CHAPTER 4

EXPERIMENT

This chapter describes the procedure of the catalyst preparation, the catalyst deactivation by propane dehydrogenation and coke catalyst regeneration to measure coke on metal active sites.

The Scope of This Study

Three types of propane dehydrogenation catalysts are used in this study

: $(0.3 \text{ wt\%})Pt/Al_2O_3$

: $(0.3 \text{ wt\%})Pt\text{-}(0.3 \text{ wt\%})Sn/Al_2O_3$

: $(0.3 \text{ wt\%})Pt\text{-}(0.3 \text{ wt\%})Sn\text{-}(0.6 \text{ wt\%})K/Al_2O_3$

The reaction conditions of the dehydrogenation reaction are as follows:

Catalyst reduction temperature	: 500 °C
Reaction temperature	: 500 °C
Operating pressure	: 1 atm.
Reaction time	: 3-120 min.
hydrogen/hydrocarbon ratio	: 0,1,3

4.1 Catalysts Preparation

Alumina support (obtained from Sumitomo Aluminium Smelting Co., Ltd., Japan) was grounded to the require mesh size of 60/80 followed by washing with distilled water 3-4 times to remove the very fine particles and other impurities, then dried at 110 °C for overnight. Subsequently, the support was calcined in air at 300 °C for 3 hours.

4.1.1 Preparation of platinum catalysts

- Preparation of impregnation solution

The impregnating solution for two grams of support was prepared by calculating the amount of the chloroplatinic acid (manufactured by Wako Pure Chemical Industries Co., Ltd., Japan.) stock solution (1 gram of chloroplatinic acid in de-ionized water 25 ml.) to the required metal loading (Appendix A). Hydrochloric acid, 5 wt% of alumina support, was then added to the solution. De-ionized water was finally added until 2 ml. of the solution was obtained

- Preparation of platinum catalyst

Two grams of alumina support was impregnated with the impregnation solution then leave the mixture for 6 hours to obtain good distribution of metal complex. After that the impregnated support was dried at 110 °C in air

overnight. Consequently,the dried material was calcined in air(100 ml/min.) at 500 $^{\circ}$C for 3 hours with heating rate 10 $^{\circ}$C/min.

4.1.2 Preparation of platinum-tin catalysts

- Preparation of impregnation solution

The same method was used as preparing platinum impregnation solution but adding stannous chloride dihydrate ($SnCL_2.2H_2O$ manufactured by Fluka Chemie AG, Swizerland) to the impregnation solution before impregnating with the support, it called "Co-impregnation method".

- Preparation of platinum-tin catalyst

The same preparation method liked preparation of platinum catalyst.

4.1.3 Preparation of platinum-tin-potassium catalyst

- Preparation of impregnation solution

a) preparation platinum tin impregnation solution used the same method as preparing platinum-tin solution.

b) preparing potassium solution by mixing potassium nitrate (KNO_3 manufactured by E.Merck, Federal Republic of Germany) which calculated to the desired amount with water into 2 ml.

- <u>Preparation of platinum-tin-potassium catalyst</u>

The preparation of Pt-Sn-K catalyst used co-impregnation method, the same method as preparing Pt-Sn catalyst but followed by re-impregnation. After calcination of co-impregnated platinum-tin catalyst, the calcined material was re-impregnated by potassium solution. The calculation of potassium loading was shown in Appendix A. The re-impregnation material was calcined again with the same condition.

4.2 Catalyst deactivation by propane dehydrogenation

4.2.1. Reaction of propane dehydrogenation

The reaction system consists of a micro reactor installed in a tube furnace. The furnace temperature is controlled by temperature controller(PF-96,RKC). The micro reactor is constructed from a quartz tube. A gas mixture (20% propane in nitrogen balance) is used as a reactant gas. Coked catalysts were prepared by passing the gas mixture through the catalyst bed. The experimental procedures are as follows :

Table 4.1 Operating condition of gas chromatograph(GC Gow-MAC Series 750)

Model	GC Gow-MAC Series 750
Detector	FID
Packed Column	VZ-10
Nitrogen flow rate	25 ml./min.
Hydrogen flow rate	30 ml./min.
Air flow rate	250 ml./min.
Column temperature	70 $^{\circ}$C
Injector temperature	100 $^{\circ}$C
Detector temperature	100 $^{\circ}$C

1. 0.1 gram of catalyst was packed in the middle of the quartz microreactor. The reactor was then placed in the furnace and the ultra high purity argon gas was introduced into the reactor at a flow rate of 30 ml./min.

2. The reactor was heated up at a heating rate of 10 $^{\circ}$C/min. until the catalyst temperature reached 200°C. Then, ultra high purity argon gas was replace by hydrogen gas at a flow rate of 100 ml/min. followed by heating up the reactor at a heating rate of 10 $^{\circ}$C/min. until the catalyst temperature reached 500 $^{\circ}$C. The catalyst was reduced at this temperature for 1 hour.

3. When the reduction process was completed,

- in the case H_2/HC=0 changed hydrogen to high purity argon for 5 min. and then changed to the 20 % propane in nitrogen.

- in the case H_2/HC was not zero , adjusted flow rate of hydrogen to the desired value. Then simultaneously introduced propane to the reactor with hydrogen.

4. The gas sampling was taken at 3, 5, 10, 30, 60 minutes of reaction intervals.

5. When desired time on stream was reached, the propane was changed to the ultra high purity argon gas. Then, the reactor was cooled down without the holding step

4.2.2 Temperature-Programmed Oxidation

Temperature-Programmed Oxidation of the catalyst was carried out in a quartz tube located in a tube (8 mm.O.D.) furnace. The furnace temperature was controlled by a microprocessor base temperature controller(DB 1000F, Chino Co.,Ltd.). A gas mixture consisted of 1 mole% oxygen in helium was used as an oxidizing gas. In one experiment, the Temperature-Programmed Oxidation process began by heating up the catalyst at a rate of 5 $^{\circ}$C/min. The oxidation process was

performed until the furnace temperature reached 700 $^{\circ}C$. During the oxidation, the amount of CO_2 in the effluent gas was first analyzed when the catalyst temperature reached 50 $^{\circ}C$, then at an interval of about 5 minutes, using a gas chromatograph (Shimadzu 8 AIT) equipped with a gas sampling valve (1 ml. sampling loop) and a thermal conductivity detector. The operating conditions of the GC. are reported in table 4.2

Table 4.2 Operating condition of gas chromatograph (GC 8-AIT, Shimadzu)

Model	GC-8AIT (Shimadzu)
Detector	TCD
Packed column	parapack QS (200x0.32 cm.)
Helium flow rate	60 ml./min.
Column temperature	90 $^{\circ}C$
Detector/injector temperature	110 $^{\circ}C$
Detector current	90 mA.

4.2.3 Determination of coke deposition on metal active site by CO adsorption

The procedure was divided into 3 parts : (1) metal active site of fresh catalyst, (2) spent catalyst, (3) regenerated catalyst after coked combustion at 200 °C. The remaining active sites was measured by CO adsorption technique on the basis that one CO molecule adsorbed on one metal active site (Biswas et.al.,1987). The amount of CO adsorbed on the catalyst was measured by the Thermal Conductivity Detector (GOW MAC). The operating condition of TCD are illustrated in table 4.3

Table 4.3 Operating condition of gas chromatograph (GOW-MAC).

Model	GOW-MAC
Detector	TCD
Helium flow rate	30 ml./min.
Detector temperature	80 °C
Detector current	80 mA.

Experimentation

1. 0.1 g. of catalyst was placed in the stainless steel tubular reactor. Helium gas was introduced into the reactor at the flow rate of 30 ml./min. The reactor was heated at an increasing rate of 10 °C/min. until the temperature reached 200 °C, then the helium gas was changed to hydrogen gas at a flow rate of 100 ml./min. The reactor

was continuous heated at the same rate until the temperature reached 500 °C. The reactor was held at this temperature for 1 hour.

2. The reactor was cooled down to room temperature.

3. The catalyst was then ready to measure metal active sites, 40 μl of the CO gas was injected to TCD at the injection port. The CO gas injection was repeated until the sample did not adsorb the CO gas.

4. The amount of metal active sites of fresh catalyst was calculated by the amount of adsorbed CO gas (Appendix B)

5. To measure the amount of spent metal active sites, the reactor was heated up to 170 °C in helium gas for 30 min. to desorb CO gas. The reactor was heated to 200 °C then change helium gas to hydrogen until the temperature reached 500 °C.

- in the case $H_2/HC=0$ changed hydrogen to high purity argon for 5 min. and then changed to the 20 % propane in nitrogen.

- in the case H_2/HC was not zero , adjusted flow rate of hydrogen to the desired value. Then simultaneously introduced propane to the reactor with hydrogen

6. When reached desired time on stream, change feed gas to helium and cooled down the reactor to room temperature. Then repeat step 3 to obtain metal active sites of spent catalyst

7. To measure the metal active sites covered by low temperature coke of the catalyst, the reactor was heated up to 170 °C in helium gas for 30 min. to desorb CO gas. The reactor was heated to 200 °C then change helium gas to 1 mole% of oxygen for 30 min. Then cooled down the reactor to 150 °C in helium, after that change oxygen to hydrogen at 150 °C and held at this temperature for 3 hours.

8. Switch from hydrogen gas to helium and cooled down the reactor to room temperature, then repeat step 3 to obtain metal active sites of regenerated catalyst.

9. Calculated total coke, high temperature coke and low temperature coke on metal active sites (Appendix C).