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Additive Effect of Silver on the Catalytic Activity of TiO_2–ZrO_2 for the Selective Reduction of NO with Propene, 2-Propanol, and Acetone

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The catalytic performance of metal-impregnated TiO_2–ZrO_2 binary metal oxide for the selective reduction of NO was investigated. The addition of silver to TiO_2–ZrO_2 catalyst caused a drastic enhancement of NO reduction activity with propene. This silver additive effect was accounted for by the assumption that silver promotes the reaction of NO_2 with propene to form a partially oxidized hydrocarbon, which is the rate-determining step. However, the catalytic activity of silver-supported TiO_2–ZrO_2 was depressed by the presence of water vapor because of its inhibiting effect on the formation of the oxygenated intermediate. Oxygen-containing compounds such as 2-propanol and acetone were also found to be good reductants on silver-supported TiO_2–ZrO_2 in the absence of water vapor. Moreover, the presence of water vapor significantly enhanced NO reduction activity of silver-supported TiO_2–ZrO_2 with these reductants. It was presumed that water vapor accelerates the selective reduction of NO by suppressing the undesirable oxidation of the reductants by O_2.

The attention paid toward environmental disruptions by harmful materials has been increasing in the past decades. For example, air pollution by nitrogen oxides (NO_x) emitted from exhaust gases is one of the most serious environmental problems. Particularly, someone must develop effective catalytic methods to remove NO_x from exhaust gases of diesel and lean-burn gasoline engine exhausts because conventional three-way catalyst does not work for these oxygen-rich exhausts.

In this connection, selective catalytic reduction of NO with hydrocarbons in the presence of oxygen has been actively studied.1,2) Metal ion-exchanged zeolites such as Cu–ZSM-5,3) Ce–ZSM-5,4) Co–Beta,5) and Ga/H–ZSM-56) are well-known catalysts for this reaction. In addition to these metal ion-exchanged zeolites, our group found that solid-acid-type materials such as H-form zeolites and alumina7) show catalytic activity for this reaction and that their solid acidity or basicity seems to play an important role in this reaction.8) However, the activity of these solid acid type catalysts at low temperatures of actual diesel exhausts was generally lower than that of metal ion-exchanged zeolite catalysts. The metals in zeolites should probably act as active catalytic species for NO reduction, and many studies have tried to clarify the role of the loaded metals in the reaction mechanism. It was also found for alumina catalyst that supporting appropriate metals promotes its activity.2)

Exhaust gases usually contain materials poisonous to the catalysts such as H_2O, SO_x, and particulate matters. Among them H_2O is said to inhibit the reaction by being strongly adsorbed on the active sites for the activation of hydrocarbons or NO. Hence, catalysts capable of reducing NO effectively in the presence of water vapor are required from a practical viewpoint. Recently, some catalysts have been reported which are not sensitive to water vapor. Ueda and Haruta9) found that the activity of Au/Al_2O_3 catalyst for NO reduction by propene in the presence of H_2O was almost the same as that in the absence of H_2O. They assumed that the oxidation of NO to NO_2 on gold, which is the first reaction step, is not inhibited by water. Miyadera and Yoshida10) reported the high catalytic activity of Ag/Al_2O_3 catalysts for the selective reduction of NO by propene in the presence of water. They also discovered11) that oxygen-containing organic compounds such as ethanol and acetone are more effective reductants than propene on Ag/Al_2O_3 in the presence of H_2O. Ukisu et al.12) investigated the catalytic performance of Ag/Al_2O_3 by FT-IR measurements and found that the formation of isocyanate (–NCO) species on the catalyst, which is regarded as a reaction intermediate, is hardly affected by coexisting water vapor.

As described above, most of the papers concerning this reaction have dealt with zeolite or single metal oxide-based catalysts. However, binary metal oxides may also exhibit catalytic activity for this reaction due to their solid acid or base property. In fact, we examined the catalytic performance of a group of binary metal oxides for NO reduction by propane and found that some of them show good catalytic activity.13) It was also found that several binary oxides showed higher activity than their corresponding single metal oxides. Thus, binary metal oxides might be promising candidates as catalyst bases. However, the effects of metal additives on the activity of binary oxides have rarely been studied in detail, although Hosose et al. reported the good additive effect of copper on SiO_2–Al_2O_3 catalyst.14)

In the present work, we investigated the catalytic performance of metal-impregnated TiO_2–ZrO_2 binary metal oxide in order to search for their usefulness as a catalyst for this reaction. TiO_2–ZrO_2 has been chosen because of its relatively good catalytic activity.13) Furthermore, TiO_2–ZrO_2 binary oxide has been reported to exhibit high surface acidity by a charge imbalance based on the generation of Ti–O–Zr bonding.[15] It is also possible that Ti ions and Zr ions on the TiO_2–ZrO_2 binary oxide act as acid sites and basic sites, respectively,[16] which may serve as catalytic active sites.

In the course of our study, we found that the catalytic activity of TiO_2–ZrO_2 for the selective reduction of NO by propene was enhanced significantly by addition of silver. Accordingly, we have investigated in detail the role of silver, the influence of water vapor and the efficiency of oxygen-containing organic compounds as a reductant for Ag/TiO_2–ZrO_2-catalyzed NO reduction. Furthermore, possible reaction mechanisms for this reaction are also discussed based on the present experimental results.

Experimental

Catalysts Preparation. The binary oxide composed of TiO_2 and ZrO_2 was prepared by a coprecipitation method.[17] A mixture of titanium(IV) tetraisopropoxide ($Ti(OC_3H_7)_4$) and zirconium(IV) tetrapropoxide ($Zr(OC_3H_7)_4$) were added into 2-propanol at 60 °C and stirred at the same temperature for 2 h. The resulting solution was hydrolyzed by adding it dropwise to an excess amount of distilled water. The precipitate thus formed was separated by centrifuging and dried at 110 °C. The sample was finally calcined at 500 °C for 5 h in flowing air. The molar ratio of TiO_2/ZrO_2 in the binary oxide was fixed to be unity. Metal-supported catalysts were prepared by impregnating TiO_2–ZrO_2 with an aqueous solution of metal nitrate (Ag(I), Fe(III), Co(II), Ni(II), Cu(II), Ga(III), and Ce(III)), followed by drying at 110 °C and calcination at 500 °C for 5 h in flowing air.

Catalytic Activity Measurements. The catalytic activity for the selective reduction of NO was measured by using a flow reactor system. A gas mixture containing NO (or NO_2), O_2, reductant (propene, 2-propanol or acetone) and/or H_2O diluted in helium was passed through the catalyst bed. The component gases supplied from cylinders were used without any purification. Water was introduced into the reaction gas by a micropump and vaporized. Some (0.2 g) of the catalyst sample placed in the quartz reactor was first treated with flowing helium at 500 °C for 30 min and then the gas was switched to the reaction gas. The gas flow rate was 66 $cm^3\,min^{-1}$ (without H_2O) or 72 $cm^3\,min^{-1}$ (with H_2O). W/F was approximately 0.2 $g\,s\,cm^{-3}$. The activity measurements were carried out with decreasing temperature in steps of 50 °C from 500 to 200 °C.

The effluent gas was analyzed by gas chromatographs equipped with a Molecular Sieve 5A column (for the analysis of N_2 and CO) and a Porapak Q column (for that of CO_2, N_2O, and hydrocarbons). The catalytic activity was evaluated by the conversion of NO to N_2 and/or N_2O and that of the reductant to CO_x (CO and CO_2).

Catalyst Characterization. Surface area of the catalyst samples was determined with a conventional flow apparatus (Shimadzu, Flowsorb II 2300) by nitrogen adsorption at −196 °C. The crystal structure was identified by XRD (Shimadzu XD-1) measurements using a Cu $K\alpha$ radiation at 40 kV and 40 mA.

TPR (Temperature Programmed Reduction) measurements were carried out to estimate the reduction behavior of the silver-supported catalysts. Before TPR measurement, an adequate amount (0.25 g) of the catalyst was placed in a quartz tube reactor and oxidized at 500 °C for 1 h in flowing 20 vol% O_2–He gas mixture. In this measurement, 10 vol% H_2–Ar gas mixture was used as a reducing gas with a flow rate of 110 $ml\,min^{-1}$ and the temperature of the catalyst bed was raised at a heating rate of 10 $°C\,min^{-1}$. After the outlet gas from the catalyst bed was passed through a molecular sieve column to eliminate H_2O produced by the TPR operation, the difference in the H_2 concentration between at the inlet and at the outlet of the reactor was detected by a thermal conductivity detector.

In order to observe the morphology of silver particles on TiO_2–ZrO_2 binary oxide, transmission electron microscope (TEM) analysis was made with a JEOL JEM-2000LX and at an accelerating voltage of 200 kV and a magnification of $\times 10^5$.

Results and Discussion

Additive Effect of Several Metals. Figure 1 shows the catalytic activity of Ag, Fe, Co, Ni, Cu, Ga, and Ce/TiO_2–ZrO_2 (metal loading: 2 wt%) along with that of TiO_2–$ZrO_2$for NO reduction by propene in the presence of 10% O_2. TiO_2–ZrO_2 itself was able to catalyze NO reduction into N_2, but the conversion level, which was about 35% at 450 °C, was not so high in spite of its high BET surface area (see in Table 1). The addition of Ce depressed the NO reduction activity of TiO_2–ZrO_2, probably due to the disappearance of the active site for NO reduction by formation of a solid solution of CeO_2 and ZrO_2, because both oxides have the same fluorite structure.[18] Fe and Co were not good additives for this reaction, either. In the case of Ag, Ni, and Ga, on the other hand, remarkable enhancement of the NO reduction activity was observed in the temperature region above 350 °C. Cu/TiO_2–ZrO_2 showed good activity in the low temperature region below 300 °C.

Among these catalysts tested here, Ag/TiO_2–ZrO_2 catalyst had excellent catalytic performance for NO reduction by propene. Similar results were reported for metal-supported alumina catalysts by Miyadera.[10,11] He found out that Ag/Al_2O_3 shows high activity for the selective reduction of NO by propene, ethanol or acetone. However, the role of silver in NO reduction on Ag/Al_2O_3 has not been clarified yet. Then we examined the effect of adding silver to TiO_2–ZrO_2 on the present reaction in detail.

Selective Reduction of NO with Propene over Ag-Supported TiO_2–ZrO_2 Catalysts. Figure 2 shows the effect of silver loading on the catalytic activity of Ag/TiO_2–ZrO_2. It can be seen that the catalytic activity of TiO_2–ZrO_2 for NO reduction is greatly enhanced by addition of silver. In addition, the temperature giving the highest NO conversion shifted to low temperature region with increasing silver content. The

Table 1. BET Surface Area of Silver-Supported TiO_2–ZrO_2 Catalysts

Catalyst	BET Surface area $m^2\,g^{-1}$
TiO_2–ZrO_2	284
1 wt% Ag/TiO_2–ZrO_2	217
2 wt% Ag/TiO_2–ZrO_2	190
5 wt% Ag/TiO_2–ZrO_2	152
10 wt% Ag/TiO_2–ZrO_2	132
15 wt% Ag/TiO_2–ZrO_2	114

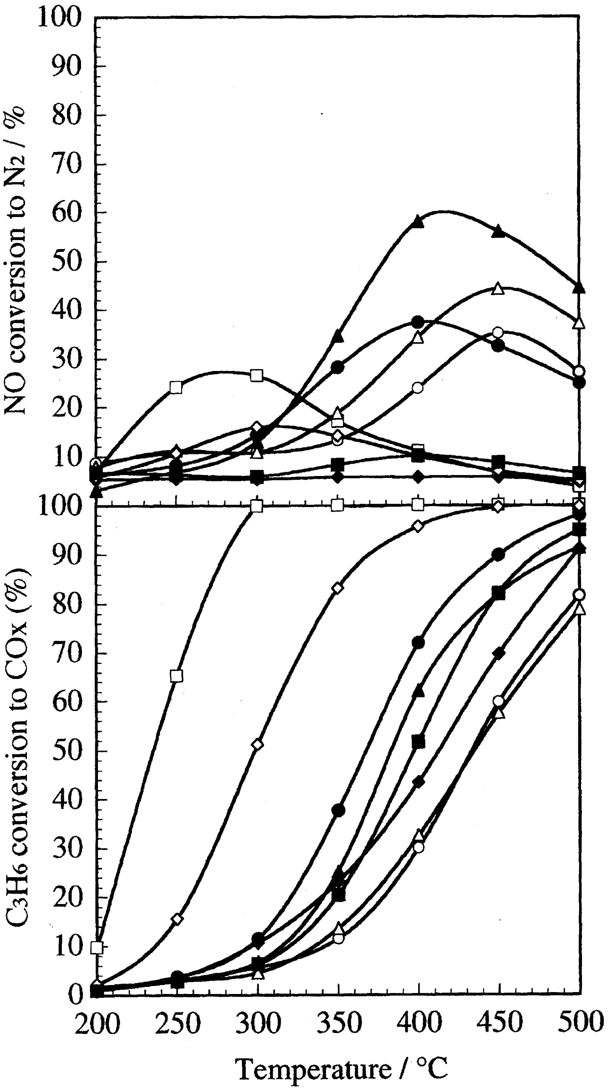

Fig. 1. Effect of metal additives on the catalytic activity of TiO_2–ZrO_2 for the selective reduction of NO with propene. Conditions: NO = 900 ppm, C_3H_6 = 850 ppm, O_2 = 10 vol%, catalyst weight = 0.2 g, gas flow rate = 66 cm^3 min^{-1}. (○); TiO_2–ZrO_2, (▲); Ag/TiO_2–ZrO_2, (□); Cu/TiO_2–ZrO_2, (◆); Ce/TiO_2–ZrO_2, (△); Ga/TiO_2–ZrO_2, (●); Ni/TiO_2–ZrO_2, (◇); Fe/TiO_2–ZrO_2, (■); Co/TiO_2–ZrO_2.

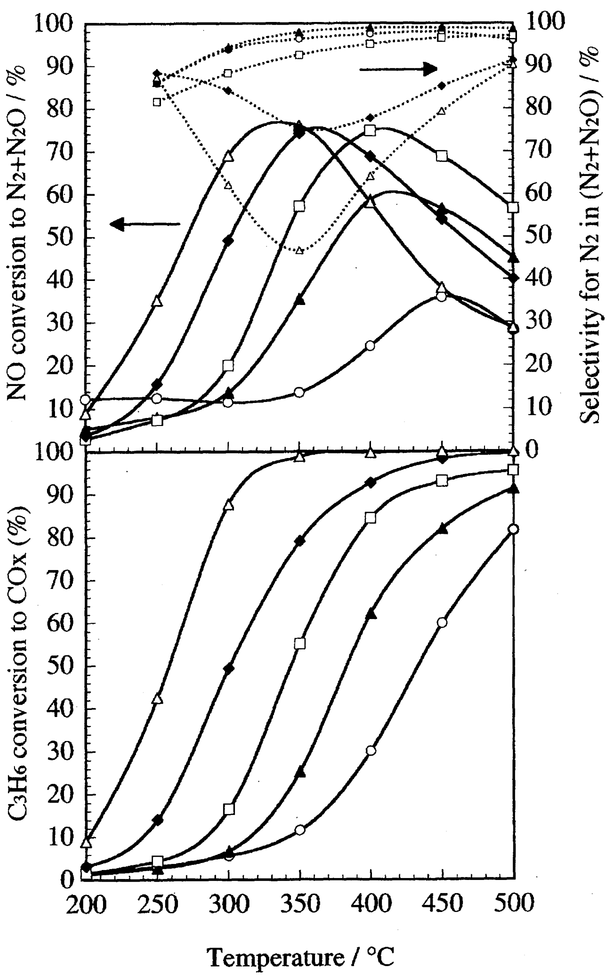

Fig. 2. Effect of silver loading on the catalytic activity of TiO_2–ZrO_2 for the selective reduction of NO with propene. The reaction conditions are the same as for Fig. 1. (○); TiO_2–ZrO_2, (▲); 2 wt% Ag, (□); 5 wt% Ag, (◆); 10 wt% Ag, (△); 15 wt% Ag.

propene oxidation activity was also highly promoted by silver addition. However, addition of an excess amount of silver lowered NO reduction selectivity for N_2, resulting in a large proportion of N_2O as a reduction product. From these results, it was concluded that 5 wt% Ag/TiO_2–ZrO_2 has the highest catalytic activity for NO reduction to N_2 with negligible formation of N_2O.

Silver oxide is generally known to be easily decomposed to metallic silver and oxygen above 300 °C. Miyadera supposed that the silver in Ag/Al_2O_3, which was reduced in flowing He at 500 °C for 1 h before the reaction, is in the metallic state under the reaction conditions of NO reduction.[11] However, the metallic silver may be converted in the oxidizing reaction gas to partially oxidized silver which seems to act as an active component. In fact we observed an induction period of about an hour before the NO conversion level reached a steady state on Ag/TiO_2–ZrO_2 which was pretreated in flowing helium at 500 °C, as shown in Fig. 3. In contrast, NO conversion level reached a steady state immediately after the reaction started, when the Ag-supported catalyst was pretreated at 500 °C in flowing O_2+He. These results suggest that the partially oxidized silver is an active species for NO reduction.

Characterization of Ag/TiO_2–ZrO_2. In order to examine the state of the supported silver, catalyst characterization was performed. The crystallite structure of silver was first examined by XRD measurements. However, no diffraction peaks assigned to silver compounds were observed even in the XRD patterns of 15 wt% Ag/TiO_2–ZrO_2. Silver seems to be highly dispersed as either metallic silver or silver oxide on TiO_2–ZrO_2 supports.

Figure 4 shows a TEM micrograph of 5 wt% Ag/TiO_2–ZrO_2 taken to estimate the particle size of silver. It was found that silver with a particle size of ca. 50—100 nm is

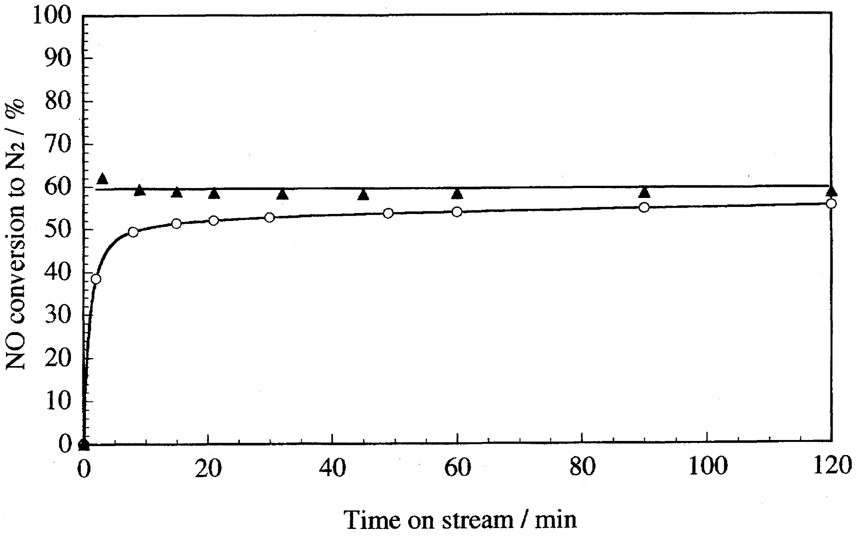

Fig. 3. Effect of pretreatment atmosphere on the catalytic activity of 5 wt% Ag/TiO$_2$–ZrO$_2$ for the selective reduction of NO with propene. The reaction conditions are the same as for Fig. 1. (○); pretreatment in flowing He, (▲); pretreatment in a flowing O$_2$+He mixture.

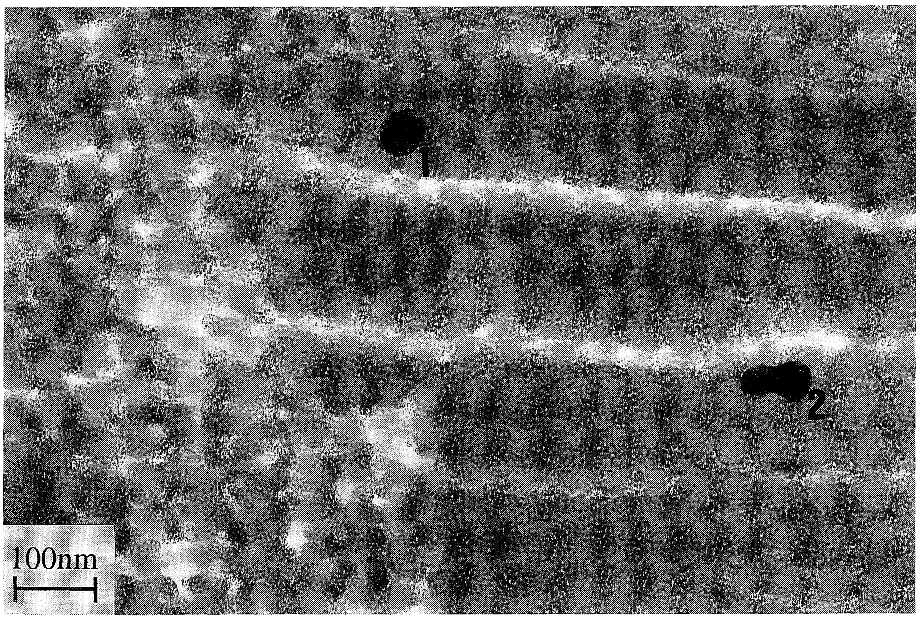

Fig. 4. TEM micrograph of 5 wt% Ag/TiO$_2$–ZrO$_2$.

dispersed on TiO$_2$–ZrO$_2$. Since no peaks were observed in the X-ray diffraction spectrum of 15 wt% Ag/TiO$_2$–ZrO$_2$, silver observed in the TEM micrograph might be supported as thin particles on TiO$_2$–ZrO$_2$. Miyadera[19] reported that the catalytic activity of Ag/Al$_2$O$_3$ for NO reduction by propene depends upon the BET surface area of alumina support. He also estimated from SEM micrographs that the particle size of silver supported on alumina, of which the BET surface area is about 250 $m^2 g^{-1}$, is ca. 100—1000 nm. Although the BET surface area of TiO$_2$–ZrO$_2$ was about 280 $m^2 g^{-1}$ and almost the same as that of the alumina used by Miyadera, the particle size of silver on TiO$_2$–ZrO$_2$ was fairly smaller than that on Al$_2$O$_3$.

TPR measurements were carried out for TiO$_2$–ZrO$_2$ and 5 wt% Ag/TiO$_2$–ZrO$_2$ to clarify the morphology of silver on TiO$_2$–ZrO$_2$. As shown in Fig. 5, no reduction peaks were detected in the TPR profile of TiO$_2$–ZrO$_2$ itself. On the other hand, two reduction peaks at 85 and 190 °C were observed on 5 wt% Ag/TiO$_2$–ZrO$_2$. These two peaks suggest that silver on TiO$_2$–ZrO$_2$ is somewhat oxygenated after calcination at 500 °C in a 20 vol% O$_2$–He gas atmosphere. Although silver oxide is thermodynamically unstable after calcination at 500 °C, metallic silver adsorbs oxygen on the surface and absorbs oxygen into the bulk, as reported by Ekern and Czanderna.[20] This oxygenated silver would behave as an active species in NO reduction by propene, as previously shown in Fig. 3. It should also be noticed that two forms of the oxygenated silver are present on TiO$_2$–ZrO$_2$, although the precise assignment of each reduction peak has not been made.

Role of Silver in NO Reduction over Ag/TiO$_2$–ZrO$_2$.

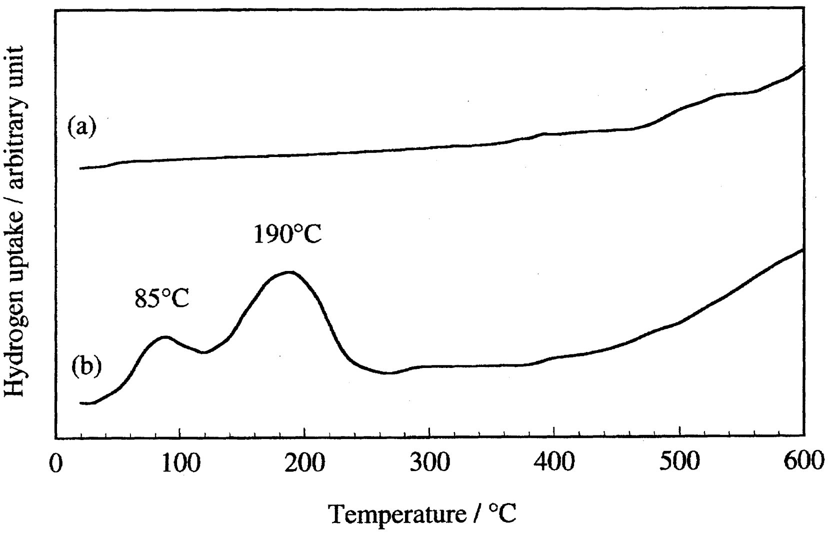

Fig. 5. TPR profiles of (a); TiO_2–ZrO_2 and (b); 5 wt% Ag/TiO_2–ZrO_2 after oxidation at 500 °C for 1 h in flowing 20 vol% O_2–He gas. Conditions: catalyst weight = 0.2 g, flow rate = 110 cm^3 min^{-1}, heating rate = 10°C min^{-1}, reducing gas; 10 vol% H_2–Ar.

(a) Effect of Nitrogen Dioxide. In a previous paper,[21] we reported that the supported cobalt species on Co/Al_2O_3 promote NO oxidation to NO_2 and that NO_2 thus formed seems to be a reaction intermediate in the overall selective reduction of NO. A similar role for active components has been proposed for Ce in Ce ion exchanged ZSM-5[22] and for Mn_2O_3 in the mechanical mixture catalyst of Au/Al_2O_3 and Mu_2O_3.[23] Accordingly, in order to explore the role of silver for NO reduction over Ag-supported TiO_2–ZrO_2, the reactivity of NO and NO_2 was compared. As shown in Fig. 6, 5 wt% Ag/TiO_2–ZrO_2 catalyst gave almost the same performance for both NO reduction and NO_2 reduction. Therefore NO_2 might directly participate in the selective reduction of NO with propene. Likewise no remarkable difference was observed between NO reduction and NO_2 reduction on TiO_2–ZrO_2, although the latter reaction occurred slightly more easily.

If the role of silver on Ag/TiO_2–ZrO_2 is to promote the oxidation of NO to NO_2, NO_2 conversion to N_2 on TiO_2–ZrO_2 has to be higher than NO conversion to N_2 on 5 wt% Ag/TiO_2–ZrO_2. However, the former activity was lower than the latter. These results suggest that NO oxidation to

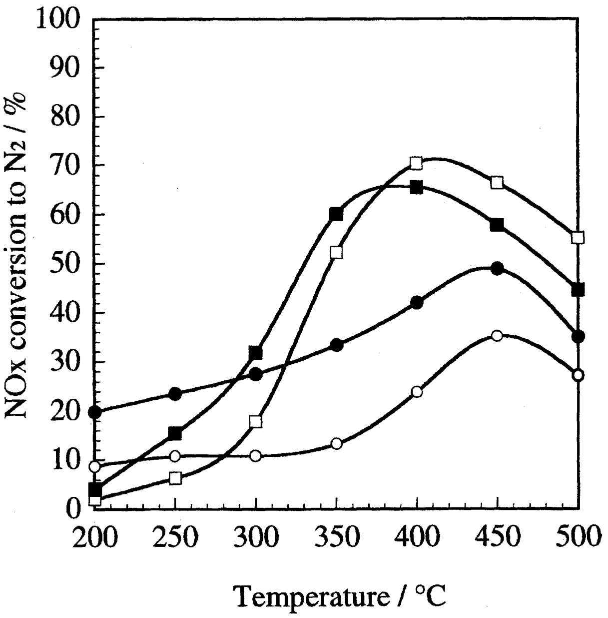

Fig. 6. Comparison of reactivity between NO (○, □) and NO_2 (●, ■) for the selective reduction over TiO_2–ZrO_2 (○, ●) and 5 wt% Ag/TiO_2–ZrO_2 (□, ■). Conditions: NO = 900 ppm, or NO_2 = 930 ppm, C_3H_6 = 850 ppm, O_2 = 10 vol%, catalyst weight = 0.2 g, gas flow rate = 66 cm^3 min^{-1}.

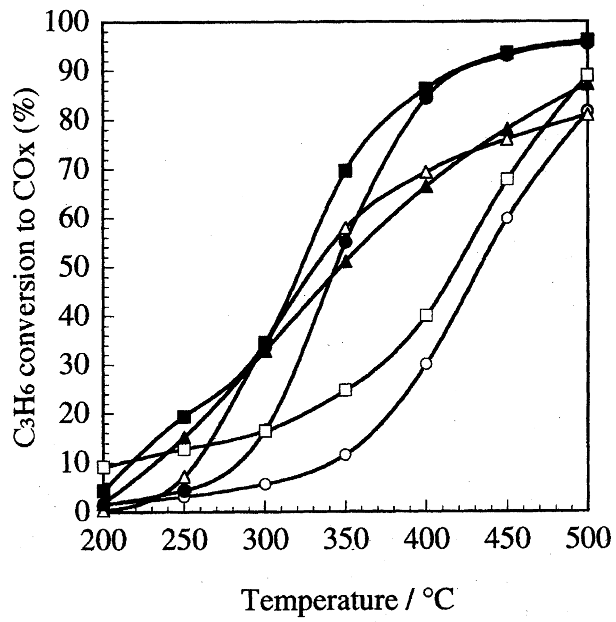

Fig. 7. Comparison of the propene conversion to CO_x for the reaction system of NO+C_3H_6+O_2 (○, ●), C_3H_6+O_2 (△, ▲), and NO_2+C_3H_6+O_2 (□, ■) over TiO_2–ZrO_2 (○, △, □) and 5 wt% Ag/TiO_2–ZrO_2 (●, ▲, ■). The reaction conditions are the same as for Fig. 6.

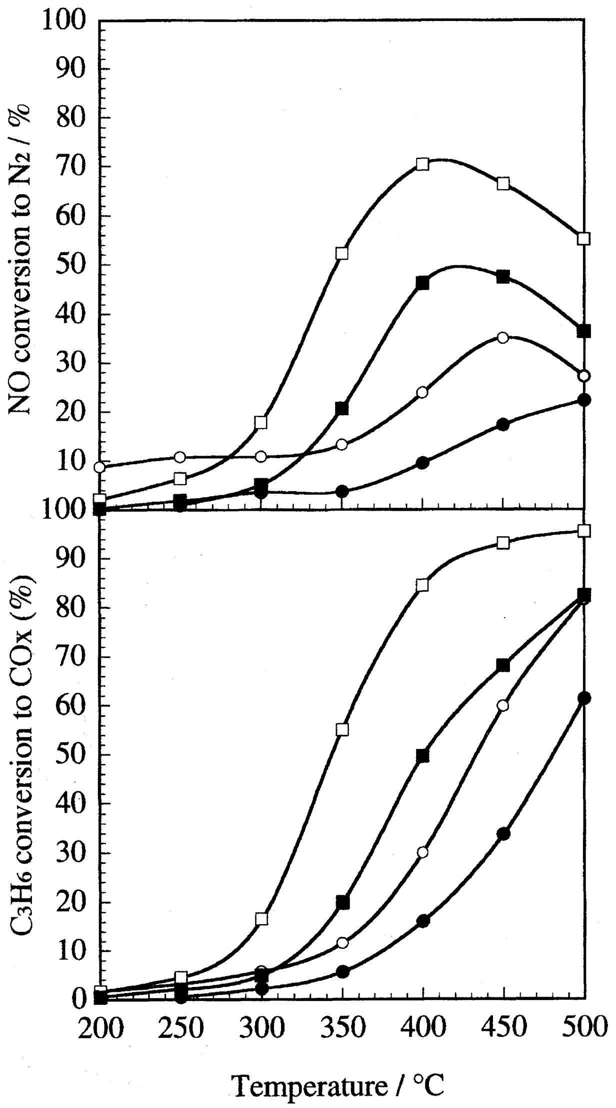

Fig. 8. Effect of water vapor on the catalytic activity of TiO_2–ZrO_2 (○, ●) and 5 wt% Ag/TiO_2–ZrO_2 (□, ■) for the selective reduction of NO with propene. Conditions: (○, □); NO = 900 ppm, C_3H_6 = 850 ppm, O_2 = 10 vol%, H_2O = 0 vol%, catalyst weight = 0.2 g, gas flow rate = 66 $cm^3 min^{-1}$. (●, ■); NO = 830 ppm, C_3H_6 = 780 ppm, O_2 = 8.6 vol%, H_2O = 8.3 vol%, catalyst weight = 0.2 g, gas flow rate = 72 $cm^3 min^{-1}$.

NO_2 is not the rate-determining step in the selective reduction of NO over Ag-supported TiO_2–ZrO_2 catalyst, although NO_2 intermediate seems to participate in NO reduction.

(b) Influence of Oxygen and Nitrogen Oxides on Propene Oxidation Activity. We examined the effect of silver toward the oxidation of propene into CO_x under these reaction systems. $NO+C_3H_6+O_2$, $C_3H_6+O_2$, and $NO_2+C_3H_6+O_2$. As shown in Fig. 7, the catalytic activity of Ag/TiO_2–ZrO_2 for propene oxidation by oxygen was almost the same as that of TiO_2–ZrO_2. However, when nitrogen oxide (NO or NO_2) was added into the reaction gas, a great difference in the propene oxidation activity of both catalysts was observed. Namely, silver on TiO_2–ZrO_2 increased propene conversion to CO_x drastically in the presence of nitrogen oxide, suggesting that nitrogen oxide reacts with propene to form CO_x.

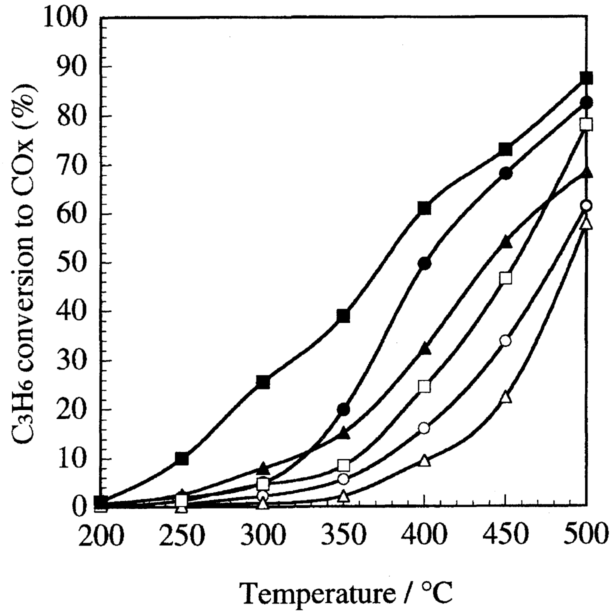

Fig. 9. Comparison of the propene conversion to CO_x for the reaction system of $NO+C_3H_6+O_2$ (○, ●), $C_3H_6+O_2$ (△, ▲), and $NO_2+C_3H_6+O_2$ (□, ■) over TiO_2–ZrO_2 (○, △, □) and 5 wt% Ag/TiO_2–ZrO_2 (●, ▲, ■) in the presence of water vapor. Conditions: NO=830 ppm or NO_2 = 850 ppm, C_3H_6 = 780 ppm, O_2 = 8.6 vol%, H_2O = 8.3 vol%, catalyst weight = 0.2 g, gas flow rate = 72 $cm^3 min^{-1}$.

Here, we tried to calculate the selectivity for NO reduction, defined as the following equation:

$$\text{Selectivity} = (\text{number of NO which reacted to } N_2)/(\text{number of } C_3H_6 \text{ which reacted to } CO_x).$$

The selectivity of TiO_2–ZrO_2 and 5 wt% Ag/TiO_2–ZrO_2 for NO reduction was 0.62 and 0.74 at 450 °C and 0.84 and 0.86 at 400 °C, respectively. This means that the addition of silver increases the selectivity of TiO_2–ZrO_2 for NO reduction, supporting the speculation described above. As NO_2 is a strong oxidizing agent, it is likely that NO is first converted to NO_2, which then reacts with propene. It is well known that silver catalysts are utilized industrially for the partial oxidation of ethylene to ethylene oxide[24] and that silver is capable of producing effectively ethylene oxide without formation of CO_2 and CO. On the basis of our experimental results and the general property of silver catalysts mentioned above, it is presumed that silver in Ag/TiO_2–ZrO_2 plays an important catalytic role for the selective formation of reaction intermediates (probably oxygenated hydrocarbons) by the reaction of nitrogen dioxide (NO_2) with hydrocarbon.

NO Reduction Activity of Ag/TiO_2–ZrO_2 in the Presence of Water Vapor. Since water vapor is contained in most exhaust gases, the influence of water vapor on NO reduction must be tested. In Fig. 8 are shown the changes of the catalytic activity of TiO_2–ZrO_2 and 5 wt%

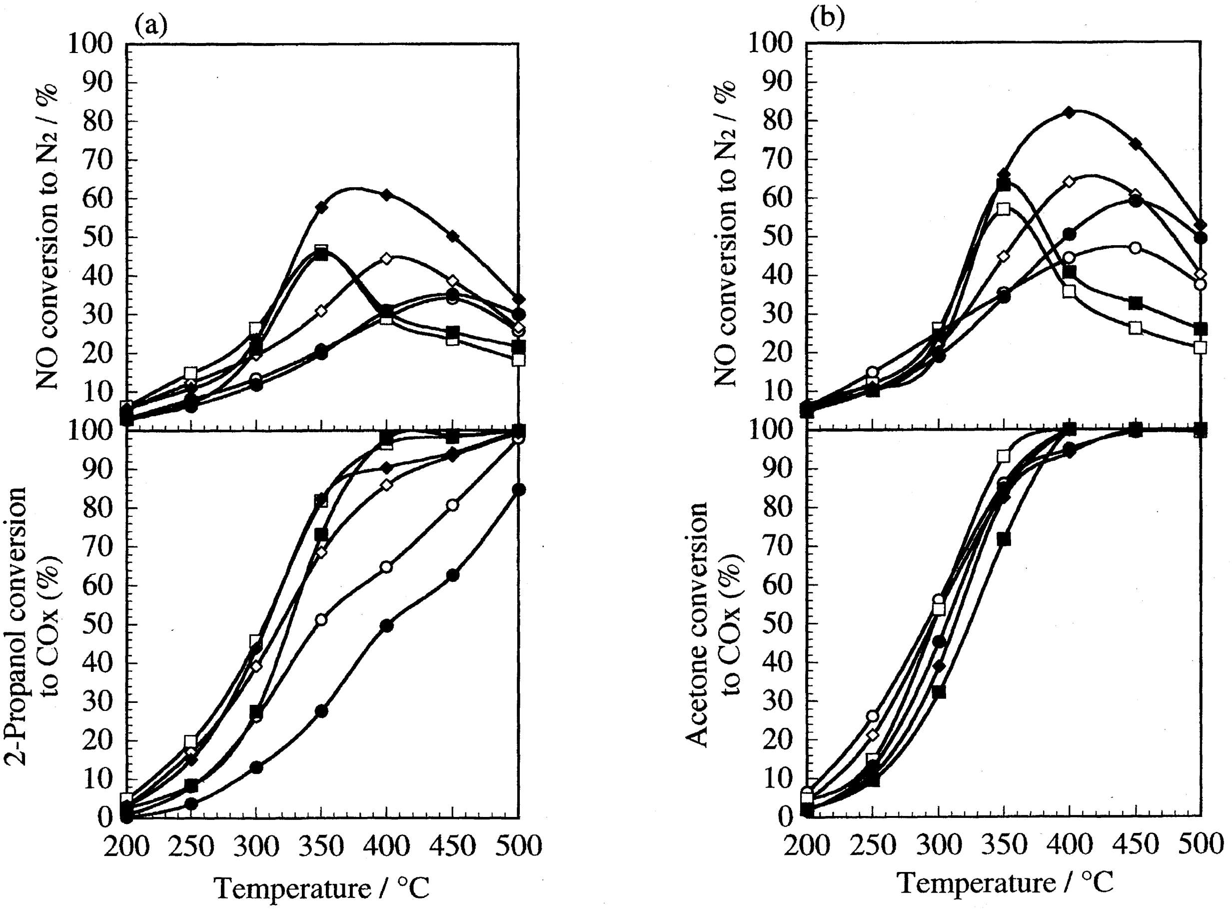

Fig. 10. Effect of water vapor on the catalytic activity of TiO_2–ZrO_2 (○, ●), 1 wt% Ag/TiO_2–ZrO_2 (◇, ◆) and 5 wt% Ag/TiO_2–ZrO_2 (□, ■) for the selective reduction of NO with (a); 2-propanol and (b); acetone. Conditions: (○, ◇, □); NO=900 ppm, 2-propanol=580 ppm or acetone=850 ppm, O_2=10 vol%, H_2O=0 vol%, catalyst weight=0.2 g, gas flow rate=66 cm^3 min^{-1}. (●, ◆, ■); NO=830 ppm, 2-propanol=530 ppm or acetone=780 ppm, O_2=8.6 vol%, H_2O=8.3 vol%, catalyst weight=0.2 g, gas flow rate=72 cm^3 min^{-1}.

Ag/TiO_2–ZrO_2 by addition of water vapor. The activity of 5 wt% Ag/TiO_2–ZrO_2 was decreased by H_2O, although the maximum NO conversion on the catalyst was still about 50% at 400—450 °C even in the presence of 8.3 vol% water vapor. On the other hand, TiO_2–ZrO_2 hardly catalyzed NO reduction in the presence of water vapor. It is well known that water vapor poisons the active sites for some reaction steps in the selective reduction of NO with hydrocarbons. Kikuchi and Yogo reported that water vapor inhibits the selective reduction of NO with CH_4 over Ga/H–ZSM-5 and In/H–ZSM-5 by poisoning the Lewis acid site responsible for the oxidation of NO to NO_2, which is the first reaction step.[6] In the present study, the retarding effect of H_2O on this reaction might be only a little, since the NO oxidation to NO_2 is not the rate-determining step.

Figure 9 presents the effect of water vapor on the propene conversion to CO_x for the reaction system of NO+C_3H_6+O_2, C_3H_6+O_2, and NO_2+C_3H_6+O_2 over TiO_2–ZrO_2 and 5 wt% Ag/TiO_2–ZrO_2. It is evident from Figs. 7 and 9 that the propene oxidation activity of both catalysts by both O_2 or nitrogen oxide (NO or NO_2) was considerably depressed by coexisting water vapor. Therefore, water vapor seems to hinder the rate-determining reaction step between propene and NO_2 on Ag sites to form oxygenated intermediates by inhibiting the activation of propene.

Selective Reduction of NO with 2-Propanol and Acetone over Ag/TiO_2–ZrO_2 in the Presence of Water Vapor. Many researchers have proposed the reaction mechanism of the selective reduction of NO with hydrocarbons.[25—27] Some references suggest that this reaction proceeds via partially oxidized hydrocarbons such as alcohols and ketones as reaction intermediates. It is expected from this hypothesis that certain oxygen-containing compounds would be more efficient reductants in the selective reduction of NO than hydrocarbons. In fact the good performances of oxygenated organic compounds have already been reported.[11,28]

We presume that a similar reaction mechanism works in the present reaction on Ag/TiO_2–ZrO_2, as mentioned above. Consequently, we examined the efficiency of 2-propanol and acetone as a reducing agent. As it was suggested that the first reaction step between propene and NO_2 to form an oxygenated intermediate is suppressed by coexisting water vapor, these reductants would be more effective for NO reduction than propene in the presence of water vapor.

Figure 10 shows the efficiency of 2-propanol and acetone for NO reduction over Ag/TiO_2–ZrO_2 with different silver loading in the presence or absence of water vapor. As for the reaction in the absence of water vapor, the behavior of 2-propanol and that of acetone are quite similar to each other, although the exact comparison of the efficiency of both reducing agents is impossible because of the different concentrations of the reducing agent. The NO reduction activity was enhanced by addition of silver up to 1 wt%. Interestingly, acetone conversion to CO$_x$ was almost unchanged for all the catalysts in spite of the different loading of silver, whereas the conversion of 2-propanol increased with increasing silver content. From these observations, it is considered that 2-propanol might be further converted to an oxygenated organic compound involving carbonyl group ($\rangle$C=O) such as acetone by the reaction with NO$_2$ or O$_2$, which is probably the final oxygeneted intermediate.

Interesting catalytic behavior of 1 wt% Ag/TiO$_2$–ZrO$_2$ for NO reduction was observed in the presence of water vapor. The presence of water vapor did not inhibit, but rather enhanced NO reduction on 1 wt% Ag/TiO$_2$–ZrO$_2$ by both reducing agents. Also, TiO$_2$–ZrO$_2$ and 5 wt% Ag/TiO$_2$–ZrO$_2$ were not sensitive to water vapor at all, the NO conversion being almost the same. Finely dispersed silver on TiO$_2$–ZrO$_2$ might be the reason for the enhancement of NO reduction efficiency of 1 wt% Ag/TiO$_2$–ZrO$_2$ by H$_2$O.

In order to make clear the reaction step, which was inhibited by H$_2$O in the overall selective reduction of NO with 2-propanol and acetone, the reactivity of NO and that of NO$_2$ were compared. As shown in Fig. 11, both NO reduction and NO$_2$ reduction proceeded more effectively in the presence of water vapor than in the absence of it. Particularly, the extent of NO$_2$ reduction was much higher than that of NO reduction in the lower temperature region. This result suggests

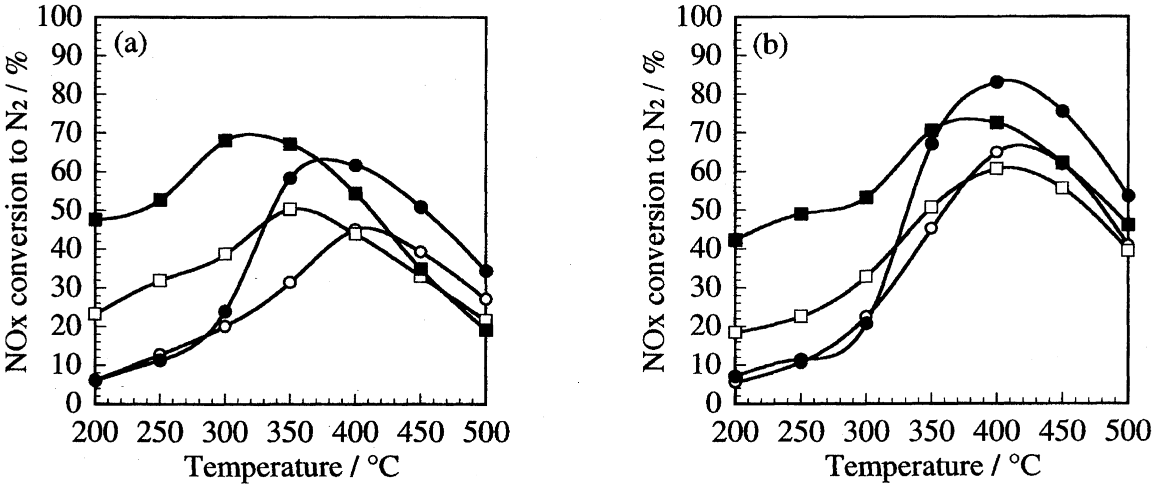

Fig. 11. Effect of water vapor on the reactivity of NO (○, ●) and NO$_2$ (□, ■) for the selective reduction over 1 wt% Ag/TiO$_2$–ZrO$_2$ by (a); 2-propanol and (b); acetone. Conditions: (○, □); NO=900 ppm or NO$_2$=930 ppm, 2-propanol=580 ppm or acetone=850 ppm, O$_2$=10 vol%, H$_2$O=0 vol%, catalyst weight=0.2 g, gas flow rate=66 cm^3 min^{-1}. (●, ■); NO=830 ppm or NO$_2$=850 ppm, 2-propanol=530 ppm or acetone=780 ppm, O$_2$=8.6 vol%, H$_2$O=8.3 vol%, catalyst weight=0.2 g, gas flow rate=72 cm^3 min^{-1}.

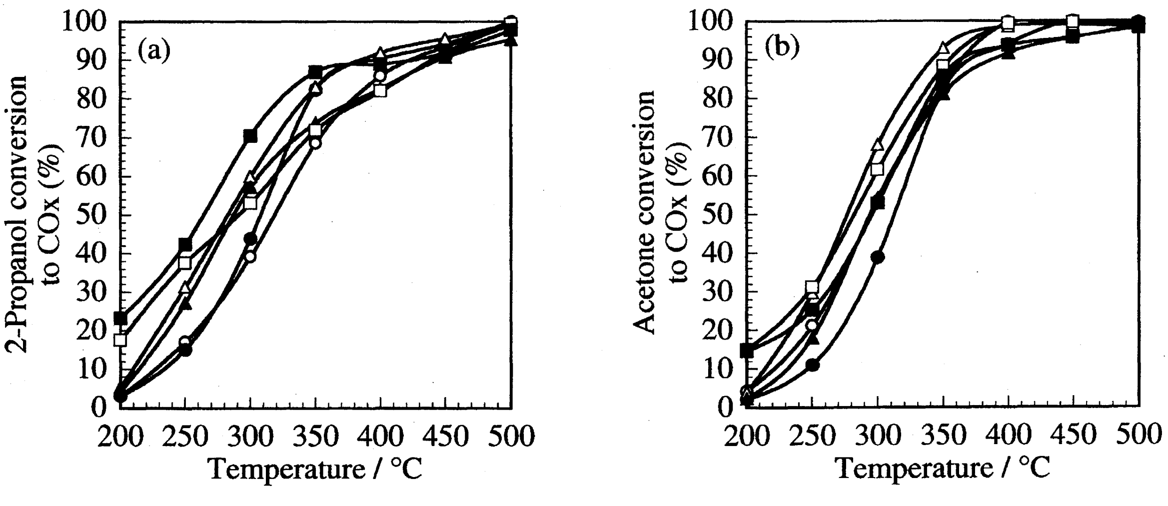

Fig. 12. Effect of water vapor on the (a); 2-propanol and (b); acetone conversions to CO$_x$ for the reaction system of NO+C$_3$H$_6$+O$_2$ (○, ●), C$_3$H$_6$+O$_2$ (△, ▲), and NO$_2$+C$_3$H$_6$+O$_2$ (□, ■) over 5 wt% Ag/TiO$_2$–ZrO$_2$. The reaction conditions of the opened symbols and the closed symbols are the same as for those in Fig. 11, respectively.

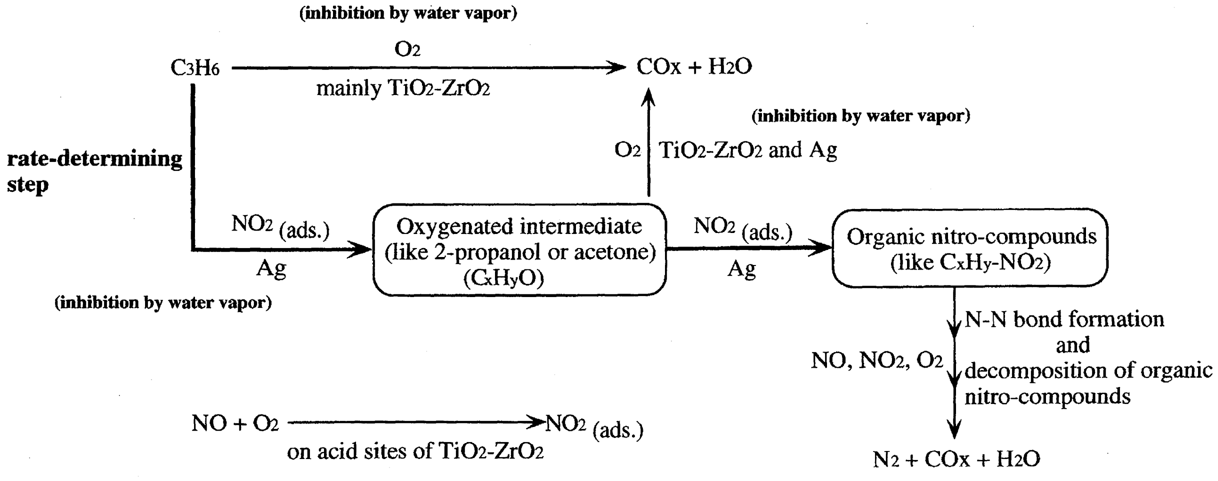

Fig. 13. Proposed reaction mechanism for the selective reduction of NO with propene on Ag/TiO_2–ZrO_2.

that NO_2 seems to participate in NO reduction when the oxygen-containing organic compounds were used as reductants, leading to the speculation that the formation of NO_2 is a key step on this reaction.

Next the oxidation of the reductant to CO_x was examined in the reaction systems of NO+reductant+O_2, reductant+O_2 and NO_2+reductant+O_2 on 1 wt% Ag/TiO_2–ZrO_2. Figure 12 shows the influence of water vapor on the catalytic activity for the oxidation of the reducing agents. When water vapor is not present in the reaction gas, the oxidation of the reducing agent by O_2 proceeded most effectively. However, when water vapor was added to the feed gas, the conversion to CO_x was accelerated by the presence of NO or NO_2. This tendency was observed more significantly for 2-propanol. Consequently, it is concluded that water vapor inhibits only the oxidation of the reducing agent by O_2 and promotes the reaction between nitrogen oxide and the reducing agent.

Presumed Reaction Mechanism for the Selective Reduction of NO with Propene over Ag/TiO_2–ZrO_2. A large number of reaction mechanisms have been proposed so far for the selective reduction of NO with hydrocarbons in the presence of oxygen. Among them, a reaction mechanism in which N_2 formation results via consecutive reaction steps consisting of the formation of partially oxidized hydrocarbons[27—30] or NO_2[4,6,31] and the formation and decomposition of nitrogen-containing intermediates[22] was supported by many investigators. We propose the same kind of mechanism for the selective reduction of NO by propene, 2-propanol and acetone in the presence of oxygen and water vapor over Ag/TiO_2–ZrO_2, as given in Fig. 13.

Since a large difference of reactivity between NO and NO_2 was not observed, as shown in Fig. 6, it is suggested that NO_2 participates in the first step of the reaction. Kikuchi and Yogo[6] showed that for NO reduction by methane over Ga/H–ZSM-5, NO oxidation to NO_2 is the first step and proceeds mainly on zeolite Lewis acid sites. It was also reported that TiO_2–ZrO_2 binary oxide has a large number of Lewis acid sites.[15,32] Moreover, Hadjiivanov et al.[33] reported that the adsorption of NO_2 on TiO_2 (anatase) gives rise to NO_3^- on coordinatively unsaturated acid-base pairs (Ti^{4+}–O^{2-}) via the formation of Ti–O_2NOH by the interaction of NO_2 with the H-bonded hydroxyl groups on TiO_2 surface. These reports suggest that the role of TiO_2–ZrO_2 on the NO reduction by propene is to stimulate the formation of NO_2 on the acid sites and to concentrate NO_2 on the acid-base pairs.

As shown in Fig. 7, the propene conversion to CO_x on Ag/TiO_2–ZrO_2 was drastically enhanced by the presence of nitrogen oxides (NO or NO_2), while an opposite tendency was observed on TiO_2–ZrO_2. Moreover, 2-propanol and acetone were as good reductants as propene on Ag/TiO_2–ZrO_2 in the absence of water vapor. Therefore, it is concluded that the initial rate-determining step is the oxidation of propene by NO_2 on the supported silver species to form a partially oxidized hydrocarbon. Since the material balance on carbon atoms was quite good in the effluent gas from the reactor, this intermediate might be stable only on the surface of the catalyst. Here, we also presume that NO reduction over TiO_2–ZrO_2 itself proceeds under a similar reaction mechanism, although the reaction rate is very low. The presence of water vapor, however, decreased the NO reduction activity of Ag/TiO_2–ZrO_2 drastically. This result would be attributed to the depression of the reaction rate of nitrogen oxide (NO or NO_2) with propene, because a retarding effect by water vapor on the propene conversion to CO_x for the reaction system of NO+C_3H_6+O_2, C_3H_6+O_2, and NO_2+C_3H_6+O_2 was observed.

Miyadera[11] found that the oxygen-containing compounds such as ethanol and acetone are more powerful reductants than propene on Ag/Al_2O_3 catalyst under the reaction conditions involving H_2O. In the present work, we found that the NO conversion to N_2 on 1 wt% Ag/TiO_2–ZrO_2 was drastically enhanced by coexisting water vapor when 2-propanol and acetone were used as the reducing agent (Fig. 10). Since water vapor did not affect the conversion of the reducing agent to CO_x in the reaction system of NO(NO_2)–reductant–O_2 but significantly decreased the conversion in the reaction system of reductant–O_2 reaction (Fig. 12), it is presumed that water vapor accelerates the selective reduction of NO with 2-propanol or acetone by suppressing the undesirable oxidation of them by O_2.

2-propanol or acetone might react with NO_2 on the supported silver particles to form a nitrogen-containing intermediate, since NO_2 conversion to N_2 for the system of NO_2–reductant–O_2 was considerably higher than NO conversion to N_2 for NO–reductant–O_2 system below 350 °C (Fig. 11). A similar reaction mechanism has been proposed by Smits and Iwasawa.[26]

Conclusions

The metal additive effect on the performance of TiO_2–ZrO_2 catalyst for the selective reduction of NO with propene, 2-propanol and acetone was investigated. When silver was added to TiO_2–ZrO_2 catalyst, NO reduction activity by propene was drastically enhanced in the region of reaction temperature tested. This silver additive effect was explained by the assumption that silver promotes the reaction of NO_2 with propene, which is the initial rate-determining step, to form a partially oxidized hydrocarbon. The presence of water vapor depressed the catalytic activity of Ag/TiO_2–ZrO_2 for NO reduction by propane because the formation of the oxygenated intermediate on silver is inhibited by coexisting water.

On the other hand, when the oxygen-containing organic compounds such as 2-propanol and acetone were used as reductants, Ag/TiO_2–ZrO_2 catalyst showed an excellent catalytic performance for NO reduction. The presence of water vapor did not inhibit, but promoted NO reduction activity. It is presumed that water vapor accelerates the selective reduction of NO by suppressing the undesirable oxidation of the reductants by O_2.

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