Enhancement of Activity of Ir Catalysts for the Selective Catalytic Reduction of NO by CO

Tetsuya Nanba,* Satoru Shinohara, Junko Uchisawa, Shouichi Masukawa, Akihiko Ohi, and Akira Obuchi
Institute for Environmental Management Technology,
National Institute of Advanced Industrial Science and Technology (AIST),
16-1 Onogawa, Tsukuba 305-8569

(Received January 16, 2006; CL-060063; E-mail: tty-namba@asit.go.jp)

The activity of Ir catalysts for selective catalytic reduction of nitrogen monoxide by carbon monoxide was drastically enhanced by combining iridium and tungsten oxide on a silica support.

Selective catalytic reduction (SCR) of NO by CO is a promising method for controlling NO_x ($NO + NO_2$) emissions from diesel engines, where catalysts are required to work in a net oxidizing atmosphere. Ogura et al. reported that Ir/silicalite at very low Ir loading exhibits high activity, with and without SO_2.[1] Haneda et al. reported that Ir/SiO_2 shows high activity only in the presence of SO_2.[2] Shimokawabe et al. suggested that Ir/WO_3 and Ir/ZnO show high activities but at a relatively low space velocity and a low oxygen concentration (2%).[3] Higher-performing catalysts should be sought for practical applications. In consideration of regulations requiring future reductions in sulfur concentrations in diesel fuel, we combined WO_3 with SiO_2 as a support material, and the resulting catalyst exhibited high performance as a CO-SCR catalyst in model diesel exhausts, in the absence of SO_2.

The peroxopolytungstic acid solution was prepared by adding 15% hydrogen peroxide to metallic tungsten powder.[4] NH_3 was then added to the solution to adjust the pH to 8.5. A predetermined amount of colloidal silica sol (Catalysis & Chemical Inc. Co., Ltd.; Cataloid S-20L, containing 20 wt % SiO_2) was mixed with the tungsten solution at various WO_3/SiO_2 ratios. The mixture was dried at 383 K and calcined at 773 K for 4 h. The supports thus prepared are designated WO_3–SiO_2(*a*), where (*a*) denotes the weight percent of WO_3 in the support. Typically 0.5 wt % iridium was loaded on each support by an impregnation method using $Ir(NH_3)_6(OH)_3$, $Ir(NH_3)_6(NO_3)_3$, H_2IrCl_6, or $Ir(NO_3)_4$ as a precursor. The impregnated samples were dried and then calcined at 773 K for 4 h in air. Details of the reactor system and analytical equipment used have been described elsewhere.[5] The powdered catalyst (0.1 g) was diluted with granular SiC (0.25–0.6 mm), and a total volume of 0.4 mL of the mixture was packed into a quartz tube reactor (inner diameter, 8 mm). The flow rate of the reactant gas was 225 mL min^{-1}. The reactant gas consisted of 500 ppm NO, 5000 ppm CO, 10% O_2, and 1% H_2O, with He or N_2 as a balance gas. The catalyst was pretreated in a 10% H_2/He flow at 873 K for 1 h. The activity was measured at temperatures ranging from 673 to 473 K in steps of 10 K. The catalysts' BET surface area (Nikkiso, Model 4232), surface morphology, and elemental analysis (Hitachi, FE-SEM; S-4700) were measured.

Figure 1 shows the temperature dependence of the CO-SCR activity of Ir/WO_3–SiO_2(10), Ir/SiO_2, and Ir/WO_3. The maximum NO_x conversions for Ir/SiO_2 and Ir/WO_3 were 11 and 39%, respectively. In contrast, Ir/WO_3–SiO_2 exhibited 86% maximum NO_x conversion and 89% maximum N_2 selectivity ($N_2/(N_2 + N_2O) \times 100$) at 533 K. These results clearly indicate that the combination of WO_3 with SiO_2 drastically enhanced the CO-SCR activity. The decrease in N_2 selectivity above 550 K was probably due to rapid consumption of the reductant CO

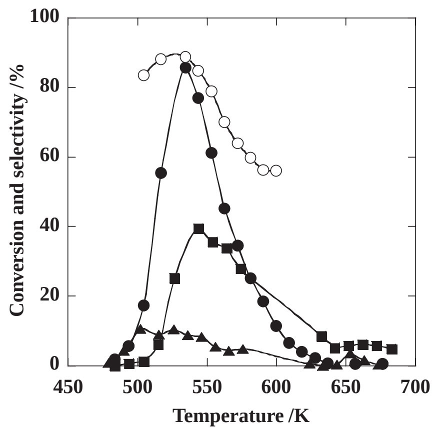

Figure 1. Temperature dependence of CO-SCR activity. Ir precursor, $Ir(NH_3)_6(OH)_3$; weight of catalysts, 0.1 g; feed gas: 500 ppm NO, 5000 ppm CO, 10% O_2, 1% H_2O, balance He; flow rate, 225 mL min^{-1}. Symbols indicate NO_x conversion for 0.5 wt % Ir/WO_3–SiO_2(10) (●), 0.5 wt % Ir/WO_3 (■), and 0.5 wt % Ir/SiO_2 (▲), and N_2 selectivity of 0.5 wt % Ir/WO_3–SiO_2(10) (○).

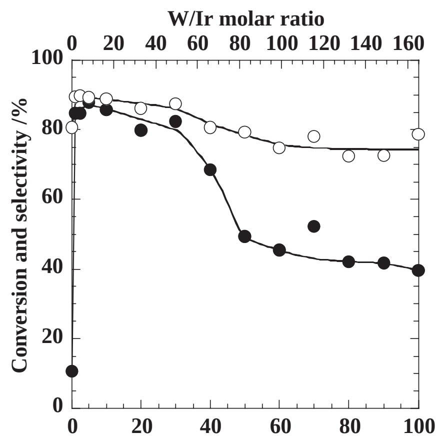

Figure 2. Dependence of CO-SCR activity on WO_3 loading in the support. Ir precursor, $Ir(NH_3)_6(OH)_3$; weight of catalysts, 0.1 g; feed gas: 500 ppm NO, 5000 ppm CO, 10% O_2, 1% H_2O, balance He; flow rate, 225 mL min^{-1}. Symbols indicate NO_x conversion (●) and N_2 selectivity (○).

Table 1. Effect of Ir precursor on CO-SCR activity

Precursor	NO_x conv./%	N_2 selec./%
$Ir(NO_3)_4$	44	84
H_2IrCl_6	43	88
$Ir(NH_3)_6(NO_3)_3$	64	86
$Ir(NH_3)_6(OH)_3$	72	89

Catalyst: 0.5 wt % $Ir/WO_3–SiO_2(10)$. Reaction conditions as in Figures 1 and 2, except that N_2 was used as the balance gas.

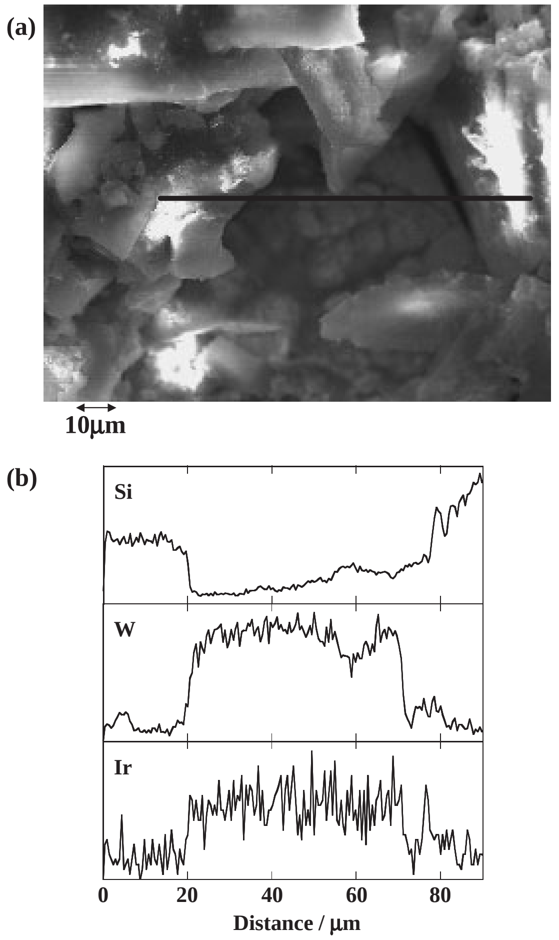

Figure 3. (a) SEM image of 0.5 wt % $Ir/WO_3–SiO_2(10)$ and (b) EDX analysis of the area indicated by the line in (a).

and would increase the rate of partial reduction of NO to N_2O.

Figure 2 shows the effect of WO_3 content in the support on the maximum NO_x conversion and N_2 selectivity. The maximum NO_x conversion and N_2 selectivity were attained between 523 and 553 K. Note that NO_x conversions exceeded 80% when the WO_3 content in the support ranged from 1 to 30%, which corresponds to a W/Ir molar ratio range of 1.7–50. Above 50% WO_3 content, the NO_x conversion was similar to that of Ir/WO_3. N_2 selectivity exhibited the same trend as NO_x conversion. This result suggests that a relatively low WO_3 content was favorable for enhanced CO-SCR activity.

Table 2. BET surface area

Area unit	WO_3 content in support/wt %					
	0	10	30	50	80	100
m^2/g	165	153	107	70	16	6
$m^2/g\text{-}SiO_2$	165	170	153	140	80	—

The choice of the iridium precursor also influenced the CO-SCR activity. Table 1 shows that the maximum NO_x conversion and N_2 selectivity over 0.5 wt % $Ir/WO_3–SiO_2(10)$ prepared with various iridium precursor. $Ir/WO_3–SiO_2(10)$ prepared with $Ir(NH_3)_6(OH)_3$ showed the highest activity.

Figure 3 shows a SEM image of $Ir/WO_3–SiO_2(10)$ prepared with $Ir(NH_3)_6(OH)_3$ as a precursor. WO_3 particles are abundant on the surface in the region near the center of the photograph (Figure 4a, line). EDX analysis of this region (Figure 4b) clearly shows that Ir is present on WO_3 rather than on SiO_2. This result suggests that $Ir/WO_3–SiO_2(10)$ consists mainly of Ir/WO_3 dispersed on SiO_2. Table 2 lists the BET surface areas of $WO_3–SiO_2$ at various composition ratios. Although the surface area per gram of support decreases linearly with increasing WO_3 content, the surface area per gram of SiO_2 decreases only slightly at WO_3 contents lower than 50%. This result suggests that at WO_3 levels up to 50%, WO_3 was finely dispersed over the SiO_2 surface without reduction in the high surface area of the SiO_2.

Because Ir/WO_3 showed high CO-SCR activities, we concluded that the increase in the WO_3 surface area due to dispersion of small particles on SiO_2 enhanced the catalytic activity. Further investigation of the role of Ir and WO_3 in CO-SCR is in progress.

References

1 M. Ogura, A. Kawamura, M. Matsukata, E. Kikuchi, *Chem. Lett.* **2000**, 146.
2 M. Haneda, Pursparatu, Y. Kintaichi, I. Nakamura, M. Sasaki, T. Fujitani, H. Hamada, *J. Catal.* **2005**, *229*, 197.
3 M. Shimokawabe, N. Umeda, *Chem. Lett.* **2004**, *33*, 534.
4 J. Oi, A. Kishimoto, T. Kudo, *J. Solid State Chem.* **1993**, *103*, 176.
5 T. Nanba, K. Sugawara, S. Masukawa, J. Uchisawa, A. Obuchi, *Ind. Eng. Chem. Res.* **2005**, *44*, 3426.
6 R. H. Yoon, T. Salman, G. Donnay, *J. Colloid Interface Sci.* **1979**, *70*, 483.

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