

CHAPTER IV



EXPERIMENTAL

This chapter consists of experimental systems and procedures used in this work, which is divided into three parts: 1) catalyst preparation, 2) catalyst characterization and 3) catalyst activities. The section 4.1 describes the procedure for catalyst preparation. The section 4.2 describes the details of catalyst characterization by various techniques such as X-ray diffraction (XRD), N₂ physisorption, Scanning Electron Microscopy (SEM), ammonia temperature-programmed desorption (NH₃-TPD), carbon monoxide temperature-programmed desorption (CO-TPD), hydrogen temperature-programmed desorption (H₂-TPD), hydrogen temperature-programmed reduction (H₂-TPR), and CO adsorption. The last part (section 4.3) describes the catalytic test in SCR of NO by propene, CO oxidation and selective CO oxidation.

4.1 Catalyst Preparation

4.1.1 Materials

The chemicals used in this study are specified as follows:

1. Aluminiumisopropoxide ($[(\text{CH}_3)_2\text{CHO}]_3\text{Al}$) from Aldrich, 98%
2. Toluene ($\text{C}_6\text{H}_5\text{CH}_3$) from Panreac, 99.5%
3. 1-Butanol ($\text{C}_4\text{H}_9\text{OH}$) from Merck, 99.5%
4. Silver nitrate (AgNO_3) from APS Finechem, 99.9%
5. Hexachloroplatinic acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) from Aldrich, 99.9%
6. Methyl alcohol (CH_3OH) from Aldrich, 99.5%
7. De-ionised water

4.1.2 Preparation of alumina support using the solvothermal method

Alumina support was prepared using 25 g of aluminiumisopropoxide (AIP). The starting material was suspended in 100 ml of solvent (butanol or toluene) in a test tube and then set up in an autoclave. In the gap between the test tube and autoclave wall, 30 ml of solvent was added. After the autoclave was completely purged with nitrogen, the autoclave was heated to desired temperature (300 °C) at the rate of 2.5 °C min⁻¹ and held at that temperature for 2 h. Autogeneous pressure during the reaction gradually increased as the temperature was raised. After the reaction, the autoclave was cooled to room temperature. The resulting powders were collected after repeated washing with methanol by centrifugation. They were then air-dried at room temperature. The as-synthesized powders were then calcined in air flow of 100 cc/min with a heating rate of 10 °C/min until the temperature reached 600 °C and holding at that temperature for 6 h.

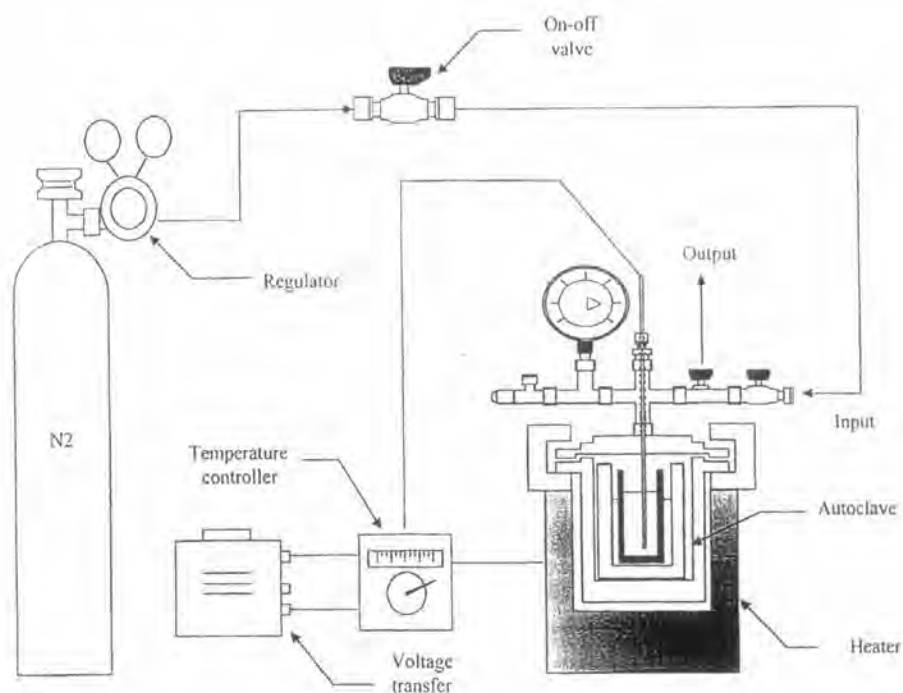


Figure 4.1 Diagram of the reaction equipment for the synthesis of alumina.

4.1.3 Preparation of Catalysts

Ag/Al₂O₃ and Pt/Al₂O₃ were prepared by the impregnation technique detailed as follows:

1. The amount of silver or platinum was calculated just enough for 2 g of the alumina support and then de-ionized water was added until the total volume of the solution became 2 ml for alumina.

2. 2 g of support was placed in a 50 ml Erlenmeyer flask and then the impregnation solution was gradually dropped into this support using a dropper. Shaking the flask continuously during impregnation was required to ensure the homogenous distribution of metal component on the support.

3. After the incipient wetness impregnation, the mixture of the impregnation solution and the alumina support was left in the atmosphere for 6 h to make a good distribution of metal complex. Subsequently, the impregnated sample was dried at 110 °C overnight in an oven.

4. The dried sample was purged under nitrogen at a flow rate of 60 ml/min with a heating rate of 10 °C/min from room temperature to 600 °C. When the temperature was reached to 600 °C, 100 ml/min of air flow was instead of nitrogen in order to make silver complex become silver oxide, which was in a stable form. The temperature was held at 600 °C for 2 h in air atmosphere. For the platinum, the temperature was held at 380 °C for 2 h in air atmosphere.

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

4.2 Catalyst characterization

This section explains the characterization of Ag/Al₂O₃ and Pt/Al₂O₃ catalyst including the crystal structure by XRD analysis, the metal active sites and the temperature programmed technique.

4.2.1 X-ray diffraction

X-ray diffraction analysis was used to analyze the crystallinity and the structure of a catalyst. 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°.

4.2.2 N₂ physisorption

The BET surface area, pore volume and pore diameter were measured by N₂ adsorption-desorption isotherm at liquid nitrogen temperature (-196°C) using a Micromeritics ASAP 2020. The surface area and pore distribution were calculated according to Brunauer-Emmett-Teller (BET) and Barret-Joyner-Halenda (BJH) methods, consecutively.

The apparatus of BET surface area measurement consisted of two feed lines for helium and nitrogen. The flow rate of the gas was adjusted by means of fine-metering valve. The sample cell made from pyrex glass. The mixture gases of helium and nitrogen flowed through the system at the nitrogen relative of 0.3. The catalyst sample (ca. 0.2 to 0.5 g) was placed in the sample cell, which was then heated up to 160°C and held at this temperature for 2 h. After the catalyst sample was cooled down to room temperature, nitrogen uptakes were measure as follows:

Step (1) adsorption step: The sample that set in the sample cell was dipped into liquid nitrogen. Nitrogen gas that flowed through the system was adsorbed on the surface of the sample until equilibrium was reached.

Step (2) desorption step: The sample cell with nitrogen gas-adsorption catalyst sample dipped into the water at room temperature. The adsorbed nitrogen gas was desorbed from the surface of the sample. This step was completed when the indicator line was in the position of base line.

4.2.3 XPS

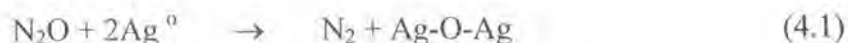
The XPS spectra and the binding energy of catalysts were determined by a Kratos Amicus X-ray photoelectron spectroscopy. The analyses were carried out with Mg K α X-ray source under a working pressure of 1×10^{-6} Pa at current of 20 mA and 12 kV, resolution 0.1 eV/step, and pass energy 75 eV. The binding energy was calibrated using the C 1s peak at 285.0 eV as reference.

4.2.4 CO-pulse chemisorption

Platinum dispersion was determined by pulsing carbon monoxide over the reduced catalyst. Approximately 0.2 g of catalyst was filled in a quartz tube, incorporated in a temperature-controlled oven and connected to a thermal conductivity detector (TCD). Prior to chemisorption, the catalyst is reduced in a flow of hydrogen (50cc/min) at 500 °C for 2 hour afterward; the sample is purged with helium. Carbon monoxide is pulsed at room temperature over the reduced catalyst until the TCD signal is constant.

4.2.5 Silver metal active sites measurement by N₂O decomposition method

The number of metal active sites were measured by N₂O decomposition technique on the assumption that only one N₂O molecule adsorbed and reacted with two silver metal sites, as the equation 4.1



A. Materials

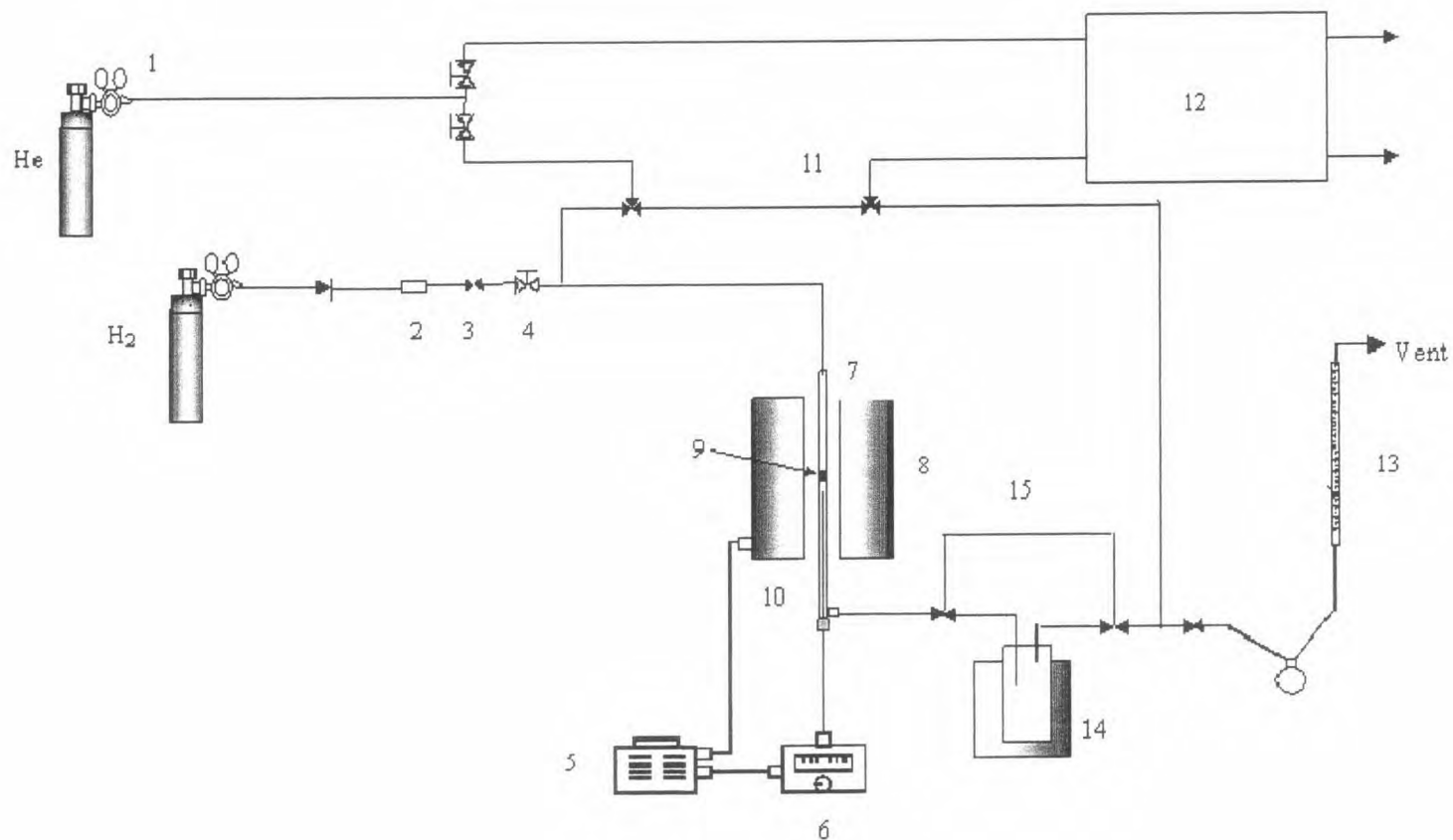
Helium in ultra high purity grade, hydrogen in ultra high purity grade and nitrous oxide in purity grade were used as a carrier gas, a reducing agent and an adsorbent gas, respectively. All gases used in this experiment were supplied by Thai Industrial Gas Limited.

B. Apparatus

The extensive diagram of instruments in measurement of the metal active sites is included in Figure 4.2. The amount of the effluent gases was measured by a thermal conductivity detector within a gas chromatograph (GOW-MAC). An operating condition of the gas chromatograph is illustrated in table 4.1.

Table 4.1 Operating condition of a thermal conductivity detector within a gas chromatograph (GOW-MAC) for measurement of the metal active sites

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



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|---------------------------|---------------|-----------------------|-----------------|---------------------------------|
| 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. Saturator | 15. Three-way Valve |

Figure 4.2 Flow diagram of measurement of N_2O decomposition

C. Procedure

1. 0.1 g of a catalyst sample was placed in a stainless steel tubular reactor. Helium gas was introduced into the reactor at a flow rate of 30 ml/min. The catalyst sample was heated at an increasing rate of 10 °C/min until a temperature reached to 300 °C. Subsequently, helium was substituted by hydrogen at a flow rate of 50 ml/min and held at this temperature for 1 h. The catalyst sample was cooled down to room temperature in helium flow.

2. At 150°C at which the catalyst sample was ready to be measured the metal active sites, 50 µl of the purity nitrous oxide gas was injected into the injection port to decompose on the metal surface of the catalyst sample. Injection of nitrous oxide was continuously repeated until the nitrous oxide did not any longer decompose on the catalyst sample. This situation was occurred when an obtained chromatogram area of any injection, after decomposition of the nitrous oxide pulse in the first injection had proceeded, was kept nearly constant compared with that of the former injection or no nitrogen product was released.

3. The amount of the metal active sites of the catalyst sample was calculated according to description in Appendix C.

4.2.6 Scanning electron microscopy (SEM)

Catalyst granule morphology and elemental distribution were obtained using a JEOL JSM-35F scanning electron microscope. The SEM was operated using the back scattering electron (BSE) mode at 20 kV at the Scientific and Technological Research Equipment Center, Chulalongkorn University (STREC)

4.2.7 Ammonia temperature-programmed desorption (NH₃-TPD)

The acidity of the catalyst samples was determined by temperature-programmed desorption of ammonia using a Micromeritics Chemisorp 2750 with a computer. In an experiment, about 0.10 g of the catalyst sample was placed in a quartz tube and pretreated at 250 °C in a flow of helium. The sample was saturated with 15%NH₃/He. After saturation, the physisorbed ammonia was desorbed in a helium gas flow for 0.5 h. Then, the sample was heated from 40 to 700 °C at a heating rate of 10 °C /min. The amount of ammonia in effluent was measured via TCD signal as a function of temperature.

4.2.8 Hydrogen and carbon monoxide temperature-programmed desorption (H₂ and CO-TPD)

Temperature programmed desorption of H₂ and CO (H₂ and CO-TPD) studies were performed in a Micromeritic ChemiSorb 2750 automated system attached with ChemiSoft TPx software. A 0.1 g of a calcined catalyst was placed in a quartz tube in a temperature-controlled oven and connected to a thermal conductivity detector (TCD). The catalyst was first purged under 50 cm³·min⁻¹ of H₂ flow at 500 °C for 1 h (using a ramp rate of 10 °C·min⁻¹) and cooled down to room temperature. The H₂ or CO was flow pass the sample at 50 cm³·min⁻¹ for 30 min. The temperature programmed desorption was performed with a constant heating rate of at 10 °C·min⁻¹ from 35 to 600 °C.

4.2.9 Temperature-programmed reduction (H₂-TPR)

Temperature programmed reduction (TPR) study was performed in a Micromeritic ChemiSorb 2750 automated system attached with ChemiSoft TPx software. A 0.1 g of a calcined catalyst was placed in a quartz tube in a temperature-controlled oven and connected to a thermal conductivity detector (TCD). The catalyst was first purged under 100 cm³·min⁻¹ of N₂ flow at 200 °C for 1 h (using a ramp rate of 10 °C·min⁻¹) and cooled down to room temperature. The reducing gas was 10% H₂ in Ar. During reduction, a cold trap was placed before the detector to remove

produced water. The temperature programmed reduction was performed with a constant heating rate at $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ from 35 to $600\text{ }^{\circ}\text{C}$. The thermal conductivity detector was conducted to measure the amount of hydrogen consumption.

4.3 Reaction study

4.3.1 Selective catalytic reduction of NO by propene

A. Materials

The gases used in the catalytic activity test are listed in table 4.2. They were all supplied by Thai Industrial Gas Limited.

Table 4.2 The details of gases used in the catalyst catalytic reduction of NO by propene

Gases	Formula	Grade
Helium	He	Ultra high purity
Oxygen	O ₂	10% in He
Nitric oxide	NO	1% in He
Propene	C ₃ H ₆	3% in He

B. Apparatus

A flow diagram of the system for testing the catalytic activity is shown in Figure 4.3. A quartz flow reactor with 0.6 cm inside diameter was used in this experiment. Feed and effluent gases were analyzed by TCD gas chromatographs, SHIMADZU GC-8ATP and SHIMADZU GC-8AIT. An operating conditions used in this experiment are given in table 4.3.

C. Procedure

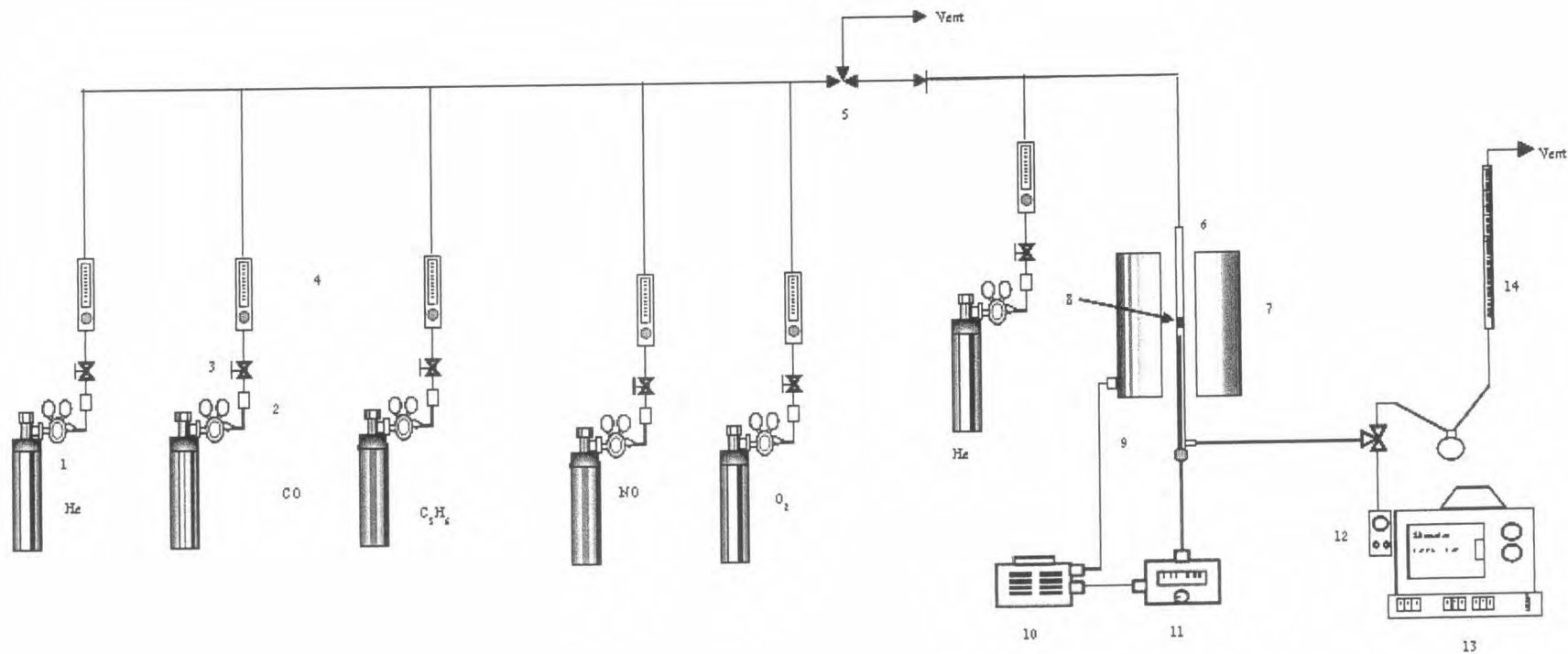
An experiment for studying catalyst activity behavior

1. 0.4 g of a catalyst sample was packed in quartz tubular down flow reactor. The reactor was placed in the furnace.

2. A gas mixture containing 1000 ppm NO, 1000 ppm C₃H₆ and 5% O₂ diluted in helium at a total flow rate of 200 ml/min (GHSV of 16000 h⁻¹) was used as a model exhaust gas to test the catalytic activity through temperature programmed reaction. The reaction gases were introduced to the reactor whose temperature was raised from 50 to 700°C stepwise. At each step, the catalyst bed was held at constant temperature until steady state was reached. This was achieved within 20 min. The effluent gases were analyzed by TCD gas chromatographs as shown in table 4.3.

Table 4.3 Operating conditions of gas chromatographs for the catalytic activity test

Gas Chromatograph	SHIMADZU GC-8ATP	SHIMADZU GC-8AIT
Detector type	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	60°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



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

Figure 4.3 Schematic diagram of the reaction line for NO and HC conversions analyzed by gas chromatographs equipped with molecular sieve 5A and porapak QS columns

4.3.2 Carbon monoxide oxidation

A. Materials

The gases used in the catalytic activity test are listed in table 4.4. They were all supplied by Thai Industrial Gas Limited.

Table 4.4 The details of gases used in the CO oxidation

Gases	Formula	Grade
Helium	He	Ultra high purity
Hydrogen	H ₂	Ultra high purity
Oxygen	O ₂	10% in He
Carbon monoxide	CO	5% in He

B. Apparatus

A flow diagram of the system for testing the catalytic activity is shown in Figure 4.3. A quartz flow reactor with 0.6 cm inside diameter was used in this experiment. Feed and effluent gases were analyzed by TCD gas chromatographs, SHIMADZU GC-8ATP and SHIMADZU GC-8AIT. An operating conditions used in this experiment are given in table 4.3.

C. Procedure

1. 0.2 g of a catalyst sample was packed in quartz tubular down flow reactor. The reactor was placed in the furnace.
2. A gas mixture containing 0.2% CO and 0.9% O₂ diluted in helium at a total flow rate of 100 ml/min (GHSV of 16000 h⁻¹) was used as a model exhaust gas to test

the catalytic activity through temperature programmed reaction. The reaction gases were introduced to the reactor whose temperature was raised from 50 to 700°C stepwise. At each step, the catalyst bed was held at constant temperature until steady state was reached. This was achieved within 20 min. The effluent gases were analyzed by TCD gas chromatographs as shown in table 4.3.

4.3.3 Selective carbon monoxide oxidation

A. Materials

The gases used in the catalytic activity test are listed in Table 4.5. They were all supplied by Thai Industrial Gas Limited.

Table 4.5 The details of gases used in the selective CO oxidation

Gases	Formula	Grade
Helium	He	Ultra high purity
Hydrogen	H ₂	Ultra high purity
Oxygen	O ₂	10% in He
Carbon monoxide	CO	5% in He

B. Apparatus

A flow diagram of the system for testing the catalytic activity is shown in Figure 4.3. A quartz flow reactor with 0.6 cm inside diameter was used in this experiment. Feed and effluent gases were analyzed by TCD gas chromatographs, SHIMADZU GC-8ATP and SHIMADZU GC-8AIT. An operating conditions used in this experiment are given in table 4.3.

C. Procedure

1. 0.2 g of a catalyst sample was packed in quartz tubular down flow reactor. The reactor was placed in the furnace.

2. A gas mixture containing 1% CO, 2% O₂ and 45% H₂ diluted in helium at a total flow rate of 100 ml/min (GHSV of 16000 h⁻¹) was used as a model exhaust gas to test the catalytic activity through temperature programmed reaction. The reaction gases were introduced to the reactor whose temperature was raised from 50 to 700°C stepwise. At each step, the catalyst bed was held at constant temperature until steady state was reached. This was achieved within 20 min. The effluent gases were analyzed by TCD gas chromatographs as shown in table 4.3.