

## CHAPTER IV

### EXPERIMENTAL

This chapter describes the experimental systems and the experimental procedures applied in this research. Section 4.1 shows the scope of this study. A description of catalyst preparation method is given in section 4.2. The experimental system of catalyst characterization is explained in section 4.3. Section 4.4 describes the experimental system of the selective catalytic reduction of NO with NH<sub>3</sub>. Details of experimental procedures, including the materials and apparatus are as follows.

#### 4.1 The scope of this study

Three types of DeNO<sub>x</sub> catalysts are used in this study:

1. 25wt%V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub>
2. 5wt%W-25wt%V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub>
3. 3wt%K-25wt%V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub>

The reaction conditions of selective catalytic reduction are as follows:

Reaction Temperature:	room temperature – 500 °C
Operating Pressure :	1 atm
Space Velocity :	40,000 hr <sup>-1</sup>

Components of reactant gas are as follows:

Nitric Oxide	:	0, 500 ppm
Ammonia	:	0, 500 ppm
Oxygen	:	0, 2% vol.
Sulfur dioxide	:	0, 50 ppm

## 4.2 Preparation of catalyst

### 4.2.1 Materials

The chemical used in this experiment is normally Analytical Grade, but only some critical chemicals have to be specified as follows:

1. Ammonium metavanadate ( $\text{NH}_4\text{VO}_3$ ) used was a commercial product of Farmitalia Carlo Erba, Italy.
2. Ammonium *para*-tungstate ( $(\text{NH}_4)_{10}\text{H}_2(\text{W}_2\text{O}_7)_6$ ), manufactured by Fluka Chemie AG, Switzerland.
3. Potassium nitrate ( $\text{KNO}_3$ ), manufactured by Eagle Manufacturing, U.S.A.
4. Titanium(IV)oxide ( $\text{TiO}_2$ ) support, obtained from Farmitalia Carlo Erba, Italy.

### 4.2.2 Preparation of 25wt% $\text{V}_2\text{O}_5/\text{TiO}_2$

Titanium(IV)oxide support was dried for 3 hours in air at 300 °C before impregnation with ammonium metavanadate in aqueous solution. The mixture was continuously stirred and heated at 70 °C until all water evaporated. After subsequent drying overnight, the sample is calcined in air at 380 °C for 3 hours. The heating rate was 10 °C/min.

### 4.2.3 Preparation of 5wt%W-25wt% $\text{V}_2\text{O}_5/\text{TiO}_2$ and 3wt%K-25wt% $\text{V}_2\text{O}_5/\text{TiO}_2$

5wt%W-25wt%  $\text{V}_2\text{O}_5/\text{TiO}_2$  and 3wt%K-25wt%  $\text{V}_2\text{O}_5/\text{TiO}_2$  were prepared by impregnation of the titania with ammonium metavanadate and ammonium *para*-tungstate, and ammonium metavanadate and potassium nitrate, respectively, also in

aqueous solution. After water evaporation each catalyst was calcined at 380 °C for 3 hours with heating rate 10 °C/min.

### **4.3 The characterization of catalyst**

#### **4.3.1 Surface area measurement**

The BET surface area was determined by nitrogen adsorption in an automatic apparatus microceritics model ASAP 2000 at Analysis Centre of Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University.

#### **4.3.2 X-ray Diffraction (XRD)**

The XRD patterns of catalysts were performed by using SIEMENS D-5000 diffractometer with  $\text{CuK}\alpha$  radiation in the  $2\theta$  range of 4-80°. The XRD spectrum is used to identify the crystal structure of catalyst.

#### **4.3.3 Determination of composition of catalyst**

The percentage of metal loading of each catalyst prepared in this study was analyzed by Atomic Absorption Spectrometer (AAS) method, at Department of Science Service.

#### **4.3.4 Fourier transform infrared spectrometer (FT-IR)**

The functional group on the catalyst surface was identified by Nicolet Impact 400 FT-IR spectrometer with the spectral resolution 4  $\text{cm}^{-1}$  over the spectral range 4000-400  $\text{cm}^{-1}$ . Each sample was mixed with KBr (ratio of sample: KBr equal to 1 : 100 ) before being forced into a thin wafer.

### **4.3.5 FT-IR pyridine adsorption**

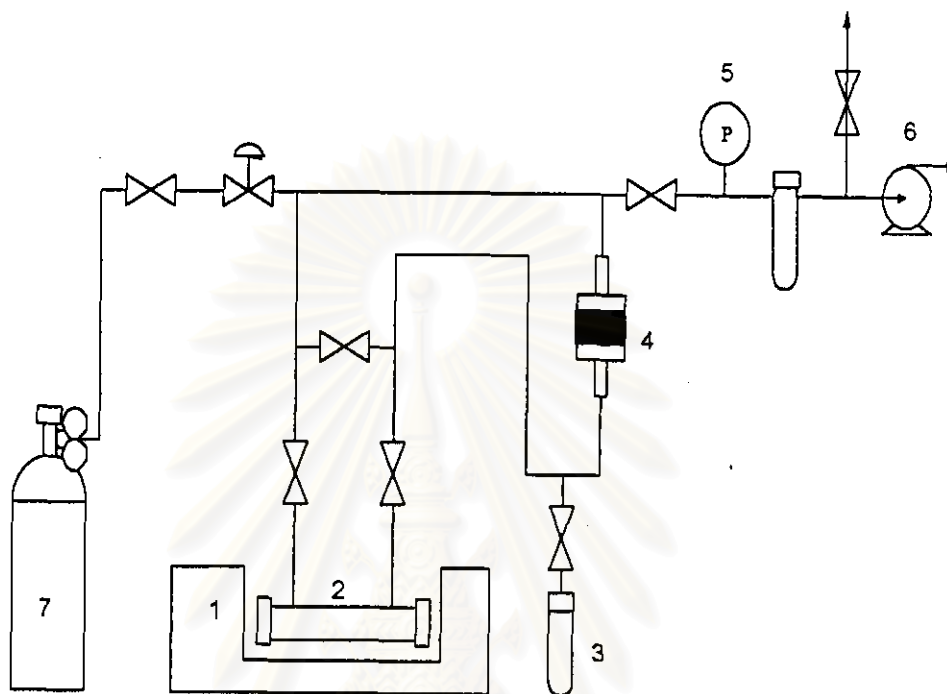
#### **4.3.5.1 Chemicals and reagents**

Ultra high purity (99.99 % ) nitrogen supplied by TIG Ltd. and Pyridine, analytical grade supplied by Univar or Ajax Chemical were used in these experiments.

#### **4.3.5.2 Instruments and apparatus**

##### **- Flow diagram**

The flow diagram of the in-situ FT-IR apparatus is depicted in Figure 4.1. All gas lines, valves and fitting in this apparatus are made of Pyrex glass except for the IR gas cell and the sample disk holder which are made of quartz glass in order to avoid the adsorption of any gas species which may remain on the inner surface of glass tube while the system was evacuated. Nitrogen was used for purging before starting the experiment. Pyridine was added to a glass tube connected with a valve which can open to the gas line system. A home-made electro-magnetic pump, fixed in the gas line, was used for circulating the gas (including the pyridine vapour) through the sample in order to accomplish the adsorption of gases or pyridine specie on the sample surface. A Labconco 195 - 500 HP vacuum pump, which theoretically has capacity at  $10^{-4}$  Torr, was used. Furthermore, a digital pressure indicator, attached to the gas line, measured the pressure of the system and checked leaking of the apparatus as well.



- |                                      |                               |
|--------------------------------------|-------------------------------|
| 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 4.1** Flow diagram of instrument used for pyridine adsorption experiment.

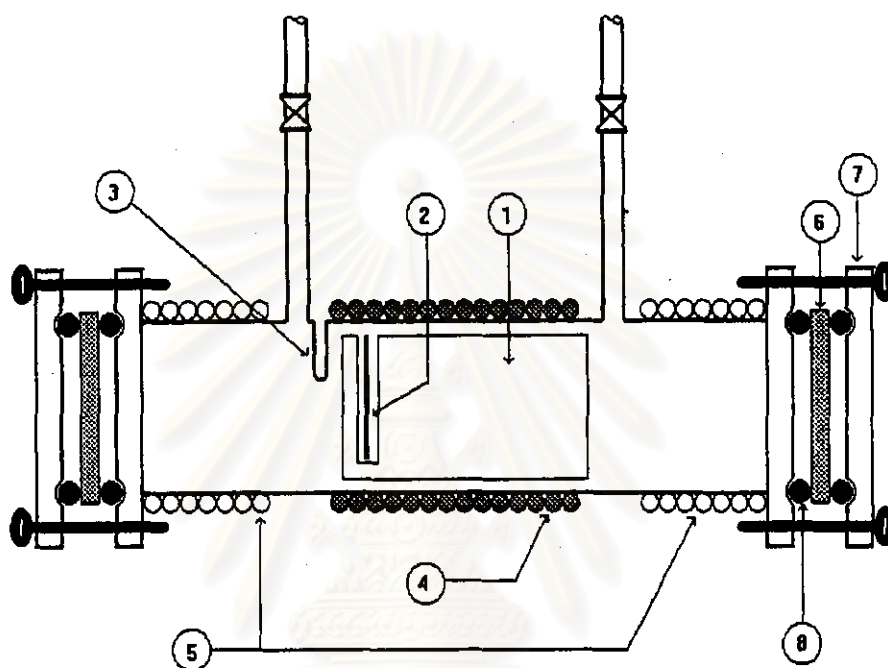
## - FT-IR

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) were applied to this study. The analyzer was placed on a movable table for convenient adjustment.

## - IR gas cell

IR gas cell used in this experiment (figure 4.2) was made of quartz glass and covered with a  $32 \times 3$  mm KBr windows at each end of the cell. The windows were sealed by two O-ring and a stainless flange fastened by a set of screws.

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



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

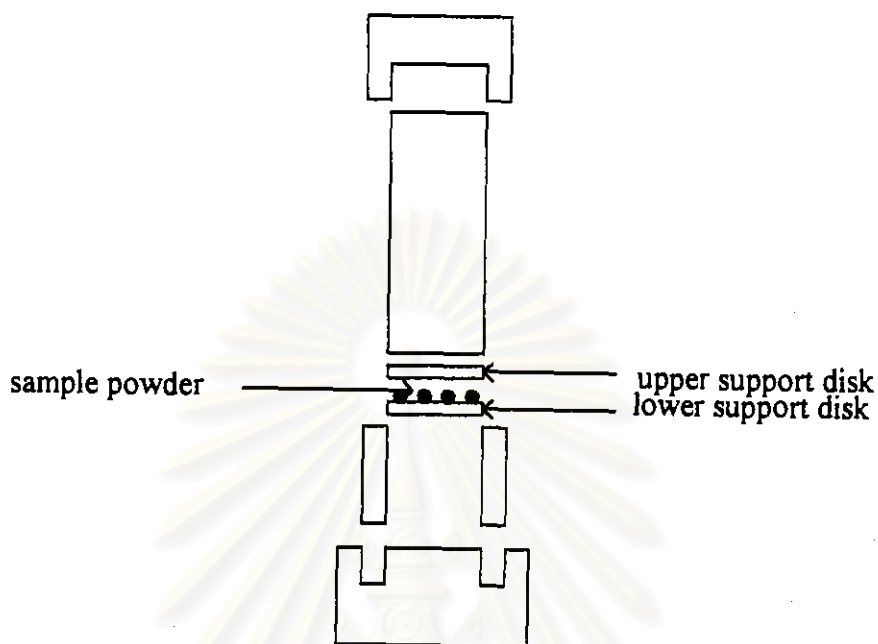
Figure 4.2 IR gas cell used for pyridine adsorption experiment.

#### 4.3.5.3 Sample disk preparation

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 die used was made of stainless steel and is shown in figure 4.3. The most important part of the die, which is directly in contact with the sample is the so-called the support disks. The support disks are composed of upper and lower disks, each 20 mm. in diameter. The support disks are 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. The powder sample, about 0.06 - 0.065g, 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/cm<sup>2</sup>. If a thick sample disk was used, a poor IR would scan result and if a too thin sample disk was employed, it would be easily cracked by thermal treating as well as broken itself. All parts of die were put together and were pressed by a manual hydraulic press at pressures of 140 -180 kg/cm<sup>2</sup> for 5 minutes. The pressure should not be too low so that a self-supporting disk cannot form. After pressing, the well-formed disk was carefully removed from the die and mounted in the IR cell.





**Figure 4.3** Body of the die for preparation of a self-supporting catalyst disk.

#### 4.3.5.4 Experimental procedure

After a well-formed sample disk is obtained, it was placed in the sample holder and then the sample holder, including sample disk, was placed into the middle of the IR gas cell. The sample disk is 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 leaks were not observed, the IR gas cell was evacuated by a vacuum pump through the gas line for at least 30 minutes to place the system under vacuum. The sample disk was evacuated in vacuum for 1 hour at room temperature. However, since no change of the IR spectrum of the sample was found during the pre-treatment, this step sometimes ignored. Pyridine vapour was brought into contact with the disk at room temperature. Under vacuum, liquid pyridine evaporates from the pyridine tube into the gas line leading to the IR gas cell. To achieve the maximum adsorption of pyridine, pyridine vapour was circulated through the system by the electro-magnetic

pump for about 1 hr or until the IR spectrum of pyridine peak did not change. After that, the IR cell and gas line were evacuated to remove not only pyridine vapour remaining in the cell and gas line but also the physisorbed pyridine from the catalyst surface too. The vacuum pump was operated till the IR spectra peaks of pyridine vapour and physisorbed pyridine totally vanished and there was no change in any other peaks of the spectra. This normally took around 1.5 hr. Then, FT-IR measurement of the spectra of the pyridine-adsorbed sample started at room temperature and were repeated at elevated temperature in 25 °C steps.

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 result spectra by such species. On the other hand, since the vibration would occur and bring about bad scans, the vacuum was switched off while the temperature was held constant for IR detection. The measurement was completed when all peaks of adsorbed pyridine disappeared so that the IR spectra of the sample was identical to the one before pyridine dosing.

#### **4.4 Nitric oxide reduction**

##### **4.4.1 Chemicals and reagents**

Nitric oxide (5% vol.) in nitrogen, ammonia (5% vol.) in nitrogen, Oxygen of ultra high purity grade (99.999% vol.), sulfur dioxide (0.5% vol.) in helium, and nitrogen of ultra high purity grade (99.999% vol.) were provided by Thai Industrial Limited.

##### **4.4.2 Instruments and apparatus**

1. Reactor: The NO reduction reactor was a conventional micro-reactor made from a quartz tube with 8.5 mm 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 NO<sub>x</sub> analyzer.

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 500 °C at the maximum voltage of 220 volts.

4. Gas controlling system: Nitric oxide, ammonia, oxygen, sulfur dioxide, and nitrogen cylinders each was equipped with mass flow controller (Kofloc 3650).

5. NO<sub>x</sub> analyzer: A NO<sub>x</sub> analyzer (model NOA-7000) equipped with a NO<sub>x</sub> detector by chemiluminescence method was used to analyze the effluent gas. The operating condition used was shown in Table 4.1.

**Table 4.1** Operating condition of NO<sub>x</sub> analyzer (model NOA-7000).

Model	NOA-7000
Measured Component	NO <sub>x</sub> at atmospheric pressure
Detector type	Chemiluminescence method
Range	0-1000 ppm
Response time	Approx. 30 seconds
Sampling flow rate	Approx. 1000 ml/min
Air flow rate	1750 ml/min
Display	LCD, 320 x 200 dots

#### 4.4.3 Procedure

The catalytic reaction test was carried out by using a conventional microreactor. The diagram of the system is exhibited schematically in Figure 4.4. A 0.5 g portion of the catalyst was packed in the middle of the quartz microreactor. A gas mixture containing NO (500ppm), NH<sub>3</sub> (500ppm), O<sub>2</sub> (2% vol.), and N<sub>2</sub> balance was fed at a total flow rate of 200 cm<sup>3</sup>/min. The reaction gas was introduced into the reactor. The temperature was raised to 500 °C at the heating rate of 5 °C/min. When the reaction temperature was 50 °C, the effluent stream was sampling every 10 minutes by the on-line gas sampler. The concentration of NO was measured by NO<sub>x</sub> analyzer. After the catalyst temperature reached 500 °C, this mixture gas in nitrogen was changed to high purity nitrogen and the reactor was cooled down.

In some run SO<sub>2</sub> was added to the reactant gas to observe their effect on the catalyst be property.

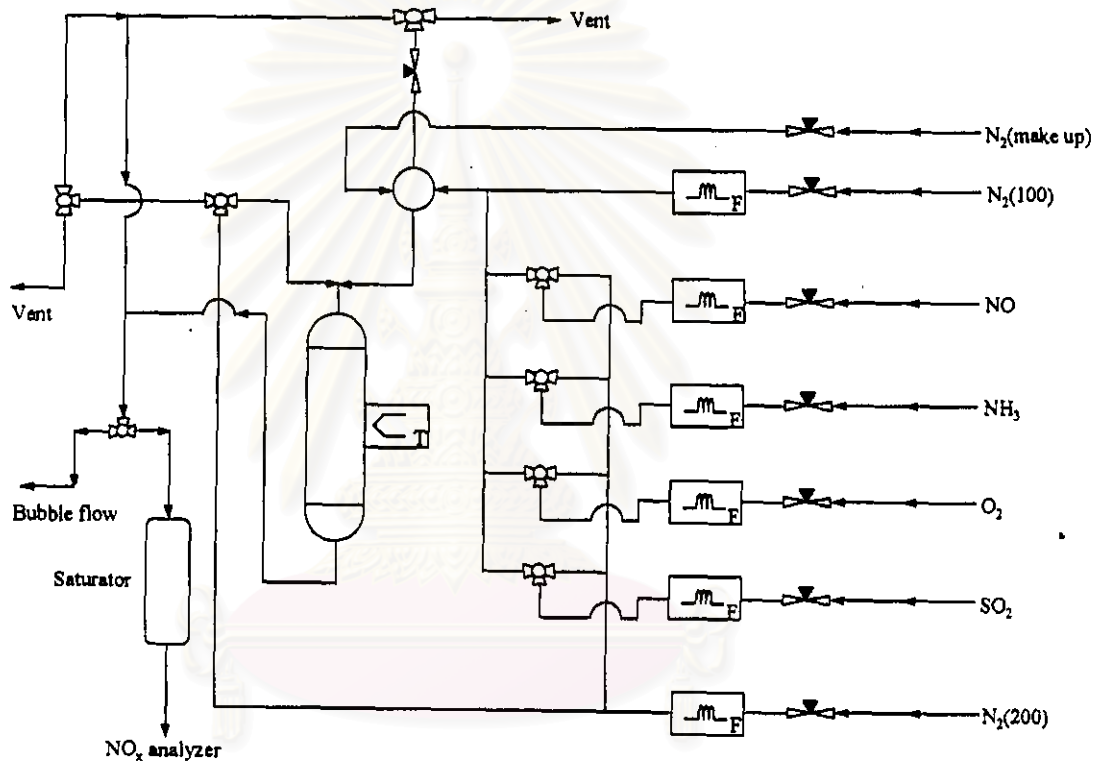


Figure 4.4 Flow diagram of NO reduction system

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