

CHAPTER IV

EXPERIMENT

Chapter IV will be devoted to the detail of experiment, which is divided into three sections. First, the method of catalyst preparation is presented in section 4.1. Second, the model reaction, i.e., hexane dehydrogenation, is described in section 4.2. Finally, the characterization methods, e.g., TPO, CO adsorption, XRD, H₂-TPD, FT-IR, BET, GC-14B with a DB1 capillary column and TEM to analyze catalysts and coked catalysts are discussed in detail.

4.1 Catalyst Preparation

4.1.1 Chemicals and Reagents

The chemicals used for the preparation are normally analytical grade. The metal precursors and supports are listed as follows:

1. Chloroplatinic acid [H₂PtCl₆.6H₂O] manufactured by Wako Pure Chemical Industries Co., Ltd., Japan.
2. Stannous Chloride Dehydrate [SnCl₂.2H₂O] manufactured by Fluka Chemie AG, Switzerland.
3. Potassium Nitrate [KNO₃] manufactured by E. Merck, Federal Republic of Germany.
4. Alumina support (Al₂O₃, type NKH-3) obtained from Sumitomo Aluminium Smelting Co., Ltd., Japan.
5. Silica support [SiO₂] manufactured by E. Merck, Federal Republic of Germany.

4.1.2 Instruments and Apparatus: Calcination Unit

This unit which uses for calcining the impregnation catalysts at high temperature is composed of an electrical furnace, an automatic temperature controller and a variable voltage transformer.

4.1.3 Preparation of Support

Alumina support and silica support were grounded to the required mesh size to 60-80 and 20-30, 40-60, 80-100 and 100-120 mesh, the minimal size, which can be used to avoid excessive pressure drop, respectively. Then they were washed with distilled water 3-4 times to remove the very fine particles and other impurities, and dried at 110°C overnight. Subsequently, the supports were calcined in air at 300°C for 3 h.

4.1.4 Preparation of Stock Solution

a) Platinum stock solution

The platinum stock solution was obtained from dissolving 1 g of chloroplatinic acid in de-ionized water 25 ml of the total volume

b) Potassium stock solution

The potassium stock solution was prepared from dissolving 1 g of potassium nitrate in de-ionized water 25 ml.

4.1.5 Preparation of Platinum Catalysts

1. To prepare the impregnation solution, the amount of stock solution to yield the required metal loading was firstly calculated for 2 g of catalyst support (Appendix A). Then, it was mixed with hydrochloric acid, 5 wt% of support. Then de-ionized water was finally added until 2 ml of solution was obtained.

2. 2 g of silica support were placed in 100 ml Erlenmeyer flask. Then, the impregnation solution was gradually dropped into the support using a dropper. Continuously stirring of the mixture in the flask while impregnating was required in order to achieve the homogeneously distributed metal component on the support.

3. The mixture was left in the flask for 6 h to obtain good distribution of metal complex.

4. The impregnated support was dried at 110°C in an oven overnight.

5. The calcination step was carried out in a quartz tube by placing the dried material obtained from (4). Nitrogen was introduced into the tube at a flow rate of 60 ml/min. Then the sample was heated up at a heating rate of 10°C/min from room temperature to 200°C. Subsequently, air was switched in to replace nitrogen with the flow rate of 100 ml/min and held at 500°C for 3 h.

6. After the catalyst was cooled down in air to 200°C, then nitrogen was switched in to cool down from 200°C to room temperature. The catalyst was stored in a glass bottle in a desiccator for further use.

4.1.6 Preparation of Bimetallic Platinum-Tin Catalyst

1. Appropriate amount of Pt and Sn ratio was calculated as described in Appendix A for 2 g of catalyst support. The impregnation solution was mixed with HCl (5 wt% of support). Continuously, de-ionized water was added to the mixture until the total volume was 2 ml.

2. The other steps were the same as the previous method described from (2) – (6).

4.1.7 Preparation of Trimetallic Platinum-Tin-Potassium Catalyst

The Pt-Sn-K catalyst was prepared by co-impregnation method. Pt-Sn was coimpregnated on the support as described previously. 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 identical conditions as used for the calcination of Pt catalyst.

4.2 Experiment

4.2.1 Chemicals and Reagents

All gases used in this study were provided by Thai Industrial Gases Limited. The hydrogen and the ultra-high purity argon were used for reducing the catalysts and for purging the system, respectively.

4.2.2 Instruments and Apparatus

A flow diagram of dehydrogenation system for liquid process is outline in Figure 4.1. The instruments used in this system are listed and explained as follows:

1) Reactor

The dehydrogenation reactor is a conventional micro reactor made from a quartz tube with 6 mm inside diameter. It can be operated from room temperature up to 1000°C under atmospheric pressure. The catalyst sample is placed between quartz glass wool layer. Sampling points are provided above and below the catalyst bed. The effluent gas was analyzed by gas chromatograph.

2) Automatic temperature controller

The automatic temperature controller consists of a magnetic switch connected to a variable voltage transformer and a RKC temperature controller series REX-C900

connected to a thermocouple attached to the catalyst bed in reactor. A dial setting establishes a set point at any temperature within the range between 0°C to 800°C.

3) Electrical furnace

This supplies the required heating to the reactor for hexane dehydrogenation reaction. The reactor can be operated from room temperature up to 800°C at a maximum voltage of 220 V.

4) Gas controlling system

The cylinders of ultra high purity argon for purging the system and hydrogen for reducing catalyst; each equipped with a pressure regulator (0-120 psig), a set of needle valves was used to adjust the flow rate of gases.

5) Gas Chromatography

Gas chromatograph (SHIMADZU GC-14A) equipped with flame ionization detector (FID) was used to analyze the composition of hydrocarbons in the feed and product streams. The operating conditions are illustrated in Table 4.1.

Table 4.1 Operating conditions for gas chromatograph

Gas chromatography	SHIMADZU GC-14A
Detector	FID
Column	OV-1 Capillary
Carrier gas	N ₂ (99.99%)
Flow rate of carrier gas	25 ml/min
Column temperature	
-Initial	60°C
-Final	140°C
Detector temperature	150°C
Injector temperature	150°C
Analyzed gas	Hydrocarbon C ₄ -C ₁₀
Split ratio	50

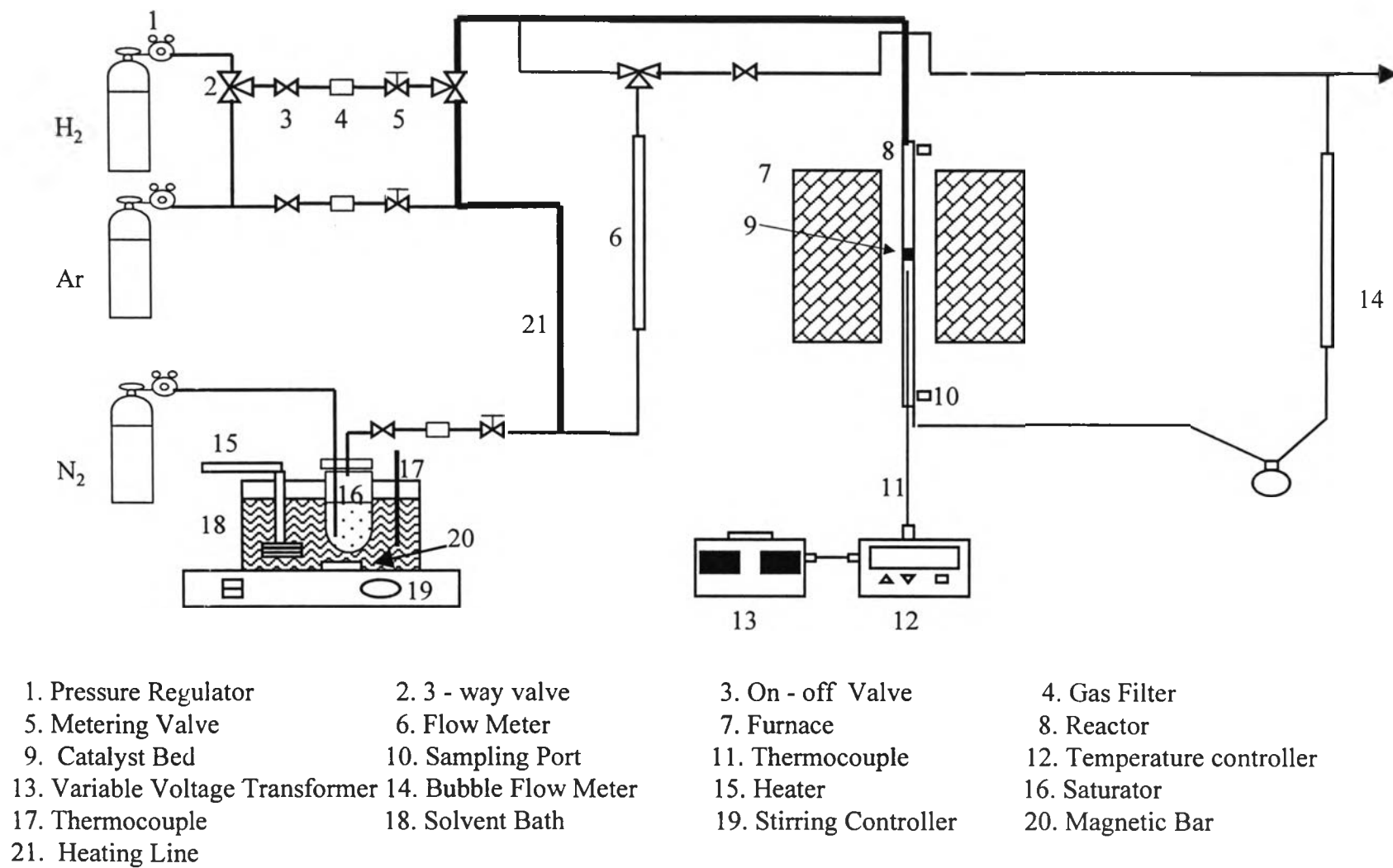


Figure 4.1 Flow diagram of dehydrogenation system

4.2.3 Experimental System

The reactor system consists of a micro reactor installed in a tube furnace. The diagram of the system for liquid reactant is exhibited schematically in Figure 4.1. The furnace temperature and the saturator temperature are controlled by temperature controllers, calculated as expressed in Appendix B. The micro reactor is constructed from quartz tube. Coked catalysts were prepared by passing the gas mixture through the catalyst bed, which was maintained at a constant temperature for a given time. The temperature was monitored using a thermocouple and a digital temperature indicator. The effluent gas was analyzed by a gas chromatography (SHIMADZU GC14-A) equipped with a flame ionization detector. The operating conditions of GC are shown in Table 4.1.

4.2.4 Experiment

A. The cooperative effect test

The cooperative effect is the combination of the metal species and acidic support. It is interesting to apply for study of coke deposition on the metal and support .

1. 0.2 g of catalyst (0.1 g of Pt/SiO₂ mixed with 0.1 g of Al₂O₃) was packed in the middle of the quartz micrometer. The reactor was placed in the furnace and argon was introduced into the reactor with a flow rate of 30 ml/min.

2. The reactor was heated up at an increasing rate of 10°C/min. until the temperature reached 200°C, and then 100 ml/min of hydrogen was switched in to replace argon with the same increasing rate until the temperature reached 500°C and the reactor was held at this temperature for 1 h. After this pretreatment was accomplished, the catalyst was ready to be used for the reaction test. Continuously, this catalyst was cool down to the reaction temperature in Ar and maintained in this temperature about 20 min. Then, 1-hexene (10% hexene in N₂) as a reactant was introduced to the reactor. The reaction conditions were undertaken at a temperature of 400°C, H₂/HC = 0 and 120 min on stream under total pressure of 1 atm. GC-14A

(Shimadzu) equipped with a capillary column and flame ionization detector was used for the analysis of gas composition. In this part, the mesh size of Pt/SiO₂ is varies with 20-30, 40-60, 80-100 and 100-120 mesh size.

3. After reaction test, the oxygen consumed and carbon dioxide of coked catalysts were determined by temperature programmed oxidation (TPO) in 1% O₂ in He. In addition, the properties of Pt-based catalysts were characterized by CO-adsorption, pyridine adsorption and H₂-TPD for measurement of the active metal sites, acidity and H₂ uptake which described H₂ spillover behavior. These characterizations were ascribed in the section 4.3

B. Coking test

Select the appropriate size of physical mixture, it was obtained in the previous result of the cooperative effect. After that, the coked catalyst was performed by the hexane dehydrogenation reaction (10% hexane in N₂). The experimental procedures are described in detail below.

1. 0.2 g of catalyst (0.1 g of Pt/SiO₂ mixed with 0.1 g of Al₂O₃) was packed in the middle of quartz micrometer. The reactor was placed in the furnace and argon was introduced into the reactor with a flow rate of 30 ml/min.

2. In this step, the reduction of catalyst was similar to the second of the cooperative effect test. After this pretreatment was accomplished, the catalyst was ready to be used for the reaction test. Continuously, this catalyst was cool down to the reaction temperature in Ar and maintained in this temperature about 20 min. Then, n-hexane (10% hexane in N₂) as a reactant was introduced to the reactor. The reaction conditions were varied and the effective parameters were studied as follows:

a) The effect of the temperature

The reaction was carried out at temperature of 475°C, 400°C and 300°C, 2 h-TOS and H₂/HC ratio = 0. The catalyst used for this research was 0.3 wt% Pt/SiO₂ physically mixed with γ -Al₂O₃.

b) The effect of promoter

The alkali metal promoters were used to incorporate on to the same support as Pt-Sn/SiO₂ with γ -Al₂O₃ and Pt-Sn-K/SiO₂ with Al₂O₃ substituted in Pt/SiO₂ mixed with Al₂O₃. For catalyst pretreatment method, it was the same category in step 1 and step 2 in section 4.2.4. The reaction conditions used for the study of this effect were 475°C, H₂/HC ratio = 0 for 2 h.

c) The effect of H₂/HC ratio

In case of present H₂, the flow rate of hydrogen was adjusted and then simultaneously introduced 10% hexane balanced in N₂ to the reactor with hydrogen. Appendix C shows calculation of H₂ flow rate compared with the ratio of H₂/HC to the total flow rate of 30 ml/min. The H₂/HC ratio used was 0-10. The experiment was tested in 475°C for 2 h.

d) The effect of reaction time

The reaction temperature was keep constant at 475°C and H₂/HC ratio was zero. The gas sampling was taken at 10, 30, 60 and 120 min of reaction intervals.

3. When the reaction conditions were finished, argon was switched in to replace. 10% Hexane in N₂ and hydrogen were switched to argon. Then, the reactor was cooled down to ambient temperature.

4. To prepare the carbonaceous deposit for analysis in different techniques, the coked catalyst was separated into coke on the metal and on the support by sieving.

4.3 Catalyst Characterization

4.3.1 Temperature-Programmed Oxidation

a) Materials

1 %vol oxygen in helium gas mixture supplied by Thai Industrial Gas was used as oxidizing agent. Ultra high purity helium was used for purging the system.

b) Apparatus

Temperature programmed oxidation of the catalyst was carried out in a quartz tube (8 mm O.D.) located in a tube furnace. The furnace temperature was controlled by a microprocessor base temperature controller (PC 600, Shinko). A gas mixture of 1 vol % oxygen in helium was used as an oxidizing gas. The oxidation process began by heating the catalyst with a flow rate of 5°C/min until the temperature reached 700°C. During the oxidation, the amount of CO₂ in the effluent gas was first analyzed when the catalyst temperature reached 50°C, then at an interval of about 5 min, using a gas chromatograph (SHIMADZU 8 AIT) equipped with a gas sampling valve (1.5 ml sampling loop) and a thermal conductivity detector. Figure 4.2 shows the flow diagram of the oxidation system.

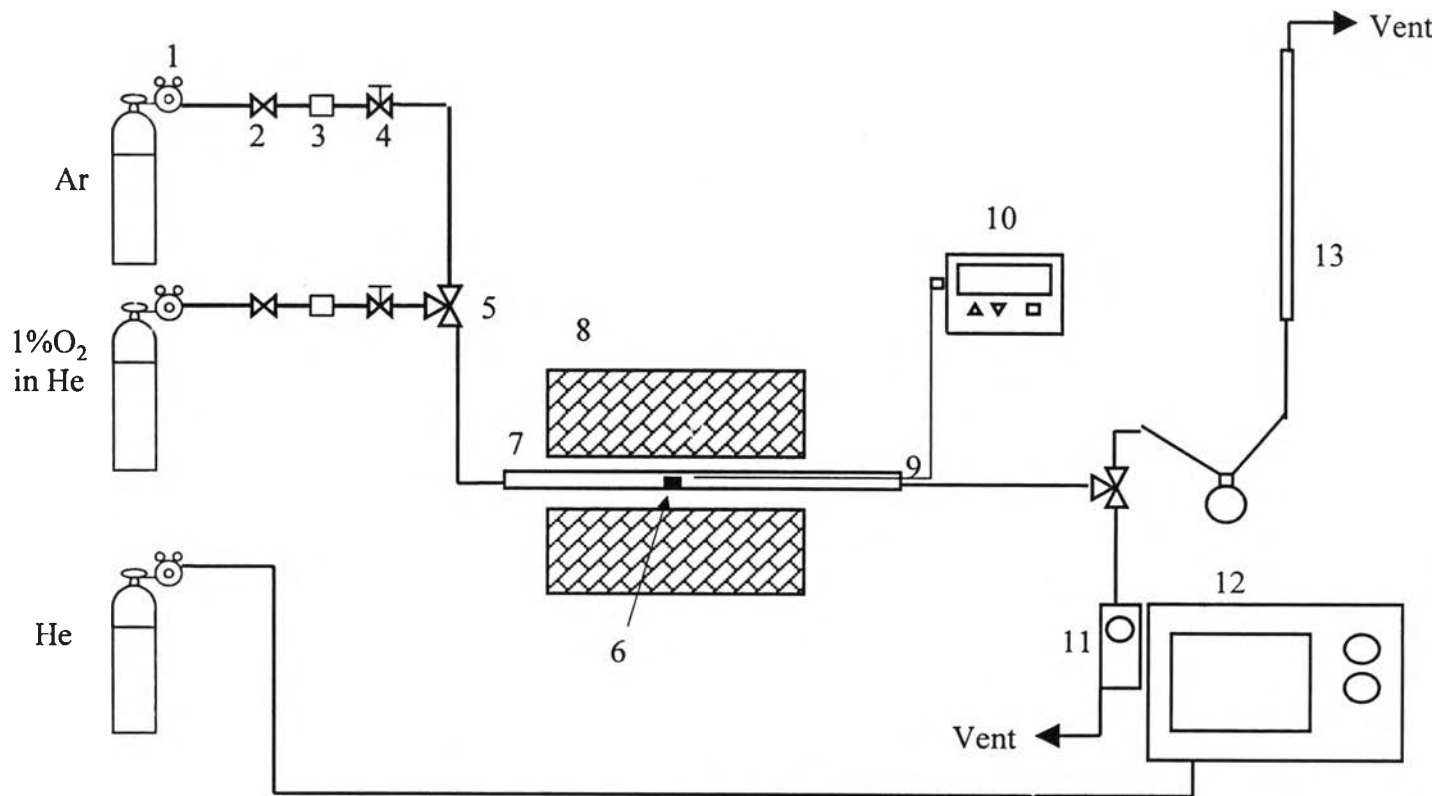
Table 4.2 Operating condition of gas chromatograph (GC-8AIT, SHIMADZU)

Model	GC-8 AIT (SHIMADZU)
Detector	TCD
Packed column	Porapack QS (200x0.32 cm)
Helium flow rate	60 ml/min
Column temperature	90°C
Detector/injector temperature	110°C
Detector current	90 mA

c) Procedure

1. The coked catalyst was packed in the middle of the quartz microreactor before placing the reactor in the furnace. The catalyst section was placed in the constant temperature zone of the furnace.

2. The 1 %vol oxygen in helium gas was flowed through the system at a flow rate of 30 ml/min.



- | | | | |
|-----------------------|----------------------------|-------------------|------------------------|
| 1. Pressure Regulator | 2. On - off Valve | 3. Gas Filter | 4. Metering Valve |
| 5. 3 - way valve | 6. Catalyst Bed | 7. Reactor | 8. Furnace |
| 9. Thermocouple | 10. Temperature controller | 11. Sampling Port | 12. Gas Chromatography |
| 13. Bubble Flow Meter | | | |

Figure 4.2 Flow diagram of Temperature Programmed Oxidation system

3. The Temperature-Programmed Oxidation of coke was started. The temperature was raised to 700°C at the heating rate of 5°C/min. When the temperature was 50°C, the effluent stream was sampled every 5 min by the on-line gas sampler.

4. The amount of oxygen consumed and carbon dioxide produced was measured.

5. After the catalyst temperature reached 700°C, The 1 %vol oxygen in helium gas was changed to ultra high purity helium and the reactor was cooled down.

6. The amount of coke (wt%) was calculated (Appendix D).

4.3.2 CO adsorption

a) Materials

Helium 99.99% was used as a carrier gas. Hydrogen was used to reduce catalyst. Carbon monoxide was used as an adsorbent and a standard gas.

b) Apparatus

The remaining active sites were measured by CO adsorption technique on the basis that one CO molecule adsorbed on one metal active site [3]. The extensive chart of instruments is included in Figure 4.3. The amount of CO adsorbed on the catalyst was measured by the thermal conductivity detector (GOW MAC). The operating conditions of GC are illustrated in Table 4.3.

Table 4.3 Operation conditions of gas chromatograph (GOW-MAC)

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

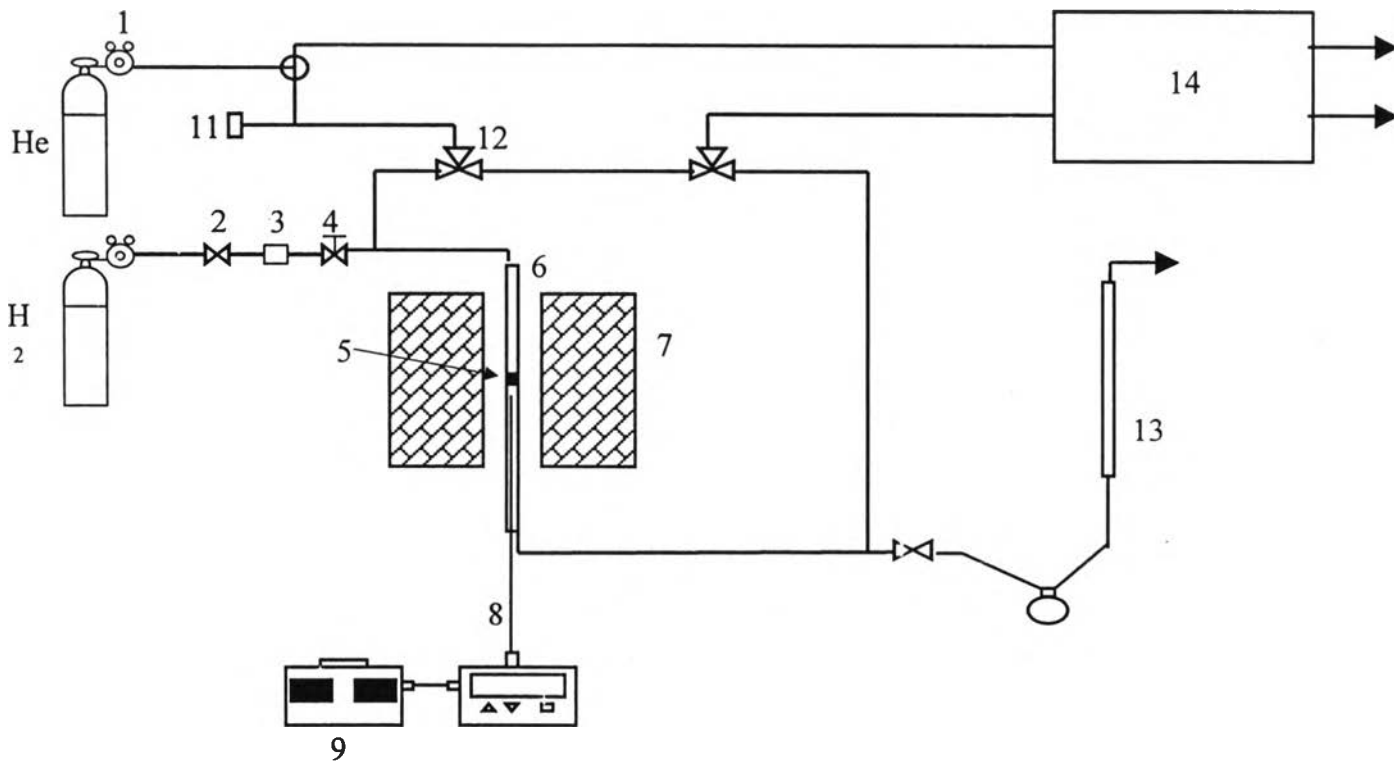
c) Procedure

1. 0.1 gram 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, and then helium was changed to hydrogen at a flow rate of 100 ml/min. The reactor was continuously heated at the same rate until the temperature reached 500°C. The reactor was held at this temperature for 1 h.

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 the system. CO was repeatedly injected until the sample did not any longer adsorb CO.

4. The amount to metal active sites of fresh catalyst was calculated by the amount of adsorbed CO gas according to the description in Appendix E.



1. Pressure Regulator

2. On-off valve

3. Gas Filter

4. Needle Valve

5. Catalyst Bed

6. Reactor

7. Furnace

8. Thermocouple

9. Variable Voltage Transformer

10. Temperature Controller

12. Three-way Valve

13. Flow Meter

14. TCD Gas chromatography

Figure 4.3 Flow diagram of CO adsorption

4.3.3 Temperature-Programmed Desorption (TPD)

a) Apparatus

The amount of H₂, which adsorbed on the surface was determined by temperature rising at a heating rate 10°C/min. The thermal conductivity detector was used to measure the amount of H₂. The operating conditions are the same as CO adsorption summarized in Table 4.3.

b) Procedures

1. 100 mg of catalyst was packed in the reactor and reduced by hydrogen flowing over catalyst at the rate of 100 ml/min. The reactor was heated up from room temperature to 500°C and maintained at this temperature for 1 h.

2. The reactor was cooled down from 500°C to the room temperature and then subsequently switched hydrogen into the reactor for 10 min. The catalyst adsorbing hydrogen was subsequently purged with He at the same temperature to remove physisorbed hydrogen.

3. The H₂-TPD experiment was carried out in quartz tube from room temperature to 550 °C at a heating rate of 10 °C/min.

4.3.4 Specific Surface Area Measurement

a) Apparatus

Specific surface areas of the catalysts were measured by physical adsorption based on BET assumption, with nitrogen as the adsorbent using a Micromeritics model ASAP 2000 at liquid-nitrogen temperature.

Table 4.4 Operating conditions for BET surface area measurement are as follows:

Model	BET
The catalyst weight	0.3-0.5 g
Degas temperature	150°C
Vacuum pressure	< 10 μ mHg
Pressure table	5 points

b) Procedure

1. The sample was heated and placed under vacuum to remove the moisture and other contaminants before analysis.

2. The catalyst sample was weighted. After that, the sample was automatically analyzed.

3. The amount of N₂ gas needed to form a monolayer on the surface of sample could be determined from the measurement the volume of gas adsorbed. The BET (Brunnauer, Emmett, and Teller) equation was used for calculating the specific surface area of the sample.

4.3.5 Infrared (IR) technique

In this work IR technique as both exsitu IR and *in situ* FT-IR analyses were adopted. For exsitu IR, we used this method to characterize the structural properties of carbonaceous deposition by the lattice vibration. The vibration bands between 400 and 4000 cm⁻¹ can indicate the structural framework of coke. Supporting wafer mixed by KBr and sample at the weight ratio of 100:1 was recorded IR spectra by Nicolet mode Impact 400 equipped with a deuterated triglycine sulfate (DTGS) detector and supported with omnic version 1.2a on windows software. Before preparing the sample disk, the mixture of sample was milled into fine powder to avoid the scattering

of IR spectra and be able to make disk. Then, fine powder was pressured by hand in a mold to become a thin film attached with a mold. Place the mold containing a thin film on the holder which IR spectra can penetrate the thin film throughly and directly.

On the other hand, we adopted *in situ* FT-IR for pyridine adsorption to investigate the acidity of the sample of Pt/Al₂O₃ and physical mixture of Pt/SiO₂ physically mixed with Al₂O₃. In this method, we used a pure sample at the weight of approximately 0.06 g that is depended on the difficulty of sample disk preparing and the ease of penetration of IR spectra. The pure sample was milled as same method as supporting disk mentioned above. Then, it was spreadly poured in the die as demonstrated in Figure 4.4. The sample was pressured using a manual hydraulic press at the pressure of 140-180 kg/cm² for 5 min. Subsequently, the thin film of sample was moved out from the die and set in the holder of IR gas cell depicted in Figure 4.5.

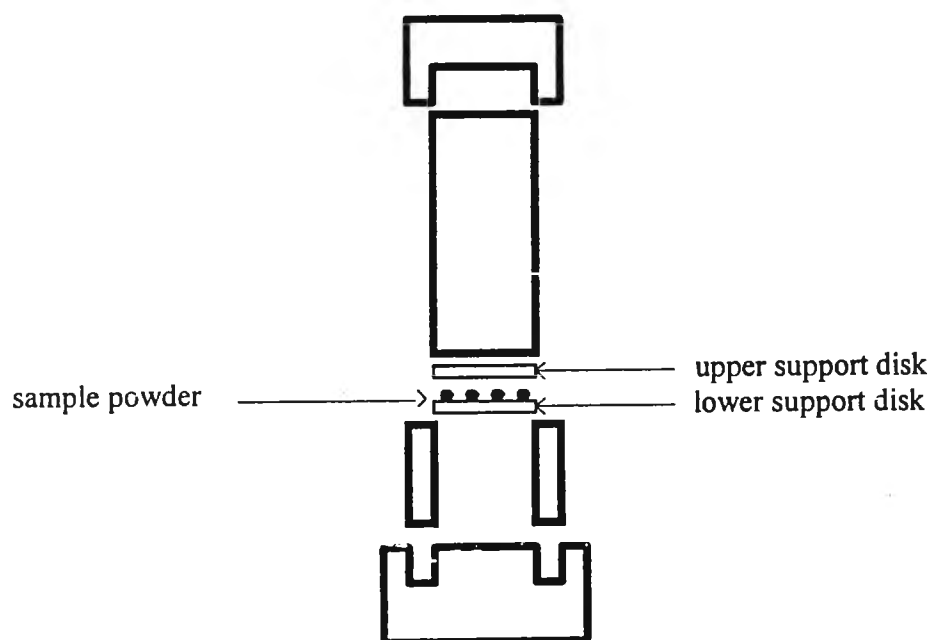
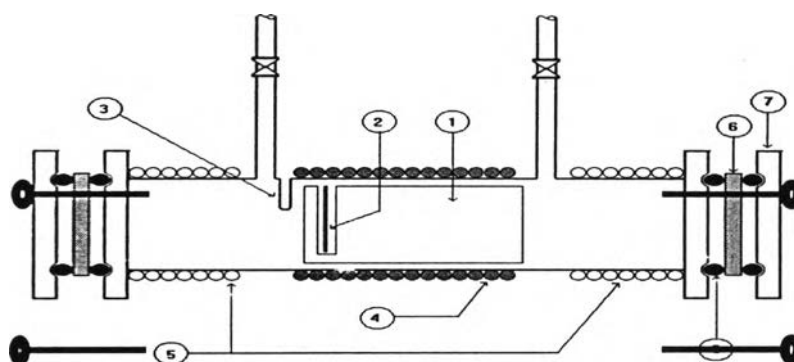


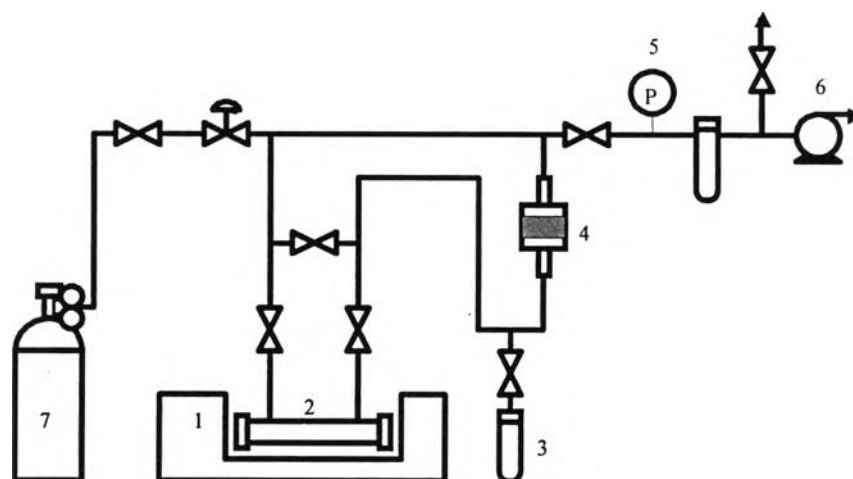
Figure 4.4 Body part of the die for preparing self-supporting sample disk.

The procedure of acidity measurement was described below. After setting the thin film of the self-supporting sample in the gas cell, both ends of the gas cell were sealed with KBr windows applied to be a closed system. The sample was evacuated using a vacuum pump model Labconco 195-500 HP at 10^{-1} torr for around 1 h to remove physisorbed species on the surface of sample. The vapor of pyridine was circulated in the system by an electro magnetic circulating pump for roughly 1 h afterwards to ensure the whole surface of sample was adsorbed by pyridine vapor. Subsequently, the system was evacuated again to remove pyridine species in the gas phase. Temperature programmed desorption was carried out to investigate the amount and strength of pyridine adsorbed on the surface of catalyst from room temperature to 500°C using 50°C increasing step by step. The evacuation was still kept continue while heating the sample and recording IR spectra at each temperature.



- | | |
|--------------------------|-----------------------|
| 1. Sample Holder | 5. Water Cooling Line |
| 2. Sample Disk | 6. KBr Window |
| 3. Thermocouple Position | 7. Flange |
| 4. Heating Rod | 8. O-ring |

Figure 4.5 Set of IR gas cell applied for the pyridine adsorption experiment



- | | |
|--------------------------------------|-------------------------------|
| 1) FT-IR Analyzer | 5) Digital pressure indicator |
| 2) IR quartz gas cell | 6) Vacuum pump |
| 3) Pyridine tube | 7) Nitrogen gas cylinder |
| 4) Electro magnetic circulating pump | |

Figure 4.6 Flow diagram of *in situ* FT-IR for acidity measurement by pyridine

4.3.6 Electron spinning resonance (ESR) analysis

Electron Spinning Resonance (ESR) analysis was chosen to study the presence or absence of the specie of deposits component which has unpaired electron. The carbon radicals on the coked sample were investigated at room temperature using X-band JEOL mode JES-RE 2X spectrometer equipped with a JEOL microwave power 0.1 mW at the Scientific and Technology Research Equipment Center, Chulalongkorn University (STREC). The samples were tested in room temperature.

4.3.7 X-ray diffraction (XRD) analysis

The crystallinity, arrangement and spacing of atom in crystalline carbon deposits materials can be analyzed using X-ray diffraction analysis. The refraction or diffraction of the x-rays was monitored at various angles with respect to the primary

beam x-ray diffraction analysis using an x-ray refractometer, SIEMENS XRD D5000, with Ni-filtered $\text{CuK}\alpha$ radiation.

4.3.8 Transmission Electron Microscopy (TEM) technique

TEM micrographs were obtained by direct observation of the fresh and coked sample by a transmission electron microscopy model JEOL JEM-200CX with an acceleration energy of 100 kV at the Scientific and Technology Research Equipment Center, Chulalongkorn University (STREC).

4.3.9 The Soxhlet extraction technique

The deactivated catalyst (50 mg) was submitted to an extraction of soluble coke in a Soxhlet apparatus with toluene. 250 ml of solvent was employed and the time of extraction was 24 h. The extracts were analyzed by GC14-B (a DB1 capillary column). The operation conditions [168] using for GC-14B are listed in Table 4.5.

Table 4.5 Operating conditions for gas chromatograph for analysis of soluble coke

Gas chromatography	SHIMADZU GC-14B
Detector	FID
Column	Capillary (DB1)
Carrier gas	N_2 (99.99%)
Flow rate of carrier gas	25 ml/min
Column temperature	
-Initial	40°C
-Final	250°C
Detector temperature	250°C
Injector temperature	200°C
Analyzed gas	Hydrocarbon
Split ratio	50