

## CHAPTER III

### EXPERIMENTAL SECTION

The experimental program can be divided into three parts: (a) catalyst preparation; (b) the activity and selectivity measurements of the catalyst by propane dehydrogenation; and (c) catalyst characterization. The details of each part are described in the following sections.

#### 3.1 Catalyst Preparation

The impregnation method is employed to prepare the catalyst. The catalyst was separately impregnated in the sequence of tin, platinum and lithium respectively.

##### 3.1.1 Materials

The  $\gamma$ -alumina, manufacturer lot No. 955x022, which has a surface area of 210 m<sup>2</sup>/g was used as a supporter. And it was sieved in the range of 170 - 400 mesh before being used.

All chemicals used in this experiment were analytical grade.

(a) Hydrogen hexachloroplatinate (IV) hydrated ( $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ ) with 37.5% platinum manufactured by Aldrich Chemicals.

(b) Tin (II) chloride hydrated ( $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ ) with tin of 98.0% purity manufactured by Ajax Chemicals.

(c) Lithium nitrate ( $\text{LiNO}_3$ ) manufactured by Merck.

(d) Aluminum oxide ( $\text{Al}_2\text{O}_3$ ) manufactured by LaRoche Chemicals.

(e) Hydrochloric acid (HCl) with the concentration of  $37.25 \pm 0.75\%$  manufactured by J.T. Baker.

(f) Hydrofluoric acid (HF) with the concentration of  $49 \pm 1\%$  manufactured by J.T. Baker.

(g) Potassium bromide (KBr) manufactured by Fluka Chemicals.

### 3.1.2 Methodology

The  $\gamma$ -alumina was dried at  $100\text{ }^\circ\text{C}$  for 6 hours in order to evaporate water in the pores. The alumina was impregnated with the tin precursor first. The tin solution was prepared by dissolving Tin (II) chloride hydrated in hot diluted hydrochloric acid to a desired amount of tin content. The tin and platinum loading were fixed at 0.8 and 0.4% by weight (These values, obtained from previous works, provided the highest activity and selectivity). The alumina was kept contacting with the impregnating solution at ambient temperature for 30 minutes and then slowly evaporated to dryness at  $150\text{ }^\circ\text{C}$ . During the evaporation step, the solution was continuously stirred at a low speed to obtain a uniform distribution of metal component on the alumina support. Then the catalyst was dried at  $100\text{ }^\circ\text{C}$  for 12 hours and followed by calcination at  $600\text{ }^\circ\text{C}$  for 6 hours in the atmospheric air with the heating rate of  $5\text{ }^\circ\text{C}/\text{min}$ .

Consequently, the calcined catalyst was impregnated again with platinum and lithium, respectively. The platinum and lithium solutions were prepared from the dissolution of  $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$  and  $\text{LiNO}_3$ , respectively, in water. And the reimpregnated catalyst was dried and calcined under the same condition as for the impregnation of tin. The concentration of lithium in the impregnating solution was adjusted to yield the final catalyst containing lithium from 0.05 to 1.5% by weight (Li/Pt ratios of 0.125, 1, 2, 2.5 and 3.75).

## 3.2 The Activity and Selectivity Studies

### 3.2.1 Materials

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

(a) The 20% purity of propane gas balanced with nitrogen was used as a feedstock for studying the deactivation of catalyst, repetitive reaction-regeneration or cycle run and coking rate measurement.

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

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

### 3.2.2 Apparatus

The apparatus used for studying the deactivation of propane dehydrogenation catalyst was schematically shown in Figure 3.1.

The details of the experimental equipment can be described as the following.

(a) Reactor: The reactor was made from a quartz tube.

(b) Gas chromatography: The compositions of feed and product streams were analyzed by an on-line gas chromatography with a Hewlett Packard model No. 5890 series II. Its specifications and operating conditions are shown in Table 3.1.

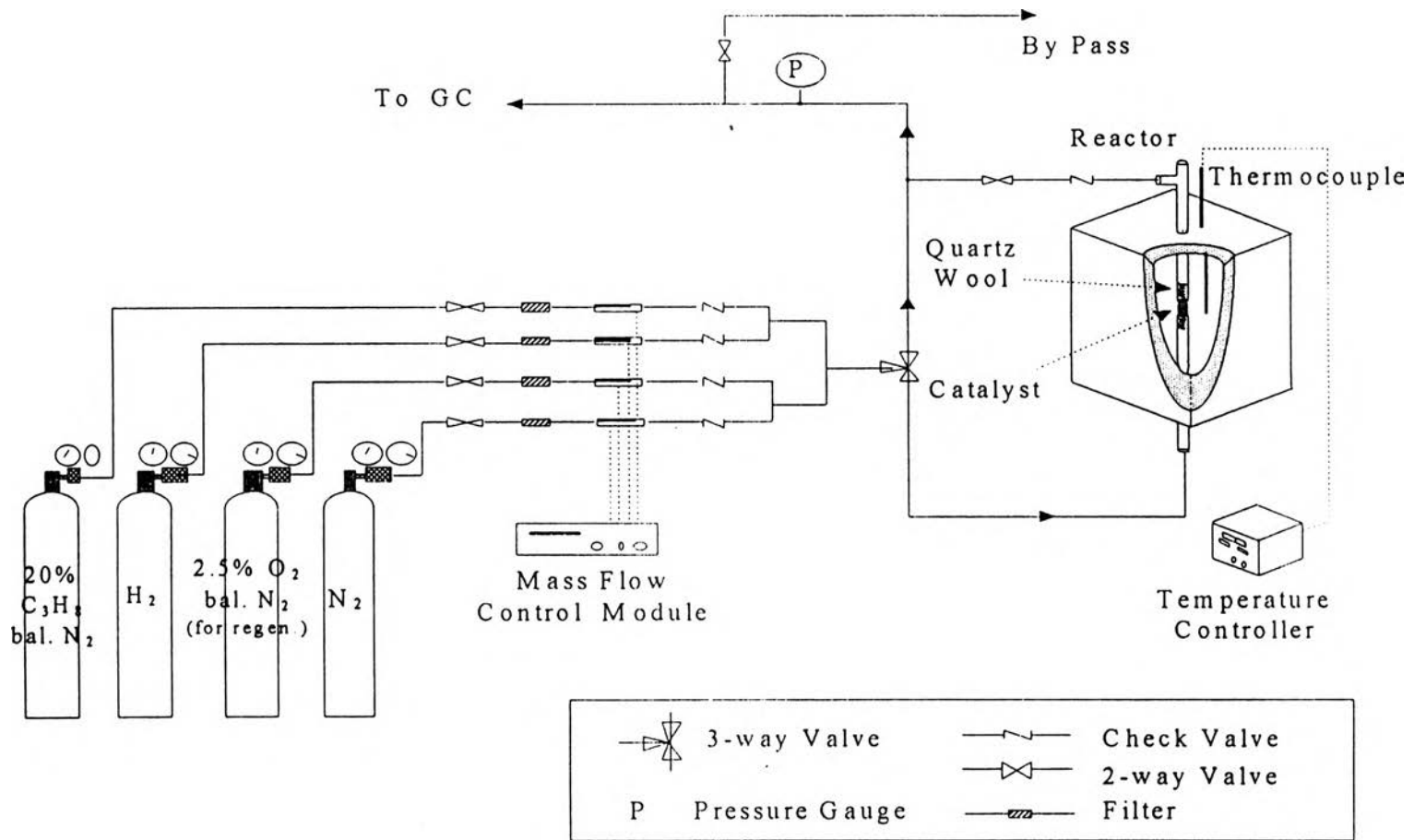


Figure 3.1 Schematic diagram of experimental equipment.

**Table 3.1** Gas chromatography specifications and operating conditions

Item	Specification and Operating condition
Column	10' x 1/8" SS
Packing	Hayesep D, 100/120
Temp.	95 °C
Carrier	12 ml/min of Nitrogen
Detector	TCD, 150 °C
Injector	120 °C

(c) Mass flow module: The flow rates of any gas streams were controlled by mass flow transducers and flow controller from SIERRA Instrument, Inc. The flow rate error was calibrated within the limit of 1%.

(d) Temperature controller: The automatic temperature controller consisted of a variable voltage transformer, a model UT37 temperature controller manufactured by YOKOGAWA, and a type-K thermocouple from Cole Palmer, probeflex 2521-mini. The heating rate was set at 5 °C/min and the desired temperature was held within 1 °C.

(e) Fittings and tubing systems: The stainless steel fittings and tubing systems having outside diameters of 1/4" and 1/8" were utilized and obtained from SWAGELOK Co., Ltd.

### 3.2.3 Methodology

Two hundred milligrams of catalyst was placed in the quartz tube reactor and sealed with quartz wool at the top and bottom of the catalyst bed. The operating temperature and pressure were maintained at 600 °C and 5 psig. The reactant gases were hydrogen and propane with a H<sub>2</sub>/C<sub>3</sub>H<sub>8</sub> ratio of 0.5.

The nitrogen at the flow rate of 85 ml/min was used as the dilution gas. The total flow rate of feed stream was 100 ml/min. The feedstock was mixed together before reaching the reactor and flowed upward over the catalyst bed. The compositions of the inlet and outlet streams were analyzed by gas chromatography to find the conversion of propane and selectivity to propylene. The conversion and selectivity were defined as the ratio of moles of reacted propane to moles of propane fed and the ratio of moles of propylene produced to moles of propane converted, respectively.

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

The activity and selectivity of the prepared catalyst were studied while contacting it with the reactants in the reactor for a long time. The procedure of this part is described below:

(a) Two hundred milligrams of catalyst was packed in the middle of the quartz tube reactor between the layer of quartz wool. The reactor was heated with the heating rate of 5 °C/min from an ambient temperature to 500 °C in flowing nitrogen gas as a purge gas with a flow rate of 50 ml/min.

(b) The catalyst was reduced in the reactor at 500 °C using hydrogen gas flow rate of 50 ml/min for an additional one and a half hours.

(c) The catalyst was then purged with nitrogen gas for another 30 minutes before introducing the feed stream.

(d) The mixture of gases which were controlled by mass flow modules had a hydrogen to hydrocarbon ratio of 0.5 with a total flow rate of 100 ml/min. The flow of the reacting gas mixture was continued through the reactor, operated isothermally at 600 °C, for 15 hours.

(e) The effluent was first sampled 2 minutes after the feed stream flowing through the reactor was initiated. The product stream was sampled

every 15 minutes by an on-line gas chromatography to determine the compositions of the product stream until the reaction time reached 15 hours.

(f) After 15 hours, the system was purged with nitrogen gas for 30 minutes.

### **Part II Repeat Reaction-Regeneration or Cycle Run**

Three catalyst compositions which provided the highest conversion and selectivity from part I were chosen to study the activity of the catalysts when they were exposed to many cycles as in the industrial applications. The details of this part are described below:

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

(b) The reactant stream was the same as in part I, but the reaction time was reduced to 8 hours with the same operating conditions.

(c) The system was purged with nitrogen gas at 600 °C for 30 minutes after the reaction was finished.

(d) A regenerating feed stream containing 1%vol O<sub>2</sub> was introduced into the reactor at 600 °C for 1 hour.

(e) Repurge the catalyst with N<sub>2</sub> at 500 °C for 30 minutes.

(f) Repeat step (a) - (c) for 8 cycles.

(g) The first sampling of the outlet gases was taken at 2 minutes after the reactant stream was introduced into the reactor. The effluent was sampling every 15 minutes until the reaction cycle was completed.

### **Part III Coking Rate Measurements**

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

(b) The reactant stream had the same compositions as part I, and the reaction conditions were the same, but the reaction time was varied to 2, 4, 6 and 8 hours.

(c) The system was purged with  $N_2$  having a flow rate of 50 ml/min for 30 minutes.

After each reaction time was completed, the total amount of carbon deposited on the spent catalyst was investigated by Elemental Analyzer or CHNS/O Analyzer which is described in section 3.3.

### **3.3 Characterization of Catalyst**

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

The CHNS/O Analyzer from the Perkin Elmer model No. 2400 series II, converts the sample which contains carbon and hydrogen completely to combustion gases ( $CO_2$  and  $H_2O$ ). The resulting gases are calibrated for exact conditions of pressure, temperature and volume. A thermal conductivity detector (TCD) is employed to detect the combustion gases which come out at different retention times. A one-mg-weight spent catalyst was used to measure the weight percentage of carbon and hydrogen after coking for each reaction time.

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

The Autosorb-1 operates by measuring the quantity of gases adsorbed onto or desorbed from a solid surface at some equilibrium vapor pressures by a static volumetric method. The sample is maintained at a constant temperature below the critical temperature of the adsorbate. An adsorption or desorption process goes on until the equilibrium is established. This volume-pressure data are utilized to calculate the BET (Brunauer, Emmett, and Teller) surface area, total pore volume and average pore diameter. Before starting analysis, the 200 mg of catalyst was dried and outgassed in the sample cell at 140 °C overnight. All analytical data were based on the dried weight of sample.



### 3.3.3 Atomic Absorption Spectroscopy (AAS)

The AAS, VARIAN model 300/400, was used to determine the content of metal loaded on the catalyst. Five hundred milligrams of catalyst was dissolved in HF and HCl with the ratio of 4 to 1 to extract the alumina before measurement. A standard solution of 1,000 ppm from Merck was used to establish a calibration curve. The amount of metal loaded on the catalyst was obtained by measuring the absorbance of those metal solutions and comparing with the calibration curve.