Reduction of lean NOx by ethanol over Ag/Al_2O_3 catalysts in the presence of H_2O and SO_2

Satoshi Sumiya [a], Mika Saito [a], Hong He [a], Qing-Cai Feng [a], Nobutsune Takezawa [b]
and Kiyohide Yoshida [a]

[a] *Research and Development Division, Riken Corporation, Kumagaya, Saitama 360, Japan*
[b] *Division of Material Science and Engineering, Graduate School of Engineering, Hokkaido University, Sapporo 060, Japan*

Received 16 July 1997; accepted 28 November 1997

The reduction of lean NOx using ethanol in simulated diesel engine exhaust was carried out over Ag/Al_2O_3 catalysts in the presence of H_2O and SO_2. The Ag/Al_2O_3 catalysts are highly active for the reduction of lean NOx by ethanol but the reaction is accompanied by side reactions to form CH_3CHO, CO along with small amounts of hydrocarbons (C_3H_6, C_2H_4, C_2H_2 and CH_4) and nitrogen compounds such as NH_3 and N_2O. The presence of H_2O enhances the NOx reduction while SO_2 suppresses the reduction. The presence of SO_2 along with H_2O suppresses the formation of acetaldehyde and NH_3. By infrared spectroscopy, it was revealed that the reactivity of NCO species formed in the course of the reaction was greatly enhanced in the presence of H_2O. The NCO species readily reacts with NO in the presence of O_2 and H_2O at room temperature, being converted to N_2 and CO_2 (CO). Addition of SO_2 suppresses the formation of NCO species and lowers the reactivity of the NCO species. However, the reduction of NOx is still kept at high conversion levels in the presence of H_2O and SO_2 over the present catalysts. About 80% of NOx in the simulated diesel engine exhaust was removed at 743 K.

Keywords: Ag/Al_2O_3, NOx, SO_2, H_2O, NCO species

1. Introduction

Recently, great interest has been aroused from the use of hydrocarbons for the reduction of NOx in diesel engine exhaust and other oxygen-rich flue gases [1–8]. However, the reduction of NOx by hydrocarbons is usually suppressed in the presence of H_2O or SO_2 [4]. Hence, effective reduction of lean NOx has not been developed yet.

Miyadera et al. [9,10] reported that oxygen-containing organic compounds such as ethanol, acetone and acetaldehyde are extremely effective for the reduction of lean NOx over Ag/Al_2O_3 even in the presence of H_2O, while H_2O inhibits the reduction of lean NOx by propene. The reduction of NOx is accompanied by side reactions to form CH_3CHO, CO along with small amounts of hydrocarbons (C_3H_6, C_2H_4, C_2H_2 and CH_4) and nitrogen compounds such as NH_3 and N_2O. We also studied the effect of H_2O on the reduction of lean NOx by ethanol and acetaldehyde and on the formation of by-products over Ag/Al_2O_3 [11]. H_2O was found to enhance the NOx reduction by ethanol or acetaldehyde.

In recent years, the involvement of surface NCO species as an intermediate of the NOx reduction by hydrocarbons has been presented [12–17]. We previously found that the surface NCO species were involved in the reduction of NOx by ethanol on Ag/Al_2O_3 as an important intermediate species [18]. The addition of O_2 was found to enhance the reaction of NCO species with NO in the absence of H_2O, and N_2 and CO_2 (CO) were produced even at room temperature. Voorhoeve et al. also postulated that NCO species are responsible for the formation of NH_3 in the reaction with H_2O or H_2 [19]. These results suggest that the formation of NCO species and the reactivity of NCO species towards NO are closely related to the NOx reduction and the formation of by-products. However, no experiments have been so far conducted for the effects of H_2O and SO_2 on the reactivity of the NCO species in the reduction of NOx by ethanol to our knowledge. Since the emissions of H_2O and SO_2 from practical diesel engines are actually unavoidable, the effects of these species on the NOx reduction should also be inspected.

Under these circumstances, the present work is aimed to study the effect of H_2O and SO_2 on the reduction of NOx by ethanol and on the reactivity of NCO species over Ag/Al_2O_3 catalysts. We show that the reactivity of the NCO species for the formation of N_2 and CO_2 is greatly enhanced in the presence of H_2O, while SO_2 suppresses the formation of the NCO species and the reactivity of the NCO species. This leads to the enhancement of the NOx reduction in the presence of H_2O and the decreased reduction of NOx in the presence of SO_2.

2. Experimental

An alumina-supported silver powder catalyst (4.0 wt% Ag) was obtained by impregnation of γ-Al_2O_3 powder (2–4 mm ⊘, 197.5 m^2/g: Mizusawa Chemicals

Co. Ltd.) with an aqueous solution of silver nitrate. The sample was dried at 393 K for 3 h and calcined at 873 K for 3 h in air.

Ag/Al_2O_3 powder thus prepared was mounted on the square-celled extruded cordierite in a honeycomb shape (200 cells/inch^2, ∅ 20 mm×16.7 mm). The reduction of NOx by ethanol was carried out over the Ag/Al_2O_3 catalyst supported on cordierite honeycomb in a fixed-bed reactor with a gas mixture containing 800 ppm NO and 10.0 vol% O_2 with a balance of N_2 or He at a total flow rate of 3,480 cm^3/min, in a temperature range of 473–873 K. An ethanol/NO mass ratio at the inlet of the reactor is always kept at 3.0. Inlet concentrations of H_2O and SO_2 were maintained at 10 vol% (or 0) and 80 ppm (or 0), respectively. GHSV was estimated to be 40,000 h^{-1}. Ethanol and H_2O were separately supplied with micropumps into the gas stream and vaporized by a coiled heater at the inlet of the reactor. The concentration of NOx ($NO + NO_2$) was determined by use of a chemiluminescence based NO/NOx analyzer (Yanagimoto Co. Ltd).

FT-IR spectra were obtained on a Nicolet Magna 550 infrared spectrophotometer with a resolution of 2 cm^{-1}. The IR sample was prepared by pressing the Ag/Al_2O_3 powder into a wafer of ca. 20 mg/cm^2 and fixed to the sample holder in an IR cell made of Pyrex glass as described in previous papers [18]. Prior to the experiments, the sample was heated to 573 K for 30 min followed by brief pumping at room temperature. All IR measurements were carried out at room temperature.

3. Results and discussion

3.1. NOx reduction in the presence of H_2O and SO_2

The effect of H_2O on the reduction of NOx by ethanol was reversible in the absence of SO_2. The steady state of the reaction was readily attained upon feeding a mixture of NO, O_2, ethanol and H_2O. When the mixture was switched over to that of NO, O_2 and ethanol, the conversion level of NOx was recovered to that in the absence of H_2O. On the other hand, the effect of SO_2 on the reaction is irreversible at the initial period of the reaction. By addition of SO_2, the conversion level of NOx decreases with the progress of the reaction. When the supply of SO_2 was switched off, the activity of the catalyst was not restored to its initial value. With the increased time, the conversion level reaches a steady state value. After exposure time over 10 h, the effect of SO_2 was reversible. When the supply of SO_2 was switched off, the conversion of NOx was improved although not recovered to the initial value. Repeated on–off cycles of the SO_2 supply reproduced the conversion level of NOx at 10 h in the presence or the absence of SO_2. Thus, the performance of the catalyst was always evaluated over the catalyst subjected to the reaction for 10 h in the presence and the absence of H_2O or SO_2 in the present experiments.

Figures 1 and 2 compare the effects of H_2O and SO_2 on the reduction of NOx and the CO_2 (CO) formation. The NO reduction and the CO_2 formation are greatly enhanced by addition of 10 vol% of H_2O in the inflow at 523–743 K. High conversion of NOx is attained. For example, at 623–743 K the reduction of NOx is achieved at conversion levels over 95% in the presence of H_2O (figure 1). Corresponding to these results, the formation of CO_2 increases by the addition of H_2O (figure 2). On the other hand, SO_2 suppresses the NOx reduction and the CO_2 formation in the 523–743 K temperature range. The CO formation increases above 653 K by addition of SO_2. It is to be noted that the conversion levels of NOx are still kept over 80% at 623–773 K in the presence of H_2O and SO_2 over the present catalyst. At temperatures above 773 K, the NOx reduction decreases with increasing temperature. Under these conditions, the effects of H_2O and SO_2 on the NOx reduction and the CO_2 formation are practically negligible. However, the conversion to CO_2 increases steadily with the increased temperature, even at temperatures above 773 K. These results suggest that the oxidation of ethanol by O_2 took place in preference to the reactions involving NOx at higher temperatures [20].

The NOx reduction was carried out in a helium flow in place of a nitrogen flow at 623 and 723 K. From the gaseous composition of the products, the selectivities to N_2 were estimated to be 80 and 74% respectively at 623 and 723 K in the presence of H_2O, while they were converted to 64 and 80% at the corresponding temperatures in the presence of both H_2O and SO_2.

Figure 3 plots the outlet concentrations of ethanol

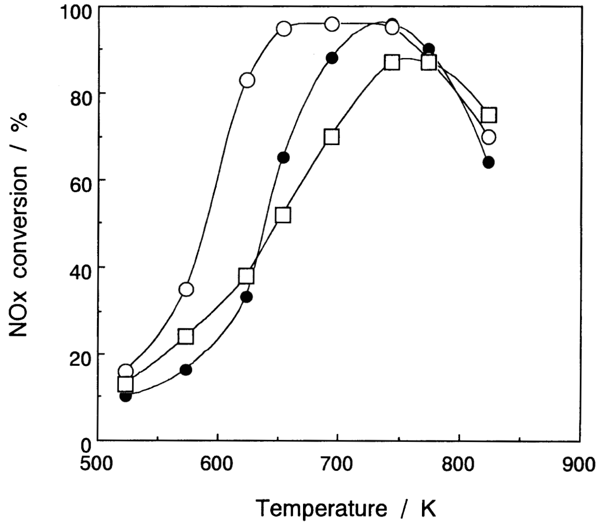

Figure 1. Effects of H_2O and SO_2 on the reduction of lean NOx over Ag/Al_2O_3 catalyst. Experimental conditions: NO = 800 ppm and O_2 = 10% at C_2H_5OH/NO mass ratio = 3. (●) H_2O = 0%, SO_2 = 0 ppm; (○) H_2O = 10%, SO_2 = 0 ppm; (□) H_2O = 10%, SO_2 = 30 ppm.

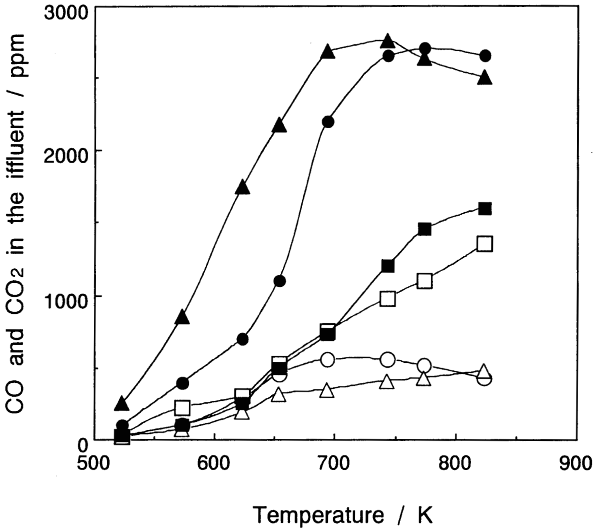

Figure 2. Effects of H_2O and SO_2 on the formation of CO and CO_2 over Ag/Al_2O_3 catalyst. Experimental conditions: NO = 800 ppm and O_2 = 10% at C_2H_5OH/NO mass ratio = 3. (○) CO (H_2O = 0%, SO_2 = 0 ppm); (△) CO (H_2O = 10%, SO_2 = 0 ppm); (□) CO (H_2O = 10%, SO_2 = 30 ppm); (●) CO_2 (H_2O = 0%, SO_2 = 0 ppm); (▲) CO_2 (H_2O = 10%, SO_2 = 0 ppm); (■) CO_2 (H_2O = 10%, SO_2 = 30 ppm).

and acetaldehyde against temperature in the NOx reduction. The concentration of ethanol in the effluent decreases greatly in the presence of H_2O as compared with that in the absence of H_2O, showing that the conversion level of ethanol increases by addition of H_2O. This confirmed previous results [11]. The conversion of ethanol increases to some extent in the presence of SO_2 as judged from the results in figure 3. The formation of acetaldehyde in the presence of both H_2O and SO_2 always exceeds that in the presence of H_2O. It was previously found that acetaldehyde produced in the NOx reduction by ethanol, works as an effective NOx-reducing reagent over Ag/Al_2O_3, and H_2O enhances the NOx reduction by acetaldehyde. These results were confirmed in the present experiments conducted over the Ag/Al_2O_3 catalyst supported on cordierite honeycomb. In contrast to H_2O, it was found that SO_2 suppressed the reduction of NOx by acetaldehyde. Thus, the increased formation of acetaldehyde in the presence of SO_2 is attributable to the inhibiting effect of SO_2 on the NOx reduction by acetaldehyde formed in the course of the reaction.

Figure 4 shows the concentration of C_2H_4 and CH_4 in the effluent against temperature. The formation of C_2H_4 increases by addition of SO_2 in the NOx reduction by ethanol. The increased formation of C_2H_4 is probably ascribed to the increased dehydration of ethanol in the presence of SO_2. The formation of CH_4 increases slightly by addition of SO_2. Very small amounts of C_3H_6 and C_2H_2 were formed in addition to C_2H_4 and CH_4 as hydrocarbon species in the NOx reduction. The effect of SO_2 on the formation of CH_4, C_3H_6 and C_2H_2 was practically negligible.

For the reactions in the mixture of NO, O_2 and ethanol in the presence of H_2O, NH_3 and N_2O were produced as nitrogen-containing products in addition to N_2. By addition of SO_2 to the mixture of NO, O_2, ethanol and H_2O, the formation of N_2O increased slightly while no NH_3 was produced.

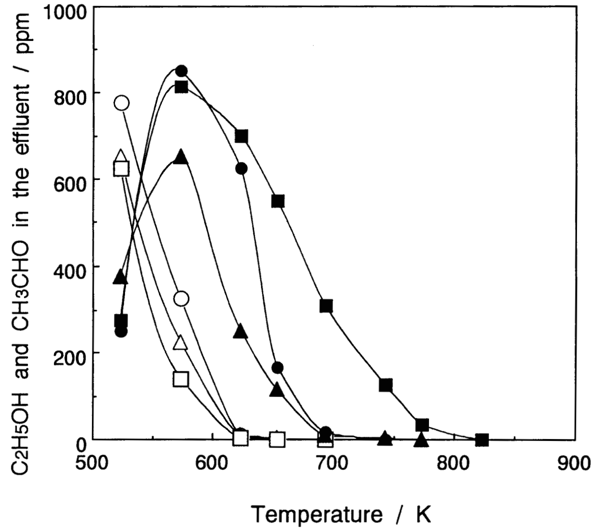

Figure 3. Effects of H_2O and SO_2 on the reduction of C_2H_5OH and the formation of CH_3CHO over Ag/Al_2O_3 catalyst. Experimental conditions: NO = 800 ppm and O_2 = 10% at C_2H_5OH/NO mass ratio = 3. (○) C_2H_5OH (H_2O = 0%, SO_2 = 0 ppm); (△) C_2H_5OH (H_2O = 10%, SO_2 = 0 ppm); (□) C_2H_5OH (H_2O = 10%, SO_2 = 30 ppm); (●) CH_3CHO (H_2O = 0%, SO_2 = 0 ppm); (▲) CH_3CHO (H_2O = 10%, SO_2 = 0 ppm); (■) CH_3CHO (H_2O = 10%, SO_2 = 30 ppm).

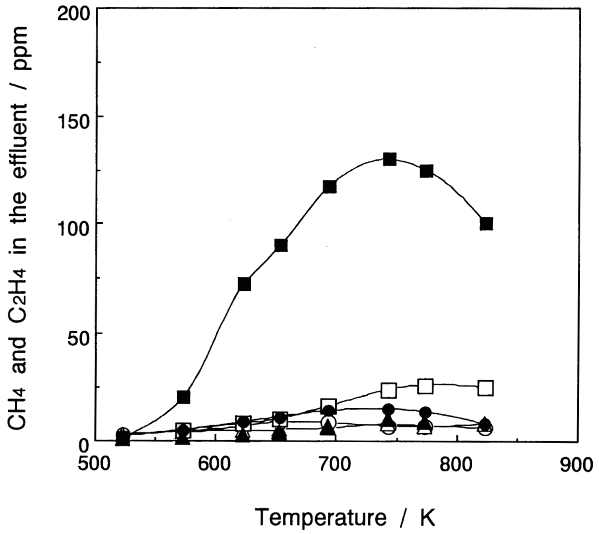

Figure 4. Effects of H_2O and SO_2 on the formation of CH_4 and C_2H_4 over Ag/Al_2O_3 catalyst. Experimental conditions: NO = 800 ppm and O_2 = 10% at C_2H_5OH/NO mass ratio = 3. (○) CH_4 (H_2O = 0%, SO_2 = 0 ppm); (△) CH_4 (H_2O = 10%, SO_2 = 0 ppm); (□) CH_4 (H_2O = 10%, SO_2 = 30 ppm); (●) C_2H_4 (H_2O = 0%, SO_2 = 0 ppm); (▲) C_2H_4 (H_2O = 10%, SO_2 = 0 ppm); (■) C_2H_4 (H_2O = 10%, SO_2 = 30 ppm).

3.2. Effects of H_2O and SO_2 on the formation and the reactivity of NCO species

We previously found that the surface NCO species were involved in the reduction of lean NOx by ethanol as an important intermediate species on Ag/Al$_2$O$_3$ [18]. The NCO species were closely correlated with the progress of the NOx reduction and the formation of by-products. Thus, the formation and the reactivity of surface NCO species were examined in the present experiments in the presence of H_2O and SO_2.

Two intense bands appear at 2260 and 2230 cm^{-1}, attributable to adsorbed Ag–NCO and Al–NCO respectively [18,21] on heating Ag/Al$_2$O$_3$ above 573 K in vacuum after exposing the IR sample to a mixture of NO (14 Torr), C_2H_5OH (11 Torr) and O_2 (15 Torr) at room temperature. The peak intensities for these NCO species further increased on heating at 673 K (figure 5a). The formation of NCO species was not suppressed in the presence of water vapor as reported in a previous paper [18]. Figure 5c shows the IR spectrum of the catalyst exposed to H_2O in the presence of Ag–NCO and Al–NCO species. The band at 1640 cm^{-1} can be ascribed to adsorbed H_2O [22]. It is seen that the IR bands for NCO species shift to lower wave numbers on addition of H_2O at room temperature. Figures 5d and 5e illustrate how the shifted NCO bands vary on evacuation of H_2O at 333 K. It shows that the bands are completely recovered on removing H_2O. This indicates that the shifts of the bands are caused by the strong interaction between NCO species and adsorbed H_2O.

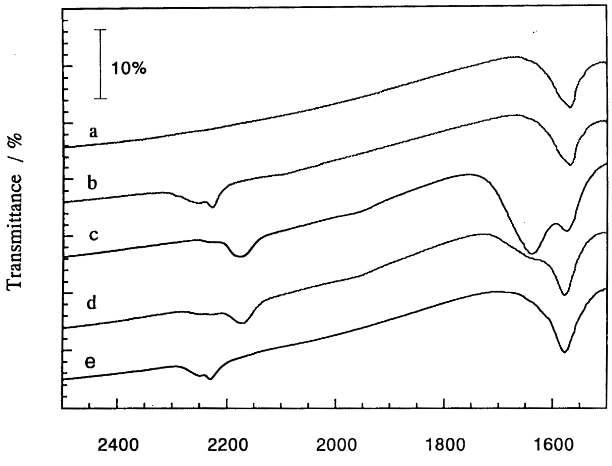

Figure 5. FT-IR spectra of Ag/Al$_2$O$_3$: effect of H_2O on NCO species. (a) Background spectrum. (b) The catalyst was heated to 673 K for 15 min in vacuum after exposing to a mixture of NO (14 Torr), C_2H_5OH (11 Torr) and O_2 (15 Torr) for 15 min at room temperature. (c) The catalyst was then exposed to 10 Torr of H_2O for 15 min at room temperature subsequently after spectrum (b) was obtained. (d) The catalyst was degassed for 15 min at room temperature subsequently after spectrum (c) was obtained. (e) The catalyst was degassed for 15 min at 333 K subsequently after spectrum (d) was obtained.

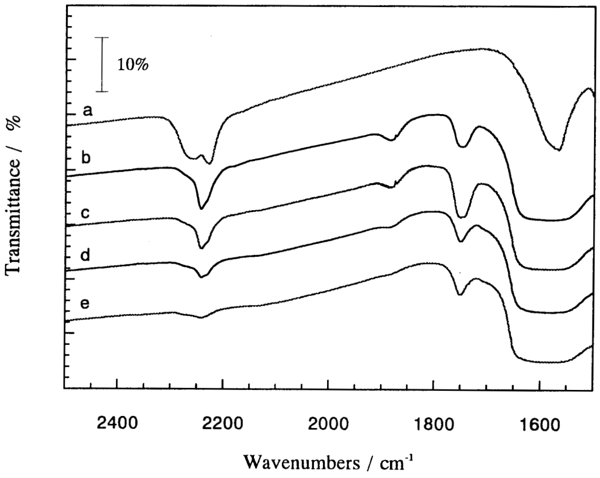

Figure 6. FT-IR spectra of Ag/Al$_2$O$_3$: effect of a mixture of NO, C_2H_5OH and O_2 on NCO species. (a) The catalyst was heated to 673 K for 15 min in vacuum after exposing to a mixture of NO (14 Torr), C_2H_5OH (11 Torr) and O_2 (15 Torr) for 15 min at room temperature. The catalyst was then exposed to a mixture of NO (14 Torr) and O_2 (15 Torr) at room temperature for (b) 2 min, (c) 5 min, (d) 15 min, (e) 30 min after spectrum (a) was obtained.

Figures 6 and 7 respectively display how the NCO species change by addition of a mixture of NO and O_2 in the absence and the presence of H_2O at room temperature. When the NCO species are exposed to the mixture of NO and O_2 in the absence of H_2O, the NCO species disappear gradually in about 60 min as shown in figure 6.

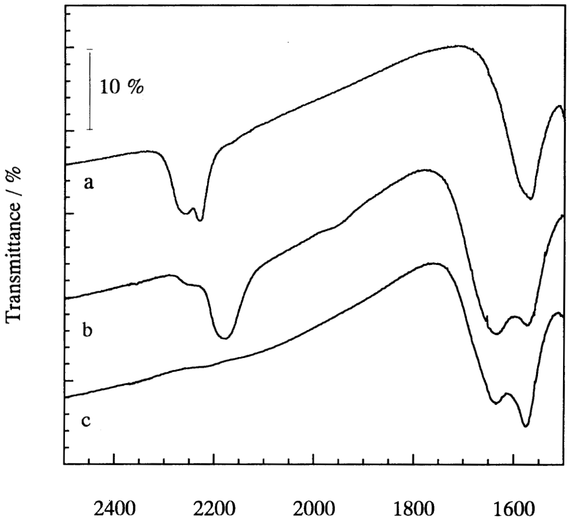

Figure 7. FT-IR spectra of Ag/Al$_2$O$_3$: effect of previous exposure of H_2O on the reaction of NCO species with a mixture of NO and O_2. (a) The catalyst was heated to 673 K for 15 min in vacuum after exposing to a mixture of NO (14 Torr), C_2H_5OH (11 Torr) and O_2 (16 Torr) for 15 min at room temperature. (b) The catalyst was then exposed to 10 Torr of H_2O for 15 min at room temperature subsequently after spectrum (a) was obtained. (c) The catalyst was exposed to a mixture of NO (14 Torr) and O_2 (15 Torr) for 5 min at room temperature subsequently after spectrum (b) was obtained.

N_2 and CO_2 (CO) were produced. In contrast to this, when the NCO species were exposed to H_2O (10 Torr) and then to a mixture of NO (14 Torr) and O_2 (15 Torr), the NCO species vanish immediately as evidenced from figure 7, to form N_2 and CO_2 (CO). These findings suggest that the strong interaction between the NCO species and adsorbed H_2O caused to increase the reactivity of the NCO species towards a mixture of NO and O_2 on Ag/Al_2O_3. Hence, it is highly probable that the increased selectivity to N_2 observed in the reduction of lean NOx in the presence of H_2O is ascribed to the increased reactivity of the NCO species towards $NO + O_2$ in the presence of H_2O.

On the other hand, two weak bands for adsorbed Ag–NCO and Al–NCO began to form above 623 K in a mixture of NO (14 Torr), C_2H_5OH (11 Torr), O_2 (15 Torr) and SO_2 (10 Torr). In comparison with the results in the absence of SO_2, the formation of NCO species from the mixture of NO, O_2 and ethanol was strongly suppressed in the presence of SO_2. No reactions between NCO species and NO occurred either in the presence or the absence of O_2 at room temperature.

A new band appeared at $\sim 1360\ cm^{-1}$ above 373 K on Ag/Al_2O_3 by addition of SO_2 to a mixture of NO, O_2 and ethanol, being ascribed to sulfate species on Al_2O_3 surface [23,24]. These findings suggest that the formation and the reactivity of surface NCO is strongly suppressed by sulfate species on the Ag/Al_2O_3 surface. Through TPD experiments [25] we previously found that sulfate species were formed on Ag and on Al_2O_3 surface on Ag/Al_2O_3. The sulfate species on the Ag surface began to decompose to SO_2 around 500 K while those on the Al_2O_3 surface were decomposed to SO_2 around 1000 K. Hence, under the present experimental conditions, sulfate species formed on Ag are reversibly held on the surface. These species most probably suppress the formation and the reactivity of NCO species in the reduction of NOx. It leads to lowering of the NOx reduction and the formation of NH_3. However, since these sulfate species are reversibly held on the surface, the reduction of NOx is still maintained at high conversion levels even in the presence of SO_2 over the present catalysts.

On the other hand, sulfate species formed on Al_2O_3 are irreversibly held on the surface in the course of the NOx reduction in the presence of SO_2, and catalyze the dehydration of ethanol. This leads to the increase in the formation of C_2H_4 in the presence of SO_2 in the NOx reduction by ethanol.

4. Summary

It was shown that the presence of H_2O enhances the lean NOx reduction by C_2H_5OH. Higher NOx reduction is ascribed to the higher reactivity of the surface intermediate, NCO species, towards $NO + O_2$. The presence of SO_2 suppresses the reduction of NOx by C_2H_5OH and the formation of NH_3 at lower temperature. The lowering of the NOx reduction in the presence of SO_2 is ascribed to the inhibiting effect of sulfate species formed on Ag on the formation and the reactivity of NCO species. However, as the temperature increased, the inhibiting effect of SO_2 on the NOx reduction was diminished. About 80% of NOx in simulated diesel engine exhaust was removed by ethanol at 743–773 K in the presence of H_2O and SO_2.

References

[1] H. Hamada, Y. Kintaichi, M. Sasaki, T. Ito and M. Tabata, Appl. Catal. 64 (1990) L1.

[2] W. Held, A. Koenig, T. Richter and L. Puppe, SAE paper 900496 (1990).

[3] M. Iwamoto, H. Yahiro, S. Shundo, Y. Tu-u and N. Mizuno, Appl. Catal. 69 (1991) L15.

[4] T. Miyadera and K. Yoshida, Chem. Lett. (1993) 1483.

[5] S. Sumiya, G. Muramatsu, N. Matsumura, K. Yoshida and R. Schenck, SAE paper 920853 (1992).

[6] Y. Torikai, H. Yahiro, N. Mizuno and M. Iwamoto, Catal. Lett. 9 (1991) 91.

[7] J.O. Petunchi, G. Sill and W.K. Hall, Appl. Catal. B 2 (1993) 303.

[8] G.P Ansell et al., Appl. Catal. B 2 (1993) 81.

[9] T. Miyadera, Appl. Catal. B 2 (1993) 199.

[10] T. Miyadera, A. Abe, G. Muramatsu and K. Yoshida, *Advanced Materials '93, A: Ecomaterials* (1994) 405.

[11] M. Saito, T. Miyadera and K. Yoshida, 68th Annual Meeting of Chem. Soc. Jpn. 2B312 (1994).

[12] Y. Ukisu, S. Sato, G. Muramatsu and K. Yoshida, Catal. Lett. 11 (1991) 177.

[13] Y. Ukisu, S. Sato, G. Muramatsu and K. Yoshida, Catal. Lett. 16 (1992) 11.

[14] Y. Ukisu, S. Sato, A. Abe and K. Yoshida, Appl. Catal. B 2 (1993) 177.

[15] V.A. Bell, J.S. Feeley, M. Deeba and R.J. Farruto, Catal. Lett. 29 (1994) 15.

[16] C. Li, K.A. Bethke, H.H. Kung and M.C. Kung, J. Chem. Soc. Chem. Commun. (1995) 813.

[17] G.R. Bamwenda, A. Obuchi, A. Ogata and K. Mizuno, Chem. Lett. (1994) 2109.

[18] Y. Ukisu, T. Miyadera, A. Abe and K. Yoshida, Catal. Lett. 39 (1996) 265.

[19] R.J.H. Voorhoeve, C.K.N. Patel, L.E. Trimble, R.J. Kerl and P.K. Gallagher, J. Catal. 45 (1976) 297.

[20] E.M. Cordi and J.L. Falconer, Appl. Catal. A 151 (1997) 179.

[21] F. Solymosi and T. Bansagi, J. Phys. Chem. 83 (1979) 552.

[22] M.L. Unland, J. Phys. Chem. 79 (1975) 610.

[23] M. Waqif, O. Saur, J.C. Lavalley, S. Perathoner and G. Centi, J. Phys. Chem. 95 (1991) 4051.

[24] M.B. Mitchell, V.N. Sheinker and M.G. White, J. Phys. Chem. 100 (1996) 7550.

[25] N. Irite, A. Abe, K. Yoshida, M. Haneda and N. Kakuta, 69th Annual Meeting of Chem. Soc. Jpn. 2A313 (1995).