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Promotive effect of additives to In/H-ZSM-5 catalyst for selective reduction of nitric oxide with methane in the presence of water vapor

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Abstract

It has been found that Ga and In/H-ZSM-5 are active catalysts for selective NO reduction with methane, while the activities are retarded by water vapor, which particularly retards the oxidation of NO to NO_2 on zeolitic Lewis acid sites, a necessary step for the reduction of NO with methane. In order to attain a H_2O-tolerant catalyst based on In/H-ZSM-5, the substitute for Lewis acid sites was searched. After testing several metal species, it was found that In/H-ZSM-5 loading Pt, Rh and Ir exhibited high catalytic activity for NO reduction even in the presence of H_2O.

Keywords: In/H-ZSM-5; Reduction; Nitric oxide; Water vapor

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1. Introduction

The HC-SCR, that is selective catalytic reduction of NO with hydrocarbons, has recently come under great attention as a countermeasure to solve the serious problem caused by emission of nitrogen oxides (NO_x) in combustion exhausts, because this process takes an advantage of using unburned hydrocarbons in the exhaust as a reductant. Although several studies [1–12] have been reported on various types of catalysts for the HC-SCR, most of them are considerably deactivated by water vapor which is inevitably contained in every combustion exhaust. In our previous study [13], it has been shown that Ga and In/H-ZSM-5 are highly active and selective for reduction of NO in the absence of water vapor even when CH_4 is used as a reductant. The problem is that their catalytic activities are strongly inhibited by water vapor, although the catalytic activity of In/H-ZSM-5 showed much higher durability against H_2O than Ga/H-ZSM-5 in the reaction system of NO_2–CH_4–O_2 [14]. The purpose of this study is to discuss the promotive effect of some additives including precious metals added to In/H-ZSM-5 on the sustainability against H_2O.

2. Experimental

Na-ZSM-5 (a molar SiO_2/Al_2O_3 ratio = 23.8) used in this work was provided by Tosoh Corp. Ga and In/H-ZSM-5 were prepared by ion exchange of NH_4-ZSM-5 derived from the Na-

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type with aqueous solutions of nitrate at 95°C for 24 h, followed by calcination at 540°C for 3 h. The level of gallium and indium ion exchange were 96% and 92%, respectively. In/H-ZSM-5 was impregnated for further improvement with an aqueous solution of $Pt(NH_3)_4Cl_2$, $Rh(NH_3)_6Cl_3$, $IrCl(NH_3)_5Cl_2$, $Cr(NO_3)_3$, $Pd(NH_3)_4Cl_2$, $Fe(NO_3)_3$, $Ce(CH_3COO)_3$, $HAuCl_4$, $Co(CH_3COO)_2$, $AgNO_3$, $Mn(NO_3)_2$, $Ni(NO_3)_2$, $Cu(CH_3COO)_2$ or NH_4VO_3. The contents of the additives to In/H-ZSM-5 were controlled to be 1 wt.-% of the catalysts. The reaction was carried out in a fixed-bed flow reactor by passing a reactant gas mixture of 1000 ppm NO_x (NO or NO_2), 1000–2000 ppm CH_4, 10% O_2 and 0–10% H_2O in helium at a rate of 100 cm^3 (STP) min^{-1} over 0.1–0.25 g of a catalyst. The tail gas from the reactor was analyzed by use of gas chromatograph and chemiluminescence NO_x analyzer. The catalytic activity was evaluated by NO_x conversion into N_2.

3. Results and discussion

From the catalytic performance of Ga and In/H-ZSM-5 in $NO–CH_4–O_2$, $NO_2–CH_4–O_2$ and $NO–O_2$ reactions, it was concluded in our previous work [13] that the reduction of NO with CH_4 on Ga and In/H-ZSM-5 catalysts proceed in the following two stages:

$$NO + 1/2O_2 \rightarrow NO_2 \qquad (1)$$

on zeolite acid sites and:

$$NO_2 + CH_4 + NOx \rightarrow N_2 + COx + 2H_2O \qquad (2)$$

on Ga or In sites.

As the catalytic activity for NO oxidation decreased and the level of NO_2 conversion in $NO_2–CH_4$ system increased with increasing Ga or In content, the role of these cations is to accelerate the reaction between NO_2 and CH_4 [reaction (2)] and not to oxidize NO to NO_2 [reaction (1)]. It has also been shown that the catalytic activity of H/Na-ZSM-5 for NO oxidation increased with increasing proton exchange level [13]. Additionally, NO conversion to NO_2 on H-ZSM-5 at 400°C increased from 30 to 35% under these reaction conditions with increasing pretreatment temperature from 500 to 800°C. Therefore, it is reasonable to consider that the zeolitic Lewis acid sites are concerned in NO oxidation to NO_2 [15].

Fig. 1 shows the effect of water vapor on the catalytic activities of H, Ga and In/H-ZSM-5 for $NO–CH_4–O_2$ and $NO_2–CH_4–O_2$ reactions. All these catalysts, particularly Ga/H-ZSM-5 and H-ZSM-5 were very sensitive to H_2O. In contrast to the $NO–CH_4–O_2$ system [Fig. 1a], the retarding effect of water vapor on In/H-ZSM-5 was relatively small in the $NO_2–CH_4–O_2$ system [Fig. 1b], while H_2O showed a significant retarding effect on Ga/H-ZSM-5 and H-ZSM-5 even in

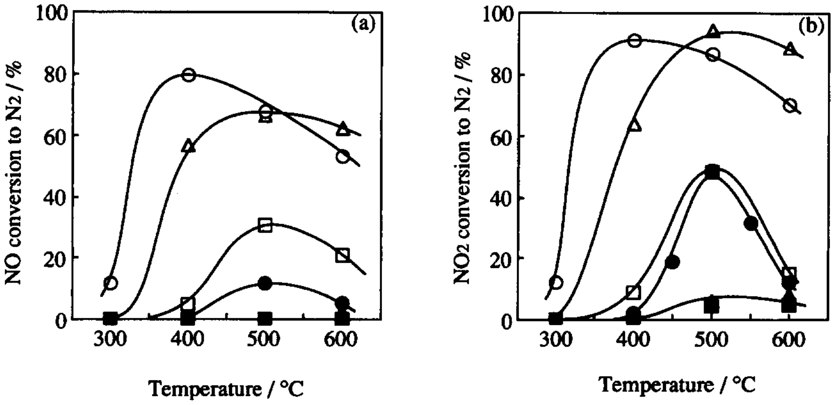

Fig. 1. Effect of water vapor on the catalytic activities of H-ZSM-5 (□ ■), Ga/H-ZSM-5 (△ ▲) and In/H-ZSM-5 (○ ●) for reduction of NO with CH_4 (a) and for reduction of NO_2 with CH_4 (b). NO or NO_2 = 1000 ppm; CH_4 = 2000 ppm; O_2 = 10%; catalyst weight = 0.25g. Open symbol, without H_2O; solid symbol, with 10% H_2O.

Table 1
Catalytic activities for NO oxidation to NO_2 in the presence of water vapor (10%) in the reactant stream

Catalyst	NO conversion to NO_2/%			
	300°C	400°C	500°C	600°C
Pt(8)/H-ZSM-5	25.6	24.4	16.1	12.3
Rh(15)/H-ZSM-5	9.5	15.7	16.1	12.5
Ir(8)/H-ZSM-5	16.5	26.5	18.4	12.1
Pd(17)/H-ZSM-5	10.3	10.9	–	12.8
Mn(72)/H-ZSM-5	10.3	11.9	11.3	–
Ni(71)/H-ZSM-5	10.8	12.4	14.3	–
Cr(17)/H-ZSM-5	10.2	12.6	14.3	–
H-ZSM-5	7.7	13.0	13.3	12.9

NO = 1000 ppm; O_2 = 10%; H_2O = 10%; total flow rate = 100 $cm^3 min^{-1}$; catalyst weight = 0.1 g.
Values in parentheses represent the level of cation exchange.

this reaction system. A larger retarding effect of water vapor in the NO-CH_4-O_2 system than in the NO_2–CH_4–O_2 system is comprehensive, because NO oxidation [reaction(1)] is strongly inhibited by H_2O molecules which are coordinated to zeolite Lewis acid sites. It is obvious that NO_2 formation is an important step for NO reduction.

These results indicate that the In sites in In/H-ZSM-5 are less inhibited by H_2O molecules than the Ga sites. The coordination of H_2O molecules to Ga and In sites may be written as follows:

$$(GaO)^+ + H_2O \rightleftarrows [Ga(OH)_2]^+$$

$$(InO)^+ + H_2O \rightleftarrows [In(OH)_2]^+$$

Coordination of bulky OH groups would block the adsorption site for NO_2 or CH_4. As OH^- group is a hard base (ligand), it can more strongly coordinate to harder Ga cations than to In cations. Namely, the coordination equilibrium is more favorable for $(InO)^+$ than for $(GaO)^+$.

As the coordination of OH groups to zeolitic Lewis acid sites cannot be avoided, these sites should necessarily be substituted by other catalytic components for NO oxidation sites, if high performance for NO reduction on In/H-ZSM-5 based catalyst could be realized even in the presence of water vapor. Table 1 summarizes the catalytic activities of various metal species added to H-ZSM-5 effective for NO oxidation. These species were added to In/H-ZSM-5 and their catalytic activities for NO reduction with methane were measured.

Fig. 2 shows typical results observed at 500°C, with their catalytic activities for NO oxidation at the same temperature. Among these metals, Pt, Rh and Ir showed promotive effects on the catalytic activity of In/H-ZSM-5, since these metal sites could work as active sites for NO oxidation even in the presence of water vapor. On the other hand, Co and Mn showed negative effect for NO reduction, although these metals species enhanced NO oxidation. It is probably due to CH_4 combustion concurrently taking place, resulting in decreased selectivity for NO reduction.

Fig. 3 shows the catalytic activities of In/H-ZSM-5, Pt/H-ZSM-5 and Pt/In/H-ZSM-5 for NO oxidation and for NO reduction with CH_4 as a function of H_2O concentration in the reactant level. Pt loaded In/H-ZSM-5 showed higher durability against H_2O than In/H-ZSM-5. The higher durability is attributed to NO oxidation activity of Pt sites, because Pt/H-ZSM-5 showed poor activity for NO reduction.

The catalytic activities of Pt, Rh and Ir/In/H-ZSM-5 are compared in Fig. 4, as a function of

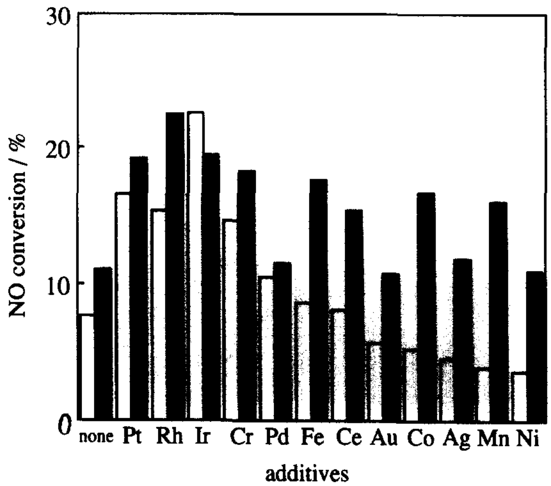

Fig. 2. Effect of the additives (1 wt.-%) to In/H-ZSM-5 on the catalytic activity for NO oxidation and reduction with CH_4 at 500°C in the presence of water vapor (10%).
NO–CH_4 system (□): NO = 1000 ppm; CH_4 = 1000 ppm; O_2 = 10%.
NO–O_2 system (■): NO = 1000 ppm; O_2 = 10%, catalyst weight = 0.1 g.

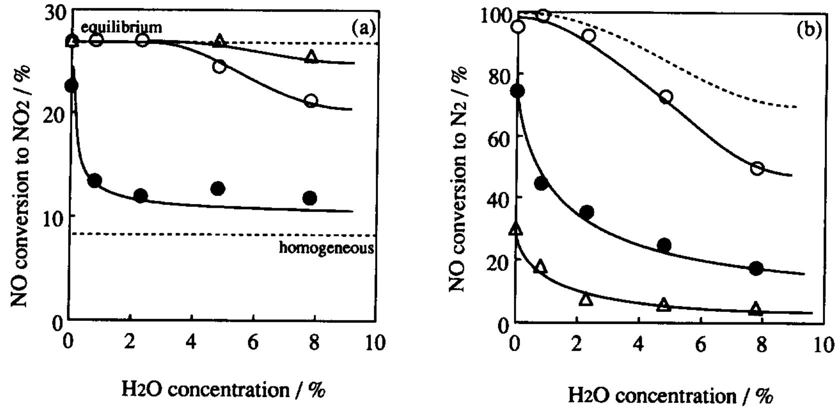

Fig. 3. Effect of water vapor on the catalytic activities of In/H-ZSM-5 (●), Pt (1 wt.-%)/H-ZSM-5 (△) and Pt (1 wt.-%)/In/H-ZSM-5 (○) for NO oxidation to NO_2 (a) and for NO reduction with CH_4 (b). (a) NO = 1000 ppm; O_2 = 10%. (b) NO (or NO_2) = 1000 ppm; CH_4 = 1000 ppm; O_2 = 10%; catalyst weight = 0.25 g. Reaction temperature = 500°C. Dotted line in Fig. (b) shows the activity of In/H-ZSM-5 in the NO_2–CH_4–O_2–H_2O system.

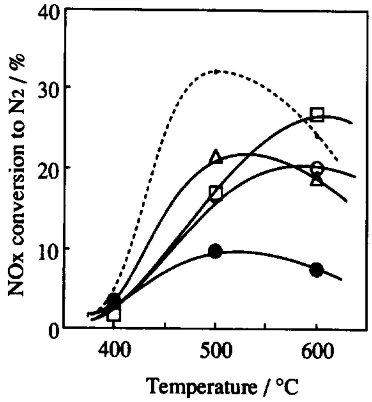

Fig. 4. Catalytic activities of In/H-ZSM-5 (●), Pt-(○), Ir-(△) and Rh-(□) loaded In/H-ZSM-5 for NO reduction with CH_4. NO = 1000 ppm; CH_4 = 1000 ppm; O_2 = 10%; H_2O = 10%; catalyst weight = 0.1 g. Dotted line, NO_2 conversion to N_2 for the NO_2–CH_4–O_2 system on the In/H-ZSM-5.

reaction temperature. The level of NO conversion on these catalysts was in between NO conversion and NO_2 conversion on In/H-ZSM-5. This means that these metals on In/H-ZSM-5 effectively act as catalytic sites for NO oxidation and CH_4 oxidation is not serious under these conditions.

On these precious metal-loaded In/H-ZSM-5 catalysts, the formation of N_2O was negligible in these experimental conditions.

Fig. 5 shows the activities of these catalysts for oxidation of NO and CH_4 independently observed in this temperature range. Among them, Pt/In/H-ZSM-5 showed the least activity for CH_4 oxidation, while Ir/In/H-ZSM-5 showed the highest. As shown in Fig. 4, Ir/In/H-ZSM-5 showed a comparable activity for NO reduction with Pt/In/

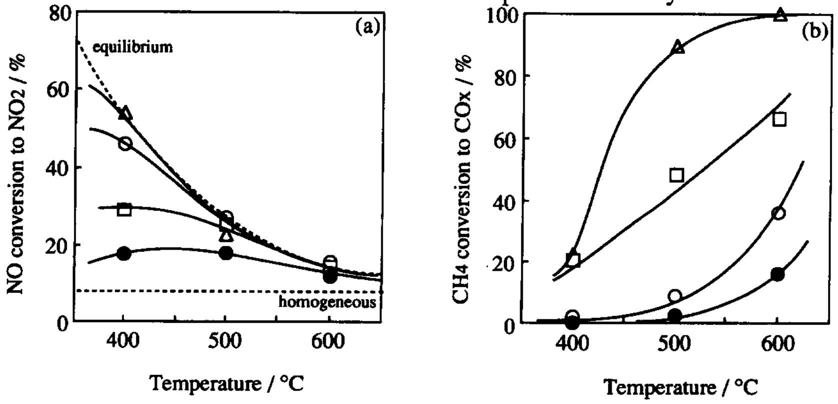

Fig. 5. Catalytic activities of In/H-ZSM-5 (●), Pt/In/H-ZSM-5 (○), Rh/In/H-ZSM-5 (□) and Ir/In/H-ZSM-5 (△) for NO oxidation to NO_2 (a) and CH_4 oxidation to CO_x (b). (a) NO = 1000 ppm; O_2 = 10%. (b) CH_4 = 1000 ppm; O_2 = 10%. Catalyst weight = 0.1 g.

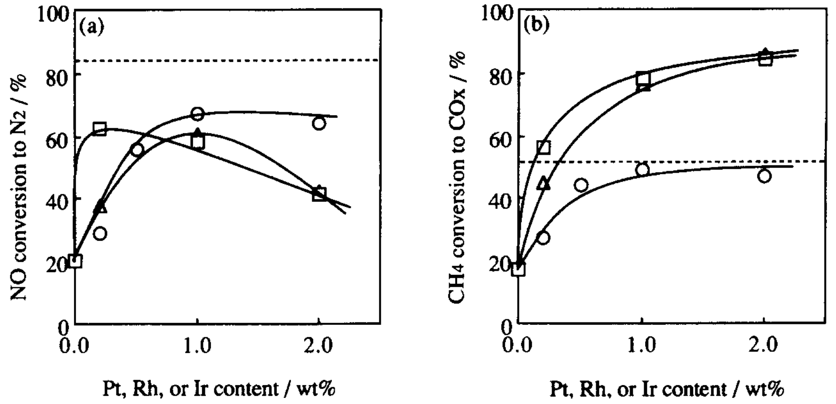

Fig. 6. The effects of the content of Pt,Rh, or Ir in In/H-ZSM-5 on the catalytic activities for NO reduction to N_2 and CH_4 conversion to CO_x at 500°C. NO = 1000 ppm; CH_4 = 1000 ppm; O_2 = 10%; H_2O = 5%; catalyst weight = 0.1 g. ○, Pt/In/H-ZSM-5; △, Rh/In/H-ZSM-5; □, Ir/In/H-ZSM-5. Dotted line shows the activity in In/H-ZSM-5 in the NO_2–CH_4–O_2–H_2O system.

H-ZSM-5 catalyst, even at 500°C, indicating that CH_4 combustion on Ir sites in the NO–CH_4–O_2 system should be somewhat retarded by NO.

As the oxidation of CH_4 takes place concurrently with that of NO, then there would be an optimum concentration of these metals to give the maximum activity and selectivity for NO reduction. Fig. 6 shows the effects of Pt, Rh or Ir content on the level of NO conversion to N_2 with the percent of CH_4 concurrently converted to CO_x. The level of CH_4 conversion increased with the content of precious metals, although more CH_4 was consumed on the Ir/In/H-ZSM-5 than other catalysts. As a result, Ir/In/H-ZSM-5 gave a maximum activity for NO reduction at 0.2 wt.-%, while the catalytic activity of Pt/In/H-ZSM-5 for NO reduction increased with increasing Pt content and gave a maximum at 1 wt.-%. Although further studies are required to explain concretly the promotive effect of these additives, it is obvious that addition of Pt and Ir to In/H-ZSM-5 is effective to enhance the catalytic activity of In/H-ZSM-5 and that these catalysts showed high activities equal to In/H-ZSM-5 for NO_2–CH_4–O_2 reaction shown by the dotted line in Fig. 6.

4. Conclusion

Effect of water vapor on the catalytic activities of Ga and In/H-ZSM-5 was significant. On both of these catalysts, NO–CH_4–O_2 reaction was more largely retarded by H_2O than NO_2–CH_4–O_2 reaction. NO_2–CH_4–O_2 reaction on In/H-ZSM-5 was, however, moderately proceed even in the presence of water vapor. It is obvious that H_2O inhibits the NO oxidation taking place on the Lewis acid sites of zeolite. It is indicated that substitution for the Lewis acid sites, on which NO oxidation proceeds, is effective for high catalytic performance in the presence of water vapor. Precious metal (Pt, Rh or Ir) loaded In/H-ZSM-5 showed high catalytic activity for NO reduction with CH_4 even in the presence of water vapor.

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