Catalytic Activity of Ir for NO-CO Reaction in the Presence of SO_2 and Excess Oxygen

Masaru Ogura, Aya Kawamura, Masahiko Matsukata, and Eiichi Kikuchi*
Department of Applied Chemistry, Waseda University, 3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555

(Received November 8, 1999; CL-990950)

Catalytic performance of Ir catalysts for reduction of nitric oxide with carbon monoxide in the presence of SO_2 and excess oxygen was investigated. NO was selectively reduced with CO on Ir/silicalite in an oxidizing atmosphere containing 1% to 10% O_2 in the temperature range of 300-500 °C. The catalytic activity was scarcely influenced by 150 ppm SO_2.

Catalytic reduction of nitric oxide (NO) in exhausts from stationary combustors and vehicles is a desirable method to apply in a practical usage. A three-way catalyst, composed of Pt, Rh, and/or Pd as active centers, facilitates NO removal from gasoline engine exhaust by use of hydrocarbons and carbon monoxide as reducing agents. However, it can be used only in a narrow window near the stoichiometry, where oxidizing molecules are balanced by reducing molecules. Because of the lean-burn combustion system, NO reduction in the exhaust from diesel engines must always be carried out in an oxidizing atmosphere.[1] Therefore, high selectivity of reductants toward NO reduction is required for the catalytic process, and the three-way catalyst is not feasible to apply for the diesel engine exhaust. Actually, NO is emitted in the exhaust gas from vehicles of diesel engine without any catalytic treatment. Moreover, the gas contains particulate matters, which bring us a problem of cancer.

Reports in the last decade have shown that many types of catalysts, such as Cu-zeolites,[2,3] or other transition metals on zeolites and oxides supports[4] can work in selective reduction of NO by hydrocarbons (HC-SCR) in the presence of excess oxygen. Zeolite-supported catalysts are attractive, because of their wider range of temperature where they can reduce NO at higher conversion levels and more selectively than alumina and the other supported catalysts. Most of the works using those types of catalysts, however, have employed milder reaction conditions than in the actual exhaust, such as lower space velocities, higher concentrations of NO and hydrocarbons, lower concentrations of oxygen, and no H_2O and SO_2 in the reactant feed. For practical clean-up of diesel exhausts, high selectivity toward NO reduction even in the presence of excess oxygen is indispensable, and much attention must be paid for the effect of SO_2 on the catalytic performance.[5] One of the authors has previously reported that a very small amount of Ir(0.02 wt%) on SiO_2 can catalyze NO reduction with CO in the presence of O_2.[6] Furthermore, it is noted that oxygen is needed to promote the NO reduction, and that 3000 ppm of NO was selectively reduced by 1% of CO in the oxidizing atmosphere up to 2% of O_2 coexisted. Utilization of CO as a reducing agent has advantages for practical application to diesel engine exhaust, because the engine works at relatively lower temperatures and the exhaust from diesel engine contains comparable or higher concentration of CO than the gasoline engine exhaust.[7] Recently Nojima et al. reported the catalytic performance of supported Ir catalysts for NO reduction by C_3H_6 as a reductant.[8,9] They have claimed that the Ir catalyst supported on MFI zeolite containing framework Co, Fe, and Al which are not ion-exchanged, exhibited a significant stability against hydrothermal treatment at 700 °C. It is, however, generally known that one of the reasons for deactivation of zeolite-based catalysts in HC-SCR is due to dealumination from the zeolite framework.[10] In this study, silicalite-1 having a MFI topology without Al in the framework was used for the support of Ir, and the effect of SO_2 on the catalytic activities of Ir catalysts for NO-CO reaction in the presence of excess oxygen was investigated.

Catalysts used in this study were Ir on three kinds of supports, SiO_2 (amorphous, Fuji Silicia Corp.), Al_2O_3 (γ, Shokubai Kasei Corp.), and silicalite (Tosoh Corp.). Ir was supported on SiO_2 and silicalite by adsorption in an aqueous solution of $[IrCl(NH_3)_5]Cl_2$. Firstly, the Ir compound was dissolved in distilled water, and the pH was adjusted to 10 with a 10% NH_4OH solution. Then, the support was added to the solution, which was stirred for 24 h at room temperature. After filtration, the Ir containing material was dried overnight in an air oven at 110 °C. Ir/Al_2O_3 catalyst was prepared by impregnating the Al_2O_3 in a H_2IrCl_6 solution. The Ir content in every catalyst was 0.02 wt%, as determined by XRF. Catalysts were pre-treated prior to a reaction: temperature was raised at a rate of 5 °C/min from room temperature to 500 °C in a 20% O_2/He stream, kept at 500 °C for 1 h, and cooled to 400 °C in a He stream, followed by reduction at that temperature for 1 h in flowing H_2. Catalytic activity tests were performed by flowing 1000 ppm NO, 7500 ppm CO, 1-10% O_2, and 0 or 150 ppm SO_2 in balancing He at a feed rate of 100 cm^3/min onto 0.1 g catalyst(GHSV: ca.40,000 h^{-1}). Under the reaction conditions employed in this study, N_2O was hardly detected; therefore, the catalytic activity was evaluated by the amount of NO converted into N_2, determined by use of a chemiluminescence NOx analyzer and a gas chromatograph.

Figure 1 shows the catalytic activities of various Ir catalysts for NO reduction by CO in the presence of 1% O_2 and in the absence of SO_2. Ir/silicalite gave slightly higher conversions of NO in lower temperature range of 300-370 °C than Ir/SiO_2. It is noted that the selectivity of CO toward NO reduction on Ir/silicalite, as expressed by the molar ratio of reacted NO/reacted CO, is much higher than that on Ir/SiO_2: at 365 °C, 0.30 and 0.13 for Ir/silicalite and Ir/SiO_2, respectively.

Figure 2 illustrates the effect of SO_2 on the NO conversions over Ir/silicalite, Ir/SiO_2, and Ir/Al_2O_3 at 400 °C. In the initial run for 30 min without SO_2, Ir/SiO_2 showed higher NO conversion than Ir/silicalite, and Ir/Al_2O_3 showed much lower activity than Ir/silicalite. As shown in the following 30 min run with 150 ppm SO_2, the catalytic activity of Ir/silicalite was hardly affected by SO_2. Moreover, NO conversion on Ir/silicalite was stable over the period of 20 h in the presence of SO_2. On the other hand, NO conversion on Ir/SiO_2 dropped by addi-

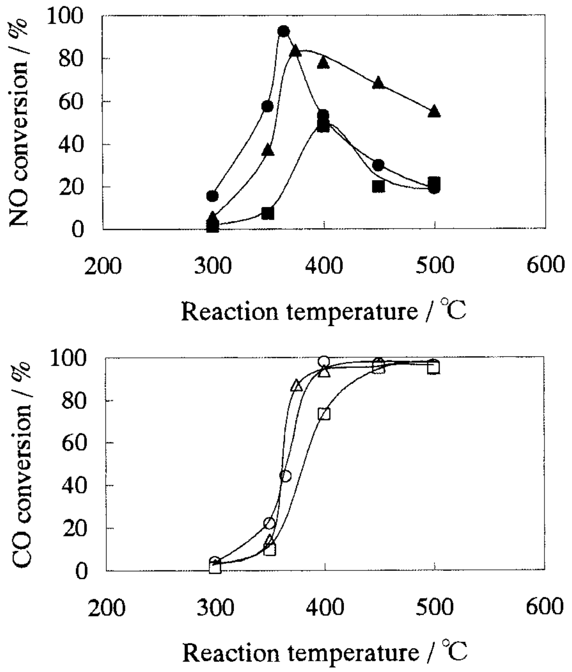

Figure 1. Catalytic activities of Ir/SiO_2(▲△), Ir/Al_2O_3(■□) and Ir/silicalite(●○) for NO reduction with CO in the presence of O_2. NO, 1000 ppm; CO, 7500 ppm; O_2, 1%; total flow rate, 100 cm^3/min. Catalyst weight, 0.1 g. Ir content, 0.02 wt%.

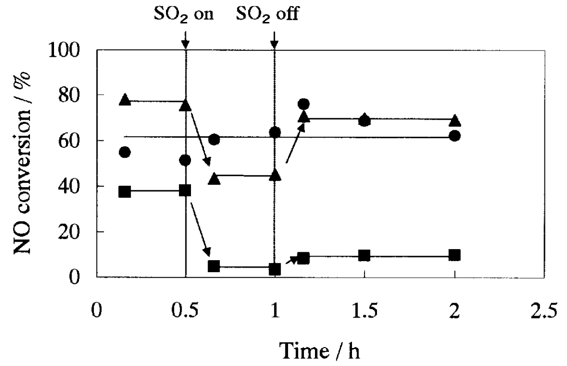

Figure 2. Effect of 150ppm SO_2 addition on the catalytic activities of Ir on SiO_2(▲), Al_2O_3(■), and silicalite(●). NO, 1000 ppm; CO, 8000 ppm; O_2, 1%; total flow rate, 100 cm^3/min. Catalyst weight, 0.1 g. Reaction temperature, 400 °C. Ir content, 0.02 wt%.

tion of SO_2, although the activity immediately recovered by excluding SO_2 from the reactant feed. It was confirmed that SO_2 poisoning on the catalytic activity of Ir/SiO_2 was reversible in the whole temperature range from 300 to 500 °C, suggesting that SO_2 competed active sites of Ir sites with NO or CO. The selectivities of CO toward NO reduction on these catalysts were almost unchanged in spite of coexisting SO_2. On the contrary, NO conversion on Ir/Al_2O_3 was significantly reduced by SO_2, and the catalytic activity of Ir/Al_2O_3 was not recovered to the level observed in the initial run of catalytic activity test after SO_2 was taken away from the reactant feed.

The effect of oxygen concentration on the NO conversion over Ir/silicalite catalyst is shown in Figure 3. NO conversion at 400 °C decreased with increasing O_2 concentration from 1 to 10%. It is noteworthy, however, that NO conversion increased with increasing O_2 concentration at lower temperatures, and 42% NO could selectively be reduced by CO at 365 °C in the presence of 10% O_2 and 150 ppm SO_2.

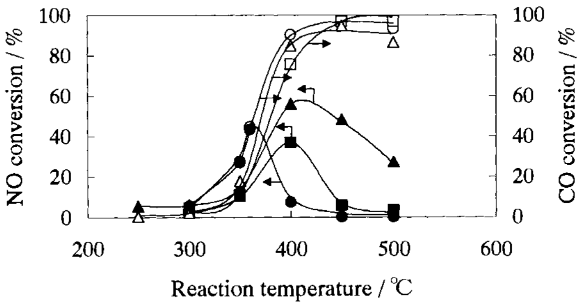

Figure 3. Effect of O_2 concentration on the catalytic activity of Ir/silicalite. NO, 1000 ppm; CO, 7500 ppm; O_2, 1%(▲△), 5%(■□), 10%(●○), SO_2, 150 ppm; total flow rate, 100 cm^3/min. Catalyst weight, 0.1 g. Ir content, 0.02 wt%.

In conclusion, Ir/silicalite was found to catalyze NO reduction with CO selectively in the presence of excess oxygen and SO_2. The promotive effect of support on the catalytic activity of Ir was critically observed in this reaction system, particularly in the presence of SO_2. It is known that Al_2O_3 is amphoteric oxide, and that an acidic gas such as SO_2 is preferably chemisorbed on Al_2O_3. The chemisorbed SO_2 may react with Al_2O_3 to form $Al_2(SO_4)_3$, resulting in the decrease of surface area of Al_2O_3 and the irreversible degradation of catalytic activity for HC-SCR.[11] As the oxides of Si can show an acidic property, no such effect of SO_2 considered for Al_2O_3 support seems possible for these supports. Moreover, silicalite is much more hydrophobic compared with SiO_2 so that hydrothermal stability of silicalite must be higher than amorphous SiO_2, in addition to the resistance against crystalline collapse due to dealumination. Considering the potential superiority of silicalite support, further and deeper investigation on Ir/silicalite catalyst seems to be needed to find a way to develop a new catalyst for practical application to diesel NOx reduction.

Reference and Notes

1 T. J. Truex, R. A. Searles, and D. C. Sun, *Platinum Met. Rev.*, **36**, 2 (1992).
2 M. Iwamoto, H. Yahiro, Y. Yuu, S. Shundo, and N. Mizuno, *Shokubai*, 32, 430 (1990).
3 W. Held, A. König, T. Richter, and L. Puppe, *SAE Trans.*, 900496 (1990).
4 Y. Traa, B. Burger, and J. Weitkamp, *Microporous and Mesoporous Materials*, **30**, 3 (1999).
5 P. Gilot, M. Guyon, and B. R. Stanmore, *Fuel*, **76**, 507 (1997).
6 E. Kikuchi, G. Takegoshi, T. Ishihara, and T. Matsuda, Preprint of 63th Annual Meeting of Chemical Society of Japan, Tokyo, March 1992, Abstr. No. 3C407.
7 P. Zelenka, W. Cartellieri, and P. Herzog, *Appl. Catal.*, **B10**, 3 (1996).
8 S. Nojima, K. Iida, and T. Kobayashi, *Shokubai*, **40**, 372 (1998).
9 S. Nojima, K. Iida, and T. Kobayashi, Japan Patent Kokai Tokkyo Koho (A), 6-296870 (1994).
10 A. Ribotta, M. Lezcano, M. Kurgansky, E. Miro, E. Lombardo, J. Petunchi, C. Moreaux, and J. M. Deeppe, *Catal. Lett.*, **49**, 77 (1997).
11 F. Suganuma, M. Tabata, K. Miyamoto, M. Kasatsuki, T. Yoshinari, H. Ueda, H. Hamada, Y. Kintaichi, M. Sasaki, and T. Ito, *Shokubai*, **35**, 114 (1993).