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The Effect of the Vanadium Component on the Life of the WO_3–TiO_2 Catalyst Used for the Reduction of NO_x with NH_3

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The 5000-h life test of the WO_3–TiO_2 catalyst for the reduction of NO_x with NH_3 has been investigated in real flue gases containing vanadium and SO_x on a pilot plant. When the present catalyst was used in a residual-oil-fired-boiler flue gas, steady activities over 90% of NO_x reduction were achieved for 5000 h at 400 °C (space velocity: 2700 h^{-1}). On the other hand, when the catalysts were taken out of the reactors at certain intervals and studied by means of a laboratory reactor, they were much more active than fresh catalyst at lower temperatures (250—350 °C). Also, the SO_2 oxidation efficiency increased with the reaction time. This activation was considered to be due to the vanadium component in the flue gas.

In many of the processes proposed hitherto, the selective reduction of NO_x with NH_3 on such catalyst systems as V_2O_5–TiO_2[1] and WO_3–TiO_2[2] has been considered to be the most promising process for removing NO_x from stationary sources. Furthermore, these catalysts are known to have an excellent activity and to be stable to SO_x; in particular, the WO_3–TiO_2 catalyst is thermally stable at 400 °C or higher temperatures and has a low oxidation activity from SO_2 to SO_3.

A mechanism for the reduction of NO_x with NH_3 in the presence of O_2 on the TiO_2–WO_3 catalyst was proposed by Imanari *et al.*[2] Kasaoka *et al.*,[3] reported the effect of the addition of WO_3 over V_2O_5 for activity on NO_x reduction with NH_3.

However, the life and effects of the vanadium component in real flue gas has not yet been reported with regard to the WO_3–TiO_2 catalyst. In this study, the life test for 5000 h as a pilot test has been investigated over WO_3–TiO_2 in connection with the reduction of NO with NH_3 using a Khafji residual-oil-fired-boiler flue gas. Also, catalysts were taken out of the reactor at certain intervals and their catalytic properties were examined by means of a X-ray photoelectron spectrometer.

Experimental

Catalyst Preparation. The 10 wt%WO_3–TiO_2 catalysts used in this study were prepared by impregnating TiO_2 (specific surface area: 70 m^2/g, mean pore radius: 320 Å, SO_4^{2-} content: 3.8%) in an aqueous solution of ammonium paratungstate ($5(NH_4)_2O12WO_3\cdot 5H_2O$). After the impregnation, the catalysts were dried for 3 h at 120 °C and then calcined for 5 h at 550 °C in an air stream.

Activity Measurement. *Pilot-plant Test*: A life test was carried out with a pilot-plant test with an apparatus which consisted of a 150 mm-id reactor containing pellet catalysts (diam. 7 mmϕ). Activity measurements were carried out at 400 °C over the space velocity of 2700 h^{-1} using the combustion flue gas at a flow rate of 100 Nm^3/h from the Khafji residual-oil-fired-boiler (sulfur content: 5.2%, vanadium content: 220—230 ppm, NO_x: 95—105 ppm).

Laboratory scale Test: The reduction of NO with a model flue-exhaust gas consisting of NO, NH_3, H_2O, SO_2, and O_2 has also been studied over the WO_3–TiO_2 catalysts which were used in the pilot test. Activity measurements were carried out between 250 and 450 °C at a space velocity of 3500 h^{-1} using a conventional flow reactor made of a quartz tube reactor (length: 500 mm, dia.: 30 mm) under atmospheric pressure. A gas mixture consisting of 150 ppm of NO, 150 ppm of NH_3, 1000 ppm of SO_2, 5% of O_2, 8% of H_2O, and balance, N_2 was used as a standard feed. The analysis of NO and SO_2 was done with a chemiluminessence-type NO_x analyzer and a NDIR type SO_x analyzer respectively.

Measurements of Catalyst Property. The surface areas were measured by means of the BET method. An X-ray photoelectron spectrometer (Dupont-Shimadzu 650) was used to examine the surface properties of the catalysts. Mg $K\alpha$ (1253.6 eV) X-ray radiation was used as the excitation source. The measurements were conducted at room temperature under a vacuum of about 10^{-7} Torr (1 Torr≈133.322 Pa). The binding energies of the C (1 s) and Au ($4f_{7/2}$) electron peaks were used as the energy standards throughout the present work; they have taken to be 285.0 and 83.6 eV respectively.

Results and Discussion

Life Test of the WO_3–TiO_2 Catalyst for NO_x Removal. The life test of the 10% WO_3–TiO_2 catalyst on the reduction of NO with NH_3 was investigated in real flue gas containing 105 ppm of NO, 8% of H_2O, 4% of O_2, 10% of CO_2, 220—230 ppm of the vanadium component, and a 5.2% sulfur component at 400 °C over the space velocity, 2700 h^{-1}. The NH_3/NO inlet ratio was 1.0. Figure 1 shows the change in the conversion of NO with the reaction time. Steady activities over an NO_x reduction efficiency of 90% were achieved for 5000 h. Thus, the WO_3–TiO_2 catalyst was revealed to be highly resistant to the large amount of SO_x which was present in the residual oil and maintained a high activity for NO_x reduction. However, the color of the catalyst in a fresh catalyst changed from light yellow to green yellow over long periods of reaction time.

Figure 2 shows the results for the reduction of NO with NH_3 at 275—450 °C. In the pilot test, they were examined by means of a laboratory scale apparatus over the WO_3–TiO_2 catalysts used after 816 h, 1150 h, 2160 h, and 4800 h. Tests were conducted with simulated flue gas containing 8% of H_2O, 5% of O_2, 1000 ppm of SO_2, and 150 ppm of NO with 150 ppm of NH_3 (balance, N_2) over a space velocity

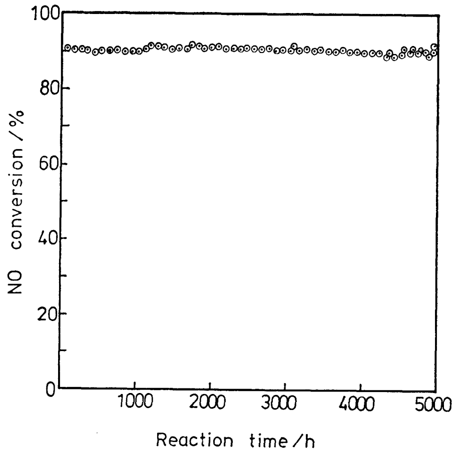

Fig. 1. Life test of WO_3–TiO_2 catalyst in real flue gas.
Reaction conditions: reaction temp; 400 °C, SV; 2700 h^{-1}. Composition of the flue gas: NO; 105 ppm, O_2; 4%, H_2O; 8%, CO_2; 10%, S component: 5.2%, vanadium component: 220—230 ppm

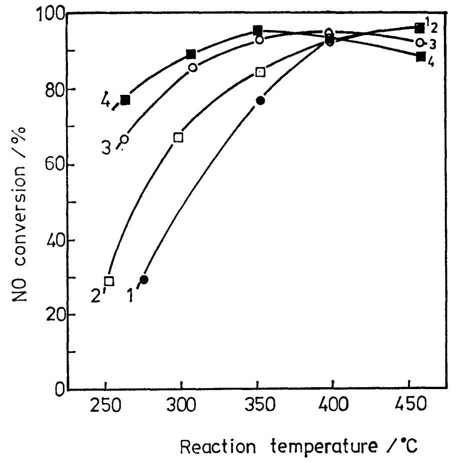

Fig. 3. Effect of amount of vanadium on activity for NO reduction.
Amounts of vanadium: 1; 0 wt%, 2; 0.5 wt%, 3; 1.5 wt% 4; 2.5 wt%. Reaction conditions are the same as for Fig. 2.

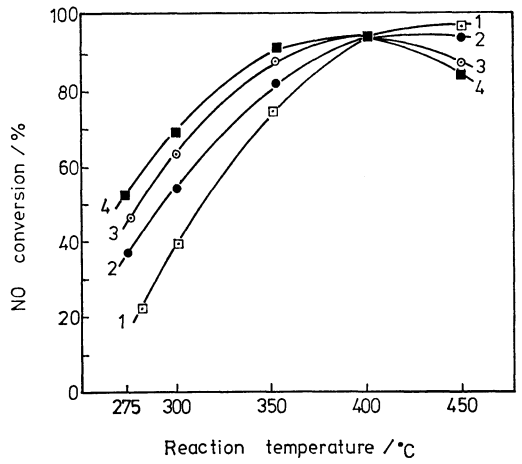

Fig. 2. Activity change in WO_3–TiO_2 catalyst with reaction time in simulated flue gas.
1: Fresh catalyst, 2: used for 1150 h, 3: used for 2160 h, 4: used for 4800 h. Reaction conditions: NO; 150 ppm, NH_3; 150 ppm, O_2; 5%, SO_2; 1000 ppm, H_2O; 8%, N_2; balance, SV; 3500 h^{-1}.

of 3500 h^{-1}. The conversion of NO was revealed to be 95% at the temperature of 400 °C, and the NO reduction efficiency did not change with the reaction time. This result fits well with that of the pilot test in Fig. 1. As shown in Fig. 2, however, the conversion of NO increased with the reaction time at 275—350 °C and decreased with the reaction time at 450 °C. In particular, the conversion of NO increased from 20 to 50% at 275 °C on a 4800-h catalyst. These observations suggest that catalysts were affected by the composition of real flue gas and changed in their surface properties. Although the present real flue gas contain a considerable amount of vanadium and sulfur components, as mentioned above, it may be supposed that such an increase in the NO reduction efficiency over a temperature range of 275—350 °C was due to the vanadium component accumulated on the catalyst, because the presence of the vanadium component is known to enhance the NO reduction efficiency at lower temperatures:[4] in contrast, SO_x is known to reduce the activities of the catalysts.[5]

To clarify the effect of the vanadium component on NO_x reduction efficiency, we prepared the V_2O_5–WO_3–TiO_2 catalysts at various V_2O_5 concentrations and examined the activity, the conversion of NO *vs.* the reaction temperature. The results are shown in Fig. 3. The vanadium-loaded catalysts appear to be superior to the WO_3–TiO_2 catalyst in the NO reduction efficiency between 250 and 350 °C, and the increase in the amount of vanadium seems to be correlated with the activity, the 2.5 wt% V_2O_5–WO_3–TiO_2 catalyst in particular revealing the highest NO reduction efficiency. By contrast, at a high temperature (450 °C) the reduction efficiency decreased as the amount of vanadium loaded was increased. Similar behavior was seen on the V_2O_5–TiO_2 catalyst.[4] Furthermore, these results are in agreement with the experimental results obtained in Fig. 2. Thus, it was found that the conversion of NO in the reaction temperature range of 250—350 °C distinctly depends on the vanadium components.

Change in the Properties of the Catalyst. Next, surface analysis of the catalyst was conducted before and after use. Figure 4 shows the variations in the X-ray photoelectron spectra of the catalyst used in the NO reduction for V $2p_{3/2}$.

In Fig. 4, the V $2p_{3/2}$ peak was not observed on a fresh catalyst, but the intensity of the V $2p_{3/2}$ peak,[6] the binding energy being 517.2, increased with the reaction time, while the spectra of W $4f_{5/2}$, O_{1s}, and S_{2p} were almost unchanged with the reaction time, except for 4800 h. Each peak of the 4800-h catalyst was slightly shifted to the higher-binding-energy side.

Furthermore, to clarify the effect of catalytic properties, Table 1 shows the results of the analysis for dust components (K_2O, Na_2O), SO_4^{2-}, V_2O_5, WO_3, surface area (BET method), pore volume, surface

TABLE 1. ANALYTICAL RESULTS OF WO_3-TiO_2 CATALYSTS WITH THE REACTION TIME

Catalyst	$\frac{V\ 2p_{3/2}}{Au\ 4f_{7/2}}$	Surface area[1)] $m^2\ g^{-1}$ (Pore volume $ml\ g^{-1}$)	Surface excess oxygen[2)] g equiv./g	Chemical analysis				
				V_2O_5(%)	WO_3(%)	SO_4^{2-}(%)	K_2O(%)	Na_2O(%)
Fresh	—	70 (0.29)	Trace	—	10.1	3.1	0.2	0.01
816 h	0.125	70 (0.29)	Trace	0.04	10.1	3.2	0.2	0.01
1150 h	0.185	71 (0.30)	2×10^{-6}	0.06	10.2	3.4	0.2	0.01
2160 h	0.250	71 (0.30)	4×10^{-6}	0.09	10.1	3.7	0.3	0.01
4800 h	0.256	71 (0.30)	7×10^{-6}	0.09	10.1	3.8	0.3	0.01

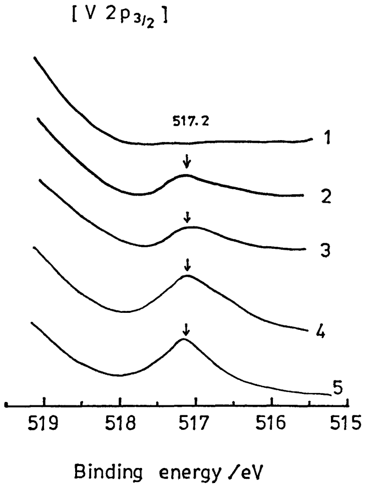

Fig. 4. Variation of photoelectron spectra for V $2p_{3/2}$. 1: Fresh catalyst, 2: used for 816 h, 3: used for 1150 h, 4: used for 2160 h, 5: used for 4800 h. Binding energies were referenced to C 1s of contaminant carbon (285.0 eV).

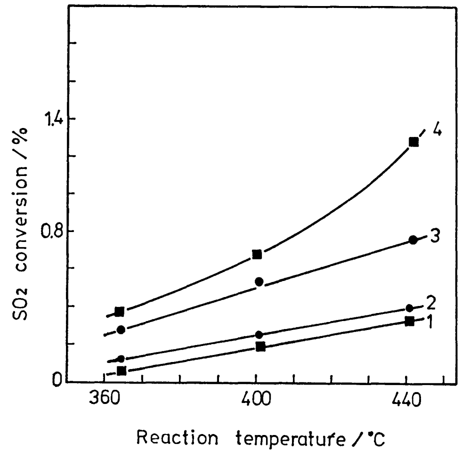

Fig. 5. Catalytic activity of WO_3–TiO_2 catalyst on SO_2 oxidation with reaction time in simulated flue gas.
1: Fresh catalyst, 2: used for 1150 h, 3: used for 2160 h, 4: used for 4800 h. Reaction conditions: NO; 150 ppm, NO/NH_3=1, H_2O; 8%, O_2; 5%, SO_2; 1000 ppm, SV; 3500 h^{-1}

excess oxygen by the KI method,[7)] and the ratio of V $2p_{3/2}$/Au $4f_{7/2}$ over fresh, 816-h, 1150-h, 2160-h, and 4800-h catalysts. It may be seen that the surface area, pore volume, potassium and sodium as dust components, and WO_3 and SO_4^{2-} contents were almost unchanged with the reaction time. The activation of a catalyst at a lower temperature was not explained sufficiently only by the change in the surface area and the pore volume. However, the concentration of V_2O_5 and the ratio of intensities between V $2p_{3/2}$ and Au $4f_{5/2}$ (standard) in the 4800-h catalyst were two times than that of the 816-h catalyst. Similar behavior was seen in the amount of surface excess oxygen on the catalyst. Judging from the results shown in Table 1, no doubt the presence of vanadium influences this increase in NO reduction efficiency at lower temperatures.

On the other hand, a previous study[4)] showed that the SO_2 oxidation was affected by the increase in vanadium concentration and enhanced by the amount of surface excess oxygen. Therefore, we examined the SO_2 oxidation over fresh and used catalysts at various temperatures. The results are shown in Fig. 5. The activity of the catalyst for SO_2 oxidation increased with an increase in the reaction time. At 365 °C, the SO_2 conversion in the 4800-h catalyst was four times that of the fresh catalyst. As is shown in Table 1, both the vanadium content and the surface excess oxygen increased with the reaction time, while the other dust components and the surface area were almost unchanged with the reaction time. Hence, it has been speculated that the increase in SO_2 conversion with the reaction time is mainly due to the vanadium accumulated on the catalyst and the amount of surface excess oxygen.

From our results, the following conclusions can be drawn. The NO reduction reached a constant value of 90%, and no change in efficiency was observed for 4500 h in real flue gases. Thus, the WO_3–TiO_2 catalyst performs well and maintains a high activity for NO reduction. However, when the WO_3–TiO_2 catalyst is used in flue gas containing a vanadium component such as Khafji residual oil, the NO reduction is not only increased at lower temperatures, but also the SO_2 oxidation is increased by accumulating vanadium on the surface of the catalyst. Therefore, for practical purposes, if the WO_3–TiO_2 catalyst is used for NO_x reduction in a residual-oil-fired-boier flue gas, it may be necessary to retard the oxidation of SO_2 to SO_3 without affecting the high activity for NO_x reduction over WO_3–TiO_2 as well as over the V_2O_5–TiO_2 catalysts.[4)]

The details of the reaction mechanism of NO with NH_3 over the WO_3–TiO_2 catalyst will be reported later.

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