Precious Metal Loaded In/H-ZSM-5 for Low Concentration NO Reduction with Methane in the Presence of Water Vapor

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Catalytic activity of In/H-ZSM-5 for selective reduction of nitric oxide at a low concentration with methane was greatly improved by supporting precious metals (Pt, Rh, Ir), which promoted not only NO oxidation, but also enhanced NO_2 adsorption in the presence of water vapor.

Nitrogen oxides (NOx) in exhaust gases is a harmful material that should be excluded in order to protect the earth from acid rain, or other environmental concerns.[1] Although a variety of approaches have been explored in the past few years and recently catalytic removal processes of NOx have received a great deal of attention. Since the discoveries by Iwamoto et al.[2] and Held et al.[3] that the reduction of NO by using hydrocarbons can be catalyzed by Cu-zeolites, this reaction has gathered increasing interest and many other catalysts have been reported to promote the selective reduction of NO with various types of hydrocarbon.[4-8] It has been shown in our previous work[9] that Ga and In/H-ZSM-5 are active for NO reduction by use of methane although the drawback of these catalysts was the strong retardation of the catalytic activity by H_2O. On the other hand, it was shown that NO_2-CH_4-O_2 reaction on In/H-ZSM-5 could moderately proceed even in the wet condition. It was reported in our previous work[10] that precious metals (Pt, Rh, and Ir) loaded In/H-ZSM-5 catalysts gave high activity for reduction of NO with CH_4 in the presence of water vapor. In this paper, the catalytic activities of the promoted In/H-ZSM-5 catalysts for removal of low concentration NOx, known as a difficult process, and promotive effects of the precious metals will be discussed.

A Na-ZSM-5(a molar SiO_2/Al_2O_3 ratio=23.8) provided by Tosoh Corp. was used. In(4.0wt%)/H-ZSM-5 was prepared by ion exchange of the NH_4-ZSM-5 derived from the Na-ZSM-5 with an aqueous solution of indium nitrate at 368 K for 8 h. 1wt% precious metals were supported on In/H-ZSM-5 by impregnation using an aqueous solution of $Pt(NH_3)_4Cl_2 \cdot H_2O$, $Rh(NH_3)_6Cl_3$, or $IrCl(NH_3)_5Cl_2 \cdot H_2O$. Each catalyst was calcined in air stream at 813 K for 3 h. Reduction of NO or NO_2 was carried out in a fixed-bed flow reactor by passing a reactant gas mixture of 100-1000 ppm NO or NO_2, 1000 ppm CH_4, 10% O_2, and 0 or 5% H_2O in helium at a rate of 100 $cm^3(STP) \cdot min^{-1}$ over 0.1 g of catalysts (GHSV = 36000 h^{-1}). The products were analyzed by means of gas chromatography and chemiluminescence NOx analysis. The catalytic activity was evaluated in terms of the conversion into N_2.

In our previous work,[9] it has been shown that the reduction of NO with CH_4 on Ga and In/H-ZSM-5 proceeds in the following two stages:

$$NO + 1/2\ O_2 \rightarrow NO_2 \quad \text{[on zeolite acid sites]} \quad (1)$$

$$NO_2 + CH_4 + NOx \rightarrow N_2 + COx + H_2O \quad \text{[on Ga or In sites]} \quad (2)$$

The catalytic activity for NO oxidation [reaction(1)] was strongly inhibited by water vapor which is inevitably contained in every combustion exhaust. This reasonably means that NO oxidation, as proposed by Brandin et al.,[11] proceeds on Lewis acid sites on zeolite. On the other hand, the catalytic activity of In/H-ZSM-5 showed a higher durability against H_2O than that of Ga/H-ZSM-5 in the reaction system of NO_2-CH_4-O_2. By addition of the precious metals, on which NO oxidation occurred instead of the zeolitic Lewis acid sites, therefore, the catalytic activity of In/H-ZSM-5 for reduction of NO with methane could considerably be promoted even in the presence of water vapor. Figure 1(a) shows the catalytic activities of the promoted In/H-ZSM-5 catalysts for 1000 ppm NO reduction in the presence of water vapor. NO conversion increased by supporting precious metals on In/H-ZSM-5 to the extent of NO_2 conversion on In/H-ZSM-5. These results indicate that these additives catalyze NO oxidation, which is a necessary step for the reduction with CH_4.

More interesting features were embodied by the promoted catalysts. When tested for the reduction of NO at a concentration as low as 100 ppm, the precious metal loaded In/H-ZSM-5 showed extremely high activity even in the wet condition, as shown in Figure 1(b). It is noted that NO conversion on precious metal loaded In/H-ZSM-5, particularly on Ir/In/H-ZSM-5, exceed the level of NO_2 conversion in NO_2-CH_4-O_2 reaction on In/H-ZSM-5. These results cannot be explained only by the improvement of the catalytic activity for NO oxidation by precious metals.

Figure 2 shows the breakthrough curves of low concentration NO in the NO-O_2 system through In/H-ZSM-5, Pt,

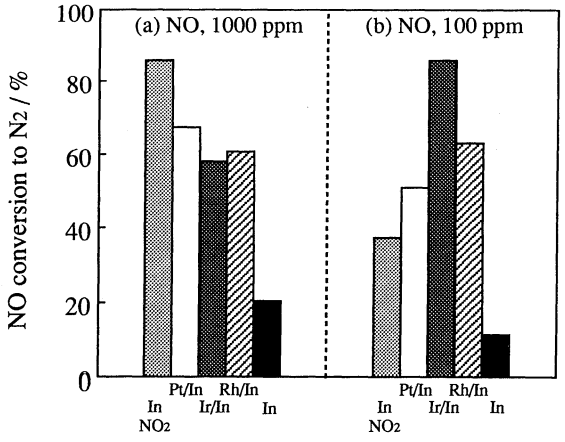

Figure 1. Promotive effects of the Pt, Rh, and Ir on the catalytic activity of In/H-ZSM-5 for NO reduction with CH_4 in the presence of water vapor.
NO, 1000 ppm (a), 100 ppm (b);
CH_4, 1000 ppm; O_2, 10%; H_2O, 5%.
Catalyst weight, 0.1 g. Reaction temperature, 773 K.

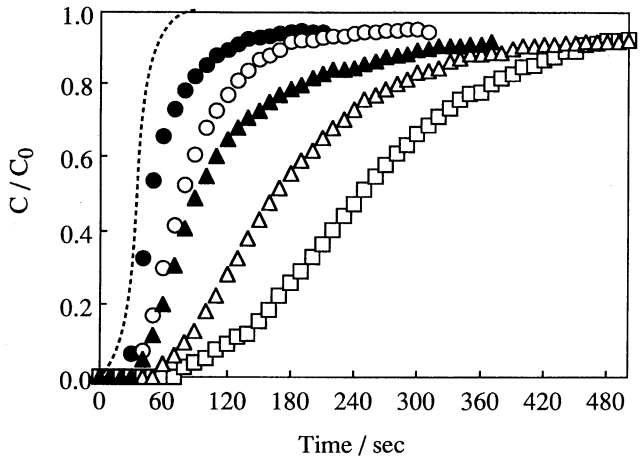

Figure 2. Breakthrough curves of NO and NO_2 through In/H-ZSM-5, and of NO through Pt/, Rh/, and Ir/In/H-ZSM-5 catalysts.
NO or NO_2, 100 ppm; O_2, 10%;
total flow rate, 100 $cm^3 \cdot min^{-1}$.
Catalyst weight, 0.1 g. Reaction temperature, 673 K.
●, NO through In/H-ZSM-5.
▲, NO_2 through In/H-ZSM-5.
NO through Pt/In/H-ZSM-5(○), Rh/In/H-ZSM-5(△), and Ir/In/H-ZSM-5(□).
Dotted line shows the curve through no catalyst.

Rh, or Ir loaded In/H-ZSM-5. It is apparent that the breakthrough point of the curves of Pt, Rh, or Ir/In/H-ZSM-5 was much later than that of In/H-ZSM-5 in the NO-O_2 system. In particular, effluent of NOx through Ir/In/H-ZSM-5 was much slower than that of NO_2 through In/H-ZSM-5. No time-lag was observed when NO was admitted to these catalysts without O_2. It was suggested in the work of Zhang et al. [12] that adsorption of NOx on the catalysts corresponds to the time-response of these curves. These results indicate that the amount of NOx (probably NO_2) was largely increased by the addition of Pt, Rh, or Ir on In/H-ZSM-5.

In conclusion, precious metal loaded In/H-ZSM-5 showed high catalytic activity for NO reduction with methane even in the presence of water vapor. These catalysts, especially Ir loaded In/H-ZSM-5, were effective for low concentration NO reduction. Promotive effect of iridium is not only to promote NO oxidation, but also probably to strengthen NOx adsorption. Although the role of precious metals is not wholly elucidated at this stage, and more study is required, it is worthwhile that reduction of low concentration of NOx with CH_4 becomes possible by use of precious metal loaded In/H-ZSM-5 catalysts. Removal of lower concentration NOx is a more difficult process and usually the concentration of NOx in practical combustion exhausts is extremely low.

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References

1 H. Bosch and F. Janssen, *Catal. Today*, **2**, 369 (1988).
2 M. Iwamoto, H. Yahiro, Y. Yuu, S. Shundo, and N. Mizuno, *Shokubai(Catalyst)*, **32**, 430 (1990).
3 W. Held, A. Koenig, T. Richter and L. Puppe, *SAE Paper*, **1990**, 900496.
4 H. Hamada, Y. Kintaichi, M. Sasaki, and T. Itoh, *Appl. Catal.*, **64**, L1 (1990).
5 M. Misono and K. Kondo, *Chem. Lett.*, **1991**, 1001.
6 K. Yogo, M. Ihara, I. Terasaki, and E. Kikuchi, *Catal. Lett.*, **17**, 303 (1993).
7 Y. Li, P. J. Battavio and J. N. Armor, *J. Catal.*, **142**, 561 (1993).
8 J. O. Petunchi, G. Sill, and W. K. Hall, *Appl. Catal.* **B2**, **303** (1993).
9 E. Kikuchi and K. Yogo, *Catal. Today*, **22**, 73 (1994).
10 E. Kikuchi, M. Ogura, N. Aratani, Y. Sugiura, S. Hiromoto, and K. Yogo, *Catal. Today*, submitted for publication.
11 J. G. M. Brandin, L. A. H. Anderson, and C. U. I. Odenbrand, *Catal. Today*, **4**, 187 (1989).
12 W. X. Zhang, H. Yahiro, N. Mizuno, J. Izumi, and M. Iwamoto, *Langmuir*, 9, 2337 (1993).