Additive Effect of Palladium on the Catalytic Activity of In/TiO_2–ZrO_2 for the Selective Reduction of Nitrogen Monoxide in the Presence of Water Vapor

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The additive effect of noble metals (Pt, Pd, Rh, and Ir) on the catalytic activity of In/TiO_2–ZrO_2 for the selective reduction of NO with propene in the presence of water vapor was investigated. Although NO reduction activity of In/TiO_2–ZrO_2 was inhibited drastically by coexisting water vapor, the addition of palladium was capable of depressing the retarding effect. The presence of both indium and palladium was necessary for the enhancement of NO reduction activity, and this was accounted for by a synergistic effect between palladium and indium. Optimum indium and palladium loadings were at 2—5 wt% and 0.005 wt%, respectively. It is suggested that the NO reduction on Pd/In/TiO_2–ZrO_2 by propene proceeds via the following consecutive steps: the formation of oxygenated intermediates by the reaction of propene with oxygen on palladium, a spillover of the intermediates from palladium to indium and reaction between the intermediates and NO_2 to form N_2 on indium.

Since nitrogen oxides (NO_x) are harmful for human health and the global environment, removal of NO_x emitted from combustion facilities is necessary. In particular new effective deNO_x technologies for diesel and lean-burn vehicles have to be developed before long. In this respect, the selective reduction of NO with hydrocarbons in the presence of oxygen has attracted much attention since Held et al.[1)] and Iwamoto et al.[2)] reported the catalytic activity of copper ion exchanged ZSM-5 towards this reaction followed by earlier patents.[3)] Afterwards many catalysts have been reported, such as metal ion-exchanged zeolites,[4—6)] H-form zeolites,[7,8)] alumina,[9)] and transition metal-supported alumina.[10)]

One of the most serious problems encountered is the retarding effect by coexisting water vapor in combustion exhaust gases. Two kinds of the retarding effect are well known: One is irreversible catalyst deactivation such as dealumination from zeolite framework. However, preventing this effect is very difficult. The other is the reaction inhibition by reversible adsorption of water vapor on catalyst surface. This effect may be solved by improving the catalyst system. For instance, Hirao et al. reported recently the unique catalytic behavior of a mechanical mixture of Mn_2O_3 and Sn–ZSM-5 that the presence of water vapor enhanced drastically the catalytic activity for NO reduction by propene over the entire temperature range.[11)] More recently, we found that the addition of water vapor increased NO conversion as well as propene conversion on silver ion-exchanged saponite, which is a clay material, at low temperatures below 400 °C.[12)] Kikuchi et al. reported that Pt, Rh, and Ir-loaded In/H–ZSM-5 exhibited high catalytic activity for NO reduction by methane even in the presence of water vapor.[13)] In addition, Au/Al_2O_3 has been reported to show a promoting effect by water vapor for the selective reduction of NO with propene.[14)] Ag/Al_2O_3 also showed the same catalytic performance as Au/Al_2O_3 when ethanol was used as a reductant.[15)]

In our previous study,[16)] it was found that indium-supported TiO_2–ZrO_2 catalyst showed high activity and selectivity for NO reduction by propene in the absence of water vapor. However, we found that the activity of the catalyst was strongly inhibited by coexisting water vapor. Therefore, we attempted to improve the tolerance of In/TiO_2–ZrO_2 against water vapor by addition of small amounts of noble metals (Pt, Pd, Rh, and Ir). We will report here the excellent catalytic behavior of the noble metal loaded In/TiO_2–ZrO_2 catalysts in the presence of water vapor.

Experimental

Catalyst Preparation. The indium-supported TiO_2–ZrO_2 catalyst was prepared by immersing TiO_2–ZrO_2 powder, which had been synthesized by hydrolysis of metal alkoxides,[17)] in an aqueous solution of $In(NO_3)_3 \cdot 2H_2O$, followed by drying and calcination at 500 °C for 5 h in flowing air. Indium loading was changed from 2 to 15 wt% as In metal. Pt, Pd, Rh, and Ir were subsequently supported on In/TiO_2–ZrO_2 by an impregnation method using an aqueous solution of $[Pt(NH_3)_4](NO_3)_2$, $[Pd(NH_3)_4](NO_3)_2$, $Rh(NO_3)_3$, and $IrCl_4$, respectively, followed by drying and calcination at 500 °C for 5 h in flowing air. Loading of the noble metals was fixed at 0.01 wt% except for palladium, the loading of which was changed from 0.005 to 0.02 wt%. The samples are denoted by noble metal (x%)/In (y%)/TiO_2–ZrO_2, where x and y are the loadings of noble metal and indium, respectively.

Catalytic Activity Measurements. The selective reduction of NO was carried out with a fixed-bed flow reactor by passing a reactant gas mixture containing 900 ppm NO, 860 ppm propene, 10% oxygen, and helium as a balance gas at a rate 66 cm^3 min^{-1} over 0.2 g of catalyst. In addition to propene, methane, ethene, propane, methanol, ethanol, 1-propanol, 2-propanol, and acetone were also tested as the reducing agent in the same mixture. In some experiments, water was introduced to the reaction gas mixture before the catalyst bed by a micropump. The concentration of water vapor was fixed at 9.1%. The analysis of the effluent gas was made with gas chromatographs equipped with a Molecular Sieve 5A column (for the analysis of N_2, CO, and CH_4) and a Porapak Q column (for that of CO_2, N_2O, C_2H_4, C_3H_8, and C_3H_6). The reaction temperature was lowered from 500 to 200 °C in steps of 50 °C.

Catalyst Characterization. BET surface area of the catalyst was measured with a conventional flow apparatus (Shimadzu, Flowsorb II 2300) by nitrogen adsorption at −196 °C. The dispersion and the particle size of the noble metals supported on In/TiO_2–ZrO_2 were determined from the amount of chemisorbed CO measured with a pulse method. In this chemisorption measurement, the sample was first reduced at 400 °C in a hydrogen flow for 30 min and then the temperature was cooled down to room temperature. Several numbers of CO pulses were introduced onto the sample until CO was not adsorbed any more. TDC was used to analyze the effluent gas.

Results and Discussion

Effect of Water Vapor on the Activity of In/TiO_2–ZrO_2. Figure 1 shows the influence of water vapor on the catalytic activity of TiO_2–ZrO_2 and In(5%)/TiO_2–ZrO_2 for the selective reduction of NO with propene. A considerable inhibiting effect by water vapor was recognized on both catalysts. Water vapor depressed the rate of NO reduction as well as that of propene oxidation over both catalysts. However, the activity of In/TiO_2–ZrO_2 in the presence of water vapor was higher than that of TiO_2–ZrO_2, suggesting that indium supported on TiO_2–ZrO_2 catalyzes this reaction even in the presence of water vapor. Figure 2 shows the effect of indium loading on the catalytic activity of In/TiO_2–ZrO_2 for NO reduction by propene at 450 °C. Apparently, the catalysts tested here were very sensitive to water vapor, irrespective of indium loading. It should be noted that a maximum NO conversion was attained at an indium loading of 5 wt%.

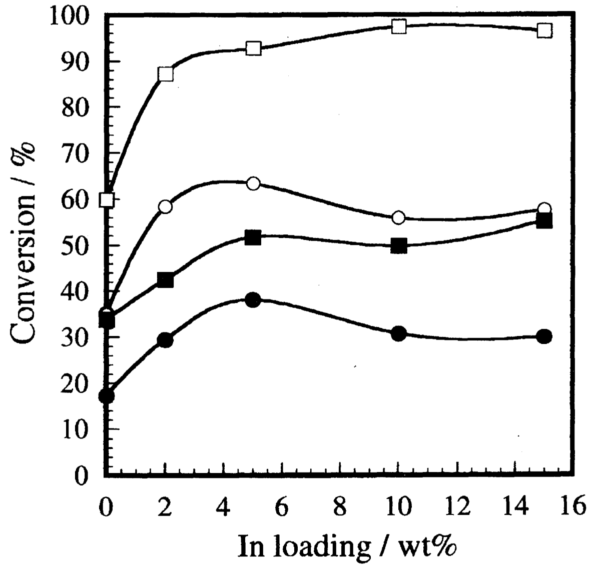

Fig. 2. Effect of indium loading on the catalytic activity of In/TiO_2–ZrO_2 at 450 °C for the selective reduction of NO with propene in the absence of and the presence of water vapor. The reaction conditions are the same as for Fig. 1. NO conversion to N_2; (○) without H_2O, (●) with H_2O. C_3H_6 conversion to CO_x; (□) without H_2O, (■) with H_2O.

In our previous paper,[16] we proposed a reaction mechanism of NO reduction by propene over In/TiO_2–ZrO_2 : N_2 is formed through the reaction of propene with NO_2, which was formed on the acid sites of TiO_2–ZrO_2, on the indium sites. In order to examine which reaction steps are inhibited by water vapor, NO_2–C_3H_6–O_2 reaction was carried out on TiO_2–ZrO_2 and In(5%)/TiO_2–ZrO_2 in the presence and ab-

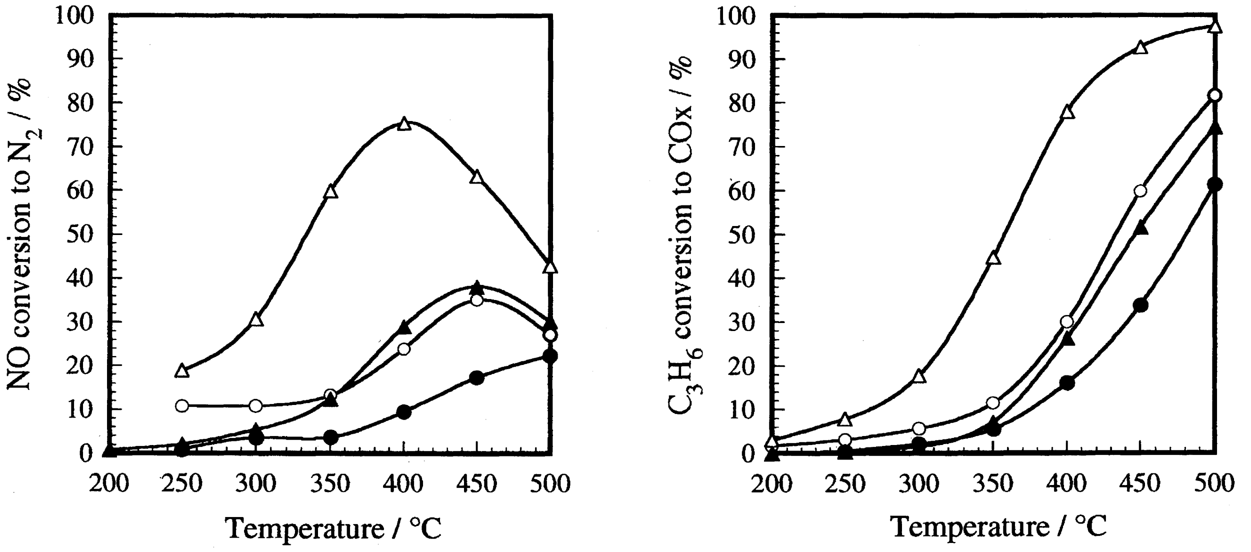

Fig. 1. Effect of water vapor on the catalytic activity of TiO_2–ZrO_2 (○, ●) and In(5%)/TiO_2–ZrO_2 (△, ▲) for the selective reduction of NO with propene in the absence of (○, △) and the presence of water vapor (●, ▲). Conditions: NO = 900 ppm, C_3H_6 = 860 ppm, O_2 = 10%, H_2O = 0 or 9.1%, catalyst weight = 0.2 g, gas flow rate = 66 cm^3 min^{-1}.

sence of water vapor. As shown in Fig. 3, the activity of both catalysts decreased significantly by water vapor, similarly to the results of the NO–C_3H_6–O_2 reaction given in Fig. 1. Almost the same activity of In(5%)/TiO_2–ZrO_2 as that of TiO_2–ZrO_2 for NO_2 reduction in the presence of water vapor suggests that the reaction steps over In sites are inhibited by water vapor. It can also be seen by comparing Figs. 1 and 3 that, as for the reaction in the presence of water vapor, the conversion of NO to N_2 on In(5%)/TiO_2–ZrO_2 was identical to that of NO_2 to N_2. Moreover, the conversion of propene to CO_x on In/TiO_2–ZrO_2 decreased significantly by water vapor in the reaction systems of NO–C_3H_6–O_2 and NO_2–C_3H_6–O_2. These results indicate that water vapor does not inhibit the oxidation of NO to NO_2 on acid site of TiO_2–ZrO_2 but does inhibit the reaction of propene with NO_2 on In sites.

Additive Effect of Noble Metals on the Activity of In/TiO_2–ZrO_2 for NO–C_3H_6–O_2–H_2O Reaction. Since the deactivation of In sites by water vapor cannot be avoided, we tried to use the noble metals, which possess high resistance to water vapor in this reaction,[5,18,19] as an additive to enhance the activity of In/TiO_2–ZrO_2 in the presence of water vapor. Figure 4 shows the additive effect of Pt, Pd, Rh, and Ir on the activity of In(5%)/TiO_2–ZrO_2 for NO reduction by propene in the presence of water vapor. The addition of Pt and Ir caused a drastic enhancement of propene conversion to CO_x on In(5%)/TiO_2–ZrO_2, whereas the conversion of NO to N_2 decreased. This is probably due to too high activity of Pt and Ir for complete oxidation of propene by oxygen,

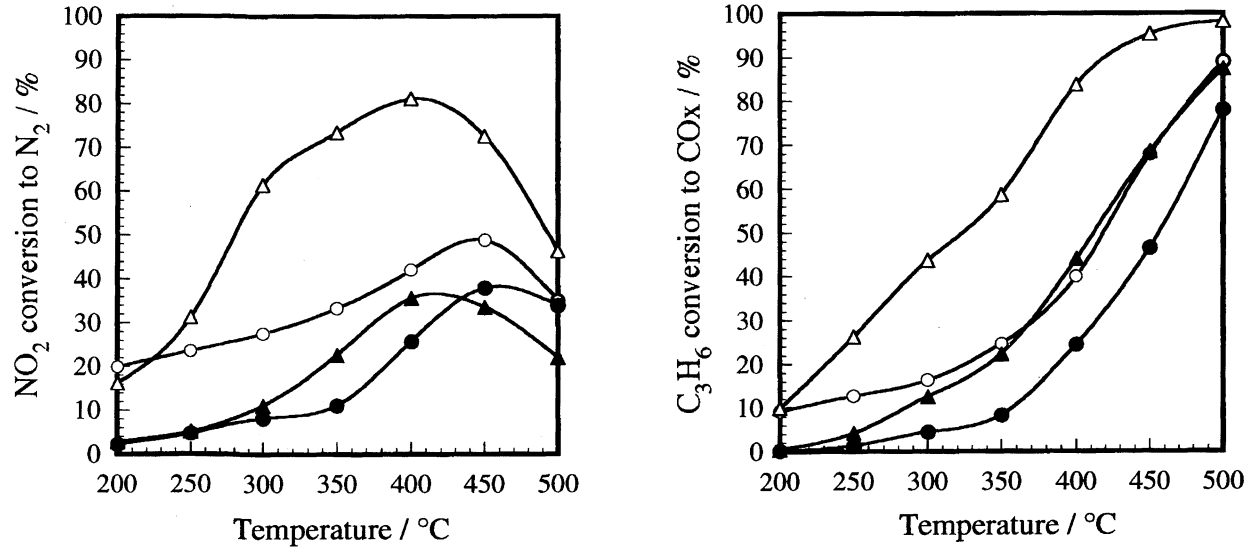

Fig. 3. Effect of water vapor on the catalytic activity of TiO_2–ZrO_2 (○, ●) and In(5%)/TiO_2–ZrO_2 (△, ▲) for the selective reduction of NO_2 with propene in the absence of (○, △) and the presence of water vapor (●, ▲). Conditions: NO_2 = 930 ppm, C_3H_6 = 860 ppm, O_2 = 10%, H_2O = 0 or 9.1%, catalyst weight = 0.2 g, gas flow rate = 66 cm^3 min^{-1}.

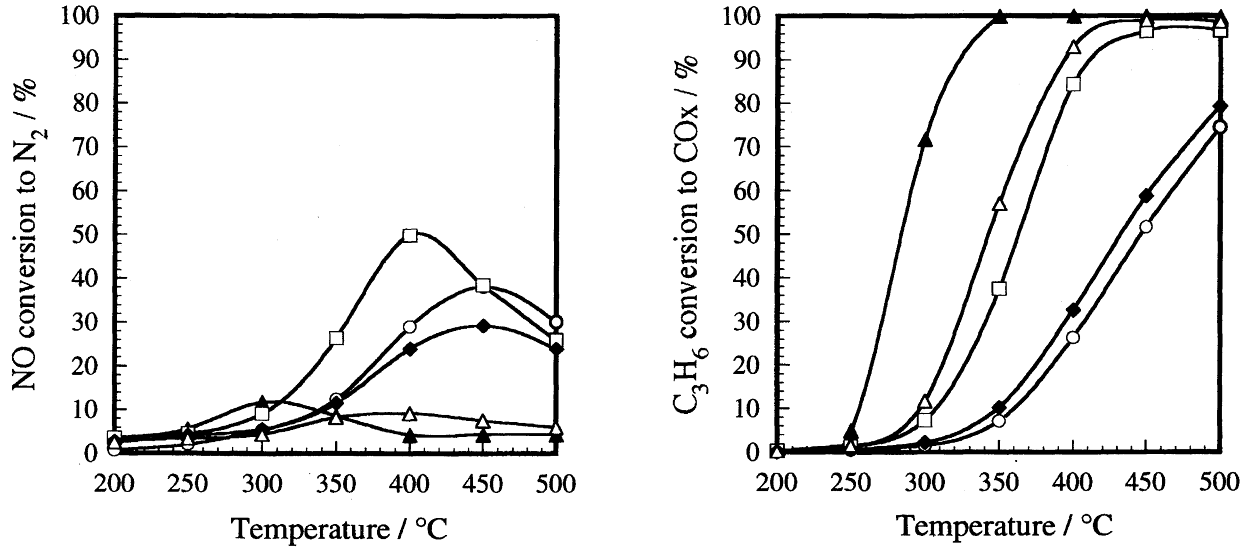

Fig. 4. Effect of noble metal additives (0.01 wt%) on the catalytic activity of In(5%)/TiO_2–ZrO_2 for the selective reduction of NO with propene in the presence of water vapor. The reaction conditions are the same as for Fig. 1. (○) In/TiO_2–ZrO_2, (▲) Pt/In/TiO_2–ZrO_2, (□) Pd/In/TiO_2–ZrO_2, (◆) Rh/In/TiO_2–ZrO_2, (△) Ir/In/TiO_2–ZrO_2.

resulting in a decrease of the selectivity for NO reduction. The addition of Rh also decreased slightly the NO reduction activity in the whole temperature range. In contrast, the loading of Pd enhanced significantly the NO reduction activity as well as the propene oxidation activity of In/TiO_2–ZrO_2 in the entire reaction temperature range and maintained high selectivity of In/TiO_2–ZrO_2 for NO reduction, although Pd is well known as a combustion catalyst.[20)] Hence, palladium loaded In/TiO_2–ZrO_2 was proved to have a good activity in the presence of water vapor.

Table 1 summarizes the BET surface area of the catalysts and the dispersion and the particle size of noble metals determined by CO chemisorption measurements. The BET surface area of TiO_2–ZrO_2 decreased by loading of indium because of a blockade of the pores of TiO_2–ZrO_2 by supported indium. However, no change in the BET surface area of In/TiO_2–ZrO_2 by addition of noble metals was observed. Theses results imply that the physical properties of In/TiO_2–ZrO_2 were not affected by the supported noble metals. Obviously, Pd, Pt, Rh, and Ir are supported on In(5%)/TiO_2–ZrO_2 with a high dispersion, more than 30%. Their dispersion decreased in the following order: Pt > Ir > Rh > Pd.

Role of Pd and In Loadings on the Activity of Pd/In/TiO_2–ZrO_2. In order to get information on the optimum loading of Pd, the activity of Pd/In(5%)/TiO_2–ZrO_2 with various Pd loadings was examined. In Table 2 is summarized the effect of Pd loading on the catalytic activity of Pd/In/TiO_2–ZrO_2 for NO reduction by propene. As for the reaction in the absence of water vapor, the conversion of propene to CO_x increased with increasing Pd loading, while the conversion of NO to N_2 decreased by addition of 0.005

Table 1. BET Surface Area of the Catalysts and the Dispersion of Noble Metal on In(5%)/TiO_2–ZrO_2

	BET surface area / m^2 g-cat^{-1}	Dispersion of noble metals[a)] / %	Particle size of noble metals / nm
TiO_2–ZrO_2	284	—	—
In(5%)/TiO_2–ZrO_2	206	—	—
Pd(0.01%)/In(5%)/TiO_2–ZrO_2	204	38.7	2.3
Pt(0.01%)/In(5%)/TiO_2–ZrO_2	203	64.1	1.4
Rh(0.01%)/In(5%)/TiO_2–ZrO_2	203	47.7	1.8
Ir(0.01%)/In(5%)/TiO_2–ZrO_2	203	53.9	1.6

a) The dispersion of noble metals was calculated by assuming a stoichiometry of CO/noble metal = 1.

Table 2. Effect of Palladium Loading on the Catalytic Activity of In(5%)TiO_2–ZrO_2 Catalyst for the Selective Reduction of NO with Propene in the Absence or the Presence of Water Vapor

Catalyst	H_2O	NO conversion to N_2 / % (C_3H_6 conversion to CO_x / %)				
	%	300 °C	350 °C	400 °C	450 °C	500 °C
In(5%)/TiO_2–ZrO_2	0	31 (18)	60 (45)	75 (78)	63 (93)	42 (97)
	9.1	5.4 (1.5)	12 (7.2)	29 (26)	38 (52)	30 (74)
Pd(0.005%)/In(5%)/TiO_2–ZrO_2	0	25 (18)	56 (57)	75 (93)	62 (99)	40 (99)
	9.1	9.0 (6.3)	30 (33)	60 (81)	47 (97)	32 (97)
Pd(0.01%)/In(5%)/TiO_2–ZrO_2	0	21 (16)	50 (55)	67 (92)	52 (99)	31 (99)
	9.1	9.1 (7.3)	26 (38)	50 (84)	39 (97)	26 (97)
Pd(0.02%)/In(5%)/TiO_2–ZrO_2	0	20 (19)	46 (69)	63 (99)	53 (99)	36 (99)
	9.1	12 (20)	40 (72)	50 (96)	39 (95)	25 (95)

Conditions: NO = 900 ppm, C_3H_6 = 860 ppm, O_2 = 10%, H_2O = 0 or 9.1%, catalyst weight = 0.2 g, gas flow rate = 66 cm^3 min^{-1}.

wt% Pd, indicating a decrease of the selectivity for NO reduction. However, in the presence of water vapor, the NO reduction activity of In/TiO_2–ZrO_2 was enhanced by addition of 0.005—0.02 wt% Pd. Among them, 0.005 wt% Pd supported catalyst gave a maximum NO conversion, which is 60%, at 400 °C.

In Table 3 is summarized the effect of indium loading on the catalytic activity of Pd(0.005%)/In/TiO_2–ZrO_2 for NO reduction by propene in the presence and absence of water vapor. The high resistance of the Pd-loaded catalysts against water vapor seems to be attributed to the presence of Pd itself, because the promotive effect by Pd was also observed on Pd/TiO_2–ZrO_2, as can be seen by comparing Fig. 1 and Table 3. The conversion of NO to N_2 on Pd/TiO_2–ZrO_2 increased significantly by the presence of indium in the catalyst. In contrast, the conversion of propene to CO_x decreased with increasing In loading. These results suggest that indium plays an important role in promoting NO reduction selectivity. Among Pd/In/TiO_2–ZrO_2 catalysts tested here, Pd(0.005%)/In(2%)/TiO_2–ZrO_2 and Pd(0.005%)/In(5%)/TiO_2–ZrO_2 gave the highest NO conversion in the presence of H_2O.

Previously, we carried out the selective reduction of NO with propene over several catalysts in the presence of water vapor.[12,17,21,22] For instance, although Al_2O_3 catalyst gave a good NO conversion, which is about 40% at 400 °C, in the absence of water vapor, the addition of it into the reaction gas depressed the NO conversion to about 10%.[21,22] The maximum NO conversion of silver ion-exchanged saponite[12] and Ag/TiO_2–ZrO_2[17] under the same reaction conditions as those in this study was about 50% at 400 °C and about 45% at 450 °C, respectively. Thus, it is evident that Pd/In/TiO_2–ZrO_2 with an optimum loading prepared here possesses a high catalytic activity for NO reduction by propene in the presence of water vapor.

Efficiency of Reducing Agents. The efficiency of various reductants for the selective reduction of NO over Pd (0.005%)/In(5%)/TiO_2–ZrO_2 was investigated. The results are summarized in Table 4. As for the reaction in the absence of water vapor, methane reduced NO slightly at high temperature. Ethene and propane showed a similar efficiency for NO reduction with the conversion of less than 40%. For these three hydrocarbons, however, the presence of water vapor inhibited NO reduction pronouncedly. On the other

Table 3. Effect of Indium Loading on the Catalytic Activity of 0.005 wt% Pd Supported In/TiO_2–ZrO_2 Catalysts for the Selective Reduction of NO with Propene in the Presence and Absence of Water Vapor

Catalyst	H_2O	NO conversion to N_2 / % (C_3H_6 conversion to CO_x / %)				
	%	300 °C	350 °C	400 °C	450 °C	500 °C
Pd(0.005%)/TiO_2–ZrO_2	0	12	30	34	29	21
		(16)	(67)	(99)	(99)	(99)
	9.1	9.1	26	27	27	20
		(18)	(77)	(97)	(96)	(95)
Pd(0.005%)/In(2%)/TiO_2–ZrO_2	0	18	38	63	57	38
		(13)	(44)	(85)	(97)	(99)
	9.1	10	32	60	46	30
		(7.7)	(37)	(85)	(94)	(96)
Pd(0.005%)/In(5%)/TiO_2–ZrO_2	0	25	56	75	62	40
		(18)	(57)	(93)	(99)	(99)
	9.1	9.0	30	60	47	32
		(6.3)	(33)	(81)	(97)	(97)
Pd(0.005%)/In(10%)/TiO_2–ZrO_2	0	27	63	74	58	37
		(18)	(58)	(90)	(98)	(98)
	9.1	5.4	15	35	45	30
		(3.5)	(19)	(50)	(84)	(97)
Pd(0.005%)/In(15%)/TiO_2–ZrO_2	0	29	70	72	53	33
		(20)	(65)	(89)	(98)	(98)
	9.1	4.6	13	36	35	25
		(2.2)	(14)	(48)	(79)	(97)

Conditions: NO = 900 ppm, C_3H_6 = 860 ppm, O_2 = 10%, H_2O = 0 or 9.1%, catalyst weight = 0.2 g, gas flow rate=66 cm^3 min^{-1}.

Table 4. Efficiency of Various Reducing Agents for the Selective Reduction of NO over Pd(0.005%)/In(5%)/TiO_2–ZrO_2

Reductant	H_2O	NO conversion to N_2 / % (Reductant conversion to CO_x / %)				
	%	300 °C	350 °C	400 °C	450 °C	500 °C
	0	1.2	2.5	4.1	5.3	6.1
CH_4		(0.3)	(0.7)	(2.3)	(6.1)	(15)
2790 ppm	9.1	0.3	0.4	0.6	1.1	1.6
		(0.1)	(0.2)	(0.3)	(1.0)	(4.1)
	0	10	16	28	39	35
C_2H_4		(4.2)	(7.4)	(17)	(37)	(72)
1410 ppm	9.1	3.3	3.2	6.5	16.0	23.0
		(1.9)	(2.6)	(9.0)	(32)	(70)
	0	25	56	75	62	40
C_3H_6		(18)	(57)	(93)	(99)	(99)
860 ppm	9.1	9.3	30	60	47	32
		(6.3)	(33)	(81)	(97)	(97)
	0	6.3	14	25	24	18
C_3H_8		(3.1)	(9.8)	(29)	(53)	(75)
890 ppm	9.1	1.5	2.6	5.8	9.2	13
		(0.5)	(2.7)	(9.8)	(27)	(61)
	0	1.9	2	1.8	1.6	1.6
CH_3OH		(97)	(99)	(99)	(100)	(99)
510 ppm	9.1	1.4	1.3	1.1	1.5	1.3
		(94)	(100)	(99)	(98)	(99)
	0	18	25	25	15	7.5
C_2H_5OH		(50)	(78)	(95)	(97)	(99)
500 ppm	9.1	15	23	22	17	10
		(39)	(76)	(90)	(93)	(96)
	0	17	28	31	20	9.7
$1-C_3H_7OH$		(48)	(79)	(98)	(99)	(99)
550 ppm	9.1	22	31	34	24	12
		(45)	(76)	(92)	(96)	(97)
	0	14	30	42	30	18
$2-C_3H_7OH$		(23)	(56)	(88)	(96)	(99)
550 ppm	9.1	13	26	36	29	18
		(19)	(46)	(83)	(94)	(97)
	0	19	28	31	17	7
$(CH_3)_2CO$		(52)	(82)	(100)	(100)	(100)
680 ppm	9.1	12	30	43	32	19
		(37)	(77)	(94)	(96)	(98)

Conditions: NO = 900 ppm, O_2 = 10%, H_2O = 0 or 9.1%, catalyst weight = 0.2 g, gas flow rate = 66 cm^3 min^{-1}.

hand, as mentioned before, propene served as an excellent reducing agent even in the presence of water vapor.

In the case of oxygenated hydrocarbons, NO reduction in the absence of water vapor proceeded at relatively low temperatures. This would be because their oxidation took place at lower temperatures than their corresponding hydrocarbons. The efficiency increased in the order of methanol≪ethanol < 1 – propanol = acetone < 2-propanol. However, this tendency was changed when water vapor was added, and acetone was the most effective reductant. It is also noteworthy that this water-promoting effect over the whole temperature range was observed for 1-propanol and acetone. We have previously reported similar results that the presence of water vapor enhanced significantly NO reduction activity of Ag-saponite[12)] and Ag/TiO_2–ZrO_2[17)] when 2-propanol and acetone were used as a reductant. We presumed that water vapor accelerates the selective reduction of NO by suppressing the complete oxidation of the reductant by oxygen. Generally, oxygenated hydrocarbons seem to serve as better reducing agents than hydrocarbon for NO reduction in the presence of water vapor.[15,23,24)] In this work, however, propene gave the highest NO reduction activity in the presence of water vapor.

Reaction Mechanism on Pd/In/TiO_2–ZrO_2. The reaction mechanism of NO reduction by propene over Pd/In/TiO_2–ZrO_2 in the presence of water vapor was investigated. Kikuchi et al. reported that the addition of Pt and Ir into In/H–ZSM-5 caused a drastic enhancement of the catalytic activity for NO reduction by methane in the presence of water vapor and that this additive effect is attributed to the high NO oxidation activity to NO_2 of Pt and Ir sites even in the presence of water vapor.[13)] In contrast, Nishizaka and Misono reported that for the selective reduction of NO with methane over Pd supported on H–ZSM-5 catalyst, the role of Pd is to activate CH_4 to promote the reaction with NO_2, which is formed on acid sites of H–ZSM-5.[25)] Thus the role of supported noble metals differs, depending upon the catalyst systems.

We examined first the difference between the reactivity of NO and NO_2 over In(5%)/TiO_2–ZrO_2 and Pd(0.005%)/In(5%)/TiO–ZrO_2 in the presence of water vapor. As shown in Fig. 5, the reactivity of NO_2 over Pd/In/TiO_2–ZrO_2 was much higher than that of NO over the whole reaction temperature range. This result suggests that NO_2 participates in the NO reduction as an intermediate. However, since NO conversion to N_2 on Pd/In/TiO_2–ZrO_2 was much higher than NO_2 conversion to N_2 on In/TiO_2–ZrO_2 for any reaction temperature, it is considered that the major role of Pd is not to promote the oxidation of NO to NO_2. Probably, the supported Pd would catalyze the propene activation by O_2, which is an important step.

Then we measured the conversion of propene to CO_x on In(5%)/TiO_2–ZrO_2 and Pd(0.005%)/In(5%)/TiO_2–ZrO_2 in the reaction systems of NO–C_3H_6–O_2, C_3H_6–O_2, and NO_2–C_3H_6–O_2 in the presence of water vapor. The results are also shown in Fig. 5. Obviously, the addition of Pd enhanced drastically the catalytic activity of In/TiO_2–ZrO_2 for

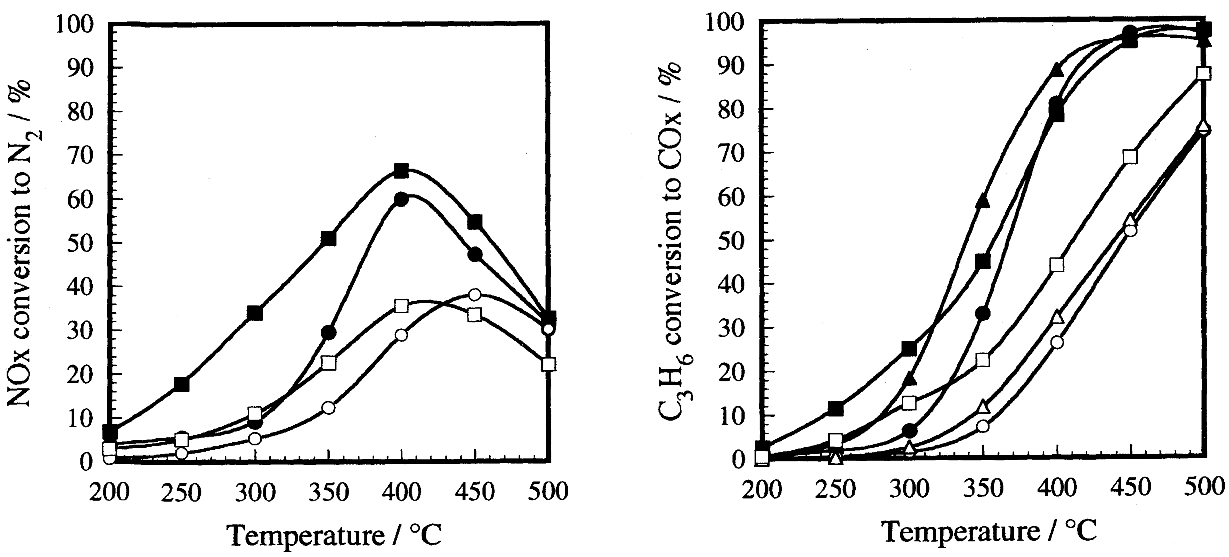

Fig. 5. Activities of In(5%)/TiO_2–ZrO_2 (○, △, □) and Pd(0.005%)/In(5%)/TiO_2–ZrO_2 (●, ▲, ■) for various reaction systems of NO+C_3H_6+O_2 (○, ●), C_3H_6+O_2 (△, ▲) and NO_2+C_3H_6+O_2 (□, ■) in the presence of water vapor. Conditions: NO = 900 ppm or NO_2 = 930 ppm, C_3H_6 = 860 ppm, O_2 = 10%, H_2O = 9.1%, catalyst weight = 0.2 g, gas flow rate = 66 cm^3 min^{-1}.

propene oxidation in all the reaction systems, suggesting that the supported Pd plays an important role for the oxidation of propene.

As can be seen in Fig. 5, the highest propene conversion on Pd/In/TiO_2–ZrO_2 was obtained in the reaction system of C_3H_6–O_2, indicating that the supported Pd promotes the oxidation of propene with O_2, which is a key reaction step. Cu–ZSM-5,[26] Pt/Al_2O_3,[27] Ag/TiO_2–ZrO_2,[17] and Co/SiO_2[28] showed a similar catalytic behavior to Pd/In/TiO_2–ZrO_2 and a reaction mechanism involving the formation of oxygenated intermediates was proposed. Therefore, oxygenated intermediates might also be formed on Pd/In/TiO_2–ZrO_2 in the present work. In order to confirm the possibility of the formation of oxygenated intermediates, we measured the activity of In(5%)/TiO_2–ZrO_2 for NO reduction by oxygenated hydrocarbons such as 1-propanol, 2-propanol, and acetone and compared with that of Pd(0.005%)/In(5%)/TiO_2–ZrO_2. The results obtained on In/TiO_2–ZrO_2 are summarized in Table 5. As for the reaction in the presence of water vapor, it can be seen by comparing Tables 4 and 5 that both catalysts showed a similar catalytic performance for NO conversion to N_2. These results lead us to conclude that oxygenated intermediates are formed on Pd sites during the selective reduction of NO by propene.

It is well known that Pd itself shows the activity for NO reduction by hydrocarbons. Actually, Pd supported on TiO_2–ZrO_2 catalyzed NO reduction by propene in the presence of water vapor (see in Table 3), because TiO_2–ZrO_2 did not show high activity for this reaction.[17] However, the direct participation of Pd in N_2 formation seems relatively small for Pd/In/TiO_2–ZrO_2 catalyzed NO reduction. Its major role is considered to be to promote propene oxidation to oxygenated intermediates, which are then converted to N_2 over In, as described above. This is because the presence of both Pd and In is necessary for achieving high NO conversion and selectivity to N_2. We reported previously that indium supported on TiO_2–ZrO_2 promotes the reaction of propene with NO_2 to yield N_2.[16] Therefore, it is supposed that NO reduction by propene over Pd/In/TiO_2–ZrO_2 proceeds on both sites of Pd and In via several reaction steps. On the basis of the experimental results, we propose the reaction mechanism that oxygenated intermediates formed on Pd sites by the oxidation of propene with O_2 react with NO_2 to yield N_2 on In sites. Here, oxygenated intermediates might be spilled over from Pd sites to In sites.

Table 5. Activity of In(5%)/TiO_2–ZrO_2 for the Selective Reduction of NO by Oxygenated Hydrocarbons

Reductant	H_2O	NO conversion to N_2 / % (Reductant conversion to CO_x / %)				
	%	300 °C	350 °C	400 °C	450 °C	500 °C
1-C_3H_7OH 550 ppm	0	19 (49)	28 (78)	29 (98)	17 (99)	3.6 (99)
	9.1	23 (44)	32 (72)	33 (93)	21 (95)	12 (98)
2-C_3H_7OH 550 ppm	0	16 (26)	32 (65)	41 (91)	33 (99)	19 (100)
	9.1	13 (8.5)	25 (34)	36 (57)	32 (73)	21 (87)
$(CH_3)_2CO$ 680 ppm	0	18 (51)	28 (81)	32 (99)	19 (100)	9.2 (100)
	9.1	14 (38)	31 (71)	50 (91)	42 (96)	24 (98)

Conditions: NO = 900 ppm, O_2 = 10%, H_2O = 0 or 9.1%, catalyst weight = 0.2 g, gas flow rate = 66 cm^3 min^{-1}.

Conclusion

The following conclusions were obtained in the present work.

(1) Although the catalytic activity of In/TiO_2–ZrO_2 for the selective reduction of NO with propene was inhibited drastically by water vapor, addition of palladium was capable of depressing the retarding effect.

(2) The presence of both indium and palladium was necessary for the enhancement of NO reduction activity, and the optimum indium and palladium loading was at 2—5 wt% and 0.005 wt%, respectively.

(3) It was suggested that the role of palladium supported on In/TiO_2–ZrO_2 is to promote the formation of oxygenated intermediates by the reaction of propene with oxygen and that N_2 was formed by the reaction between the oxygenated intermediates and NO_2 on indium.

(4) Propene served as the most efficient reducing agent.

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