The Reduction of Nitrogen Monoxide with Ammonia on the Activated Surface of Steel Plates (Part 2)

Catalyst with High Durability against Sulfuric Acid

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The resistance to the effects of SO₃ on the activity of the catalyst prepared from a mild steel plate was improved by addition of a vanadium compound and by calcination at temperature above 600°C. The reaction kinetics of NO reduction with NH₃ on the modified catalyst can also be expressed by the equation,

$$\frac{-1}{K_{\text{NH}_3}(P_{\text{NH}_3}^{\text{in}} - P_{\text{NO}}^{\text{in}})} \cdot \ln \frac{(1-x)P_{\text{NH}_3}^{\text{in}}}{P_{\text{NH}_3}^{\text{in}} - xP_{\text{NO}}^{\text{in}}} - \ln(1-x) = \frac{k'RP_T \sqrt{K_{\text{O}_2}^{\text{in}} P_{\text{O}_2}^{\text{in}}}}{1 + K_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}}^{\text{in}} + \sqrt{K_{\text{O}_2}^{\text{in}} P_{\text{O}_2}^{\text{in}}}} \cdot \frac{A}{F}$$

which was originally proposed for the reaction kinetics on the unmodified catalyst.¹⁾

The durability of a modified catalyst of the honeycomb form was verified by the results of the catalyst life tests done with the flue gas from a heavy oil fired boiler.

1. Introduction

The reduction of NO with NH₃ was catalyzed by the activated steel¹⁾. In order to improve the resistance of steel plate catalyst to the effect of SO₃, the effects of modification with various metal compounds were investigated and it was found that vanadium compounds were most effective.

Thus the relation between the composition and the catalytic activity of the catalyst modified with vanadium and the reaction kinetics were studied. Further, the catalyst life of this modified catalyst was tested with the flue gas from a heavy oil fired boiler.

2. Experimental

2.1 Material

Commercial reagents and gases were used without farther treatment. FeVO₄ was prepared according to the method of Kurina²⁾ by completely drying an aqueous solution of Fe(NO₃)₃ and NH₄VO₃, and calcining the resulting residue at 450 °C.

2.2 Catalyst Preparation

The steel plate catalyst was made from a plate of mild steel plate (50 mm × 33 mm × 2 mm) as described in the previous paper¹⁾. It was coated

with a layer of Fe₂O₃ and Fe₃O₄; the roughness factor of the catalyst surface was about 6,000. The catalyst was modified by impregnating it with various solutions of metal compounds as given in **Table 1** and calcinating at 450 °C for an hour. When the catalyst was modified with vanadium, the amount of vanadium added and the calcination temperature were varied.

A honeycomb block which had been made of 18Cr-8Ni stainless steel (0.3 mm thick), as shown in **Fig. 1**, was activated in the same manner as described above for the steel plate and it was used in the practical catalyst life test. The geometrical surface area of the honeycomb-catalyst was about 0.85 m²_G.

2.3 Catalytic Activity Measurement

The procedures and the apparatus used for the

Table 1 Catalytic Activities of Modified Catalysts

Impregnating Solution	NO-Conversion (%) at 350°C*	
	Before	After
None	58.7	[32.0]
0.5 mol/l Ti(C ₂ O ₄) ₂ -H ₂ O	80.3	[48.3]
0.5 mol/l NH ₄ VO ₃ -0.5 mol/l H ₂ C ₂ O ₄ -H ₂ O	83.5	[65.0]
0.5 mol/l Cr(NO ₃) ₃ -H ₂ O	83.0	[45.1]
0.1 mol/l WO ₃ -conc. NH ₄ OH _{aq}	68.2	[33.0]
0.5 mol/l Mn(NO ₃) ₃ -H ₂ O	48.2	not measured
0.5 mol/l Co(NO ₃) ₃ -H ₂ O	52.1	〃
0.5 mol/l Ni(NO ₃) ₂ -H ₂ O	62.4	〃
0.5 mol/l Cu(NO ₃) ₂ -H ₂ O	83.3	[45.0]
0.5 mol/l Sn Cl ₂ -C ₂ H ₅ OH-H ₂ O	80.2	[41.0]

* Measured before and after the H₂SO₄ treatment under the standard reaction conditions (Table 2)

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Fig. 1 Apparatus for Catalyst Life Test

Table 2 Standard Reaction Conditions

Gas Composition (vol%)	NO	NH ₃	SO ₂	O ₂	H ₂ O	N ₂
	0.042	0.042	0.023	6.1	10	balance
Flow Rate : 0.066 m ³ (STP)/h						
Total Pressure (P _T) : 10 ⁵ Pa						

NO reduction with NH₃ were the same as described in the previous paper¹⁾. The standard reaction conditions are given in Table 2.

2.4 Pretreatment with Sulfuric Acid Vapor

The treatment of the catalyst with H₂SO₄ was carried out by the use of an usual flow system. The catalyst was exposed at 400 °C for an hour to a stream (0.06 m³/h) of air mixed with H₂SO₄ vapor (about 0.2 vol %) by bubbling the air through conc. H₂SO₄ at 180 °C.

2.5 Catalyst Life Test

Fig. 1 shows a flow sheet of the test apparatus used for testing the catalyst life. Four honeycomb-catalyst blocks were piled up in a reactor, and the flue gas from the oil fired boiler was passed through the reactor at the rate of 25 m³ (STP)/h. The amount of ammonia, equimolar to NO, was added to the flue gas at the inlet of the reactor. The reaction temperature was maintained at ca. 400 °C by heating the flue gas with an electric preheater. The concentration of NO was measured with the NO_x-meters (YANAGIMOTO ECL 77) located at the inlet and the outlet of the reactor.

3. Results and Discussion

3.1 Modified Plate-form Catalysts

Activities of modified catalysts are given in Table 1 as determined NO-conversion measured at 350°C under the standard reaction conditions (Table 2). The data in the brackets are the NO-conversions measured on the catalysts heated at 400°C for an hour in the H₂SO₄-air mixture. We see that some of the modified catalysts were more active than the unmodified ones, but, all of them were deactivated by the H₂SO₄-pretreatment. However, the catalyst modified with vanadium was the most resistant to the H₂SO₄-pretreatment.

Fig. 2 shows the effect of calcination temperature on the catalytic activity of the catalyst modified with vanadium (8 g-V/m²_G) (The amount of

Catalyst modified with vanadium (8 g-V/m²_G) calcined for an hour, ● : with, ○ : without H₂SO₄ treatment Under standard reaction conditions (Table 2)

Fig. 2 Effect of Calcination Temperature on Catalytic Activity

Catalyst calcined at 680°C for an hour, ● : with, ○ : without H₂SO₄ treatment Under standard reaction conditions (Table 2)

Fig. 3 Effect of Vanadium on Catalytic Activity

vanadium compound carried on). The activity of the catalyst without H_2SO_4 -pretreatment decreased with calcination temperature, while the activity of the catalyst with the pretreatment increased with the calcination temperature and attained a maximum at ca. 630°C . Activities of catalysts calcined above 600°C were rather increased by the H_2SO_4 -pretreatment.

The activity of the catalyst modified with vanadium and calcined at 680°C for an hour depended on the amount of vanadium compound added as shown in **Fig. 3**, and the optimum amount was $2.5 \text{ g-V/m}^2_{\text{G}}$ for both catalysts with and without the H_2SO_4 -pretreatment.

In **Fig. 4** IR-spectra of the catalysts are compared with IR-spectra of the related materials. The unmodified catalyst showed IR-absorption bands in the range from 800 cm^{-1} to 400 cm^{-1} due to iron oxide. The IR-spectrum of the catalyst with vanadium added but not calcined showed additional two absorption bands at ca. 850 cm^{-1} and $1,000 \text{ cm}^{-1}$ which were identified as those of V_2O_5 , indicating that this catalyst is consisted of V_2O_5 and iron oxide, while the IR-spectrum of the catalyst modified with vanadium and calcined at 640°C was similar to the IR-spectrum of FeVO_4 at upper 800 cm^{-1} . It is clear that FeVO_4 is formed by the calcination.

- ① unmodified catalyst
- ② Catalyst without calcination ($8 \text{ g-V/m}^2_{\text{G}}$)
- ③ Catalyst calcined at 680°C for an hour ($8 \text{ g-V/m}^2_{\text{G}}$)
- ④ FeVO_4
- ⑤ Fe_3O_4
- ⑥ $\alpha\text{-Fe}_2\text{O}_3$
- ⑦ $\gamma\text{-Fe}_2\text{O}_3$
- ⑧ V_2O_5

Fig. 4 IR-Spectra of Catalysts without H_2SO_4 -Pretreatment

Catalyst modified with vanadium ($8 \text{ g-V/m}^2_{\text{G}}$, calcined at 680°C for an hour, without the H_2SO_4 -Pretreatment)

Under standard reaction conditions (Table 2) except where specified

Plots : Observed NO-Conversion ($\square$: 400°C , $\blacktriangle$: 350°C , $\bullet$: 325°C , $\triangle$: 300°C , $\circ$: 275°C)
Dotted lines : Calculated NO-Conversion

Fig. 5 Kinetic Results on Modified Catalyst

Table 3 Rate Parameters for Catalyst Modified with Vanadium
(8 g-V/m²G, calcined at 680°C for an hour)

	Before H ₂ SO ₄ -Pretreatment					After H ₂ SO ₄ -Pretreatment				
Temp.	275°C	300°C	325°C	350°C	400°C	275°C	300°C	325°C	350°C	400°C
k' k mol h·Pa	6.6×10^{-6}	(1.2×10^{-5})	4.5×10^{-5}	(3.1×10^{-5})	(7.5×10^{-5})	3.1×10^{-6}	(6.3×10^{-6})	1.2×10^{-5}	(2.2×10^{-5})	(6.6×10^{-5})
	$k' = 2.72 \exp(-7,070/T)$					$k' = 37.4 \exp(-8,930/T)$				
K_{NH_3} (Pa ⁻¹)	5.8×10^{-2}	(4.9×10^{-2})	4.2×10^{-2}	(3.7×10^{-2})	(2.8×10^{-2})	2.5×10^{-1}	(1.9×10^{-1})	1.6×10^{-1}	(1.4×10^{-1})	(1.0×10^{-1})
	$K_{\text{NH}_3} = 1.49 \times 10^{-3} \exp(2,000/T)$					$K_{\text{NH}_3} = 1.97 \times 10^{-3} \exp(2,640/T)$				
K_{O_2} (Pa ⁻¹)	9.7×10^{-3}	(7.9×10^{-3})	6.5×10^{-3}	(5.5×10^{-3})	(4.1×10^{-3})	6.5×10^{-4}	(5.6×10^{-4})	4.8×10^{-4}	(4.2×10^{-4})	(3.3×10^{-4})
	$K_{\text{O}_2} + 1.01 \times 10^{-4} \exp(2,500/T)$					$K_{\text{O}_2} + 1.97 \times 10^{-5} \exp(1,930/T)$				
$K_{\text{H}_2\text{O}}$ (Pa ⁻¹)	6.0×10^{-4}	(5.0×10^{-4})	4.2×10^{-4}	(3.6×10^{-4})	(2.7×10^{-4})	1.7×10^{-4}	(1.3×10^{-4})	1.1×10^{-4}	(0.9×10^{-4})	(0.6×10^{-4})
	$K_{\text{H}_2\text{O}} = 8.16 \times 10^{-6} \exp(2,360/T)$					$K_{\text{H}_2\text{O}} = 7.26 \times 10^{-7} \exp(3,000/T)$				

() : Value calculated by temperature dependence equation for each of the rate parameters.

Table 4 Molar Ratio of Consumed NH₃ to NO Catalyst
Modified with Vanadium (8 g-V/m²G, calcined
at 680°C for an hour) Under standard reaction
conditions (Table 2)

Reaction Temperature (°C)	250	300	350	400
Molar Ratio of Consumed NH ₃ to NO	0.98	1.00	1.05	1.13

3.2 Kinetics of Reduction of Nitrogen Monoxide with Ammonia on Catalyst Modified with Vanadium

The reduction of NO with NH₃ on the catalyst modified with vanadium (8 g-V/m²G, calcined at 680°C for an hour) was carried out. The results are given in **Fig. 5**, where the dotted lines show the NO-conversions calculated by Eq. (1),

$$\frac{-1}{K_{\text{NH}_3}(P_{\text{NH}_3}^{\text{in}} - P_{\text{NO}}^{\text{in}})} \cdot \ln \frac{(1-x)P_{\text{NH}_3}^{\text{in}}}{P_{\text{NH}_3}^{\text{in}} - xP_{\text{NO}}^{\text{in}}} - \ln(1-x) \\ = \frac{k'RP_T\sqrt{K_{\text{O}_2}P_{\text{O}_2}^{\text{in}}}}{1 + K_{\text{H}_2\text{O}}P_{\text{H}_2\text{O}}^{\text{in}} + \sqrt{K_{\text{O}_2}P_{\text{O}_2}^{\text{in}}}} \cdot \frac{A}{F} \quad (1)$$

[when $P_{\text{NH}_3}^{\text{in}}$ is equal to $P_{\text{NO}}^{\text{in}}$, the first term on the left side is $x/K_{\text{NH}_3}P_{\text{NH}_3}^{\text{in}}(1-x)$] which was proposed for the kinetics observed with the unmodified catalyst¹⁾. The values of the rate parameters given in **Table 3** for the present modified catalyst were determined by the same procedures reported in the previous paper¹⁾. We see that Eq. (1) satisfactorily reproduces the observed results except for the case of reaction at 400 °C.

Referring to the molar ratio of consumed NH₃ to NO given in **Table 4**, oxidation of NH₃ might occur at 400 °C in addition to the equimolar reaction between NO and NH₃¹⁾,

to cause the disagreement between the observed NO-conversion and the calculated NO-conversion.

Vanadium modified catalyst (8 g-V/m²G, calcined at 680°C for an hour)
Under standard reaction conditions (Table 2)
Plots : Observed NO-conversion (○ : before, ● : after H₂SO₄ treatment)
Dotted lines : Calculated NO-conversion (① : before, ② : after H₂SO₄ treatment)

Fig. 6 Temperature Dependence of NO-Conversion

The kinetic data, which were obtained by use of catalyst (8 g-V/m²G, calcined at 680°C for an hour) modified with vanadium and treated with the H₂SO₄-air mixture, were also analyzed by Eq. (1) and the rate parameters were also evaluated as shown in **Table 3**. We see in **Table 3** the H₂SO₄-pretreatment decreases K_{O_2} , but increases K_{NH_3} .

Fig. 6 shows the effect of the H₂SO₄-pretreatment on the temperature dependence of NO-conversion. The conversion efficiency of NO above 350°C, which increased by the H₂SO₄-pretreatment, which could be interpreted as the increase in K_{NH_3} with the H₂SO₄-pretreatment.

Composition of flue gas : 0.004%NO, 0.035%SO₂, 0.0032%SO₃, 4~5%O₂,
8~10%H₂O, 13~15%CO₂, balance N₂
Flow rate of flue gas : 25 m³ (STP)/h
Reaction Temperature : 400°C
Catalyst : ● : unmodified, ○ : modified with vanadium

Fig. 7 Results of Catalyst Life Test

3.3 Catalyst Life

The plots of NO-conversion (%) with the modified and the unmodified catalyst versus. reduction time are shown in Fig. 7. It is clear that the catalyst life is improved by modification with vanadium.

Nomenclature

- A: geometrical area of the catalyst (m²_G)
- F: flow rate of reaction gas (STP-m³/h)
- K_j: equilibrium constant of adsorption for jth component (1/pa)
- k': apparent rate constant per unit geometrical

- area of catalyst (k·mol/h·m²_G·pa)
- m²_G: dimension of geometrical area of catalyst (m²)
- Pⁱⁿ_j: partial pressure of jth component at the inlet of the reaction cell (pa)
- P_T: total pressure at the inlet of the reaction cell (pa)
- x: NO-conversion
- R: gas constant (22.4 m³(STP)/k·mol)

References

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要 旨

鋼板の活性化表面上でのアンモニアによる一酸化窒素の還元反応 (第2報)

耐 硫 酸 性 触 媒

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表面が Al 合金化された鋼板を活性化して作られる, NO の NH₃ 還元触媒は¹⁾, 重油燃焼排ガス中では短寿命であった (Fig. 7)。触媒の耐久性を改良することを目的として, 活性成分の多元化を行った。その中で, V で多元化したものは, 硫酸蒸気で処理された後でも比較的高い活性を示した (Table 1)。V 添加触媒を 600°C 以上で焼成することによって, 耐硫酸性能をさらに高めることができた (Fig. 2)。焼成によって FeVO₄ が生成することが確認された (Fig. 4)。最適添加V量は 2.5 g/m²G であった (Fig. 3)。

焼成V添加触媒上では, 350°C 以下で NO と NH₃ との等

モル反応が起こったが (Table 4), 高温度 (400°C) で NH₃ の酸化によるものと考えられる, NH₃ の過剰消費が認められた。焼成V添加触媒上での Reaction Kinetics は (Fig. 5), 400°C での結果を除けば, 未添加触媒上での結果を説明するために提出された反応速度式¹⁾ Eq. (1) で説明された。硫酸蒸気で予め処理された触媒上での Reaction Kinetics も Eq. (1) で説明された。そして硫酸処理された触媒の方が 350°C 以上でむしろ高い NO 変化率を示す (Fig. 6) という結果は, 主として, 硫酸処理によって K_{NH_3} が増加したためであるとして解釈された。

焼成V添加触媒は, 重油燃焼排ガス中においても, 長期間高い活性を維持することが確かめられた (Fig. 7)。

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