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 butane 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

All chemicals used in this experiment are analytical grade.

(a) Hydrogen hexachloroplatinate (IV) hydrated ($H_2PtCl_6.xH_2O$) with 37.5% platinum manufactured by Aldrich Chemicals.

(b) Tin (II) chloride hydrated ($SnCl_2.2H_2O$) with tin of 98.0% purity manufactured by Ajax Chemicals.

(c) Lithium nitrate ($LiNO_3$) manufactured by Merck.

(d) Aluminum oxide 90 active (Al_2O_3), neutral manufactured by Merck.

(e) Hydrochloric acid (HCl) with the concentration of 37.25 ± 0.75 wt. % manufactured by J.T. Baker.

(f) Hydrofluoric acid (HF) with the concentration of 49 ± 1 wt.% manufactured by J.T. Baker.

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

3.1.2 Methodology

The γ-alumina support was dried at 100 °C for 6 hours before use. 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 alumina was kept contacting with the impregnating solution at ambient temperature and then slowly evaporated to dryness at 150 °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 °C for 12 hours and followed by calcination at 600 °C for 6 hours in the atmospheric air with the heating rate of 5 °C/min.

Consequently, the calcined catalyst was impregnated again with platinum and lithium, respectively. The platinum and lithium solutions were prepared from the dissolution of $H_2PtCl_6 \cdot xH_2O$ and $LiNO_3$, respectively, in water. And the reimpregnated catalyst was dried and calcined under the same condition as for the impregnation of tin.

The concentration of 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 (0.5, 1.0, 1.5, 2.0 and 2.5 Sn/Pt ratio). The concentration of lithium in the impregnating solution was selected to yield final catalysts containing 0.40 wt% of lithium.

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 purity of 99.5% butane gas was used as feed stream for studying in catalyst deactivation, coking rate measurement and repetitive reaction-regeneration or cycle run.

(b) Ultra high purity nitrogen gas (99.999%) was used as a dilute gas for butane 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 butane dehydrogenation and for reducing catalyst before used.

3.2.2 Apparatus

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

The details of the experimental equipment were described as the following.

(a) Reactor: The reactor was made from 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.

(c) Mass flow module: The flow rates of butane, nitrogen and hydrogen 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%.
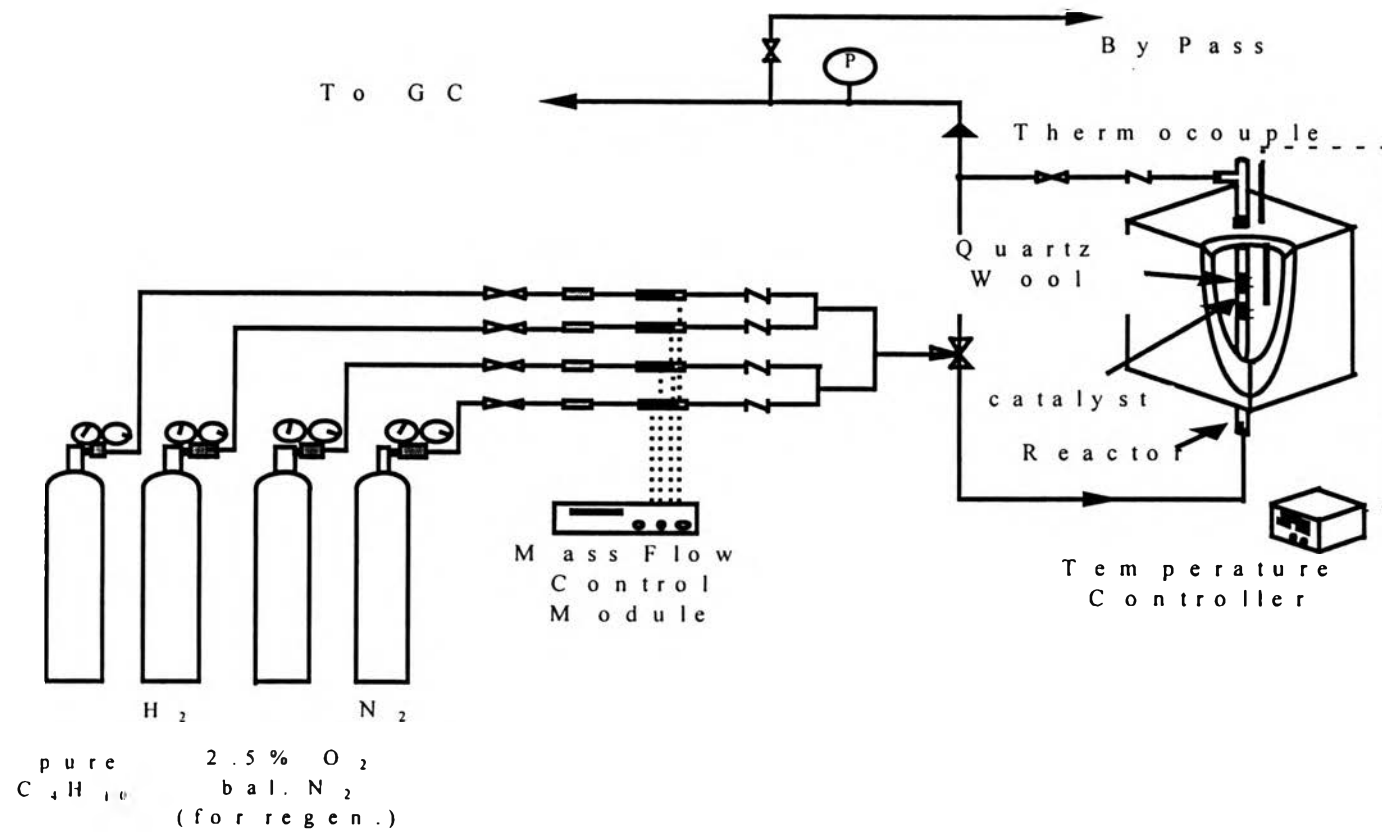
By Pass

To GC

Thermocouple

Quartz
Wool

catalyst

Reactor

Mass Flow
Control
Module

Temperature
Controller

H₂

N₂

pure
C₄H₁₀

2.5% O₂
bal. N₂
(for regen.)

Figure 3.1 Schematic diagram of experimental equipment.

Table 3.1   Gas chromatography specifications and operating conditions

Item	Specifications and Operating conditions
Column	24 ft × 1/8" OD., S.S.
Packing	20% BMEA on Chromosorb P-AW, 60/80
Temp.	85 °C
Carrier	12 ml/min of Nitrogen
Detector	TCD, 200 °C
Injector	120 °C

(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 system: The stainless steel fittings and tubing system 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 butane with a H_2/C_4H_{10} ratio of 0.5 and 85 ml/min of N_2 gas is 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 butane and selectivity to 1-butene, trans-2-butene, cis-2-butene and 1,3 butadiene. The conversion and selectivity were defined as the ratio of moles of reacted butane to moles of butane fed and the ratio of moles of that product produced to moles of butane converted, respectively.

Part I Catalyst Deactivation

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 catalyst was first sampled after the feed stream flowing through the reactor for 2 minutes. 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   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.

Part III   Repeated 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_2 was introduced into the reactor at 600 °C for 1 hour.

(e) Repurge the catalyst with N_2 at 500 °C for 30 minutes.

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

(g) The first sampling 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.

3.3 Characterization of Catalyst

3.3.1 CHNS/O Analysis

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 Surface Area Measurement

The Autosorb-1 is used for surface area measurement. It 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 50-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, is used to determine the content of metal loaded on the catalyst. The five hundred milligram 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.

3.3.4 Energy-Dispersive X-Ray Spectrometry (EDX)

EDX, model ISIS-3000, is used to measure the energy and intensity distribution of X-ray signal generated by a focused electron beam. This is a method for detecting and measuring these X-rays as well as converting them into a useful form for qualitative and quantitative elemental analysis. EDX can analyze an element from Be to U. Therefore it is applied to measure the amount of platinum, tin and chloride in the catalysts.

3.3.5 Transmission Electron Microscopy (TEM)

Electron microscope, JEOL model JEM-200 CX, serve to magnify minute objects normally invisible to the naked eye. An electron microscope uses an electron beam as a specimen illuminating medium for this purpose. Since the illuminating beam of an electron beam and the medium is vacuous, there are certain limitations. However, by effectively using a wealth of attachments, many advantages can be realized. This is espetially true when the microscope combines scanning image microscopy, electron diffraction and X-ray analysis. This microscope provides good image at low to high magnifications (100x to 450,000x).