Intrapore Catalysis in NO Reduction with Methane on Ir/In/H-ZSM-5 Catalyst

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Chemisorption of NOx on In/H-ZSM-5, Ir/In/H-ZSM-5, and the physical mixture of Ir/H-ZSM-5 and In/H-ZSM-5, and the catalytic activities of these catalysts for NO reduction with methane are studied to understand the role of Ir onto In/H-ZSM-5. The amount of NOx chemisorption on Ir/In/H-ZSM-5 was largest among the catalysts tested. The catalytic activities for NOx reduction on these catalysts were well correlated to the amount of chemisorbed NOx. The dual-functional mechanism, that is, NO oxidation and NO_2 reduction with CH_4 works effectively on Ir and $[InO]^+$ sites, respectively, in the same zeolite pore, as an intrapore catalysis.

Selective catalytic reduction of nitric oxides by hydrocarbons (SCR-NOx) has been attracting a lot of attention as the substitution for the conventional technologies such as NH_3-SCR and three-way catalysis. Several catalysts show high activities for the reduction of NOx using various hydrocarbons: Cu and various metal loaded zeolites, H-ZSM-5, and metal oxides such as Al_2O_3.[1-5] It has been understood that zeolite-based catalysts are more effective than metal oxides from the viewpoint of wide temperature range in which these catalysts show high activity. We have already shown that the addition of precious metals (Pt, Rh, and Ir) improves the catalytic activity of In/H-ZSM-5 for NO reduction by CH_4 even in the presence of H_2O.[6] These catalysts catalyze NO reduction with CH_4 in a dual-functional mechanism: precious metal catalyzes oxidation of NO to NO_2, which is the necessary step for NO reduction by use of CH_4, and $[InO]^+$ catalyzes subsequent reduction of NO_2 with CH_4. By the studies of breakthrough curves of NOx, it has been concluded that precious metals, especially Ir, increase the amount of NOx chemisorption on $[InO]^+$ sites.[7] At present, the role of zeolitic structure for this reaction remains a point in dispute. In this study, we will propose a concept of "intrapore catalysis" to explain why Ir loaded In/H-ZSM-5 shows high catalytic activity for the reduction of NO with CH_4, and discuss the role of zeolitic structure for this reaction.

In(4 wt%)/H-ZSM-5 and Ir(1 wt%)/H-ZSM-5 catalysts were prepared by the ion exchange of NH_4-ZSM-5 derived from Na-ZSM-5 (a molar SiO_2/Al_2O_3 ratio=23.8) supplied by Tosoh Corp. with aqueous solutions of $In(NO_3)_3$ (Mitsuwa Pure Chemicals Corp.) at 95 °C for 8 h and $[IrCl(NH_3)_5]Cl_2$ (N. E. Chemcat Corp.) at room temperature for 24 h, respectively. 1 wt% Ir was loaded onto In/H-ZSM-5 by impregnating the In/NH_4-ZSM-5 with an aqueous solution of $[IrCl(NH_3)_5]Cl_2$. These catalysts were calcined at 540 °C for 3 h prior to the reaction. Reactions were carried out in a fixed-bed flow reactor by passing a reactant gas mixture of 100 ppm NOx (NO or NO_2), 1000 ppm CH_4, 10% O_2 and 0 or 5% H_2O in He at a rate of 100 cm^3(STP)·min^{-1} over 0.1 g of catalysts (GHSV = 36000 h^{-1}). Reaction products were analyzed by means of on-line gas chromatography with a TCD detector and chemiluminescence NOx analysis. The catalytic activity was evaluated by the conversion of NOx into N_2. Chemisorption of NOx was measured by the pressure swing adsorption method reported elsewhere[7] under the same conditions as those for reaction, using the same gas mixture as that for reaction excluding CH_4 and H_2O. The concentration of NOx passing through the catalyst bed was detected using a NOx analyzer (NOA-305 A, Shimadzu Corp.). The amount of adsorbed NOx was calculated from a breakthrough curve, as shown in Figure 1. The curve through a catalyst was measured till the slope of the curve was below 5 mmol·sec^{-1}. The dispersion of Ir was measured by chemisorption of hydrogen by use of Belsorp 28SA (Bel Japan Corp.).

Figure 2 compares the amounts of chemisorbed NOx and the catalytic activities for NOx+CH_4+O_2 reactions for various catalysts containing In and/or Ir on H-ZSM-5. NOx was hardly adsorbed on Ir/H-ZSM-5. A larger amount of NOx was adsorbed on In/H-ZSM-5 when NO_2+O_2 was introduced than when NO+O_2 was admitted. NOx was scarcely adsorbed from NO without oxygen. These results mean that the adsorbed species is NO_2 on $[InO]^+$ sites. The amount of chemisorbed NOx was larger on Ir/In/H-ZSM-5 than that on In/H-ZSM-5. Furthermore, the larger amount of chemisorbed NOx was observed from NO+O_2 than from NO_2+O_2. It is also interesting to note that the amounts of NOx chemisorbed on the physical mixture of Ir/H-ZSM-5 and In/H-ZSM-5 from NO and NO_2 was comparable and they were also comparable to that on In/H-ZSM-5 from NO_2+O_2. It is obvious from Figure 2 that the catalytic activities for NOx reduction were well correlated to the amounts of chemisorbed NOx on these catalysts. CH_4 was hardly adsorbed on these catalysts in our experimental conditions. These results indicate that chemisorbed NO_2 on $[InO]^+$ sites is the important species in the reduction of NO with CH_4, and the rate-determining step of this reaction exists in the reaction between chemisorbed NO_2 species and CH_4, taking place on $[InO]^+$ sites.

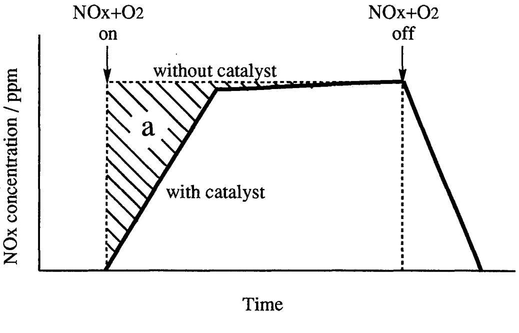

Figure 1. Measurement of NOx chemisorption by use of breakthrough curve.
a, corresponds to the amount of chemisorbed NOx.

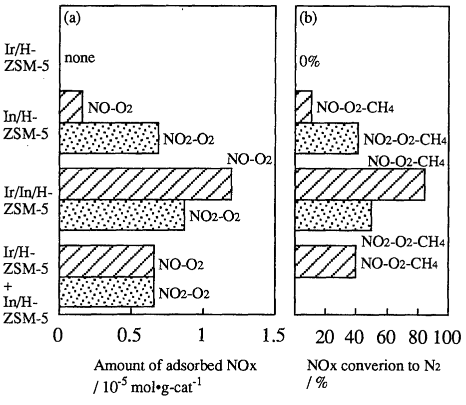

Figure 2. NOx chemisorption at 400 °C (a) and reduction with CH_4 (b) using NO or NO_2 with O_2 admitted onto Ir/H-ZSM-5, In/H-ZSM-5, Ir/In/H-ZSM-5, and physical mixture of Ir/H-ZSM-5 and In/H-ZSM-5.
NOx adsorption: NO (or NO_2), 100 ppm; O_2, 10%.
NOx reduction: NO (or NO_2), 100 ppm; CH_4, 1000 ppm; O_2, 10%; H_2O, 5%.
Total flow rate, 100 $cm^3 \cdot min^{-1}$.
Catalyst weight: Ir/H-ZSM-5, In/H-ZSM-5, and Ir/In/H-ZSM-5, 0.1 g; Ir/H-ZSM-5+In/H-ZSM-5, 0.2 g.

Figure 3 shows the concentrations of NO and NO_2 in the outlet for the experiments shown in Figure 1. Equilibrium of NOx concentration in the outlet gas was not completely accomplished within 10 min exposure of NO_2 to In/H-ZSM-5. When NO_2+O_2 is switched off, adsorbed NOx is desorbed. The desorbed NOx was almost NO_2, which came out slowly. In the case of Ir/In/H-ZSM-5, however, 10 min was almost enough to reach equilibrium of NOx concentration in the outlet gas. When NO+O_2 was switched off, NOx was desorbed rapidly with an overshooting. Desorption of NOx was completed within 5 min, and the desorbed NOx was mainly detected as NO. These results suggest that NO_2 adsorbed on Ir/In/H-ZSM-5 decomposes on Ir sites to NO which diffuses faster than NO_2.

As In/H-ZSM-5 did not chemisorb hydrogen, dispersion of Ir on H-ZSM-5 and In/H-ZSM-5 was determined by H_2 chemisorption at room temperature as H/Ir to be 0.8 and 0.9, respectively. These values mean that Ir is highly dispersed on these catalysts and may be mostly located inside the zeolite pore. From these results, we propose the effective catalysis of Ir/In/H-ZSM-5 as shown in Figure 4. Reduction of NO with CH_4 proceeds in a dual-functional mechanism on Ir/In/H-ZSM-5: Ir catalyzes NO oxidation to NO_2, followed by reduction of NO_2 with CH_4 into N_2 on $[InO]^+$ sites. Ir is well dispersed on ZSM-5 not only on outer surface of the zeolite but also inside the zeolite pores. NO diffuses into the zeolite pores faster than NO_2. Therefore, NO is oxidized with O_2 on Ir sites inside the zeolite pore, and formed NO_2 can be adsorbed on $[InO]^+$ sites in the same pore. On the other hand, NO_2 can be adsorbed more readily on $[InO]^+$ sites near the outer surface of the zeolite pores rather than inside the zeolite pores. Increasing NO_2 concentration in the zeolite pores leads to the enhancement of the catalytic activity for the CH_4-SCR of NO. High catalytic activity for reduction of NO with CH_4 on Ir/In/H-ZSM-5 will be accounted for by this "intrapore catalysis".

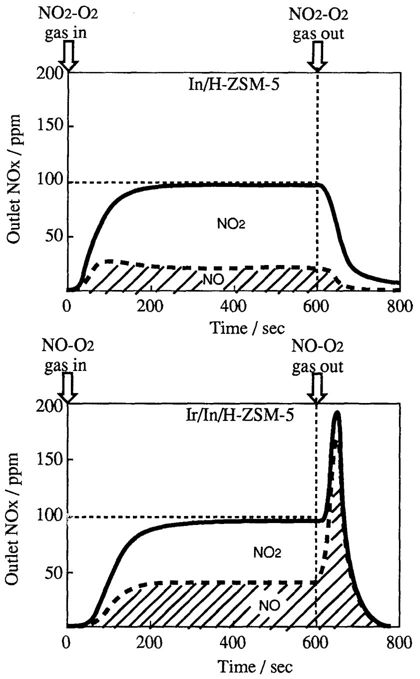

Figure 3. Concentrations of NO and NO_2 in the outlet through In/H-ZSM-5 and Ir/In/H-ZSM-5 catalysts at 400 °C.
Catalyst weight, 0.1 g.

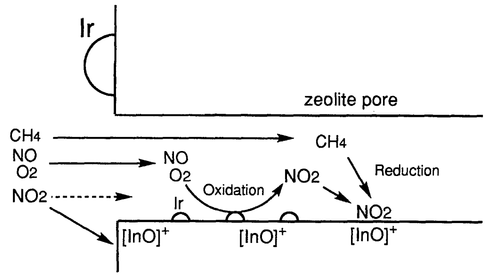

Figure 4. Intrapore catalysis of Ir/In/H-ZSM-5.

References

1 M. Iwamoto, H. Yahiro, Y. Yuu, S. Shundo, and N. Mizuno, *Shokubai(Catalyst)*, **32**, 430 (1990).
2 K. Yogo, M. Ihara, I. Terasaki, and E. Kikuchi, *Catal. Lett.*, **17**, 303 (1993).
3 H. Hamada, Y. Kintaichi, M. Sasaki, and T. Itoh, *Appl. Catal.*, **64**, L1 (1990).
4 K. Yogo, M. Umeno, H. Watanabe, and E. Kikuchi, *Catal. Lett.*, **19**, 131 (1993).
5 Y. Kintaichi, H. Hamada, M. Tabata, M. Sasaki, and T. Ito, *Catal. Lett.*, **6**, 239 (1990).
6 E. Kikuchi, M. Ogura, N. Aratani, Y. Sugiura, S. Hiromoto, and K. Yogo, *Catal. Today*, **27**, 84 (1996).
7 M. Ogura, S. Hiromoto, and E. Kikuchi, *Chem. Lett.*, **1995**, 1135.