

## **CHAPTER IV**

### **EXPERIMENTAL**

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., nitrogen oxide reduction, is described in section 4.2. Finally, the characterization methods, TPO, ESR, IR, BET, XRD and TEM to analyze catalysts and carbonaceous deposit catalysts are discussed in detail.

#### **4.1 Catalysts Preparation**

##### **4.1.1 Chemicals and Reagents**

The HY and HMOR zeolites were obtained from TOSOH Corporation, 3-8-2, Shiba, Minato-ku, Tokyo 105-8623, Japan, HY (JRC-Z-HY 5.5) and HMOR (JRC-Z-HM-20(4)). The parent Na-ZSM-5 zeolite was obtained from ALSI-PENTA Zeolithe GmbH, Alustr. 50, 92421 Schwasdorf, Germany, with Si/Al molar ratio of 25. The preparation of H-ZSM-5 and Cu-ZSM-5 were described as follows:

##### **4.1.2 NH<sub>4</sub>- and H-form ZSM-5**

To make NH<sub>4</sub>-ZSM-5, parent Na-ZSM-5 powder was firstly mixed with 1 M NH<sub>4</sub>NO<sub>3</sub> solution at 30 ml per gram of catalyst. In the procedure, catalyst amount did not exceed 5 grams to approach complete exchange. The slurry of zeolite and solution was then stirred and heated on a hot plate, maintained at 80 °C by applying a condenser. After heating the mixture for about 1 hr, the mixture was cooled down to room temperature and centrifuged to remove the use solution. The remained crystals were mixed again with NH<sub>4</sub>NO<sub>3</sub> solution in the same amount. The previous step was repeated. The exchanged catalyst was then washed twice with deionized water using centrifuge. Subsequently, the exchanged crystals were dried in an oven at 110-120 °C for at least 3 hrs. The dried catalyst obtained is the NH<sub>4</sub>-form of ZSM-5. The NH<sub>4</sub>-ZSM-5 was converted to H-form ZSM-5 by removing NH<sub>3</sub> species from the catalyst

surface.  $\text{NH}_3$  can be removed by thermal treatment of the  $\text{NH}_4$ -ZSM-5 zeolite. This was done by heating a sample in a furnace from ambient temperature to  $540^\circ\text{C}$  in 1 hr and holding the sample at  $540^\circ\text{C}$  for 3.5 hrs. After the catalyst was cooled down, it was stored in a glass bottle in a desiccator for future use.

#### **4.1.3 Copper ion-exchanged ZSM-5**

The Cu-ZSM-5 catalysts were prepared by the ion-exchanged method as follows. Approximately 5 g of Na-ZSM-5 was ion-exchanged in an 250 ml, 0.01 M aqueous solution of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  as the Cu source. Then, 10%  $\text{NH}_4\text{OH}$  solution was gradually dropped into the mixture to get the appropriate pH level (pH~9-11) to achieve a high loading. The ion-exchange was performed for 24 h at room temperature under continuous stirring by a magnetic stirrer. After the ion exchange process, the preparation was thoroughly washed with deionized water for 3-5 times to get rid of some ions using centrifuge separator and dried at  $110^\circ\text{C}$  for at least 3 h in an oven. The Cu-ZSM-5 catalyst was calcined up to  $540^\circ\text{C}$  for 3.5 h. Copper loading was 2% by weight.

#### **4.1.4 Pelletization**

All catalysts were pelletized by using a stainless steel die which has about a 1 cm diameter opening inside the die. The pelletization was performed at the pressure of about 3,000 psi, by applying a manual press, for 3 minutes for the approximate 0.25 g. catalyst sample per one pellet. The pellets obtained then were cut by a clean cutter into small granular pieces and were sieved to acquire grain sized to 8-16 mesh for use in the steady state reaction experiments.

## 4.2 Nitrogen oxide Reduction

### 4.2.1 Chemicals and Reagents

Nitrogen oxide (1% by vol) in helium, propene (3% by mole) in helium, Oxygen of ultra high purity grade (99.999% by vol) and helium with the same grade as oxygen (99.999% by vol) were provided by Thai Industrial Gases Limited.

Toluene ( $C_6H_5CH_3$ ) available from Carlo Erba Reagenti, 99.5%.

### 4.2.2 Instruments and Apparatus

A flow diagram of the steady state nitrogen oxide reduction system is shown in figure 4.1. The system consists of a reactor, an automation temperature controller, an electrical furnace, a gas control system and a saturator. The instruments used in this system is listed and explained below:

1. Reactor: The nitrogen oxide 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 gas was sampled and analyzed by an on-line gas chromatograph.

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 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 heating to the reactor for NO reduction reaction. The reactor could be operated from room temperature up to 600°C at maximum voltage of 220 volts.

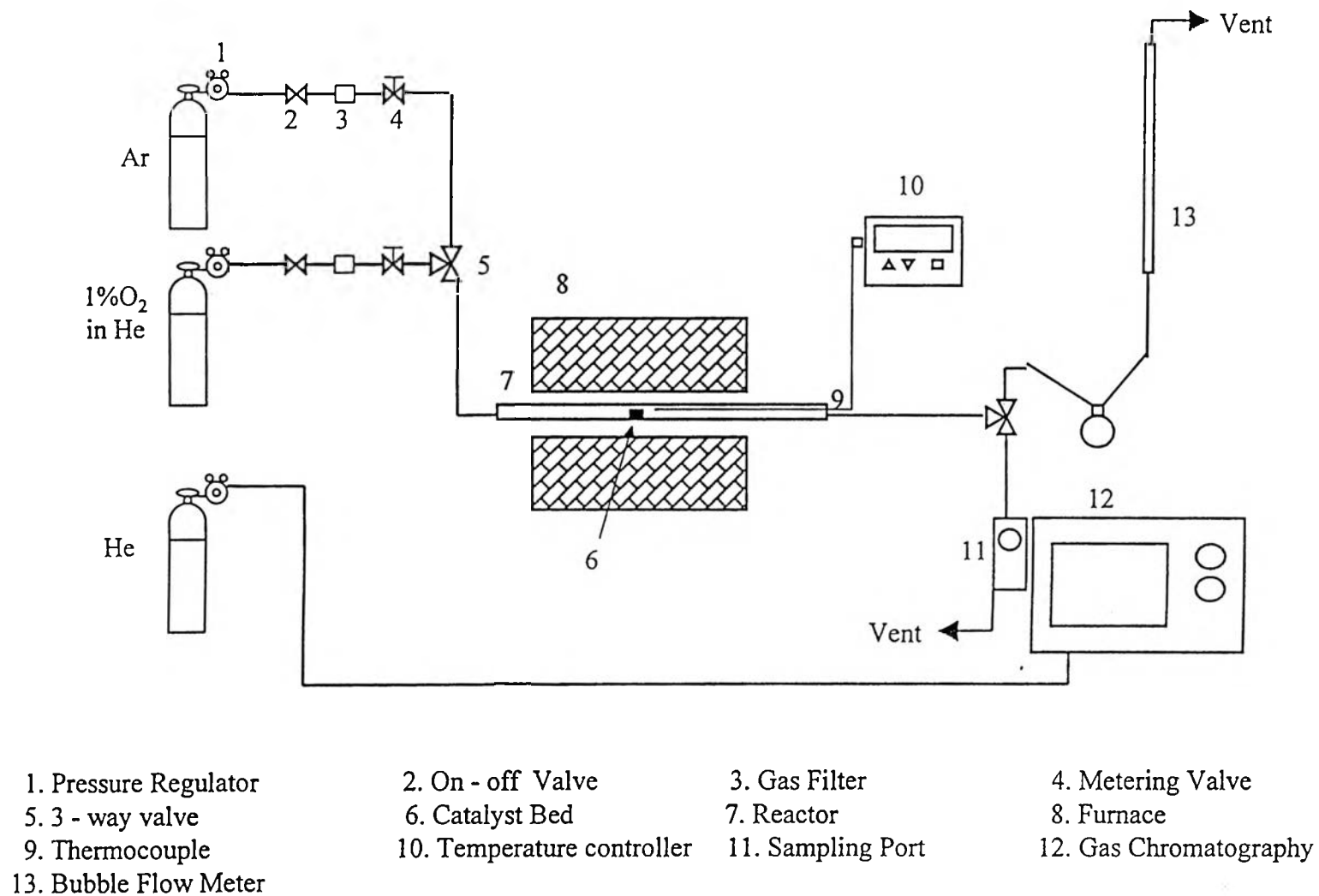


Figure 4.1 Flow diagram of Temperature Programmed Oxidation system

4. Gas controlling system: Nitrogen oxide, methane, oxygen, and helium cylinders each was equipped with a pressure regulator, and an on-off valve. Needle valves were used to adjust flow rate of gases. A gas-sampling valve was used to take sample of effluent gas.

5. Gas chromatography: The apparatus consist of thermal conductivity detector (TCD) gas chromatographs, SHIMADZU GC8-ATP and SHIMADZU GC-8AIT were used to analyze feed and effluent gas. Operating condition used was shown in table 4.1.

**Table 4.1** Operating condition of gas chromatograph

Gas Chromatography	SHIMADZU GC-8ATP	SHIMADZU GC-8AIT
Detector	TCD (on-line)	TCD (on-line)
Packed column	MS-5A	PORAPAK-Q
Carrier gas	He (99.999%)	He (99.999%)
Flow rate of carrier gas	40 ml/min	80 ml/min
Column temperature	70°C	90°C
Detector temperature	100°C	110°C
Detector current (mA)	80	90
Analyzed gas	O <sub>2</sub> , N <sub>2</sub>	C <sub>3</sub> H <sub>6</sub> , CO <sub>2</sub>

### 4.2.3 Experiment

The carbonaceous deposits catalysts were performed by nitrogen oxide reduction. It is interesting to apply for study of carbonaceous deposition on the catalysts. The experimental procedures are described in detail below.

1. 0.2 g portion of the catalyst was packed in the quartz tube reactor. The reactor was placed in the furnace and helium was introduced into the reactor with a flow rate of 100 ml/min (GHSV  $\sim$  20000 h<sup>-1</sup>).

2. The reactor was heated up at an increasing rate of 10°C/min. until the temperature reached 500°C and the reactor was held at this temperature for 1 h. After that, the catalyst was ready to be used for the reaction test. Continuously, this catalyst was cool down to the reaction temperature in helium and maintained in this temperature about 20 min. The reaction conditions were varied and the effective parameters were studied as follows:

**a.) The influence of hydrocarbons on deposits**

Hydrocarbons used to adsorb on the catalysts were C<sub>3</sub>H<sub>6</sub> (3% mole of carbon) and toluene (3% mole of carbon) in helium balance with the total flow rate of 100 ml/min (GHSV  $\sim$  20000 h<sup>-1</sup>). The reaction conditions used for the study of this effect were 400°C.

**b.) The influence of the catalysts on deposits**

Catalysts used in this reaction were HY, HM, H-ZSM-5 and Cu-ZSM-5. The reaction conditions used for the study of this effect were 400°C.

**c.) The influence of adsorption time on deposits**

The reaction temperature was kept constant at 400°C. The gas sampling was taken at 5, 20 and 60 min of reaction intervals.

**d.) The influence of the adsorbed gas mixtures on deposits**

The adsorbed gas mixtures were used to adsorb on to the catalysts as C<sub>3</sub>H<sub>6</sub> only (3% mole of carbon) in helium balance, C<sub>3</sub>H<sub>6</sub> (3% mole of carbon) + 1000ppm NO in helium balance and C<sub>3</sub>H<sub>6</sub> (3% mole of carbon) + 1000ppm NO + O<sub>2</sub>(10%vol) in helium balance with the total flow rate of 100 ml/min (GHSV  $\sim$  20000 h<sup>-1</sup>) and toluene (3% mole of carbon) substituted in C<sub>3</sub>H<sub>6</sub> all cases. The reaction conditions used for the study of this effect were 400°C.

3. When the reaction conditions were finished, helium was switched in to replace the adsorbed gas mixtures. Then, the reactor was cooled down to ambient temperature.

After reaction test, the used catalyst were characterized by different methods. The carbon dioxide and nitrogen produced during the combustion of carbonaceous deposits catalysts were determined by temperature programmed oxidation (TPO). In addition, the properties of the catalysts were characterized by ESR, FT-IR, BET, XRD and TEM. These characterizations were ascribed in section 4.3

### **4.3 Catalyst Characterization**

#### **4.3.1 Temperature-Programmed Oxidation**

##### **a) Materials**

1 %vol oxygen in helium gas mixture and nitrogen oxide (1% vol) in helium 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. A microprocessor base temperature controller (PC 600, Shinko), controlled the furnace temperature. 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 10°C/min until the temperature reached 800°C. During the oxidation, the amount of CO<sub>2</sub> in the effluent gas was first analyzed when the catalyst temperature reached 100°C, then at an interval of about 10 min, using a gas chromatograph (SHIMADZU 8 AIT) equipped with a gas sampling valve (1.5 ml sampling loop) and a thermal conductivity detector

### c) Procedure

1. The carbonaceous deposit 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 oxidizing gas mixtures used to remove carbon on the catalysts by TPO technique were flowed through the system at a flow rate of 100 ml/min. The oxidizing gas mixtures used oxygen 1% vol in helium (1%O<sub>2</sub>/He), 1000ppm of nitrogen oxide (1000 ppm NO) and 1000ppm of nitrogen oxide (1000ppmNO) + 1% vol in helium (1%O<sub>2</sub>/He).

3. The Temperature-Programmed Oxidation of carbonaceous deposit catalyst was started. The temperature was raised to 800°C at the heating rate of 10°C/min. When the temperature was 50°C, the effluent stream was sampled every 10 min by the on-line gas sampler.

4. To take up the concentration measurement; the gas samples were analyzed by using gas chromatograph GC-8ATP (for N<sub>2</sub>) and GC-8AIT (for CO<sub>2</sub>). From the area of CO<sub>2</sub> and N<sub>2</sub>, the concentrations of CO<sub>2</sub> and N<sub>2</sub> from reactor outlet were calculated with calibration equation analyzed from C<sub>3</sub>H<sub>6</sub> consumption.

5. After the catalyst temperature reached 800°C, The oxidizing gas was changed to ultra high purity helium and the reactor was cooled down.

6. The amount of carbon and nitrogen (wt%) was calculated (Appendix A).

#### 4.3.2 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.

#### **4.3.3 Infrared (IR) technique**

In this work IR technique were adopted. This method is used to characterize the structural properties of carbonaceous deposition by the lattice vibration. The vibration bands between 400 and 4000  $\text{cm}^{-1}$  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 enable 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.

#### **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 boiling point temperature.

##### **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<sub>2</sub> 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.

**Table 4.2** 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 μmHg
Pressure table	5 points

#### 4.3.5 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 CuK $\alpha$  radiation.

#### 4.3.6 Transmission Electron Microscopy (TEM) technique

TEM micrographs were obtained by direct observation of the fresh and carbonaceous deposit samples 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).