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Characterization of highly active silver catalyst for NOx reduction in lean-burning engine exhaust

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A new Ag/Al_2O_3 catalyst for removing NOx in lean exhaust gas was developed. Oxidized Ag/Al_2O_3 catalyst is highly active for reduction of NOx with ethanol and propene, whereas reduced Ag/Al_2O_3 catalyst is less active for these reactions. Selectivity to N_2 is also high on the oxidized Ag/Al_2O_3 compared to that on the reduced Ag/Al_2O_3. XRD and SEM studies of these two types of Ag catalysts suggest that oxidation induces an interaction between Ag and the support, where the particles are grown in large size. In contrast, the metallic Ag particles are finely dispersed by the reduction process. Although dispersion of Ag particles is decreased by the oxidation process, the catalytic activity is increased. This suggests that the Ag–alumina sites created in the high temperature oxidizing environment are active in catalytic reduction of NOx.

Keywords: silver, alumina, nitric oxide, catalytic reduction

1. Introduction

The amount of nitrogen oxides (NOx) released by most internal combustion engines and furnaces exceeds the maximum tolerable level specified in health and environmental protection regulations. Specifically, a large number of diesel engines and lean-burning gasoline engines are the major sources of NOx. An effective catalyst for reducing the amount of NOx in lean-burning engine exhaust, however, is yet unavailable.

Studies of catalytic reduction of NOx with hydrocarbons in the presence of oxygen have been carried out on alumina [1], zeolites [2–4], metal-supported catalysts [5–7], and copper-exchanged ZSM-5 [8]. Among these, Cu-ZSM-5 was reported to be a promising catalyst for reduction of NOx in lean-burning engine exhaust. However, the activity of the Cu-ZSM-5 catalyst decreases in the presence of water vapor, and the catalyst loses its activity when the temperature exceeds 800 K. Therefore, the Cu-ZSM-5 catalyst is still far from being effective for reduction of NOx in lean-burning engine exhaust.

In these circumstances, a new promising catalyst has been found for NOx reduction in oxidizing atmosphere by the present authors. This is an alumina-supported silver (Ag/Al_2O_3) catalyst [9]. When ethanol is used as the reducing reagent, about 80% of NOx in diesel engine exhaust can be removed [10,11]. At present, this Ag/Al_2O_3 catalyst is being used in practice for cleaning oxygen-rich exhaust gas from industrial stationary sources [11]. Catalytic activity and selectivity of this Ag/Al_2O_3 catalyst, however, are highly dependent on the catalyst preparation and pretreatment conditions, especially the atmosphere in which the catalyst is calcined [12].

In this paper, the effects of calcination of Ag/Al_2O_3 in an oxidative atmosphere and a reductive atmosphere were examined, the structure of the silver on Al_2O_3 was studied using XRD, SEM, and XPS, and the activity for NOx reduction was discussed in terms of the surface structure of the Ag/Al_2O_3 catalyst.

2. Experimental

The Ag/Al_2O_3 catalyst was prepared by impregnating γ-Al_2O_3 pellets (2–4 mm ø, 200 m^2/g, Catalysts and Chemicals Ind. Co., Ltd.) with an aqueous solution of silver nitrate (4.63×10^{-2} mol/cm^3), and drying the impregnated pellets at 393 K for 3 h. The pellets were then calcined in a H_2 flow of 500 cm^3/min at 573 K for 3 h and calcined again in a N_2 flow of 1000 cm^3/min at 873 K. The Ag content was 5 wt%. The Ag/Al_2O_3 catalyst produced by this procedure was named "reduced Ag/Al_2O_3 catalyst". The oxidized Ag/Al_2O_3 catalyst (5 wt% of Ag) for comparison was obtained by calcining the reduced Ag/Al_2O_3 catalyst in a N_2/O_2 flow containing 10% oxygen and balance N_2 of 1000 cm^3/min at 873 K for 3 h.

The catalytic activity of the reduced and the oxidized catalysts (approximately 3.68 g, 8.84 cm^3) for NOx reduction was evaluated using a fixed-bed flow reactor. In the reactor, a simulated exhaust gas stream containing 800 ppm NO, 10% O_2, 1714 ppm C_3H_6 (or 1516 ppm C_2H_5OH) and balance N_2 was flowing at a rate of 4420 cm^3/min. The N_2 selectivity of the reduced and the oxidized catalysts during NOx reduction was evaluated using gas chromatography, where a simulated gas containing 800 ppm NO, 10% O_2, 1714 ppm C_3H_6, 10%

H_2O and balance He of a flow rate of 4420 cm ^{3}/min was used.

The Ag/Al_2O_3 catalysts were crushed into powder and characterized using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) measurements, and the catalytic activities of these catalysts for reduction of NOx were compared.

XRD spectra were obtained with a MAC Science-MXP3 using nickel-filtered copper Kα ($\lambda = 1.54050$ Å) radiation. The mean particle size and the morphology of the silver on Al_2O_3 were determined by SEM analysis (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^{-5} Torr.

3. Results and discussion

Catalytic reduction of NOx over the reduced and the oxidized Ag/Al_2O_3 catalysts was studied using a simulated exhaust gas stream containing propene or ethanol as the reductant. Fig. 1 shows the reduction of NOx with propene over the reduced Ag/Al_2O_3 catalyst and over the oxidized Ag/Al_2O_3 catalyst. The conversion rate of NOx at approximately 700 K was about 50% over the reduced Ag/Al_2O_3 catalyst, while with the oxidized Ag/Al_2O_3 catalyst the conversion rate was greater than 80%. In other words, the oxidized Ag/Al_2O_3 was more efficient for NOx reduction. This result shows that, in any case, the Ag/Al_2O_3 catalyst is promising for NOx reduction under lean-burning conditions.

Fig. 2 shows the reduction of NOx by ethanol over the reduced catalyst and the oxidized Ag/Al_2O_3 catalyst. By comparing figs. 1 and 2, it can be clearly seen that the optimum NOx reduction temperature was lowered by the use of ethanol, as opposed to propene, for both catalysts. The activity windows were similar, however. These results show that, compared to the reduced Ag/Al_2O_3 catalyst, the oxidized Ag/Al_2O_3 catalyst has a higher activity for NOx reduction by hydrocarbon ($NOx + O_2 + HC \rightarrow N_2 + CO_2(CO) + H_2O$) as well as by ethanol in the presence of oxygen.

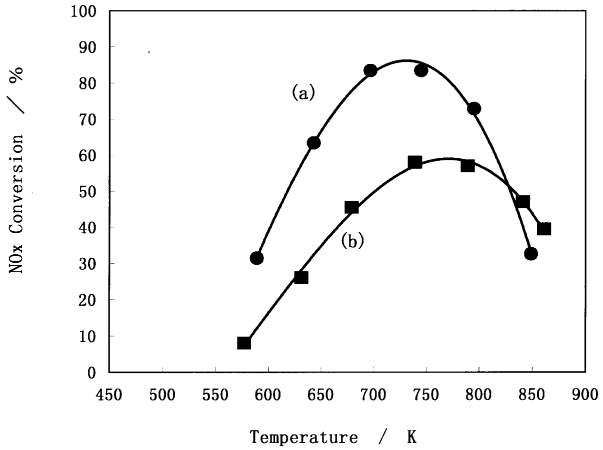

Fig. 1. Reduction of NOx by propene on the oxidized Ag/Al_2O_3 catalyst (a) and the reduced Ag/Al_2O_3 catalyst (b). Test conditions: 800 ppm NO, 10% O_2, 1714 ppm C_3H_6, SV = 30000 h^{-1}, flow rate = 4420 cm^3/min, catalyst volume = 8.84 cm^3.

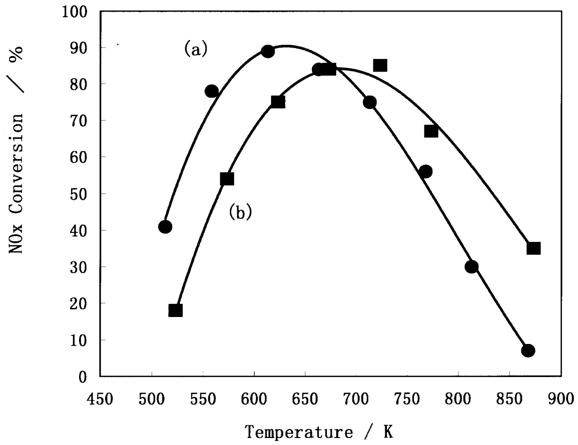

Fig. 2. Reduction of NOx by ethanol on the oxidized Ag/Al_2O_3 catalyst (a) and the reduced Ag/Al_2O_3 catalyst (b). Test conditions: 800 ppm NO, 10% O_2, 1563 ppm C_2H_5OH, balance N_2, SV = 30000 h^{-1}, flow rate = 4420 cm^3/min, catalyst volume = 8.84 cm^3.

Conversion of NOx to N_2 measured using a simulated gas flow containing 10% water vapor over the oxidized Ag/Al_2O_3 catalyst is shown in fig. 3. According to observation, the activity of the oxidized Ag/Al_2O_3 catalyst for NOx reduction is high in the presence of water vapor, and its selectivity to N_2 is also high as compared to those of the reduced Ag/Al_2O_3 catalyst.

To emphasize the differences between the oxidized

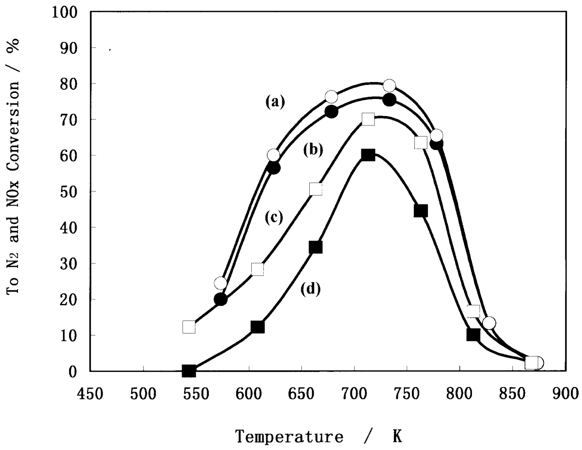

Fig. 3. Selectivity to N_2 and activity of NOx reduction in water vapor. (a) NOx conversion over oxidized Ag/Al_2O_3 catalyst; (b) conversion to N_2 over oxidized Ag/Al_2O_3 catalyst; (c) NOx conversion over reduced Ag/Al_2O_3 catalyst; (d) conversion to N_2 over reduced Ag/Al_2O_3 catalyst. Test conditions: 800 ppm NO, 10% O_2, 1714 ppm C_3H_6 ($C_3H_6/NO = 3$), balance He, SV = 30000 h^{-1}, flow rate = 4420 cm^3/min, catalyst volume = 8.84 cm^3.

Table 1
Characteristics of silver/silver compounds in the oxidized Ag/Al_2O_3 catalyst and the reduced Ag/Al_2O_3 catalyst analyzed with SEM, XRD, and XPS

	Oxidized Ag/Al_2O_3	Reduced Ag/Al_2O_3
SEM		
particle size (nm)	~ 50	~ 10
dispersion	poor	good
XRD		
structure of Ag	no XRD peaks	metal silver
crystallite size (nm)	–	7.4
XPS		
BE of Ag(3d) (eV)	367.92	367.92
Ag content (at%)	4.40	2.49

catalyst and the reduced catalyst, the two Ag/Al_2O_3 catalysts were characterized using XRD, SEM and XPS. The results are summarized in table 1.

Fig. 4 shows the XRD spectra of the reduced Ag/Al_2O_3 catalyst, the oxidized Ag/Al_2O_3 catalyst and a reference alumina sample. Distinct XRD patterns attributable to crystallized silver metal and γ-alumina were observed from the reduced Ag/Al_2O_3 catalyst. However, no XRD pattern attributable to crystallized silver metal or compounds could be obtained from the oxidized Ag/Al_2O_3 catalyst. The average size (7.4 nm) of the silver crystallites was estimated from the broadening of the corresponding X-ray diffraction line.

Fig. 5 shows SEM photographs of reduced Ag/Al_2O_3 and oxidized Ag/Al_2O_3 catalysts to demonstrate the distribution of Ag particles and their morphology on the surface of Al_2O_3. As shown in fig. 5, the reduced Ag/Al_2O_3 catalyst had spherical Ag particles of a mean particle size of 10 nm that were well dispersed over the Ag/Al_2O_3 surface. On the other hand, the particles of the oxidized catalyst were larger, attributable to the oxidation of Ag/Al_2O_3, and averaged about 50 nm in size.

Fig. 6 shows the XPS of the Ag($3d_{5/2}$) on the oxidized Ag/Al_2O_3 catalyst and the reduced Ag/Al_2O_3 catalyst. The binding energy (BE) of the Ag($3d_{5/2}$) electron on the oxidized Ag/Al_2O_3 catalyst was 367.9 eV, which is very close to that on the reduced Ag/Al_2O_3 catalyst. Therefore, it is difficult to distinguish metallic silver from oxidized silver by using the BE of the Ag($3d_{5/2}$) electron [13]. It is worth noting that the integrated area of the Ag($3d_{5/2}$) electron peak may be proportional to the silver content on alumina. However, the results showed a discrepancy in silver content between the two catalysts. That is, the apparent silver content on the oxidized Ag/Al_2O_3 catalyst estimated from XPS results (Ag(3d) to Al(2p) peak area ratio) is about 1.7 times larger than on the reduced catalyst, while the two catalysts were supposed to have the same bulk silver content (5 wt%). The results obtained by XRD, SEM and XPS are summarized in table 1.

The results of this study show that oxidizing the silver particles on alumina is effective for lean NOx reduction. The interaction of oxygen with silver surface and supported silver particles has been studied by other researchers using XRD, IR, TPD, SEM and XPS [13–16]. Yanase and Komiyama reported that silver particles on silver undergo a change in shape to become oblate spheroids when exposed to oxygen at elevated temperature [17]. Tanaka et al. showed a reconstructive growth of (–Ag–O–) chains on a silver(110) surface using STM and that these (–Ag–O–) chains make a complex arrangement on the surface [18]. Bao et al. also showed the reconstruction of an Ag(111) surface in O_2 at temperatures higher than 800 K using STM, which was explained in terms of formation of an oxygen containing phase in the subsurface [19]. Meima et al. concluded from TPD measurements that a substantial quantity of oxygen could dissolve into the bulk silver lattice of supported polycrystalline silver causing reordering of the surface [15]. These results suggest that oxidation of Ag/Al_2O_3 changes the surface structure as well as the morphology of silver particles on alumina. It should be pointed out that no XRD patterns relating either to

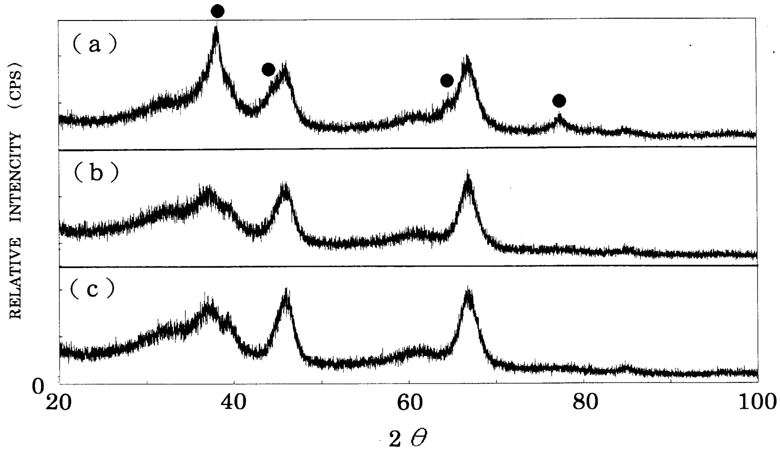

Fig. 4. XRD spectra from the oxidized Ag/Al_2O_3 catalyst (a) and the reduced Ag/Al_2O_3 catalyst (b). (●) XRD peaks from metallic silver.

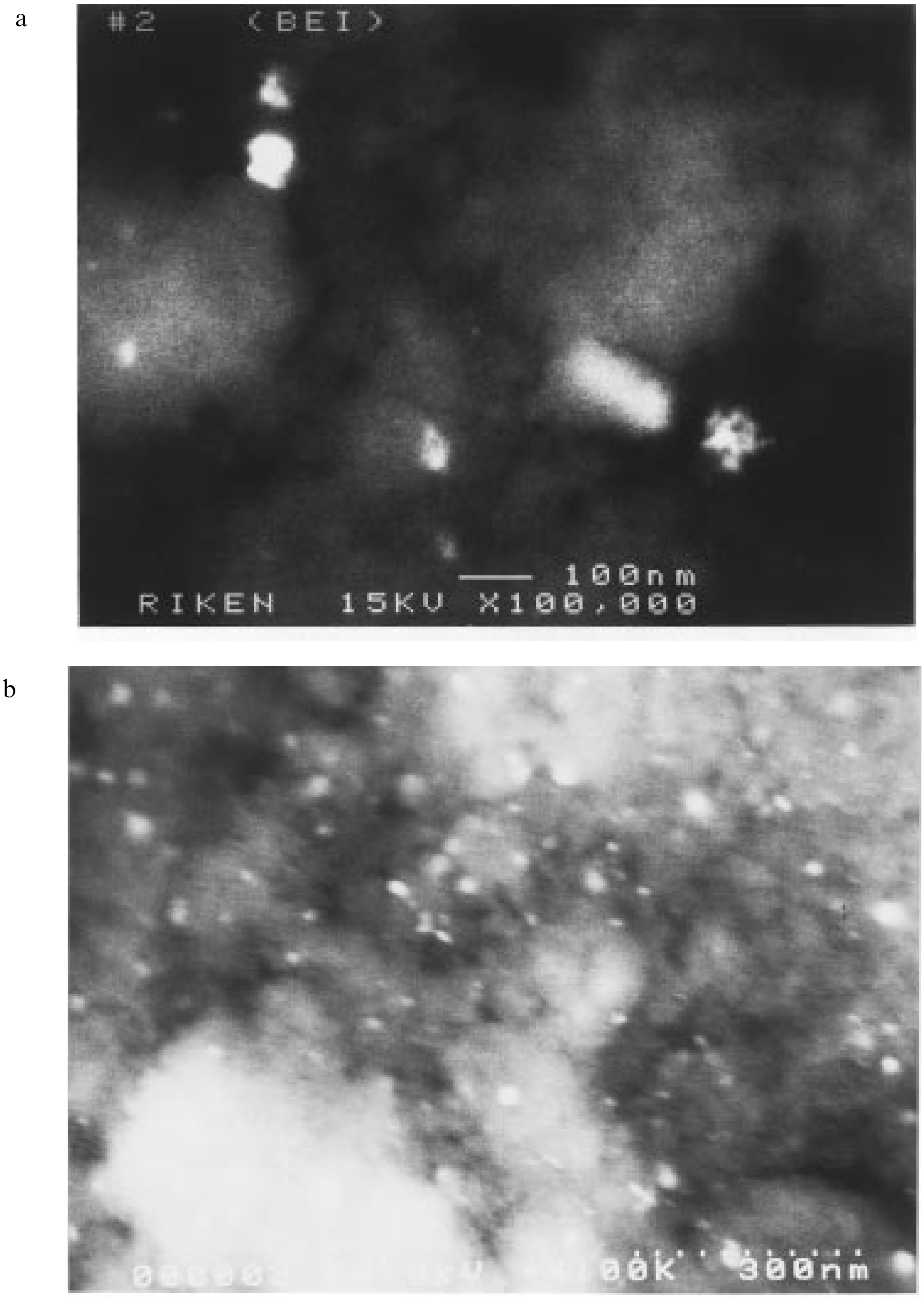

Fig. 5. SEM photographs from the oxidized Ag/Al_2O_3 catalyst (a) and the reduced Ag/Al_2O_3 catalyst (b).

metallic silver crystal or to silver compounds were found for oxidized Ag/Al_2O_3 catalyst, although the corresponding SEM image indicated particle growth on the surface. Therefore, it can be concluded that the particles were not metallic silver but some kind of silver compounds. The observed particle growth by oxidation may not be related to the aggregation of small particles, as commonly observed in sintering of metallic particles, because the XPS signal for Ag(3d) was almost doubled in peak area by oxidation. Consequently, high catalytic activity and selectivity for NOx reduction under lean-burn conditions was attained on the oxidized catalyst but not on the surface of the reduced catalyst.

It should be pointed out that Ag catalyst on Al_2O_3 has a rather high catalytic activity for NOx reduction, but Ag catalyst on other oxides is far less active for the reaction [20]. This suggests the importance of metal–support interaction in NOx reduction. The authors also found that Ag compounds such as sulfate and chloride supported on Al_2O_3 exhibit a rather high catalytic activ-

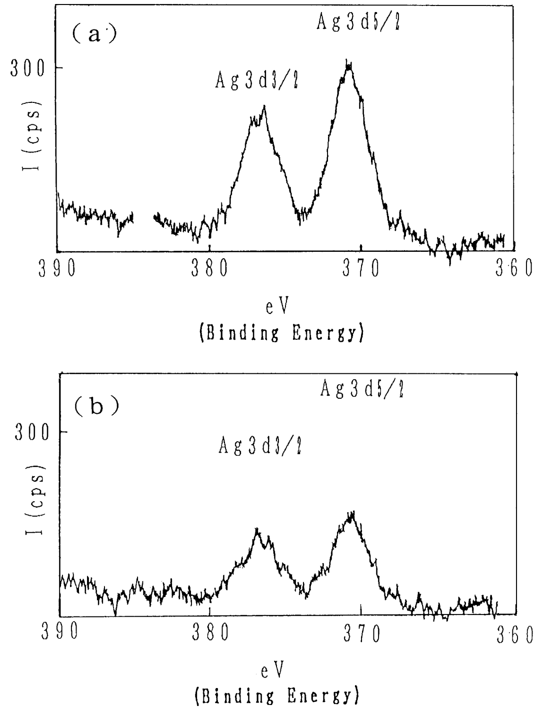

Fig. 6. XPS spectra of Ag(3d) from the oxidized Ag/Al_2O_3 catalyst (a) and the reduced Ag/Al_2O_3 catalyst (b).

ity for NOx reduction. Taking these facts into account, it may be concluded that the Ag compounds formed during catalysis are stabilized on the Al_2O_3 surface, which, in turn, is responsible for the high catalytic activity exhibited by Ag/Al_2O_3.

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