

CHAPTER III

EXPERIMENTS

3.1 Materials

All gases in this experiment provided by Thai Industrial gas Co. Ltd..

The Ultra high purity (UHP) Nitrogen was used in purging the system, Gas Chromatography(GC) carrier, Thermal Conductivity Detector(TCD) reference gas, Simultaneous Thermal Analysis balance gas and mixing the diluted Oxygen for regeneration procedure.

The 5 vol.% Oxygen in Nitrogen mixture was mixed with UHP Nitrogen by Mass flow controller to give 1 vol.% Oxygen in Nitrogen.

The Ultra high purity Helium was used as balance gas in Elementary Analyzer.

The Air zero grade was used as combustion gas in Elementary Analyzer and STA.

For Infra-Red (IR) spectroscopy, Potassium Bromide (KBr) AR grade supplied by Fluka Chemicals was used.

Hydrochloric acid (HCl) ($37 \pm 0.75\%$ Conc.) and Hydrofluoric acid (HF) ($49 \pm 1\%$) AR grade provided by J.T. Baker

200 mg. of fresh and spent Pt-Sn-Li/Al₂O₃ catalyst from propane dehydrogenation experiment were taken for the study. Three types of catalysts in different Sn/Pt ratios were studied . Its physical properties are described in Table 3.1.

Table 3.1 Identification of the catalysts used in study

Catalyst name	Pt (wt.%)	Sn (wt.%)	Li (wt.%)	Sn/Pt ratio	S (m ² /g)	Vp (cc/g)	dp (°A)	active site
D ₃	0.42	0.65	0.45	1.55	98.62	0.22	87.34	
D ₄	0.44	0.85	0.45	1.93	98.30	0.21	85.22	
D ₅	0.37	0.90	0.45	2.43	97.53	0.22	89.64	

^a S = surface area

Vp = pore volume

dp = pore radius

3.2 Equipment

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

3.2.1 Gas Chromatography

The quantitative analysis of CO₂ gas produced by combustion reaction and O₂ unconverted gas was detected by the thermal conductivity detector (TCD). GC Hewlett packard 5890 Series II was used. The GC operating conditions are shown in Table 3.2.

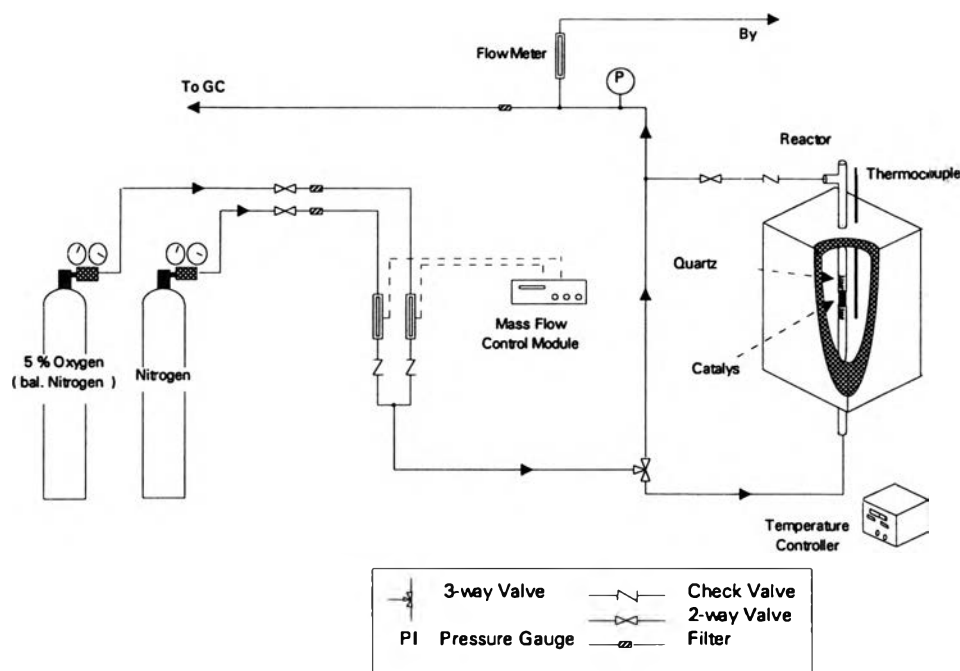


Figure 3.1 Flow diagram of cycle regeneration equipment

Table 3.2 Operating condition of GC,TCD

Packing	60/80HayeSep P	Oven Temp.	90 °C
Injector Temp.	120 °C	Carrier flow rate	N ₂ , 10 ml/min.
Detector Temp.	90 °C	Column	8' * 1/8" SS

3.2.2 Furnace

This set was assembled from refractory brick and the resistant wire to give a simple furnace with square hole in the core. Its reliable operating range about 200-700 °C corresponds to the temperature control device.

3.2.3 Temperature control device

The furnace temperature was controlled by YOKOGAWA Digital Indicating controller model UT37. It gives the linearized temperature, 5 °C/min. for ramp up and 10 °C/min. for cool down the furnace. Thermocouple type K, Cole Palmér probe-flex 2521- mini, was used to measure the furnace temperature.

3.2.4 Mass flow Controller

All gas species in this experiment were controlled by Mass flow transducers with control box supplied by SIERRA instrument, Inc. With a flow rate error smaller than 1%

3.2.5 Tubing

Valves, filters and tubes are provided by Sweagelok company. The tube system was assembled in 1/4" stainless steel. Except the GC inlet line, it is 1/8" stainless steel tube.

3.3 Methodology

3.3.1 Cycle regeneration

This experimental section was operated on a simple quartz tube reactor as shown in Figure 3.1 and was constructed in conjunction with the Propane dehydrogenation over Pt catalyst experiment (See K. Wongkolkitsilp, 1996). The dehydrogenation reaction dealt with cyclic

operation, i.e., 8 cycles were investigated. The reaction part of this cycle was operating at 600 °C. The spent catalyst from the last cycle was regenerated for 1 hr. Then the next dehydrogenation reaction cycle was started. The regeneration time was measured by burning the spent catalyst with dilute Oxygen gas until no carbondioxide, produced by combustion reaction, was found by GC.

The cycle regeneration procedure is as follow.

(a) 200 mg. of spent catalyst was hold in the quartz reactor. The reactor was kept at a temperature of 500 °C. Nitrogen gas was used as the purging gas with a flow rate 50 ml/min. After purging the system for 10 min., then isolating the reactor from the purging gas stream.

(b) Mixed 5 % O₂ in N₂ with N₂ and waited for the mixed gas concentration go to the steady state in order to get a steady O₂ signal which corresponds to 1% O₂ in N₂, total flow rate 50 ml/min. also.

(c) Switch the 1% O₂ in N₂ reactor for 1 hr. Start measuring CO₂, O₂.

(d) Purge the system for 5 min. with N₂ and prepare to run dehydrogenation reaction.

(e) After running the 8th reaction cycle., cool down the system to 100 °C with purging gas.

(f) When the reactor temperature reaches 100 °C kept this condition for 10 min. then start temperature program oxidation.

(g) Isolate the reactor and Mix diluted O₂ gas as described in 3.1.3 (a, b)

(h) Switch the dilute O₂ to the reactor and start the temperature program from 100 °C to 700 °C, increasing rate 5 °C/min. and begin measuring CO₂ and O₂ concentration.

(i) Purge the system for 5 min. and cool down the furnace.

3.3.2 The partial regeneration

The objective of this part is to investigate how coke deposits on the catalyst were changed during regeneration. Using gases as described in section 3.1. Spent catalyst from the 1st cycle of propane dehydrogenation was investigated. The catalyst properties are shown in Table 3.1 with the same equipment in Figure 3.1.

The partial regeneration procedure.

(a) Follow section 3.3.1 (a)-(b)

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

(c) Cool down the furnace with purging gas, took the catalyst and characterized the partial regenerated catalyst. (See section 3.3)

3.3.3 Coked catalyst characterization

3.3.3.1 Infra-red spectroscopy

A Bio Rad FTIR (Model FTS - 45A), single beam spectrophotometer was used. The instrument range is 400-4000 cm⁻¹. The FTIR operation as shown in Table 3.3

Table 3.3 FTIR conditions

Scan speed	20 kHz	Aperture	2 cm ⁻¹
Low pass filter	5 kHz	Spectrum	Absorbance
Resolution	16	No. Scan	16

To extend the IR signal, the spent catalyst was by dissolving alumina support as following

(a) 50 mg. of coked catalyst was mixed with a solution of 0.1 ml of 37wt.% HCl and 0.4 ml of 47 wt.% HF at room temperature for 2 hr.

(b) The suspension was filtered by 45 micron membrane filter, washed with distillate water and dried for a night at room temperature.

(c) The extracted coke from (b) 1 mg. and KBr 99 mg. were mixed and pressed in to disk.

(d) Scan the prepared disk with FTIR instrument.

3.3.3.2 *Measuring Hydrogen and Carbon*

A Perkin Elmer Elementary Analyzer (CHNS/O) was applied to measure Hydrogen and Carbon weight percentage contains in 1 mg. of Spent and partially regenerated catalyst. Fresh catalyst was used as reference.

3.3.3.3 *Measuring Weight loss*

Netzsch Simultaneous Thermal Analysis (STA 409 EP) was used. The STA parameters are shown in Table 3.4.

Table 3.4 STA parameters

Sample	Treated catalyst	Atmosphere	1.25 % O ₂
Reference	Fresh catalyst	Flow rate cm ³ /min.	50
Crucible	Alumina	Heating rate K/min.	8
Sample carrier	TG/DTA	Start temperature °C	20
Range TG mg	100	End temperature °C	700
Range DTA uV	40	Sampling time /sec	4