

CHAPTER IV

EXPERIMENT

This chapter will be devoted to the detail about the experimental systems and the experimental procedures used in this research work. This topic is classified into three sections. The procedure for catalyst preparation is first presented in section 4.1. Subsequently, the section 4.2 explains the characterization of catalysts including the determination of chemical content by atomic absorption spectroscopy (AAS) method, the specific surface area measurement by the Brunauer-Emmett-Teller (BET) single point method, the metal active sites measurement by CO adsorption technique, the crystal structure by X-ray diffraction (XRD) analysis, the acidity measurements by pyridine adsorption as well as NH₃ temperature programmed desorption (NH₃-TPD) techniques and the basicity measurement by CO₂ temperature programmed desorption (CO₂-TPD) procedure. Finally, the detailed procedure for catalyst evaluation to study the catalytic activity and the nature of surface species is pronounced in section 4.3.

4.1 Catalyst Preparation

4.1.1 Materials

A support and the metal precursors used in this catalyst preparation are all analytical grades. They are listed in Table 4.1. It is noted that the specification of alumina support about the chemical composition and the physical properties will be exhibited in Appendix A.

Table 4.1 The details of chemicals used in the catalyst preparation

Chemicals	Formula	Manufacture
1. Alumina pellet (type NKH-3)	$\gamma\text{-Al}_2\text{O}_3$	Sumitomo Aluminum Smelting Co., Ltd., Japan
2. Chloroplatinic acid hexahydrate	$\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$	Wako Pure Chemical Industries Co., Ltd., Japan
3. Lithium nitrate	LiNO_3	J.T. Baker Inc., USA
4. Chromium(III) nitrate nonahydrate	$\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	Fluka Chemie AG, Switzerland
5. Ferric nitrate nonahydrate	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	Carlo Erba Reagenti, Italy
6. Nickel(II) nitrate hexahydrate	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	Carlo Erba Reagenti, Italy
7. Gallium(III) nitrate hydrate	$\text{Ga}(\text{NO}_3)_3$	Sigma Chemical Co., USA
8. Cobaltous acetate tetrahydrate	$\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$	Carlo Erba Reagenti, Italy
9. Stannous chloride dihydrate	$\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$	Fluka Chemie AG, Switzerland
10. Ammonium (para)-tungstate	$(\text{NH}_4)_{10}\text{H}_2(\text{W}_2\text{O}_7)_6$	Fluka Chemie AG, Switzerland

4.1.2 Procedure

A. Preparation of Support

Alumina pellets, spherical shape, were grounded to the required mesh size of 40-60 mesh and then washed by distilled water for 2-3 times to remove the very fine particles and other impurities. Subsequently, they were dried at 110°C overnight and then calcined in stagnant air at 300°C for 2 h.

B. Preparation of Platinum Stock Solution

The platinum stock solution was obtained by dissolving 1 g of chloroplatinic acid hexahydrate in 25 ml of de-ionized water.

C. Preparation of Monometallic Platinum Based Catalyst

1. To prepare the impregnation solution, the amount of platinum stock solution to yield the required platinum loading was calculated just enough for 2 g of alumina support (Appendix C) and then de-ionized water was added until the total volume of solution became 2 ml.

2. 2 g of alumina support was placed in 100 ml Erlenmeyer flask and then the impregnation solution obtained from step 1 was gradually dropped into this support using a dropper. Continuously shaking of the mixture in the flask while impregnating was required in order to achieve the homogeneously distributed metal component on the support.

3. After the incipient wetness impregnation, the mixture of impregnation solution and alumina support was left in the atmosphere for 6 h to make a good distribution of metal complex.

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

5. The dried sample obtained from step 4 was proceeded through the calcination step in order to make platinum complex become platinum oxide, which was in a stable form. This step was conducted by using a quartz tube in which the ceramic boat containing the dried sample was placed. This sample was heated under nitrogen at a flow rate of 60 ml/min with the heating rate of 10°C/min from room temperature to 200°C. When the temperature was reached to 200°C, 100 ml/min of air flow was instead of nitrogen. The sample was next heated under air flow with the heating rate of 10°C/min from 200 to 500°C and then held at 500°C for 3 h.

6. After the calcined sample was cooled down, it was stored in a glass bottle into a dessicator for further use.

D. Preparation of Bimetallic Platinum-Second Metal Based Catalysts

1. The impregnation solution obtaining the mixture of platinum stock solution and the second metal precursor (Li, Cr, Fe, Co, Ni, Ga, Sn or W) was prepared by calculating the appropriate amount of platinum and second metal for 2 g of alumina support (Appendix C). Continuously, de-ionized water was added to the mixture until the total volume became 2 ml. It was remarked that the impregnation solution containing Pt and Sn must be mixed with HCl (5wt% of support). While, using W as the second metal, the impregnation solution was necessarily heated by a hot plate.

2. The other steps were following to the steps of (2)-(6) in the preparation of monometallic platinum based catalyst as described in section 4.1.2 (C).

4.2 Catalyst Characterization

4.2.1 Determination of the Chemical Content on Catalysts

The actual percentage of metal loading for all catalysts prepared in this study was measured by atomic absorption spectroscopy (AAS) method at Thailand Institute of Science and Technology Research.

4.2.2 Specific Surface Area Measurement

The specific surface area (S_{BET}) of the catalyst was calculated by using the Brunauer-Emmett-Teller (BET) single point method on the basis of nitrogen uptake measured at liquid-nitrogen boiling point temperature.

A. Materials

Ultra high purity of nitrogen and helium supplied by Thai Industrial Gas Limited were used as the adsorbate and balance gases, respectively.

B. Apparatus

The experimental apparatus of the single point BET surface area measurement consisted of two feed lines of helium and nitrogen. The flow rates of both gases were adjusted by means of fine-metering valves connected with a thermal conductivity detector. The sample cell made from pyrex glass. The schematic diagram of the experimental apparatus is shown in Figure 4.1 and the operating condition of a thermal conductivity detector within a gas chromatograph (GOW-MAC) is illustrated in Table 4.2.

Table 4.2 Operating condition of a thermal conductivity detector within a gas chromatograph (GOW-MAC) for the measurement of the specific surface area

Model	GOW-MAC
Detector type	TCD
Helium flow rate	30 ml/min
Detector temperature	35°C
Detector current	80 mA

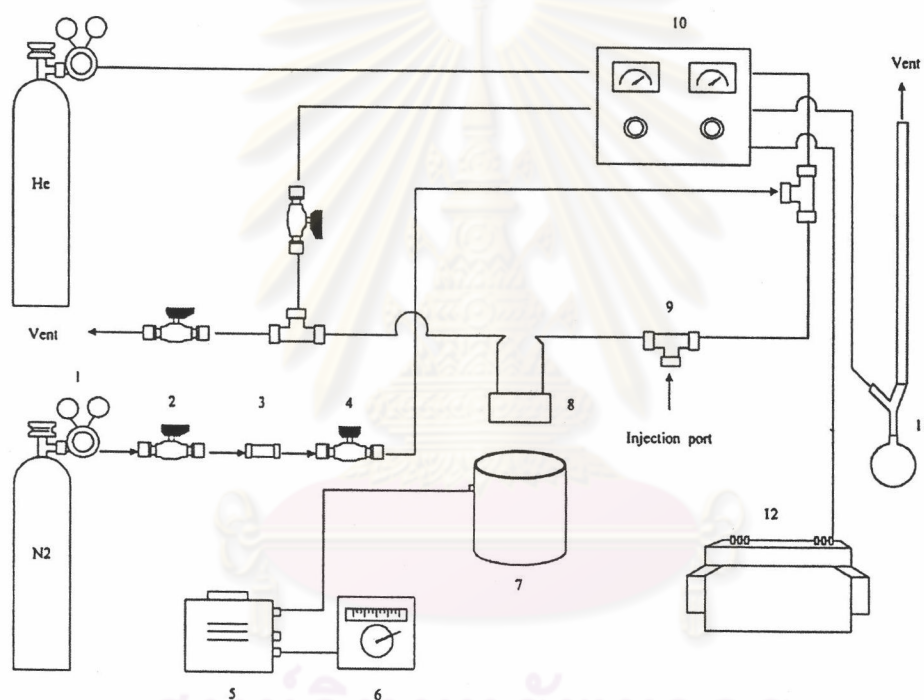
C. Procedure

The mixture gases of helium and nitrogen flowed through the system at the nitrogen relative pressure of 0.3. The catalyst sample was placed in the sample cell, ca. 0.2 g, which was heated up to 160°C and then held at that temperature for 2 h in order to remove the remaining water on the catalyst surface. Subsequently, it was cooled down to room temperature and measured the specific surface area containing three steps as follows:

1. Adsorption step: The catalyst sample set in the sample cell was dipped into the liquid nitrogen. Nitrogen gas flowing through the system was adsorbed on the catalyst surface of a sample until equilibrium was reached.

2. Desorption step: The sample cell containing the nitrogen-adsorbed catalyst sample was rapidly dipped into the water at room temperature. The adsorbed nitrogen gas was desorbed from the catalyst surface. This step was absolutely completed when the apparent signal on the recorder was back in the position of the base line drift.

3. Calibration step: 1 ml of nitrogen gas at atmospheric pressure was injected through the injection port. The obtained integral area of this gas was used as the reference area for the calibration. The calculation method will be explained separately in Appendix C.



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|-----------------------------------|------------------------|---------------------------|
| 1. Pressure Regulator | 2. On-off Valve | 3. Gas Filter |
| 4. Needle Valve | 5. Voltage Transformer | 6. Temperature Controller |
| 7. Heater | 8. Sample Cell | 9. Three-way |
| 10. Thermal Conductivity Detector | 11. Bubble Flow Meter | 12. Recorder |

Figure 4.1 Schematic diagram of the single point BET specific surface area measurement

4.2.3 Metal Active Sites Measurement

A. Materials

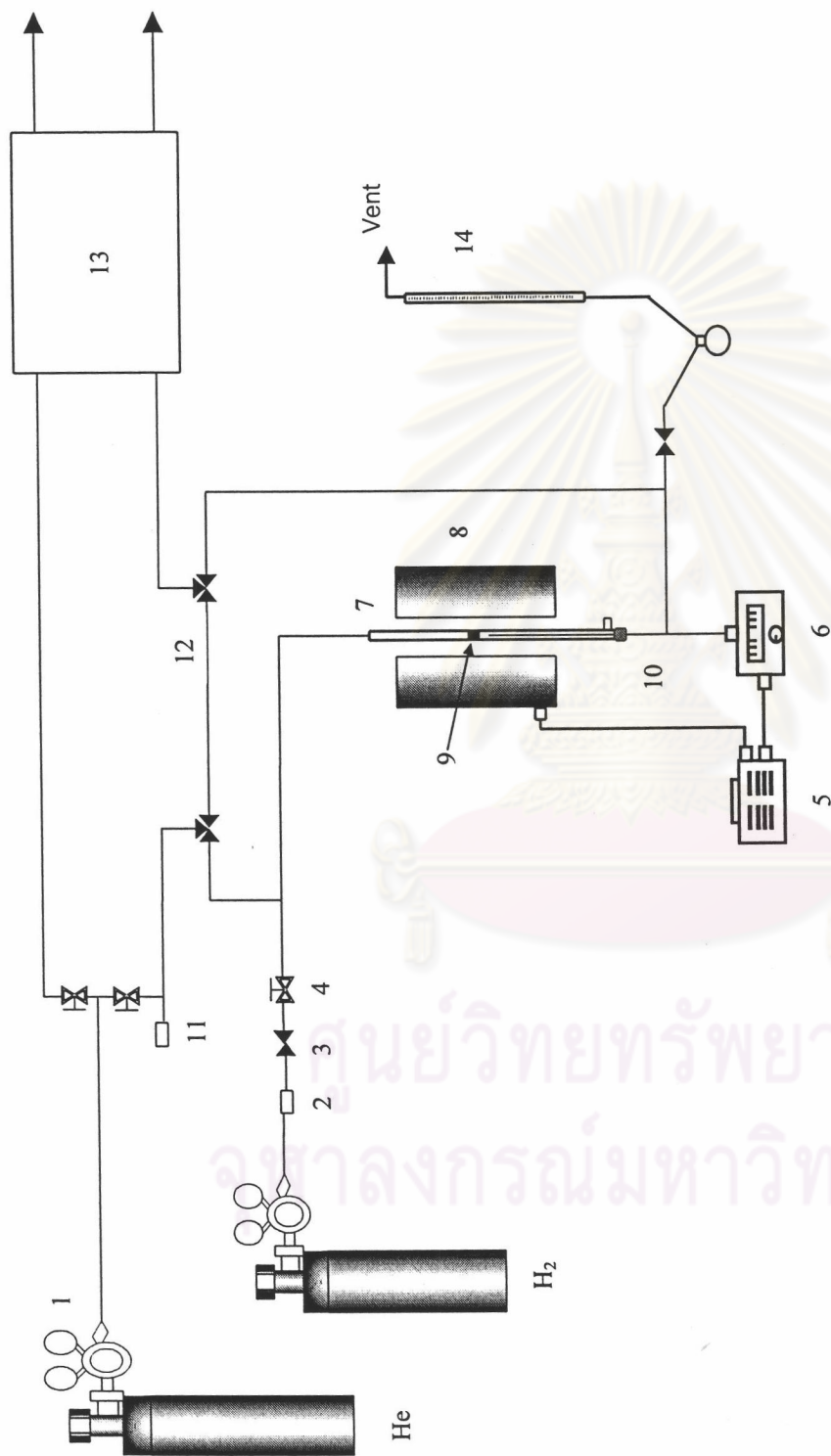
Helium in ultra high purity grade, hydrogen in ultra high purity grade and carbon monoxide in purity grade were used as a carrier gas, a reducing agent and an adsorbent gas, respectively. All gases used in this experiment were supplied by Thai Industrial Gas Limited.

B. Apparatus

The number of metal active sites was measured by CO adsorption technique on the basic assumption that only one CO molecule adsorbed on one metal active site [205]. The extensive diagram of instruments in the measurement of the metal active sites is included in Figure 4.2. The amount of carbon monoxide adsorbed on the metal surface was measured by a thermal conductivity detector within a gas chromatograph (GOW-MAC). The operating condition of gas chromatograph is illustrated in Table 4.3.

Table 4.3 Operating condition of a thermal conductivity detector within a gas chromatograph (GOW-MAC) for the measurement of the metal active sites

Model	GOW-MAC
Detector type	TCD
Helium flow rate	30 ml/min
Detector temperature	35°C
Detector current	80 mA



- | | | | | |
|---------------------------|---------------------|-----------------|-----------------------|---------------------------------|
| 1. Pressure Regulator | 2. Gas Filter | 3. On-Off Valve | 4. Needle Valve | 5. Variable Voltage Transformer |
| 6. Temperature Controller | 7. Reactor | 8. Furnace | 9. Catalyst Bed | 10. Thermocouple |
| 11. Injection Port | 12. Three-way Valve | 13. TCD | 14. Bubble Flow Meter | |

Figure 4.2 Flow diagram of the measurement of CO adsorption

C. Procedure

1. 0.1 g of the catalyst sample was placed in a stainless steel tubular reactor. Helium gas was introduced into the reactor at the flow rate of 30 ml/min. Prior to the measurement of the metal active sites, the catalyst sample was heated at an increasing rate of 10°C/min until the temperature reached to 200°C, and then helium was substituted by hydrogen at a flow rate of 100 ml/min. The catalyst sample was continuously heated at the same rate from 200 to 500°C and subsequently held at 500°C for 1 h.

2. The catalyst sample was cooled down to room temperature in helium flow.

3. At room temperature at which the catalyst was ready to be measured the metal active sites, 50 µl of the purity carbon monoxide gas was injected into the injection port to adsorb on the metal surface of the catalyst sample. The injection of carbon monoxide was continuously repeated until the catalyst sample did not any longer adsorb carbon monoxide. This situation was occurred when the obtained chromatogram area of any injection, after the adsorption of CO pulse in the first injection had proceeded, was kept nearly constant compared with that of the former injection.

4. The amount of the metal active sites of the catalyst sample will be calculated according to the description in Appendix C.

4.2.4 X-ray Diffraction Analysis

The crystallinity and structure of the catalyst 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 CuK α radiation in the 2 θ range of 10 to 80°.

4.2.5 Acidity Measurement by Pyridine Adsorption

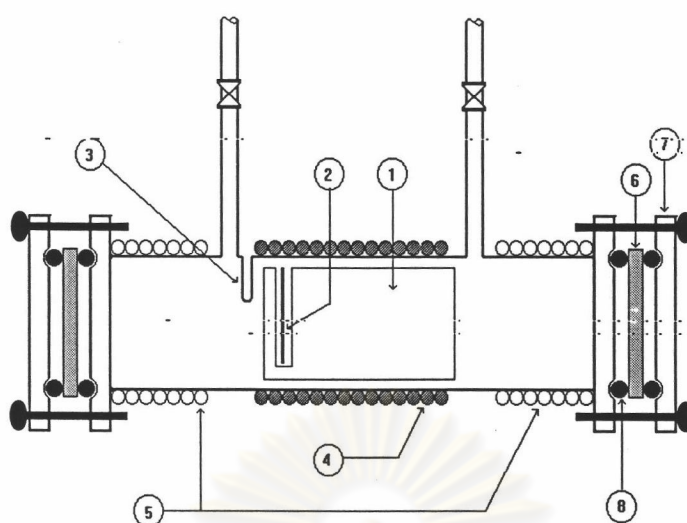
A. Materials

Pyridine supplied by Ajax Chemical in analytical grade was used as a probe molecule for the measurement of acidity in this experiment.

B. Apparatus

Fourier transform infrared (FT-IR) spectrometer was used as a detector in the experiment of the pyridine adsorption. A Nicolet model Impact 400 FT-IR equipped with a deuterated triglycine sulfate (DTGS) detector and connected to a personal computer with Omnic version 1.2a on Windows software (to fully control the functions of the IR analyzer) was applied to this study. The analyzer was placed on a movable table for convenient adjustment. IR gas cell used in this experiment is shown in Figure 4.3. It was made of quartz glass and covered with a 32×3 mm KBr window at each end of the cell. Each window was sealed by two O-rings and a stainless flange fastened by a set of screws.

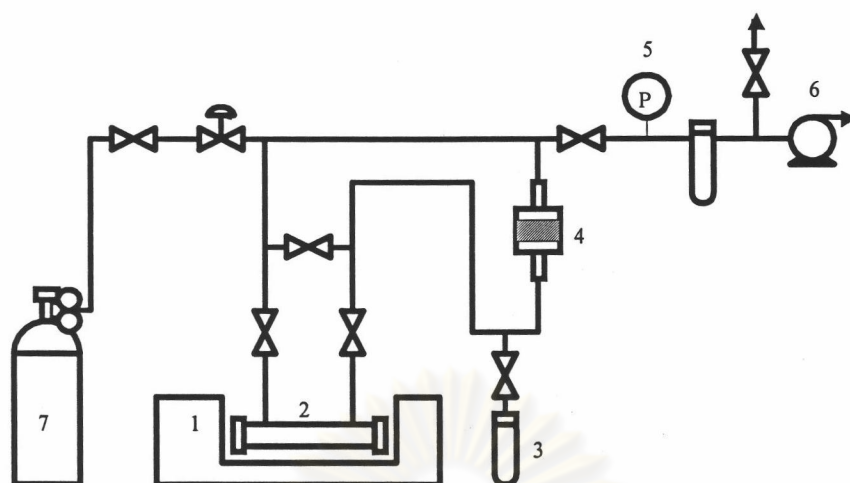
The cell was roughly divided into two zones involving the heating and cooling parts with respect to its temperature. The function of the heating zone at the middle of the IR cell was to increase the temperature for the sample disk. The quartz sample holder for the sample disk to keep it perpendicular to the IR beam was arranged inside the IR cell in the heating zone. A thermocouple was used to measure the sample disk temperature, which was controlled by a variable voltage transformer and a temperature controller. At both ends of the IR cell were connected with a cooling water line. They were applied to reduce the excessive heating, which may damage O-ring seals and the windows.



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

Figure 4.3 IR gas cell used for the pyridine adsorption experiment

The flow diagram of *in situ* FT-IR apparatus is depicted in Figure 4.4. All gas lines, valves and fittings in this apparatus were made of pyrex glass except for the IR gas cell and the sample disk holder, which were made of quartz glass in order to avoid the adsorption of any gas species remaining on the inner surface of glass tube while the system was evacuated. Pyridine was added to a glass tube connected with a valve, which could be opened to the gas line system. A homemade electro magnetic pump, which was fixed in the gas line, was used for circulating the pyridine vapor through the sample in order to accomplish the adsorption of pyridine species on the sample surface. A Labconco 195 - 500 HP vacuum pump, which theoretically had capacity at 10^{-4} Torr, was installed. Furthermore, a digital pressure indicator, which was attached to the gas line, could measure the pressure of the system and check for leaking of the apparatus as well.



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|-------------------------------|--------------------------------------|
| 1. FT-IR Analyzer | 2. IR Quartz Gas Cell |
| 3. Pyridine Tube | 4. Electro Magnetic Circulating Pump |
| 5. Digital Pressure Indicator | 6. Vacuum Pump |
| 7. Nitrogen Gas Cylinder | |

Figure 4.4 Flow diagram of the instruments used for the pyridine adsorption experiment

Another important apparatus is the die made of stainless steel to use for preparing the sample in form of the disk as shown in figure 4.5. The most important part of the die, which was directly in contact with the sample, was the so-called the support disks. The support disks were composed of upper and lower disks, each 20 mm in diameter and highly polished to a mirror like finish in order to overcome the sticking of sample to the surface of the die, the main problem in pressing disks.

C. Procedure

1. To produce a self-supporting catalyst sample disk for an IR experiment, the catalyst was milled thoroughly in a small quartz mortar to obtain a very fine powder. This minimized the scattering of infrared radiation and provided a high quality of spectrum. The powder sample about 0.06 g was spread to totally cover the surface of the lower support disk placed in the die to make a sample having a weight 15-20 mg/cm². If a thick sample disk was used, the result from IR scan would be very poor.

While, if a too thin sample disk was employed, it would be easily cracked by thermal treating as well as broken itself.

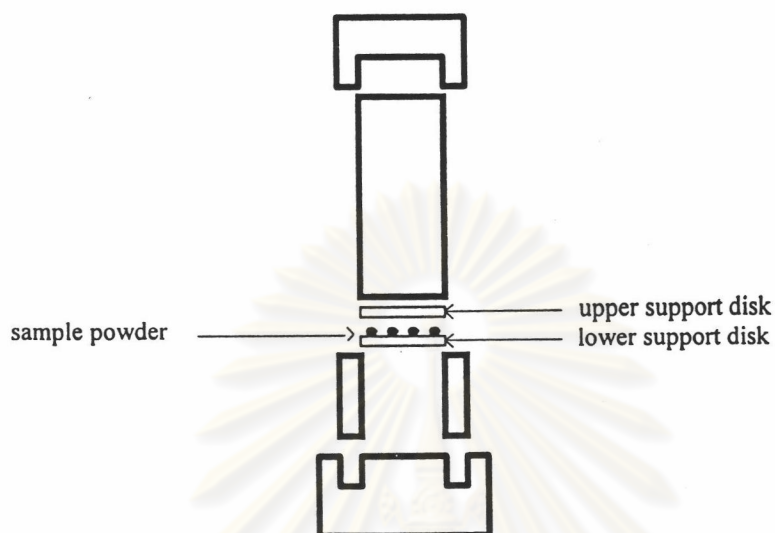


Figure 4.5 Body of the die for preparation of a self-supporting catalyst disk

2. All parts of die were put together as shown already in Figure 4.5 and were pressed by a manual hydraulic press at pressures of 140-180 kg/cm² for 5 min. The pressure should not be too low so that a self-supporting disk could not be formed. After pressing, the well-formed disk was carefully removed from the die and mounted in the IR cell.

3. After a well-formed sample disk was obtained, it was placed in the sample holder and then the sample holder including the sample disk was placed into the middle of the IR gas cell. The sample disk was located as close to the thermocouple probe hole as possible. Once the KBr windows were sealed at both ends of the IR gas cell and the leaks were not observed, the IR gas cell was evacuated by a vacuum pump through the gas line for at least 30 min to place the system under vacuum.

4. Under vacuum, pyridine vapor was brought into contact with the disk at room temperature by evaporating liquid pyridine from the pyridine tube into the gas line leading to the IR gas cell. To achieve the maximum adsorption of pyridine,

pyridine vapor was circulated through the system by the electro-magnetic pump for about 1 h or until the IR spectrum of pyridine peak did not change.

5. After the saturation in pyridine adsorption, the IR cell and gas line were evacuated to remove not only pyridine vapor remaining in the system but also the physisorbed pyridine from the catalyst surface. The vacuum pump was operated till the IR spectra peaks of pyridine vapor and physisorbed pyridine totally vanished and there was no change in any other peaks of the spectra.

6. FT-IR measurement of the spectra of the pyridine-adsorbed sample was started at room temperature and repeated at the elevated temperature in 25°C stepwise. The vacuum pump was kept running while the sample disk and the IR gas cell were heating to remove all species desorbed from the sample surface out of the system in order to avoid disturbing the spectra by such species.

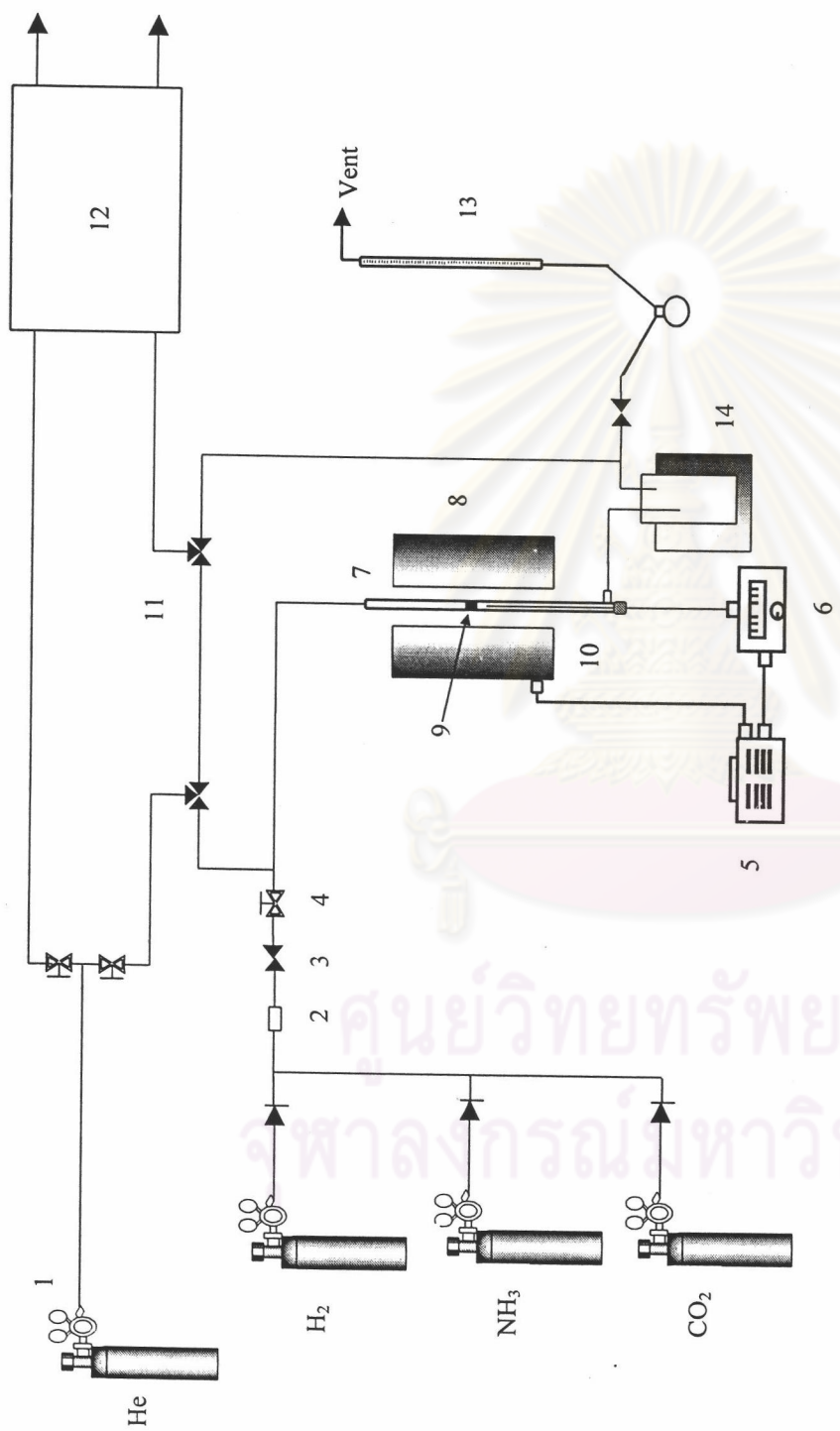
4.2.6 Acidity Measurement by NH₃-TPD

A. Materials

Helium in ultra high purity grade and ammonia in purity grade were used as a carrier gas and a probe molecule gas, respectively. Both gases used in this experiment were supplied by Thai Industrial Gas Limited.

B. Apparatus

The temperature programmed desorption of ammonia was used to measure the acid strength and the total amount of acid sites on the catalyst surface. The flow diagram of instruments in the measurement of acid sites by NH₃-TPD is shown in Figure 4.6. The amount of ammonia desorbed from the catalyst surface was measured by a thermal conductivity detector within a gas chromatograph (SHIMADZU GC 8A). The operating condition of gas chromatograph is illustrated in Table 4.4.



- 1. Pressure Regulator
- 2. Gas Filter
- 3. On-Off Valve
- 4. Needle Valve
- 5. Variable Voltage Transformer
- 6. Temperature Controller
- 7. Reactor
- 8. Furnace
- 9. Catalyst Bed
- 10. Thermocouple
- 11. Three-way Valve
- 12. TCD
- 13. Bubble Flow Meter
- 14. H₂O Trap

Figure 4.6 Flow diagram of the measurement of NH₃-TPD and CO₂-TPD

Table 4.4 Operating condition of a thermal conductivity detector within a gas chromatograph (SHIMADZU GC 8A) for the acidity measurement by NH_3 -TPD

Model	SHIMADZU GC 8A
Detector type	TCD
Helium flow rate	50 ml/min
Detector temperature	80°C
Detector current	80 mA

C. Procedure

1. 0.2 g of the catalyst sample was placed in a quartz tubular reactor. Under helium atmosphere at the flow rate of 50 ml/min, the catalyst sample was heated up to 500°C at a heating rate of 10°C/min and held for 1 h at this temperature in order to eliminate the adsorbed water. Then, the system was cooled down to room temperature.

2. At room temperature, the adsorption step was carried out in pure ammonia at the flow rate 30 ml/min for 1 h. After the adsorption step, the catalyst sample was swept in helium until the base line of the TCD signal was constant.

3. The desorption step was performed under a helium flow of 50 ml/min from room temperature to 700°C at a heating rate of 10°C/min. It was noted that during the desorption step the remaining water on the catalyst sample was trapped by the dry ice as well.

4.2.7 Basicity Measurement by CO₂-TPD

A. Materials

Helium in ultra high purity grade and carbon dioxide in purity grade were used as a carrier gas and a probe molecule gas, respectively. Both gases used in this experiment were supplied by Thai Industrial Gas Limited.

B. Apparatus

The temperature programmed desorption of carbon dioxide was used to measure the basic strength and the total amount of basic sites on the catalyst surface. The flow diagram of instruments in the measurement of basic sites by CO₂-TPD is the same as NH₃-TPD shown in Figure 4.6. The amount of carbon dioxide desorbed from the catalyst surface was measured by a thermal conductivity detector within a gas chromatograph (SHIMADZU GC 8A). The operating condition of gas chromatograph is summarized in Table 4.5.

Table 4.5 Operating condition of a thermal conductivity detector within a gas chromatograph (SHIMADZU GC 8A) for the basicity measurement by CO₂-TPD

Model	SHIMADZU GC 8A
Detector type	TCD
Helium flow rate	50 ml/min
Detector temperature	80°C
Detector current	80 mA

C. Procedure

1. 0.2 g of the catalyst sample was placed in a quartz tubular reactor. Under helium atmosphere at the flow rate of 50 ml/min, the catalyst sample was heated up to

500°C at a heating rate of 10°C/min and held for 1 h at this temperature in order to eliminate the adsorbed water. Then, the system was cooled down to room temperature.

2. At room temperature, the adsorption step was carried out in pure carbon dioxide at the flow rate 30 ml/min for 1 h. After the adsorption step, the catalyst sample was swept in helium until the base line of the TCD signal was constant.

3. The desorption step was performed under a helium flow of 50 ml/min from room temperature to 700°C at a heating rate of 10°C/min. It was noted that during the desorption step the remaining water on the catalyst sample was trapped by the ice as well.

4.3 Catalyst Evaluation

4.3.1 Catalytic Activity Test

A. Materials

The gases used in the catalytic activity test are listed in Table 4.6. They were all supplied by Thai Industrial Gas Limited.

Table 4.6 The details of gases used in the catalyst activity test

Gases	Formula	Grade
Helium	He	Ultra high purity
Hydrogen	H ₂	Ultra high purity
Oxygen	O ₂	10% in He
Nitric oxide	NO	1% in He
Propene	C ₃ H ₆	3% in He
Propane	C ₃ H ₈	3% in He
Sulfur dioxide	SO ₂	0.5% in He

B. Apparatus

A flow diagram of the system for testing the catalytic activity is shown in Figure 4.7. The apparatus consisted of a quartz tubular reactor, an automation temperature controller, an electrical furnace, a gas controlling system and two sets of gas chromatography. The instruments used in this system were listed and explained as follows:

1. Reactor: The NO reduction reactor was a conventional micro-reactor made from quartz tube with 0.6 cm inside diameter. The reaction was carried out under ordinary gas flow and atmospheric pressure. The effluent gases were sampled and analyzed by two on-line sets of gas chromatography.

2. Automation temperature controller: This unit consisted 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 a reactor. A dial setting established a set point at any temperature within the range between 0 to 999°C.

3. Electrical furnace: The furnace supplied the required heated to the reactor for NO reduction reaction. The reactor could be operated from room temperature up to 800°C at maximum voltage of 220 volts.

4. Gas controlling system: Helium, hydrogen, oxygen, nitric oxide, propene, propane and sulfur dioxide cylinders were each equipped with a pressure regulator, and an on-off valve. Needle valves were used to adjust a volumetric flow rate of gases. Two gas-sampling valves were used to take the sample of effluent gases.

5. Gas chromatography: The instruments consisted of thermal conductivity detector equipped within gas chromatographs, SHIMADZU GC8-ATP and SHIMADZU GC-8AIT, were used to analyze feed and effluent gases. The operating condition used in this experiment is given in Table 4.7.

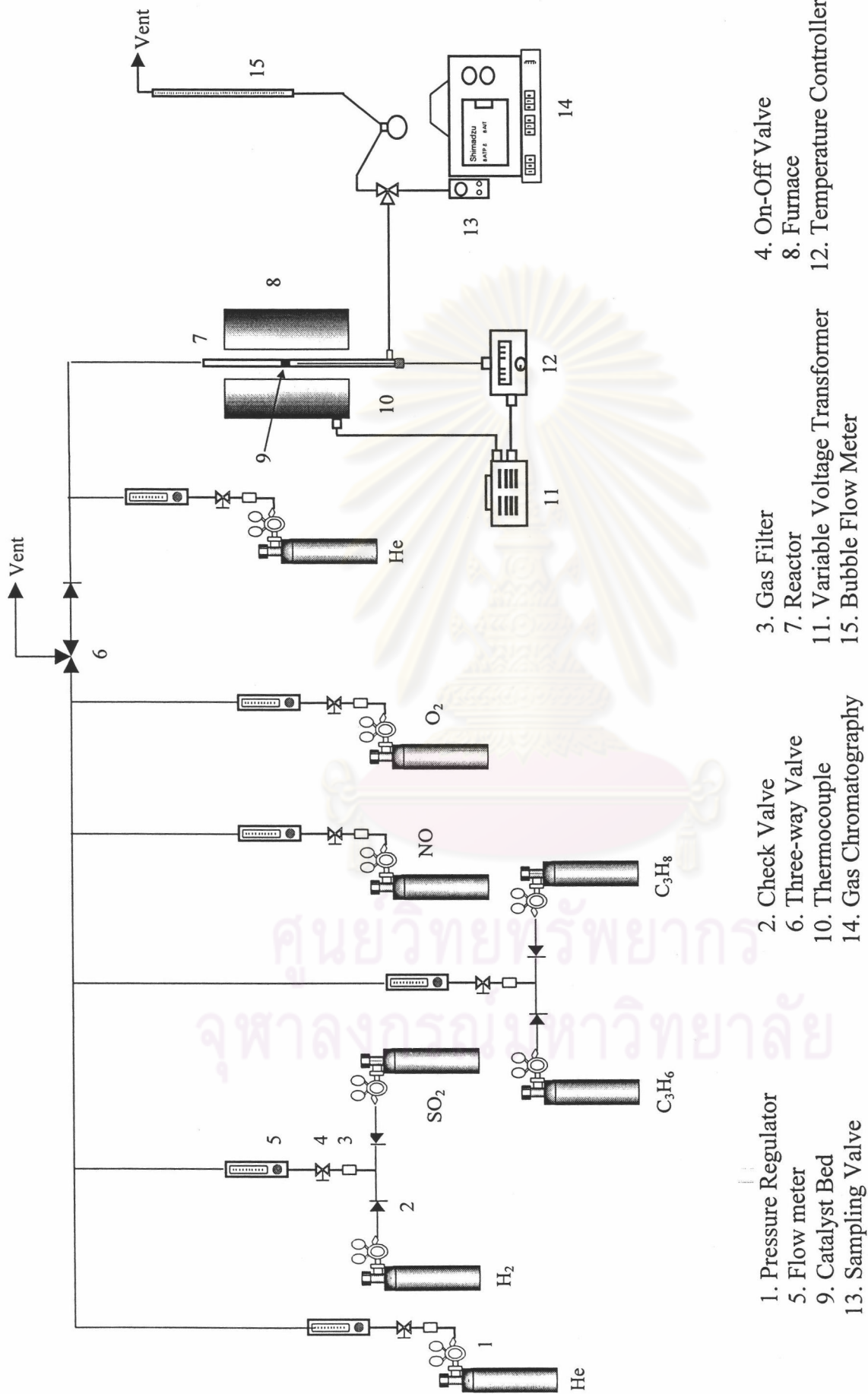


Figure 4.7 Schematic diagram of the reaction line for NO and HC conversions analyzed by gas chromatographs equipped with molecular sieve 5A and porapak QS columns

Table 4.7 Operating conditions of gas chromatographs for the catalytic activity test

Gas Chromatograph	SHIMADZU GC8A-ATP	SHIMADZU GC8A-AIT
Detector	TCD	TCD
Packed column	Molecular sieve 5A	Porapak QS
Carrier gas	He (UHP)	He (UHP)
Flow rate of carrier gas	45 ml/min	85 ml/min
Injector temperature	100°C	110°C
Column temperature	70°C	80°C
Detector temperature	100°C	110°C
Current	80 mA	90 mA
Analyzed gas	O ₂ , N ₂ , CH ₄ , CO	CH ₄ , CO ₂ , N ₂ O, C ₃ H ₆ , C ₃ H ₈ , SO ₂

C. Procedure

1. 0.1 g of catalyst was packed in a quartz tubular downflow reactor and the height of the catalyst bed was about 0.6 cm. The reactor was placed in the furnace and helium was introduced into the reactor in order to remove the remaining air out of the system.

2. Prior to the catalytic activity test, some of catalyst was reduced by hydrogen at a flow rate of 100 ml/min from room temperature to 500°C and held at 500°C for 1 h. After that, the helium was switched into the reactor to replace hydrogen and held at the same temperature for 10 min in order to remove the remaining hydrogen. Subsequently, the helium was substituted by 10% O₂ in He under a flow rate of 100 ml/min at the same temperature. The catalyst was reoxidized under this condition for 1 h and then cooled down to room temperature.

3. A gas mixture contained 1000 ppm NO, 1000 ppm C₃H₆ or C₃H₈ and 5% O₂ diluted in helium at a total flow rate of 200 ml/min (GHSV of 60000 h⁻¹) was used as a model exhaust gas to test the catalytic activity through temperature programmed

reaction. The reaction gases were introduced at elevated temperature from 100 to 600°C. At each given temperature, the catalyst sample was held until a true steady state was reached. This was achieved within 20 min. The samples of effluent gases were taken by two sampling loops each connected with a sampling valve and analyzed by using gas chromatograph equipped with molecular sieve 5A column for separating O₂, N₂ and CO and porapak QS column for separating CO₂, N₂O and hydrocarbons. Peak areas were automatically determined by using Shimadzu C-R6A integrator data system. The concentrations of the hydrocarbon reductant before and after reaction were used to calculate the C₃H₆ consumption. While the conversion of NO was calculated based on the concentration of N₂ and N₂O formed as described in Appendix C.

4. It was noted that for the effect of SO₂ on the catalytic activity, 500 ppm SO₂ was added into the feed stream. The experimental testing was conducted through the cycle of switching reaction. Switches were carried out after the system had reached equilibrium at a particular temperature. Generally, the helium inert tracer was switched out and the SO₂ was switched in after 1 h. The feed stream containing the SO₂ was held and switched back in after 1 h. Two cycles of this switching experiment were continuously repeated.

4.3.2 An Experimental Set for Studying the Nature of Surface Species

A. Materials

The gases used in the investigation of the surface species are similar to those in the catalytic activity test as already listed in Table 4.6.

B. Apparatus

The instruments and a flow diagram of the system for studying the nature of surface species are the same as those for testing the catalytic activity as seen in Figure 4.7.

C. Procedure

1. 0.1 g of catalyst was packed in a quartz tubular downflow reactor and the height of the catalyst bed was about 0.6 cm. The reactor was placed in the furnace and helium was introduced into the reactor in order to remove the remaining air out of the system.

2. Before the testing, some of catalyst sample was reduced by hydrogen at a flow rate of 100 ml/min from room temperature to 500°C and held at 500°C for 1 h. After that, the helium was switched into the reactor to replace hydrogen and held at the same temperature for 10 min in order to remove the remaining hydrogen. Subsequently, the helium was substituted by 10% O₂ in He under a flow rate of 100 ml/min at the same temperature. The catalyst was reoxidized under this condition for 1 h and then cooled down to room temperature.

3. The observation of surface species was performed by an experimental set of three continuous steps as follows:

a. Reaction step: A selected reactant gas mixture contained 1000 ppm NO, 1000 ppm C₃H₆ or C₃H₈ and 5% O₂ diluted in helium at a total flow rate of 200 ml/min (GHSV of 60000 h⁻¹) was used as a model exhaust gas to produce the surface species. This reactant gas mixture was introduced at a given temperature for 2 h. The samples of effluent gases were taken for the concentration measurement and analyzed by gas chromatograph every 10 min to check the steady state conversions of HC and NO at a particular temperature. When the time on stream was equal to 2 h, the catalyst was immediately purged by helium at a reaction temperature for 10 min and then cooled down to room temperature.

b. Temperature programmed desorption (TPD) step: After reaction step, it was continuously followed by the temperature programmed desorption to remove the adsorbed surface species in the same apparatus. This step was carried out under 50 ml/min helium flow with the heating rate of 5°C/min from 100 to 800°C. The effluent gases were analyzed by using gas chromatograph equipped with molecular

sieve 5A column for separating O_2 , N_2 and CO and porapak QS column for separating CO_2 , N_2O and hydrocarbons. Peak areas were automatically determined by using Shimadzu C-R6A integrator data system. The amount of surface species was calculated from the obtained releasing gases as described in Appendix C. The catalyst through TPD step was cooled down at room temperature.

c. Temperature programmed oxidation (TPO) step: After temperature programmed desorption step, the removal of the remaining deposits was performed by heating the catalyst sample under 1% O_2 in He at a flow rate of 50 ml/min with the heating rate of $5^\circ C/min$ from 100 to $800^\circ C$. The effluent gases were also analyzed by using gas chromatograph.

4. It was remarked that the experiment for reactivity test of surface species to the oxidizing gas was similar to that for investigating the nature of surface species but the TPD step was negligible. Additionally, the oxidizing gases in TPO step were varied as 1000 ppm NO, 1% O_2 and the gas mixture of 1000 ppm NO and 1% O_2 .



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