

CHAPTER IV

EXPERIMENT

This work can be divided into 3 parts: the catalyst preparation, the selective hydrogenation of acetylene and the catalyst characterization. In each part, the details of the experiments are described as follows:

4.1 The preparation of catalyst

4.1.1 Materials

The chemicals used in this experiment are normally analytical grade, but only some critical chemicals are to be specified as follows:

(a) Palladium [II] nitrate ($\text{Pd}[\text{NO}_3]_2$) manufactured by Nacalai Tesque Inc., Kyoto, Japan.

(b) Silver nitrate (AgNO_3) manufactured by E. Merck, Federal Republic of Germany.

(c) Alumina ($\alpha\text{-Al}_2\text{O}_3$) support (CS-303) was obtained from United Catalyst Incorporation (UCI), USA.

4.1.2 Apparatus

4.1.2.1 Unit for grinding and screening support

This unit consists of a pestle, a mortar and sieve trays. It was used for reducing the size of alumina support to the desired one, 40/60 mesh.

4.1.2.2 Unit for dry impregnation

This unit comprises pipettes, flask, beaker, droppers and volumetric flasks. It was used for preparing aqueous catalyst solution and impregnating the solution onto the support.

4.1.2.3 Unit for calcination

This unit is composed of an electrical furnace, an automatic temperature controller and a variable voltage transformer. It was used for calcining catalysts at high temperature.

4.1.3 Preparation of the palladium catalyst

4.1.3.1 Preparation of support and stock solution

4.1.3.1.1 Preparation of support

Alumina support was ground to the required mesh size of 40/60 and then washed with distilled water 3-4 times to remove fine particles and other impurities. Subsequently, the support was dried in an oven at 110°C overnight. Finally, it was calcined under air flow at 300 °C for 3 hours.

4.1.3.1.2 Preparation of stock solution

1) Palladium stock solution

The palladium complex solution was prepared by dissolving 0.1 gram of palladium nitrate in de-onized water and then making the total volume of the solution to 25 ml.

2) Silver stock solution

The silver complex solution was prepared by dissolution 0.5 gram of silver nitrate in de-ionized water to the total volume of 25 ml.

4.1.3.2 Preparation of palladium-based catalyst

1) The impregnating solution for 2 grams of support was prepared by calculating the amount of the stock solution to obtain the required metal loading. The de-ionized water was then added to obtain 2-ml solution.

2) 2 grams of alumina support was placed in a 100-ml erlenmeyer flask and then the impregnating solution from the palladium stock solution was gradually dripped into the support. Shaking the flask continuously during impregnation was required to ensure the homogeneous distribution of metal component on the support.

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

4) For calcination, the dried material was placed in a quartz tube. Nitrogen was subsequently introduced into the tube with the flow rate of 60 ml/min. The tube was then heated with the rate of 10 °C/min until the temperature reached 500 °C. After that, air with the flow rate of 100 ml/min was switched into the tube to replace nitrogen and the material was held for 2 hours.

4.1.3.3 Preparation of palladium-silver catalyst

The serial impregnation method was used to prepare the silver promoted 0.4% palladium on alumina support. The order of catalyst impregnation was the deposition of palladium followed by silver, respectively. For palladium, the impregnation and calcination methods were the same as mentioned above. For silver, both methods were quite similar to those of palladium with the exception that the calcination conditions were 370 °C for temperature and 1 hour for holding time.

4.2 The selective hydrogenation of acetylene

4.2.1 Chemicals and reagents

- Reaction gas mixture consisting of 0.8% H₂, 0.3% C₂H₂ and C₂H₄ balanced was manufactured by Thai Industrial Gas Limited (TIG).
- Hydrogen was bought from TIG.
- Argon was bought from TIG.

4.2.2 Instruments and apparatus

4.2.2.1 Reactor

The reactor is a conventional microreactor made from quartz tube. It can be operated at high temperature.

4.2.2.2 Automatic temperature controller

This unit consists of a magnetic switch connected to a variable voltage transformer and controlled by an RKC temperature controller of PF-4 series. The controller receives signal from thermocouple adjacent to the bed of catalyst in the reactor. A dial setting of the controller establishes a set point of any temperature within the range of 0 to 800 °C.

4.2.2.3 Electric furnace

Electric furnace was used to heat up the reactor during the reduction of catalyst and the reaction of gas mixture. The heating rate was controlled by the variable voltage transformer. By using the automatic temperature controller, the furnace could generate heat for the reactor ranging from room temperature to 800 °C.

4.2.2.4 Gas controller system

The system includes the following items:

- 1) Gas pressure regulators
- 2) on-off valves
- 3) needle valves to adjust gas flow rate

4.2.2.5 Gas chromatograph (GC)

Gas chromatograph was used to analyse the quantity of gas compositions obtained from the reactor outlet. This GC is an FID type of

SHIMADZU GC 14B with Carbosieve column S-2. The operating conditions of gas chromatograph are shown in Table 4.1.

Table 4.1 Operating conditions of gas chromatograph

Detector type	FID*
Detector temperature	180 °C
Column type	Carbosieve S-2
Column temperature	145 °C
Carrier gas	Nitrogen

* FID = Flame Ionization Detector

4.2.3 Procedure

The performance of catalyst for acetylene hydrogenation was measured in a conventional microreactor made from quartz tube. Reaction was carried out in an ordinary flow reactor under atmospheric pressure.

1) 0.2 g of catalyst was packed in the reactor and heated up from room temperature to 100 °C in argon flow at a rate of 30 ml/min. The catalyst was then reduced by replacing argon with hydrogen at a flow rate of 100 ml/min and maintained at this temperature for 2 hours.

2) After the reduction of the catalyst had been completed, the reactor was cooled down from 100 °C to a reaction temperature of 60 °C under argon flow and held at this temperature for 10 minutes. Later, the gas mixture from another line was switched to replace argon at the same flow rate of 30 ml/min. Consequently, the gas mixture was reacted under catalytic hydrogenation, i.e., acetylene was selectively hydrogenated to ethylene. However, in case of nitrous oxide treatment, the reactor was cooled down from 100 °C to 90 °C under argon flow and held for 10 minutes before nitrous oxide injection. After the temperature was reduced to 60 °C, the following procedures were similar to those without nitrous oxide addition.

3) The products taken from the sample at the reactor outlet were analysed by gas chromatograph. Conversion and selectivity were then calculated from the data obtained.

The flow diagram of acetylene hydrogenation is illustrated in Figure 4.1.

4.3 Characterization of the catalysts

4.3.1 Metal site measurement

4.3.1.1 Introduction

Generally, activity of catalyst is a function of metal site. Therefore, in order to describe changes in catalyst activity, it is necessary that the metal site measurement be used to characterize the catalyst. In this work CO adsorption technique was used for this measurement. Furthermore, it was assumed that the ratio of adsorbed CO:site was 1:1 and adsorption of CO was irreversible.

4.3.1.2 Procedure

The CO adsorption was detected by TCD detector and the flow diagram of this apparatus is shown in Figure 4.2. The procedure of CO adsorption technique was as follows:

1) 0.5 g of catalyst was packed in the sample tube and heated up from room temperature to 100 °C in helium flow at a rate of 30 ml/min. It was then reduced by replacing helium with hydrogen flow at a rate of 100 ml/min and maintained at this temperature for 2 hours.

2) After the reduction of catalyst had been completed, the sample tube was cooled down from 100 °C to 60 °C under helium flow and held at this temperature for 10 minutes. While cooling the catalyst, TCD detector was turned on and the set conditions were shown in Table 4.2. However, in case of nitrous oxide

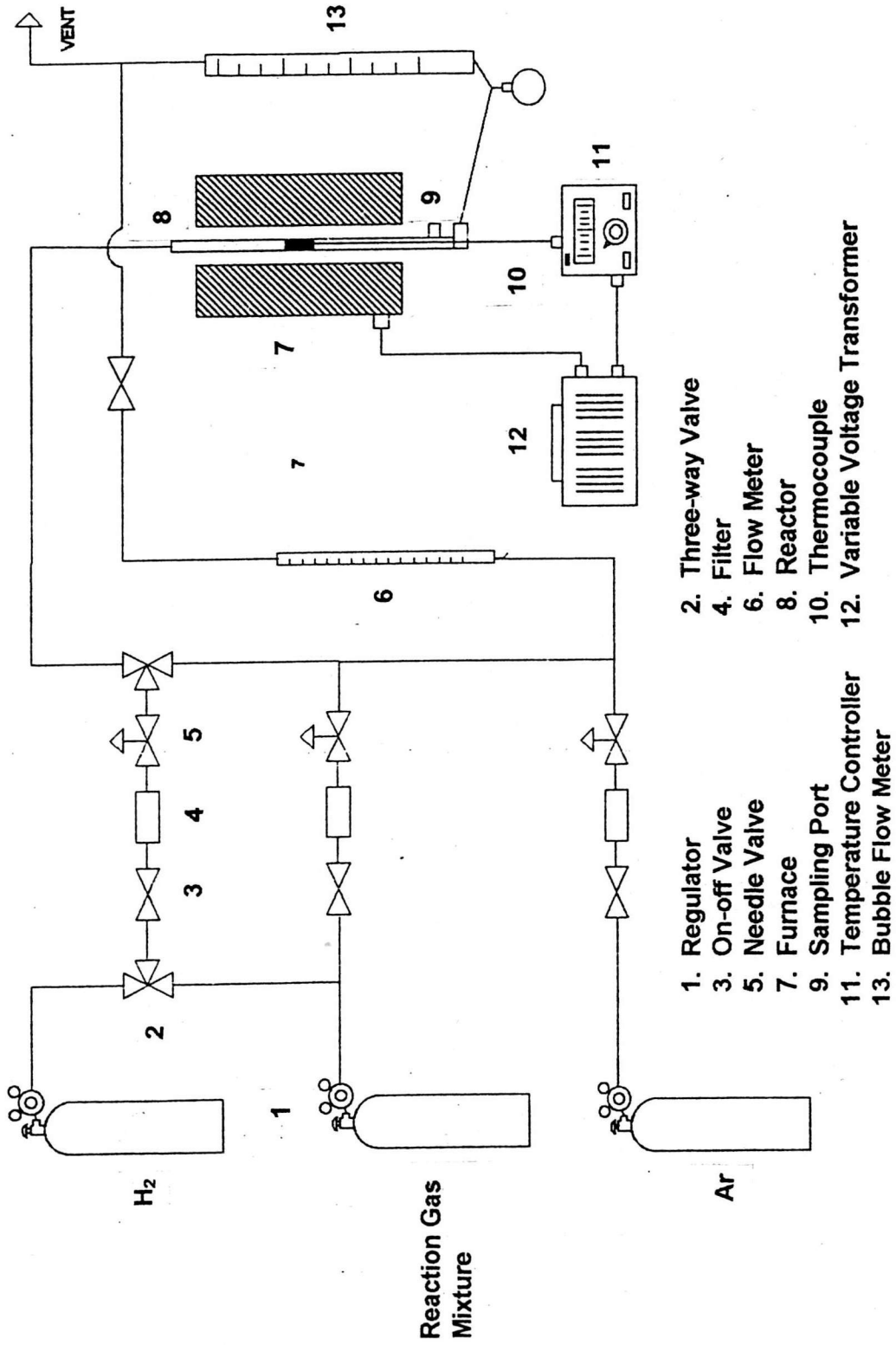


Figure 4.1 A flow diagram of acetylene hydrogenation

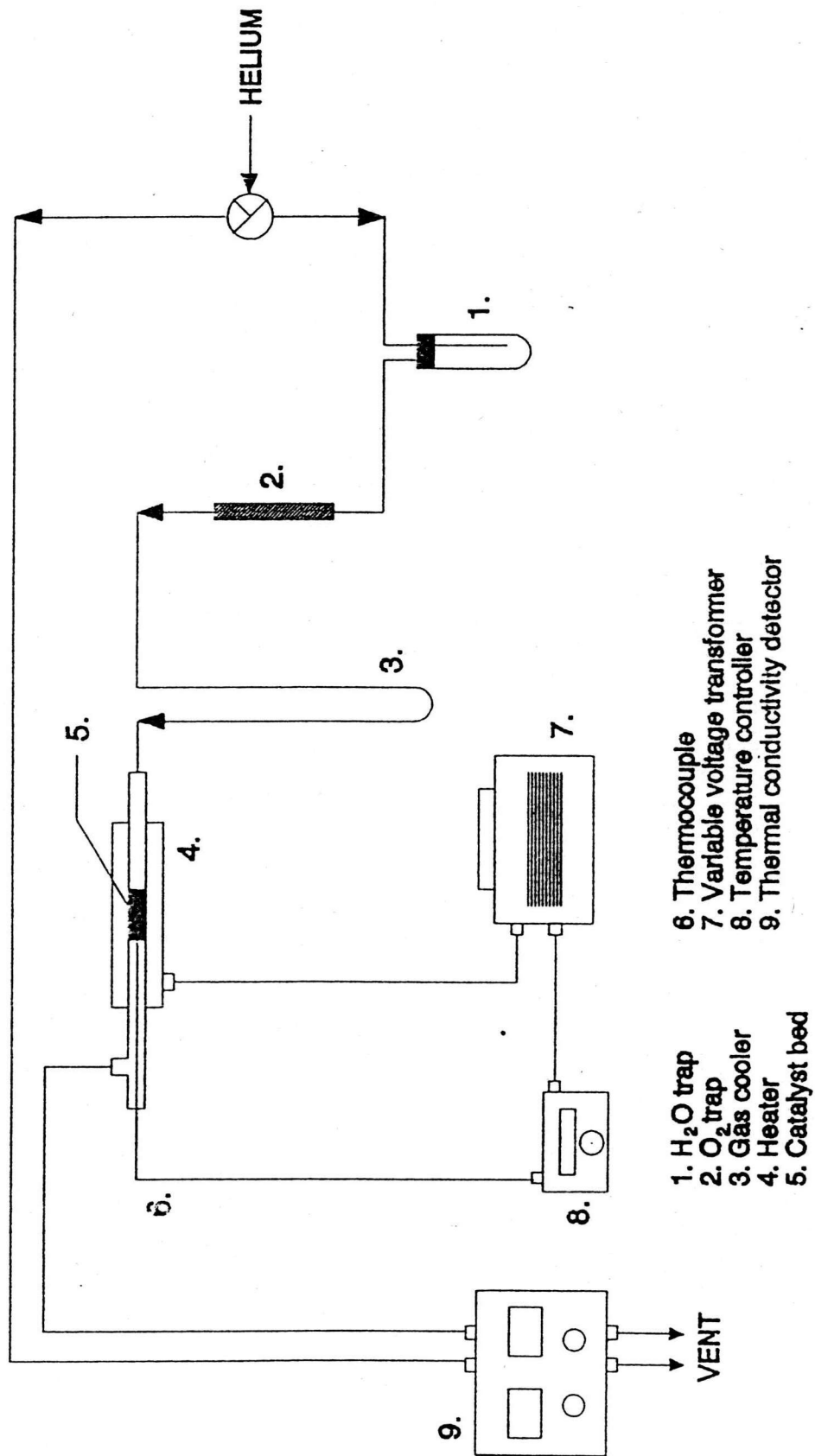


Figure 4.2 A flow diagram of the CO adsorption apparatus

treatment, the reactor was cooled down from 100 °C to 90 °C under helium flow and held for 10 minutes before nitrous oxide injection. After the temperature was reduced to 30 °C, the following procedures were similar to those without nitrous oxide addition.

Table 4.2 Conditions of TCD detector

variable	condition
Carrier gas flow	He 30 ml/min
Temperature of detector	80 °C
Current detector	80 mA

3) 0.18 ml of CO was injected to the injection port. The result was shown by recorder. Injection of CO was repeated until the sample did not adsorb CO gas, i.e., size of CO peak remained unchanged.

4.3.2 BET surface area measurement

Specific surface area of the catalyst was measured by a BET surface area analyzer (model ASAP 2000). This method was a physical adsorption of N₂ on the surface of the catalyst to find the specific area.

BET surface was measured by a BET analyzer at the Analytical center of Chemical Engineering Department, Chulalongkom University. The operating conditions are given in Table 4.3.

Table 4.3 Operating conditions of BET surface area measurement

The catalyst weight	0.2-0.4 g
Degas temperature	150 °C
Vacuum pressure	10 μHg
Pressure table	5 point.