CHEMISTRY LETTERS, pp. 1483-1486, 1993. © 1993 The Chemical Society of Japan

# Alumina-supported Catalysts for the Selective Reduction of Nitric Oxide by Propene

Tatsuo MIYADERA* and Kiyohide YOSHIDA†
National Institute for Resources and Environment, Onogawa, Tsukuba, Ibaraki 305,
† Riken Corporation, Suehiro, Kumagaya, Saitama 360

The effect of water vapor and $SO_2$ on the selective reduction of nitric oxide over alumina-supported Ag, In, Ga, Sn, and Zn catalysts has been investigated. Water vapor and $SO_2$ had large effect on the reactivity of propene and on the reduction of NO over those catalysts.

Selective reduction of NOx by hydrocarbons over copper-exchanged ZSM-5 and other cation-exchanged zeolites have been reported.[1-4] However, the activities of those catalysts decreased in the presence of water vapor or at high temperatures.[1,5-6] From a practical point of view, it is important to develop catalysts which are heat-resistant and active in the presence of water vapor and $SO_2$. Alumina-supported catalysts were also found to be effective for selective reduction of NOx.[7,8] Although alumina base catalysts have lower activities, they are expected to be more heat-resistant than the ones with zeolite. Alumina base catalysts are also subject to the interference of water.[9,10] The authors of this paper investigated the effect of water vapor and $SO_2$ on the selective reduction of NO over alumina-supported Ag, In, Ga, Zn, and Sn catalysts which showed high activities in the absence of water and $SO_2$.

An alumina-supported silver catalyst was prepared according to the previously outlined procedure.[11] Other catalysts were prepared by impregnating pellet type alumina (Catalysts and Chemicals Co.) with aqueous solutions of metal nitrate (In, Ga, Zn) or ethanol solution of tin chloride. The alumina-impregnated tin chloride which was dried at 200 ℃ in a dry nitrogen stream was converted to tin hydroxide by treating with an aqueous solution of ammonia at a room temperature. After being dried at 70 ℃, the alumina-supported In, Ga, Zn, and Sn catalysts were calcined at temperatures in a range between 110 and 550 ℃ in an air stream.

Activities of the catalysts were measured with a fixed-bed flow reactor at a constant space velocity of 6400/h. Inlet gas composition was 500 ppm NO, 500 ppm $C_3H_6$, 0 or 200 ppm $SO_2$, 0-10% $O_2$, 10% $CO_2$, balance $N_2$ (dry basis) plus 0 or 10% $H_2O$. Water was injected into the gas stream and vaporized before the reactor. Water vapor in the post-catalyst stream was removed by two condensers. The concentrations of NO and NOx (NO + $NO_2$) were measured with a chemiluminescence-based NO/NOx analyzer. Nitric oxide was partially oxidized to nitrogen dioxide over the catalysts and a small part of the $NO_2$ was trapped out while passing through the condensers. The concentration of outlet NOx was corrected by adding the lost $NO_2$ which was estimated according to the

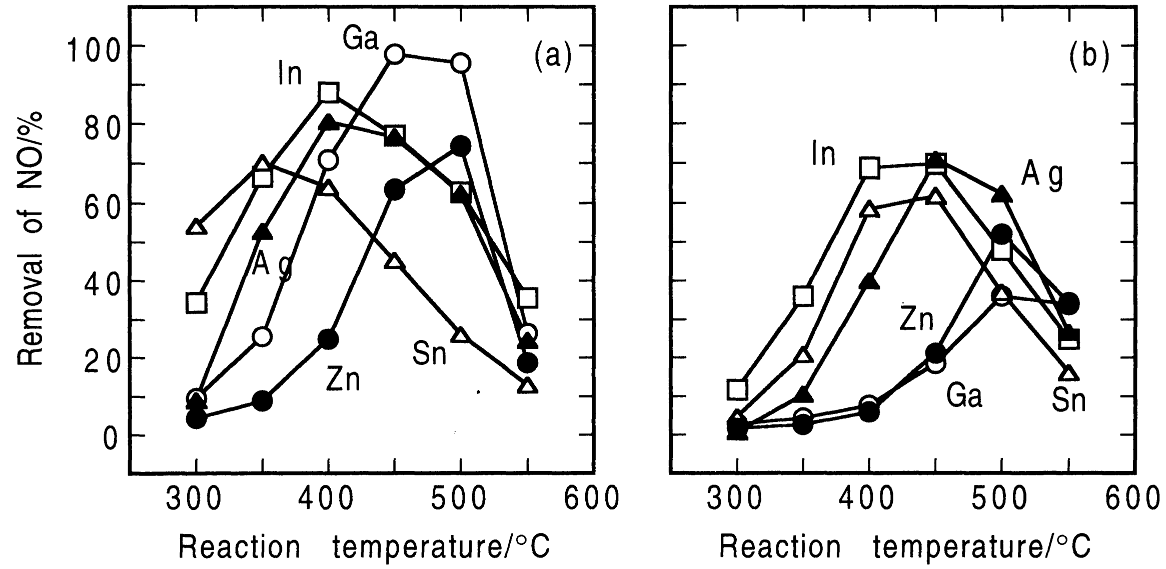

Fig. 1. Effect of water vapor on the reduction of NO over alumina-supported catalysts. Reaction conditions: NO 500 ppm, $C_3H_6$ 500 ppm, $CO_2$ 10%, balance $N_2$, $H_2O$ 0%(a) 10%(b); SV 6400/h.

way described in the previous work.[11] The percent of NO removal(dry basis) was defined as 100*(NO in - corrected NOx out)/(NO in). In another experiment, helium-balanced gas mixture (1021 ppm NO, 667 ppm $C_3H_6$, 0 or 200 ppm $SO_2$, 10% $O_2$ (dry basis) plus 0% or 10% $H_2O$) was used as a reactant and the post-catalyst sample was analyzed by gas chromatography with columns: molecular sieve 5A (for $N_2$ and CO), Porapak Q (for $CO_2$ and $N_2O$), and silica gel (for $C_3H_6$). More than 90% of the reacted NOx (measured with NO/NOx analyzer) was detected as $N_2$ and there was no formation of $N_2O$. Therefore, it seems that there is no problem in estimating the NOx reduction activity of the catalysts on measuring NOx with NO/NOx analyzer.

Figure 1a shows the NO removal activities of alumina-supported catalysts (2.0 wt% metal loading) in the absence of water vapor and sulfur dioxide. The order of catalytic activities was Ga(98%, maximum NO removal) > In(88%) > Ag(81%) > Zn(74%) > Sn(70%). In the absence of water, the Ga/$Al_2O_3$ catalyst showed extremely high activity as well as Ga-exchanged zeolites.[4] However, the activities of those catalysts were decreased by water as can be seen in Fig. 1b. The order of catalytic activities in the presence of 10% water was Ag(71%), In(70%) > Sn(62%) > Zn(52%) > Ga(36%). The activity of Ga/$Al_2O_3$ was significantly decreased by water. In order to investigate the effect of water on the reduction of NO and the oxidation of propene, the conversion rates of NO to $N_2$ and propene to COx (CO + $CO_2$) in NO - $C_3H_6$ - $O_2$ - He - ($H_2O$) system were measured at temperatures where NO were removed effectively. The result is shown in Table 1. The conversion of propene on every catalysts decreased by the addition of water vapor over all the temperature range. On the other hand, the selectivities of $C_3H_6$ for $N_2$ formation (defined as formed $N_2$*2/consumed $C_3H_6$) over all catalysts except Ga/$Al_2O_3$ increased in the presence of water vapor. It can be said that water vapor suppressed the undesirable $C_3H_6$ oxidation where $C_3H_6$ did not contribute to NO reduction, and hence it increased

Table 1. Activities of alumina-supported catalysts

| Catalyst (2wt%) | Temp (℃) | Conv. of NO to $N_2$/% (1) | (2) | (3) | Conv. of $C_3H_6$ to COx/% (1) | (2) | (3) | Selectivity for $N_2$ a) (1) | (2) | (3) |
|---|---|---|---|---|---|---|---|---|---|---|
| $Ag/Al_2O_3$ | 450 | 56.7 | 47.2 | 45.0 | 100 | 77.2 | 75.8 | 0.87 | 0.94 | 0.91 |
| | 400 | 48.4 | 20.3 | 34.5 | 80.5 | 28.0 | 57.0 | 0.92 | 1.11 | 0.93 |
| $In/Al_2O_3$ | 450 | 50.6 | 57.7 | 27.9 | 100 | 91.7 | 57.0 | 0.77 | 0.96 | 0.75 |
| | 400 | 55.8 | 52.8 | 15.9 | 94.8 | 64.8 | 23.0 | 0.90 | 1.25 | 1.06 |
| $Sn/Al_2O_3$ | 450 | 37.3 | 50.1 | 31.6 | 100 | 95.1 | 98.5 | 0.57 | 0.81 | 0.49 |
| | 400 | 52.9 | 44.2 | 30.8 | 100 | 58.3 | 74.7 | 0.81 | 1.16 | 0.63 |
| $Ga/Al_2O_3$ | 500 | 77.9 | 24.8 | 16.1 | 100 | 36.7 | 36.6 | 1.19 | 1.03 | 0.67 |
| | 450 | 60.5 | 14.5 | 5.9 | 82.2 | 18.8 | 16.6 | 1.13 | 1.18 | 0.54 |
| $Zn/Al_2O_3$ | 500 | 59.5 | 34.6 | 12.3 | 100 | 58.0 | 31.0 | 0.91 | 0.91 | 0.61 |
| | 450 | 24.0 | 12.9 | 6.6 | 43.9 | 16.2 | 12.9 | 0.84 | 1.22 | 0.78 |

Inlet gas composition: (1) NO 1021 ppm, $C_3H_6$ 667 ppm, $O_2$ 10%, balance He (2) + $H_2O$ 10% (3) + $H_2O$ 10%, $SO_2$ 200 ppm; SV 6400/h.
a) defined as formed $N_2$*2/consumed $C_3H_6$.

the selectivity for $N_2$ formation. Alumina-supported Ag, In, and Sn catalysts exhibited higher NO reduction activities in the presence of water at 450 ℃ than in the absence of water; this might have been due to the large increase of selectivity for $N_2$ formation and small decrease in the reactivity of $C_3H_6$ caused by water vapor. The significant decrease of NO reduction activity of $Ga/Al_2O_3$ was probably due to the extreme decrease of $C_3H_6$ reactivity in the presence of water.

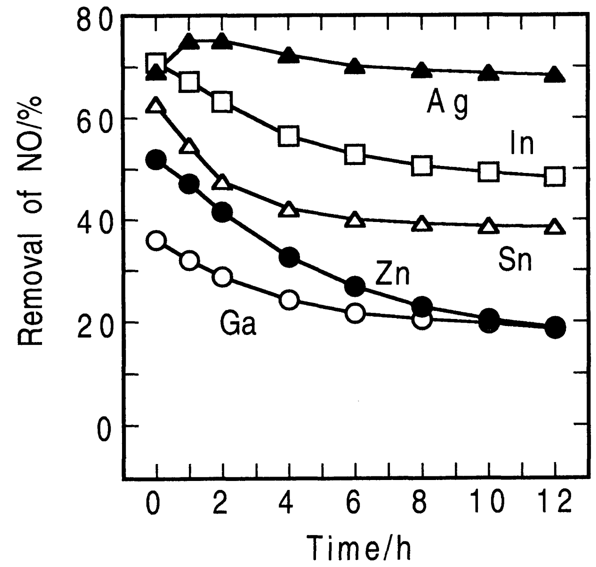

Fig. 2. Effect of $SO_2$ on the reduction of NO over alumina-supported catalysts. Reaction temp: Ag, In, Sn 450 ℃; Ga, Zn 500 ℃, $SO_2$ 200 ppm, Other conditions are the same as in Fig. 1b.

Figure 2 shows the change of NO removal activities of the alumina-supported catalysts in the presence of 200 ppm $SO_2$ and 10% water. The activities of $Ga/Al_2O_3$ and $Zn/Al_2O_3$ decreased significantly by $SO_2$ and they became the same level of alumina support in 12 h. Though the effect of $SO_2$ on the $In/Al_2O_3$ and $Sn/Al_2O_3$ catalysts was rather small, the activities of those catalysts decreased by 30% in 12 h. Among the tested catalysts, only $Ag/Al_2O_3$ showed as high NO reduction activity as in the absence of $SO_2$. When the addition of $SO_2$ to the feed gas was stopped, the activity of $Sn/Al_2O_3$ was restored gradually, whereas the activities of In, Ga, and $Zn/Al_2O_3$ catalysts were not restored.

The conversion rates of propene and NO and the selectivities of $C_3H_6$ for $N_2$ formation over the alumina-supported catalysts (exposed to 200 ppm of $SO_2$ for 24 hr) in the presence of $SO_2$ are shown in Table 1. In the presence of $SO_2$ and $H_2O$, the conversions of $C_3H_6$ over $In/Al_2O_3$ and $Zn/Al_2O_3$ were extremely low, while the conversions over $Sn/Al_2O_3$ and $Ag/Al_2O_3$ were rather high. The selectivities of $C_3H_6$ for $N_2$ formation over alumina-supported Sn, Ga, and Zn were decreased significantly by the addition of $SO_2$ to the water containing system. It can be said that the decrease of NO reduction activity in the presence of $SO_2$ and $H_2O$ was mainly due to the suppression of $C_3H_6$ reaction ($In/Al_2O_3$) or due to the decrease of selectivity for $N_2$ formation ($Ga/Al_2O_3$). The extreme decrease of the NO reduction activity of $Zn/Al_2O_3$ in the presence of $SO_2$ and $H_2O$ seems to have been caused by the large decrease in both the reactivity of $C_3H_6$ and selectivity for $N_2$ formation. On the other hand, $Ag/Al_2O_3$ suffered only a small interference from $SO_2$ at 450 ℃. In addition, the NO reduction activity of $Ag/Al_2O_3$ in the presence of $SO_2$ and $H_2O$ was higher than in the absence of $SO_2$ at 400 ℃; this was probably due to the large increase of reactivity of $C_3H_6$ and small decrease of selectivity for $N_2$ formation. This promoting effect of $SO_2$ on the NO reduction was unique to the $Ag/Al_2O_3$ catalyst. Though the rate of NO removal over the $Ag/Al_2O_3$ catalyst decreased with the increase of space velocity, it can be concluded that, among the tested catalysts, $Ag/Al_2O_3$ is the most promising one to be put to practical use.

## References

1) W. Held, A. Konig, T. Richiter, and L. Puppe, SAE Paper, 900496(1990).
2) M. Iwamoto, H. Yahiro, S. Shundo, Y. Yu-u, and N. Mizuno, Shokubai(Catalyst), **32**, 430(1990); Appl. Catal., **69**, L15(1991).
3) M. Misono and K. Kondo, Chem. Lett., **1991**, 1001.
4) K. Yogo, S. Tanaka, M. Ihara, T. Hishiki, and E. Kikuchi, Chem. Lett., **1992**, 1025.
5) S. Sato, H. Hosose, W. X. Zhang, H. Yahiro, N. Mizuno, M. Iwamoto, M. Kobayashi, M. Konno, T. Chikahisa, and T. Murayama, Shokubai(Catalyst), **33**, 448(1991).
6) S. Kasahara, K. Sekizawa, and M. Kimura, 61th Annual Meeting of the Chem. Soc. Jpn., No. 3H203(1991); K. Yokota, M. Kimura, H. Doi, and K. Sekizawa, ibid., No. 3H204(1991).
7) H. Hamada, Y. Kintaichi, M. Sasaki and T. Ito, Appl. Catal., **75**, L1(1991).
8) A. Obuchi, A. Ohi, M. Nakamura, A. Ogata, K. Mizuno and H. Ohuchi, Appl. Catal., B **2**, 71(1993).
9) T. Miyadera and K. Yoshida, 62th Annual Meeting of the Chemical Society of Japan, No. 4D411(1991).
10) H. Hamada, Y. Kintaichi, T. Yoshinari, M. Sasaki, and T. Ito, 63th Annual Meeting of the Chemical Society of Japan, No. 2C448(1992).
11) T. Miyadera, Appl. Catal., B **2**, 199(1993).

(Received May 27, 1993)