© 1989 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 62, 1226—1232 (1989) [Vol. 62, No. 4

Vanadium Oxides (V_2O_x) Catalysts for Dry-Type and Simultaneous Removal of Sulfur Oxides and Nitrogen Oxides with Ammonia at Low Temperature

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(Received August 11, 1988)

In order to develop highly functional catalysts for a dry-type, simultaneous removal of sulfur oxides (SO_x) and nitrogen oxides (NO_x) the catalytic activities of V_2O_x/TiO_2, V_2O_x/TiO_2/AC(activated carbon) and V_2O_x/AC ($4<x<5$) were studied using a fixed bed flow reactor. In this process SO_2 is catalytically oxidized to SO_3 and then fixed on the catalyst as ammonium sulfates by reactions with H_2O and NH_3; NO_x are reduced to N_2 with NH_3 over the same catalyst at low temperature (ca. 130 °C). The sulfates deposited on the catalyst must be periodically removed for regeneration in order to realize repeated use of the catalyst. V_2O_x/TiO_2 was found to be a suitable catalyst for the simultaneous removal and to have an acceptable tolerance for reiterative regeneration. Also, water washing of the used catalyst after a NH_3 pretreatment was found to be preferable for regeneration. The sulfates deposited on the catalyst could be recovered as $(NH_4)_2SO_4$ by this type regeneration. The deposited sulfates were amorphous and could be regarded as being a mixture of NH_4HSO_4 and $(NH_4)_2SO_4$. These sulfates reacted with NO_x to produce N_2.

SO_x and NO_x in the flue gases emitted from stationary sources have been removed by two consecutive processes. NO_x in flue gas are catalytically reduced to N_2 with NH_3 by a dry process at around 350 °C; SO_x are absorbed by a wet process at around 50 °C. These processes are well established, though complicated and not very energy saving-type processes. Furthermore, in wet-type desulfurization, waste water must be cleaned. For both simplification and energy saving, it is desirable to estabish a low-temperature, dry-type process for the removal of SO_x and NO_x.

The authors have already reported a dry-type, simultaneous removing process, in which CuO containing metal oxides (TiO_2, SiO_2, etc.) are used as the catalyst and sorbent. In this case SO_2 is oxidized to SO_3, and then fixed as $CuSO_4$ ($SO_3 \rightarrow CuO$). NO_x are catalytically reduced to N_2 with NH_3 over the $CuSO_4$ formed. This dry-type process gives a high completion rate for the simultaneous removal of SO_x and NO_x at around 350 °C. Furthermore, it was found that CuO containing multi-component metal oxides has sufficient tolerance for reiterative regeneration from $CuSO_4$ to CuO.[1-3]

A new dry-type, simultaneous process using active carbon or coke was proposed[4,5] and studied regarding practical applications.[6-9] In this process SO_2 is oxidized to SO_3 over the catalyst and then fixed on the catalyst:

$$SO_2+(1/2)O_2+H_2O=H_2SO_4, \quad (1)$$

and

$$H_2SO_4+NH_3=NH_4HSO_4. \quad (2)$$

NO is reduced to N_2 with NH_3 over the same catalyst:

$$NO+(1/4)O_2+NH_3=N_2+(3/2)H_2O. \quad (3)$$

The catalysts are claimed to be highly active for simultaneous removal, even when a lot of the sulfate is fixed on the catalyst surface. Furthermore, the catalyst which lost its activity at last has to be regenerated, because of the deposition of sulfate. That is, the sulfate has to be removed from the used catalyst without loss and deactivation of the catalyst.

The regeneration of the used catalyst can be achieved according to the reactions:

$$H_2SO_4+(1/2)C=SO_2+H_2O+(1/2)CO_2, \quad (4)$$

and

$$NH_4HSO_4+(1/2)C=NH_3+H_2O+SO_2+(1/2)CO_2. \quad (5)$$

Therefore, loss of the carbon catalysts during regeneration is unavoidable.

In the present study, vanadium oxides catalysts were studied to develop a dry-type, simultameous removal process; reiterative regeneration by a wet-type method was also studied in order to establish a regeneration method in which the used catalyst could be regenerated without loss and deactivation. Vanadium oxides catalysts have been used as a commercial denitrification catalyst, and are highly active even at low temperature if the preparation is adequate.[10] The sulfation of SO_x with H_2O and NH_3 over the vanadium oxides catalysts were also studied.[11-14] The object of this work is to clarify the performance and the possibility of any practical applications of vanadium oxides catalysts.

Experimental

Materials. Gases (NO, SO_2, NH_3, O_2, N_2, and He) from commercial cylinders were used. NH_3 and H_2O were supplied as aqueous ammonia. All chemicals used for the preparation of catalysts were reagent grade. Before use, AC(activated carbon) was washed with hot water (ca. 100 °C), dried at 110 °C for 25 h and then calcined at 900 °C for 1 h in a stream of N_2.

Catalysts. The support TiO_2(anatase) was prepared by the precipitation method. A 10 wt% $TiCl_4$ aqueous solution was poured instantly into a 7 wt% NH_3 aqueous solution under intensive mixing at room temperature. The precipitate was washed with repeated decantation, filtered, dried at 110 °C for 25 h, calcined at 400 °C for 3 h in the stream of air, crushed, and then sieved to average diameter of 1.0 mm (surface area: 90 $m^2 g^{-1}$, bulk density: 0.83 g cm^{-3}). The AC as a support was crushed and sieved to an average diameter of 1.0 mm (surface area: 1460 m^2 g^{-1}, bulk density: 0.42 g cm^{-3}). TiO_2/AC was prepared by a chemical vapor deposition method. That is, the AC was packed in a glass tube reactor and dried at 150 °C for 1 h in a N_2 stream, cooled down to room temperature, exposed to $TiCl_4$ vapor using a mixed gas of 1% $TiCl_4$ and N_2(100 $cm^3N\,min^{-1}$) for 3 h, and then exposed to a mixed gas of 40% NH_3, 2% H_2O and N_2 (180 $cm^3N\,min^{-1}$) for 3 h. After this procedure, the sample was washed with water, dried at 110 °C for 25 h and calcined at 400 °C for 3 h in a N_2 stream (surface area: 1040 $m^2 g^{-1}$, bulk density: 0.53 $g\,cm^{-3}$). The TiO_2 content in the TiO_2/AC was ca. 21 wt%.

Catalysts, V_2O_x/TiO_2, V_2O_x/AC, and V_2O_x/TiO_2/AC, were prepared by an impregnation method. The supports were impregnated in aqueous ammonia of NH_4VO_3 at room temperature for 25 h, dried in a rotary evaporator under evacuation at 40 °C, and then dried at 110 °C for 25 h. The amount of NH_4VO_3 loaded on the support was ca. 5 wt% as V_2O_5. The NH_4VO_3 loaded on the support was changed to an active state V_2O_x ($4<x<5$)[10] by a pretreatment with a mixed gas of 250 ppm NO, 250 ppm NH_3, 5% O_2 and N_2(500 $cm^3N\,min^{-1}$) at 200 °C for 3 h.

Reaction Procedure. The simultaneous removal of SO_x and NO_x was carried out in a fixed bed flow reactor under an atmospheric pressure, in the temperature range 130 to 150 °C (mainly 130 °C). Two glass tube reactors were used. The one (inner dia.: 12 mm) was used for 3 ml of catalyst (SV: 1.0×10^4 h^{-1}) and the another (inner dia.: 20 mm) was used for 12 ml (SV: $2.5\times10^{-3}\,h^{-1}$) or 18 ml (1.7×10^3 h^{-1}) of catalyst. Inlet gases were a mixture of 250 ppm SO_2, 250 ppm NO, (0—750) ppm NH_3, 5% O_2, 10% H_2O and N_2, and were fed with the total flow rate of 500 $cm^3N\,min^{-1}$. The concentrations of SO_x and NO_x in inlet and outlet gas were measured by the method of Arsenazo III (JIS K0103) and a chemiluminescence-type NO_x meter (YANACO ECL300), respectively. The concentration of NH_3 was measured by the conventional absorption-titration method.[15] Confirmation of the reduction of NO_x to N_2 with NH_3 was carried out using helium instead of N_2 as a balanced gas. The concentration of N_2 was measured by a gas chromatograph using a column packed with Molecular Sieves 5A (zeolite).

The reactivity of NH_4HSO_4 with NH_3 and the thermal stability of NH_4HSO_4, $(NH_4)_3H(SO_4)_2$ and $(NH_4)_2SO_4$ were measured with a flow-type auto-recording micro-thermobalance. Identifications of the sulfates were carried out by X-ray diffraction (XRD) analysis. The pore volume of the catalyst was measured using a mercury porosimeter (Erba MOD-220).

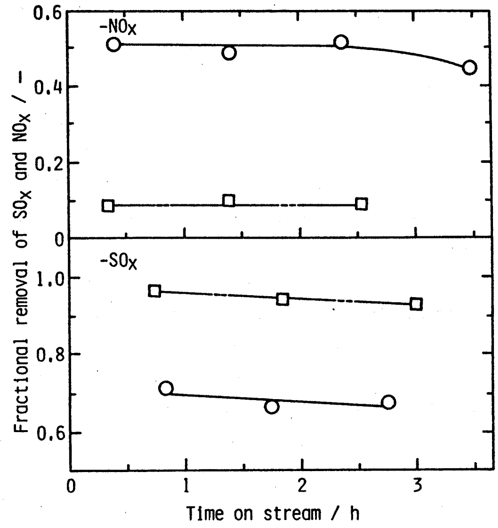

Fig. 1. Simultaneous removal of SO_x and NO_x with V_2O_x/TiO_2 and V_2O_x/AC. Catalysts: virgin, 3.0 ml, reaction conditions: 250 ppm SO_2–250 ppm NO–500 ppm NH_3–5% O_2–10% H_2O–N_2(500 $cm^3N\cdot min^{-1}$, 1.0×10^4 h^{-1}), 403.2 K.
○: V_2O_x/TiO_2, □: V_2O_x/AC.

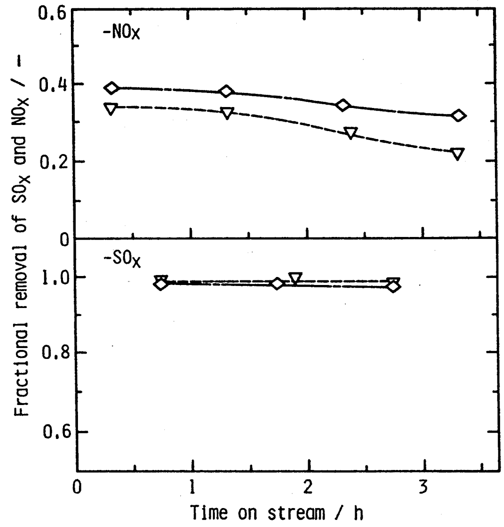

Fig. 2. Simultaneous removal of SO_x and NO_x with V_2O_x/TiO_2/AC and mixture of equi-volume of V_2O_x/TiO_2 and V_2O_x/AC. Catalysts: virgin, 3.0 ml, reaction conditions: 250 ppm SO_2–250 ppm NO–500 ppm NH_3–5% O_2–10% H_2O–N_2(500 $cm^3N\cdot min^{-1}$, 1.0×10^4 h^{-1}) 403.2 K.
▽: V_2O_x/TiO_2/AC, ◇: V_2O_x/TiO_2+V_2O_x/AC.

Results and Discussion

Simultaneous Removal of SO_x and NO_x with V_2O_x/AC, V_2O_x/TiO_2, and V_2O_x/TiO_2/AC. Results on the simultaneous removal of SO_x and NO_x over V_2O_x/AC and V_2O_x/TiO_2 are shown in Fig. 1. A comparison of the catalytic activities of the two catalysts led to the conclusion that V_2O_x/AC is more suitable for SO_x removal than V_2O_x/TiO_2, and that V_2O_x/TiO_2 is more suitable for NO_x removal than V_2O_x/AC.

For the utilization of the characteristics of V_2O_x/AC and V_2O_x/TiO_2, the combination of the two catalysts was studied. That is, the activity of V_2O_x/TiO_2/AC was measured and compared with that of a mixture of the equi-volume of V_2O_x/AC and V_2O_x/TiO_2. These results are shown in Fig. 2. The order of catalytic activities was as follows:

For NO_x removal: $V_2O_x/TiO_2 > (V_2O_x/AC + V_2O_x/TiO_2) > V_2O_x/TiO_2/AC \gg V_2O_x/AC$

For SO_x removal: $V_2O_x/TiO_2/AC$, $(V_2O_x/AC + V_2O_x/TiO_2)$, $V_2O_x/AC > V_2O_x/TiO_2$

Unfortunately, the expected effect with the combination was not found. From the above results, it was found that V_2O_x/TiO_2 is most suitable among the three catalysts for the simultaneous removal of SO_x and NO_x (especially, for the concentration of $NO_x >$ that of SO_x).

Confirmation of the Fixation of SO_x on the Catalyst and the Reduction of NO_x to N_2. The fixation of SO_x on the catalyst was confirmed by the following procedure. The used catalysts (V_2O_x/AC and V_2O_x/TiO_2 used for 3.5 h (Fig. 1)) were washed with water at room temperature, and the amount of ammonium sulfates in the filtrate was measured by Arsenazo III method. The ratios of the amount recovered by the above method to the amount of SO_x removal were from 0.9 to 1.0.

For the comfirmation that NO_x are reduced to N_2 with NH_3, helium was used instead of N_2 as a balance gas. As the results, it was found that almost all of SO_x and NO_x were removed.

Effects of Reaction Temperature and Concentration of NH_3 on the Simultaneous Removal of SO_x and NO_x. The effect of the reaction temperature on the removal of SO_x and NO_x with V_2O_x/TiO_2 is shown in Fig. 3. With the temperature rise, the activity for NO_x removal increased and that for SO_x removal decreased. Although the reason for the decrease of SO_x removal is unknown, it may be possible that the sulfate (such as NH_4HSO_4 (mp 147 °C)) melted and plugged the pores of the catalyst. This plugging probably disturbed the removal of SO_x more than that of NO_x.

The effect of the inlet concentration of NH_3 on the removal of SO_x and NO_x with V_2O_x/TiO_2 is shown in Fig. 4. The fractional removal of NO_x increased with increasing NH_3 concentration, and then reached a constant value above the stoichiometric concentration of NH_3 (calculated from Eq. 3). This means that the dependency of the reduction rate of NO on the concentration of NH_3 is zero order. This result is consistent with the previous results reported.[1,16,17] On the other hand, the fractional removal of SO_x increased with increasing NH_3 concentration. This suggests that NH_3 plays an important role in SO_x removal, and that the rate-determining step of SO_x removal is not the oxidation of SO_2 to SO_3 with O_2.

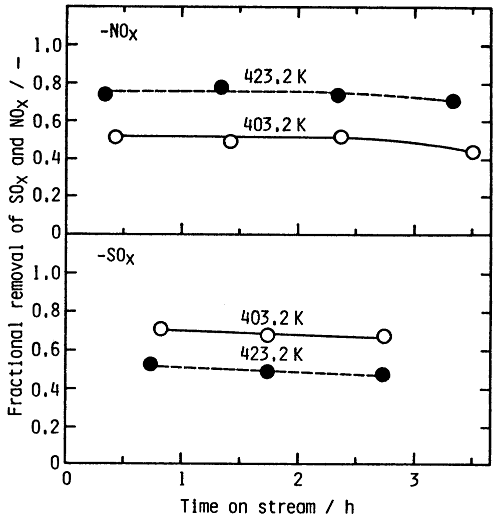

Fig. 3. Effect of reaction temperature on simultaneous removal of SO_x and NO_x with V_2O_x/TiO_2. Catalyst: virgin, 3.0 ml, reaction conditions: 250 ppm SO_2–250 ppm NO–500 ppm NH_3–5% O_2–10% H_2O–N_2 (500 $cm^3N \cdot min^{-1}$, 1.0×10^4 h^{-1}).

Stabilities of V_2O_x/TiO_2 and V_2O_x/AC for Regeneration. The experiments on the regeneration of the used catalyst were tried by wet-type methods. In the early stage, the used catalysts were washed with water at room temperature without any pretreatment. In this method part of the V_2O_x on the supports was slightly dissolved with the water. This was due to the acidity of the solution. Therefore, to prevent leaching of V_2O_x from the catalysts, the used catalysts were treated with NH_3 (0.5% NH_3–5% O_2–N_2, 450 cm^3N min^{-1}, 130→100 °C, 0.5 h); that is, the sulfates deposited on the catalyst were neutralized with NH_3. After this treatment, the ammonium salts formed on the catalysts were extracted with water. the ammonium salts taken out from the aqueous solution by drying were identified as $(NH_4)_2SO_4$ by XRD analysis.

The stabilities of V_2O_x/TiO_2 and V_2O_x/AC for reiterative regeneration by the improved regeneration

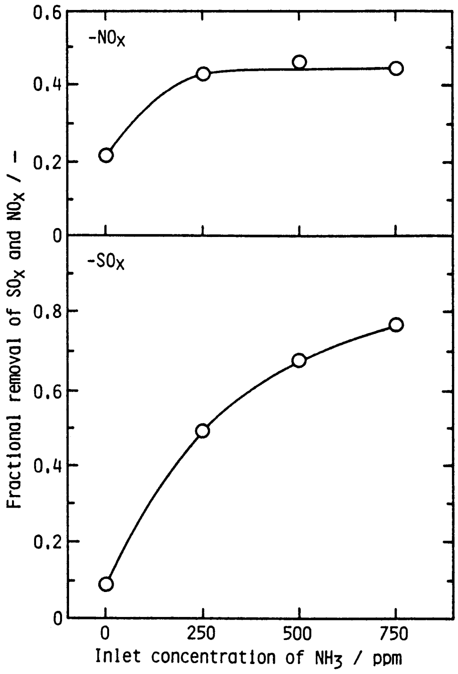

Fig. 4. Effect of inlet concentration of NH_3 on simultaneous removal of SO_x and NO_x with V_2O_x/TiO_2. Catalyst: virgin, 3.0 ml, reaction conditions: 250 ppm SO_2–250 ppm NO–0—750 ppm NH_3–5% O_2–10% H_2O–N_2(500 cm^3 $N \cdot min^{-1}$, 1.0×10^4 h^{-1}), 403.2 K.

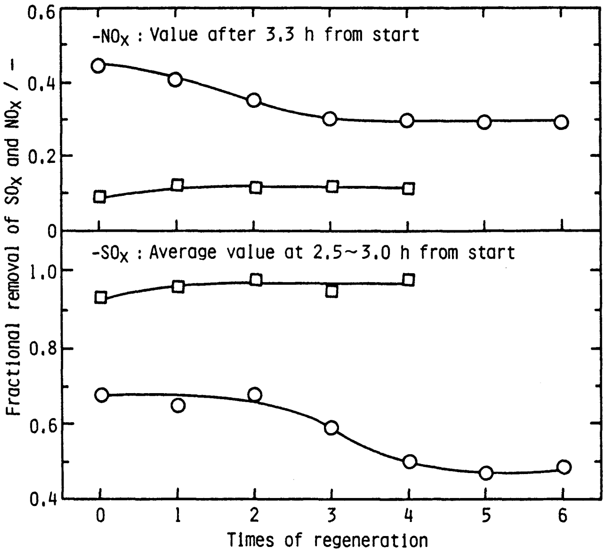

Fig. 5. Regeneration stability of V_2O_x/TiO_2 and V_2O_x/AC for simultaneous removal of SO_x and NO_x catalysts: 3.0 ml, reaction conditions: 250 ppm SO_2–250 ppm NO–500 ppm NH_3–5% O_2–10% H_2O–N_2 (500 $cm^3N\cdot min^{-1}$, 1.0×10^4 h^{-1}),403.2 K.
○: V_2O_x/TiO_2, □: V_2O_x/AC.

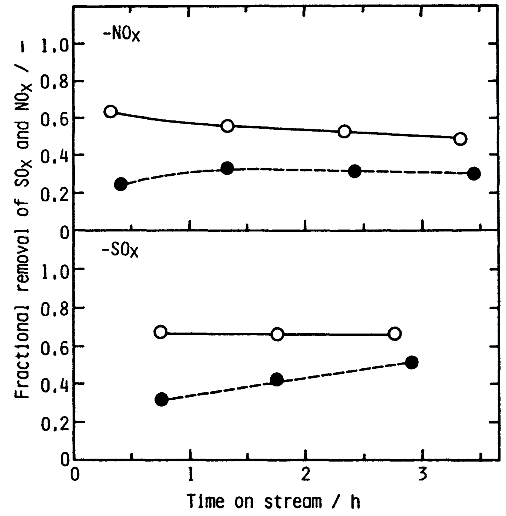

Fig. 6. Comparison of catalytic activity of V_2O_x/TiO_2* and V_2O_5/TiO_2* for simultaneous removal of SO_x and NO_x. TiO_2*: calcined at 550 °C for 3 h in air stream, catalysts: virgin, 3.0 ml, reaction conditions; 250 ppm SO_2–250 ppm NO–500 ppm NH_3–5% O_2–10% H_2O–N_2 (500 cm^3 $N\cdot min^{-1}$, 1.0×10^4 h^{-1}), 403.2 K.
○: V_2O_x/TiO_2*, ●: V_2O_5/TiO_2*.

method are shown in Fig. 5. V_2O_x/AC was found to have good stability, but the activity of V_2O_x/TiO_2 decreased up to the fifth regeneration, and then sustained adequate activity. One of the reasons for the deactivation of V_2O_x/TiO_2 up to fifth regeneration run might be a decrease of the specific surface area; however, the difference of the surface area of the virgin catalyst and that of the seventh regenerated catalyst was small (94→87 $m^2 g^{-1}$). Another reason might be the change of V_2O_x to another vanadium oxide, such as V_2O_5. Therefore, the activities of V_2O_x/TiO_2 and V_2O_5/TiO_2 were compared. TiO_2, which were calcined at 550 °C for 3 h, were used (surface area: 72 $m^2 g^{-1}$, bulk density: 1.1 $g\,cm^{-3}$). V_2O_5/TiO_2 was prepared from TiO_2 supported NH_4VO_3 by calcining at 550 °C for 3 h in a stream of air. The activity of V_2O_x/TiO_2 for the simultaneous removal was higher than that of V_2O_5/TiO_2, as shown in Fig. 6. It was indicated that the change of V_2O_x to V_2O_5 might be one of the causes of the deactivation.

Identification of the Sulfates Deposited on the Catalyst. As described previously, SO_x were fixed on a catalyst, though the kinds of sulfates were unknown. Therefore, the identification of deposited sulfates was carried out by XRD analysis; however, no clear X-ray diffraction pattern was found. This indicated that the sulfates were amorphous.

Because of the difficulty of a direct identification of the sulfates by XRD analysis, an indirect identification was tried by the following method. The used catalyst was washed with water; then, the filtrate was dried in a rotary evaporator under evacuation at 40 °C. The sulfates from the filtrate were dried at 110 °C for 25 h, and were then analyzed by XRD. As a result, $(NH_4)_3H(SO_4)_2$(equi-gram-mole mixture of NH_4HSO_4) and $(NH_4)_2SO_4$),$^{17)}$ and $(NH_4)_2SO_4$ were identified. Since these sulfates might be produced via NH_4HSO_4, the possibility of conversion from NH_4HSO_4 to another sulfate was studied. That is, the reactivity of NH_4HSO_4 with NH_3 under the coexistence of water vapor was studied at 130 °C using a thermobalance. The conversions of the NH_4HSO_4 to $(NH_4)_3H(SO_4)_2$ and $(NH_4)_2SO_4$ were confirmed by thermal gravimetrical and XRD analysis. Furthermore, it was confirmed by a gravimetrical method that the decompositions of NH_4HSO_4, $(NH_4)_3H(SO_4)_2$ and $(NH_4)_2SO_4$ are not detectable by a temperature-programmed method (2 °C min^{-1}) in the temperature range 130 to 150 °C.

From the above results, it was suggested that the sulfates could be regarded as a mixture of NH_4HSO_4 and $(NH_4)_2SO_4$, and that the side reaction of NH_4HSO_4 with NH_3 proceeds according to the following equation:

$$NH_4HSO_4+NH_3=(NH_4)_2SO_4. \qquad (6)$$

It was also suggested that $(NH_4)_2SO_4$ is the final product from SO_x on the catalyst, if it does not react with SO_x and NO_x.

Reactivities of the Sulfates Deposited on the Catalyst. Shikada et al.$^{18)}$ already reported that NH_4HSO_4 in a molten salt of $NH_4HSO_4/NaHSO_4$ reacted with NO under the coexistence of V_2O_5. Therefore, the reactivities of the sulfates deposited on the catalyst with NO_x were measured by the following procedure.

For the complete removal of NH_3 remaining on V_2O_x/TiO_2 after the activation step of $NH_4VO_3 \rightarrow V_2O_x$,the sample V_2O_x/TiO_2 was further treated with a mixed gas (250 ppm NO-5% O_2-N_2) at 200 °C. This treatment was stopped when the outlet concentration of NO_x became equal to the concentration in the inlet gas. The treated catalyst was crushed under 100 mesh, mechanically mixed with NH_4HSO_4 or $(NH_4)_2SO_4$ using a mortar, pelletized, crushed, again, and then sieved to an average dieameter of 1.0 mm. The content of the sulfate was ca. 10 wt%. Figure 7 shows the reactivity of the NH_4HSO_4 or $(NH_4)_2SO_4$ loaded on V_2O_x/TiO_2 with NO_x. It was obviously found that $(NH_4)_2SO_4$ and NH_4HSO_4 reacted with NO_x. Furthermore, the reduction of NO_x to N_2 with the sulfates was confirmed by using helium as a balanced gas, and the gas chromatograph, as follows:

$$NO + (1/4)O_2 + NH_4HSO_4 = N_2 + (3/2)H_2O + H_2SO_4, \tag{7}$$

and

$$NO + (1/4)O_2 + (NH_4)_2SO_4 = N_2 + (3/2)H_2O + NH_4HSO_4. \tag{8}$$

On the other hand, small amount of SO_x were removed; the fracional removal of SO_x was almost the same as the value measured without the coexistence of NH_3 (Fig. 4).

The active site of the catalst for the reactions of Eqs. 7 and 8 will finally be covered by the deposited sulfates. Therefore, any NH_4HSO_4 formed will be converted to $(NH_4)_2SO_4$ with NH_3.

Evaluation of V_2O_x/TiO_2 as a Catalyst for the Simultaneous Removal of SO_x and NO_x. For practical applications, the life of a catalyst and the reaction conditions demanding an almost complete removal of both SO_x and NO_x are important. From these view points, the fractional conversions of SO_x and NO_x were measured for 30 h. The results under the conditions that the inlet concentration of NH_3 was set to be equal to the stoichiometric value in Eqs. 2 and 3 (NO: 250 ppm, SO_2: 250 ppm, $NH_3/(SO_2+NO)$ mole ratio: 1.0) are shown in Fig. 8. At a higher space velocity (1.0×10^4 h^{-1}), both of the conversions of SO_x gradually decreased with the time on stream. From a comparison of the fractional removal of SO_x and NO_x, the SO_x removal proceeded predominantly under this conditions. Since the reason for the decline of the fractional removal of both SO_x and NO_x was considered to be the deposition of the sulfates, the surface area and pore volume of a virgin catalyst and that of a used catalyst were measurd. In this case, NH_4HSO_4 in the used catalyst absorbed water vapor and melt if the catalyst was exposed to the atmosphere at room temperature. Therefore, before the measurements of the surface area and the pore volume, the used catalyst was treated with NH_3, and NH_4HSO_4 was converted to $(NH_4)_2SO_4$ by the same procedure as that of the NH_3 treatment in the regemeration. The surface area of the catalyst decreased ca. 40% after the use (94→54 m^2 g^{-1}) and the pore volume of the catalyst also fell down ca.30% after the use (pore diameter>6 nm : 0.26→0.17 cm^3 g^{-1}). From these results it was confirmed that the reason of the declines of the fractional removal of SO_x and NO_x was the deposition of the sulfates.[11-13] At lower space velocity (2.5×10^3 h^{-1}), NO_x were almost completely removed up to 6 h from the start, but the fractional removal of SO_x fell down gradually up to 12 h. The effect of the space velocity (SV) on the removal of SO_x is not justified, because the conversion of SO_x at the lower SV should be considerably larger than that of the

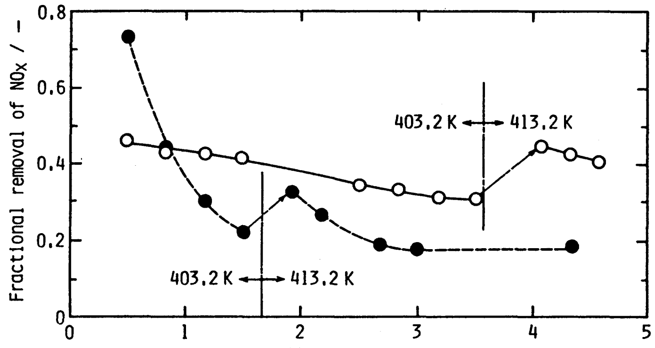

Fig. 7. Reactivity of NH_4HSO_4 and $(NH_4)_2SO_4$ loaded on V_2O_x/TiO_2 with NO_x. 10 wt% $NH_4HSO_4/(V_2O_x/TiO_2)$, 10 wt% $(NH_4)_2SO_4/(V_2O_x/TiO_2)$:Virgin, 3.0 ml, reaction conditions: 250 ppm SO_2-250 ppm NO-5% O_2-10% H_2O-N_2 (500 cm^3 N·min^{-1}, 1.0×10^4 h^{-1}).
O: $(NH_4)_2SO_4/(V_2O_x/TiO_2)$, ●: $NH_4HSO_4/(V_2O_x/TiO_2)$.

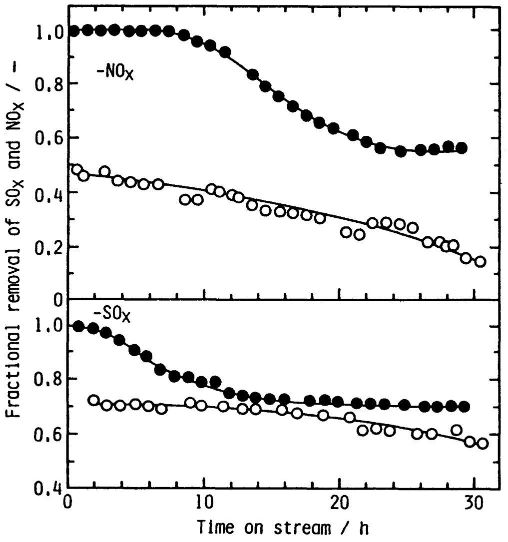

Fig. 8. Effect of space velocity on simultaneous removal of SO_x and NO_x with V_2O_x/TiO_2 in long run. Catalyst: virgin, 3.0, 12.0 ml, reaction conditions: 250 ppm SO_2-250 ppm NO-500 ppm NH_3-5% O_2-10% H_2O-N_2(500 cm^3 N·min^{-1}), 403.2 K.
O: 3.0 ml, 1.0×10^4 h^{-1}, ●: 12.0 ml, 2.5×10^3 h^{-1}.

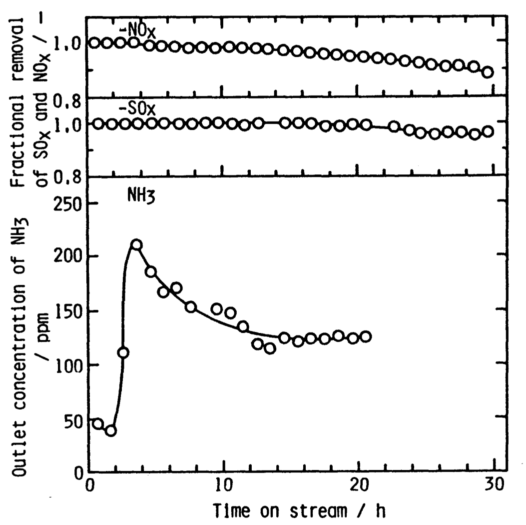

Fig. 9. Complete simultaneous removal of SO_x and NO_x with V_2O_x/TiO_2. Catalyst: virgin, 12.0 ml, reaction conditions: 250 ppm SO_2–250 ppm NO–750 ppm NH_3–5% O_2–10% H_2O–N_2(500 cm^3 N·min^{-1}, 2.5×10^3 h^{-1}), 403.2 K.

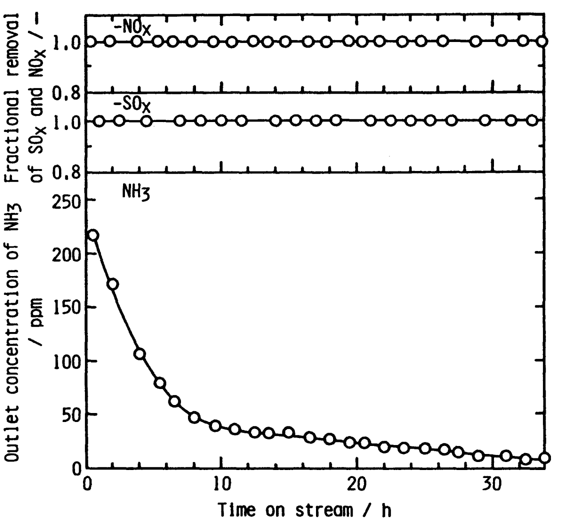

Fig. 10. Complete simultaneous removal of SO_x and NO_x with V_2O_x/TiO_2. Catalyst: virgin, 18.0 ml, reaction conditions: 100 ppm SO_2–250 ppm NO–400 ppm NH_3–5% O_2–10% H_2O–N_2(500 cm^3 N·min^{-1}, 1.7×10^3 h^{-1}), 403.2 K.

higher SV. Furthermore, the NO_x removal proceeded predominantly in the early time at the lower SV, being inconsistent with the results obtained at the higher space velocity. It was suggested that these results were due to the insufficiency of the amount of NH_3 supplied. In these experiments, the amount of NH_3 used was just sufficient to form NH_4HSO_4 and to reduce NO_x to N_2; however, $(NH_4)_2SO_4$ was produced in addition to NH_4HSO_4. This formation of $(NH_4)_2SO_4$ caused the insufficiency of the amount of NH_3 for the complete removal of SO_x and NO_x.

Based on the above results, in a following experiment, NH_3 was used in stoichiometric amount (750 ppm NH_3 for 250 ppm SO_2 and 250 ppm NO) according to Eqs. 2 to 6. That is, this amount of NH_3 is just sufficient to form $(NH_4)_2SO_4$ and to reduce NO_x to N_2. SO_x were almost completely removed from start up to 20 h, and the fractional removal of NO_x was kept above 90% for 20 h, as shown in Fig. 9. However, in this case, a considerable amount of NH_3 was detected in the reactor outlet. Furthermore, during the early hours the concentration of NH_3 changed abnormally. It may be considered that the adsorption of NH_3 onto the catalyst occurred, and also that the contributions of the reactions of Eqs. 2 to 6 to the consumption of NH_3 depended on the time on stream. Using the data at the quasi-steady state in Fig. 9 (from 14 to 20 h), the consumption mole ratio of NH_3 to (SO_x +NO_x) was obtained as ca. 1.25. This means that the sulfates produced seem to be a mixture of equi-gram-mole of NH_4HSO_4 and $(NH_4)_2SO_4$. Although, the simultaneous complete removal of SO_x and NO_x was possible under a sufficient amount of NH_3, the practical application of the catalyst claims the almost complete removal of SO_x and NO_x without any leakage of NH_3. Therefore, in the next experiment the inlet mole ratio of NH_3 to (SO_x+NO_x) was decreased from 1.5 to 1.25, and the space velocity was lowered to 1.7×10^3 h^{-1}. In this case, from the start up to 20 h, NO_x were almost completely removed, and SO_x were almost completely removed after 12 h. From these results and the dependency of the removal of SO_x on the concentration of NH_3, it was suggested that the removal rate of SO_x is lower under a smaller amount of NH_3 and, hence, the amount of the catalyst was not sufficient for a complete removal of SO_x.

From the results shown in Fig. 4, it was also suggested that the removal rate of SO_x could be kept higher under a higher mole ratio of NH_3 to SO_x. This claim for the removal of SO_x was satisfied by the application of a catalyst to the NO_x-rich flue gas(concentration of NO_x>that of SO_x). In the next experiment, SO_2, NO, and NH_3 were set to be 100, 250, and 400 ppm, respectively. The almost complete simultaneous removal of SO_x and NO_x without leakage of NH_3 was achieved, except during the early hours, as shown in Fig. 10.

The above-mentioned results might suggest that a just sufficient amount of NH_3 to form a mixture of equi-gram-mole of NH_4HSO_4 and $(NH_4)_2SO_4$, and to reduce NO_x to N_2, had to be used for the complete removal of SO_x and NO_x without leakage of NH_3. However, from previous fundamental studies, it was concluded that the most stable form of the sulfate was $(NH_4)_2SO_4$, and that the mole ratio of NH_4HSO_4 to $(NH_4)_2SO_4$ depended on the time on stream and/or the concentration of NH_3. In any case, it was experimentally clarified that the simultaneous complete removal of SO_x and NO_x in a NO_x-rich gas without leakage of NH_3 was possible.

Conclusion

V_2O_x/TiO_2 was found to be a suitable catalyst for the simultaneous removal of SO_x and NO_x in NO_x-rich flue gas by reactions with NH_3, even at low temperature, such as 130 °C.

V_2O_x/AC was suitable only for the removal of SO_x, and the activity for the removal of SO_x was better than that of the V_2O_x/TiO_2. The water washing of the used catalyst after treatment with NH_3 was found to be a preferable regeneration method for the prevention of the V_2O_x leaching. By this method the SO_x fixed on the catalysts could be recovered as $(NH_4)_2SO_4$. It was found that sulfates deposited on the catalysts are amorphous and can be regarded as being a mixture of NH_4HSO_4 and $(NH_4)_2SO_4$. It was also found that these sulfates reacted with NO_x and did not react with SO_x.

Although, the amount of NH_3 for the complete removal of SO_x and NO_x without leakage of NH_3 for a given flue gas could not be theoretically predicted, it was experimentally confirmed that for the NO_x-rich flue gas, SO_x and NO_x could be completely removed without the leakage of NH_3. For the SO_x-rich flue gas, the use of (V_2O_x/AC+V_2O_x/TiO_2) or V_2O_x/TiO_2 /AC may be suitable. Furthermore, we already found another type catalyst containing Cr_2O_3 for SO_x-rich flue gas.$^{19)}$ Details of the characteristics of this catalyst will be reported later.

The present work was partially supported by a Grant-in-Aid for Scientific Research No. 61035044 from the ministry of Education, Science and Culture.

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