

## CHAPTER III

### EXPERIMENTAL SECTION

#### 3.1 Materials

##### 3.1.1 Gases

All gases used in this experiment were commercially obtained from Thai Industrial Gas Public Co., Ltd. and Praxair Korea Co., Ltd.

The ultra high purity (UHP) nitrogen was used for purging the system, gas chromatography carrier, thermal Conductivity Detector reference gas, simultaneous thermal analysis balance gas and mixing the diluted oxygen for regeneration procedure.

The pure butane and UHP hydrogen were used as reactants for the butane dehydrogenation reaction.

The 2.5 vol% oxygen balance in nitrogen was mixed with the UHP nitrogen by using mass flow controller to obtain 1 vol% oxygen in nitrogen.

The ultra high purity (UHP) helium was used as a carrier gas in an elemental analyzer.

The air zero grade was used as the combustion gas in elemental analyzer and simultaneous thermal analysis. It was used for driving the auto sampling valve in gas chromatography also.

##### 3.1.2 Chemicals

Potassium bromide (KBr), AR grade, supplied by Fluka Chemicals was used for preparing sample of Infra-Red spectroscopy.

Concentrated hydrochloric acid (HCl),  $37\pm 0.75$  wt% of concentration, and Concentrated hydrofluoric acid (HF),  $49\pm 1$  wt% of concentration, provided by J.T. Baker were used.

### 3.1.3 Catalysts

Catalyst samples were prepared by the impregnation method discussed by Suthasut (1998). Two hundred milligrams of fresh and spent Pt-Sn-Li/Al<sub>2</sub>O<sub>3</sub> catalysts obtained from the butane dehydrogenation experiment were used in this study. The tin content was varied from the 0.2 to 1.0 wt% whereas Pt and Li content were kept at 0.4 wt% and 0.45 wt%, respectively to give the difference in Sn/Pt weight ratios from 0.5 to 2.5. Their metal contents and physical properties, obtained from AAS, EDX and BET, are given in Table 3.1 to 3.3. Three types of catalysts in different Sn/Pt ratios which are D<sub>1</sub>, D<sub>3</sub>, and D<sub>5</sub> were studied in the cyclic regeneration while all catalysts were studied in the partial regeneration.

**Table 3.1** Characteristics of the catalysts investigated by AAS\*

Catalyst name	Pt (wt.%)	Sn (wt.%)	Li (wt.%)	Sn/Pt ratio
D <sub>1</sub>	0.42	0.25	0.42	0.59
D <sub>2</sub>	0.40	0.45	0.42	1.12
D <sub>3</sub>	0.40	0.66	0.48	1.65
D <sub>4</sub>	0.42	0.79	0.45	1.88
D <sub>5</sub>	0.42	0.96	0.48	2.28

\* Atomic Absorption Spectroscopy

**Table 3.2** Characteristics of the catalysts investigated by EDX\*

Catalyst name	Pt (wt.%)	Sn (wt.%)	Cl (wt.%)	Sn/Pt ratio
D <sub>1</sub>	0.43	0.29	0.12	0.67
D <sub>2</sub>	0.42	0.41	0.10	0.98
D <sub>3</sub>	0.42	0.68	0.13	1.62
D <sub>4</sub>	0.41	0.88	0.12	2.15
D <sub>5</sub>	0.42	1.09	0.16	2.60

\* Energy-Dispersive X-Ray Spectrometry

**Table 3.3** Physical properties of the catalysts investigated by BET\*

Catalyst name	Surface area (m <sup>2</sup> /g)	Total pore volume (cc/g)	Avg. pore radius (Å)
D <sub>1</sub>	112.6	0.040	7.128
D <sub>2</sub>	109.6	0.039	7.286
D <sub>3</sub>	120.0	0.041	6.870
D <sub>4</sub>	112.8	0.040	7.101
D <sub>5</sub>	111.2	0.040	7.257

\* Brunauer, Emmett, and Teller

## 3.2 Apparatus

The experimental system as shown in Figure 3.1 can be divided into three parts. The first part is the gas blending system, the second part is the differential flow reactor, and the last part is the gas chromatography used for analysis of the reactor effluent samples.

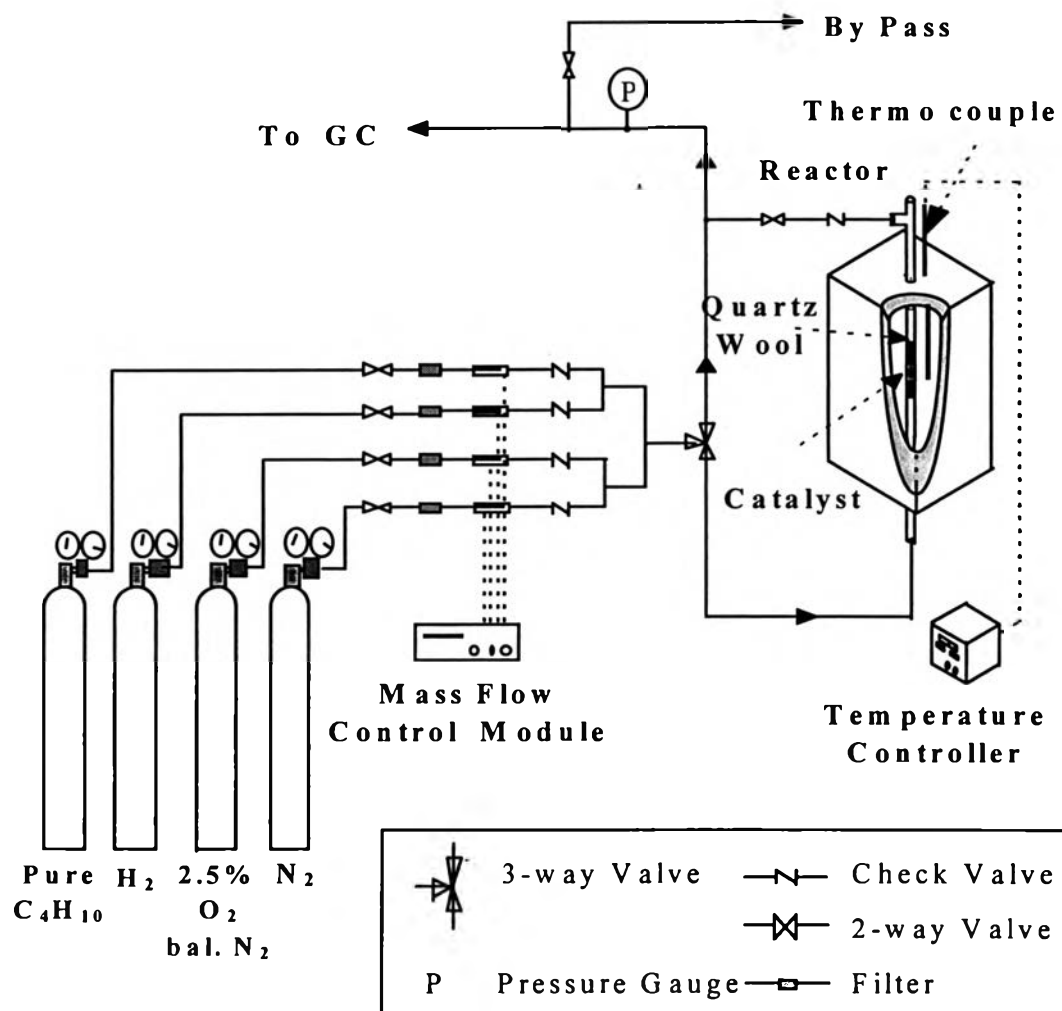
### 3.2.1 Gas Blending System

The flow rate of each gas was controlled by mass flow transducers associated with a control box supplied by Sierra Instruments to achieve the desired feed stream composition. All gases were first passed through a 7 micron filter in order to remove any small particles and then flowed through the mass flow controller at a constant pressure of 20 psig. Check valves were also installed to prevent the back flow of gases. All the feed stream were mixed before feeding into the reactor.

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

### 3.2.2 Differential Flow Reactor

Butane dehydrogenation and combustion reactions were carried out in a 1/4 inch diameter simple quartz tube reactor at 5 psig by adjusting the metering valve. The catalyst, packed between two plugs of 0.1 g and 0.15 g of zirconia wool at the top and the bottom of the catalyst respectively, was placed in the middle of the reactor. The reactor was held in an electrical heater equipped with a PID controller. The furnace temperature was controlled by a Yokogawa digital indicating controller model UT37. It gives a linearized temperature rate of 5°C/min for heating up and of 10°C/min for cooling down



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

the furnace. The reliable operating range is about 200-700°C. A type-K thermocouple obtained from Cole Palmer probe-flex 2521-mini was used for measuring the furnace temperature.

### 3.2.3 Analytical Instrumentation

Gas chromatography was used to analyze both quantitative and qualitative composition of effluent gas up and down stream of the reactor. A Hewlett Packard (Model 5890 Series II) was used in this work with a thermal conductivity detector (TCD).

Both qualitative and quantitative analyses were obtained from the chromatogram. Qualitative analysis was obtained by comparison of the retention times with standard gases. Quantitative analysis was achieved using the calibration factors obtained from known concentration gases. From the combustion reaction, the quantitative analysis of CO<sub>2</sub> gas produced and O<sub>2</sub> unconverted gas were determined. The gas chromatography specifications and operating conditions are given in Table 3.4.

**Table 3.4** Specifications and operating conditions of Gas Chromatography

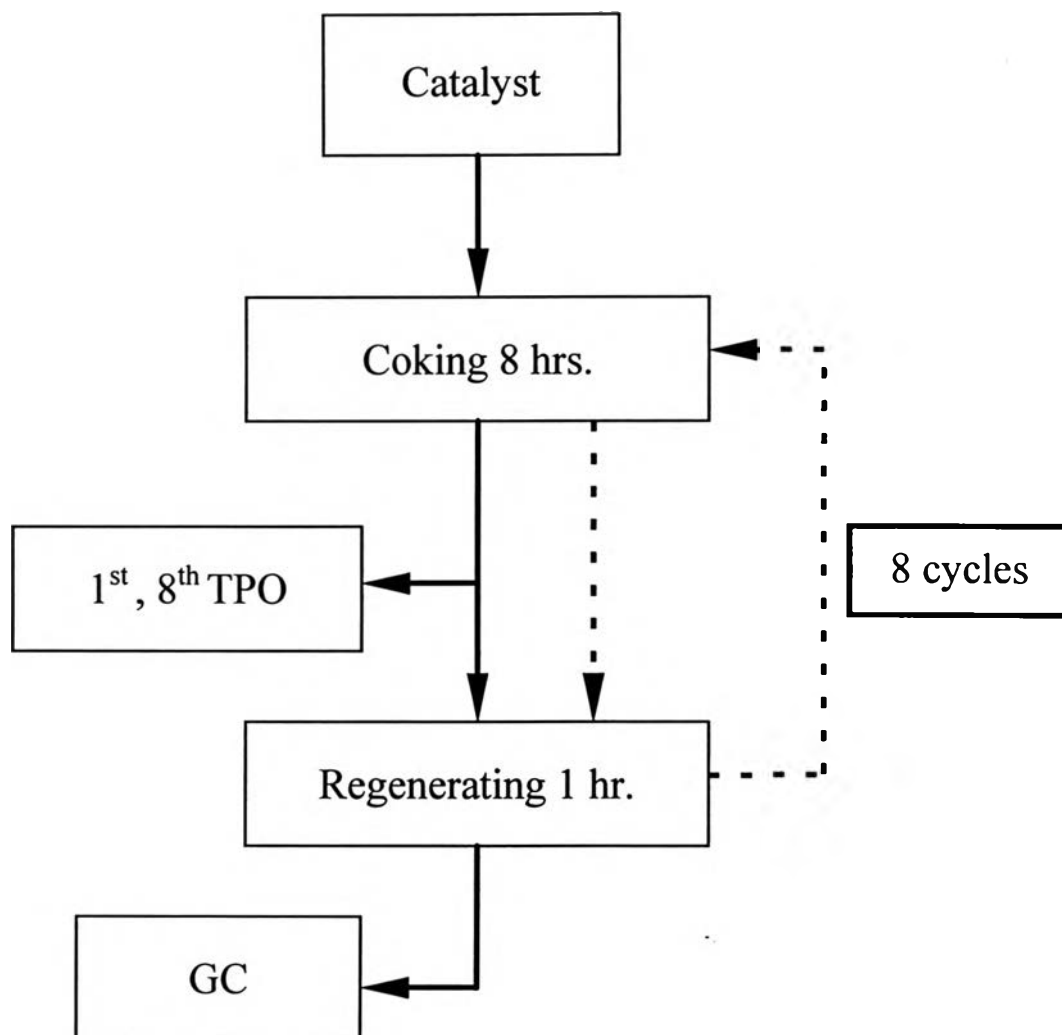
Item	Specifications and operating conditions
Packing	20 % BMEA on Chromosorb P-AW, 60/80
Column	24 ft × 1/8" OD., S.S.
Carrier flow rate	N <sub>2</sub> , 12 ml/min
Injector temperature	120°C
Detector temperature	200°C
Oven temperature	85°C
Detector	TCD

### 3.3 Methodology

This experimental section was operated on a simple quartz tube reactor as shown in Figure 3.1 and was constructed in conjunction with the butane dehydrogenation over Pt catalyst experiment (See Suthasut, 1998). The reaction gas was 5 vol% hydrogen and 10 vol% butane by using N<sub>2</sub> as a dilution gas.

#### 3.3.1 Cycle Regeneration

After loading 200 mg of fresh catalyst into the reactor, the catalyst bed temperature was raised to 500°C in pure nitrogen stream at a flow rate of 50 ml/min. After the temperature reached 500°C, the pure hydrogen with a flow rate of 50 ml/min was fed into the reactor instead of nitrogen. The temperature was held at 500°C for 1.5 hours, and then the hydrogen stream was stopped and the bed was heated up to the reaction temperature of 600°C with a heating rate of 5°C/min. After that, reactant gases and dilution gas, set at the desired compositions, were allowed to flow to the reactor and then the catalyst bed was operated with the butane dehydrogenation reaction for 8 hours. The bed temperature was cooled down to 500°C and then purging the system with 50 ml/min of N<sub>2</sub> for 30 minutes. Mix 2.5 vol% O<sub>2</sub> in N<sub>2</sub> with UHP N<sub>2</sub> to obtain 1 vol% O<sub>2</sub> and wait until the mixed gas concentration was constant. The total flow rate of mixed gas was 100 ml/min. After that 1 vol% O<sub>2</sub> in N<sub>2</sub> was switched to the reactor. The CO<sub>2</sub> and O<sub>2</sub> concentrations were read from gas chromatography. This step took 1 hour in order to regenerate the spent catalyst. The system was purged with 50 ml/min of N<sub>2</sub> for 30 minutes. 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. After finishing the first and the eighth reaction cycle, catalyst samples were characterized by TPO (See Section 3.3.3).



**Figure 3.2** Schematic diagram of cyclic regeneration experiment.



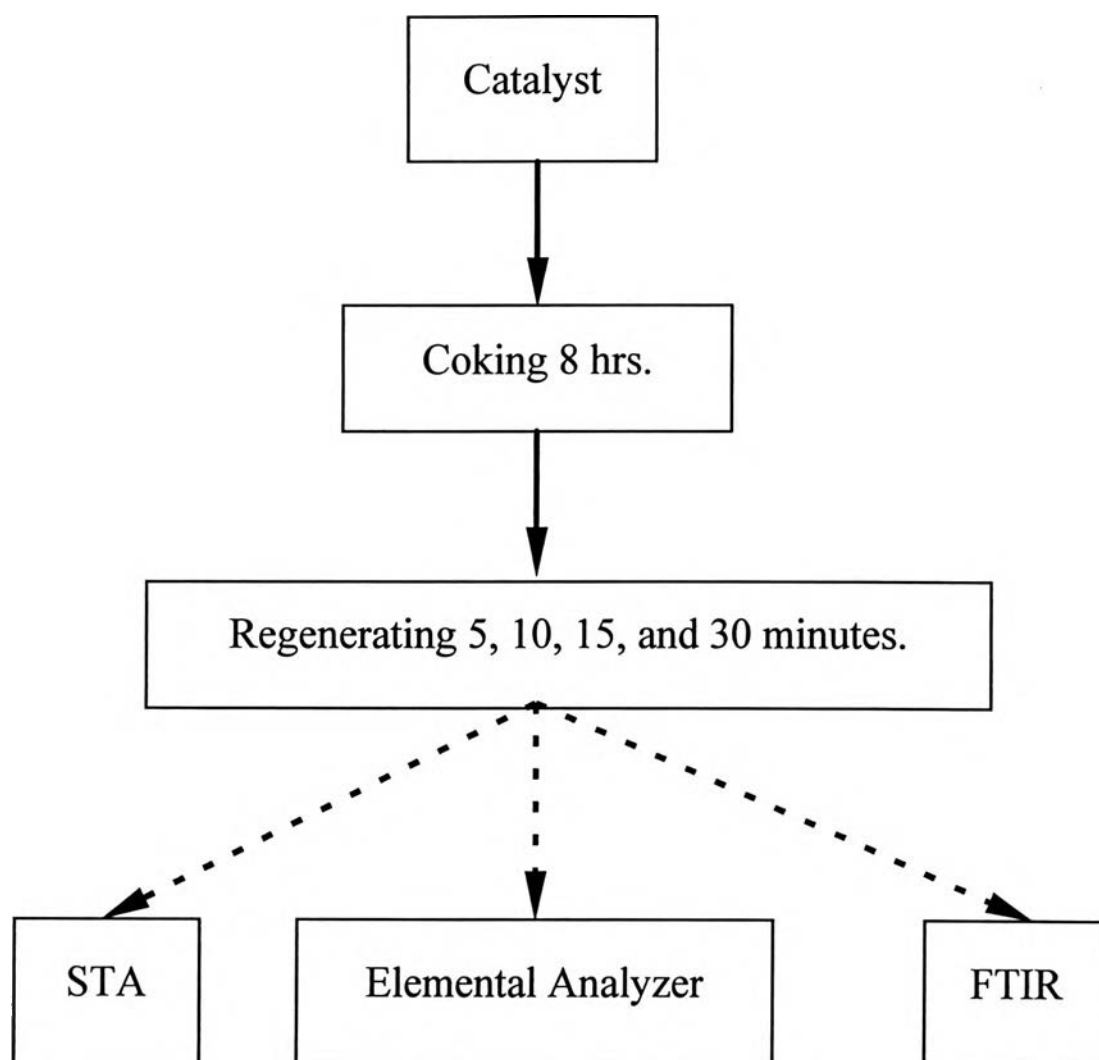
### 3.3.2 Partial Regeneration

The objective of this part is to investigate how coke deposits on the catalyst change during regeneration. The catalyst was operated in the butane dehydrogenation reaction. The procedure is the same as described in the cycle regeneration part, but only the first cycle of the dehydrogenation reaction was operated. After that the spent catalyst was regenerated by varying the burning time from 5 to 30 minutes. Then the spent and partially regenerated catalysts were characterized by FTIR, STA and elemental analyzer (See Section 3.3.3). The schematic diagram is shown in Figure 3.3.

### 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. After finishing the first and the eighth reaction cycles, the system was purged with 50 ml/min of N<sub>2</sub> while cooling down the system to 100°C. The reactor temperature was kept at 100°C for 30 minutes and then stop the purging gas. Mix the dilute O<sub>2</sub> gas to achieve 1 vol% O<sub>2</sub> in N<sub>2</sub> and switch it to the reactor. The temperature programmed oxidation was started by increasing a temperature from 100°C to 700°C with a heating rate of 5°C/min and simultaneously measuring CO<sub>2</sub> and O<sub>2</sub> concentrations.

*3.3.3.2 Measurement of Carbon Content.* The elemental analyzer is the equipment used to evaluate the basic elements in the sample which are carbon, hydrogen, nitrogen and sulfur. The sample is burnt in an oxidizing atmosphere and the products are then separated by a column and detected with the TCD detector.



**Figure 3.3** Schematic diagram of partial regeneration experiment.

A Perkin Elmer Series II CHNS/O Analyzer 2400 was used to determine the carbon weight percentage of 1 mg of spent and partially regenerated catalyst.

The operating conditions were :

Combustion furnace temperature = 975°C

Reduction furnace temperature = 501°C

Detector oven temperature = 82.6°C

*3.3.3.3 Measurement of Weight Loss.* A Netzsch simultaneous thermal analysis (model STA 409 EP) was used to measure the weight loss from the catalyst due to the burning of coke deposits. The instrument parameters are shown in Table 3.5.

**Table 3.5** Simultaneous thermal analysis parameters

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

*3.3.3.4 Infrared Spectroscopy.* Infrared Spectroscopy is one of the techniques used to determine the functional groups of the substances by taking the advantage of the infrared absorption.

A Bio-Rad FTIR (model FTS-45A), single beam spectrophotometer was used. The FTIR conditions are given in Table 3.6.

**Table 3.6** Fourier transform infrared spectroscopy conditions

Condition	Value
Scan speed, kHz	5
Low pass filter, kHz	1.2
Resolution	16
Spectral range, $\text{cm}^{-1}$	400-4000
Aperture, $\text{cm}^{-1}$	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). Seventy 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 an hour. Then 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. One milligram of extracted coke and 99 mg of potassium bromide were mixed together and pressed into disk. Finally, scan the prepared disk with the FTIR instrument.