New Type of Active Carbon Catalyst for Simultaneous Removal of SO_x and NO_x

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Active carbons prepared from nitrogen containing compounds were found to show high activity for SO_2 removal. Enhancement of the activity for NO reduction was realized by supporting vanadium ions on these active carbons. Regeneration of the catalyst was examined with various reducing agents. The activity for SO_2 removal was recovered by removing sulfate ions on the catalyst with NH_3 at 350 °C. The 200 h life test of the present catalyst was carried out for the simultaneous removal of SO_x and NO_x.

Development of the technique for removal of sulfur oxides (SO_x) and nitrogen oxides (NO_x) in a flue gas emitted from a stationary combustion equipment involves complicated problems. Recently, active carbons have been used for the simultaneous removal of SO_x and NO_x in a flue gas.[1,2] SO_x is removed by adsorption on a catalyst as sulfate compounds, NO_x being reduced by NH_3 added in a flue gas as a reducing agent. However, active carbon (AC) developed so far are applied at a low space velocity below 1000 h^{-1} because of lower activities at the temperature range in which AC is of use. Development of active catalysts which can be used at a higher space velocity is desirable. According to studies by Sano and Ogawa[3] on new types of catalysts with higher activity for SO_2 removal, certain impurities such as surface nitrogen species seem to have a good effect on activity. Investigation was carried out in order to improve the activity for simultaneous removal of NO and SO_2. Develpoment of technique for regeneration is also important in connection with the simultaneous reduction. In this paper, the method of regeneration and result of the life test for 200 h are described.

Experimental

Catalyst. As raw materials for active carbons, nitrogen-containing compounds such as polyacrylonitrile or urea resin, a sulfur-containing compound (ashaltene) and a silica-containing compound (chaff) were used. Materials were put into a reactor made of quartz (length 500 mm, diam 60 mm) and were carbonized at *ca.* 250 °C in N_2 flow (1 *l*/h). Activation was carried out in the temperature range 600—1000 °C using water vapor or $ZnCl_2$ as an activating reagent. Some commercial AC were also used as a reference. The nitrogen-containing AC preapred from polyacrylonitrile was found to show superior activity for SO_2 removal and was selected as a carrier for the simultaneous removal of SO_2 and NO. Metal salts were supported by the impregnation method. Impregnation was carried out at 30 °C for 5 h, and the catalysts obtained were dried at 120 °C for 3 h, and then calcined at 250 °C in N_2 stream (1 *l*/h). Catalysts prepared are summarized in Table 1.

Activity Measurement. Activity measurements were carried out at 200 °C at a space velocity of 5000 h^{-1} using a conventional flow reactor made of stainless steel (length 300 mm, diam 25 mm). A gas mixture consisting of SO_2 500 ppm, NH_3 500 ppm, O_2 5 vol%, H_2O 10 vol%, and N_2 was used as standard feed, 300 ppm of NO being added in the case of simultaneous removal. The activities for SO_2 removal and NO reduction were determined by measurements of the concentrations before and after the reaction. Analyses of SO_2 and NO were made with a NDIR type SO_x analyzer and a chemiluminescence type NO_x analyzer, respectively. The analysis of NH_3 was performed by the chemical method (JIS-K-0099).

Measurement of Catalyst Property. Measurement of surface areas and elemental analysis of C and N were carried out by the BET method and CHN corder (Yanaco MT-2), respectively. An X-ray photoelectron spectrometer (Dupont 650B) was used to examine surface properities of the catalysts. An ion microanalyzer (Hitachi IMA-2) and an electron microprobe (Hitachi HU-12) were also used to estimate the line profile of each element and the despersion of supported vanadium ions, respectively.

Results and Discussion

Comparison of AC as Regards Activity for SO_2 Removal. The activities of various AC for SO_2 removal are shown in Fig. 1. AC prepared from nitrogen-containing compounds showed superior activity to other AC, while

Table 1. Preparation of AC from raw material

Raw material	Activating conditions	Surface area	Nitrogen content
Polyacrylonitrile	600—1000 °C	300—1000 m^2/g	2—12 wt %
Urea resin	800 °C	525 m^2/g	6.4 wt %
Melamine resin	800 °C	517 m^2/g	8.1 wt %
Aniline-formaldehyde resin	800 °C	662 m^2/g	5.2 wt %
m-Phenylenediamine-formaldehyde resin	800 °C	420 m^2/g	5.5 wt %
Asphaltene	800 °C	520 m^2/g	—
Chaff	800 °C	625 m^2/g	—

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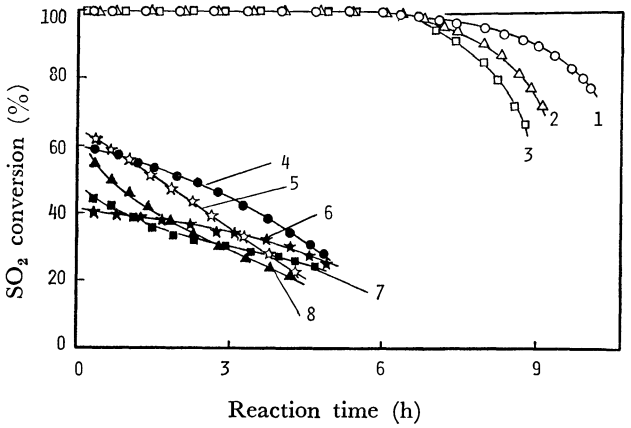

Fig. 1. Comparison of performance of various AC for SO_2 removal. Raw materials;
1 ○: Polyacrylonitrile, 2 △: *m*-phenylenediamine-formaldehyde resin, 3 □: urea resin, 4 ●: commerical type A, 5 ☆: commercial type B, 6 ★: commercial type C, 7 ■: asphaltene, 8 ▲: chaff.
Reaction conditions;
Reaction temp: 200 °C, SV: 5000 h^{-1}, SO_2: 500 ppm, NH_3: 500 ppm, O_2: 5 vol%, H_2O: 10 vol% N_2: balance.

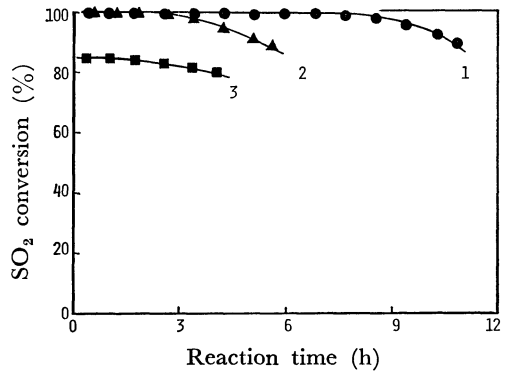

Fig. 2. Effect of space velocity on activity for SO_2 removal.
Space velocities;
1 ●: 5000 h^{-1}, 2 ▲: 10000 h^{-1}, 3 ■: 15000 h^{-1}.
Reaction conditions;
Reaction temp 200 °C,
SO_2: 500 ppm, NH_3: 500 ppm, O_2: 5 vol%, H_2O: 10 vol%, N_2: balacne.

those prepared from asphaltene and chaff showed lower activity than commercial ones. Figure 2 shows the effect of space velocity on activity for the removal of SO_2. AC prepared from polyacrylonitrile (PAN) showed high activity at space velocity higher than 10000 h^{-1}, indicating the merit of the AC prepared from nitrogen-containing compounds.

Effect of Preparation Conditions on the Catalytic Activity for SO_2 Removal. Figure 3 shows the effect of activating conditions on activities and capacities of active carbons from PAN for SO_2 removal. When $ZnCl_2$ was used as an activating agent, the catalysts obtained were not active, probably due to the blocking of SO_2 adsorption sites by zinc atom. In fact, the results obtained with the ion micronalyzer showed that the surface concentration of Zn on AC with lower

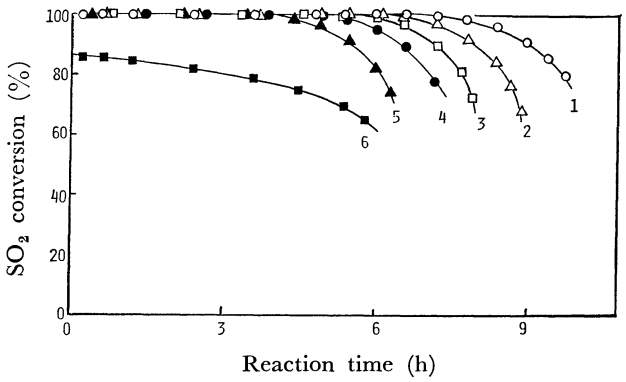

Fig. 3. Effect of preparation conditions on the catalytic activity for SO_2 removal.
Activating conditions;
1 ○: 800 °C, 30 min, water vapor, 2 △: 900 °C, 15 min, water vapor, 3 □: 900 °C, 30 min, water vapor, 4 ●: 700 °C, 30 min, water vapor, 5 ▲: 1000 °C, 20 min, water vapor, 6 ■: $ZnCl_2$, 700 °C, 30 min, N_2.
Reaction conditions;
Reaction temp: 200 °C, SV: 5000 h^{-1}, SO_2: 500 ppm, NH_3: 500 ppm, O_2: 5 vol%, H_2O: 10 vol%, N_2: balance.

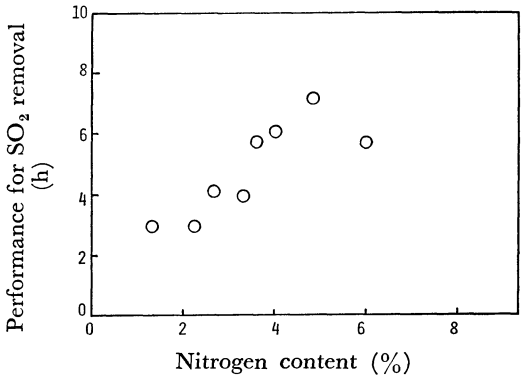

Fig. 4. Relation between performance of SO_2 removal and nitrogen content in present AC.
Performance of SO_2 removal: hours to keep 100% of SO_2 removal.

activity for SO_2 removal is higher than that on AC with higher activity. Though highly active ones were obtained when activated by H_2O, capacity performance of SO_2 removal was found to be deeply dependent on activating conditions. The specific surface area of the AC prepared under various conditions is in the range 300—1000 m^2/g, the activity of these AC being superior to that of commerical ones whose specific surface area is 700—1000 m^2/g. Surface functional groups of carriers play an important role in the catalysis.[4,5] It seems that some kinds of surface species contribute to the performance of SO_2 removal. A few percent of nitrogen atom remained after activation. Nitrogen species seem to exist in the state of C–N or N–N.[6] Thus the nitrogen species existing on the surface of the AC seem to be effective for the SO_2 removal. The amount of SO_2 adsorbed on AC was enhanced when nitrogen species were formed on the usual AC by impregnation with aqueous solutions of

Table 2. Binding energy of photoelectron spectra for N 1s, V $2p_{3/2}$, and S 2p on catalyst

	N 1s (eV)	V $2p_{3/2}$ (eV)	S 2p (eV)
Fresh catalyst	396.1	517.7	—
	397.5		
Deactivated catalyst	396.1	517.2	169.0
	397.6		

Binding energies were obtained based on C 1s spectra of contaminant carbon (285.0 eV).

nitrogen-containing compounds.[3] The amount of nitrogen in the AC we prepared was in the range 2—12 wt%. The relation between the amount of nitrogen and the performance is shown in Fig. 4. The increase in the amount of nitrogen seems to be correlated with activity. We thus examined the nitrogen species on the surface of AC in order to study the chemical states. Two peaks of N ls spectra were observed on the surface (Table 2), their binding energies being 396.1 and 397.5 eV, respectively. This indicates that two different chemical states of nitrogen atoms exist on the surface of the AC (probably C–N and C–N–N) and that one of them would be more effective for the removal of SO_2.

Effect of Coexisting Gas on Activity for SO_2 Removal. In the removal of SO_2 with NH_3, the following reactions are considered as the mechanism:[1]

$$SO_2 + 1/2O_2 \longrightarrow SO_3 \quad (1)$$

$$SO_3 + H_2O \longrightarrow H_2SO_4 \quad (2)$$

$$H_2SO_4 + NH_3 \longrightarrow NH_4HSO_4 \quad (3)$$

$$NH_4HSO_4 + NH_3 \longrightarrow (NH_4)_2SO_4 \quad (4)$$

Figure 5 shows the effect of coexisting gases on the activity for SO_2 removal. When O_2 or H_2O was removed from the feed gas, the activity decreased rapidly, indicating that the existence of both O_2 and H_2O is indispensable for the removal of SO_2 (Reactions 1 and 2). The activity for SO_2 removal increased to some extent in the absence of NO in the feed gas (Fig. 5). In the case of commercial AC, the activity increased when NO was added to the feed gas. This might be explained by the catalysis of NO for the formation of SO_3. On the other hand, in the AC prepared from polyacrylonitrile, the activity for SO_2 removal was higher in the absence of NO. This is also one of the features of AC from polyacrylonitrile, suggesting that the activity for SO_2 removal depends on C–N–N and/or C–N species on AC. When NH_3 was removed from the feed gas, the activity was found to decrease gradually because of the lack of NH_3 for SO_2 removal (Reactions 3 and 4). The effect of the amount of NH_3 in the feed gas for SO_2 removal is shown in Fig. 6. The capacity SO_2 removal increased with increase in the amount of NH_3 added. Leak of NH_3 was observed at the outlet of the reactor when the concentration of NH_3 in the feed gas exceeded 500 ppm. Thus in the present work, 500 ppm of NH_3 was introduced in the feed gas.

Enhancement of Activity for NO Reduction. Activities of AC for NO reduction do not differ much

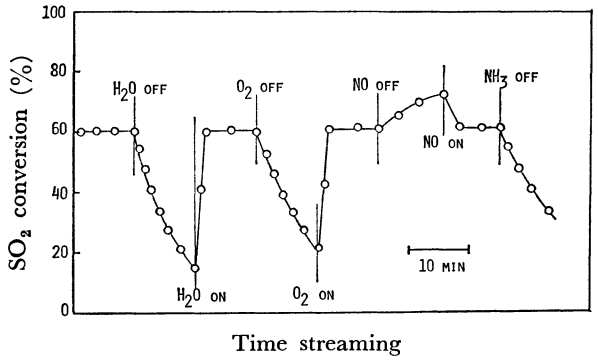

Fig. 5. Effect of coexisting gas on acetivity for SO_2 removal.
Reaction conditions;
Reaction temp: 230 °C, SV: 15000 h^{-1}, SO_2: 500 ppm, NO: 300 ppm, NH_3: 500 ppm, O_2: 5 vol%, H_2O: 10 vol%, N_2: balance.

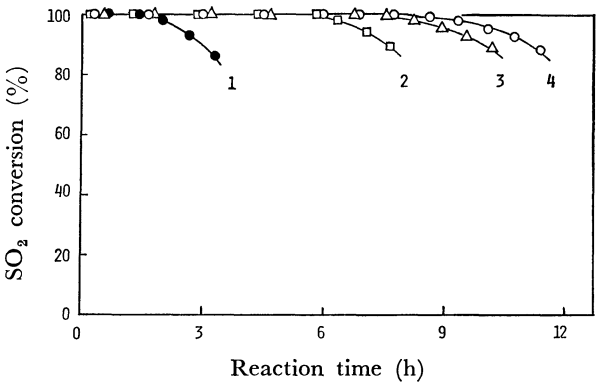

Fig. 6. Effect of amount of NH_3 on performance of SO_2 removal.
Amounts of NH_3;
1 ●: 0 ppm, 2 □: 300 ppm, 3 △: 500 ppm, 4 ○: 700 ppm.
Reaction conditions;
Reaction temp. 200 °C, SV: 5000 h^{-1}, SO_2: 500 ppm, O_2: 5 vol%, H_2O: 10 vol%, N_2: balance.

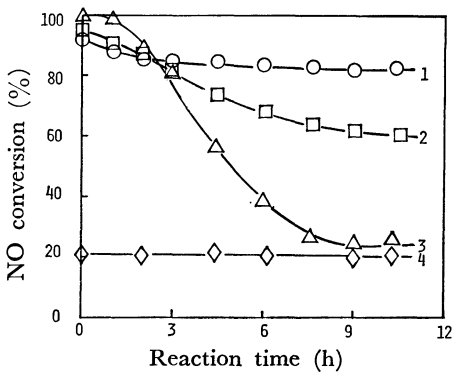

Fig. 7. Enhancement of activity for NO reduction.
1 ○: 5 wt% V_2O_5–AC, 2 □: 5 wt% CeO-AC, 3 △: 5 wt% MnO_2–AC, 4 ◇: AC
Reaction conditions;
Reaction temp: 220 °C, SV: 5000 h^{-1}, SO_2: 500 ppm, NO: 300 ppm, NH_3: 600 ppm, O_2: 5 vol%, H_2O: 10 vol%, N_2: balance.
AC used in this study was prepared from polyacrylonitrile.

from those of commercial ones. Under the reaction conditions, the activity of AC was so low that only 20% of NO was removed. Enhancement of activity for NO reduction was attempted by supporting various metal salts. Metals such as V or Mn which were found effective for NO reduction when supported on Al_2O_3 or TiO_2[7] were loaded on AC for the enhancement of the activity for NO reduction. Cerium, vanadium and manganese oxides supported catalysts were found to be highly active (Fig. 7). However, the activity of manganese or cerium supported catalyst decreased gradually with formation of the sulfate, regeneration of activity being difficult by the conventional technique. Since vanadium oxide supported catalyst exhibits a high activity for more than 10 h, vanadium ions were supported on the AC to improve the activity. The effect of the content of vanadium ions on both SO_2 removal ability and NO reduction activity was investigated in order to know the optimum content. The activity of the AC for SO_2 removal decreased with increase in the amount of vanadium supported (Fig. 8). On the contrary, the activity for NO reduction increased with increase in the amount of vanadium, apporaching a ceiling value at a certain vanadium content. AC with 2 wt% of vanadium supported showed optimum performance for the simultaneous removal.

Regeneration of Catalyst. The activity of catalyst for SO_2 removal decreases over a certain reaction time (Fig. 1 or 6); that for NO reduction does not decrease over 10 h. Sulfuric acid or ammonium sulfates formed during the course of reaction would diminish the number of active sites for successive adsorption of SO_2. Thus the removal of these compounds from the catalyst is indispensable for the regeneration of the catalyst. Deactivated catalysts were usually regenerated by (a) heating above 400 °C in nitrogen or (b) washing with water. In (a) surface compounds seem to react with AC as follows.

$$2H_2SO_4 + C \longrightarrow 2SO_2 + 2H_2O + CO_2 \quad (5)$$

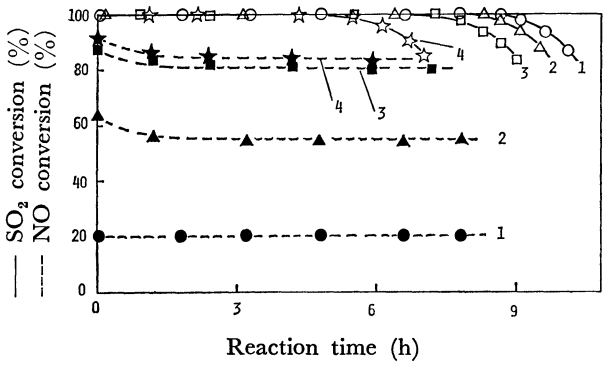

Fig. 8. Effect of amount of vanadium on activity for SO_2 removal and NO reduction.
Amounts of vanadium;
1 ○●: 0 wt%, 2 △▲: 1 wt%, 3 □■: 2 wt%, 4 ☆★: 4 wt%.
Reaction conditions;
Reaction temp: 220 °C, SV: 5000 h^{-1}, SO_2: 500 ppm, NO: 300 ppm, NH_3: 600 ppm, O_2: 5 vol%, H_2O; 10 vol%, N_2: balance.

$$NH_4HSO_4 + C \longrightarrow 2NH_3 + 2H_2O + 2SO_2 + CO_2 \quad (6)$$

Consumption of AC is unavoidable. In (b) elusion of vanadium salt takes place because of its change from oxide to soluble sulfate state in water. A new method free from the loss of active components is desirable.

In an industrial SO_2 removal process using $Cu–Al_2O_3$ catalyst, H_2, CO or low molecular HC is effective.[8] We have found that CO and H_2 are effective and that the consumption of AC caused by the regeneration with H_2 or CO was less than that by heating in nitrogen. When deactivated catalysts are treated with NH_3 gas, however, H_2SO_4 on the deactivated catalyst changes to NH_4HSO_4 or $(NH_4)_2SO_4$ (Reactions 3 and 4), and the consumption of the catalyst (Reactions 5 and 6) decrease as compared with the case in which other reducing agents are used.

Figure 9 shows the variation of photoelectron spectra for S 2p and V $2p_{3/2}$ on the catalyst. The intensity of S 2p peak increased with reaction time, that of V $2p_{3/2}$ peak decreasing gradually. No S 2p peak was observed after regeneration with NH_3. Analysis of sulfate ions (JIS-K-0101) showed no sulfate ions after the regeneration. The results show that sulfur was removed perfectly from the catalyst by regenerating with NH_3 gas. The electronic state of vanadium ions turned electronegative with reaction time (Fig. 9). The change of the electronic state of the active component would affect the activity for NO reduction. The activity of the AC catalyst was found to decrease at the initial state of the reaction (Fig. 8). After regeneration with NH_3 gas, both the electronic state of vanadium ions and the activity for NO reduction were recovered. For practical purposes, repeated regeneration is desirable.

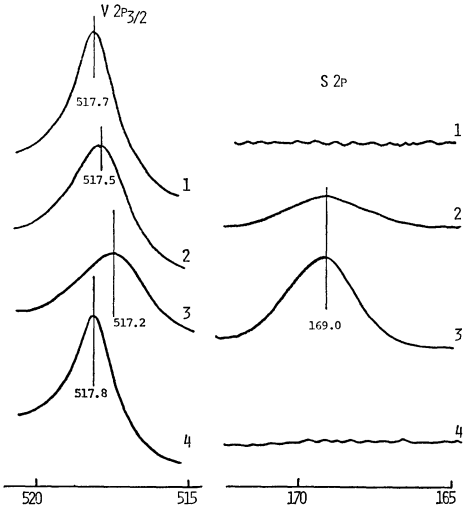

Fig. 9. Variation of photoelectron spectra for S 2p and V $2p_{3/2}$.
1: Fresh catalyst, 2: used for 2 h, 3: deactivated (used for 10 h), 4: regenerated with NH_3 at 350 °C. Catalyst: 2 wt% on AC prepared from polyacrylonitrile. Binding energies were referenced to C ls of contaminant carbon (285.0 eV).

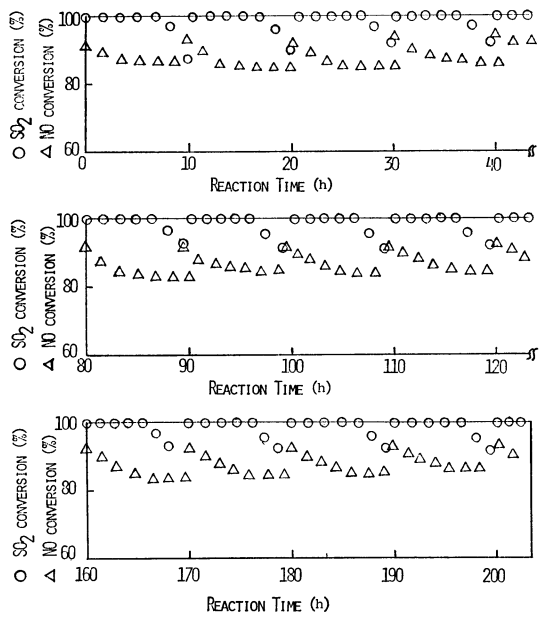

Fig. 10. Life test of simultaneous removal of SO_2 and NO.
Reaction conditions;
Reaction temp: 220 °C, SV: 5000 h^{-1}, SO_2: 500 ppm, NO: 300 ppm, NH_3: 600 ppm, O_2: 10 vol%, H_2O: 10 vol%, N_2: balance.
Regeneration conditions;
Reaction temp: 350 °C, Reaction time: 2 h, SV: 130 h^{-1}, NH_3: 2 vol%, N_2: balance.

Life Test of AC Catalyst for Simultaneous Removal. Figure 10 shows the result of the life test of AC catalyst for the simultaneous removal of SO_2 and NO. After every 10 h, regeneration was performed using NH_3 gas at 350 °C for 2 h. Steady activities over 90% of SO_2 removal and 80% of NO reduction were achieved. The consumption of the catalyst for 200 h of the life test was less than 0.1 ml (20 ml of the catalyst). After the life test, the dispersion of vanadium ions on regenerated catalysts was examined. The particle size of vanadium (smaller than 20 Å) and the highly dispersed state did not change after 20 repetitions of regeneration.

The results indicate that the simultaneous removal of SO_2 and NO with space velocity higher than 5000 h^{-1} is feasible.

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