Promotional effect of H_2O on the activity of In_2O_3-doped Ga_2O_3–Al_2O_3 for the selective reduction of nitrogen monoxide

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Effect of metal oxide additives on the catalytic performance of Ga_2O_3–Al_2O_3 prepared by the sol–gel method for the selective reduction of NO with propene in the presence of oxygen was studied. Of several metal oxide additives, the addition of In_2O_3 enhanced drastically the activity of Ga_2O_3–Al_2O_3 for NO reduction by propene in the presence of H_2O. In addition, the activity of In_2O_3-doped Ga_2O_3–Al_2O_3 catalyst was extremely intensified by the presence of H_2O below 350 °C. The promotional effect of H_2O was interpreted by the suppression of undesirable propene oxidation and the removal of carbonaceous materials deposited on the catalyst surface. We also found that close interaction of In_2O_3 and Ga_2O_3 is necessary for the enhancement of activity by H_2O. A lot of hydrocarbons except methane and oxygenated compounds served as good reducing agents, among which propene and 2-propanol were the most efficient ones. In_2O_3-doped Ga_2O_3–Al_2O_3 catalyst was capable of reducing NO into N_2 quite efficiently in the presence of H_2O at a very high space velocity.

Keywords: nitrogen monoxide, selective reduction, H_2O, In_2O_3–Ga_2O_3–Al_2O_3, sol–gel method

1. Introduction

Air pollution by nitrogen oxides (NO_x) emitted from exhaust gases is one of the most serious environmental problems. Particularly, it is described to develop effective methods to remove NO_x from diesel and lean burn gasoline engine exhaust gases, which contain high concentrations of oxygen. In this respect, the selective catalytic reduction of NO with hydrocarbons in the presence of oxygen has attracted much attention [1,2]. Among many effective catalysts reported so far [3–8], alumina-supported metal (oxide) catalysts would be promising candidates for practical applications because of their high activity and stability. However, in many cases the catalytic activity is depressed considerably by the presence of H_2O contained in combustion gases.

Miyadera and Yoshida [8] investigated the influence of H_2O on the activity of alumina-supported metal (oxide) catalysts for NO reduction by propene. They reported that the activity of Ga/Al_2O_3 and Zn/Al_2O_3 was significantly decreased by H_2O, while for Ag/Al_2O_3 and In/Al_2O_3 the activity depression by H_2O was very little. Miyadera et al. [9] also revealed that the activity of Ag/Al_2O_3 was increased evidently by addition of H_2O when ethanol was used as a reducing agent. There are several reports concerning the intensifying effect of H_2O on NO reduction by oxygenated hydrocarbons [10–12]. Recently, Hirao et al. [13] reported the promotional effect of H_2O for a mechanical mixture of Mn_2O_3 and Sn-ZSM-5 for NO reduction by propene. We also found that the addition of H_2O to the reaction gas containing NO, propene, oxygen and helium increased NO conversion on silver ion-exchanged saponite at low temperatures below 400 °C [12]. In addition, Ueda et al. [14] reported a similar positive effect of H_2O on NO reduction by propene over Au/Al_2O_3. Although the activity enhancement by H_2O has been reported for many catalytic systems and its reasons have been investigated, there are a lot of ambiguous points yet.

Recently, we found that gallium oxide supported on alumina (Ga_2O_3–Al_2O_3) showed quite high catalytic activity for NO reduction by propene when the catalyst was prepared by the sol–gel method [15]. However, a decrease of NO reduction activity by coexisting H_2O was observed. Moreover, the effective temperature window was relatively narrow and was located in a high-temperature region. In the present study, we investigated the effect of metal oxide additives on Ga_2O_3–Al_2O_3 for the selective reduction of NO with propene, in order to promote the activity of Ga_2O_3–Al_2O_3 in the presence of H_2O at lower temperatures. In the course of our study, we found that In_2O_3-doped Ga_2O_3–Al_2O_3 showed good catalytic activity for NO reduction by propene in the presence of H_2O. It was also discovered that coexisting H_2O accelerated NO reduction over In_2O_3–Ga_2O_3–Al_2O_3 at low temperatures. We report here the unique catalytic behavior of In_2O_3-doped Ga_2O_3–Al_2O_3 for the selective reduction of NO with propene in the presence of oxygen and H_2O.

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2. Experimental

2.1. Catalyst preparation

Metal oxide-doped Ga_2O_3–Al_2O_3 catalysts were prepared by coprecipitation through the sol–gel process. In, Sn, Co, Cu, Fe, Ni and Ag were selected as the metal oxide additive. The aluminium boehmite sol was prepared first by hydrolysis of aluminium(III) tri-isopropoxide in hot water (90 °C) with a small amount of nitric acid, and then mixed with a solution of gallium(III) nitrate and metal nitrate of the doped metal oxide, except for Sn for which chloride was used, dissolved in ethylene glycol. After the sol solution was stirred for 1 day, the solvents were eliminated by heating under reduced pressure and the residue was dried and calcined at 600 °C for 5 h in flowing air. The samples are abbreviated as $M_nO_m(x)$–$Ga_2O_3(y)$–Al_2O_3, where x and y are the loading of metal oxide and Ga_2O_3, and M is the metal element. In the case of Ag, the loading was calculated as Ag-metal.

In order to examine the effect of preparation method on the catalytic activity, we prepared In_2O_3(5)-doped Ga_2O_3(30)–Al_2O_3 by the co-impregnation method in which alumina powder was immersed in an aqueous solution of gallium(III) nitrate and indium(III) nitrate, followed by drying and calcination at 600 °C for 5 h in flowing air. This sample is expressed as In_2O_3(5)–Ga_2O_3(30)/Al_2O_3. In_2O_3(5)/Al_2O_3 as a reference sample was also prepared by the impregnation method using alumina powder and an aqueous solution of indium(III) nitrate. The catalyst powder thus obtained was dried and calcined at 600 °C for 5 h in flowing air. Alumina powder used here was synthesized by hydrolysis of aluminium(III) tri-isopropoxide in the same manner as described in a previous paper [16]. BET surface area of alumina was found to be 200 $m^2\,g^{-1}$.

Cu-ZSM-5 (Cu, 3.2 wt%) was also prepared by the ion exchange method using ZSM-5 ($SiO_2/Al_2O_3 = 34.5$) and an aqueous solution of copper(II) acetate. The catalyst powder thus obtained was dried and calcined at 500 °C for 5 h in flowing air.

2.2. Catalytic activity measurements

The catalytic activity was measured by using a fixed bed flow reactor. The feed gas mixture contained 900 ppm NO, a reducing agent, 10% oxygen and helium as the balance gas. CH_4, C_2H_4, C_3H_8, C_3H_6, n-C_6H_{14}, cyclo-C_6H_{12}, C_6H_6, CH_3OH, C_2H_5OH, 2-C_3H_7OH and $(CH_3)_2CO$ were used as the reducing agents. The concentration of the reducing agents was adjusted to about 3000 ppm C. The gas flow rate was fixed at 66 $cm^3\,min^{-1}$. The contact time (W/F) was changed from 0.18 to 0.02 $g\,s\,cm^{-3}$ by controlling the catalyst weight, corresponding to a space velocity (SV) between 10 000 and 100 000 h^{-1}. In some experiments, H_2O was introduced into the reaction gas mixture at a concentration of 9.1% with a micropump. In this case, the W/F was kept constant by controlling the helium flow. The reaction temperature was changed with steps of 50 °C from 600 to 250 °C. The effluent gas was analyzed by gas chromatography. A Molecular Sieve 5A column was used for the analysis of N_2, CO and CH_4 and a Porapak Q column for that of N_2O, CO_2, C_2H_4, C_3H_6 and C_3H_8. The catalytic activity was evaluated in terms of NO conversion to N_2 and that of the reducing agent to CO_x ($CO + CO_2$). The formation of N_2O was negligible.

2.3. Catalyst characterization

Thermogravimetric analysis (TGA) was carried out using a Shimadzu DTG-50. 15 mg of a sample used for NO reduction in the presence and absence of H_2O at 350 °C for 5 h was placed in a platinum sample pan and heated at a rate of 10 °C min^{-1} in flowing air with a flow rate of 40 $cm^3\,min^{-1}$. BET surface area was measured by nitrogen adsorption at −196 °C with a conventional flow type apparatus (Shimadzu, Flowsorb II 2300). The crystal structure was identified by XRD (Shimadzu XD-D1) measurements using Cu Kα radiation at 40 kV and 40 mA.

3. Results and discussion

3.1. Additive effect of metal oxides

BET surface areas of the metal oxide-doped Ga_2O_3–Al_2O_3 catalysts are summarized in table 1. BET surface areas ranged from 176 to 203 m^2g^{-1} depending upon the doped metal oxides.

Table 2 summarizes the activity of metal oxide-doped Ga_2O_3–Al_2O_3 catalysts for NO reduction by propene in the presence and absence of H_2O. In this experiment, the loading of the metal oxide additives and Ga_2O_3 was fixed at 2 and 30 wt%, respectively. As for the reaction in the absence of H_2O, Ga_2O_3(30)–Al_2O_3 catalyzed NO reduction effectively at temperatures above 400 °C, but the activity at temperatures below 350 °C was not so high. The addition of several metal oxides into Ga_2O_3(30)–Al_2O_3 caused an enhancement of NO reduction activity in the low-temperature region below 350 °C, although the activity of these catalysts was lower than that of Ga_2O_3(30)–Al_2O_3 at elevated temperatures. Of the metal oxide additives tested here, CoO, CuO, Fe_2O_3 and Ag showed good effect on the title reaction.

Table 1

BET surface area of metal oxide (2 wt%)-doped Ga_2O_3(30)–Al_2O_3.

Catalyst	BET surface area ($m^2\,g^{-1}$)
Ga_2O_3(30)–Al_2O_3	200
In_2O_3(2)–Ga_2O_3(30)–Al_2O_3	178
SnO_2(2)–Ga_2O_3(30)–Al_2O_3	176
CoO(2)–Ga_2O_3(30)–Al_2O_3	203
CuO(2)–Ga_2O_3(30)–Al_2O_3	180
Fe_2O_3(2)–Ga_2O_3(30)–Al_2O_3	186
NiO(2)–Ga_2O_3(30)–Al_2O_3	198
Ag(2)–Ga_2O_3(30)–Al_2O_3	193

Table 2
Activities of metal oxide (2 wt%)-doped Ga_2O_3(30)–Al_2O_3 catalysts prepared by the sol–gel method for the selective reduction of NO with propene in the presence and absence of H_2O.[a]

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	550 °C
Ga_2O_3(30)–Al_2O_3	0	14 (5.9)	31 (23)	100 (98)	100 (100)	95 (100)	59 (100)
	9.1	13 (3.6)	20 (8.1)	35 (22)	66 (56)	89 (97)	59 (100)
In_2O_3(2)–Ga_2O_3(30)–Al_2O_3	0	21 (7.5)	48 (33)	94 (100)	84 (100)	72 (100)	53 (100)
	9.1	30 (11)	81 (42)	92 (81)	87 (100)	69 (100)	45 (100)
SnO_2(2)–Ga_2O_3(30)–Al_2O_3	0	23 (14)	39 (37)	64 (75)	74 (93)	61 (96)	29 (99)
	9.1	23 (12)	45 (21)	66 (47)	82 (82)	73 (95)	37 (99)
CoO(2)–Ga_2O_3(30)–Al_2O_3	0	25 (7.9)	97 (82)	97 (100)	88 (100)	73 (100)	46 (100)
	9.1	22 (5.3)	32 (9.7)	74 (38)	96 (82)	88 (99)	54 (100)
CuO(2)–Ga_2O_3(30)–Al_2O_3	0	62 (94)	55 (100)	46 (100)	34 (100)	30 (100)	27 (100)
	9.1	14 (24)	31 (82)	31 (100)	30 (100)	20 (100)	14 (100)
Fe_2O_3(2)–Ga_2O_3(30)–Al_2O_3	0	57 (46)	73 (96)	54 (99)	37 (100)	26 (100)	20 (100)
	9.1	17 (9.4)	34 (30)	43 (68)	41 (97)	26 (99)	17 (100)
NiO(2)–Ga_2O_3(30)–Al_2O_3	0	18 (4.5)	32 (16)	76 (61)	99 (99)	96 (100)	64 (100)
	9.1	9.7 (1.9)	15 (4.9)	27 (14)	54 (44)	88 (95)	61 (100)
Ag(2)–Ga_2O_3(30)–Al_2O_3	0	49 (97)	51 (100)	52 (100)	55 (100)	52 (100)	36 (100)
	9.1	27 (47)	42 (81)	52 (94)	60 (100)	58 (100)	34 (100)

[a] Reaction conditions: NO = 900 ppm, C_3H_6 = 860 ppm, O_2 = 10%, H_2O = 0 or 9.1%, gas flow rate = 66 $cm^3\,min^{-1}$, $W/F = 0.18$ $g\,s\,cm^{-3}$.

Table 3
Reaction rates and specific activities of metal oxide (2 wt%)-doped Ga_2O_3(30)–Al_2O_3 catalysts prepared by the sol–gel method for NO reduction into N_2 by propene in the presence and absence of H_2O at 300 °C.[a]

Catalyst	Without H_2O (0%)		With H_2O (9.1%)	
	Reaction rate ($mol\,min^{-1}\,g^{-1}$)	Specific activity ($mol\,min^{-1}\,m^{-2}$)	Reaction rate ($mol\,min^{-1}\,g^{-1}$)	Specific activity ($mol\,min^{-1}\,m^{-2}$)
Ga_2O_3(30)–Al_2O_3	9.29×10^{-7}	4.64×10^{-9}	8.62×10^{-7}	4.31×10^{-9}
In_2O_3(2)–Ga_2O_3(30)–Al_2O_3	1.39×10^{-6}	7.83×10^{-9}	1.99×10^{-6}	1.12×10^{-8}
SnO_2(2)–Ga_2O_3(30)–Al_2O_3	1.53×10^{-6}	8.67×10^{-9}	1.53×10^{-6}	8.67×10^{-9}
CoO(2)–Ga_2O_3(30)–Al_2O_3	1.66×10^{-6}	8.17×10^{-9}	1.46×10^{-6}	7.19×10^{-9}
CuO(2)–Ga_2O_3(30)–Al_2O_3	4.11×10^{-6}	2.29×10^{-8}	9.29×10^{-7}	5.16×10^{-9}
Fe_2O_3(2)–Ga_2O_3(30)–Al_2O_3	3.78×10^{-6}	2.03×10^{-8}	1.13×10^{-6}	6.06×10^{-9}
NiO(2)–Ga_2O_3(30)–Al_2O_3	1.19×10^{-6}	6.03×10^{-9}	6.43×10^{-7}	3.25×10^{-9}
Ag(2)–Ga_2O_3(30)–Al_2O_3	3.25×10^{-6}	1.68×10^{-8}	1.79×10^{-6}	9.28×10^{-9}

[a] Reaction conditions: NO = 900 ppm, C_3H_6 = 860 ppm, O_2 = 10%, H_2O = 0 or 9.1%, gas flow rate = 66 $cm^3\,min^{-1}$, temperature = 300 °C, catalyst weight = 0.2 g.

On the other hand, when H_2O was introduced into the reaction gas, interesting behavior was observed for some catalysts. The activity of Ga_2O_3(30)–Al_2O_3 was depressed considerably by the presence of H_2O and the temperature window became narrow and shifted to higher temperature region. A similar retarding effect of H_2O was observed for CoO(2)–, CuO(2)–, Fe_2O_3(2)–, NiO(2)– and Ag(2)–Ga_2O_3(30)–Al_2O_3. In the case of In_2O_3(2)–Ga_2O_3(30)–Al_2O_3, however, a pronounced promotional effect of H_2O on NO reduction activity was observed at lower temperatures below 350 °C. The activity of SnO_2(2)–Ga_2O_3(30)–Al_2O_3 was also enhanced by the presence of H_2O, but the increment was not so prominent as that of In_2O_3(2)–Ga_2O_3(30)–Al_2O_3. Accordingly, In_2O_3(2)–Ga_2O_3(30)–Al_2O_3 was the most active catalyst for NO reduction by propene in the presence of H_2O.

In order to clarify the difference in the activity of metal oxide additives on the catalyst surface, we calculated reaction rate ($mol\,min^{-1}\,g^{-1}$) and specific activity ($mol\,min^{-1}\,m^{-2}$) normalized by BET surface area for NO reduction into N_2. The results obtained at 300 °C, where NO conversion is relatively low, are summarized in table 3. Obviously, the specific activity for N_2 formation was increased by addition of metal oxide into Ga_2O_3(30)–Al_2O_3, irrespective of coexisting H_2O, suggesting that NO reduction into N_2 proceeds mainly on the doped metal oxide. As for the reaction in the absence of H_2O, CuO(2)–, Fe_2O_3(2)– and Ag(2)–Ga_2O_3(30)–Al_2O_3 showed relatively high specific activity. On the other hand, In_2O_3(2)–Ga_2O_3(30)–Al_2O_3 gave the highest specific activity for N_2 formation in the presence of H_2O.

Table 4
Change of NO and propene conversions on $Ga_2O_3(30)$–Al_2O_3 and $In_2O_3(2)$–$Ga_2O_3(30)$–Al_2O_3 with H_2O concentration.[a]

Catalyst	Reaction temperature	NO conversion to N_2 (%) (C_3H_6 conversion to CO (%)/ to CO_2 (%))			
		$H_2O = 0\%$	$H_2O = 1.0\%$	$H_2O = 4.1\%$	$H_2O = 9.1\%$
$Ga_2O_3(30)$–Al_2O_3	400 °C	100 (44/55)	57 (22/12)	41 (15/7.9)	35 (15/7.1)
$In_2O_3(2)$–$Ga_2O_3(30)$–Al_2O_3	350°C	48 (13/21)	78 (29/29)	79 (23/22)	81 (20/22)

[a] Reaction conditions: NO = 900 ppm, C_3H_6 = 860 ppm, O_2 = 10%, H_2O = 0–9.1%, gas flow rate = 66 $cm^3\,min^{-1}$, $W/F = 0.18\ g\,s\,cm^{-3}$.

3.2. Promotional effect of H_2O

As mentioned above, the presence of H_2O accelerated NO reduction over In_2O_3–Ga_2O_3–Al_2O_3 at low temperatures. Two reasons for the promotional effect of H_2O can be considered. One is the suppression of the undesirable oxidation of hydrocarbons by oxygen, resulting in the improvement of hydrocarbon utilization for NO reduction into N_2 [8,11,17,18]. The other is the removal of surface carbonaceous materials deposited on the catalytically active sites [17–21].

First, we examined the effect of H_2O concentration on the catalytic activity of $Ga_2O_3(30)$–Al_2O_3 and $In_2O_3(2)$–$Ga_2O_3(30)$–Al_2O_3 for NO reduction at 400 and 350 °C, respectively. The results are summarized in table 4. Apparently, the catalytic activity of $Ga_2O_3(30)$–Al_2O_3 for NO reduction decreased monotonously with H_2O concentration. On the other hand, the addition of a slight amount of H_2O (1%) into the reaction gas increased NO conversion to N_2 as well as propene conversion to CO_x ($CO + CO_2$) on $In_2O_3(2)$–$Ga_2O_3(30)$–Al_2O_3. Further increase of H_2O concentration did not cause an additional enhancement of NO and propene conversion. The propene conversion to CO as well as that to CO_2 on $Ga_2O_3(30)$–Al_2O_3 decreased gradually with H_2O concentration, suggesting that coexisting H_2O inhibits the propene oxidation by adsorption onto the active sites. In the case of $In_2O_3(2)$–$Ga_2O_3(30)$–Al_2O_3, the propene conversion to CO increased with increasing H_2O concentration, whereas that to CO_2 hardly changed. If propene oxidation proceeds through a consecutive reaction of CO formation and subsequent CO oxidation to CO_2, these results would lead us to the consideration that there is some involvement of coexisting H_2O in the reaction path, probably propene oxidation.

In order to get information on the promotional effect of H_2O, we investigated the response of NO reduction by propene and propene oxidation by oxygen in the absence of NO to the supply of H_2O on $In_2O_3(2)$–$Ga_2O_3(30)$–Al_2O_3 at 350 °C. The reaction was carried out as follows: (1) reaction in the absence of H_2O (1st stage), (2) introduction of H_2O into the reaction gas after 1st stage (2nd stage), (3) removal of H_2O from the reaction gas after 2nd stage (3rd stage). The results are shown in figures 1 and 2. In the case of the NO–C_3H_6–O_2 reaction (figure 1), the catalytic activity for NO reduction in the absence of H_2O, which is the 1st stage of the reaction, decreased gradually with reaction time and then reached steady state in 2 h. The carbon balance, which was estimated from a sum of unreacted propene and formed CO_x, approached to 100% more slowly through the reaction. When H_2O was introduced into the reaction gas, the 2nd stage of the reaction, an enhancement of NO conversion to N_2 as well as CO_x yield was observed. The catalytic activity returned gradually to approximately the same initial level by the interruption of H_2O, the 3rd stage of the reaction. In the case of propene

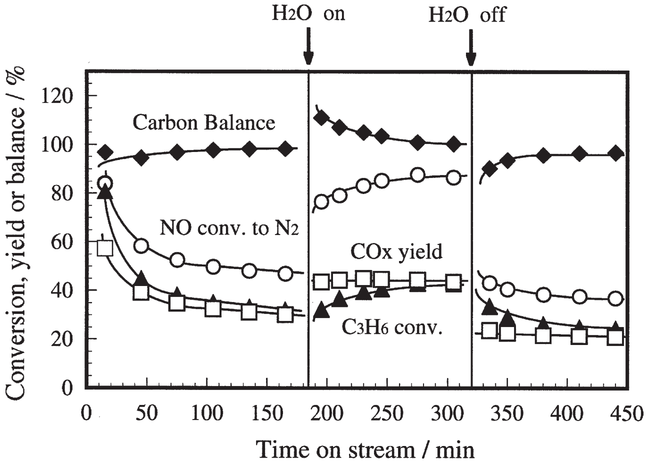

Figure 1. Effect of H_2O on the catalytic activity of $In_2O_3(2)$–$Ga_2O_3(30)$–Al_2O_3 for NO reduction by propene at 350 °C. Conditions: NO = 900 ppm, C_3H_6 = 860 ppm, O_2 = 10%, H_2O = 0 or 9.1%, catalyst weight = 0.2 g, $W/F = 0.18\ g\,s\,cm^{-3}$. (○) NO conversion to N_2, (▲) C_3H_6 conversion, (□) CO_x yield, (♦) carbon balance.

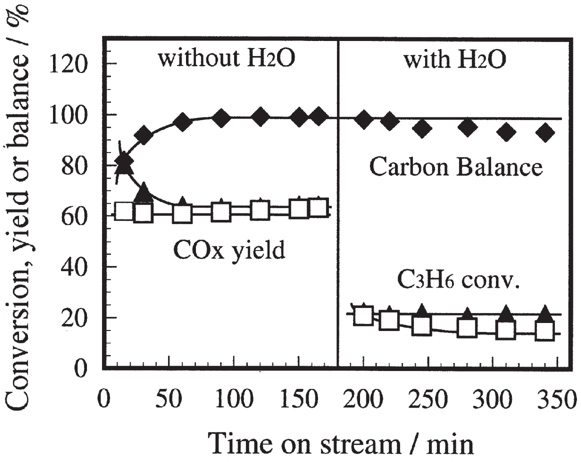

Figure 2. Effect of H_2O on the catalytic activity of $In_2O_3(2)$–$Ga_2O_3(30)$–Al_2O_3 for propene oxidation by oxygen in the absence of NO at 350 °C. Conditions: C_3H_6 = 860 ppm, O_2 = 10%, H_2O = 0 or 9.1%, catalyst weight = 0.2 g, $W/F = 0.18\ g\,s\,cm^{-3}$. (▲) C_3H_6 conversion, (□) CO_x yield, (♦) carbon balance.

combustion by oxygen in the absence of NO (figure 2), propene conversion and CO_x yield were significantly decreased by the presence of H_2O. These results would lead us to consider that coexisting H_2O inhibits mainly the undesirable propene combustion, resulting in the improvement of propene utilization for NO reduction. This is one of the reasons for the promotional effect of H_2O on the activity of In_2O_3–Ga_2O_3–Al_2O_3.

It should be noted from figure 1 that the carbon balance for NO reduction increased sharply after the addition of H_2O and then decreased slowly to the original level observed in the absence of H_2O. We reported recently a similar experimental result for NO_2 reduction by propene over proton-exchanged saponite [20]. Misono et al. [21] also reported that the carbon balance of NO reduction by propene over $Mn_2O_3 +$ Sn-ZSM-5 in the absence of H_2O was much worse than that in the presence of H_2O. They explained this phenomenon by assuming that oligomerization or polymerization leading to carbon deposits took place during NO reduction in the absence of H_2O and then the carbon deposits thus formed are removed by reactions such as steam reforming to form reductants like H_2 and CO. The same phenomenon should take place in the present study, because we observed an increase of CO yield in NO–C_3H_6–O_2 reaction over In_2O_3(2)–Ga_2O_3(30)–Al_2O_3 with H_2O concentration (see in table 4) and the formation of relatively high concentrations of H_2 during the reaction in the presence of H_2O compared with that in its absence.

In order to confirm the above possibility for the promotional effect of H_2O, TGA profiles of In_2O_3(2)–Ga_2O_3(30)–Al_2O_3 used for NO reduction in the presence or absence of H_2O at 350 °C for 5 h were taken in flowing air. In the experiments, the catalysts are designated as "cat(with H_2O)" and "cat(w/o H_2O)". The results are depicted in figure 3. The TGA profiles of the two samples were obtained by subtracting the TGA profile of a fresh catalyst. As can be seen in figure 3, a weight loss attributed to oxidation of carbon deposits was recognized around 400–500 °C in the TGA profiles of both catalysts. However, the weight loss from "cat(w/o H_2O)" was much larger than that from "cat(with H_2O)", indicating that a large amount of carbon is deposited on the former catalyst. The amount of carbon deposits on the catalyst was estimated to be ca. 1.44 wt% for "cat(w/o H_2O)" and ca. 0.95 wt% for "cat(with H_2O)". This means that carbon deposited on the catalyst surface should be removed efficiently by H_2O.

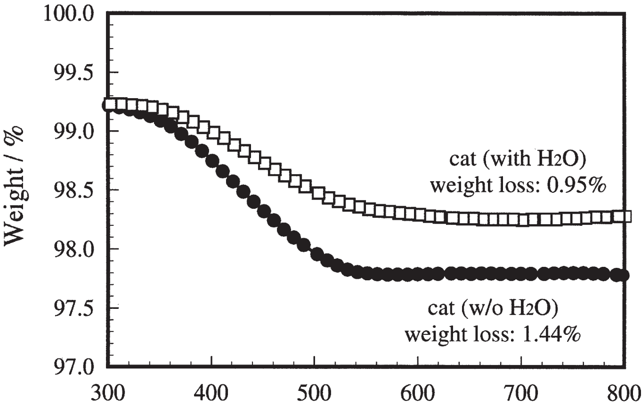

Figure 3. TGA profiles of In_2O_3(2)–Ga_2O_3(30)–Al_2O_3 used to NO reduction in the presence (□) or absence of H_2O (●) at 350 °C for 5 h. The composition of the reaction gas is the same as for figure 1. Conditions for TGA: catalyst weight = 15 mg, gas flow rate = 40 $cm^3\,min^{-1}$, heating rate = 10 $°C\,min^{-1}$.

Consequently, we conclude that there are two reasons for the enhancement effect of H_2O for NO reduction on In_2O_3(2)–Ga_2O_3(30)–Al_2O_3; one is the suppression of the undesirable oxidation of propene by oxygen, resulting in the improvement of propene utilization for NO reduction. The other is the removal of surface carbonaceous materials deposited on the catalytically active sites by reactions such as steam reforming.

3.3. *Optimum loading of In_2O_3 for In_2O_3–Ga_2O_3(30)–Al_2O_3*

In order to get information on the optimum loading of In_2O_3, the effect of In_2O_3 loading on the activity of In_2O_3–Ga_2O_3(30)–Al_2O_3 for NO reduction by propene in the presence of H_2O was examined. As shown in figure 4, the NO conversion as well as the propene conversion on Ga_2O_3(30)–Al_2O_3 was greatly enhanced by addition of

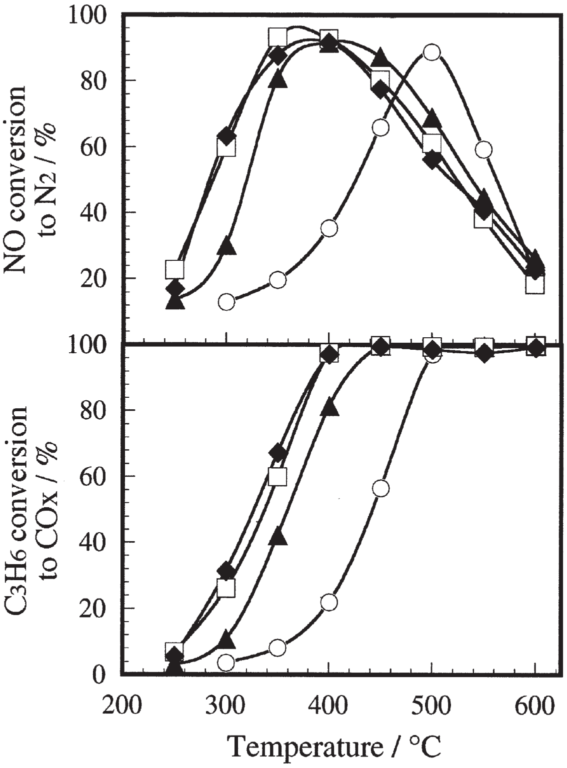

Figure 4. Effect of indium loading on the catalytic activity of In_2O_3–Ga_2O_3(30)–Al_2O_3 for NO reduction by propene in the presence of H_2O. Conditions: NO = 900 ppm, C_3H_6 = 860 ppm, O_2 = 10%, H_2O = 9.1%, catalyst weight = 0.2 g, $W/F = 0.18\ g\,s\,cm^{-3}$. (○) 0 wt% In_2O_3, (▲) 2 wt% In_2O_3, (□) 5 wt% In_2O_3, (◆) 10 wt% In_2O_3.

In_2O_3. Moreover, the added In_2O_3 brought about an extension and a shift of the active temperature window to lower temperature region, although no great change of the maximum NO conversion was observed. Obviously, In_2O_3 loading of more than 5 wt% did not cause a considerable change of the catalytic performance. It was concluded that optimum In_2O_3 loading is around 5 wt%.

3.4. Effect of preparation method on the activity of $In_2O_3(5)$–$Ga_2O_3(30)$–Al_2O_3

We studied the effect of preparation method on the catalytic activity of $In_2O_3(5)$–$Ga_2O_3(30)$–Al_2O_3 for NO reduction by propene in the presence and absence of H_2O. The results obtained for $In_2O_3(5)/Al_2O_3$, $In_2O_3(5)$–$Ga_2O_3(30)/Al_2O_3$ and $In_2O_3(5)$–$Ga_2O_3(30)$–Al_2O_3 are given in figure 5. As for the reaction in the absence of H_2O (figure 5(a)), $In_2O_3(5)$–$Ga_2O_3(30)$–Al_2O_3 prepared by the sol–gel method showed higher catalytic activity than $In_2O_3(5)$–$Ga_2O_3(30)/Al_2O_3$ prepared by the co-impregnation method at temperatures below 400 °C. Interestingly, the activity of $In_2O_3(5)$–$Ga_2O_3(30)/Al_2O_3$ was a little less than that of $In_2O_3(5)/Al_2O_3$, indicating that Ga_2O_3 seems to decrease the activity of In_2O_3/Al_2O_3.

As for the reaction in the presence of H_2O, interesting catalytic behavior was observed depending upon the presence or absence of Ga_2O_3. As described before, the activity of $In_2O_3(5)$–$Ga_2O_3(30)$–Al_2O_3 was enhanced considerably by coexisting H_2O. A slight increase in NO reduction activity was observed for $In_2O_3(5)$–$Ga_2O_3(30)/Al_2O_3$, while there was no increase in the activity of $In_2O_3(5)/Al_2O_3$. This means that the presence of In_2O_3 and Ga_2O_3 is essential for the activity enhancement by H_2O.

In order to obtain information on the effect of Ga_2O_3, the catalyst samples were analyzed by various characterization techniques. The BET surface areas of the catalysts were found to be as follows: $In_2O_3(5)/Al_2O_3$ 150 $m^2\,g^{-1}$, $In_2O_3(5)$–$Ga_2O_3(30)/Al_2O_3$ 115 $m^2\,g^{-1}$, $In_2O_3(5)$–$Ga_2O_3(30)$–Al_2O_3 155 $m^2\,g^{-1}$. A difference in BET surface area was observed among the catalysts. The smallest BET surface area was attained on $In_2O_3(5)$–$Ga_2O_3(30)/Al_2O_3$ because of a blockage of the pores of Al_2O_3 by supported In_2O_3 and Ga_2O_3.

The rate ($mol\,min^{-1}\,g^{-1}$) and specific activity ($mol\,min^{-1}\,m^{-2}$) for NO reduction into N_2 at 300 °C were calculated for the three catalysts. As summarized in table 5, the specific activity was increased by the presence of Ga_2O_3, irrespective of coexisting H_2O. A great difference in the specific activity was also observed between $In_2O_3(5)$–$Ga_2O_3(30)/Al_2O_3$ and $In_2O_3(5)$–$Ga_2O_3(30)$–Al_2O_3. Since the sol–gel technique is capable of preparing catalysts with highly dispersed species [16], the presence of In_2O_3 and Ga_2O_3 interacting strongly with alumina would be related to the high activity of $In_2O_3(5)$–$Ga_2O_3(30)$–Al_2O_3.

The XRD measurements were carried out to examine the crystallite structure of indium oxide and gallium oxide. As shown in figure 6, the diffraction peaks assigned to In_2O_3 as well as γ-Al_2O_3 were observed for $In_2O_3(5)/Al_2O_3$, indicating that In_2O_3 seems to be aggregated as large parti-

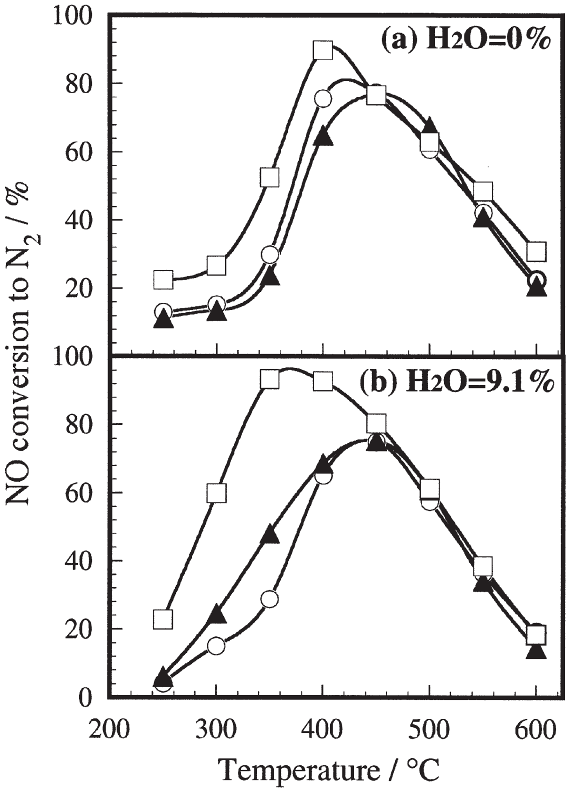

Figure 5. Effect of preparation method on the catalytic activity of $In_2O_3(5)$–$Ga_2O_3(30)$–Al_2O_3 for NO reduction by propene in the (a) absence and (b) presence of H_2O. The reaction conditions are the same as for figure 1. (○) $In_2O_3(5)/Al_2O_3$, (▲) $In_2O_3(5)$–$Ga_2O_3(30)/Al_2O_3$, (□) $In_2O_3(5)$–$Ga_2O_3(30)$–Al_2O_3.

Table 5
Reaction rates and specific activities of $In_2O_3(5)/Al_2O_3$, $In_2O_3(5)$–$Ga_2O_3(30)/Al_2O_3$ and $In_2O_3(5)$–$Ga_2O_3(30)$–Al_2O_3 for NO reduction into N_2 by propene in the presence and absence of H_2O at 300 °C.[a]

Catalyst	BET surface area ($m^2\,g^{-1}$)	Without H_2O (0%)		With H_2O (9.1%)	
		Reaction rate ($mol\,min^{-1}\,g^{-1}$)	Specific activity ($mol\,min^{-1}\,m^{-2}$)	Reaction rate ($mol\,min^{-1}\,g^{-1}$)	Specific activity ($mol\,min^{-1}\,m^{-2}$)
$In_2O_3(5)/Al_2O_3$	150	1.01×10^{-6}	6.70×10^{-9}	9.95×10^{-7}	6.65×10^{-9}
$In_2O_3(5)$–$Ga_2O_3(30)/Al_2O_3$	115	9.00×10^{-7}	7.80×10^{-9}	1.64×10^{-6}	1.42×10^{-8}
$In_2O_3(5)$–$Ga_2O_3(30)$–Al_2O_3	155	1.77×10^{-6}	1.14×10^{-8}	3.97×10^{-6}	2.56×10^{-8}

[a] Reaction conditions: NO = 900 ppm, C_3H_6 = 860 ppm, O_2 = 10%, H_2O = 0 or 9.1%, gas flow rate = 66 $cm^3\,min^{-1}$, temperature = 300 °C, catalyst weight = 0.2 g.

cles on γ-Al_2O_3. However, for In_2O_3(5)–Ga_2O_3(30)/Al_2O_3 and In_2O_3(5)–Ga_2O_3(30)–Al_2O_3, no diffraction peaks ascribed to In_2O_3 were observed. This means that the dispersion of In_2O_3 on these two catalysts is much higher than that on In_2O_3(5)/Al_2O_3. Accordingly, the coexisting Ga_2O_3 seems to contribute to the improvement of the dispersion of In_2O_3 by the interaction between both oxides. We think that the highly dispersed In_2O_3 is responsible for the enhancement of NO reduction activity by H_2O. Figure 6 also indicates the difference in the structure of gallium oxide between the two In_2O_3-doped Ga_2O_3–Al_2O_3 catalysts. Namely, the diffraction peaks assigned to β-Ga_2O_3 were observed for In_2O_3(5)–Ga_2O_3(30)/Al_2O_3, while the peaks assigned to $GaAlO_3$ [22] were detected for In_2O_3(5)–Ga_2O_3(30)–Al_2O_3. The difference in the structure of gallium oxide would be one of the reasons for the difference in the catalytic activity between the two catalysts.

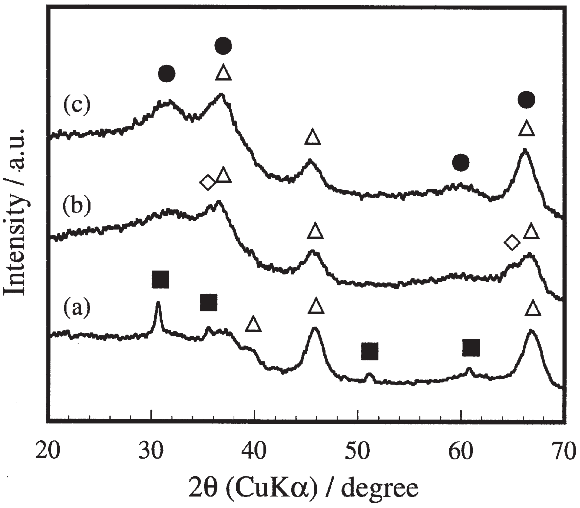

Figure 6. XRD patterns of (a) In_2O_3(5)/Al_2O_3, (b) In_2O_3(5)–Ga_2O_3(30)/Al_2O_3 and (c) In_2O_3(5)–Ga_2O_3(30)–Al_2O_3. (◇) for β-Ga_2O_3, (△) for γ-Al_2O_3, (●) for $GaAlO_3$, (■) for In_2O_3.

3.5. *Efficiency of the reducing agent*

Next, we studied the efficiency of various reductants for the selective reduction of NO in the presence of H_2O over In_2O_3(5)–Ga_2O_3(30)–Al_2O_3. The results are summarized in table 6. As for NO reduction by saturated hydrocarbons, methane was not an effective reducing agent at all. Propane showed relatively high NO reduction activity in the temperature region between 450 and 550 °C. n-hexane and cyclohexane also acted as effective reducing agents in the temperature range between 400 and 550 °C and were more efficient than propane. The maximum NO conversion and the effective temperature changed depending strongly upon carbon number as follows: CH_4 (14%, 600 °C) $<$ C_3H_8 (70%, 500 °C) $<$ cyclohexane (83%, 400 °C) $=$ n-hexane (87%, 450 °C).

In the case of unsaturated hydrocarbons, a similar behavior as of saturated hydrocarbons was observed. Propene was more efficient for NO reduction than ethene at the lower temperatures below 400 °C. The maximum NO conversion and the effective temperature observed are as follows: C_2H_4 (84%, 450 °C) $<$ C_3H_6 (93%, 350–400 °C). However, the efficiency of benzene, which is one of the aromatics, for NO reduction was worse than that of the corresponding saturated hydrocarbon, namely, n-hexane and cyclohexane. In_2O_3(5)–Ga_2O_3(30)–Al_2O_3 seems to catalyze NO reduction by unsaturated hydrocarbons more effectively.

Oxygenated hydrocarbons were also effective reducing agents for NO reduction at relatively low temperatures, compared with corresponding hydrocarbons. Particularly, methanol showed the highest NO reduction activity at 300 °C, but the effective temperature window was narrow. When ethanol, 2-propanol and acetone were employed as reductants, high activity for NO reduction was attained in a wide temperature range. Almost the same effective temperature window was observed for ethanol, 2-propanol and acetone. Maximum NO conversion was obtained for 2-propanol. The maximum NO conversion and the effective temperature changed depending upon carbon number as follows: ethanol (68%, 400 °C) $<$ methanol (81%,

Table 6

Efficiency of various reducing agents for the selective reduction of NO over In_2O_3(5)–Ga_2O_3(30)–Al_2O_3 in the presence of H_2O.[a]

Reduct	NO conversion to N_2 (%) (CH conversion to CO_x (%))							
	250 °C	300 °C	350 °C	400 °C	450 °C	500 °C	550 °C	600 °C
CH_4	–	–	–	–	2.8 (1.0)	4.7 (4.6)	8.4 (17)	14 (52)
C_2H_4	–	4.0 (1.0)	25 (14)	71 (54)	84 (87)	79 (98)	57 (98)	29 (100)
C_3H_6	–	60 (26)	93 (60)	93 (98)	80 (99)	61 (99)	38 (99)	18 (100)
C_3H_8	–	–	–	6.2 (2.0)	45 (28)	70 (71)	61 (92)	40 (100)
n-C_6H_{14}	–	–	18 (8.0)	86 (90)	87 (98)	73 (98)	57 (99)	43 (100)
cyclo-C_6H_{12}	–	–	25 (15)	83 (78)	80 (94)	65 (98)	51 (100)	45 (100)
C_6H_6	–	–	12 (6.3)	29 (22)	67 (57)	70 (78)	64 (92)	44 (99)
CH_3OH	21 (12)	81 (90)	55 (93)	28 (100)	10 (100)	–	–	–
C_2H_5OH	–	26 (25)	65 (75)	68 (92)	67 (99)	55 (99)	37 (99)	–
2-C_3H_7OH	–	58 (24)	93 (65)	94 (94)	74 (95)	56 (98)	38 (99)	–
$(CH_3)_2CO$	–	46 (22)	83 (72)	87 (80)	70 (89)	56 (99)	36 (99)	–

[a] Reaction conditions: NO $=$ 900 ppm, O_2 $=$ 10%, reductant $=$ 3000 ppm C, H_2O $=$ 9.1%, gas flow rate $=$ 66 $cm^3\,min^{-1}$, $W/F = 0.18$ $g\,s\,cm^{-3}$.

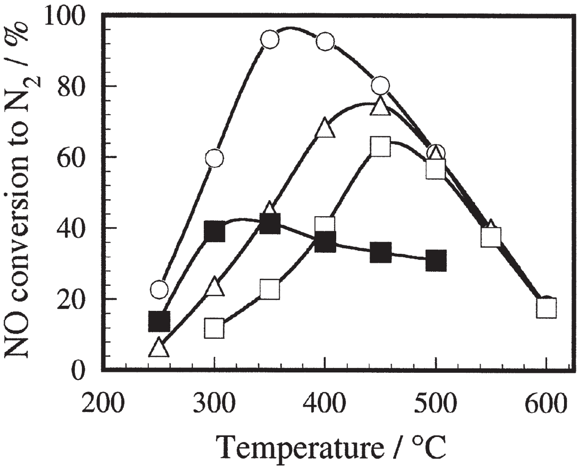

Figure 7. Effect of space velocity (SV) on the catalytic activity of $In_2O_3(5)$–$Ga_2O_3(30)$–Al_2O_3 for NO reduction by propene in the presence of H_2O. In this figure, (■) indicates the activity of Cu-ZSM-5 for NO reduction at SV = 100 000 h^{-1} examined for comparison. Conditions: NO = 900 ppm, C_3H_6 = 860 ppm, O_2 = 10%, H_2O = 9.1%, catalyst weight = 0.02–0.2 g, W/F = 0.02–0.18 $g\,s\,cm^{-3}$. (○) SV = 10 000 h^{-1}, (△) SV = 40 000 h^{-1}, (□) SV = 100 000 h^{-1}.

300 °C) < acetone (87%, 400 °C) < 2-propanol (94%, 400 °C).

We can conclude that propene and 2-propanol served as the most efficient reducing agents for NO reduction in the presence of H_2O.

3.6. Comparison of NO reduction activity of $In_2O_3(5)$–$Ga_2O_3(30)/Al_2O_3$ and Cu-ZSM-5

Figure 7 shows the influence of space velocity on NO reduction activity of $In_2O_3(5)$–$Ga_2O_3(30)$–Al_2O_3 in the presence of H_2O. Although the catalytic activity decreased with increasing space velocity, NO conversion at 450 °C was found to be as much as 75 and 65% at SV = 40 000 and 100 000 h^{-1}, respectively. In figure 7 is also shown the NO conversion profile for Cu-ZSM-5, which has been reported as one of the most active catalysts at high space velocity. Although Cu-ZSM-5 showed excellent activity at temperatures below 350 °C, the activity of $In_2O_3(5)$–$Ga_2O_3(30)/Al_2O_3$ was much higher than that of Cu-ZSM-5 at higher temperatures above 400 °C. Therefore, In_2O_3–Ga_2O_3–Al_2O_3 is one of the most active catalysts for the selective reduction of NO in the presence of H_2O and at high space velocity.

4. Conclusions

The catalytic performance of metal oxide-doped Ga_2O_3–Al_2O_3 prepared by the sol–gel method for the selective reduction of NO with hydrocarbons or oxygenated hydrocarbons in the presence of oxygen was investigated. As for NO reduction by propene in the presence of H_2O, In_2O_3-doped Ga_2O_3–Al_2O_3 catalyst showed the highest NO reduction activity among other metal oxide-doped catalysts in the lower temperature region below 400 °C. The presence of H_2O enhanced drastically the catalytic activity of In_2O_3-doped Ga_2O_3–Al_2O_3. The promotional effect of H_2O was accounted for by the following two reasons: one is the suppression of undesirable oxidation of propene by oxygen, resulting in the improvement of propene utilization for NO reduction into N_2; the other is the removal of surface carbonaceous materials deposited on the catalytically active sites by reactions such as steam reforming.

The effect of preparation method on the catalytic activity of In_2O_3-doped Ga_2O_3–Al_2O_3 for NO reduction by propene was investigated. The highest activity was attained on In_2O_3–Ga_2O_3–Al_2O_3 prepared by the sol–gel method. This was considered to be due to the difference in the crystallite structure of gallium oxide. It is also noteworthy that the activity of In_2O_3-doped Ga_2O_3–Al_2O_3 prepared by sol–gel and co-impregnation methods was enhanced by addition of H_2O, while the promotional effect of H_2O was not observed on In_2O_3/Al_2O_3 prepared by the impregnation method. We considered that the highly dispersed In_2O_3 produced by the interaction between In_2O_3 and Ga_2O_3 is responsible for the enhancement of NO reduction activity by H_2O.

A lot of hydrocarbons except methane and oxygenated compounds served as good reducing agents, among which propene and 2-propanol were the most efficient ones. In_2O_3-doped Ga_2O_3–Al_2O_3 catalyst was also capable of reducing NO into N_2 quite efficiently in the presence of H_2O at very high space velocities.

References

[1] M. Shelef, Chem. Review 95 (1995) 209.
[2] M. Iwamoto and H. Yahiro, Catal. Today 22 (1994) 5.
[3] M. Iwamoto, H. Yahiro, Y. Yu-u, S. Shundo and N. Mizuno, Shokubai (Catalyst) 32 (1990) 430.
[4] E. Kikuchi and K. Yogo, Catal. Today 22 (1994) 73.
[5] C. Yokoyama and M. Misono, J. Catal. 150 (1994) 9.
[6] Y. Kintaichi, H. Hamada, M. Tabata, M. Sasaki and T. Ito, Catal. Lett. 6 (1990) 239.
[7] H. Hamada, Catal. Today 22 (1994) 21.
[8] T. Miyadera and K. Yoshida, Chem. Lett. (1993) 1483.
[9] T. Miyadera, A. Abe, G. Muramatsu and K. Yoshida, *Advanced Materials '93, V/A: Ecomaterials*, ed. R. Yamamoto (Elsevier, Amsterdam, 1994) p. 405.
[10] C.N. Montreuil and M. Shelef, Appl. Catal. B 1 (1992) L1.
[11] M. Haneda, Y. Kintaichi, M. Inaba and H. Hamada, Bull. Chem. Soc. Jpn. 70 (1997) 499.
[12] K. Sato, T. Fujimoto, S. Kanai, Y. Kintaichi, M. Inaba, M. Haneda and H. Hamada, Appl. Catal. B 13 (1997) 27.
[13] Y. Hirao, C. Yokoyama and M. Misono, J. Chem. Soc. Chem. Commun. (1996) 597.
[14] A. Ueda, T. Oshima and M. Haruta, Appl. Catal. B 12 (1997) 81.
[15] M. Haneda, Y. Kintaichi, H. Shimada and H. Hamada, Chem. Lett. (1998) 181.
[16] M. Haneda, T. Mizushima, N. Kakuta, A. Ueno, Y. Sato, S. Matsuura, K. Kasahara and M. Sato, Bull. Chem. Soc. Jpn. 66 (1993) 1279.
[17] M. Misono, Y. Hirao and C. Yokoyama, Catal. Today 38 (1997) 157.
[18] H.Y. Chen and W.M.H. Sachtler, Catal. Lett. 50 (1998) 125.

[19] Y. Hirao, C. Yokoyama and M. Misono, *78th Meeting of Catal. Soc. Jpn.* A (1996) 6B20.

[20] T. Fujimoto, K. Sato, T. Yoshinari, Y. Kintaichi, M. Inaba, M. Haneda and H. Hamada, Sekiyu Gakkaishi 40 (1997) 510.

[21] M. Misono, H. Niiro and Y. Hirao, Res. Chem. Intermed. 24 (1998) 123.

[22] J. Macdonald, J.A. Gard and F.P. Glasser, J. Inorg. Nucl. Chem. 29 (1967) 661.