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Selective reduction of NO on Ag/Al_2O_3 catalysts prepared from boehmite needles

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Abstract

Ag/Al_2O_3 catalysts prepared from boehmite needles (ca. 10 nm×100 nm), which were formed by a hydrolysis of aluminium tri-isopropoxide (AIP), showed good performances for selective catalytic reduction of NO_x compared with the previously reported catalysts [N. Aoyama, K. Yoshida, A. Abe, T. Miyadera, Catal. Lett. 43 (1997) 249], especially when ethanol is employed as a reducing agent in the presence of water. Temperature programmed reduction (TPR) study revealed that the Ag species are attractively interacted with the alumina surface and the oxidized Ag species contribute positively for the improvement of the catalytic activity at the temperatures above 750 K. It is concluded that the boehmite needles as a precursor of alumina support are useful to create the catalytically active sites for NO_x reduction. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: NO_x reduction; Ag/Al_2O_3 catalyst; Boehmite needles; SO_2

1. Introduction

Many efforts have still been continuing to develop new catalysts for reduction of NO_x in lean-burning engine exhaust since the report of the novel Cu-ZSM5 catalyst by Iwamoto et al. [2]. Selective catalytic reduction of NO_x has been studied on alumina [3], zeolite [4–6] and metal-supported catalysts [7,8] with hydrocarbons in the presence of excess oxygen. Among those catalysts, Cu-ZSM5 seems to be a promising catalyst for the selective catalytic reduction of NO_x. However, the Cu-ZSM5 catalyst is deactivated by the presence of water vapor or when the temperature exceeds 800 K. In these circumstances, Miyadera and Yoshida [9] found a new catalyst, Ag/Al_2O_3 catalyst, for NO_x reduction in oxidizing atmosphere and reported that oxygen-containing organic compounds such as ethanol and acetone are effective in the reduction of lean NO_x even in the presence of water vapor. They concluded that the reduced Ag/Al_2O_3 catalyst loses its activity but the oxidized Ag species act effectively for the NO_x reduction. In addition, they also mentioned that the interaction between Ag and Al_2O_3 support is important to inhibit the deactivation caused by the reduction of the oxidized Ag species during the reaction.

In this study, we have attempted to prepare Ag/Al_2O_3 catalysts, where Ag species are interacted successfully with alumina to act for active sites. For this purpose, a sol solution containing boehmite

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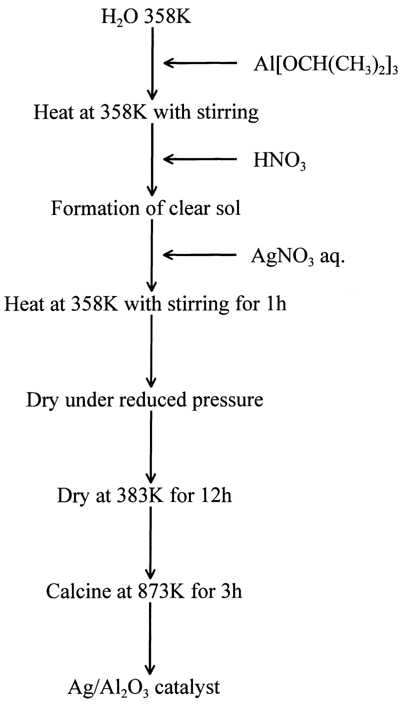
needles (ca. 10 nm×100 nm) has been employed as a precursor of alumina support. It is expected that the boehmite needle (i.e. large surface area) might contribute Ag species to disperse and anchor on the alumina surface, and then the attractive interaction is also expected during the activation procedure from boehmite to γ-alumina. The catalytic activity for NO_x reduction was examined using propene and ethanol as a reducing agent, and the effect SO_2 was also studied. The catalyst was characterized by X-ray diffraction (XRD) and temperature programmed reduction (TPR) method. The activity for NO_x reduction was discussed in terms of the reducing property of Ag species on the Ag/Al_2O_3 catalyst.

2. Experimental

The preparation procedure of Ag/Al_2O_3 catalyst is summarized in Table 1. The sol solution containing boehmite needles was prepared in the following manner. Aluminum tri-isopropoxide (AIP) was added to hot water (358 K) under vigorous stirring, and then a small amount of nitric acid (the mole ratio of "nitric acid/AIP" was 0.11) was introduced into the hot slurry for the peptization of aluminum hydroxide to a clear sol. The boehmite needles in the clear sol solution were confirmed by a transmission electron microscope (TEM) as reported previously [10]. The sol solution was subsequently mixed with an aqueous solution with an adequate amount of $AgNO_3$. After the solution was stirred at 358 K for 1 h, the solvents were eliminated by heating them under reduced pressure, drying, and calcining at 873 K for 3 h. The catalyst thus formed was named Ag/Al_2O_3(Alk). Bare alumina was also prepared from the clear sol solution using the same procedure but the calcination was carried out at 773 K for 4 h. The surface area was 175 $m^2 g^{-1}$. The other catalyst was prepared by an impregnation method using the bare alumina and an aqueous solution of silver nitrate. The catalyst formed was called Ag/Al_2O_3(Imp). Silver content varied from 2.5 to 20 wt% in the catalysts. The Ag/Al_2O_3(Alk) and Ag/Al_2O_3(Imp) catalysts showed no obvious difference in the surface area and the values were around 160–170 $m^2 g^{-1}$.

The catalytic activities of Ag/Al_2O_3 catalysts for NO_x reduction were evaluated using a fixed-bed flow reactor. Several simulated exhaust gas streams consisting of NO, O_2, C_3H_6(or C_2H_5OH) and N_2 were employed. Effect of SO_2 was also examined. The analysis of NO_x was performed using a chemiluminescence detector. Conversion efficiencies of NO_x were plotted as a function of inlet-gas temperature.

Table 1
Preparation procedure of Ag/Al_2O_3 catalysts from boehmite needles



A powder X-ray diffraction apparatus (XRD, Rigaku, Rint-2000) with a Cu K_α source (30 kV, 20 mA) was used for the examination of compounds in the catalysts. In order to characterize the oxidized Ag species on the catalysts, temperature programmed reduction (TPR) measurements were carried out, elevating the temperature up to 873 K with a temperature raising rate of 10 K min^{-1}. During the measurements 10 vol% H_2/Ar was introduced into the reactor, where 0.3 g of the catalyst powder was placed, with a flow rate of 100 ml min^{-1}.

3. Results and discussion

XRD results show that diffraction peaks assigned to γ-Al_2O_3 were observed for the Ag/Al_2O_3(Alk) and the Ag/Al_2O_3(Imp) catalysts, while the peaks assigned to Ag species were detected for the Ag/Al_2O_3(Imp) catalyst above 7.5 wt% of Ag content. No diffraction peaks corresponding to Ag species were detected, however, for the Ag/Al_2O_3(Alk) catalyst up to 20 wt% of Ag content. This indicates that Ag species in the Ag/Al_2O_3(Alk) catalyst are highly dispersed on Al_2O_3. It is presumed that the Ag species is more attractively interacted with the boehmite than the alumina, and then the interaction acts positively for the generation of highly dispersed Ag species when the boehmite is transformed to γ-Al_2O_3 by the activation procedure.

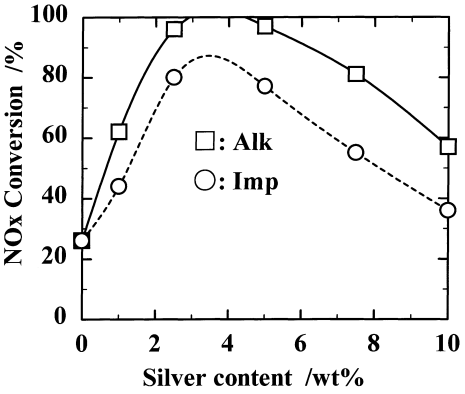


Fig. 1. Reduction of NO_x by propene on Ag/Al_2O_3 catalysts.

In order to survey the catalytic activities of Ag/Al_2O_3 catalysts in various Ag loadings, NO_x reduction was carried out at 773 K, where a simulated gas containing 1000 ppm NO, 5% O_2, 2000 ppm C_3H_6 and balance of N_2 was used. The result is displayed in Fig. 1. The conversion efficiency of NO_x was about 80% on the Ag/Al_2O_3(Imp) catalyst while it was greater than 90% on the Ag/Al_2O_3(Alk) catalyst. In addition, the optimum Ag content for NO_x reduction in both catalysts was found to be around 2.5–5 wt%. This is in agreement with the previous report which suggested that 5 wt% of Ag was the optimum concentration [1]. It is also found that the Ag/Al_2O_3(Alk) catalyst acts effectively for NO_x reduction at the Ag content as low as 2.5 wt%, indicating that the boehmite needles might play an important role for the formation of active Ag species on alumina.

Thus, 5 wt%-Ag/Al_2O_3(Alk) and 5 wt%-Ag/Al_2O_3(Imp) catalysts were chosen to examine the detailed catalytic activities for comparison. The catalysts were submitted to further NO_x reduction using a model gas flow containing 300 ppm NO, 10% O_2, 429 ppm C_3H_6, 10% H_2O and balance of N_2 with *W*/*F* being 0.03 g s cm^{-3}. The effect of SO_2 was also investigated by the addition of 30 ppm SO_2 into above simulated gas. The results are shown in Fig. 2. The activities increased with an increase of temperature but the conversion efficiencies of NO_x at 773 K were about 30% on both catalysts in the presence of water vapor. The effect of SO_2 was not clear. The difference in the activity by the preparation method either the sol–gel or the impregnation was not realized in the conditions.

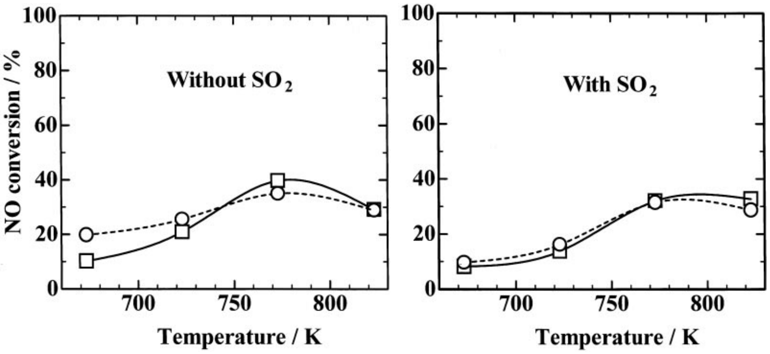


Fig. 2. Effect of SO_2 for reduction of NO_x by propene on 5 wt% Ag/Al_2O_3 catalysts. (□) Alk, (○) Imp.

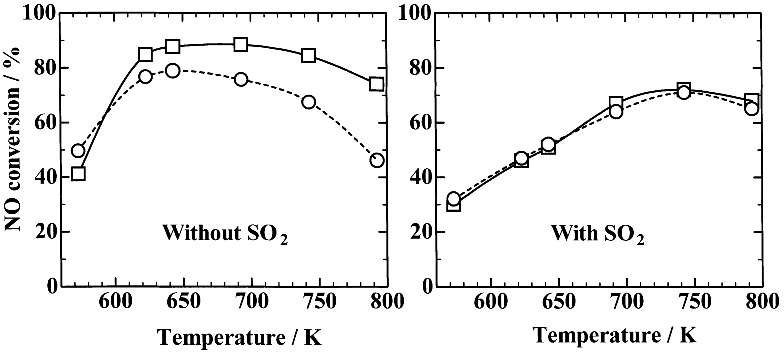


Fig. 3. Effect of SO_2 for reduction of NO_x by ethanol on 5 wt% Ag/Al_2O_3 catalysts. (□) Alk, (○) Imp.

The NO_x reduction by ethanol as the reductant was also carried out using the simulated gas containing 800 ppm NO, 10% O_2, 1565 ppm C_2H_5OH, 10% H_2O and balance of N_2 with W/F being 0.01 g s cm^{-3}. The effect of SO_2 was investigated by the addition of 30 ppm SO_2, too. Fig. 3 shows the reduction of NO_x by ethanol over 5 wt%-Ag/Al_2O_3(Alk) and 5 wt%-Ag/Al_2O_3(Imp) catalysts. The conversion efficiencies were enhanced from 30% to 70–90% in the presence of ethanol instead of propene, indicating that ethanol is a more favorable reducing agent than propene for NO_x reduction, especially on Ag/Al_2O_3 catalysts. By comparing Figs. 2 and 3, it can be clearly seen that the optimum NO_x reduction temperature was lowered by the use of ethanol for the catalysts. It was also found that the activity on the Ag/Al_2O_3(Alk) catalyst was improved, especially at high temperature, in the absence of SO_2 compared with a previous result [1]. The conversion efficiency of NO_x around 650–750 K was more than 80% while it was suppressed strongly below 650 K when SO_2 was present. On the other hand, the Ag/Al_2O_3(Imp) catalyst showed relatively lower activity in the NO_x reduction than the Ag/Al_2O_3(Alk) catalyst in the absence of SO_2. When SO_2 existed, the conversion efficiency of NO_x was also lowered below 650 K, resulting in that the profile of NO_x conversion was almost the same as with the Ag/Al_2O_3(Alk) catalyst. High reduction of NO_x was however, attainable around 700 K even in the presence of SO_2. The behavior of SO_2 on Ag/Al_2O_3 catalysts was evaluated using temperature programmed desorption (TPD) spectra of sulfur compounds from SO_2 treated Ag/Al_2O_3 catalyst. The SO_2 desorption started from around 500 K and two peaks were observed around 700 and 1000 K, respectively. No other sulfur oxide was detected in the gas phase. The desorbed SO_2 could be ascribed to the decomposition of SO_4 species. Thus, we suppose that the lowering of NO_x reduction activity below 650 K might be due to the occupation of sulfates on catalytically active site of Ag/Al_2O_3 catalyst. The SO_2 desorption around 700 K suggested that Ag species might promote both the decomposition of the sulfates and the desorption of SO_2, resulting in the high activity. The detailed study will be published elsewhere [11]. This result shows that the Ag/Al_2O_3 catalyst is still promising for NO_x reduction under lean-burning conditions.

The clear difference between Ag/Al_2O_3(Alk) and Ag/Al_2O_3(Imp) catalysts was only observed in the NO_x reduction when ethanol and water vapor coexisted in the simulated gas. No difference in the activity was realized in the other conditions since the property of active Ag species, probably, seem to be modified by SO_2. As described before, the catalytically active Ag species were the oxidized Ag species, which were formed by the interaction between Ag and the alumina support [1]. Thus, in order to measure the stability of the oxidized Ag species, the catalysts were characterized by the TPR measurements in temperatures from 300 to 873 K. Displayed in Fig. 4, the Ag/Al_2O_3(Alk) and Ag/Al_2O_3(Imp) catalysts provided the peaks with almost the same temperature around 373 K and no other peaks were detected at the temperatures up to 873 K. However, large hydrogen consumption was observed on the Ag/Al_2O_3(Imp) catalyst, indicating that the oxidized Ag species are easily reduced at

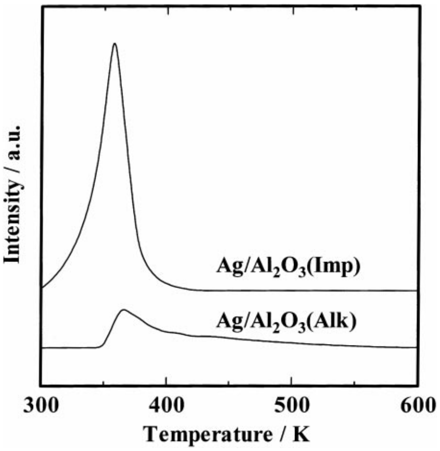


Fig. 4. TPR spectra of the 5 wt% Ag/Al_2O_3 catalysts.

temperatures as low as 373 K. On the other hand, the consumption of hydrogen was small on the Ag/Al_2O_3(Alk) catalyst. This means that the Ag species are stabilized by the interaction between Ag and the alumina support, and then the oxidized Ag species play as the catalytically active species. Consequently, the Ag/Al_2O_3(Alk) catalyst shows a good catalytic performance by the use of ethanol as the reducing agent. Furthermore, this attractive interaction could lead to high activity at a temperature above 750 K, at which the activity usually was lowered as reported previously [1]. We believe that this interaction could be generated during the structural change from boehmite to γ-alumina and deposited Ag species may be anchored with the relatively strong force on the alumina. It could be concluded that the boehmite needles are the efficient precursors of alumina support for this purpose.

Acknowledgements

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