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APPENDIX A

SAMPLE OF CALCULATION

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

Reagent: Ammonium metavanadate, NH₄VO₃ (Farmitalia Carlo Erba)

Molecular weight = 116.98 grams.

(Atomic weight of vanadium = 50.9419)

Support: Titanium dioxide, TiO₂ – anatase phase (Farmitalia Carlo Erba)

Calculation for the preparation of 25 wt.% V₂O₅/TiO₂

Based on: 25 wt.% V₂O₅/TiO₂, 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 NH₄VO₃ used as precursor salt.

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

$$= 1.0 \text{ grams.}$$

Vanadium 1.0 grams was prepared from NH₄VO₃.

Vanadium content in NH₄VO₃ is 50.9419 grams, therefore:

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

$$= 2.2964 \text{ grams.}$$

2. Preparation of 5%WO₃ - 25%V₂O₅/TiO₂ (% by weight) catalyst with the wet impregnation method.

- Reagent: Ammonium metavanadate, NH₄VO₃ (Farmitalia Carlo Erba)
 Molecular weight = 116.98 grams.
 (Atomic weight of vanadium = 50.9419)
- Ammonium paratungstate, (NH₄)₁₀H₂(W₂O₇)₆ (Fluka Chemika)
 Molecular weight = 3060.59 grams.
 (Atomic weight of Tungsten = 183.85)
- Support: Titanium dioxide, TiO₂ – anatase phase (Farmitalia Carlo Erba)

Calculation for the preparation of 5%WO₃ - 25%V₂O₅/TiO₂ (% by weight)

From (1); Calculation for 25%V₂O₅/TiO₂, we used NH₄VO₃ 2.2964 grams.

Based on: 5%WO₃ - 25%V₂O₅/TiO₂, catalyst weight = 100 grams.

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

Then, 25%V₂O₅/TiO₂ = 100 - 5 = 95 grams.

25%V₂O₅/TiO₂ weight used for all preparations is 4.0 grams.

(TiO₂ 3.0 grams + V₂O₅ 1.0 grams)

For (NH₄)₁₀H₂(W₂O₇)₆ used as precursor salt..

$$\text{Tungsten required} = 4.0 \times (5/95) \text{ grams.}$$

$$= 0.2105 \text{ grams.}$$

Tungsten 0.2105 grams was prepared from (NH₄)₁₀H₂(W₂O₇)₆.

Tungsten content in (NH₄)₁₀H₂(W₂O₇)₆ is 3060.59 grams, therefore:

$$\text{The required salt} = 0.2105 \times 3060.59 / (183.85 \times 12) \text{ grams.}$$

$$= 0.2921 \text{ grams.}$$

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

Reagent: Ammonium metavanadate, NH₄VO₃ (Farmitalia Carlo Erba)
 Molecular weight = 116.98 grams.
 (Atomic weight of vanadium = 50.9419)
 Potassium nitrate, KNO₃ (Eagle Manufacturing, U.S.A.)
 Molecular weight = 101.1069 grams.
 (Atomic weight of Potassium = 39.102)

Support: Titanium dioxide, TiO₂ – anatase phase (Farmitalia Carlo Erba)

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

From (1); Calculation for 25%V₂O₅/TiO₂, we used NH₄VO₃ 2.2964 grams.

Based on: 3%K₂O - 25%V₂O₅/TiO₂, catalyst weight = 100 grams.

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

Then, 25%V₂O₅/TiO₂ = 100 - 3 = 97 grams.

25%V₂O₅/TiO₂ weight used for all preparations is 4.0 grams.

(TiO₂ 3.0 grams + V₂O₅ 1.0 grams)

For KNO₃ used as precursor salt.

$$\text{Potassium required} = 4.0 \times (3/97) \text{ grams.}$$

$$= 0.1237 \text{ grams.}$$

Potassium 0.1237 grams was prepared from KNO₃.

Potassium content in KNO₃ is 101.1069 grams, therefore:

$$\text{The required salt} = 0.1237 \times 101.1069 / 39.102 \text{ grams.}$$

$$= 0.3198 \text{ grams.}$$

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 N₂.

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



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APPENDIX B
CHEMICAL COMPONENT OF TiO₂ SUPPORT

Table B-1: Chemical component of TiO₂ 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

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APPENDIX C

THE OPERATING CONDITIONS OF 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 conditions of NO_x analyzer (model NOA-7000)

Model	NOA-7000
Measured component	NO _x at Atmospheric pressure
Detector type	Chemiluminescence
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

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APPENDIX D

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.

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APPENDIX E

DATA OF EXPERIMENTS

Table E-1: The data of 25V catalyst in reaction test

Temperature (°C)	Reactions						
	NO conversion (%)					NO generation (%)	
	NO+NH ₃	NO+NH ₃ +O ₂	NO+NH ₃ +O ₂ +SO ₂	NO+NH ₃ +O ₂ +H ₂ O	NO+NH ₃ +O ₂ +SO ₂ +H ₂ O	NH ₃ +O ₂	NH ₃ +O ₂ +SO ₂ +H ₂ O
50	2.7	6.3	6.7	6.2	4.2	0	0
100	5.2	13.2	14.8	26.0	13.7	0	0
150	9.4	34.5	34.9	31.1	20.5	0	0
200	16.7	45.2	48.7	43.5	23.5	0	0
250	26.5	78.1	85.4	65.2	59.4	0	0
300	34.9	90.1	96.4	80.6	80.5	0	0
350	37.2	85.2	62.3	72.7	65.0	1.8	1.8
400	42.3	62.4	-1.8	38.6	53.5	9.6	11.6
450	45.8	21.3	-56.8	35.3	17.2	29.4	33.6
500	49.1	-20	-100	22.1	-50.1	63.1	67

Table E-2: The data of co-25V5W catalyst in reaction test

Temperature (°C)	Reactions						
	<i>NO conversion (%)</i>					<i>NO generation (%)</i>	
	NO+NH ₃	NO+NH ₃ +O ₂	NO+NH ₃ +O ₂ +SO ₂	NO+NH ₃ +O ₂ +H ₂ O	NO+NH ₃ +O ₂ +SO ₂ +H ₂ O	NH ₃ +O ₂	NH ₃ +O ₂ +SO ₂ +H ₂ O
50	2.25	9.1	3.9	1.1	1.5	0	0
100	15.6	25.8	8.2	32.1	28.6	0	0
150	22.8	38.5	17.1	44.1	48.3	0	0
200	31.2	63.1	33.9	61.7	65.2	0.4	0.4
250	40.1	88.2	62.7	78.8	75.1	0.4	0.4
300	56.5	99.6	82.6	93.9	80.8	0.8	0.8
350	61.4	96.3	93.7	98.7	91.7	0.8	0.8
400	62.5	88.2	93.0	82.5	86.8	6.4	6.4
450	63.1	44.1	69.1	31.7	57.3	32.6	35.3
500	61.9	-40.0	-28.2	-48.9	-37.2	68.6	76.8

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Table E-3: The data of co-25V3K catalyst in reaction test

Temperature (°C)	Reactions						
	NO conversion (%)					NO generation (%)	
	NO+NH ₃	NO+NH ₃ +O ₂	NO+NH ₃ +O ₂ +SO ₂	NO+NH ₃ +O ₂ +H ₂ O	NO+NH ₃ +O ₂ +SO ₂ +H ₂ O	NH ₃ +O ₂	NH ₃ +O ₂ +SO ₂ +H ₂ O
50	5.8	9.7	12.2	3.3	5.3	0.2	0.2
100	9.4	13.4	16.6	11.7	11.5	0.4	0.4
150	14.4	24.6	35.5	18.2	25.1	0.4	0.4
200	17.3	32.8	56.0	32.9	31.5	0.4	0.4
250	20.0	34.6	59.5	41.3	48.5	0.4	0.4
300	22.6	43.7	62.2	60.1	65.0	0.4	0.4
350	32.6	50.2	36.5	61.2	67.8	1.0	2.4
400	34.1	52.8	14.7	54.5	54.8	3.0	8.8
450	36.1	56.0	-1.9	32.9	25.3	6.2	13.9
500	36.5	56.4	-20	21.3	0.8	9.0	22.0

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Table E-4: The data of 25V5W3K catalyst in reaction test

Temperature (°C)	Reactions						
	<i>NO conversion (%)</i>					<i>NO generation (%)</i>	
	NO+NH ₃	NO+NH ₃ +O ₂	NO+NH ₃ +O ₂ +SO ₂	NO+NH ₃ +O ₂ +H ₂ O	NO+NH ₃ +O ₂ +SO ₂ +H ₂ O	NH ₃ +O ₂	NH ₃ +O ₂ +SO ₂ +H ₂ O
50	1.95	9.3	9.6	7.78	7.7	0	0
100	10.9	29.2	16.7	23.3	24.4	0	0
150	18.9	40.0	24.1	24.8	26.4	0.3	0.3
200	24.8	43.1	42.4	34.2	30.8	0.4	0.4
250	27.1	65.0	51.6	39.8	46.8	0.4	0.4
300	33.9	78.7	76.9	64.0	73.8	0.6	0.6
350	40.3	60.9	46.1	58.3	60.0	1.0	1.0
400	40.0	29.5	25.8	17.4	38.7	8.6	8.0
450	44.2	14.5	-26.2	-6.4	20.0	22.0	19.8
500	43.5	-6.5	-100	-7.8	-6.3	47.2	50.0

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Table E-5: The data of the catalysts that add tungsten in reaction test

Temperature (°C)	NO conversion (%)				
	25V2W	Co-25V5W	25V5W	5W25V	25V10W
50	2.8	1.4	4.3	2.7	2.1
100	8.2	28.5	24.9	17.5	10.5
150	20.1	48.3	26.2	25.8	12.1
200	35.3	65.2	39.5	34.7	22.9
250	50.5	75.1	50.2	51.1	50.3
300	80.2	80.8	69.0	72.8	73.8
350	70.2	91.7	73.8	75.9	75.4
400	60.0	86.8	44.5	45.1	66.7
450	30.8	57.3	14.1	13.8	33.7
500	-56.3	-37.2	-20.0	-17.8	-55.3

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Table E-6: The data of the catalysts that add potassium in reaction test

Temperature (°C)	NO conversion (%)				
	25V1K	Co-25V3K	25V3K	3K25V	25V5K
50	4.9	5.3	4.6	3.8	12.8
100	8.7	11.5	7.6	7.5	30.0
150	22.8	25.1	11.5	20.9	38.7
200	29.8	31.5	22.3	22.2	44.6
250	54.4	48.5	44.2	30.9	48.1
300	74.8	65	54.2	60.0	59.8
350	61.8	67.8	43.5	63.2	48.2
400	45.6	54.9	24.8	45.5	27.3
450	26.8	25.3	-52.1	10.9	8.5
500	-3.0	0.8	-100	-25.8	-17.5

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APPENDIX F

PUBLISHED PAPERS

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



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ผลของลำดับการเติมทั้งสแตนบนตัวเร่งปฏิกิริยาวานาเดียมออกไซด์บนตัวรองรับไททานเนียมออกไซด์ที่ใช้ในการเลือกกำจัดแก๊สไนตริกออกไซด์

นิพนธ์ คนองชัยยศ, ธรรพร มงคลศรี และปิยะสาร ประเสริฐธรรม

ภาควิชาวิศวกรรมเคมี คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

กรุงเทพ 10330

บทคัดย่อ

ตัวเร่งปฏิกิริยาวานาเดียมออกไซด์บนตัวรองรับไททานเนียมออกไซด์ถูกนำมาใช้กันอย่างกว้างขวางในปฏิกิริยาการเลือกกำจัดแก๊สไนตริกออกไซด์โดยใช้แก๊สแอมโมเนีย ในงานวิจัยนี้ได้มีการพัฒนาตัวเร่งปฏิกิริยานี้โดยการเติมทั้งสแตนออกไซด์เข้าไปบนตัวเร่งปฏิกิริยา 25%วานาเดียมออกไซด์เพื่อเพิ่มประสิทธิภาพและการเลือกกำจัดแก๊สไนตริกออกไซด์และทำการวัดความเป็นกรดบนพื้นผิวตัวเร่งปฏิกิริยาโดยใช้เทคนิคการดูดซับของไฮรดิน จากผลการทดลองพบว่าลำดับการเติมทั้งสแตนจะมีผลต่อประสิทธิภาพของตัวเร่งปฏิกิริยา ทั้งนี้อาจเนื่องมาจากเกิดการเปลี่ยนแปลงความเป็นกรดบนพื้นผิวตัวเร่งปฏิกิริยา

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Effect of loading sequence on the SCR activity of tungsten promoted V_2O_5/TiO_2 DeNO_x catalyst

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Abstract

V_2O_5/TiO_2 catalyst used in the selective catalytic reduction (SCR) of NO_x by NH₃ is frequently doped with second metal oxide to modify its catalytic activity and selectivity. Tungsten is a second metal oxide added to enhance Bronsted acidity of the catalyst. This paper reports the effect of loading sequence during the preparation of a W promoted V_2O_5/TiO_2 catalyst (25 wt% V_2O_5 , 5 wt% WO_3). The SCR of NO by NH₃ was used as test reaction. The acidity of the catalyst surface was measured using pyridine adsorption technique. It is observed that the sequence of W loading has some effects on the catalytic activity of the catalyst. Possibly by the changing in surface acidity of the catalyst.

Keywords: V_2O_5/TiO_2 , SCR, nitric oxide removal, WO_3

Introduction

Selective reduction (SCR) of NO_x by ammonia is an important process in reducing the amount of NO_x released from a stationary source. Among several catalyst systems studied, such as tungsten oxide, molybdenum oxide, rhenium oxide, chromium oxide [Duffy et al. 1994, Matralis et al. 1995, Wachs et al. 1996, Nova et al. 1998] vanadium (V) oxide (V_2O_5) supported titanium oxide catalyst is the most widely employed in this process. [Kotter et al. 1989, Clarebout et al. 1991, Tufano & Turco 1993] Although the V_2O_5/TiO_2 system possesses high SCR activity, its performance can be further enhanced by adding metal oxides (e.g. oxides of W, Mo, Nb). [Weng et al. 1993, Vikulov et al. 1994, Lietti et al. 1996, Ramis et al. 1996] W is a widely used promoter of V_2O_5 in SCR catalyst. Because WO_3 can widen the temperature window of SCR, increase the poison resistance to alkali metal oxides and arsenious oxide, and reduce ammonia oxidation as well as SO_2 oxidation. [Alemang et al. 1995]

It is known that the V_2O_5/TiO_2 system will have the highest turnover frequency (TOF) when the amount of V_2O_5 loaded is about theoretical monolayer coverage. [Amiridis et al. 1996, Ciambelli et al. 1996, Ramis et al. 1996] Hence, many research groups have focused their studies in these regions. [Shikada & Fujimoto 1983, Blanco et al. 1989, Clarebout et al. 1991, Weng & Lee 1993, Turco et al. 1994, Vikulov et al. 1994, Marshneva et al. 1995, Ciambelli et al. 1996, Kijlstra et al. 1996, Lietti et al. 1996, Ramis et al. 1996, Kanata et al. 1998] But in this work, we will base on high rate per unit mass or unit volume of the catalyst. Research in our laboratory has shown that the maximum rate per unit mass could be obtained at vanadia loading about 25 wt%. [Teratrakoonwicha 1997]

In the present paper, we have demonstrated the effect of loading sequence during the preparation of a W promoted V_2O_5/TiO_2 catalyst (25 wt% V_2O_5 , 5 wt% WO_3) for the SCR of NO by NH_3 in the presence of oxygen.

Experimental

Preparation of catalysts

V_2O_5/TiO_2 catalyst was prepared by the conventional wet impregnation method. TiO_2 (manufactured by Farmitalia Carlo Erba) was grounded to a require mesh size of 60-80 mesh. The XRD analysis showed it to be pure anatase. Then, the support was put into an aqueous solution containing an appropriate amount of ammonium metavanadate, NH_4VO_3 (Farmitalia Carlo Erba).

Three type 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 were calcined in air at 653 K 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 same condition. In the second type of sample, 25V5W, vanadia was that 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 653 K. The last 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.

Characterization of catalysts

The specific surface areas of the catalysts were measured using the BET method, in a Micromeritics ASAP 2000, using nitrogen as adsorption gas. XRD pattern was recorded using X-ray diffractometer Siemen model D-500 with $CuK\alpha$ radiation ($\lambda = 1.5432 \text{ \AA}$). Ni was used as X-ray filter. Percentage of metal vanadium and tungsten loading was analyzed by Atomic Absorption Spectrometry (AAS) method. The IR spectra of all samples were recorded by a Nicolet Impact 400 FT-IR spectrometer equipped with a TGS detector. The pyridine adsorption method with the KBr disc were used for measuring surface acidity of the catalysts. Spectra of samples were taken in transmittance at room temperature (RT) up to 723 K at a spectral resolution of 4 cm^{-1} .

Reactivity measurement

Steady state catalytic activity measurement was evaluated in a quartz tubular fixed bed microreactor (ID. = 6 mm.) load with 0.5 g of catalyst. The furnace temperature was 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 . The reactant gas flow rates were controlled using a set of mass flow

controller (Kofloc 3650). NO concentration in the effluent gas was analysed using a NO_x analyser (Shimadzu model NOA-7000).

Results and Discussion

Catalyst characterization

Table 1 shows the compositions and BET surface area of the catalysts; 25V, 25V5W, 5W25V and co-25V5W. The XRD patterns of all catalysts are depicted in figure 1. Crystalline tungsten oxide was not found on the ternary catalysts. The samples like the binary catalyst. This may be because the amount of tungsten loading was too low or the calcination temperature was lower than 1023 K in moist air, therefore WO₃ could not formed. [Engweiler 1996]

Table 1: shows the compositions and BET surface of the catalysts; 25V, 25V5W, 5W25V and co-25V5W.

Sample	BET surface area (m ² /g)	% Metal loading	
		Vanadium	Tungsten
25V	9.87	23	-
25V5W	10	18	3.4
5W25V	12.59	20	2.4
co-25V5W	12.44	21	3.5

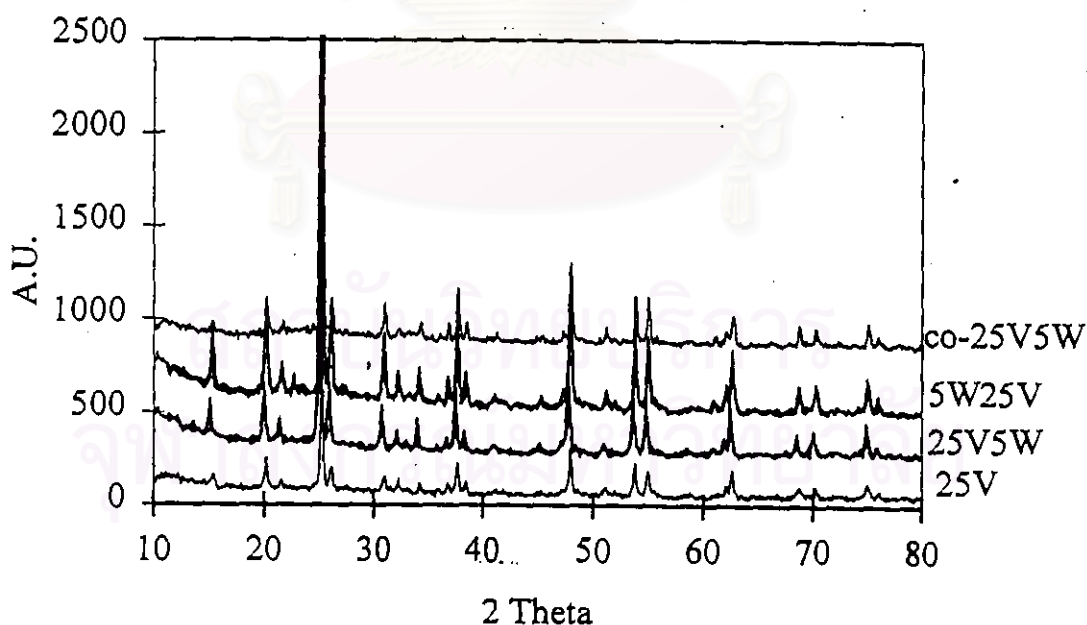


Figure 1: XRD patterns of all catalysts

Figure 2 show IR spectra of all-samples including pure V_2O_5 . When compares IR band for all samples, it appears that all samples show absorption IR bands around 1022 cm^{-1} and 833 cm^{-1} . The bands around 1022 cm^{-1} and 833 cm^{-1} have been assigned to the V=O stretching vibration of bulk V_2O_5 , and characteristic vibration of V_2O_5 , respectively. [Teratrakoonwicha 1997] In addition, a band around 983 cm^{-1} , characteristic of stretching W=O bond [Ramis et al. 1992], can't be observed in all three V_2O_5 - WO_3 /TiO₂ catalysts.

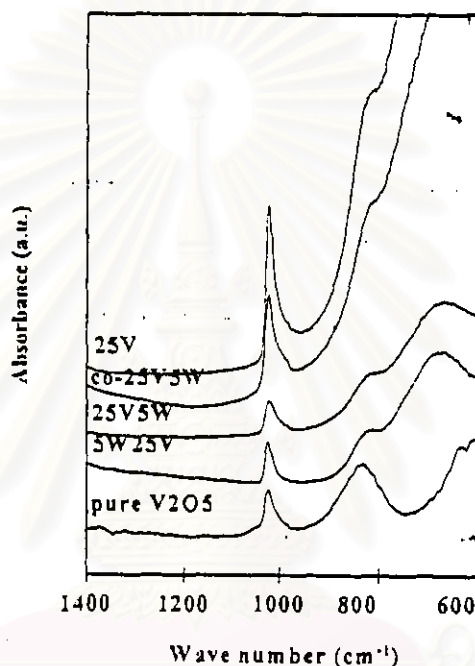


Figure 2: IR absorption spectra of all catalysts

NO reduction activity

The activity of all samples were determined over the temperature range of 323-773 K which the reactant gas feed were kept in the presence of equimolar amounts of NO and NH_3 , and excess oxygen.

Figure 3 shows the comparison of catalytic activity for the SCR of NO with NH_3 on all samples; 25V, 25V5W, 5W25V and co-25V5W. For the catalyst without WO_3 addition, the conversion increases with temperature up to 75% at 623 K. At reaction temperature beyond 623 K, the NO conversion began to drop as the result of NH_3 oxidation to nitrogen oxides which is a undesired side reaction. This side reaction becomes significant only at high temperature (above 623 K). [Teratrakoonwicha 1997]

The behavior of the ternary catalysts is similar to the binary catalyst. For co-25V5W catalyst, the NO conversion could reached about 90% at temperature around 573 K while the NO conversions of 25V5W and 5W25V catalysts level off at 70-75% at temperature range 523-623 K. At high reaction temperature, a significant drop in NO conversion as the result of NH_3 oxidation as in the binary catalyst.

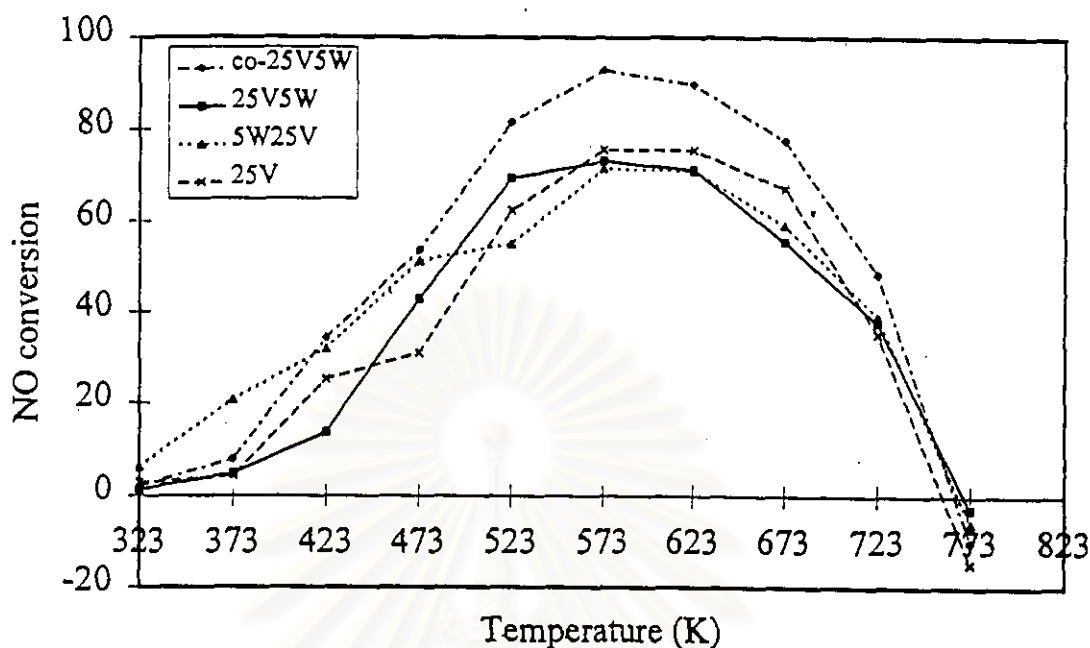


Figure 3: NO conversions over W promoted and unpromoted V_2O_5/TiO_2

Surface acidity measurement

IR spectra of pyridine adsorbed on fresh catalysts; 25V, 25V5W, 5W25V and co-25V5W are shown in figures 4-7 respectively. The band around 1450 cm^{-1} is assigned to molecularly coordinated species, pyridine adsorbed on Lewis acid site. Another important band is the band around 1540 cm^{-1} . This band belongs to protonated species, normally used to indicate the presence of Brønsted acid site. On fresh 25V catalyst (figure 4), the intensity of the molecularly coordinated species (1450 cm^{-1}) is more than the protonated species (1540 cm^{-1}). When the temperature of the catalyst was increased, the peak of the molecularly coordinated species decline faster than the peak of the protonated species. That means Lewis acid site is weaker acid site.

Regarding ternary catalysts, the peak of the protonated species is stronger than that of the binary catalyst (figure 5-7). These peaks disappear around 573 K which is higher than the peak in the binary catalyst. This results indicate that acid strength of Brønsted acid site is increased with the presence of W. [Ramis et al. 1992] However, no clear effect on the acid strength of Lewis acid site could be observed in the presence and absence of W. Maybe, depend on loading sequence during the preparation of W promoted V_2O_5/TiO_2 catalysts. Consequently, after raising up the temperature of the 25V5W, 5W25V catalysts, the peak of the molecularly coordinated species, $1440\text{--}1450\text{ cm}^{-1}$, drop and disappear about 473 K while in co-25V5W (figure 7) still appear. This peak of co-25V5W disappear about 523-548 K.

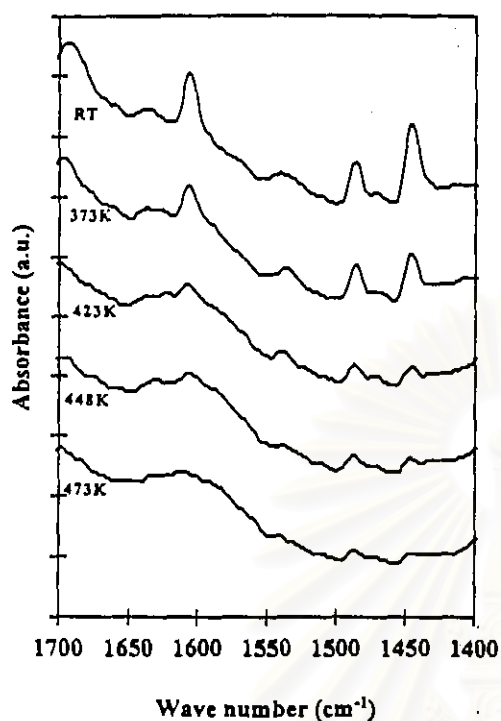


Figure 4: Pyridine adsorption on 25V catalyst

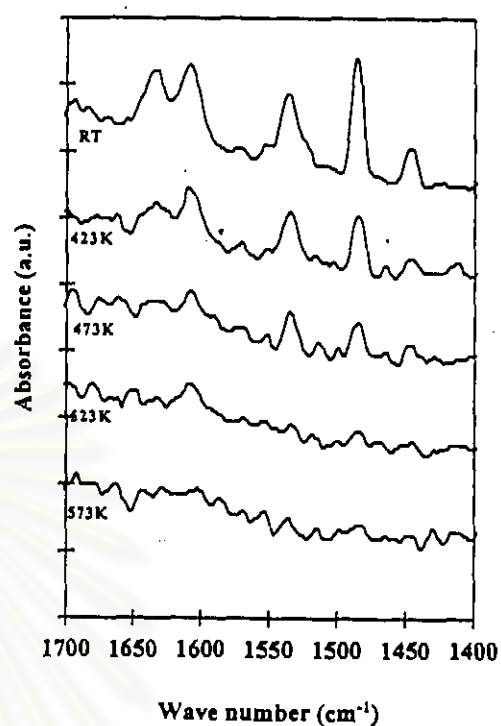


Figure 5: Pyridine adsorption on 25V5W catalyst

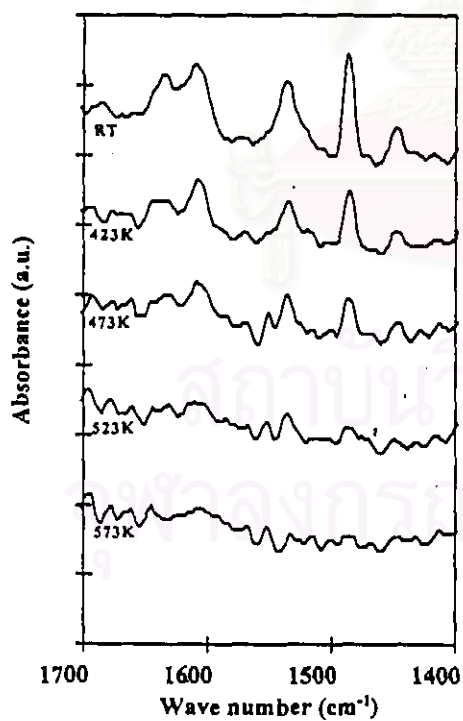


Figure 6: Pyridine adsorption on 5W25V catalyst

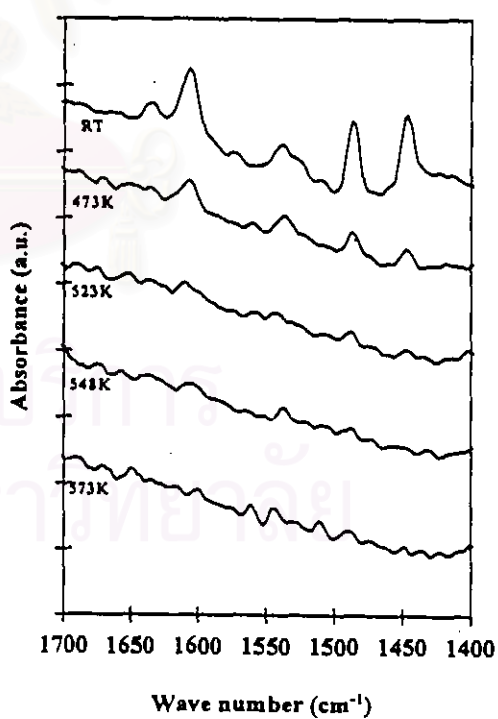


Figure 7: Pyridine adsorption on co-25V5W catalyst

From the results shown in figures 3-7, the conversion of NO can be explained using changes in acidity of the catalyst surface. A significant difference among the binary catalyst and the ternary catalysts is the ternary catalysts show higher acid strength of Brönsted acid site. This result suggest that Brönsted acid site is not active center in the SCR mechanism [Ramis et al. 1996] because in the ternary catalysts show the same acid strength of Bronstead acid site but difference on activity. However, we can use the strength of Lewis acid site to explain about the difference on activity. The strength of Lewis acid site on 25V5W, 5W25V are less than co-25V5W showed in figure 5-7, therefore activity of 25V5W, 5W25V are less than co-25V5W too. Although some literature presented that increased the Brönsted acidity did increase the reactivity [Kijlstra et al. 1996], our results are not clear to say that. On the whole results, we believe that increased Lewis acid site by W addition increase the SCR activity.

Conclusions

The binary (25V) and ternary (25V5W, 5W25V, co-25V5W) catalysts showed a good performance on the SCR of NO by NH₃. Tungsten is added to enhance both Brönsted acidity and Lewis acidity of catalysts. The sequence of W loading has some effects on the catalytic activity of the catalysts. It is found that can change in surface acidity of the catalysts (the sequence of W loading).

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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 deactivated 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 compounds with NH_3 which covers catalyst surface, thus, leading to catalyst deactivation. In addition it can also deactivate the catalyst by poisoning 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 amoxidation 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.

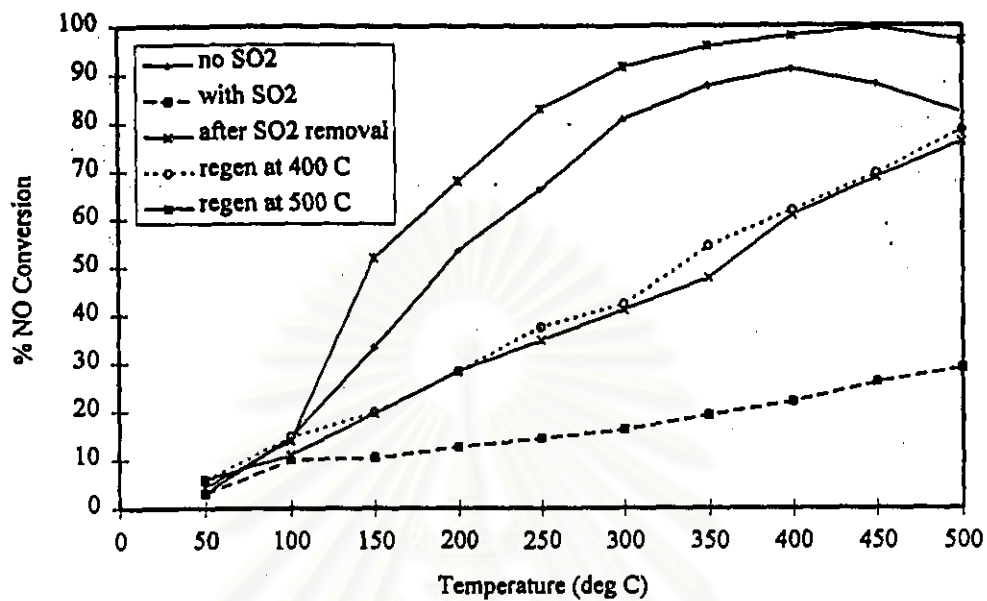


Figure 1 Effect of SO₂ on the SCR of NO by NH₃ over 23%V₂O₅/TiO₂ catalyst

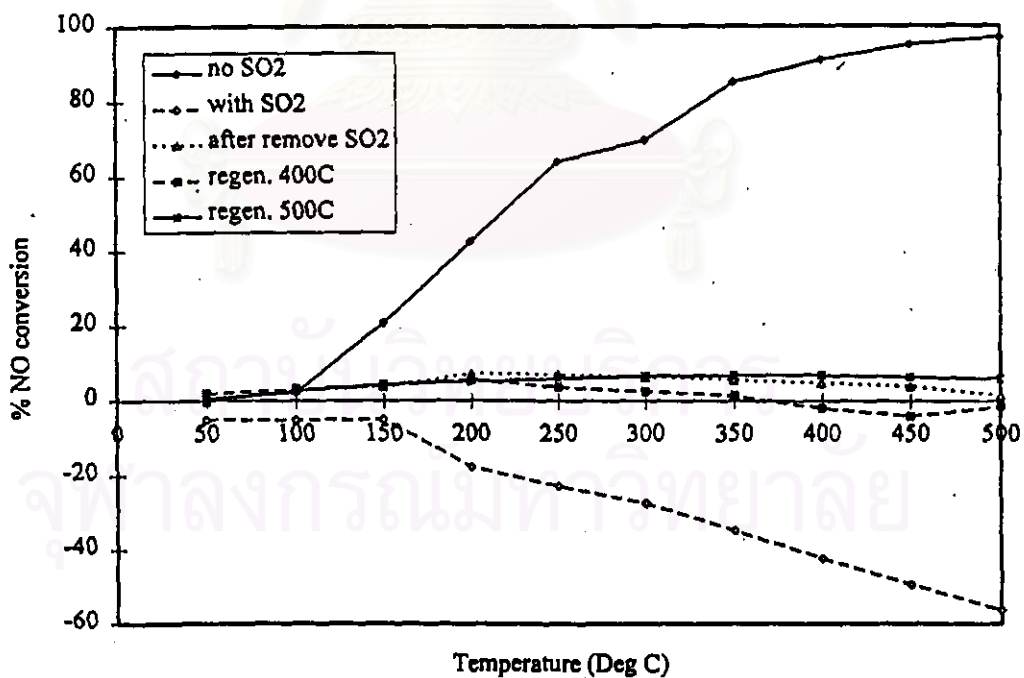


Figure 2 Effect of SO₂ on the SCR of NO by NH₃ over 6%V₂O₅/TiO₂ catalyst

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 /TiO₂ 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.

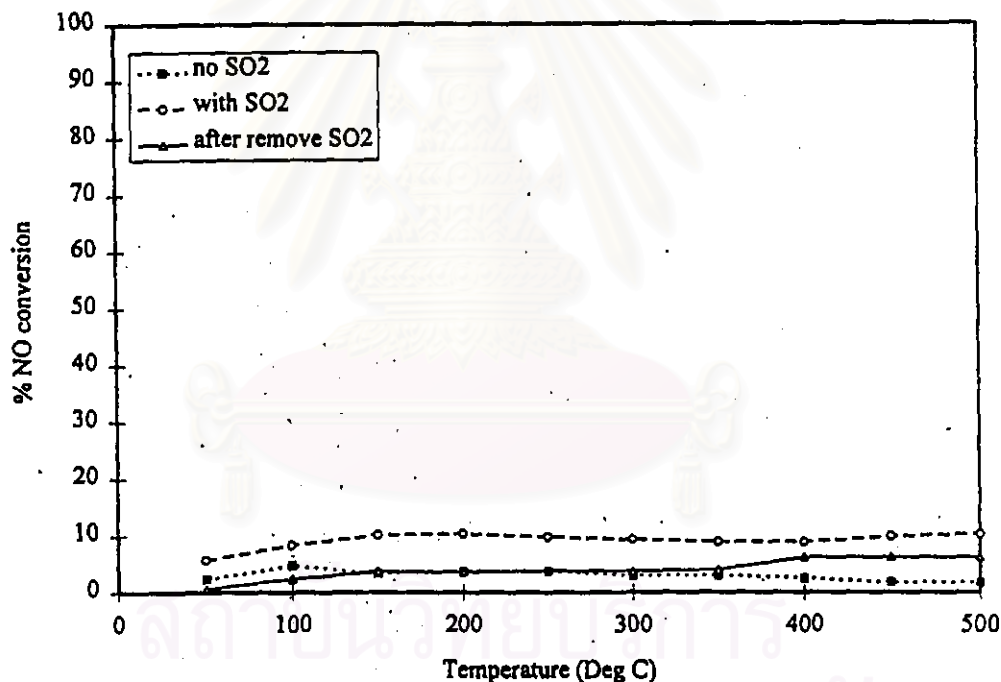


Figure 3 Effect of SO_2 on the SCR of NO by NH_3 over V_2O_5 catalyst

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