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IMPROVEMENT OF V_2O_5-TiO_2 CATALYST FOR NO_x REDUCTION WITH NH_3 IN FLUE GASES

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A study was made to retard the oxidation of SO_2 to SO_3 over V_2O_5-TiO_2 catalysts developed for the NO_x reduction in flue gases. An addition of oxide, which has small amounts of excess oxygen, to the V_2O_5-TiO_2 was proved to be effective. Especially, the GeO_2-V_2O_5-TiO_2 revealed a high NO_x conversion and a retardation for the SO_3 formation.

A lot of catalysts have been developed for the catalytic removal of NO_x in flue gases. A V_2O_5-TiO_2 catalyst is used in practice as one of the best catalysts for the reduction of NO_x by NH_3, because of its high activity at low temperature and of its high resistance to the poisoning by SO_x.[1)] However, flue gases contain SO_2, O_2, CO_2 and H_2O with NO_x, in particular, the SO_2 is oxidized to SO_3 on the V_2O_5-TiO_2 catalyst, and then some NH_3-SO_3 compound such as NH_4HSO_4 and $(NH_4)_2S_2O_7$ are formed by the reaction of NH_3 and H_2O with the above SO_3, which may bring about a corrosion and plugging of the reactor and heat-exchanger. Hence, it is desired to retard the oxidation of SO_2 to SO_3 without affecting the high activity for NO_x reduction over the V_2O_5-TiO_2 catalyst. This letter reports the retardation of the SO_2 oxidation over the V_2O_5-TiO_2 catalyst improved by the addition of a third component such as GeO_2, ZnO and Y_2O_3.

The V_2O_5-TiO_2 catalyst was prepared by impregnating TiO_2(anatase type) in an aqueous NH_4VO_3 solution and by drying and calcinating in O_2 at 550°C. Six different M_xO_y-V_2O_5-TiO_2 catalysts (where M=Ge, Zn, Ta, Y, Mo, or W, $x=1\sim2$, $y=2\sim5$) were prepared by impregnating the V_2O_5-TiO_2 into aqueous solution in which a third component was dissolved in calculated amounts and by drying and calcinating in O_2 at 550°C. Table 1. shows the chemical composition and the surface area of the above catalysts. The experiments were carried out using a conventional flow reactor under the following conditions; the space velocity was 1.5×10^4 h^{-1} with 5 ml of catalysts at 1 mm in diameters and the reaction temperatures were in the range of 200∼500°C. The gases were furnished directly from cylinders to make mixtures of desired concentrations of NO, NH_3, SO_2 and O_2. N_2 was used as a balance gas. The concentrations of NO_x was measured by an analyzer of chemiluminescence type and that of SO_2 by IR analyzer. An amount of surface excess oxygen was determined by the KI (pH 7.7) method.[2)]

Fig. 1. shows the effect of the concentration of V_2O_5 on V_2O_5-TiO_2 catalyst for NO_x reduction and SO_2 oxidation at various temperatures. It can be seen that for the whole range of temperature, the conversion of SO_2 increased with an increase in concentration of V_2O_5. On the other hand, the conversion of NO_x also increased with an increase in concentration of V_2O_5 at temperature of 250-350°C. However, the conversion of NO_x decreased with an increase in concentration of V_2O_5 when the temperature was raised above the range of 400∿450°C. This decrease in the conversion of NO_x could be caused by the oxidation of NH_3 to NO_x or N_2. Over the 1wt% V_2O_5-TiO_2, a reduction level greater than 90 % was obtained at temperatures of 300-450°C. Therefore, the 1wt% V_2O_5-TiO_2 was used as a parent catalyst at present work.

Fig. 2. shows the catalytic activities of M_xO_y-V_2O_5-TiO_2, whose composition is given in Table 1., for the oxidation of SO_2. It can be seen that for all the catalysts, SO_2 conversion increased with an increase in temperature, and the activity for SO_2 oxidation on these catalysts are in the following order :

$$WO_3\text{-}V_2O_5\text{-}TiO_2 > MoO_3\text{-}V_2O_5\text{-}TiO_2 > V_2O_5\text{-}TiO_2 > Ta_2O_5\text{-}V_2O_5\text{-}TiO_2 >$$
$$Y_2O_3\text{-}V_2O_5\text{-}TiO_2 > GeO_2\text{-}V_2O_5\text{-}TiO_2 > ZnO\text{-}V_2O_5\text{-}TiO_2$$

The addition of WO_3 or MoO_3 to the V_2O_5-TiO_2 enhanced the activity of SO_2 oxidation. On the other hand, the addition of GeO_2 or ZnO to the V_2O_5-TiO_2 was effective for the retardation of SO_3 formation, the conversion of SO_2 on them were reduced by one-third against that of V_2O_5-TiO_2 at temperature of 300-500°C. The addition of Ta_2O_5 to the V_2O_5-TiO_2 did not affect the oxidation activity. From these results, of all oxides employed as the third component, the oxides which were composed of the cation in low valence states against V^{5+} were proved to be effective for the retardation of SO_3 formation.

The catalytic activities of M_xO_y-V_2O_5-TiO_2 on the NO_x reduction at various temperatures are shown in Fig. 3. The conversion of NO_x on WO_3-V_2O_5-TiO_2 and GeO_2-V_2O_5-TiO_2 were higher than that of V_2O_5-TiO_2 over the whole range of temperature studied, and the reduction level reached above 95 % at temperatures of 350-450°C. However, the decreases of the conversion of NO_x at any temperature were observed by the addition of a third component to the V_2O_5-TiO_2 except for WO_3 or GeO_2. Especially, the ZnO-V_2O_5-TiO_2 revealed the lowest activity in the reduction of NO_x and its conversion was 30 % lower than that of the 1wt%-V_2O_5-TiO_2 at 350°C.

Table 1. Catalyst composition and surface area

catalyst	raw material	composition, wt%		S.A. (m^2/g) b)
		V_2O_5	M_xO_y a)	
TiO_2	—	—	—	40
V_2O_5-TiO_2	NH_4VO_3	0.99	—	40
ZnO-V_2O_5-TiO_2	$ZnSO_4$	0.98	1.05	40
Y_2O_3-V_2O_5-TiO_2	$Y(NO_3)_36H_2O$	1.07	1.04	40
GeO_2-V_2O_5-TiO_2	$Gecl_4$	0.98	1.00	39
Ta_2O_5-V_2O_5-TiO_2	$Tacl_5$	0.97	1.98	40
MoO_3-V_2O_5-TiO_2	$(NH_4)_6Mo_7O_{24}$	0.95	1.76	39
WO_3-V_2O_5-TiO_2	$(NH_4)_2O12WO_35H_2O$	0.97	0.62	40

a) Amount of oxides employed as a third component

b) BET surface area (N_2 adsorption)

Thus, the order of activity for the NO_x reduction was not necessary the same as that of SO_2 oxidation over the present catalysts.

The presence of oxygen is known to enhance the reduction of NO_x.[3)4)] Inomata et al.,[5)] have been reported that the rate of the $NO-NH_3$ reaction was in proportion to the amount of the $V^{5+}=O$ species in the $V_2O_5-TiO_2$ catalyst. Thus, a function of oxygen is of considerable importance for the activation of both NO_x reduction and SO_2 oxidation, then, a relationship between the conversion of SO_2 and the surface excess oxygen by KI (pH 7.7) method was examined over the present catalysts.

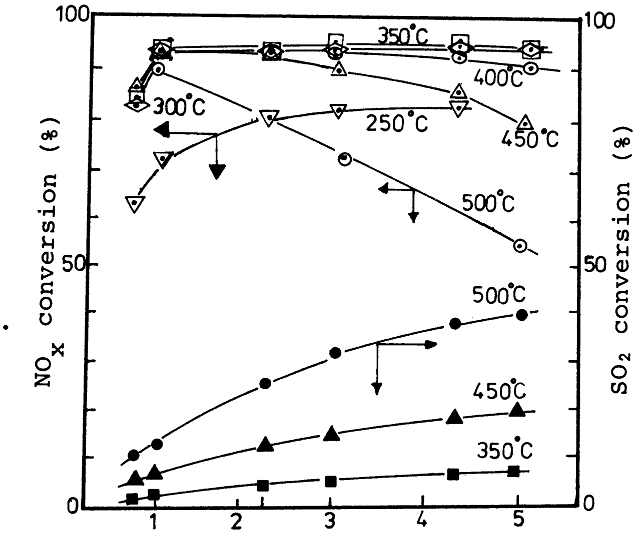

Fig. 1. The effect of the concentration of V_2O_5 for NO_x reduction and SO_2 oxidation

Space velocity; 15000 hr^{-1}

Reaction gas; 150 ppm NO, 150 ppm NH_3, 3% O_2, 7.3 % H_2O, 1000 ppm SO_2, balance N_2

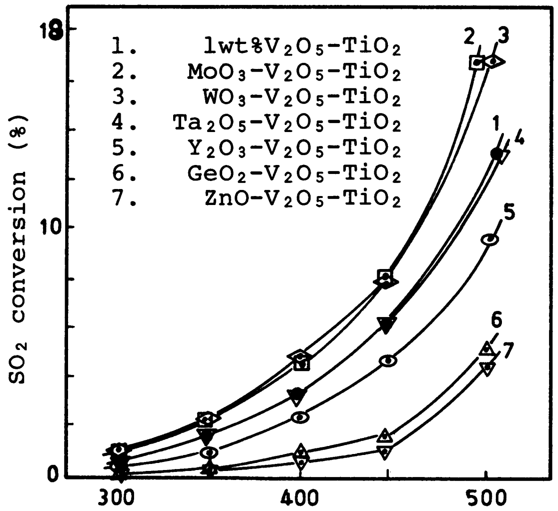

Fig. 2. Catalytic activity of $M_xO_y-V_2O_5-TiO_2$ on SO_2 oxidation

Reaction conditions are the same as for Fig. 1.

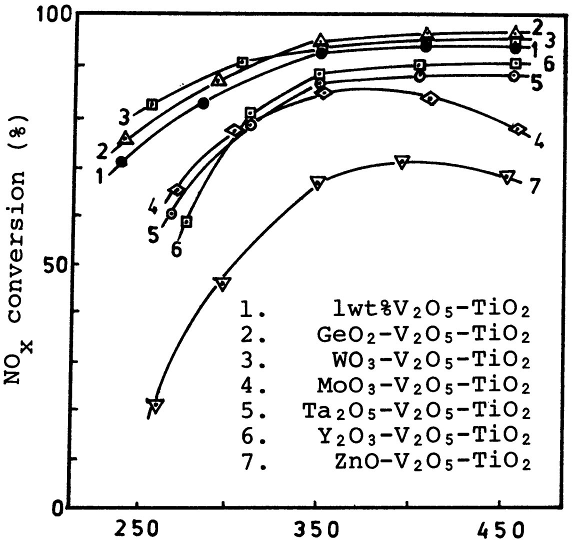

Fig. 3. Catalytic activity of $M_xO_y-V_2O_5-TiO_2$ on NO_x reduction

Reaction conditions are the same as for Fig. 1.

As shown in Fig. 4., a linear relation between the conversion of SO_2 and the surface excess exygen was obtained. The surface area of the present catalysts were almost the same as shown in Table 1. The results described above suggest that the SO_2 oxidation can be retarded by decreasing the surface excess oxygen on the catalyst, in other words, by adding the oxides which were composed of the cation in low valence states against V^{5+} to V_2O_5-TiO_2. On the other hand, no good linearity was obtained on the NO_x reduction with the surface excess oxygen. Hence, the active sites for SO_2 oxidation and NO_x reduction could be different. Unfortunately, we could not determine both the species of surface excess oxygen and the active sites on the present catalysts. Further work is needed to clarify the actual scheme of these phenomena.

In conclusion, the addition of relatively small amount of the GeO_2 to the V_2O_5-TiO_2 lowered the oxidation efficiency of SO_2 to SO_3 and also raised the NO_x reduction efficiency against those of the parent V_2O_5-TiO_2 catalyst.

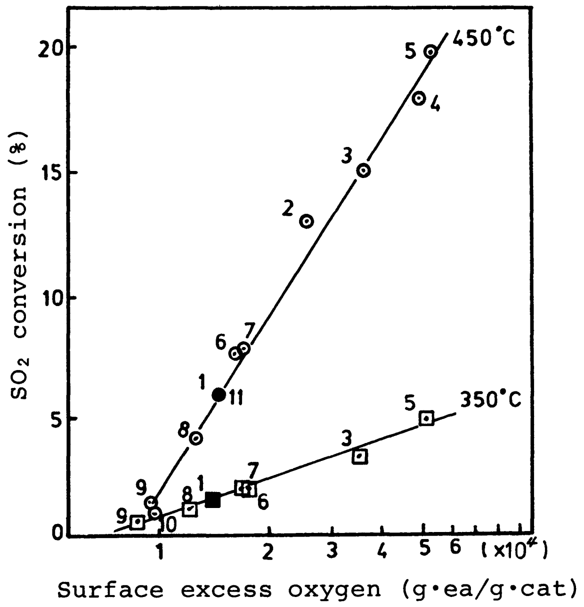

Fig. 4. Relationship between surface excess oxygen and SO_2 conversion
Reaction Temp. 350°C, 450°C
The other conditions are the same as for Fig. 1.

1. 1 wt%V_2O_5-TiO_2
2. 2.3wt%V_2O_5-TiO_2
3. 3 wt%V_2O_5-TiO_2
4. 4.4wt%V_2O_5-TiO_2
5. 5 wt%V_2O_5-TiO_2
6. WO_3-V_2O_5-TiO_2
7. MoO_3-V_2O_5-TiO_2
8. Y_2O_3-V_2O_5-TiO_2
9. GeO_2-V_2O_5-TiO_2
10. ZnO-V_2O_5-TiO_2
11. Ta_2O_5-V_2O_5-TiO_2

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