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Study on V_2O_5–Al_2O_3 Catalyst by Means of XPS for the Reduction of Nitric Oxide with Ammonia

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Synopsis. The V_2O_5–Al_2O_3 catalyst used for the NO reduction in flue gas from a sintering furnace was studied by means of X-ray photoeloctron spectroscopy and X-ray microanalysis. Effects of dust components accumulated on the catalyst and of electronic states of vanadium ions on catalytic activities were discussed.

Of various methods for the removal of nitrogen monoxide in flue gas emitted from stationary combustion equipments, the catalytic reduction of NO with ammonia seems to be most effective.[1–3] Supported V_2O_5 catalysts have been used for industrial gases. It is desirable to know the influence of dust components (Fe, Si, K, Ca, Na, C, S) in flue gas on the life of the catalysts. A pilot plant test using flue gas from a boiler or a coke oven showed that sulfur oxides (SO_x) reduce the activities of the catalysts.[4,5] However, it was observed that K in the flue gas from a sintering furnace lowers the catalytic activities to a greater extent than SO_x.[6,7] In this study, characterization of the V_2O_5–Al_2O_3 catalyst used in the flue gas from a sintering furnace was made by means of X-ray photoelectron spectrometer and X-ray microanalyzer.

Experimental

The catalyst was prepared by impregnating γ-Al_2O_3 (diam. 6 mm, surface area 210 m^2/g, average pore radius 60 Å) with an aqueous solution of vanadium(IV) oxalate.[6] A life test was carried out with a moving bed type reactor (1000 Nm^3/h) at a space velocity of 10000 h^{-1}. The composition of the dust in the flue gas was Fe 28 wt %, SO_4 25 wt %, K 1.5 wt %, Na 0.6 wt %, that of the flue gas from the sintering furnace being NO 170—280 ppm, SO_2 130—260 ppm, O_2 13—15 vol %, H_2O 10—15 vol %, CO_2 10 vol %, and dust 30—120 mg/Nm^3. 200 ml of catalyst taken from the reactor every 100 h of the reaction time was subjected to examination of the change in catalytic properties. The line profile of each element in the catalyst was obtained with a X-ray microanalyzer (Shimadzu). Dust components on catalyst particles and electronic states of the elements in the catalyst were measured with a X-ray photoelectron spectrometer (Dupont 650 B). The values of the binding energies were referred to C 1s photoelectron spectra of contaminant carbon (285.0).

Results and Discussion

Figure 1 shows line profiles of dust components accumulated on the catalyst. S, Si, and Ca were found in inner parts of the catalyst, K and Fe being restricted to surface layers of catalyst particles (Fig. 1 A). On Fe_2O_3–Al_2O_3 catalysts, K permeated into the catalyst particles to form a complex of $[K_2Fe(SO_4)_2]$. The difference in the behavior of K remains unclarified.

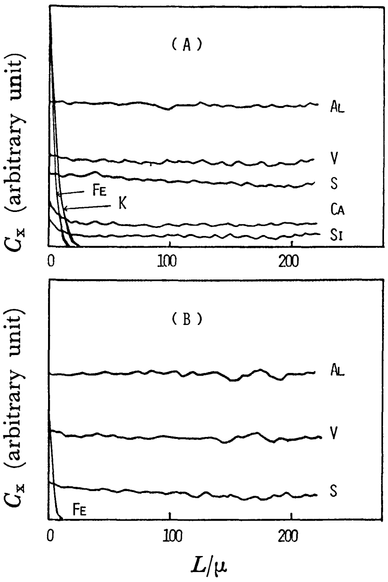

Fig. 1. Distribution analysis of each component in V_2O_5–Al_2O_3 catalyst confirmed by X-ray microanalyzer.
The sample was prepared in a form of hemi-sphere particle to obtain the depth profile. (A): Used for 2000 h, (B): regenerated (heating, washing, and treating with SO_2), L: depth from the surface, C_x: concentration of each component in the catalyst.

The amount of S increased with the reaction time, becoming constant after a certain time. Increase in the concentrations of K, Fe, Ca, and Si continued even after 1000 h.[7] Dust components except S and Fe were removed from the catalyst after regeneration (heating at 550 °C for 2 h and washing at 80 °C for 2 h and subsequent treatment with 500 ppm of SO_2 at 300 °C for 15 h). From the fact that the activity recovered after the regeneration, the effects of S and Fe on the activity are considered to be less than those of the other components.

Figure 2 shows the changes in photoelectron spectra of some dust components on the catalyst. Binding energies of K 2p spectra show that K exists in the form of K_2SO_4. Intensities of these photoelectron spectra, especially those of K and Fe, increased with reaction time. As regards S 2p spectra, the intensity was saturated after 800 h of the reaction. Changes of V $2p_{3/2}$ and Al 2p photoelectron spectra of the catalyst are shown in Fig. 3. The intensity of V $2p_{3/2}$ spectrum decreased more rapidly than that of Al 2p spectrum. This indicates that K sticks predominently on V, the active component, rather than on the carrier, causing a decrease of catalytic activity. The electronic states of vanadium and aluminium ions turned electronegative with reaction time (Fig. 3). The change of elec-

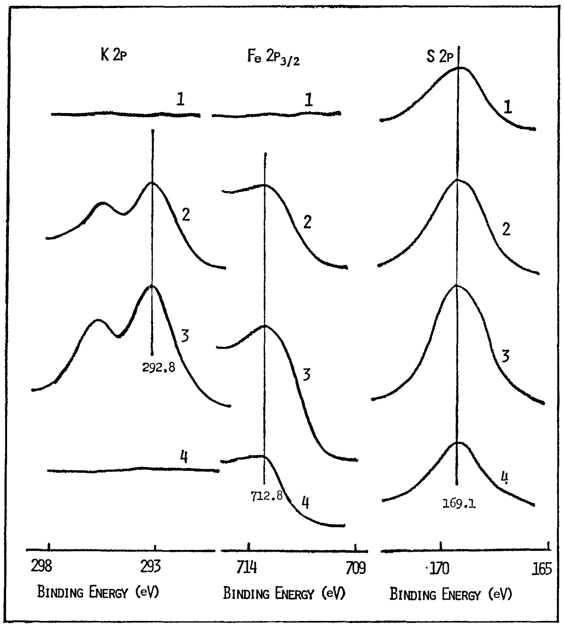

Fig. 2. Change in photoelectron spectra of dust component on V_2O_5–Al_2O_3 catalyst.
1: Fresh (treating with SO_2), 2: used for 600 h, 3: used for 2000 h, 4: regenerated (heating, washing, and treating with SO_2).

tronic state of aluminium ions is due to the formation of $Al_2(SO_4)_3$.[4] The binding energy of vanadium ions of the catalyst subjected to the reaction using the flue gas from the sintering furnace decreased by 1.0 eV, while the value obtained for the catalyst used for a gas without dust components decreased only by 0.5 eV. The difference would be ascribed to the effects of K adhered on V. The optimum electronic state of the cation in the active component shows high activity, the catalytic activity decreasing when the electronic state of the cation deviates from the optimum state to electronegative or electropositive state.[8] Changes in electronic states of vanadium ions would affect the activity of the catalyst for NO reduction. A large decrease in the binding energy would give the result[6] in which the catalytic activity decreases much more rapidly when the catalyst is used in the flue gases containing dust components. The ratio of intensities between V $2p_{3/2}$ and Al 2p spectra and the electronic state of vanadium ions returns to the original one by the regeneration.

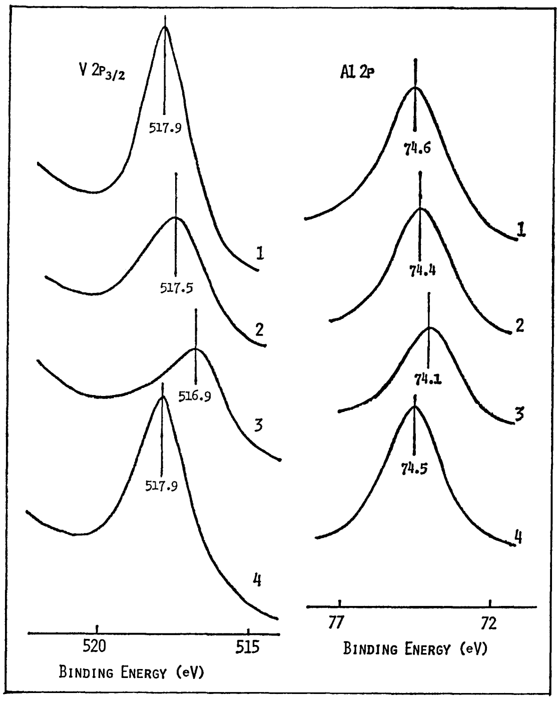

Fig. 3. Change in photoelectron spectra of active component and carrier on V_2O_5–Al_2O_3 catalyst.
1: Fresh (treating with SO_2), 2: used for 600 h, 3: used for 2000 h, 4: regenerated (heating, washing, and treating with SO_2).

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