

## CHAPTER III

### EXPERIMENT

This experimental part was divided into 3 parts: (a) Catalyst preparation, (b) Catalyst activity by propane dehydrogenation, (c) Catalyst characterization. In each part the details of procedure and apparatus were described as the following.

#### 3.1 Catalyst Preparation

The catalysts were prepared by the impregnation method. Material used as a support for the catalysts was  $\gamma$ -alumina, ground and sieve to 80/170 mesh. Table 3.1 summarizes the differences in the various preparation reported in this work, i.e., surface area, pore volume, pore diameter of catalyst and amount of active sites.

**Table 3.1** Characteristics of the catalysts investigated <sup>a</sup>

Catalyst	Pt (wt%)	Sn (wt%)	Li (wt%)	Cl (wt%)	Sn/Pt ratio	S (m <sup>2</sup> /g)	V <sub>p</sub> (cc/g)	d <sub>p</sub> (°A)
A	0.41	-	-	1.10	-	106.3	0.23	82.48
B	0.42	-	0.45	1.10	-	103.5	0.22	82.14
C	0.44	0.81	-	1.10	1.84	105.8	0.21	82.98
D1	0.45	0.22	0.45	1.10	0.49	98.55	0.22	89.22
D2	0.41	0.40	0.45	1.10	0.98	98.73	0.22	90.14
D3	0.42	0.65	0.45	1.10	1.55	98.62	0.22	87.34
D4	0.44	0.85	0.45	1.10	1.93	98.30	0.21	85.22
D5	0.37	0.90	0.45	1.10	2.43	97.53	0.22	89.64

<sup>a</sup> S = surface area      V<sub>p</sub> = pore volume      d<sub>p</sub> = pore radius

### 3.1.1 Materials

All chemicals used in this experiment are analytical grade and used as received.

(a) Hydrogen hexachloroplatinate (IV) hydrate ( $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ ) manufactured by Aldrich chemicals which platinum of 37.5% purity.

(b) Tin (II) chloride hydrated (Stannous chloride;  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ ) manufactured by Ajax chemicals which tin of 98.0-103.0% purity.

(c) Lithium nitrate ( $\text{LiNO}_3$ ) manufactured by Riedel-de haen ag. which lithium of 95% purity.

(d) Hydrochloric acid (HCl)  $37.25 \pm 0.75$  % of concentration from J.T.Baker.

(e) Hydrofluoric acid (HF)  $49 \pm 1$  % of concentration from J.T.Baker.

(f) Aluminium oxide 90 active ( $\text{Al}_2\text{O}_3$ ), neutral was supplied by Merck.

(g) Potassium bromide AR grade supplied by Fluka Chemicals was used.

### 3.1.2 Methodology

The alumina support was dried at  $100^\circ\text{C}$  overnight before used. The impregnating solution is prepared to contain a complex trichlorostannate (II) chloroplatinate anionic species (Wilhelm, 1976) by dissolving hexachloroplatinic acid in distilled water and mixed with a solution of stannous chloride in diluted hydrochloric acid in the required amount for the metal loading.

The concentration of tin and platinum in the impregnating solution being adjusted to yield a final catalyst containing from 0.20 to 1.00 wt% of tin and 0.40 wt% of platinum in all type of prepared catalyst (0.5, 1.0, 1.5, 2.0, 2.5 Sn/Pt ratio). The pH of the impregnating solution is controlled at less than about 3 prior to contact with the carrier material. The carrier material is preferably maintained in contact with the impregnating solution at ambient temperature for 6 hours before evaporated substantially to dryness at 100 °C with continuous slow speed stirring of the mixture of carrier material and the impregnating solution to obtain the homogeneously distributed metal component on the alumina support. Thereafter, the catalysts were dried overnight at 100 °C followed by calcined in air atmosphere for 6 hours with the heating rate of 5 °C/min.

The catalysts were then impregnated with a lithium nitrate aqueous solution to neutralize the acid used in the first impregnation procedure with a mixture of hexachloroplatinic acid and stannous chloride solution. The concentration of lithium in the impregnating solution was selected to yield final catalysts containing 0.45wt% of lithium. Then the catalysts were treated by the same drying and calcining as described.

## **3.2 Catalyst Activity Test by Propane Dehydrogenation**

### **3.2.1 Materials**

All gases used in this part were supplied by Thai Industrial Gases Public Co., Ltd.

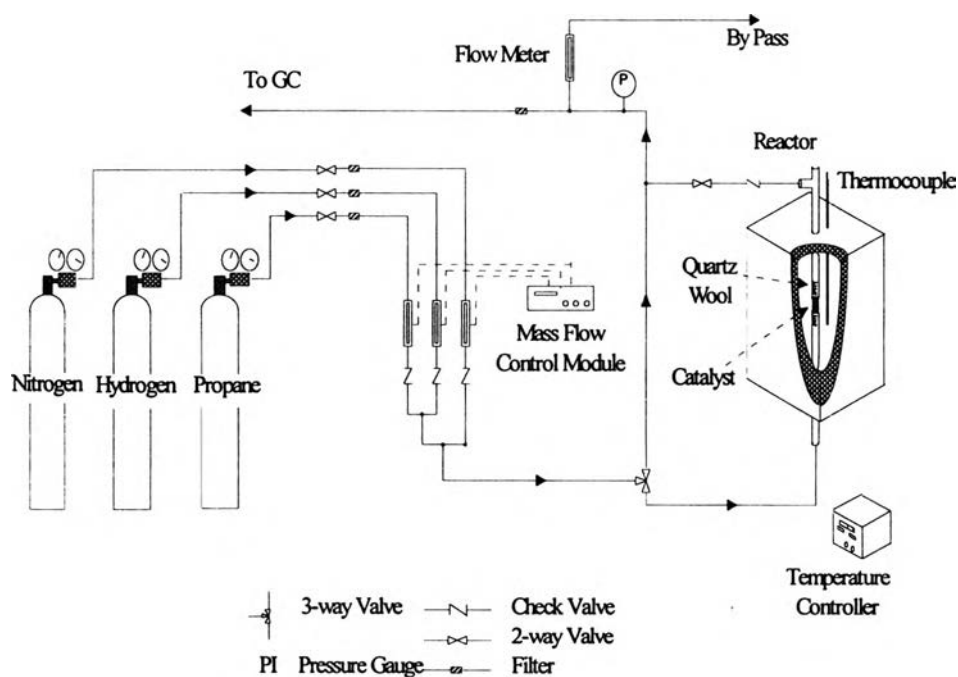
(a) The purity of 99.5% propane gas was used as feed stream for studying in catalyst deactivation, cycle of propane dehydrogenation, and coking rate measurement.

(b) Ultra high purity nitrogen gas (99.999%) was used as dilute gas in propane dehydrogenation and as a carrier gas for gas chromatography.

(c) Ultra high purity hydrogen gas (99.999%) was used as feed stream for propane dehydrogenation and for reducing catalyst before used.

### 3.2.2 Apparatus

The apparatus for study in catalyst deactivation of propane dehydrogenation was shown schematically in Figure 3.1.



**Figure 3.1** Schematic diagram of experimental apparatus.

(a) Reactor: The reactor used in catalytic tests was made of quartz tube. 200 mg of catalyst were placed between layers of quartz wool.

(b) Gas chromatography (GC): The composition of feed and effluent stream were analyzed by on-line GC, HEWLETT PACKARD series II 5890, with flame ionization detector (FID). The operating conditions were shown in Table 3.2.

**Table 3.2** GC operating conditions

Column	1m * 1/8" SS
Packing	Phenyl isocyanate/Poracil C, 80/100
Temp.	28 °C
Flow rate	Nitrogen, 10 ml/min
Detector	FID, 250 °C
Injector	120 °C

(c) Mass flow controller: All gases were controlled by mass flow transducer with control box supplied by SIERRA instrument, Inc. The flow rate error is smaller than 1%.

(d) Temperature controller: The automatical temperature controller consisted of a variable voltage transformer, a temperature controller, YOKOGAWA model UT37, and a thermocouple type K, Cole Palmer probe-flex 2521-mini, The heating rate amounted to 5 °C/min and controlled to desired temperature within 1 °C.

(e) Tubing system: Tubing system was obtained by SWAGELOK Co. Ltd., with a stainless steel tube diameter of 1/4" & 1/8" for GC inlet line.

### 3.2.3 Methodology

The activity of the catalyst samples for the dehydrogenation of propane was tested in quartz tube reactor at 600 °C, 5 psig. Using the catalyst charge of 200 mg with a range of mesh size of 80/170. A gaseous mixture of 8.157% propane in N<sub>2</sub> at total flow rate of 105 ml/min as a feed. Reactant and effluent products were analyzed by GC to find the conversion and selectivity to propylene which were expressed as mole percentage. Conversion and selectivity to propylene were calculated as the ratio of moles of converted propane to the mole of fed propane and the ratio of formed propylene to the moles of converted propane, respectively.

#### **Part I Catalyst Deactivation**

For catalyst life on-stream studies of the differently prepared catalysts, the following procedure is described:

(a) 200 mg of catalyst were placed in the quartz tube reactor between the layer of quartz wool in the middle of reactor. The reactor was heated with linear temperature programming from ambient temperature to 500 °C in a flowing N<sub>2</sub> as a purged gas with a flow rate of 50 ml/min and heating rate of 5 °C/min.

(b) Prior to the run, the catalyst samples were reduced in the reactor under H<sub>2</sub> at 500 °C for an additional 1 hr with flow rate of 50 ml/min.

(c) Purged the system in N<sub>2</sub> for 5 min before introduction of the hydrocarbon feed.

(d) The mixture of gas was controlled by mass flow controller to give 8.157 mole% of propane in N<sub>2</sub> with 0.5321 H<sub>2</sub> to hydrocarbon ratio at the

total flow rate of 105 ml/min. The mixture gas was introduced into the reactor which is operated isothermally at 600 °C, 5 psig, for 17 hr.

(e) The first sampling was started at 2 min after the feed stream of 8.157 mole% of propane in N<sub>2</sub> was fed to the reactor. The effluent products were sampled every 15 min until the reaction time was completed.

(f) After 17 hr of propane dehydrogenation, purged the system in N<sub>2</sub> for 5 min.

### **Part II Repeated Reaction-Regeneration Cycles**

In this part, 3 types of catalyst which give the high conversion and selectivity to propylene were selected from part I results to test the activity of these catalysts when they were operated in many cycles of reaction as in the industrial work.

(a) Follow part I step (a)--(c).

(b) The mixture of gas was similar to part I step (d) but the reaction time was decreased to 8 hr with the same operating condition.

(c) After 8 hr of propane dehydrogenation, purged the system in N<sub>2</sub> for 5 min.

(d) Start the regeneration step with 1 vol% O<sub>2</sub> in N<sub>2</sub> at 500 °C for 1 hr.

(e) Purged the system in N<sub>2</sub> for 5 min.

(f) Repeated step (a)--(e) for 8 cycles.

(g) Compare the conversion and selectivity to propylene in each cycle by on-line GC. The first sampling was start at 2 min after introducing feed stream. The effluent products were sampling in every 15 min until the reaction time was completed.

### **Part III Coking Rate Measurement**

(a) Follow part I step (a)--(c).

(b) Mixed 8.157 mole% of propane in N<sub>2</sub> with 0.5321 H<sub>2</sub> to hydrocarbon ratio at the total flow rate of 105 ml/min. The reaction was operated at 600 °C for 2, 4, 6 and 8 hr respectively.

(c) Purged the system in N<sub>2</sub> for 5 min.

After each reaction time was completed, the total amount of carbon deposited on the spent catalyst was characterized by Elementary Analyzer as described in Section 3.3.

### **3.3 Catalyst Characterization**

#### **3.3.1 CHNS/O Analyzer**

In the CHNS/O operating mode the Perkin Elmer 2400 Series II employs a combustion method to convert the sample elements which contain carbon and hydrogen to simple gases (CO<sub>2</sub> and H<sub>2</sub>O). The resulting gases are homogenized and controlled to exact conditions of pressure, temperature, and volume. The spent catalyst of 1 mg was used as a sample combustion so we can measure carbon and hydrogen weight percentage after complete combustion.

#### **3.3.2 Quantachrome Autosorb-1**

The Autosorb-1 operates by measuring the quantity of gas adsorbed onto or desorbed from a solid surface at some equilibrium vapor pressure by the static volumetric method. The solid sample maintained at a



constant temperature below the critical temperature of the adsorbate. An adsorption or desorption occurs the pressure in the sample cell changes until equilibrium is established. This volume-pressure data can be reduced by the Autosorb-1 into BET (Brunauer, Emmett, and Teller) surface area, total pore volume and average pore diameter. 200 mg of sample were dried and degassed in the sample holder overnight at 120 °C before use. All the data was calculated based on the dried weight of the sample after analysis.

### **3.3.3 Atomic Absorption Spectroscopy (AAS)**

The content of metal (Pt and Sn) loaded in the catalyst were characterized by Atomic Absorption Spectroscopy, VARIAN model 300/400. Standard solutions used in this work manufactured by Merck contained Pt and Sn of 1000 ppm respectively. 500 mg of catalysts were dissolved in mixture solution of hydrofluoric acid and hydrochloric acid to dissolve the alumina support before use. The amounts of metal loaded in the catalyst were obtained by measuring the absorbance of those metal solutions.