the reported gas flow rates.

^{*} 7 hour reaction running for kinetics study.

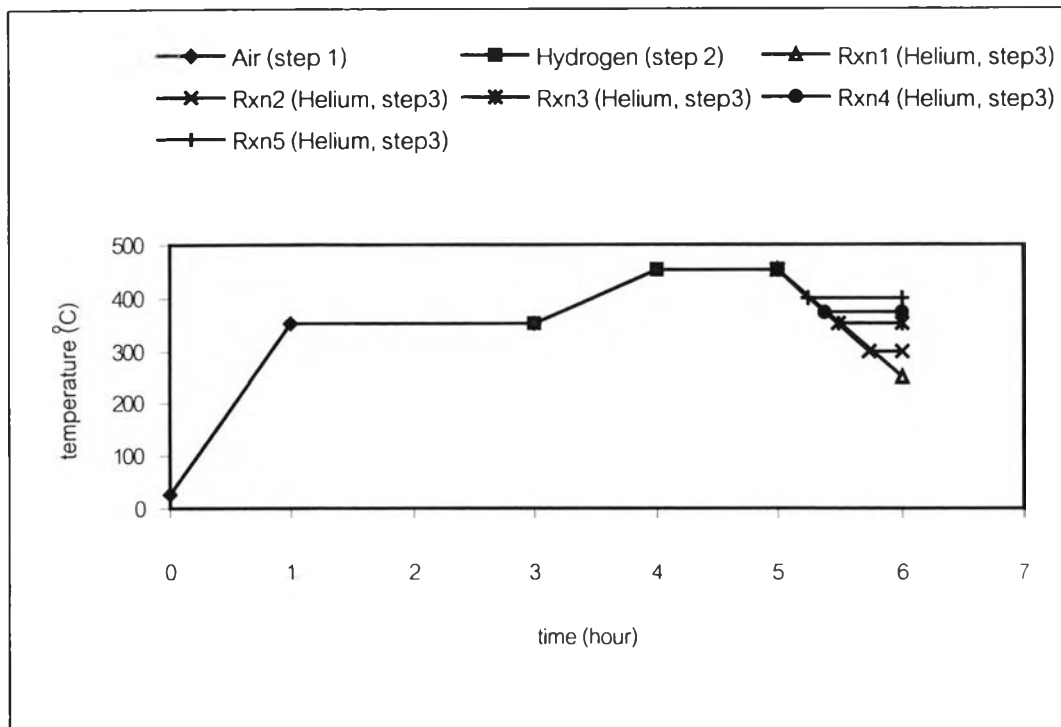


Figure 3.2 Temperature distribution in pretreatment steps before running reactions.