

CHAPTER III

EXPERIMENTAL SECTION

3.1 Materials

3.1.1 Gases

All gases used in this experiment were provided by Thai Industrial Gas Public Co., Ltd.

The ultra high purified (UHP) nitrogen was used for purging the system, Gas chromatography (GC) carrier, Thermal conductivity detector (TCD) reference gas, Simultaneous thermal analysis (STA) balance gas and mixing the diluted oxygen for regeneration procedure.

The 2.5 vol% oxygen in nitrogen mixture was mixed with nitrogen using a mass flow controller to give 1 vol% oxygen in nitrogen.

The ultra high purified helium was used as a carrier gas in an Elemental analyzer.

The zero graded air was used for driving the auto inject valve in Gas chromatography. It was also used as the combustion gas in Elemental analyzer and STA.

3.1.2 Chemicals

Potassium bromide (KBr), AR grade, supplied by Fluka Chemicals was used for Infrared (IR) spectroscopy.

Hydrochloric acid (HCl) ($37 \pm 0.75\%$ conc.) and hydrofluoric acid (HF) ($49 \pm 1\%$ conc.), AR grade, were provided by J.T. Baker.

3.1.3 Catalysts

Two hundred milligrams of fresh and spent Pt-Sn-Li/Al₂O₃ catalysts obtained from the propane dehydrogenation experiment were used in this study. The weight percentage of Pt and Sn was kept to 0.4 and 0.8 respectively. The lithium content was varied from 0.05 to 1.5 wt%. Their compositions are given in Table 3.1. The three best catalysts from the dehydrogenation part, which are D₁, D₂ and D₃, were studied in the cyclic regeneration while all catalysts were studied in the partial regeneration.

Table 3.1 Compositions of the catalysts used in this study

Catalyst name	Pt (wt%)	Sn (wt%)	Li (wt%)	Li/Pt ratio
D ₁	0.39	0.78	0.04	0.10
D ₂	0.44	0.81	0.39	0.89
D ₃	0.41	0.80	0.78	1.90
D ₄	0.40	0.79	1.02	2.55
D ₅	0.39	0.79	1.47	3.77

3.2 Equipment

The experiments were operated in a simple quartz tube reactor as shown in Figure 3.1.

3.2.1 Gas Chromatography

A Hewlett Packard gas chromatograph (model 5890 Series II) was used to detect CO₂ and O₂ signals. The quantitative analysis of CO₂ gas produced by the combustion reaction and O₂ unreacted gas was detected by

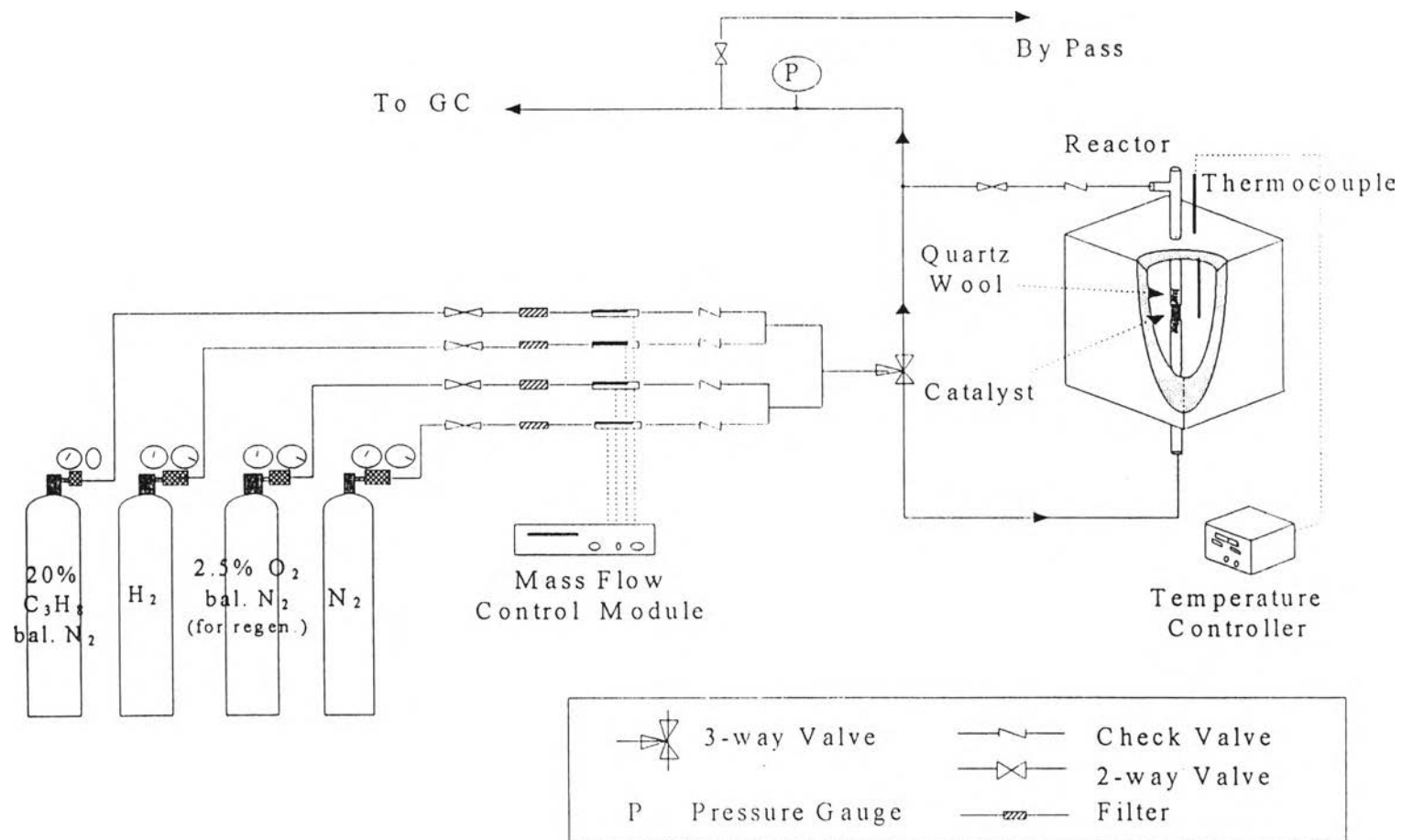


Figure 3.1 Schematic diagram of experimental equipment.

the thermal conductivity detector (TCD). The gas chromatography specifications and operating conditions are given in Table 3.2.

Table 3.2 Specifications and operating conditions of GC

Item	Specification and operating condition
Packing	100/120 HayeSep D
Detector	TCD
Column	10' x 1/8" S.S.
Carrier flow rate	N ₂ , 12 ml/min
Injector temp., °C	150
Detector temp., °C	200
Oven temp., °C	60

3.2.2 Furnace

This set was assembled from refractory bricks and the resistance wires to give a simple furnace with square hole in the core. Its reliable operating range is about 200-700 °C corresponding to a temperature control device.

3.2.3 Temperature Control Device

The furnace temperature was controlled by YOKOGAWA digital indicating controller model UT37. It gives a linearized temperature rate of 5 °C/min for ramping up and of 10 °C/min for cooling down the furnace. A type-K thermocouple, Cole Palmer probe-flex 2521-mini, was used for measuring the furnace temperature.

3.2.4 Mass Flow Controller

All gases in this experiment were controlled by mass flow transducers associated with a control box supplied by SIERRA instrument, Inc. The flow rate error is less than 1%.

3.2.5 Tubing and Fittings

Valves, filters and tubing were provided by Swagelok company. All tubes in the system were assembled with 1/4" stainless steel tubes, except for the GC inlet line, a 1/8" stainless steel tube was installed.

3.3 Methodology

This experimental section was conducted in conjunction with the propane dehydrogenation over Pt catalyst experiment (see Saimongkol, 1997). The catalyst was packed in a simple quartz tube reactor as shown in Figure 3.1 and then was operated in the propane dehydrogenation reaction at 600 °C for 8 hours. The reaction gas was hydrogen and 10 vol% propane with a H₂/C₃H₈ ratio of 0.5 and N₂ was used as the dilution gas.

3.3.1 Cycle Regeneration

After the reaction was finished, the spent catalyst was regenerated for an hour. Then the next dehydrogenation reaction cycle was started. This procedure was repeated for 8 cycles as its schematic diagram is shown in Figure 3.2.

The cycle regeneration procedure is as follows:

(a) Two hundred milligrams of spent catalyst from the propane dehydrogenation reaction was held in the quartz reactor. The reactor was

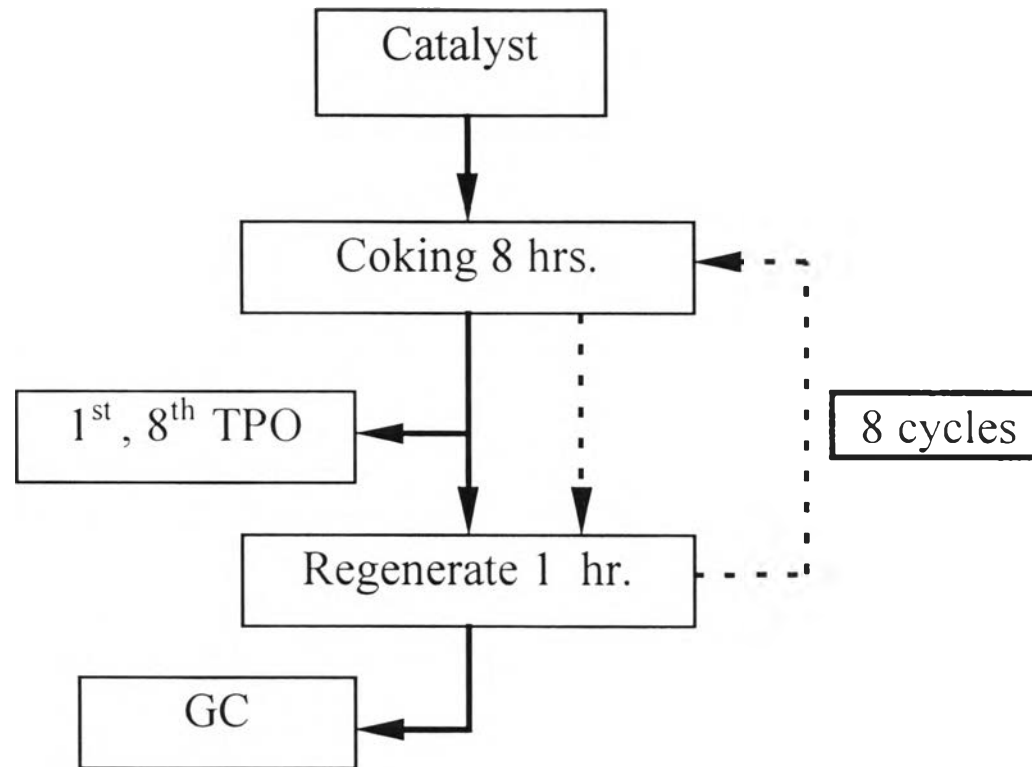


Figure 3.2 Schematic diagram of cyclic regeneration experiment.

cooled down to 500 °C and it was maintained at this temperature throughout the regeneration time. Nitrogen gas was used to purge the system with a flow rate of 50 ml/min. for 30 minutes;

(b) Mix 2.5 % O₂ in N₂ with UHP N₂ to obtain 1% O₂ and wait until the mixed gas concentration was constant. The total flow rate of mixed gas was 100 ml/min;

(c) Switch 1% O₂ in N₂ to the reactor for an hour and then start measuring CO₂ and O₂ signal;

(d) Purge the system for 30 minutes with N₂ at a flow rate of 50 ml/min and prepare to run the dehydrogenation reaction;

(e) Repeat the step (a) - (d);

(f) After finishing the first and the eighth reaction cycle, catalyst samples were characterized by TPO (see Section 3.3.3).

3.3.2 Partial Regeneration

The objective of this part is to investigate how coke deposits on the catalyst change during regeneration. The catalyst was also operated in the propane dehydrogenation. The spent catalyst from the first cycle of dehydrogenation reaction was regenerated by varying the burning time from 5 to 60 minutes. The schematic diagram is shown in Figure 3.3.

The partial regeneration procedure is as follows:

(a) Follow the step (a) - (b) in Section 3.3.1;

(b) Switch the 1% O₂ in N₂ to reactor for 5,10,15 and 30 minutes respectively;

(c) Purge the system for 5 minutes and cool down the furnace;

(d) Characterize the spent and partially regenerated catalyst (see Section 3.3.3).

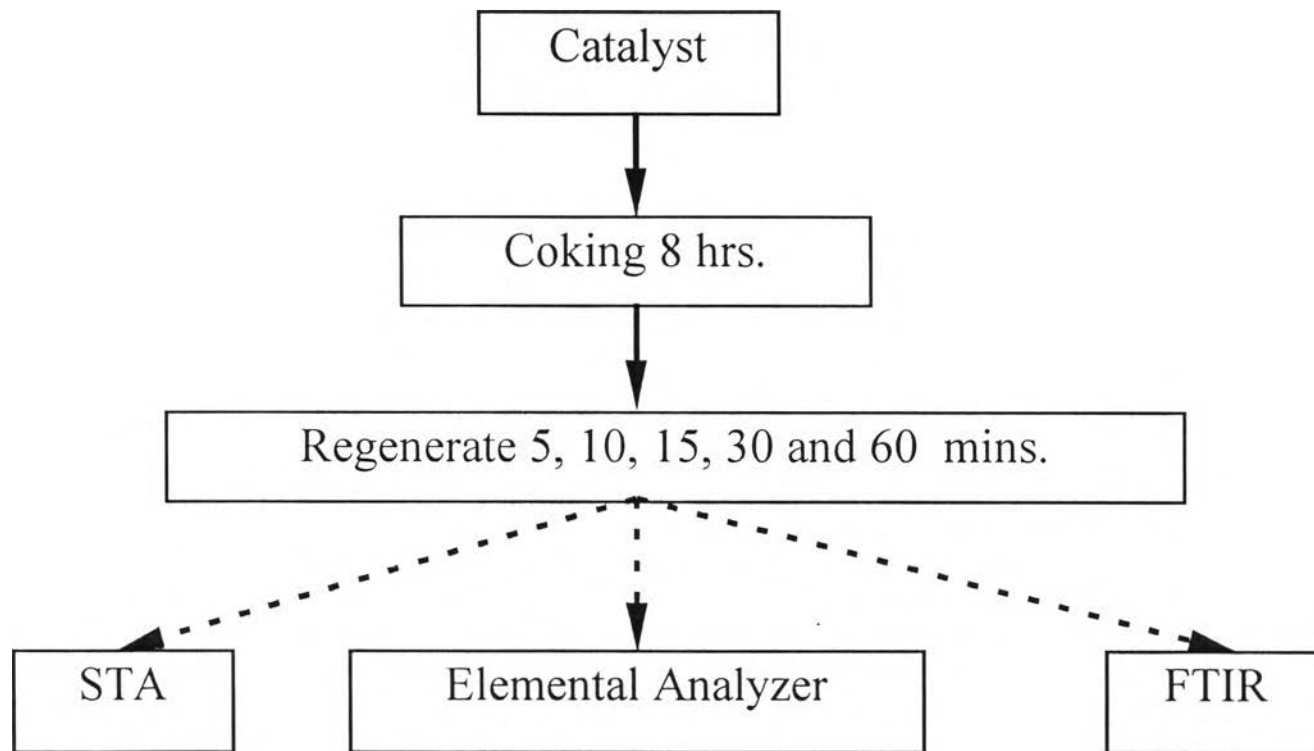


Figure 3.3 Schematic diagram of partial regeneration experiment.

3.3.3 Coked Catalyst Characterization

3.3.3.1 *Temperature-Programmed Oxidation (TPO)*

The temperature programmed oxidation was investigated *in-situ* in the catalyst bed as shown in Figure 3.1. The spent catalysts of the first and the eighth reaction cycle were studied.

The TPO procedure is as follows:

- (a) After finishing the first and the eighth reaction cycle, purge the system with N₂ gas while cooling down the system to 100 °C;
- (b) Keep the reactor temperature at 100 °C for 30 minutes and then stop the purging gas;
- (c) Mix the diluted O₂ gas as described in section 3.3.1 (b);
- (d) Switch the diluted O₂ to the reactor and start the temperature programmed oxidation (TPO) by increasing a temperature from 100 °C to 700 °C with a heating rate of 5 °C/min and then begin measuring CO₂ and O₂ concentrations;
- (e) Purge the system for 5 minutes and cool down the furnace.

3.3.3.2 *Measurement of Carbon Content*

A Perkin Elmer elemental analyzer (CHNS/O) was applied to measure the carbon weight percentage which contained in 1 mg of spent and partially regenerated catalyst.

3.3.3.3 *Measurement of Weight Loss*

A Netzsch simultaneous thermal analysis (model STA 409 EP) was applied to measure the weight loss from the catalyst. The instrument parameters are shown in Table 3.3.

Table 3.3 STA parameters

Parameter	Value	Parameter	Value
Sample	Treated catalyst	Sample weight, mg	50
Reference	Fresh catalyst	Flow rate, cm ³ /min	50
Crucible	Alumina	Heating rate, K/min	5
Sample carrier	TG/DTA	Start temperature, °C	20
Range TG, mg	100	End temperature, °C	700
Range DTA, uV	40	Sampling time, /sec	4
Atmosphere	1 % O ₂		

3.3.3.4 Infrared Spectroscopy

A Bio-Rad FTIR (model FTS - 45A), single beam spectrophotometer was used. The FTIR conditions are given in Table 3.4.

Table 3.4 FTIR conditions

Condition	Value
Scan speed, kHz	5
Low pass filter, kHz	1.2
Resolution	16
Spectral range, cm ⁻¹	400 - 4000
Aperture, cm ⁻¹	2
Spectrum	Absorbance
No. Scan	16
Sensitivity	1

For attainment of adequate signal levels, the concentration of coke was increased by dissolving the alumina support in an acid mixture by the following procedure proposed by Magnoux et al. (1987):

(a) Fifty milligrams of spent or partially regenerated catalysts were attacked under vigorous stirring with a solution of 0.1 ml of 37 wt% hydrochloric acid and 0.4 ml of 47 wt% hydrofluoric acid at room temperature for 2 hours;

(b) The suspension was filtered by a 45 micron membrane filter and the solid was washed with distilled water and then dried overnight at room temperature;

(c) One milligram of extracted coke from (b) and 99 mg of potassium bromide were mixed together and pressed into disk;

(d) Scan the prepared disk with the FTIR instrument.