CHAPTER IV

EXPERIMENTAL SYSTEMS
AND EXPERIMENTAL PROCEDURES

This chapter will explain about the experimental system and the experimental procedures that were used in this work. This chapter is classified into 3 main sections. The catalyst preparation is presented in section 4.1. The experimental system is described in section 4.2. The section 4.3 finally explains about catalyst characterization including the temperature programmed oxidation (TPO), chemical analysis, differential thermal analysis, CO adsorption, BET surface area, and XRD presented in section 4.3.1, 4.3.2, 4.3.3, 4.3.4, 4.3.5 and 4.3.6, respectively.

The scope of this study

The composition of reactant

Ethanol	30 vol%
Helium	70 vol%

The catalysts used in this study are as fallows:

2 wt% Pd / SiO_2

2 wt% Pd / 0.5 wt% La_2O_3 / SiO_2

2 wt% Pd / 3 wt% La_2O_3 / SiO_2

The reaction conditions of ethanol decomposition are as follows:

Reaction temperature	200-500°C
Operation pressure	1 atm

4.1 Preparation of catalyst

4.1.1 Materials

The chemicals used in this study have to be specified as follows:

1. Palladium (II) chloride ($PdCl_2$), manufactured by Wako Pure Chemical Industries CO., Ltd., Japan.

2. Lanthanum nitrate hydrate ($La(NO_3)_3 \cdot 6H_2O$), manufactured by Wako Pure Chemical Industries CO., Ltd., Japan.

3. Silica gel (SiO_2), manufactured by Strem Chemical CO., Ltd., USA.

4. Ethanol (CH_2CH_3OH), (99.99%) manufactured by E.Merch, Federal Republic of Germany.

4.1.2 Apparatus: unit for calcination

This unit which consists of an electrical furnace and automatic temperature controller was used for calcining the impregnated catalysts at high temperature.

4.1.3 Preparation of support

Silica support was obtained by grinding Grade 57 silica gel (SiO_2) granulars and collecting particles in the 16-20 mesh range. The silica support particles were calcined at 550°C for 8 hr in a furnace to eliminate adsorbed water and other impurities. The temperature of furnace was increased from ambient temperature to 550°C at the heating rate 2°C/min. The calcined silica was removed from the furnace, cooled down to room temperature and stored in a desiccator.

4.1.4 Impregnation of promoter and active species

4.1.4.1 Lanthana loading

1. The wetability (or water capacity) of the support was determined by adding deionized water to a 1.0 g sample of silica. Water was added until the particles began to visibly stick together. The result from that provided us that the wetability was 1.0 ml/g of silica.

2. A lanthanum nitrate solution was applied to dry silica support using the standard catalyst impregnation method. The lanthanum nitrate solution was added to the dried silica support as the lanthanum oxide source. An example of preparation is described as follows: lanthanum nitrate hydrate 0.1644 g was added to 2.0 ml of deionized water. The entired lanthanum nitrate solution was slowly added to 2.0 g of silica support. This recipe produced a 3.0 weight percent loading of La_2O_3 on the SiO_2 substrate.

3. The lanthanum nitrate impregnated silica support was dried overnight at $110^{\circ}C$.

4. The dried impregnated silica was calcined at $550^{\circ}C$ for 8 hr in furnace to decompose the lanthanum nitrate salt into lanthana (La_2O_3) and to firmly fix it to the silica surface. The temperature of furnace was increased from ambient temperature to $550^{\circ}C$ by heating rate of $2^{\circ}C/min$. The support was removed from the furnace, cooled to room temperature and stored in a desiccator. The lanthana-modified silica (La_2O_3/SiO_2) was used as a support material for the palladium catalysts. The modified silica supports were designated as 0.5% La_2O_3/SiO_2 and 3% La_2O_3/SiO_2 in which 0.5 and 3.0 weight percent loading of lanthanum oxide was fixed to the silica surface.

4.1.4.2 Palladium loading

For palladium-based catalysts, the supports were silica and lanthana-modified silica. The preparation procedures are as follows:

1. The previously calcined SiO_2 and La_2O_3/SiO_2 support were impregnated with a solution of palladium by the incipient wetness technique. The solution used was prepared by dissolving palladium (II) chloride in a 1:1 by volume mixture of water and concentrated hydrochloric acid. In this preparation, the solution was heated at 80°C for 30 min to promote dissolution of the palladium salt. Using the water capacity measurement obtained previously for the silica particles, a sufficient amount of the palladium salt was added to obtain a two weight percent of palladium.

2. After an impregnation, the catalyst was dried at 110°C for 8 hr.

3. The dried catalyst was calcined 550°C for 8 hr in a furnace. The temperature of furnace was increased from ambient temperature to 550°C by the heating rate of 2°C/min. The palladium salt was, consequently, decomposed into small palladium metal or metal oxide crystallites. Finally, the catalyst was cooled down and stored in a disiccator. The prepared catalysts are designated as 2%Pd/SiO$_2$, 2Pd%/0.5%La$_2$O$_3$/SiO$_2$, and 2%Pd/3%La$_2$O$_3$/SiO$_2$

4.2 Experiment system

4.2.1 Chemicals and reagents

Thai Industrial Gasses limited provided all gases used in this study. They are high purity helium (99.995%), ultra high purity helium (99.999%), and high purity hydrogen (99.995%). The high purity helium was used as a purge gas and diluent gas in the catalytic reactor system. The ultra high purity helium was used as a carrier gas for gas chromatograph. The high purity hydrogen was used to reduce the catalyst to the active metal form. Ethanol (99.99%) reactants, supplied by Aldrich, were used in this study.

4.2.2 Instrument and apparatus

A flow diagram of the decomposition system is shown in Figure4.1. The parts used in this study are listed and explained as follows:

1. Reactor

The decomposition reactor employed was a conventional micro reactor made from quartz tube with 8 mm. inside diameter. The catalyst was placed between quartz wool layers. The effluent gas was analyzed by an online gas chromatograph.

2. Electrical furnace

It supplied the required heat to the reactor for the ethanol decomposition reaction. It could be operated from room temperature up to $800^{\circ}C$. The reaction temperature was controlled by an automatic temperature controller.

3. Gas chromatograph

Gas chromatograph (SHIMADZU GC-14B) equipped with a thermal conductivity detector (TCD) was used to analyze the composition of gas effluent from the reactor. The GC operating conditions are listed in the Table 4.2

Figure 4.1 Flow diagram of ethanol decomposition system.
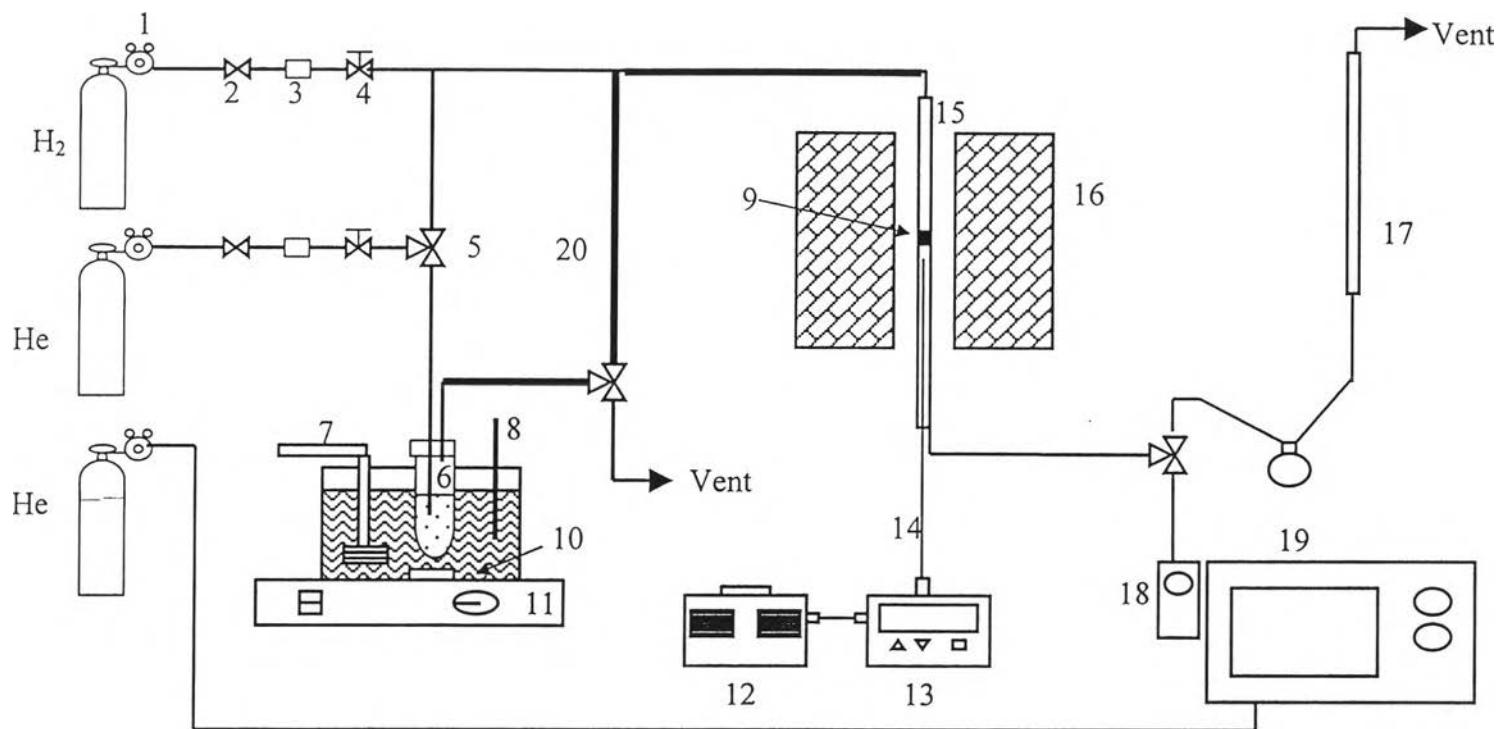
1. Pressure regulator
2. On - off valve
3. Gas filter
4. Metering valve
5. 3 - way valve
6. Saturator
7. Heater
8. Thermometer
9. Catalyst bed
10. Magnetic bar
11. Stirring controller
12. Variable voltage transformer
13. Temperature controller
14. Thermocouple
15. Reactor
16. Furnace
17. Bubble flow meter
18. Sampling valve
19. Gas chromatography
20. Heating line

Table 4.1 Operating conditions of gas chromatograph (SHIMADZU 14B)

Model	SHIMADZU 14B
Detector	TCD
Column	Porapak N (300x0.32cm)
Carrier gas	Ultra high purity helium
Flow rate of carrier gas	50 ml/min
Column temperature	
- Initial temperature	$60^{\circ}C$
- Initial time	5 min
- Rate	$5^{\circ}C/min$
- Final temperature	$150^{\circ}C$
Detector temperature	$150^{\circ}C$
Injector temperature	$150^{\circ}C$
Detector current	80 mA

4.2.3 Catalytic reactor system

Catalyst evaluations were conducted in a tubular flow reactor. The catalyst was heated by an electric furnace. Thermocouple type K was placed in the center of catalyst bed in order to measure the catalyst temperature, which was controlled by an automatic temperature controller. Liquid ethanol was placed in a saturator set at $51^{\circ}C$. It was vaporized in helium balanced, in order to produce 30%vol in reactant feed. The effluent gas from reactor was analyzed by an on-line gas chromatograph (SHIMADZU GC14-B) equipped with a thermal conductivity detector.

4.2.4 Experimental procedure

1. 0.1 g of 2%Pd/SiO$_2$ catalyst was packed in the middle of the quartz microreactor, which was placed in an electrical furnace. Helium gas was introduced into the reactor with a flow rate of 30 ml/min for 30 min.

2. The reactor was heated up with the heating rate of 5°C/min until the temperature reached 400°C, and then hydrogen gas with the flow rate of 60 ml/min was switched to replace helium for the reduction process. The catalyst was reduced at this temperature for 2 hr before cooling down to room temperature in helium flow. After this pretreatment was accomplished, the catalyst was ready to be used for the reaction.

3. The reactor was heated up to the reaction temperature in helium atmosphere with the heating rate of 5°C/min before the reactant gas was introduced to start the reaction. The reaction temperature was carried out at temperature 200, 300, 400 and 500°C. The sampled gas was taken at 5, 60, 120, 180, 240 and 360 min of reaction intervals.

4. After the reaction was completed, the 30% ethanol in helium was switched to helium and the reactor was cooled down to room temperature.

5. In case that the catalysts were 2%Pd/0.5%La$_2$O$_3$ SiO$_2$ and 2%Pd/3La$_2$O$_3$/SiO$_2$, the same procedure as previously described were performed.

4.3 Characterization of catalysts

4.3.1 Temperature programmed oxidation

a) **Materials**

The 1% vol oxygen in helium gas mixture supplied by Thai Industrial Gas was used as an oxidizing agent. The ultra high purity helium was used for purging the system before starting the experiment.

b) **Apparatus**

Temperature Programmed Oxidation of catalyst was carried out in a quartz tube reactor (8 mm. OD) placed inside an electrical furnace. The furnace temperature was controlled by a temperature controller (PC 600, Shinko). During the oxidation the effluent gas was analyzed 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 this system.

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

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

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 chromatograph
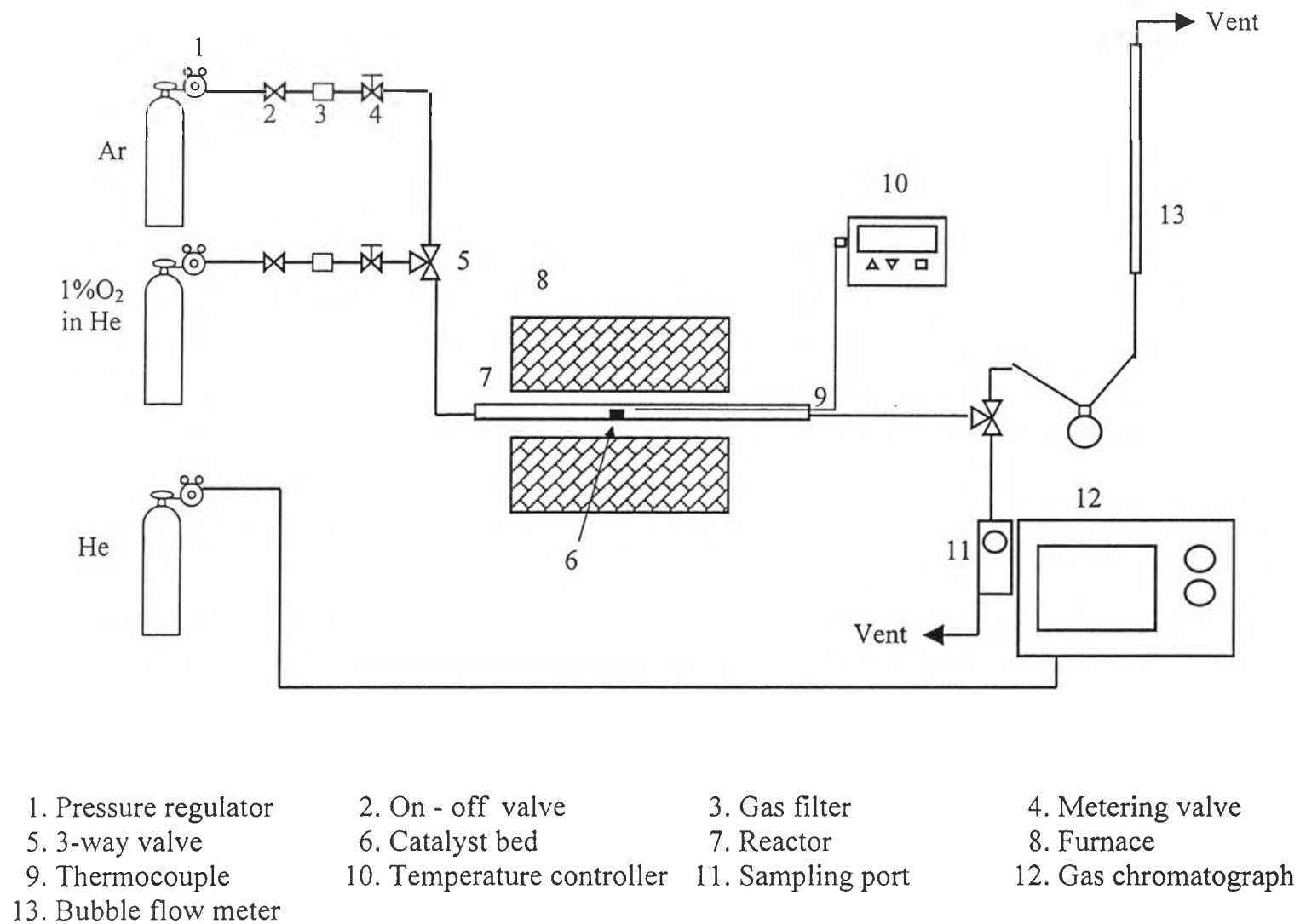13. Bubble flow meter

Figure 4.2   Flow diagram of temperature programmed oxidation system.

c) TPO procedure

1. The coke catalyst was packed in the middle of a quartz microreactor before placing the reactor inside the furnace.

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

3. The temperature programmed oxidation of coke was started. The temperature was raised to $900^{o}C$ with the heating rate of $5^{o}C/min$. When the temperature reached $50^{o}C$, the effluent was sampled and analyzed every 5 min by the on-line gas sample.

4. The amounts of carbon dioxide produced and oxygen consumed were measured.

5. After the catalyst temperature reached $700^{o}C$, the 1% vol oxygen in helium gas was changed to ultra high purity helium and the reactor was cooled down.

4.3.2 Chemical analysis

Atomic Absorption Spectrometry (AAS) method is a technique for determining the composition for metallic elements in solution. The sample was analyzed at Department of Chemical Engineering, Faculty of Engineering, Khon Kaen University.

4.3.3 Differential thermal analysis (DTA)

DTA is a technique in which the difference in temperature between a substance and reference material is measured as a function of temperature while the substance and reference material are subjected to a controlled temperature program.

This analysis was carried out by using a Shimadzu DTA-50 at Department of Chemical Engineering, Faculty of Engineering, Thammasat University.

4.3.4 CO adsorption

a) Materials

0.1 g of catalyst was used. The ultra high pure helium was used as a carrier gas. The ultra high pure hydrogen was used to reduce the catalyst. The carbon monoxide was used as an adsorbent and a standard gas.

b) Apparatus

The remaining active sites were measured by the CO adsorption technique on the basis that one CO molecule adsorbed on one metal active site. An extensive chart of instrument 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 TCD are listed 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
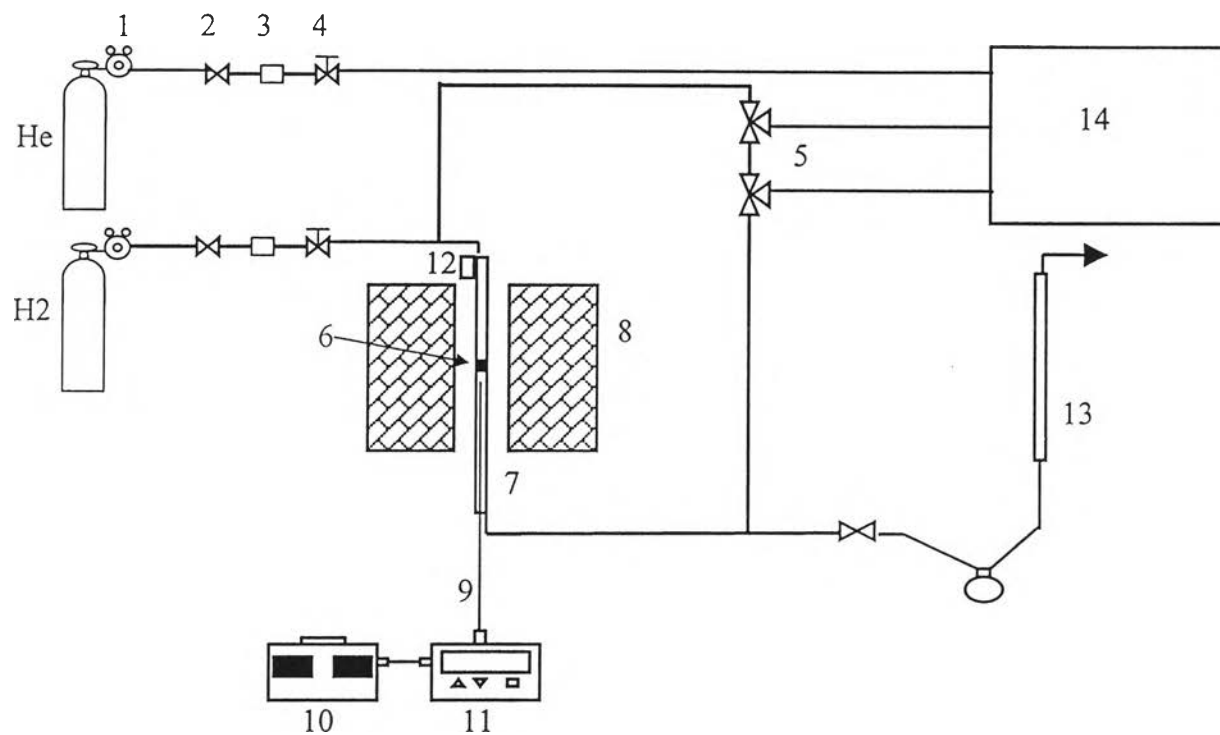
1. Pressure regulator   2. On - off valve   3. Gas filter   4. Metering valve
5. 3-way valve   6. Catalyst bed   7. Reactor   8. Furnace
9. Thermocouple   10. Variable voltage transformer   11. Temperature controller   12. Injection port
13. Bubble flow meter   14. Gas chromatography

Figure4.3   Flow diagram of CO adsorption system.

c) Procedure

1. 0.1 g of the catalyst was placed in a stainless steel tubular reactor. The 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 switched to hydrogen gas at the 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 hr.

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 could not adsorb CO gas.

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 D.

4.3.5 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 adsorbate using a Micromeritics model ASAP 2000 at liquid-nitrogen temperature. This unit is located at Analysis Center of Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University.

Table 4.4 Operating conditions for BET surface area measurement

The catalyst weight	0.3-0.5 g
Degas temperature	150°C
Vacuum pressure	< 10 µHg
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 N_2 gas needed to form a monolayer on the surface of sample could be determined form measurements the volume of gas adsorbed. The BET (Brunnauer, Emmett, and Teller) equation was used for calculating the specific surface area of the sample.

4.3.6 X-ray diffraction (XRD) analysis

The crystallinity, structure and composition, of sample was analyzed using x-ray diffraction analysis. The refraction or diffraction of the x-ray was monitored at various angles with respect to the primary beam x-ray diffraction analysis was carried out using an x-ray refractometer, SIEMENS XRD D5000, with Cu K_α radiation, accurately measured in the 4-40° 2θ angular region, at Petrochemical Engineering Research Laboratory, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University.