

CHAPTER III

EXPERIMENTAL

This chapter describes experimental system procedure used in this work which can be divided into three parts. Catalyst preparation is shown in section 3.1. Details of catalyst evaluation to study catalytic activity are given in section 3.2. Finally, properties of the catalyst characterized by various techniques are explained in section 3.3.

3.1 Catalyst Preparation

3.1.1 Chemicals

All chemicals using in this experiment are as following:

1. JRC ALO-2 Alumina (Al_2O_3)
2. Palladium (II) nitrate hydrate ($\text{Pd}(\text{NO}_3)_2$) from Aldrich Chemical Company, USA.
3. Silver nitrate (AgNO_3) from APS Finechem

3.1.3 Preparation Procedures

3.1.3.1 Preparation of Alumina Support

Alumina support used to synthesize simulated catalysts was prepared by calcination of JRC ALO-2 at 1150°C for 128 minutes.

3.1.3.2 Preparation of Palladium and Palladium-Silver Catalyst

Simulated catalysts, 1wt%Pd-3wt%Ag/ Al_2O_3 , were prepared by sequential or co-incipient wetness impregnation method. The details of preparation are as following:

1) The impregnating solution for 2 grams of support was prepared by calculating the amount of palladium salt to obtain the required metal loading (see Appendix A). The sufficient amount of de-ionised water was then added to obtain palladium solution.

2) 2 grams of alumina support was placed in a crucible then the impregnating solution was gradually dripped into support. Stirring the sample continuously was required to ensure homogeneous distribution of metal component on support.

3) The impregnated support was left to stand for 6 h to assure adequate distribution of metal complex. The support was subsequently dried at 110°C in air overnight.

4) The dried impregnated support was calcined under 60 ml/min nitrogen with the heating rate of 10°C/min until the temperature reached 500°C. A 100 ml/min of flowing air was then switched into the reactor to replace nitrogen and the temperature was held at 500°C for 2 h.

5) The palladium impregnated sample was re-impregnated with silver complex using a similar procedure except that calcination were performed at 370°C and held at that temperature for 1 h.

3.2 Catalyst Evaluation

Catalytic performance was studied in selective hydrogenation of acetylene with GHSV of 5400 h⁻¹. Reaction test was performed as a function of time-on-stream with and without N₂O pretreatment. Material, apparatus, and operating procedure are detailed as below:

3.2.1 Materials

The reactant gas used for the catalyst evaluation was the ethylene feedstream to the acetylene converter as supplied by the Rayong Olefins Co.,Ltd., Thailand. Ultra high purity hydrogen and high purity argon manufactured by Thai Industrial Gas Co., Ltd. (TIG) were used for reduction and cooling processes.

3.2.2 Apparatus

The catalytic test was performed in a flow system as shown diagrammatically in Figure 3.1. Detail of instruments in this system are listed and explained as follow:

1) Reactor

The reaction was performed in a conventional vertical quartz tubular reactor (inside diameter = 0.9 cm) at atmospheric pressure.

2) Electric furnace

The furnace was used to apply required temperature to the reactor. The temperature of catalysts bed can vary in the range of 30 to 600°C.

3) Automation temperature controller

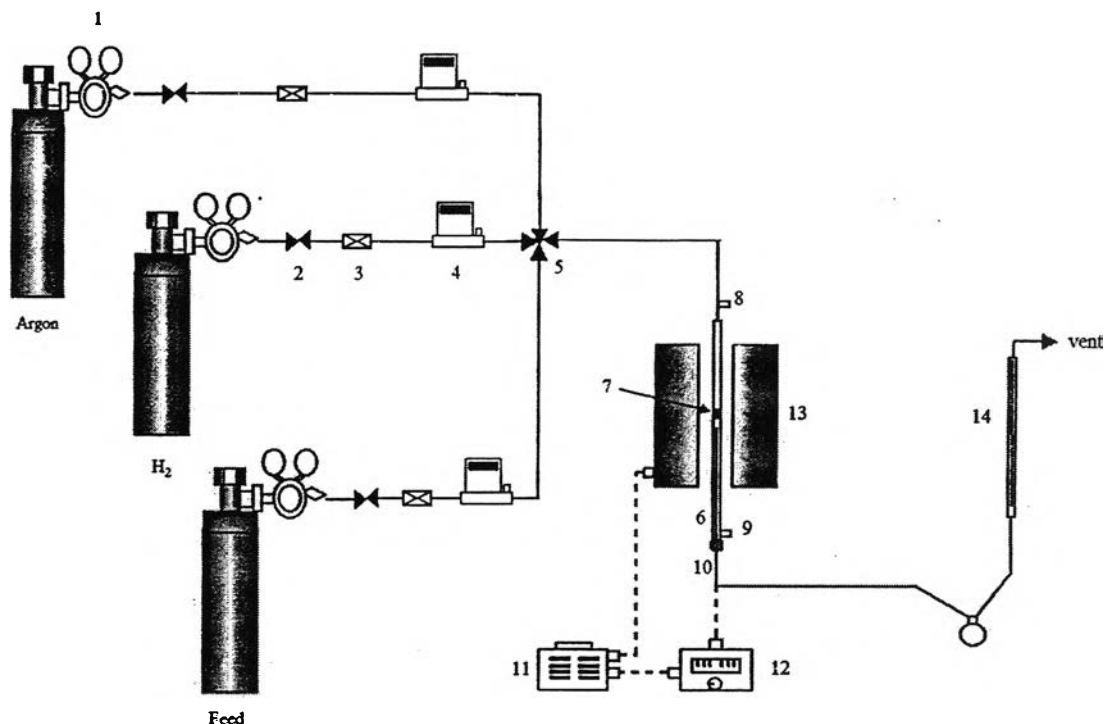
The temperature of catalysts bed is automatic controlled by this unit. This unit consisted of variable transformer with connected to a magnetic switch and a RKC temperature controller. Temperature is measured by a thermocouple attached to the catalysts bed.

4) Gas controlling system

All gas used in system were separately equipped with a pressure regulator and a on-off valve. Gas flow rates were adjusted by mass flow controller.

5) Gas chromatograph

Products and feeds were analyzed by a gas chromatograph equipped with a FID detector for separating C_2H_2 , C_2H_4 and C_2H_6 . H_2 was analyzed by a gas chromatograph equipped with a TCD detector. The operating conditions are summarized in Table 3.1



- | | |
|-------------------------|----------------------------------|
| 1. pressure regulator | 8. sampling point (feed) |
| 2. on-off valve | 9. sampling point (product) |
| 3. filter | 10. thermocouple |
| 4. mass flow controller | 11. variable voltage transformer |
| 5. 4-ways fitting | 12. temperature controller |
| 6. reactor | 13. electric furnace |
| 7. catalyst bed | 14. bubble flow meter |

Figure 3.1 Flow diagram of the selective hydrogenation of acetylene

3.2.3 Procedures

Approximately 0.5 g of catalyst was packed in quartz tubular down flow reactor. The catalyst bed length was about 1 cm. The reactor was placed into the

furnace and argon was introduced into the reactor in order to remove remaining air. Prior to reaction, the catalyst was reduced with 100 ml/min hydrogen flow at a temperature of 200°C and held at that temperature for 2 h. Afterwards, catalyst bed was switched into argon in order to remove the remaining hydrogen. If pretreatment with N₂O was performed, catalyst bed must be cooled down to pretreatment temperature and known amount of N₂O was introduced into the bed and held at that temperature for 10 min.

The reactant was introduced at 70°C temperature and 1 atm, sampling was taken every 1 hour. Effluent gases were sampled to analyze the concentration of CH₄, C₂H₂, C₂H₄ and C₂H₆ using GC-8A (FID) installed with a carbosieve S-II column, whereas H₂ concentration was analyzed by GC-8A (TCD) installed with a molecular sieve 5A column. Details of the calculation of the catalyst activity to convert acetylene and the selectivity are given in Appendix C.

Table 3.1 Operating conditions of gas chromatographs.

Gas Chromatograph	SHIMADZU GC-8A	SHIMADZU GC-8A
Detector	FID	TCD
Packed column	Carbosieve column S-II	Molecular sieve 5A
Carrier	Ultrahigh purity N ₂	Ultrahigh purity Ar
Carrier gas flow rate (ml/min)	30	30
Injector temperature (°C)	180	80
Initial column temperature (°C)	100	50
Program rate (°C/min)	10	-
Final column temperature (°C)	160	50
Current (mA)	-	70
Analyzed gas	CH ₄ , C ₂ H ₂ , C ₂ H ₄ , C ₂ H ₆	H ₂

3.3 Catalyst Characterization

Various characterization techniques were used in this studied in order to clarify the catalyst structure and morphology and surface composition. The structure and morphology of prepared and spent catalysts were studied using surface area measurements, Determination of coke concentration and X-ray diffractometer (XRD) and the details of each technique will be described in section 3.3.1. In the second part 3.3.2, the surface analysis of catalysts was investigated employing CO pulse chemisorption, X-ray photoelectron spectroscopy (XPS), Ethylene temperature programmed technique, temperature programmed oxidation (TPO) and infrared spectroscopy (FT-IR).

3.3.1 Bulk Structure and Morphology of the Catalyst

3.3.1.1 Specific Surface Area Measurement

Surface area measurements were carried out by low temperature nitrogen adsorption in a Micromeritic ChemiSorb 2750 system. Calculations were performed on the basis of the BET isotherm. 0.2 grams of sample was loaded into u-shape cell made from Pyrex and heated in helium to 200°C for 2 h in order to eliminate trace amount of water adsorbed on surface, then cooled down to room temperature. The analysis gas consist of 30%N₂ in helium was introduced to Pyrex cell. Sample adsorbed nitrogen at low temperature by dipped cell into liquid nitrogen dewar until it's surface was saturated with nitrogen and desorbed nitrogen at room temperature by moved away the dewar. The nitrogen that was desorbed from sample was measured by TCD detector.

3.3.1.2 X-ray Diffraction (XRD) Analysis

The crystallinity, structure and composition of catalysts were analyzed by XRD analysis. The X-ray diffraction patterns of the catalysts were carried out using an X-ray refractometer, SIEMENS D5000, with Cu K_α radiation, accurately measured in the 20–80° 2 theta angular region.

3.3.1.3 Determination of coke concentration

Samples with coke deposited were burned off in air at 500°C and the weight losses were measured. Reference sample of fresh catalyst was given the same treatment and the difference in weight loss was attributed to coke.

3.3.2 Surface Analysis

3.3.2.1 Metal Active Site Measurement

Metal active sites were measured using CO chemisorption technique performed in a Micromeritic ChemiSorb 2750 automated system. The known amount of CO was pulsed into the catalyst bed at room temperature. Carbon monoxide that was not adsorbed was measured using thermal conductivity detector. Pulsing was continued until catalyst surface was saturated with CO. the number of metal active sites was calculated in the basic assumption that only one CO molecule adsorbed on one metal active site (Vannice *et al.*, 1981; Anderson *et al.*, 1985; Ali *et al.*, 1998 and Mahata *et al.*, 2000) Calculation details of %metal dispersion are given in Appendix D.

3.3.2.2 X-ray Photoelectron Spectroscopy(XPS)

The XPS analysis was performed originally using an AMICUS spectrometer equipped with a Mg K_α X-ray radiation. For a typical analysis, the source was operated at voltage of 15 kV and current of 12 mA. The pressure in the analysis chamber was less than 10⁻⁵ Pa. The AMICUS system is computer controlled using the AMICUS “VISION2” software.

3.3.2.3 Ethylene temperature programmed technique

The amount of C₂H₄ adsorbed on the surface of catalyst was determined by means of temperature program technique. Experiment was performed in a

Micromeritic ChemiSorb 2750 automated system attached with ChemiSoft TPx software. The details of procedure are described below:

1) 0.2 grams of catalyst sample was loaded in a u-shape quartz cell and installed to the instrument. The catalyst must be reduced first in hydrogen flowing at the rate of 50 ml/min. The sample tube was heated in hydrogen to 200°C and holding at this temperature for 1 h and then cooled down to room temperature in helium.

2) The sample was heated up to 70°C and switched ethylene into reactor for 3 h, afterward ethylene was switched to helium and reactor was cooled down to room temperature.

3) The ethylene temperature program technique was carried out from room temperature to 800°C at a heating rate of 10°C/min.

3.3.2.4 Temperature programmed oxidation (TPO)

Temperature program oxidation (TPO) was used to determine amount of coke deposit and the temperature that coke was completely burned off. TPO was performed in a Micromeritic ChemiSorb 2750 automated system attached with ChemiSoft TPx software. The details of procedure are described below:

1) 0.25 grams of catalyst sample was loaded in a u-shape quartz cell and installed to the instrument. To eliminate trace amount of water, the catalysts were heated in helium to 200 °C and holding at this temperature for 2 h and then cooled to room temperature.

2) TPO was carried out from room temperature to 800°C at a heating rate of 5°C/min in 25 ml/min of 1%O₂ in helium. The amount of oxygen consumed was detected by TCD.