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APPENDIX

APPENDIX A

REDUCTION OF NO$_x$

A major source of nitric oxide emissions is fuel combustion in engines and power plants. NO$_x$ emissions also can be significant in chemical operations such as nitric acid plants. More recently, the emission of nitrous oxides (N$_2$O) from fiber production plants has received attention because of it global warming effects. The nitric oxide and SO$_x$ emissions are component of acid rain since, when mixed with water vapor in the clouds, they form nitric and sulfuric acid, respectively. Furthermore, NO$_x$ participates in photochemical ozone (smog) generation by reaction with hydrocarbons.

NO$_x$ is formed in combustion processes by combining the N$_2$ and O$_2$ present in air. At temperatures greater than 1500 °C, this reaction proceeds at appreciable rates through a well characterized mechanism called the Zeldovich equation. If a compound in the combustion process has bound nitrogen (e.g., pyridine), NO$_x$ is readily formed at much lower temperature through an oxidation process.

A.1 Nonselective catalytic reduction (NSCR) of NO$_x$

One of the earliest techniques used to abate NO$_x$ emissions from engines and nitric acid plants was to deplete the oxygen by operating the engines near stoichiometric or by adding a hydrocarbon or purge gas to deplete the oxygen via a chemical reaction in the exhaust.

For stationary engine operation, the engine is normally operated near stoichiometric conditions, whereby the catalytic chemistry is very similar to automotive three-way catalyst technology. The main differences from this application relative to automotive exhaust control are in the operating conditions (temperature, steady-state operation) and the aging phenomena.

The major reactions involved NSCR NO_x are as follows :

$$CO + 1/2O_2 \longrightarrow CO_2 \qquad (A.1)$$

$$H_2 + 1/2O_2 \longrightarrow H_2O \qquad (A.2)$$

$$HC + O_2 \longrightarrow CO_2 + H_2O \qquad (A.3)$$

$$NO_x + CO \longrightarrow CO_2 + N_2 \qquad (A.4)$$

$$NO_x + H_2 \longrightarrow H_2O + N_2 \qquad (A.5)$$

$$NO_x + HC \longrightarrow CO_2 + H_2O + N_2 \qquad (A.6)$$

A typical commercial catalyst ranges from 0.1 to 0.5 percent platinum, plus rhodium supported on a high surface area γ-Al_2O_3 washcoated onto a ceramic honeycomb.

A.2 Selective catalytic reduction (SCR) of NO_x

SCR of NO_x using NH_3 was first discovered in 1957. The discussion that follows is a historical perspective of the development of SCR technology. It was discovered that NH_3 could react selectively with NO_x, producing elemental N_2 over a Pt catalyst in excess amounts of oxygen. The major desired reactions are:

$$4NH_3 + 4NO + O_2 \longrightarrow 4N_2 + 6H_2O \qquad (A.7)$$

$$4NH_3 + 4NO_2 + O_2 \longrightarrow 3N_2 + 6H_2O \qquad (A.8)$$

One undesirable reaction produces N_2O which, given its strong infrared absorptivity, is considered to be a powerful greenhouse gas:

$$2NH_3 + O_2 \longrightarrow N_2O + 3H_2O \qquad (A.9)$$
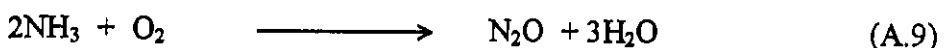
The injected ammonia can be wasted by catalytic partial oxidation to elemental nitrogen. This is a nonselective reaction.

$$4NH_3 + O_2 \longrightarrow N_2 + 6H_2O \qquad (A.10)$$
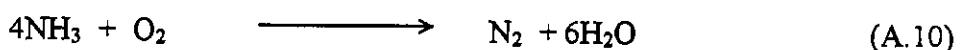
It can also be completely oxidized to NO, another nonselective reaction.

$$4NH_3 + O_2 \longrightarrow 4NO + 6H_2O \qquad (A.11)$$

At temperature below about 100-200 °C, the ammonia can be react with the NO_2 present in the process gas producing explosive NH_4NO_3.

$$2NH_3 + 2NO_2 + H_2O \longrightarrow NH_4NO_3 + NH_4NO_2 \qquad (A.12)$$
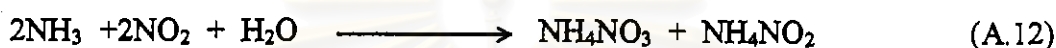
The reaction can be avoided by never allowing the temperature to fall below about 200 °C. The tendency for formation of NH_4NO_3 can also be minimized by metering into the gas stream less than the precise amount of NH_3 necessary to react stoichiometrically with the NO_x (1 to 1 mole ratio). By doing so, there is little excess NH_3 that can "slip" out of the reactor. In all applications, there is always a specification on permitted NH_3 slip. Frequently, this is < 5-10 vppm.

When sulfur is present in the flue gas, such as in coal-fired boilers or power plants, or in petroleum-derived liquid fuels such as distillate or diesel, the oxidation of SO_2 to SO_3 (reactions A.13 and A.14) results in formation of H_2SO_4 upon reaction with H_2O. Obviously, this results in condensation downstream and excessive corrosion of process equipment.

$$2SO_2 + O_2 \longrightarrow 2SO_3 \qquad (A.13)$$
$$SO_3 + H_2O \longrightarrow H_2SO_4 \qquad (A.14)$$

The reaction of NH_3 with SO_3 also results in formation of $(NH_4)_2SO_4$ and/or NH_4HSO_4 (reactions 3.15 and 3.16), which deposits on and fouls downstream process equipment such as heat exchangers and causes a loss in to thermal efficiencies.

$$NH_3 + SO_3 + H_2O \longrightarrow NH_4HSO_4 \qquad (A.15)$$
$$2NH_3 + SO_3 + H_2O \longrightarrow (NH_4)_2SO_4 \qquad (A.16)$$
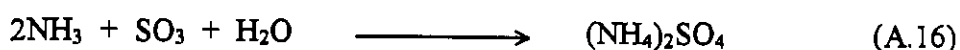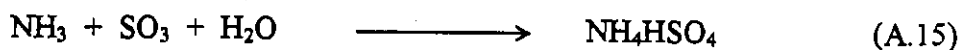
Few applications of SCR NO_x catalysts existed until the early 1970s, when reduction of the emission of NO_x became an important control issue for stationary power sources in Japan. The Pt technology was not applicable in this exhaust temperature region (i.e. >250 °C) because of its poor selectivity for NO_x reduction at these higher temperatures, so it was during this period that the base metal catalysts were invented. Note that the Pt catalysts lose selectivity above 250 °C. At >250 °C, V_2O_5/Al_2O_3 catalyst was used first. However, its use was restricted to sulfur-free exhaust gases because the alumina reacted with SO_3 to form $Al_2(SO_4)_3$ and deactivated the catalyst. This problem led to another key development-the use of nonsulfating TiO_2 carrier for the V_2O_5, which then became the catalyst of choice. These catalysts functioned at higher temperatures and over a broader range than Pt.

Finally, quite recently, zeolite based catalysts have been developed that function at higher temperatures.

Since each general class of catalyst material has different temperature performance characteristics, the engineer has considerable design flexibility to select the most cost-effective catalyst composition, structure, and operating system to optimize the abatement process. The active catalytic component and temperature ranges may be classified as indicated below:

Low temperature (175-250 °C): platinum

Medium temperature (300-450 °C): vanadium

High temperature (350-600 °C): zeolite

IR SPECTRA OF SPENT CATALYSTS
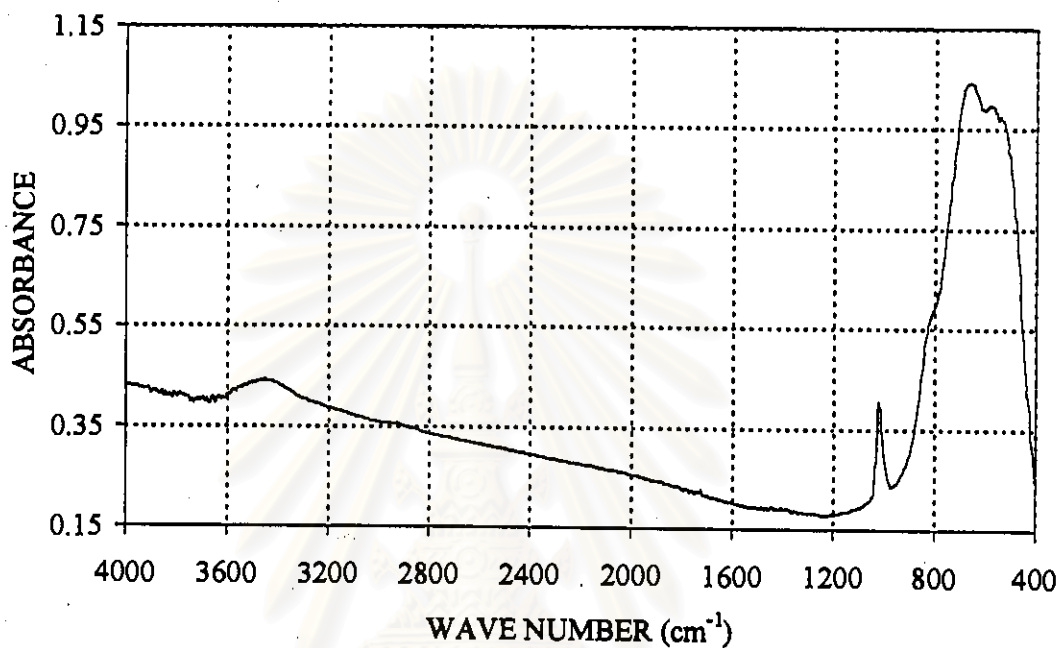
Figure B-1 IR spectrum of spent 25wt%V_2O_5/TiO_2 without SO_2
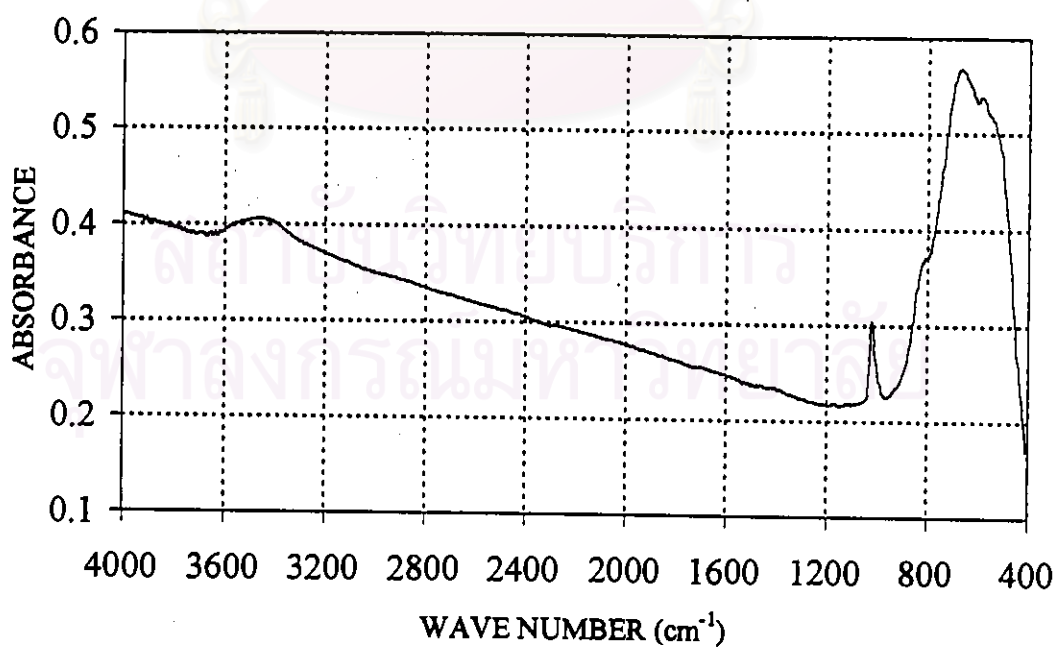
Figure B-2 IR spectrum of spent 25wt%V_2O_5/TiO_2 with SO_2
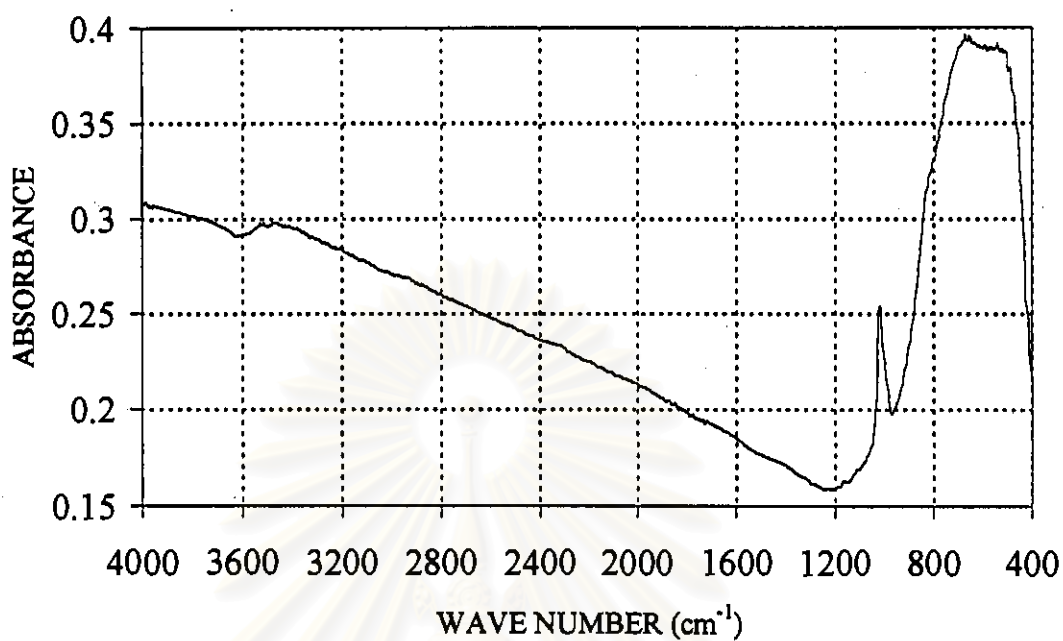
Figure B-3 IR spectrum of spent 5wt%W-25wt%V_2O_5/TiO_2 without SO_2
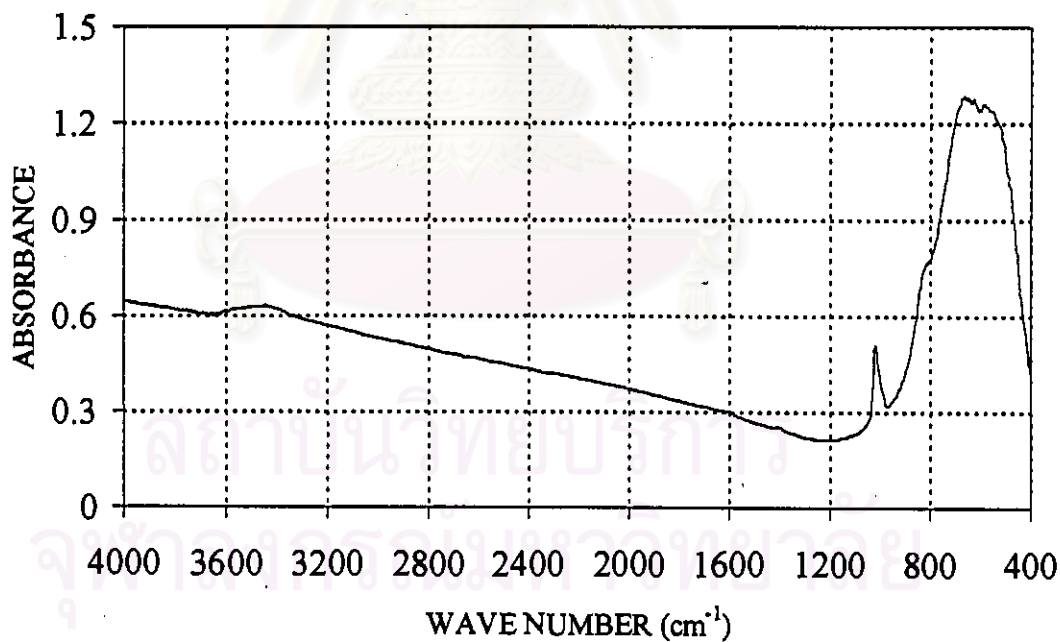
Figure B-4 IR spectrum of spent 5wt%W-25wt%V_2O_5/TiO_2 with SO_2
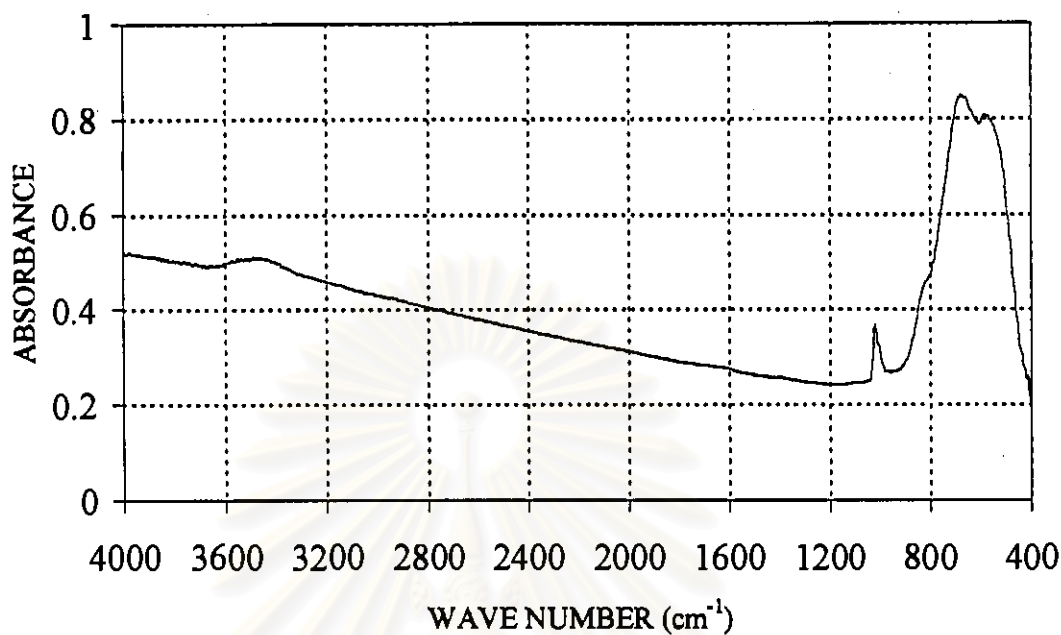
Figure B-5 IR spectrum of spent 3wt%K-25wt%V_2O_5/TiO_2 without SO_2
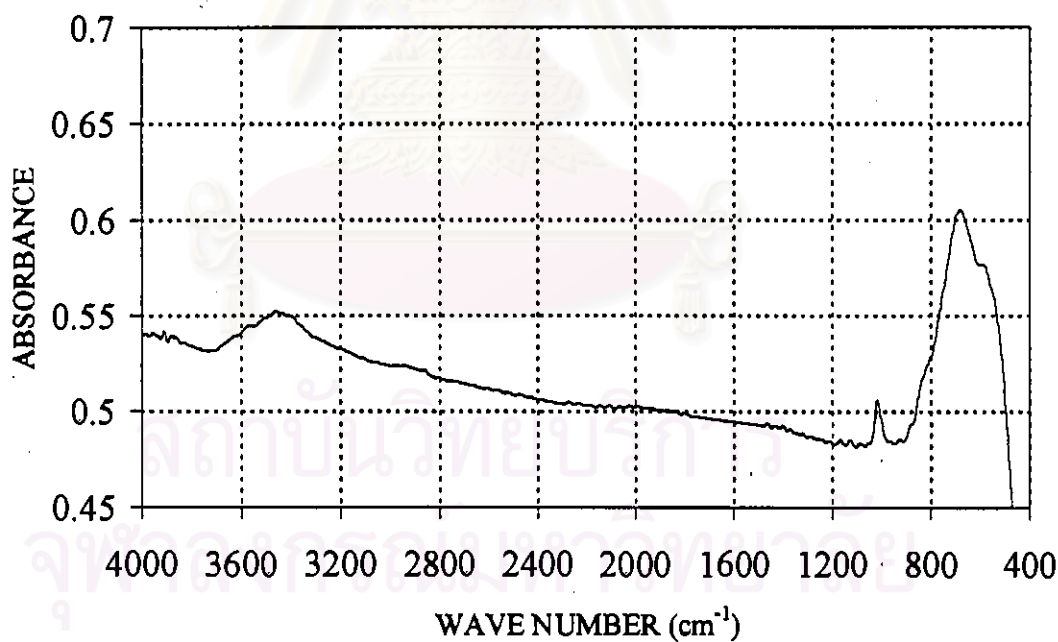
Figure B-6 IR spectrum of spent 3wt%K-25wt%V_2O_5/TiO_2 with SO_2

APPENDIX C

SAMPLE OF CALCULATION

1. **Preparation of 25%V_2O_5/TiO_2 (% by weight) catalyst with the wet impregnation method.**

    Reagent: Ammonium metavanadate, NH_4VO_3 (Farmitalia Carlo Erba)

                Molecular weight = 116.98 grams.

                (Atomic weight of vanadium = 50.9419)

    Support: Titanium dioxide, TiO_2 – anatase phase (Farmitalia Carlo Erba)

Calculation for the preparation of 25 %wt. V_2O_5/TiO_2

    Based on: 25 %wt. V_2O_5/TiO_2, catalyst weight = 100 grams.

    So that, the catalyst 100 grams would composed of vanadium oxide 25 grams.

    Then, titanium dioxide (support) = 100 – 25 = 75 grams.

The titanium dioxide support weight used for all preparations is 3.0 grams.

For NH_4VO_3 used as precursor salt.

        Vanadium required   = $3.0 \times (25/75)$ grams.

                            =   1.0   grams.

    Vanadium 1.0 grams was prepared from NH_4VO_3.

Vanadium content in NH_4VO_3 is 50.9419 grams, therefore:

        The required salt   = $1 \times 116.98 / 50.9419$ grams.

                         =   2.2964   grams.

2. **Preparation of 5%WO$_3$ - 25%V$_2$O$_5$/TiO$_2$ (% by weight) catalyst with the wet impregnation method.**

Reagent: Ammonium metavanadate, NH$_4$VO$_3$ (Farmitalia Carlo Erba)

Molecular weight = 116.98 grams.

(Atomic weight of vanadium = 50.9419)

Ammonium paratungstate, (NH$_4$)$_{10}$H$_2$(W$_2$O$_7$)$_6$ (Fluka Chemika)

Molecular weight = 3060.59 grams.

(Atomic weight of Tungsten = 183.85)

Support: Titanium dioxide, TiO$_2$ – anatase phase (Farmitalia Carlo Erba)

Calculation for the preparation of 5%WO$_3$ - 25%V$_2$O$_5$/TiO$_2$ (% by weight)

From (1); Calculation for 25%V$_2$O$_5$/TiO$_2$, we used NH$_4$VO$_3$ 2.2964 grams.

Based on: 5%WO$_3$ - 25%V$_2$O$_5$/TiO$_2$, catalyst weight = 100 grams.

So that, the catalyst 100 grams would composed of tungsten oxide 5 grams.

Then, 25%V$_2$O$_5$/TiO$_2$ = 100 – 5 = 95 grams.

25%V$_2$O$_5$/TiO$_2$ weight used for all preparations is 4.0 grams.

(TiO$_2$ 3.0 grams + V$_2$O$_5$ 1.0 grams)

For (NH$_4$)$_{10}$H$_2$(W$_2$O$_7$)$_6$ used as precursor salt.

Tungsten required   =   4.0 × (5/95)   grams.

=   0.2105   grams.

Tungsten 0.2105 grams was prepared from (NH$_4$)$_{10}$H$_2$(W$_2$O$_7$)$_6$.

Tungsten content in (NH$_4$)$_{10}$H$_2$(W$_2$O$_7$)$_6$ is 3060.59 grams, therefore:

The required salt   =   0.2105 × 3060.59 / (183.85 × 12) grams.

=   0.2921   grams.

3. Preparation of 3%K₂O - 25%V₂O₅/TiO₂ (% by weight) catalyst with the wet impregnation method.

Reagent: Ammonium metavanadate, NH_4VO_3 (Farmitalia Carlo Erba)

Molecular weight = 116.98 grams.

(Atomic weight of vanadium = 50.9419)

Potassium nitrate, KNO_3 (Eagle Manufacturing, U.S.A.)

Molecular weight = 101.1069 grams.

(Atomic weight of Potassium = 39.102)

Support: Titanium dioxide, TiO_2 – anatase phase (Farmitalia Carlo Erba)

Calculation for the preparation of 3%K₂O - 25%V₂O₅/TiO₂ (% by weight)

From (1); Calculation for $25\%V_2O_5/TiO_2$, we used NH_4VO_3.2.2964 grams.

Based on: $3\%K_2O$ - $25\%V_2O_5/TiO_2$, catalyst weight = 100 grams.

So that, the catalyst 100 grams would composed of tungsten oxide 3 grams.

Then, $25\%V_2O_5/TiO_2$ = 100 – 3 = 97 grams.

$25\%V_2O_5/TiO_2$ weight used for all preparations is 4.0 grams. (TiO_2 3.0 grams + V_2O_5 1.0 grams)

For KNO_3 used as precursor salt.

Potassium required   =   4.0 × (3/97)   grams.

=   0.1237   grams.

Potassium 0.1237 grams was prepared from KNO_3.

Potassium content in KNO_3 is 101.1069 grams, therefore:

The required salt   =   0.1237 × 101.1069 / 39.102   grams.

=   0.3198   grams.

4. Calculation of NO conversion

The effluent gas was analyzed by NO_x analyzer. The SCR activity was evaluated in terms of the conversion of NO into N_2.

NO conversion (%) $= \{([NO]_{in} - [NO]_{out}) / [NO]_{in}\} \times 100$

APPENDIX D

CHEMICAL COMPONENT OF TiO$_2$ SUPPORT

Chemical component	% by weight
TiO$_2$	99.0
Cl	0.01
PO$_4$	0.10
SO$_4$	0.10
Pb	0.0010
As	0.0002
Fe	0.0050
Cu	0.0005
Zn	0.0050

APPENDIX E

THE OPERATING CONDITIONS NO$_x$ ANALYZER

NO$_x$ analyzer (model NOA-7000) was used to analyze the concentrations of nitric oxide. Operating conditions are as follows:

Table C-1: Operating condition of NO$_x$ analyzer (model NOA-7000)

Model	NOA-7000
Measured component	NO$_x$ by Atmospheric pressure Chemiluminescence method
Range	0 – 1000 ppm
Response time	Approx. 30 seconds
- NO$_x$	- can be changed in 20-60 seconds
- O$_2$	- can be changed in 30-60 seconds
Sampling flow rate	Approx. 1000 ml/min
Air flow rate	1750 ml/min

APPENDIX F

THE CONDITIONS OF CALCINATION THE CATALYSTS

Temperature controller parameter:

Alarm 1, (A1)	=	0
Alarm 2, (A2)	=	0
Xp %, (Pb)	=	1.5
T integral [sec], (τ_I)	=	400
T derivative [sec], (τ_D)	=	400
Approach, (Ap)	=	1.0
Cycle time [sec], (Hc)	=	80
Maximum power [heat], (H_L) =		100
Set point [celcius]	=	380

Conditions of calcination:

Air flow rate	=	100 ml/min.
Rate of temperature program	=	10°C / min.

APPENDIX G

PUBLISHED PAPERS

These published paper emerged during this study were presented at Academic Conference, 8th, Mahidol University, 17-18 December 1998, and 7th, Chiangmai University, 23-25 October 1997.

บทบาทความเป็นกรดของพื้นผิวตัวเร่งปฏิกิริยาวานาเดียม(V)ออกไซด์บนไททาเนียม(IV)ออกไซด์ต่อความว่องไวในการเกิดปฏิกิริยาการเลือกรีดิวซ์ไนตริกออกไซด์ด้วยแอมโมเนีย

ภาวิณี สินทรโก ธราธร มงคลศรี และปิยะสาร ประเสริฐธรรม

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บทคัดย่อ

งานวิจัยนี้ได้นำตัวเร่งปฏิกิริยาวานาเดียม(V)ออกไซด์ที่มีเปอร์เซ็นต์สูง (25%โดยน้ำหนัก)บนไททาเนียม(IV)ออกไซด์มาใช้ในปฏิกิริยาการเลือกรีดิวซ์ไนตริกออกไซด์ด้วยแอมโมเนียและศึกษาความเป็นกรดของพื้นผิวตัวเร่งปฏิกิริยาทั้งก่อนและหลังการทำปฏิกิริยาด้วยเทคนิคการดูดซับด้วยไพริดีน ซึ่งจากผลการทดลองพบว่า ความเป็นกรดบรอนสเตดมีส่วนสำคัญต่อการเกิดปฏิกิริยาการเลือกรีดิวซ์ไนตริกออกไซด์ด้วยแอมโมเนียมากกว่าความเป็นกรดลิวอิส และจากการทดสอบประสิทธิภาพของตัวเร่งปฏิกิริยา พบว่าในบรรยากาศที่มีซัลเฟอร์ไดออกไซด์จะไปช่วยส่งเสริมการเกิดปฏิกิริยาการเลือกรีดิวซ์ไนตริกออกไซด์ด้วยแอมโมเนียให้ดีขึ้นที่อุณหภูมิต่ำกว่า 623 เคลวิน แต่ที่อุณหภูมิสูงกว่านี้จะไปส่งเสริมปฏิกิริยาแอมโมเนียออกซิเดชัน

คำสำคัญ: วานาเดียม(V)ออกไซด์, ไททาเนียม(IV)ออกไซด์, ความเป็นกรด

Role of surface acidity on the SCR activity of V_2O_5/TiO_2 DeNO$_x$ catalyst

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Abstract

In our study, a high loaded catalyst 25wt%V_2O_5/TiO_2 was developed. Surface acidity of the catalyst before and after the SCR reaction was measured using pyridine adsorption technique. The results suggest that Brönsted acidity rather than Lewis acidity involves in the selective reduction path of NO$_x$ by NH$_3$. For the catalytic activity test, the presence of SO$_2$ in a feed composition seems to promote the SCR reaction at the reaction temperature below 623 K and NH$_3$ oxidation at higher temperature.

Key words: V_2O_5/TiO_2, SCR, Surface acidity.

1. Introduction

Selective catalytic reduction (SCR) of NO with NH$_3$ over V_2O_5/TiO_2 catalysts has been extensively employed for controlling the pollution due to nitrogen oxides released from stationary sources. Although it is generally accepted that the vanadia portion of the catalyst is essential for this reaction, the nature of the active sites and the mechanism of the reaction over the catalyst are quite controversial (1-7). Several literatures have suggested that the reactivity of V_2O_5/TiO_2 catalysts on the SCR relates to the surface acidity of the catalysts (7-16).

Recently, evidence was presented that $V^{5+}=O$ and Brönsted acid sites are involved in the catalytic cycle on V_2O_5/TiO_2 catalysts (7-9). The NH$_4^+$ acts as the active ammonia species and reacts with NO from the gas phase according to an Eley-Rideal mechanism (7). Moreover, the Lewis acidity of the surface is decreased with the loading of V_2O_5 on the titania support (10). Ammonia is adsorbed predominantly on the Lewis acid sites of the catalyst, blocking the access of N$_2$O to these sites.

In contrast, the results were published which showed that the reaction between ammonia and NO involves ammonia species coordinated to Lewis acid sites and not ammonium ions bonded to Brönsted acid sites (11-12).

In addition, typical DeNO$_x$-SCR process specifications include NO$_x$ reduction efficiencies ≥ 80 percent with an ammonia slip of 1-5 ppm and SO$_2$ conversions lower than 1-2 percent. The low levels imposed to NH$_3$ slip and SO$_2$ conversion are intended to prevent SO$_3$, NH$_3$, and water forming ammonium sulfates which may deposit in the cold equipment downstream from the reactor, causing severe corrosion

and pressure drop problems (13-14). Several authors (15-17) reported the Brönsted acidity of V_2O_5/TiO_2 catalyst increased after SO_2 treatment. Enhanced Brönsted acidity due to the formation of surface sulphate (15) or $(TiO)_3S=O$ formation (16)promotes the SCR activity, whereas deposition of ammonium (bi) sulphates may cause severe deactivation.

In this work we will discuss the surface acidity of 25 wt% V_2O_5/TiO_2 catalysts before and after SCR reaction in both presence and absence of SO_2. Surface acidity was investigated using pyridine adsorption technique.

2. Experimental

2.1 Catalyst preparation

The titania support used was commercial product of Farmitalia Carlo Erba. The XRD results indicated that it is pure anatase (result not shown here). The support was dried for 3 hours in air at 573 K before impregnation with ammonium metavanadate (Farmitalia Carlo Erba) in aqueous solution. After subsequent drying overnight, calcining in air at 653 K for 3 hours.

2.2 Surface acidity measurement

Surface acidity of the catalyst was measured using pyridine adsorption method. Self-supporting wafers of ca. 200 mg/cm^2 were prepared and inserted into a quartz glass cell equipped with KBr windows connected to a gas manifold. Spectra were recorded with Nicolet Impact400 spectrometer at room temperature up to 573 K. The spectral resolution under the conditions of the measurements was 4 cm^{-1} over the spectral range 1700-1300 cm^{-1}. The samples were in-situ pretreated at room temperature for 1 hour in vacuum and subsequently exposed to pyridine at room temperature until they became saturated. Spectra recording was performed after gas phase pyridine was evacuated from the cell. The effect of SO_2 on surface acidity was investigated by purging the sample with SO_2 at room temperature until the sample became saturated. Then, evacuating the system before introducing pyridine. In some experiments, the samples were pretreated at 473 K in different gases (NH_3, SO_2 and $NH_3 + SO_2$) for 2 hours. After cooling down to room temperature in vacuum, pyridine was introduced into the system.

2.3 Catalytic activity test

Steady state catalytic activity measurement was performed in a quartz tubular fixed-bed microreactor (ID=8.5mm) loaded with 0.5 g of catalyst. The reactant gas mixture, flow rate 200 ml/min, contains 500 ppm NO, 500 ppm NH_3, 2%O_2 balanced with N_2. In some runs, 50ppm SO_2 were added to the system. The reactant gas flow rate were controlled using a set of mass flow controller (Kofloc 3650). The outlet of the reactor was connected directly to a NO and O_2 analyzer (Shimadzu model NOA-7000) with Chemiluminescent detector.

3. Results and discussion

Figure 1 shows the FT-IR spectra obtained from adsorption of pyridine on fresh 25 wt%V_2O_5/TiO_2 at room temperature up to 573 K. It is clear from the present work and other published works (18-19) that the spectra of the adsorbed pyridine at room temperature, spectrum 1a, show band at 1445 cm^{-1} due to coordinatively adsorbed pyridine, while the weaker band at 1540 cm^{-1} is due to pyridinium ions adsorbed on Brönsted acid sites. The band around 1480 cm^{-1} is ascribed to proton acidity (20). In addition, the bands near 1640 and 1600 cm^{-1} can be assigned to pyridinium ions and to coordinated pyridine, respectively. After heating under evacuation at room temperature up to 573 K, spectra 1a-1g, it can be observed that the absorbance of the coordinated pyridine (1445 cm^{-1}) is stronger than the absorbance of the pyridinium ions (1540 cm^{-1}). The pyridinium adsorbed on Brönsted acid sites can not be observed at 473 K, whereas the coordinated pyridine is still detectable and completely disappeared at 573 K. This means that the Lewis acid sites are stronger than the Brönsted acid sites.

Figure 2 shows the FT-IR spectra of pyridine adsorption on fresh 25wt%V_2O_5/TiO_2 after SO_2 adsorption and evacuation. The figure shows again the presence of both coordinated pyridine (1445 and 1600 cm^{-1}) and pyridinium ions (1540 and 1640 cm^{-1}). A Comparison of the spectra relative to adsorbed pyridine on fresh 25wt%V_2O_5/TiO_2 (Figure 1), showing that the intensity of the band belongs to pyridinium ions adsorbed on Brönsted acid sites (1540 cm^{-1}) increased while the band of the coordinatively adsorbed pyridine (1445 cm^{-1}) seems to be relatively constant. After heating under vacuum at 523 K, the band of pyridine adsorbed on Brönsted acid sites still appears. This is equivalent to saying that the preadsorbed SO_2 increases the acid strength and the amount of the Brönsted acid sites. In the case of pyridine adsorbed on Lewis acid sites, it looks the same to the result of the pyridine adsorption on fresh 25wt%V_2O_5/TiO_2 (Figure 1).
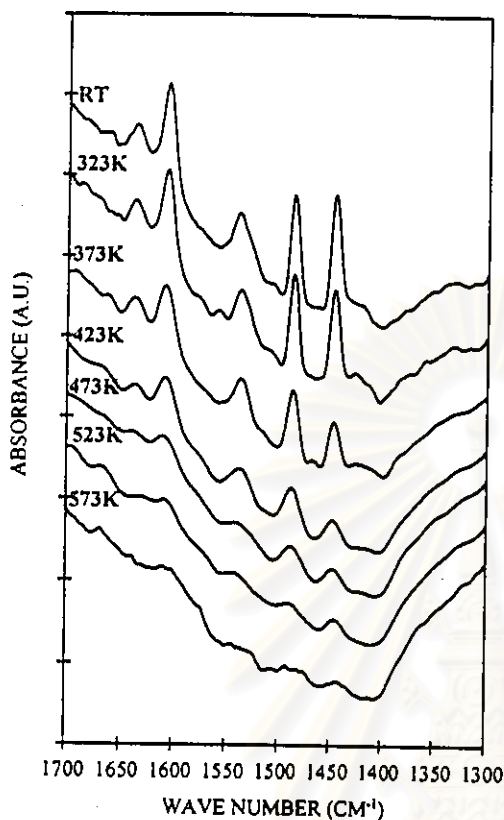
Figure 1 Pyridine adsorption on fresh 25wt%V_2O_5/TiO_2.
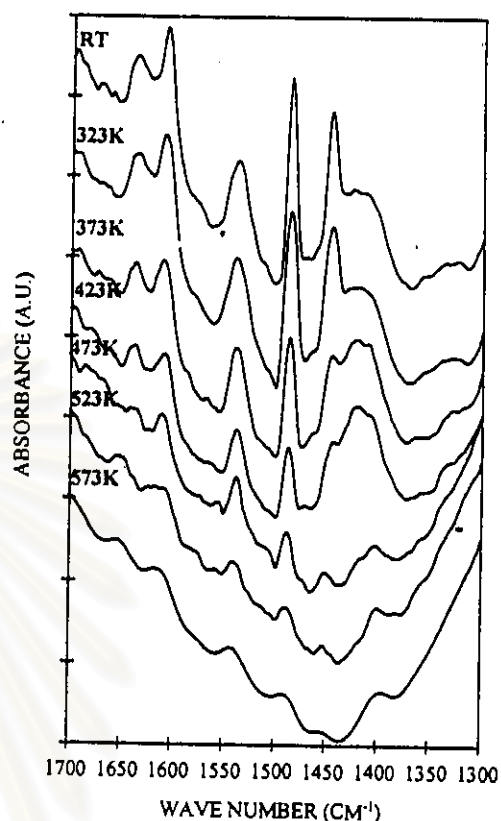
Figure 2 Pyridine adsorption on fresh 25wt%V_2O_5/TiO_2 after SO_2 adsorption.

Figure 3 shows that at the reaction temperature of 473 K, NO conversion of 25 wt%V_2O_5/TiO_2 with the presence of SO_2 was higher than that without the presence of SO_2 in a feed composition. From these results, spent catalysts after reaction at 473 K with and without SO_2 were characterized by in-situ FT-IR in order to investigate the effect of acidity on NO conversion. Figures 4 and 5 show the spectra of the pyridine adsorption over V_2O_5/TiO_2 after SCR reaction at 473 K with and without SO_2, respectively. It is found that both spent catalysts show similar acid strength and amount of both Brönsted acid sites and Lewis acid sites such as that of the fresh 25 wt%V_2O_5/TiO_2 (Figure 1). FT-IR spectra of pyridine adsorption on fresh 25wt%V_2O_5/TiO_2 after preadsorption by SO_2 at 473 K (Figure 6) is also similar to the FT-IR spectra of pyridine adsorption on fresh 25wt%V_2O_5/TiO_2. It is possible that SO_2 is a weakly adsorbed species and easy to desorb at 473 K. From this reason, SO_2 might not interfere in the surface acidity when the catalyst is cooled down to room temperature.

FT-IR spectra of pyridine adsorption on fresh 25wt%V_2O_5/TiO_2 after preadsorption by NH_3 at 473 K is shown in Figure 7. The bands due to pyridinium ions (1540 and 1640 cm^{-1}) disappear, while the bands near 1445 and 1660 cm^{-1} can still be presented and slightly decreased in intensity. This suggests that the protonated
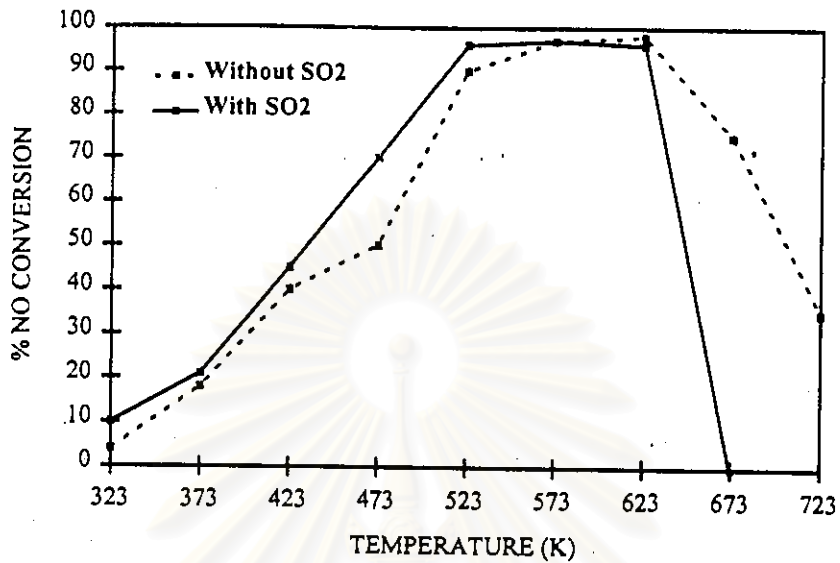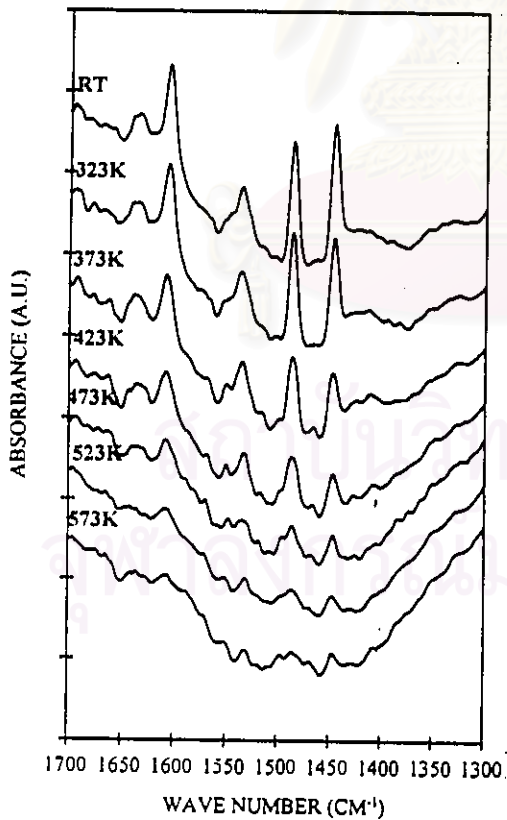
Figure 3 SCR activities of 25wt%V$_2$O$_5$/TiO$_2$.

Figure 4 Pyridine adsorption on spent 25wt%V$_2$O$_5$/TiO$_2$ without SO$_2$ at 473 K.
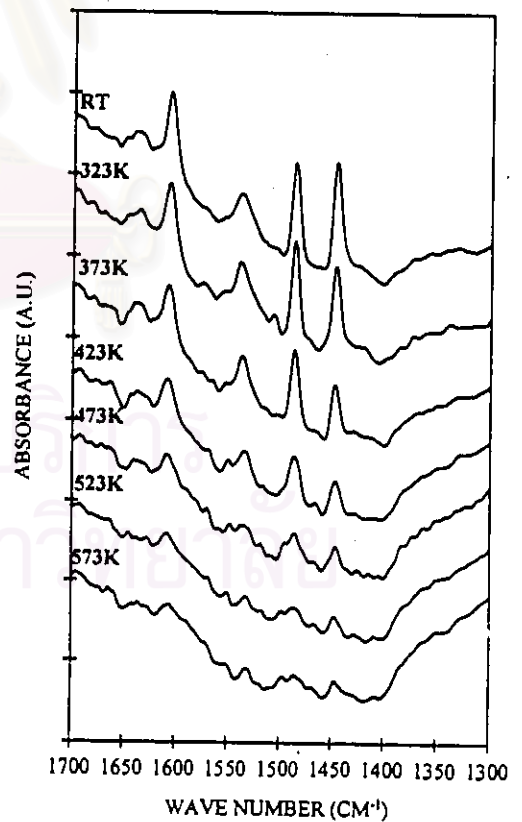
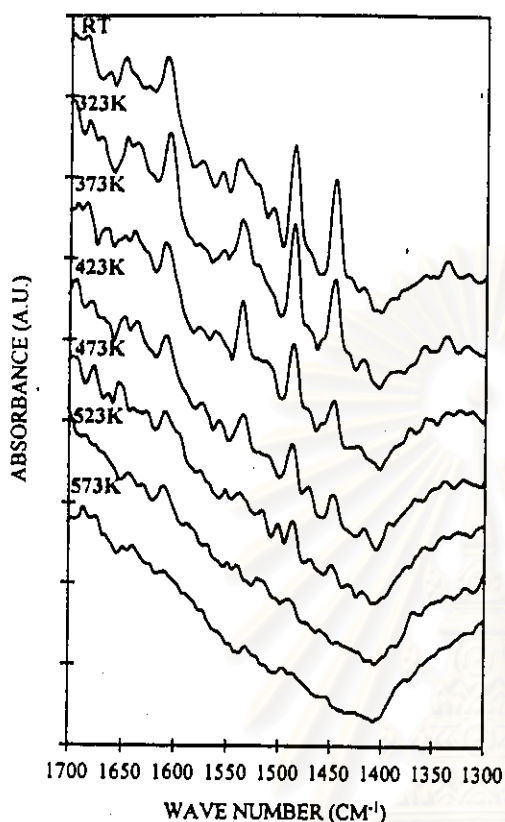**Figure 5** Pyridine adsorption on spent 25wt%V$_2$O$_5$/TiO$_2$ with SO$_2$ at 473 K.

Figure 6 Pyridine adsorption on fresh
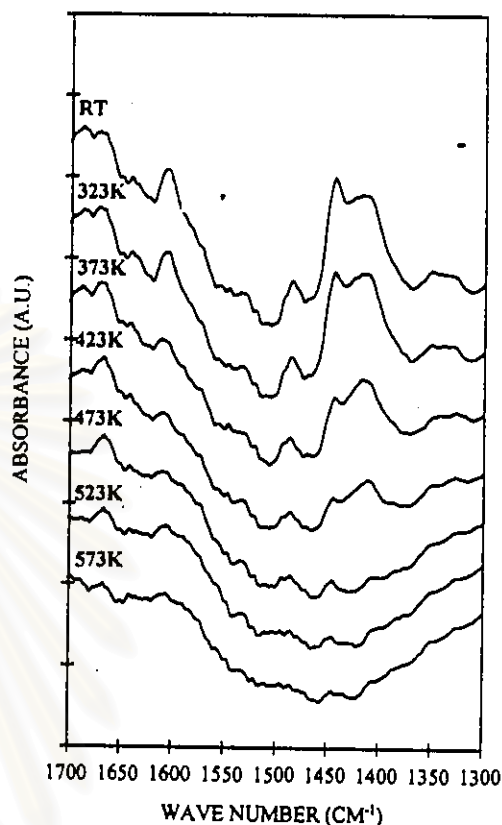25wt%V$_2$O$_5$/TiO$_2$ after SO$_2$
adsorption at 473K.

Figure 7 Pyridine adsorption on fresh
25wt%V$_2$O$_5$/TiO$_2$ after NH$_3$
adsorption at 473 K.

ammonia species are more strongly bonded than the coordinated ammonia species and the most of ammonia are adsorbed on Brönsted acid sites.

Pyridine adsorption after pre-coadsorption of SO$_2$ and NH$_3$ at 473 K on fresh 25wt%V$_2$O$_5$/TiO$_2$ shown in Figure 8. The band at 1540 cm^{-1} decreases significantly with respect to the fresh sample, whereas the band at 1445 cm^{-1} is slightly decreased. No new band of NH$_4$HSO$_4$ and (NH$_4$)$_2$SO$_4$ can be observed. It is possible that the observed Brönsted acid sites are due to the SO$_2$ adsorption on the surface.

The comparison of NO conversion over 25 wt%V$_2$O$_5$/TiO$_2$ in the presence and absence of SO$_2$ has been previously shown in Figure 3. From figure 3 one can see that in the absence of SO$_2$, the NO conversion increased up to a maximum near 100% at around 573 K and can maintain this conversion up to 623 K. The decrease in NO conversion was observed when the reaction temperature was further increased up to 723 K. This decreasing is caused by the direct oxidation of ammonia to nitric oxide which takes place over crystalline V$_2$O$_5$ (19). In the present of SO$_2$, at temperature below 573 K SO$_2$ seems to promote the SCR reaction. As for higher temperature, the NO conversion in this region rapidly drop, indicating severe oxidation of NH$_3$ to nitrogen oxide especially when SO$_2$ was present.
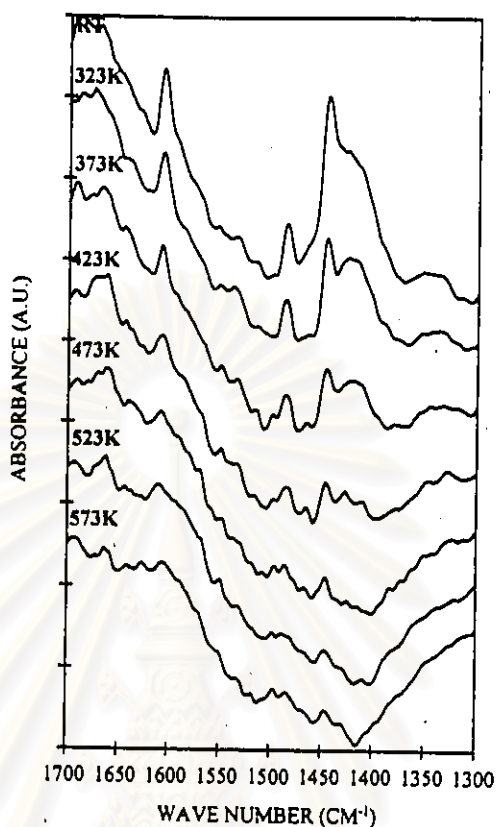
Figure 8 Pyridine adsorption on fresh $25wt\%V_2O_5/TiO_2$ after $NH_3 + SO_2$ adsorption at 473 K.

The conversion of NO shown in figure 3 can be explained using changes in surface acidity of the catalyst. As shown in figures 1 and 2, the preadsorbed SO_2 increases both acidity and acid strength of Brönsted acid site of 25 $wt\%V_2O_5/TiO_2$ catalyst resulting in some improvement in the SCR activity in the reaction temperature region below 623 K. Our result agrees with that reported by some authors (17,21-22) showing that sulphate addition during the preparation of a low loaded V_2O_5/TiO_2 catalyst or surface sulphate formation during the reaction can increase the SCR activity. ' The increase in Brönsted acidity and acid strength, however, have some negative effects. By considering at the reaction temperature higher than 623 K, figure 3, NO conversion with the presence of SO_2 decreased more steeply than that without SO_2 addition. Surprisingly, in-situ FT-IR (figures 1 and 2) showed that the catalyst preadsorbed by SO_2 has higher both Brönsted acidity and acid strength then the fresh catalyst. These results suggest that at the higher reaction temperature, Brönsted acidity promotes NH_3 oxidation rather than SCR reaction.

4. Conclusions

SO_2 addition promotes the selective catalytic reduction of NO with NH_3 over 25wt%V_2O_5/TiO_2 at the reaction temperature below 623 K. As for higher temperature reaction condition, SO_2 introduced enhances ammonia oxidation. In-situ FT-IR data using pyridine as probe molecule, showing the Brönsted acid site plays more important role for SCR of NO with NH_3 than the Lewis acid site.

Acknowledgement

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Deactivation of V_2O_5/TiO_2 catalyst by SO_2 during the selective catalytic reduction of NO by NH_3

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ABSTRACT

A series of V_2O_5/TiO_2 catalyst used for the selective catalytic reduction (SCR) of NO by ammonia were tested using simulated exhaust gas in the temperature range 50-500°C in the presence and the absence of SO_2. Experimental results reveal that the addition of only a small amount of SO_2 can significantly but not completely deactivate the V_2O_5/TiO_2 catalyst. The deactivation experiment suggests that the V_2O_5/TiO_2 catalyst is deacivated by two mechanism. The first mechanism is the irreversible adsorption of SO_2 at low temperature. This deactivation mode may be able to be eliminated by raising regeneration temperature. The monolayer structure of V_2O_5 on TiO_2 seems to be very sensitive to this mode of deactivation. The second deactivation mechanism is the equilibrium adsorption of SO_2. Crystalline V_2O_5 shows higher SO_2 tolerance than the monolayer structure.

Introduction

Selective catalytic reduction (SCR) of NO_x by ammonia is an important process in reducing the amount of NO_x released from a stationary source. In this process, NO_x is reacted with NH_3 over a V_2O_5/TiO_2 catalyst to form water and nitrogen. The amount of NH_3 fed and reaction temperature must be carefully control to ensure maximum NO_x conversion with minimum NH_3 slip [1-6].

Not only NO_x, SO_2 is also a species normally presents in effluent gas from fossil fuel burning. The amount of SO_2 depends on type of fuel used. SO_2 can strongly affects catalytic activity of some V_2O_5/TiO_2 catalysts in some cases. For example, it can form some sulphate compouds with NH_3 which covers catalyst surface, thus, leading to catalyst deactivation. In addition it can also deactivate the catalyst by poinsoning mechanism [7,8]. However, it has been reported that in some cases SO_2 could enhance the SCR activity of the catalyst [7].

V_2O_5/TiO_2 (anatase form) is a catalyst system that exhibits strong interaction between the active phase and the support. On the anatase surface and at low V_2O_5 loading, the V_2O_5 will not form a crystal structure but form a structure known in the name "monolayer" instead. This monolayer structure shows a drastically difference in catalytic property from the crystalline structure [3].

In the present paper, we have demonstrated the effects of SO_2 on the SCR activity of V_2O_5/TiO_2 catalysts. The effects were related to the surface structure of V_2O_5.

Experiment

V_2O_5/TiO_2 catalysts were prepared by the conventional wet impregnation method. TiO_2 (anatase phase, manufactured by Farmitalia Carlo Erba, Italy) was grounded to a require mesh size of 60-80 mesh. Then, the support was put into an aqueous solution containing an appropriate amount of NH_4VO_3. The mixture was continuously stirred and heated until all water evaporated. The obtained catalyst was further dried in air overnight. After drying the catalyst was further calcined in air for another 3-5 hours.

The reaction system consists of a quartz microreactor installed in a tube furnace. The furnace temperature was controlled by a digital temperature controller. A gas mixture containing NO, NH_3, O_2 balanced with N_2 was used as reactant gas. The concentrations of NO, NH_3 and O_2 were 500 ppm, 500 ppm and 2 vol% respectively. The reactor was operated at gas hourly space velocity 5000-20000 hr^{-1}. NO concentration in the effluent gas was analysed using a NO_x analyser (Shimadzu model NOA-7000). Further details of the experimental system and experimental procedure are already described elsewhere [9].

Results and discussion

Figure 1 shows the effect of SO_2 on the SCR activity of a 23wt% V_2O_5/TiO_2 catalyst. Without SO_2 the catalyst can achieve about 90% NO conversion at 400°C. When 50 ppm of SO_2 was added to the feed gas, however, the conversion of NO drastically drops to only 20%. Since the NO conversion never decrease to zero, SO_2 should deactivate the catalyst by reversible adsorption on the active site of the catalyst. However, when SO_2 was removed from the system the catalyst can partially regain its activity. This result means that some active site must be strongly poisoned by SO_2 adsorption.

Catalyst regeneration at 400°C does not recover any activity of the catalyst. Further regeneration at a higher temperature, 500°C, seems to be more effective. The catalyst after the regeneration at 500°C exhibits slightly higher activity than before SO_2 was added. This result indicates that the catalyst surface may have two types of active site. The first one is weakly deactivated by SO_2 while the other one is strongly deactivated. To test the hypothesis, a 6wt% V_2O_5/TiO_2, which represents the monolayer structure of V_2O_5 on anatase surface, and V_2O_5 were run in the same condition as the 23wt% V_2O_5/TiO_2 catalyst.

Figure 2 demonstrates catalytic property of 6% V_2O_5/TiO_2 under the influence of SO_2. When SO_2 was added to the sytem, the NO concentration in the effluent gas increases obviously, resulting in minus value of NO conversion. The additional NO may come from the ammoxidation of NH_3 in the feed gas. When SO_2 was removed from the system the catalyst activity drastically drops to near zero. Further regeneration at 400°C or 500°C can not recover any activity of the catalyst. Therefore, we may conclude that the monolayer structure of V_2O_5 can be severely deactivated by SO_2 in the SCR process.
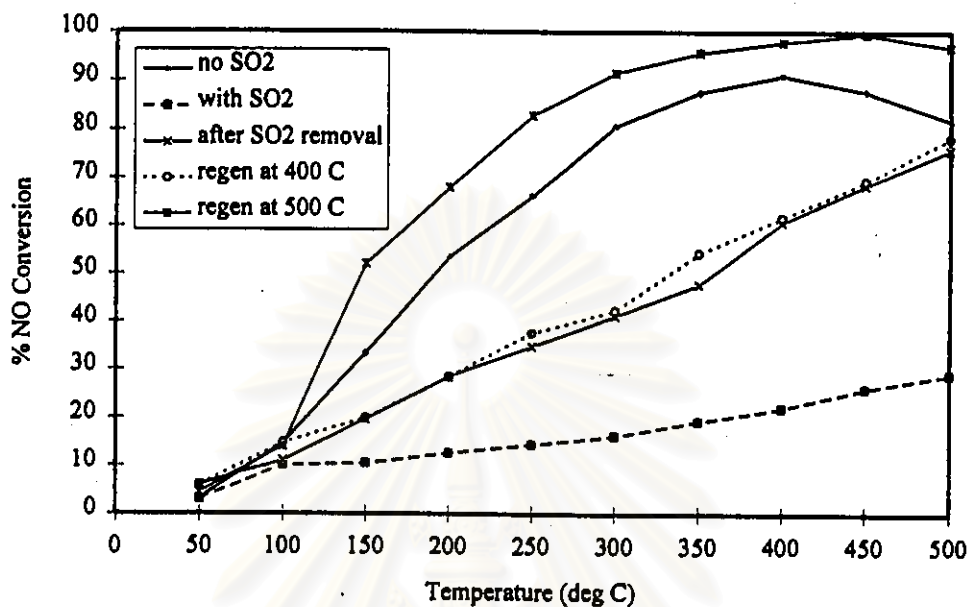
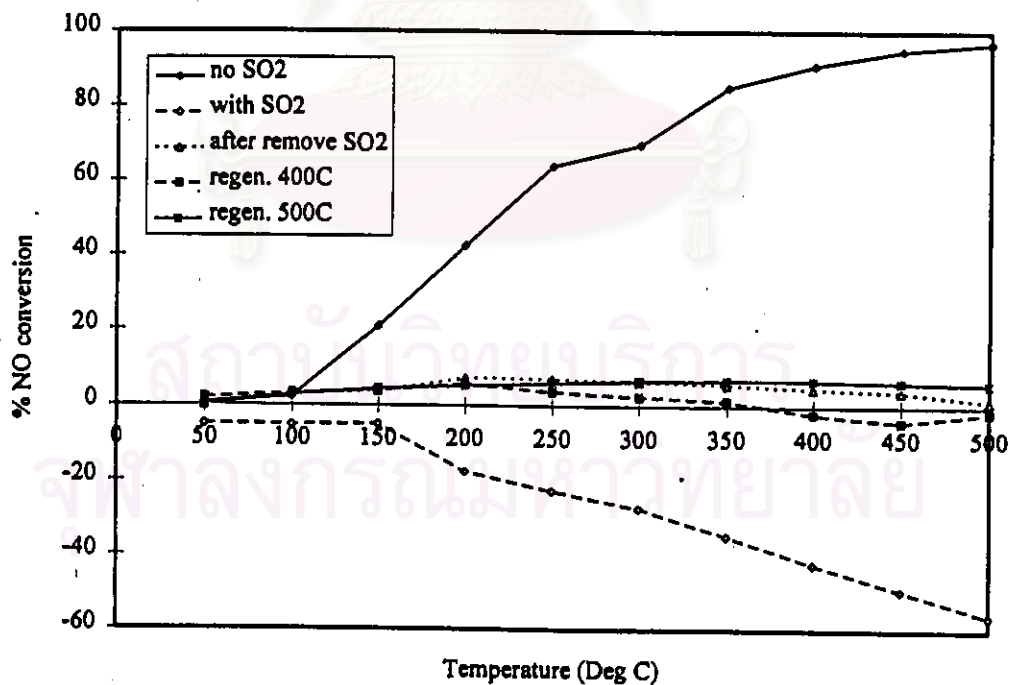Figure 1 Effect of SO_2 on the SCR of NO by NH_3 over 23%V_2O_5/TiO_2 catalyst

Figure 2 Effect of SO_2 on the SCR of NO by NH_3 over 6%V_2O_5/TiO_2 catalyst

When pure V_2O_5, which represents of crystalline V_2O_5 structure, was used another different result was obtained (figure 3). Although unsupported V_2O_5 is not a good SCR catalyst, the presence of SO_2 does increase its activity. V_2O_5 is known as a good catalyst for the oxidation of SO_2 to SO_3 in sulfuric manufacturing process. Since V_2O_5 does not show any deactivation phenomenon by SO_2, no regeneration experiment was performed.

In conclusion, the crystalline structure of V_2O_5 has higher SO_2 resistance than the monolayer structure. The $23\%V_2O_5/TiO_2$ catalyst contains crystalline structure, mono- and multilayer structures of V_2O_5. When SO_2 was removed from the feed stream, the crystalline structure could regain its activity by releasing adsorbed SO_2 from its surface. The mono- and multilayer structures, however, need a higher temperature to remove the adsorbed SO_2 from their surface since SO_2 was strongly adsorbed. Thus leading to the partial loss of the SCR activity after SO_2 was eliminated from the feed gas.
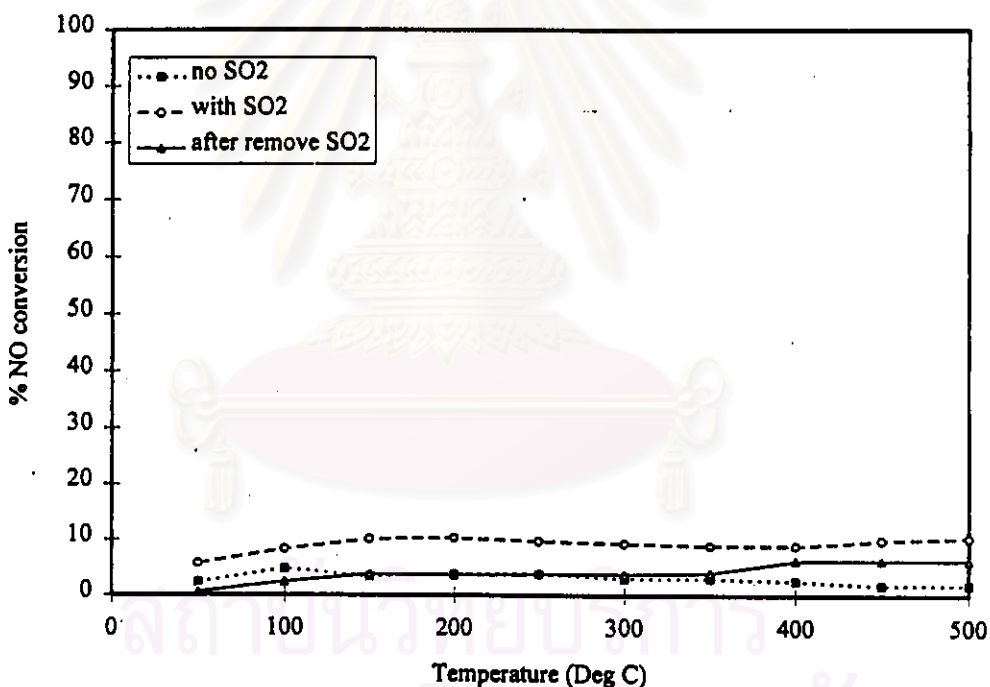

Figure 3 Effect of SO_2 on the SCR of NO by NH_3 over V_2O_5 catalyst

Acknowledgement

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