

CHAPTER IV

EXPERIMENTAL

This chapter contains details about catalyst preparation method, selective catalytic reduction (SCR) of nitric oxide with ammonia system and characterization of catalyst. In each section, details of experimental procedures, including the materials and apparatus are described.

The scope of this study

Type of DeNO_x catalyst used in this study:

- Pure TiO₂, pure V₂O₅, 25 wt.% V₂O₅/TiO₂ (based catalyst)
- The catalyst which additional tungsten; 2 wt.% WO₃- 25 wt.% V₂O₅/TiO₂ (co-loading), 10 wt.% WO₃- 25 wt.% V₂O₅/TiO₂ (co-loading), three types of 5 wt.% WO₃- 25 wt.% V₂O₅/TiO₂; co-loading, load V first, load W first
- The catalyst which additional potassium; 1 wt.% K₂O - 25 wt.% V₂O₅/TiO₂ (co-loading), 5 wt.% K₂O - 25 wt.% V₂O₅/TiO₂ (co-loading), three types of 3 wt.% K₂O - 25 wt.% V₂O₅/TiO₂; co-loading, load V first, load W first
- The catalyst which additional both tungsten and potassium; 3 wt.% K₂O - 5 wt.% WO₃- 25 wt.% V₂O₅/TiO₂

Reaction condition:

Reaction temperature	:	room temperature – 500°C
Operation pressure	:	1 atm.
Space velocity	:	20,000 (1/hr)

Component of feed gas:

Nitric oxide	:	0, 500 ppm
Ammonia	:	0, 500 ppm
Oxygen	:	0, 2 %
Nitrogen	:	balance

4.1 Preparation of catalysts

V_2O_5/TiO_2 catalyst was prepared by the conventional wet impregnation method. TiO_2 support (manufactured by Farmitalia Carlo Erba) was grounded to the required mesh size of 60-80 mesh. Then, 3 grams of the support was put into an aqueous solution containing an appropriate amount of ammonium metavanadate, NH_4VO_3 (Farmitalia Carlo Erba). The mixture was continuously stirred and heated to $70^\circ C$ until all water evaporated. The obtained catalyst was further dried in air at overnight. After drying the catalyst was calcined in air, 100 ml/min., at $380^\circ C$ for 3 hours. The heating rate was $10^\circ C/min.$

Three types of $V_2O_5-WO_3/TiO_2$ catalysts were prepared. In the first type of preparation, denoted further in the text by symbols 5W25V, vanadium was introduced on TiO_2 surface doped previously with tungsten. The doping was performed by impregnation from the ammonium paratungstate (Fluka Chemika), obtained after water evaporation and then calcined in air at $380^\circ C$ for 3 hours. Vanadia was then deposited on the calcined WO_3/TiO_2 sample by the incipient wetness method from NH_4VO_3 solution. The obtained powder was again dried and calcined in the same condition. In the second type of sample, 25V5W, vanadia was firstly introduced in the way given above onto pure titania surface, then tungsten was deposited on the calcined V_2O_5/TiO_2 samples by the incipient wetness method. The catalyst was dried and calcined in air for 3 hours at $380^\circ C$. The third sample, co-25V5W, was prepared by co-impregnation of the titania with ammonium metavanadate and ammonium paratungstate, also in aqueous solution. The conditions of drying and calcination liked previous samples. About co-25V2W, co-25V10W were the symbols of 2 wt.% WO_3 - 25 wt.% V_2O_5/TiO_2 , 10 wt.% WO_3 - 25 wt.% V_2O_5/TiO_2 , respectively. 25V2W, 25V10W were prepared by co-impregnation.

Three types of $V_2O_5-K_2O/TiO_2$ catalysts were prepared using similar method to the three types of $V_2O_5-WO_3/TiO_2$ catalysts. The symbols of the three types of $V_2O_5-K_2O/TiO_2$ catalysts liked the three types of $V_2O_5-WO_3/TiO_2$ catalysts too *i.e.*

3K25V, 25V3K, co-25V3K). Also, co-25V1K and co-25V5K were prepared like the catalysts which additional tungsten by co-impregnation method.

The last sample, 25V5W3K, was prepared by wet-impregnation. Titania with ammonium metavanadate, ammonium paratungstate and potassium nitrate were mixed together in aqueous solution. Then, the mixture was dried and calcined.

4.2 The system of the catalytic activity test

Steady state catalytic activity measurement was evaluated in a quartz tubular fixed bed microreactor (ID. = 6 mm.). The diagram of the system is exhibited schematically in figure 4.1. The furnace temperature is controlled by a digital temperature controller. The reactant mixture, total flow rate 200 ml/min, composes 500 ppm NH_3 , 500 ppm NO , 2% O_2 balanced with N_2 . In some runs, SO_2 and water vapor were added to the system. The reactant gas flow rates were controlled using a set of mass flow controller (Kofloc 3650). De NO_x catalyst was tested by passing the gas mixture through the catalyst bed. During the experiments, the reaction temperature is monitored using a thermocouple and a digital temperature indicator. NO concentration in the effluent gas was analyzed using a NO_x analyzer (Shimadzu model NOA-7000). The operating conditions of NO_x analyzer are shown in appendix C (table C-1).

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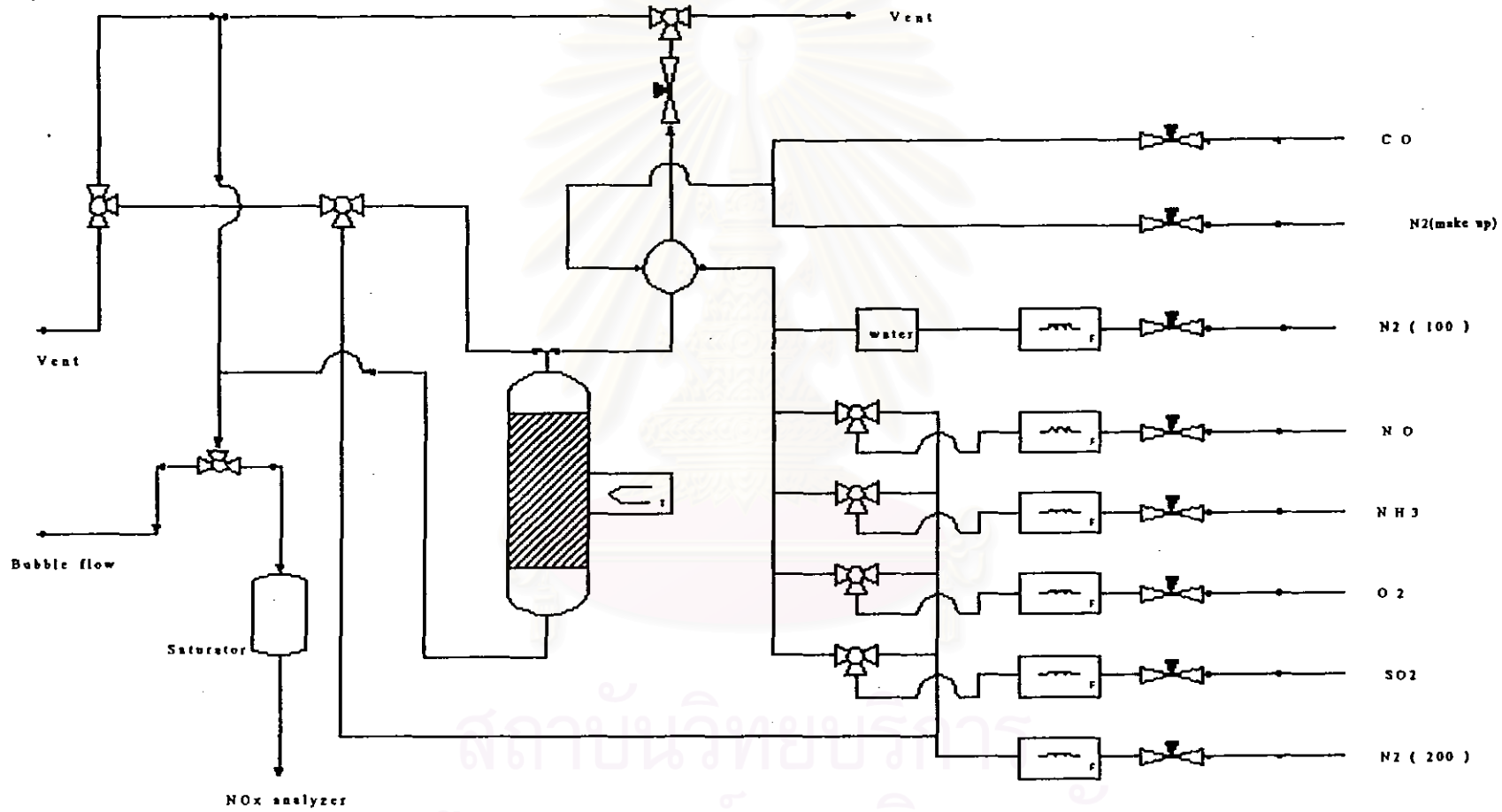


Figure 4.1: Flow diagram of the reactor system for NO reduction

4.3 Experimentation

The experimental procedures are described in detail below.

1. 0.5 grams of catalyst was packed in the middle of the quartz microreactor. The reactor was then placed in the furnace and the gas mixture ($\text{NO} + \text{NH}_3 + \text{O}_2 + \text{N}_2$) was introduced into the reactor at a flow rate of 200 ml/min.

2. The reduction of NO_x was started up at room temperature. The temperature was raised to 500°C at the heating rate of $5^\circ\text{C}/\text{min}$. When the temperature was 50°C , the effluent stream was sampled continuously by the on-line gas sampler.

3. The amount of nitric oxide in the effluent gas was measured by NO_x analyzer.

4. After the catalyst temperature reached 500°C , the mixture gas in nitrogen was changed to high purity nitrogen and the reactor was cooled down.

Note: In some runs, SO_2 and H_2O were added to the reactant gas to observe their effect on the catalyst property.

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4.4 Characterization of the catalysts

- X-ray Diffraction Pattern

X-ray Diffraction (XRD) analysis of the catalysts was performed using X-ray diffractor (model D-5000, SEIMENS), using $\text{CuK}\alpha$ radiation in the 2θ range of $4\text{-}80^\circ$.

- Specific surface area Measurement

Surface area of the catalysts were measured by the BET method, with nitrogen as absorbent using a micrometrics model ASAP-2000 at the boiling point of liquid-nitrogen.

- Chemical Analysis

Atomic Absorption Spectrometry (AAS) method is a technique for determining the concentration for metallic elements in solution. The samples were analysed at the Center of Service Science.

- Fourier Transform Infrared Spectrometer (FT-IR)

The functional group on the catalyst surface was determined by FT-IR using Nicolet model Impact 400. Each sample was mixed with KBr with ratio of sample : KBR equal to 1 : 100 before being formed into a thin wafer. Infrared spectra were recorded between 4000 to 400 cm^{-1} on a microcomputer. FT-IR spectra were measured at room temperature with a resolution of 4 cm^{-1} and an average of 50 scans.

- Surface acidity measurement

Infrared spectroscopy and temperature programmed desorption of pyridine have been used to investigate the acidic properties of the catalysts. The experimental procedures are described in detail below.

The catalyst (0.06 grams) was pressed into a self-supporting wafer and placed into a quartz in-situ IR gas cell with sample disk holder. The gas cell was attached with two KBr windows at both ends. Prior to adsorption the sample was evacuated to about 10^{-4} torr at room temperature for 1 hour. Pyridine was introduced into the IR

cell by self-vaporizing in vacuum condition and was circulated through the system by an electromagnetic pump. After 1 hour of adsorption, the excess and weakly adsorbed pyridine was removed by evacuating at room temperature for 1 hour. Presumably only the chemisorbed pyridine remained on the surface. Desorption was then continued by evacuation at progressively higher temperature, every 25°C, and IR spectra were recorded on a Nicolet Impact 400 FT-IR equipped with a TGS detector. Each spectrum consisted of 500 scans at a resolution of 4 cm⁻¹. Background spectra, *i.e.*, prior to adsorption, were subtracted from all spectra such that the effects of adsorption and thermal treatments could be more clearly seen.



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