Effect of SO_2 on NO_x reduction by ethanol over Ag/Al_2O_3 catalyst

Akira Abe [a], Naoko Aoyama [a], Satoshi Sumiya [a], Noriyoshi Kakuta [b] and Kiyohide Yoshida [a]

[a] *Riken Corporation, Suehiro 4-14-1, Kumagaya, Saitama 360, Japan*
[b] *Department of Materials Science, Toyohashi University of Technology, Tempaku, Toyohashi, Aichi 441, Japan*

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A new Ag/Al_2O_3 catalyst for removing NO_x in diesel engine exhaust gas was developed. The influence of SO_2 on the reduction of lean NO_x by ethanol over the Ag/Al_2O_3 catalyst was evaluated in simulated diesel exhaust and characterized using TPD, XRD, XPS, SEM and BET measurements. The Ag/Al_2O_3 catalyst was highly active for the reduction of NO_x with ethanol in the presence of SO_2 although the reduction of NO_x is suppressed at lower temperatures. The activity for NO_x reduction is high even on the Ag/Al_2O_3 catalyst exposed to a SO_2 (200 ppm)/O_2 (10%)/H_2O (10%) flow for 20 h at 723 K and comparable to that on the fresh Ag/Al_2O_3 catalyst. No crystallized Ag metal and Ag compounds were formed by the $SO_2/O_2/H_2O$ exposure. On the other hand, crystallized Ag_2SO_4 was easily formed when the Ag/Al_2O_3 catalyst was exposed to a SO_2 (200 ppm)/O_2 (10%)/NO (800 ppm)/H_2O (10%) flow for 10 h at 723 K. XRD, SEM and XPS studies showed that the formation of crystallized Ag_2SO_4 results in growing of Ag particles in larger size and lowering the surface content of Ag particles. In addition, the specific surface area of the Ag/Al_2O_3 catalyst decreases from 221 to 193 m^2/g. Although the dispersion of Ag particles was decreased by the formation of Ag_2SO_4, the activity for the reduction of lean NO_x was, remarkably, not affected. This suggests that the Ag–alumina sites created by the Ag_2SO_4 formation are still active for the lean catalytic reduction of NO_x.

Keywords: silver, silver sulfate, alumina, nitric oxide, catalytic reduction

1. Introduction

The amount of nitrogen oxides (NO_x) exhausted from internal combustion engines and furnaces is now over a tolerable level for both health and environmental protection. Especially, the large number of diesel engines and lean-burning gasoline engines are the major sources of NO_x. A prominent catalyst for reducing NO_x in lean-burning engine exhaust, however, has not been developed.

Catalytic reduction of NO_x with hydrocarbons in the presence of oxygen has been studied on alumina [1], zeolites [2–4], metal-supported catalysts [5–7], and copper-exchanged ZSM-5 [8]. However, the reduction of lean NO_x over these catalysts is, usually, suppressed in the presence of water vapor and SO_2 [5].

In these circumstances, Miyadera et al. reported that oxygen-containing organic compounds such as ethanol and acetone are extremely effective in the reduction of lean NO_x over an alumina-supported silver (Ag/Al_2O_3) catalyst in the presence of water vapor [9,10]. When ethanol is used as the reducing agent, about 80% of lean NO_x was removed [11–14]. Now, the Ag/Al_2O_3 catalyst has been developed for cleaning oxygen-rich exhaust gas [12]. A most interesting fact is that lean NO_x is effectively reduced on the Ag/Al_2O_3 catalyst even in the presence of SO_2.

In this paper, the influence of SO_2 on reduction of lean NO_x over the Ag/Al_2O_3 catalyst was studied by TPD. In addition, the Ag/Al_2O_3 catalyst exposed to a $SO_2/O_2/NO/H_2O$ flow was characterized by means of XRD, SEM and XPS, and the activity for the NO_x reduction was discussed in relation to the surface structure of the SO_2-treated Ag/Al_2O_3 catalyst.

2. Experimental

The Ag/Al_2O_3 catalyst was prepared by impregnating Al_2O_3 powders (230 m^2/g, CONDEA Pural-SB) with an aqueous solution of silver nitrate (4.68×10^{-2} mol/l) and then drying at 393 K for 3 h. The powders were then calcined in air at 873 K for 3 h. Ag content was 4.6 wt%, as revealed by atomic absorption spectroscopy. The catalytic activity of the Ag/Al_2O_3 catalyst for lean NO_x reduction was evaluated in the presence and absence of 80 ppm SO_2 under a model gas flow containing 800 ppm NO, 10% O_2, 10% H_2O and 1565 ppm C_2H_5OH (N_2 balance, 1800 cm^3/min). Interaction between the Ag/Al_2O_3 surface and SO_2 was evaluated by temperature-programmed desorption (TPD) with mass spectroscopy measurements.

The SO_2-treated Ag/Al_2O_3 catalysts (4.6 wt% of Ag) were obtained by exposing the Ag/Al_2O_3 catalysts to the $SO_2/O_2/H_2O$ flow containing 200 ppm SO_2, 10% O_2 and 10% H_2O (N_2 balance, 1000 cm^3/min) at 723 K for 20 h (SO_2-treated (i)) and the $SO_2/O_2/NO/H_2O$ flow containing 200 ppm SO_2, 10% O_2, 800 ppm NO, and 10% H_2O (N_2 balance, 1000 cm^3/min) at 723 K for 4, 10 and 20 h (SO_2-treated (ii)).

The catalytic activity of the SO_2-treated catalyst (∅ 0.5–1 mm, about 0.5 g, 0.6 cm^3) for NO_x reduction was evaluated using a fixed-bed flow reactor containing a model gas stream consisting of 800 ppm NO, 10% O_2, 10%

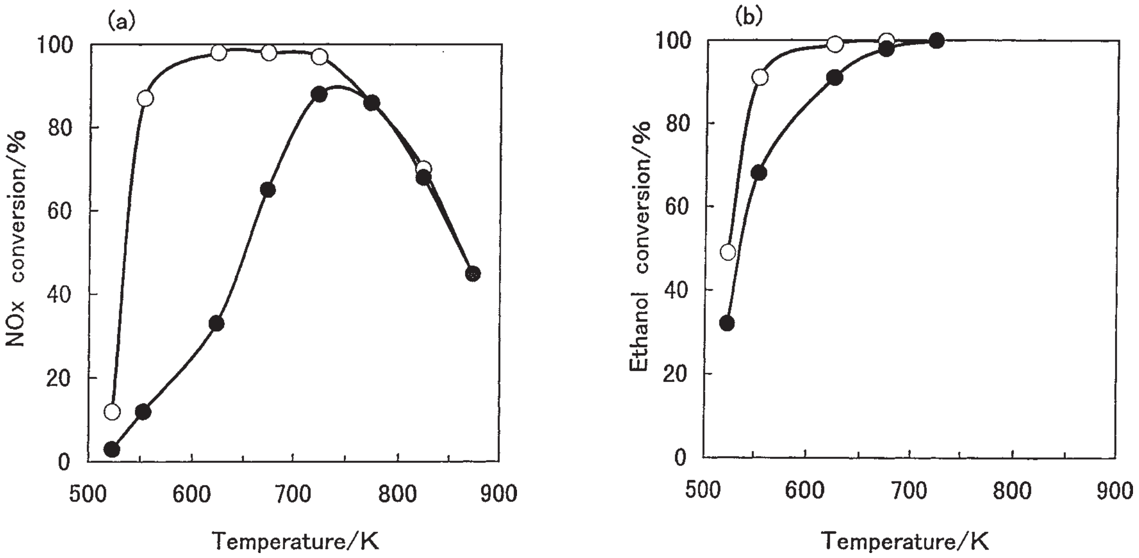

Figure 1. Conversion of NO_x (a) and ethanol (b) on the Ag/Al_2O_3 catalyst. Test conditions: NO 800 ppm, O_2 10%, C_2H_5OH 1565 ppm, H_2O 10%, (○) SO_2 0 ppm, (●) SO_2 80 ppm, N_2 balance, $W/F = 0.05$ g s/m^3, flow rate 1800 cm^3/min, catalyst weight 1.5 g.

H_2O, 1565 ppm C_2H_5OH and 30 ppm SO_2 (N_2 balance, 1500 cm^3/min).

The SO_2-treated Ag/Al_2O_3 catalysts were characterized using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM).

XRD patterns were obtained with a Mac Science MXP3 using nickel-filtered copper Kα ($\lambda = 0.15405$ nm) radiation. The mean particle size and the morphology of the silver on Al_2O_3 were observed by SEM (Hitachi S-5000). XPS spectra (Shimadzu ESCA-750) were obtained with a Mg Kα source ($h\nu = 1253.6$ eV) and a background pressure below 3×10^{-7} Torr.

3. Results and discussion

Catalytic reduction of lean NO_x over the Ag/Al_2O_3 catalyst was studied using a model gas flow containing ethanol as a reductant. Figure 1 shows the conversions of NO_x and C_2H_5OH over the Ag/Al_2O_3 catalysts in the presence or absense of SO_2. The conversion of C_2H_5OH was high above 600 K in the absence of SO_2 and more than 80% of the NO_x was reduced around 600–700 K while the conversions of C_2H_5OH and NO_x were suppressed below 700 K in the presence of SO_2. High reduction of NO_x was, however, attainable above 700 K even in the presence of 80 ppm SO_2.

The behavior of SO_2 on the Ag/Al_2O_3 catalyst was evaluated by the TPD method with mass spectroscopy after exposing the Ag/Al_2O_3 catalyst (3.0 g) to a gas mixture of 200 ppm SO_2, 10% O_2 and N_2 balance (flow rate 1000 cm^3/min) at 573 K for 30 min and then evacuating. Figure 2 shows the TPD spectrum of SO_2. The desorption peaks were observed around 700 K and 1000 K, respectively. In the present work, no other sulfur oxides were detected in the gas phase and the TPD spectrum from the Al_2O_3 exposed to SO_2 and O_2 showed a small SO_2 desorption around 1000 K. Studies by XPS [15,16], TPD [15] and IR [16] show that SO_2 reacts with oxygen to form sulfate on the Ag surface above 500 K [15] and on the Al_2O_3 surface [16] at 673 K. From these results the SO_2 desorbed around 700 K and 1000 K could be ascribed to the decomposition of SO_4 species on Ag sites and on Al_2O_3, respectively.

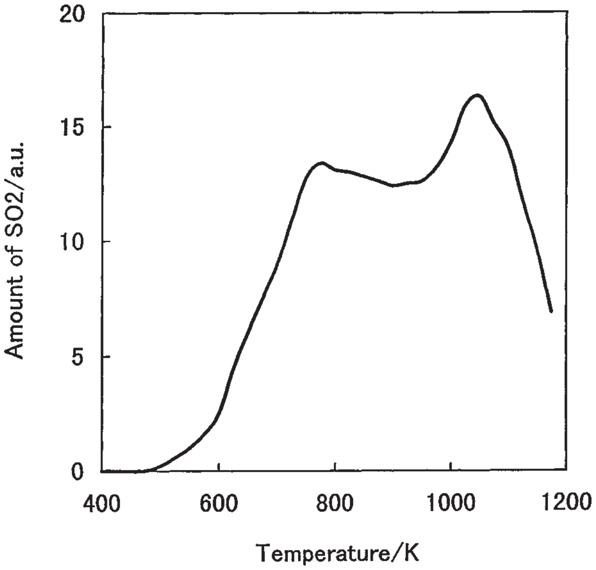

Figure 2. TPD spectrum of SO_2 from the Ag/Al_2O_3 catalyst exposed to the SO_2/O_2 flow. Treatment conditions: SO_2 200 ppm, O_2 10%, N_2 balance, 573 K for 30 min, flow rate 1000 cm^3/min, catalyst weight 3.0 g.

Thus, we suppose that lowering of the NO_x reduction rate as observed in figure 1 can be arisen from occupation of sulfates on catalytically active sites of the Ag/Al_2O_3 catalyst. A large SO_2 desorption peak around 1000 K observed on the Ag/Al_2O_3 catalyst suggests that SO_2 oxidation to SO_3 species is promoted on the Ag site and then the SO_3 species migrate to form sulfate on the Al_2O_3 surface. On

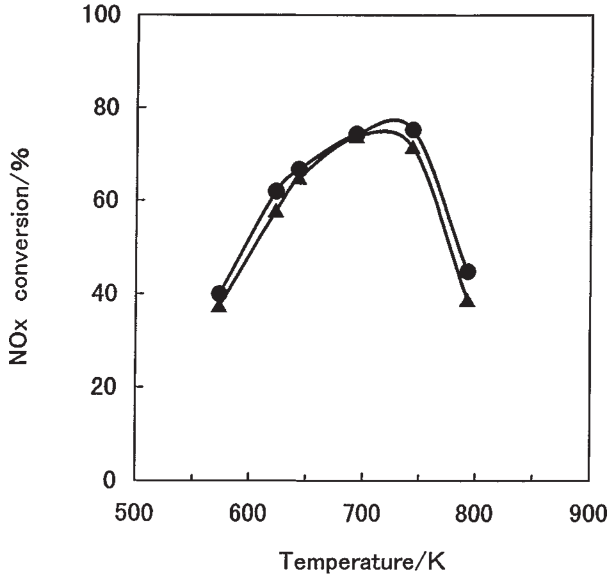

Figure 3. Conversion of NO_x on the fresh Ag/Al_2O_3 catalyst and the SO_2-treated (i) Ag/Al_2O_3 catalyst. (●) Fresh Ag/Al_2O_3, (▲) SO_2-treated (i) Ag/Al_2O_3. Test conditions: NO 800 ppm, O_2 10%, C_2H_5OH 1565 ppm, H_2O 10%, SO_2 30 ppm, N_2 balance, $W/F = 0.02$ g s/cm^3, flow rate 1500 cm^3/min, catalyst weight 0.5 g.

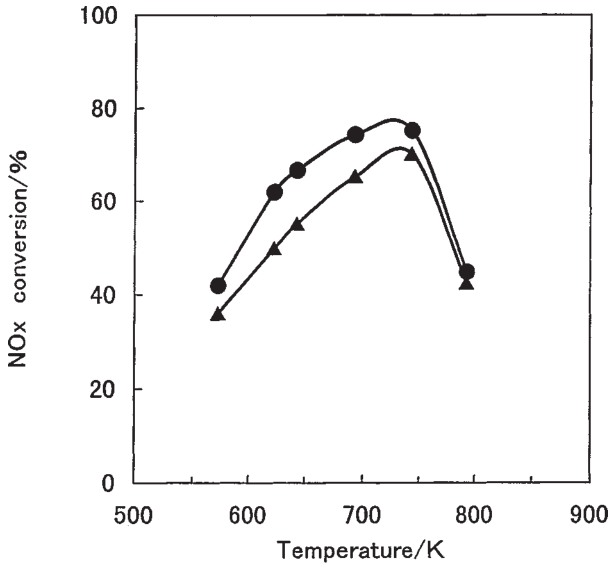

Figure 4. Conversion of NO_x on the fresh Ag/Al_2O_3 catalyst and the SO_2-treated (ii) Ag/Al_2O_3 catalyst. (●) Fresh Ag/Al_2O_3, (▲) SO_2-treated (ii) Ag/Al_2O_3. Test conditions: NO 800 ppm, O_2 10%, C_2H_5OH 1565 ppm, SO_2 30 ppm, H_2O 10%, N_2 balance, $W/F = 0.02$ g s/m^3, flow rate 1500 cm^3/min, catalyst weight 0.5 g.

the other hand, SO_2 desorption from the Ag/Al_2O_3 catalyst at lower temperatures suggests that Ag sites also promote the decomposition of the sulfates for SO_2 desorption.

Table 1
Characteristics of silver or silver compounds in the fresh Ag/Al_2O_3 catalyst and the SO_2-treated (ii) Ag/Al_2O_3 catalyst analyzed by SEM, XRD, XPS and the BET method.

Method	Characteristic	Fresh Ag/Al_2O_3	SO_2-treated (ii) Ag/Al_2O_3
SEM	particle size	∼50 nm	500–1000 nm
XRD	structure of Ag	no XRD peaks	Ag_2SO_4
XPS	BE of Ag(3d)	367.9 eV	367.9 eV
	Ag content	4.4 at%	2.5 at%
BET	specific surface area	221 m^2/g	193 m^2/g

Next, the fresh Ag/Al_2O_3 catalyst was exposed to the $SO_2/O_2/H_2O$ flow around 723 K for 20 h (SO_2-treated (i) Ag/Al_2O_3 catalyst) to evaluate its durability against SO_2. Figure 3 shows the comparison of the NO_x reduction performance between the fresh and the SO_2-treated (i) Ag/Al_2O_3 catalyst evaluated using the model gas. The surprising result is the high NO_x reduction performance on the SO_2-treated (i) Ag/Al_2O_3 catalyst, comparable to the fresh Ag/Al_2O_3 catalyst. On the other hand, the fresh Ag/Al_2O_3 catalyst was exposed to the $SO_2/O_2/NO/H_2O$ flow around 723 K for 20 h (SO_2-treated (ii) Ag/Al_2O_3 catalyst). Figure 4 shows the comparison of the NO_x reduction performance between the fresh and the SO_2-treated (ii) Ag/Al_2O_3 catalyst evaluated using the model gas. The activity of NO_x reduction was still high over the SO_2-treated (ii) Ag/Al_2O_3 catalyst although it decreased at lower temperatures. The characterization of these catalysts was carried out by XRD, as shown in figure 5. As reported in a previous paper [14], no XRD pattern attributable to crystallized silver metal or compounds was observed for the fresh Ag/Al_2O_3 catalyst. Since oxidation of the Ag/Al_2O_3 catalyst in the calcination procedure induces interaction between Ag particles and Al_2O_3, where the Ag particles are grown in size such as thin layers, we concluded that the oxidized Ag particles were not metallic silver but some kinds of silver compounds, and the silver compounds seemed to be stabilized by an interaction between Ag and alumina support. No crystallized silver metal or compounds were detected for the SO_2-treated (i) Ag/Al_2O_3 catalyst either (figure 5(a)). We suppose that catalytically active sites still remained on the Ag/Al_2O_3 surface exposed to the $SO_2/O_2/H_2O$ flow for 10 h on the fresh Ag/Al_2O_3 catalyst. On the other hand, when the fresh Ag/Al_2O_3 catalyst was exposed to the $SO_2/O_2/NO/H_2O$ flow at 723 K for 10 h (SO_2-treated (ii) Ag/Al_2O_3 catalyst), developing of crystallized Ag_2SO_4 was observed by XRD (figure 5(b)).

The SO_2-treated (ii) Ag/Al_2O_3 catalyst was also characterized by SEM and XPS measurements. The characterization of the fresh and the SO_2-treated (ii) Ag/Al_2O_3 catalysts is summarized in table 1.

The size of the SO_2-treated (ii) Ag particles observed by SEM was larger compared to the fresh Ag on Al_2O_3 and averaged about 500–1000 nm.

Figure 6 shows the XPS spectra for the Ag($3d_{5/2}$) region of the fresh and the SO_2-treated (ii) Ag/Al_2O_3 catalysts. The binding energy (BE) for the Ag($3d_{5/2}$) electron appeared at 367.9 eV on the SO_2-treated (ii) Ag/Al_2O_3 catalyst, which was very close to that on the fresh Ag/Al_2O_3 catalyst. Therefore, it is difficult to find the difference of chemical conditions between the fresh and the SO_2-treated (ii) Ag from the BE of the Ag($3d_{5/2}$) electron. However, the peak area for the Ag($3d_{5/2}$) electron was ap-

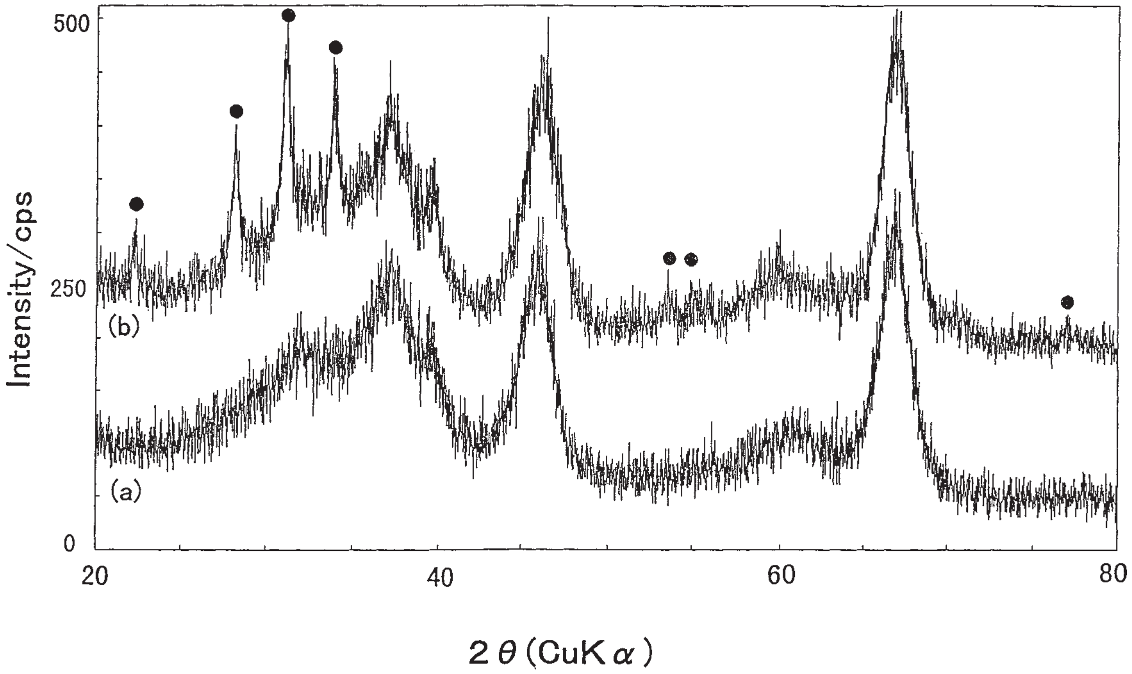

Figure 5. XRD patterns of the SO_2-treated Ag/Al_2O_3 catalysts. Treatment conditions (a): SO_2 200 ppm, O_2 10%, H_2O 10%, N_2 balance, 723 K for 20 h. Treatment conditions (b): SO_2 200 ppm, O_2 10%, NO 800 ppm, H_2O 10%, N_2 balance, 723 K for 10 h. (●) XRD peaks of crystallized Ag_2SO_4.

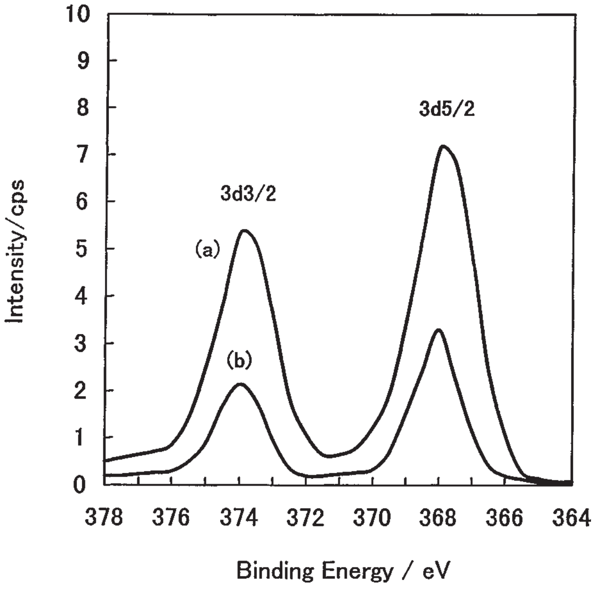

Figure 6. XPS spectra of Ag(3d) from the fresh Ag/Al_2O_3 catalyst (a) and the SO_2-treated (ii) Ag/Al_2O_3 catalyst (b).

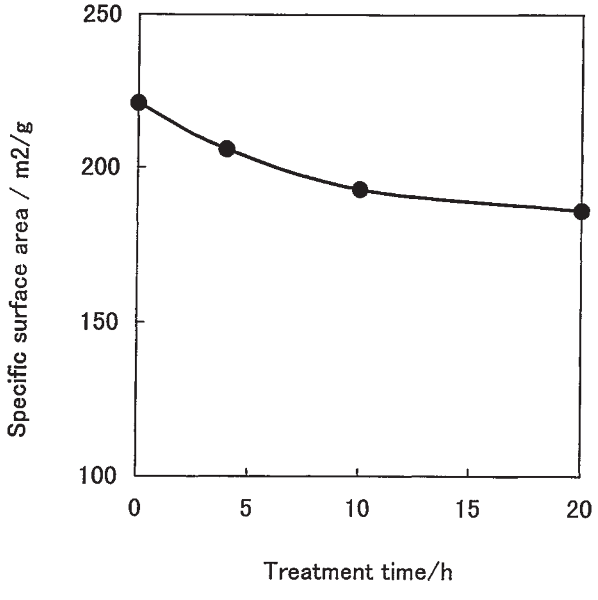

Figure 7. Specific surface area of the SO_2-treated (ii) Ag/Al_2O_3 catalyst. Treatment conditions: SO_2 200 ppm, O_2 10%, NO 800 ppm, H_2O 10%, 723 K for 0–20 h, flow rate 1000 cm^3/min, catalyst weight 3.0 g.

parently different for the two catalysts. That is, the apparent amount of silver estimated by XPS (Ag(3d) to Al(2p) peak area ratio) was about 0.56 times smaller on the SO_2-treated (ii) Ag/Al_2O_3 surface than on the fresh Ag/Al_2O_3 surface. We suppose that the amount of silver on the Al_2O_3 surface is actually comparable to that on the fresh Ag/Al_2O_3 catalyst and the formation of larger Ag_2SO_4 particles leads to decreasing of apparent amount of silver on the surface.

A most interesting result is that the SO_2-treated (ii) Ag/Al_2O_3 catalyst exhibits excellent catalytic performance, as shown in figure 4, although crystallized Ag_2SO_4 was partially developed on Al_2O_3. Growing of crystallized Ag_2SO_4 leads to lowering of activity for lean NO_x reduction at lower temperatures.

These results suggest that the SO_2-treated Ag particles supported on the Al_2O_3 surface are also responsible for effective reduction of lean NO_x although the growing of crystallized Ag_2SO_4 leads to lowering of the activity for lean NO_x reduction at lower temperatures. Figures 7 and 8 show the changes of specific surface area and sulfur content observed from Ag/Al_2O_3 catalyst exposed to

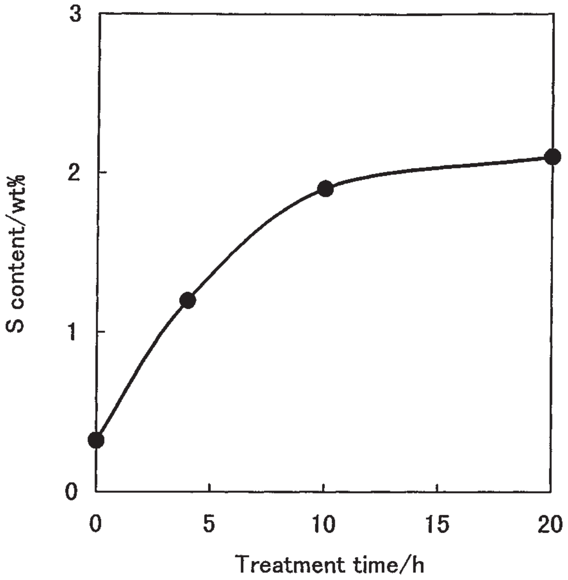

Figure 8. Sulfur content of the SO_2-treated (ii) Ag/Al_2O_3 catalyst. Treatment conditions: SO_2 200 ppm, O_2 10%, NO 800 ppm, H_2O 10%, 723 K for 0–20 h, flow rate 1000 cm^3/min, catalyst weight 3.0 g.

the $SO_2/O_2/NO/H_2O$ flow at 723 K against exposing time (0–20 h). The behavior of sulfur content and specific surface area suggests that the concentration of sulfur is almost saturated at around 2 wt% and the high specific surface area around 190 m^2/g is still kept even after exposure to the $SO_2/O_2/NO/H_2O$ flow for 20 h. At present, the Ag/Al_2O_3 catalyst has been evaluated at 623–823 K in stationary diesel engine exhaust and high NO_x reduction was kept even after the repeated evaluation for 500 h. These results suggest that the Ag/Al_2O_3 catalyst will be a promising candidate for the reduction of NO_x from stationary diesel engine exhaust.

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