Excellent Promoting Effect of Ba Addition on the Catalytic Activity of Ir/WO_3–SiO_2 for the Selective Reduction of NO with CO

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The catalytic performance of Ba-doped Ir/WO_3–SiO_2 for the selective reduction of NO with CO in an oxidizing atmosphere was investigated. The NO reduction activity and durability of the Ir/WO_3–SiO_2 catalyst were drastically improved by the addition of Ba. Ba played an important role to stabilize the catalytically active Ir–WO_x ($x < 3$) sites of Ir/WO_3–SiO_2 during the reaction.

The selective reduction of NO in an oxidizing atmosphere is one of the most desirable technologies for removing NO_x emitted from diesel engines and lean-burn engines. Currently, the selective reduction of NO using CO as a reductant attracts attention for which Ir catalysts are known to exhibit a high activity. Ogura et al. reported that Ir/silicate gave a high NO conversion in the presence of 1% O_2.[1] Haneda et al. reported that Ir/SiO_2 shows a high activity under oxidizing atmosphere when SO_2 coexists.[2] Simokawabe et al. also showed that the selective reduction proceeds effectively on Ir/WO_3 and Ir/ZnO.[3] Recently, Nanba et al. found that the NO reduction activity of Ir/SiO_2 was drastically enhanced by the addition of W.[4] However, the development of catalysts to show higher activity and durability in a wide temperature range is desired from a practical point of view. Accordingly, we have investigated the activity of various Ir/WO_3-based catalysts for the selective reduction of NO with CO in an oxidizing atmosphere and found that only Ba-doped Ir/WO_3–SiO_2 catalysts show a significantly high activity and durability under wide reaction conditions. In this paper, we report the excellent performance of Ba-doped Ir/WO_3–SiO_2 catalysts with discussions of the roles of Ba additive in the activity.

$(NH_4)_{10}W_{12}O_{41}\cdot 5H_2O$ and citric acid were dissolved in distilled water to which SiO_2 (Fuji Silysia Chemicals, Cariact G-10, 300 $m^2\cdot g^{-1}$) was added. The weight ratio of WO_3:SiO_2 was 1:9. The mixture was dried in air at 110 °C overnight and calcined in air at 500 °C for 4 h to obtain WO_3–SiO_2 support. Ir/WO_3–SiO_2 was prepared by impregnation of the WO_3–SiO_2 support with an aqueous solution of H_2IrCl_6. The impregnated catalyst precursor was dried at 110 °C overnight, followed by calcination at 600 °C for 6 h in air. The loading of Ir metal was fixed at 5 wt %. Then, Ba was doped to Ir/WO_3–SiO_2 using $Ba(NO_3)_2$ solution, followed by drying at 110 °C overnight, and calcined at 600 °C for 6 h in air. The loading of Ba was varied from 1/20 to 1/1 (molar ratio of Ba/Ir). The catalytic activity was measured using a fixed bed flow reactor. Prior to each reaction, the catalyst was pretreated in a flow of 10% H_2/He at 600 °C for 2 h. The reaction gas mixture consisting of 500 ppm NO, 3000 ppm CO, 5% O_2, 6% H_2O, 1 ppm SO_2 and He balance was passed through the catalyst at a gas flow rate of 90 $cm^3\cdot min^{-1}$ (SV = ca. 75,000 h^{-1}). The effluent gas was analyzed by gas chromatography. In order to investigate the durability of catalysts, the activities were measured by repeating the heating sequence from 140 to 600 °C and the cooling sequence from 600 to 140 °C. We also examined the oxidation properties of the catalysts by means of temperature-programmed oxidation (TPO).

Figure 1 shows the NO conversion to $N_2 + N_2O$ and CO conversion to CO_2 over Ba–Ir/WO_3–SiO_2 with different Ba loadings, where the conversions indicate the initial catalytic activities. In the absence of Ba, the NO reduction occurred at temperatures below 450 °C and a maximum NO conversion of 53% was obtained at 280 °C. The NO reduction activity of Ir/WO_3–SiO_2 was drastically promoted by the addition of Ba. The maximum NO conversion over Ba–Ir/WO_3–SiO_2 (Ba/Ir = 1/5) was about 2 times higher (94%) than that of Ir/WO_3–SiO_2. Since the activity for the CO conversion was also increased by the addition of Ba in the range of 240–300 °C, It seems that the enhancement of the NO reduction activity is due to the CO activation as reductant by the addition of Ba.

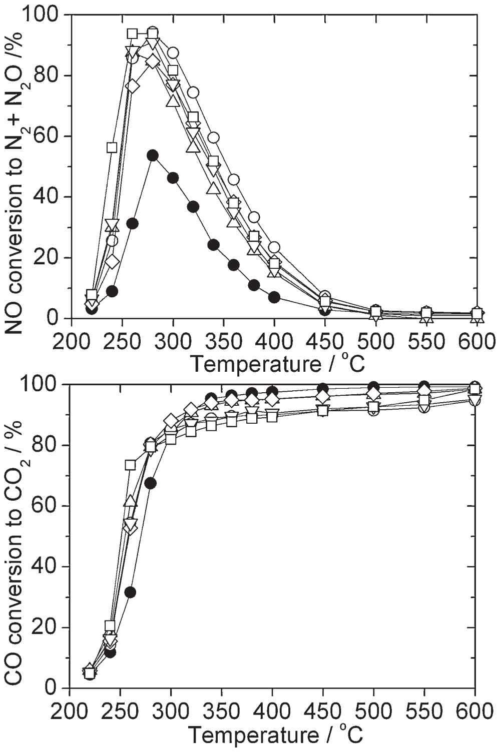

Figure 1. Catalytic activities of Ba–Ir/WO_3–SiO_2. Reaction conditions: 500 ppm NO, 5% O_2, 3000 ppm CO, 6% H_2O, 1 ppm SO_2, Ba/Ir ratio: 0 (●), 1/20 (◇), 1/10 (△), 1/5 (○), 1/3 (▽), and 1/1 (□).

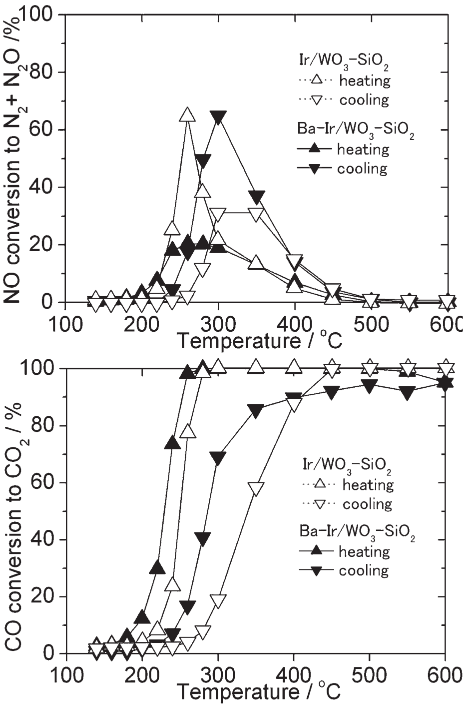

Figure 2. Catalytic activities of Ir/WO_3–SiO_2 (△, ▽) and Ba–Ir/WO_3–SiO_2 (Ba/Ir = 1/10) (▲, ▼) in heating and cooling sequences. Reaction conditions: 500 ppm NO, 5% O_2, 3000 ppm CO, 6% H_2O, 1 ppm SO_2.

The activities, which indicate the steady-state conversions, on Ir/WO_3–SiO_2 and Ba–Ir/WO_3–SiO_2 (Ba/Ir = 1/10) during the heating and cooling sequence were shown in Figure 2. On Ir/WO_3–SiO_2, the maximum NO conversion reached 65% at 260 °C in the heating sequence. However, the maximum NO conversion was decreased to 30% in the cooling sequence, which was 1/2 of that in the heating sequence. In addition, the temperature giving the maximum NO conversion shifted from 260 to 350 °C. After the heating and cooling sequences were repeated several times, the maximum NO conversion significantly decreased to 10% (not shown). For the CO conversion, the active temperature in the cooling sequence was 50–150 °C higher than that in the heating sequence. After repeating both sequences several times, the active temperature range became higher, indicating that the CO oxidation activity decreased monotonously during the reaction. CO oxidation reaction is well known to proceed mainly on metal surface,[5] indicating that the decrease in the CO oxidation activity of Ir/WO_3–SiO_2 is caused by oxidation of Ir metal during the reaction. Thus, we consider that the deactivation of NO reduction on the Ir/WO_3–SiO_2 catalyst is due to the oxidation of Ir metal during the reaction. On the other hand, the maximum NO conversion on Ba–Ir/WO_3–SiO_2 in the heating sequence was 20% at 260 °C, which was lower than that on Ir/WO_3–SiO_2 (65% at 260 °C). However, the NO conversion in the cooling sequence became higher in the wide range of reaction temperatures. After repeating both sequences several times, no change in the NO reduction activity was observed and the maximum conversion was kept constant at about 60%. For the CO conversion, the active temperature range in the cooling sequence was shifted to higher temperature than that in the heating sequence. However, the CO oxidation activity of Ba–Ir/WO_3–SiO_2 was higher than that of Ir/WO_3–SiO_2, considering that the oxidation of Ir metal during the reaction was suppressed by Ba.

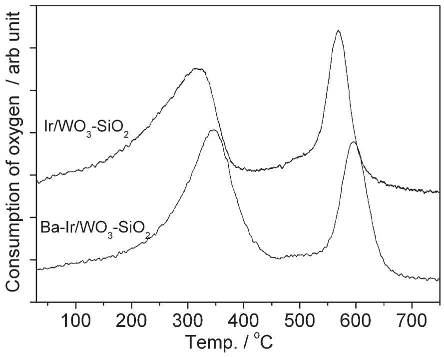

Figure 3. TPO profiles of Ir/WO_3–SiO_2 and Ba–Ir/WO_3–SiO_2 (Ba/Ir = 1/10). Pretreatment: 600 °C, H_2 (10%)/He, Operating conditions: O_2 (5%)/He, 10 °C/min. Sample weight, 0.1 g.

To get information on the oxidation property of Ir/WO_3–SiO_2 and Ba–Ir/WO_3–SiO_2, we carried out TPO measurements for the reduced catalysts (Figure 3). The O_2 consumption peaks appeared at 300 and 570 °C for Ir/WO_3–SiO_2 were due to the oxidation of W and Ir, respectively.[6–8] The temperatures for the oxygen consumption of both W and Ir shifted 50 °C higher by the addition of Ba, clearly indicating that Ir and W in Ba–Ir/WO_3–SiO_2 are difficult to be oxidized than those in Ir/WO_3–SiO_2.

The promotional effect of W on the catalytic activity of Pt/SiO_2 for NO + CO reaction was reported by Regalbuto et al.[9] They suggested that the Pt–WO_x adliniation sites, which are located on Pt particles decorated by partially reduced tungsten oxides, have a high NO dissociation activity. Nanba et al.[4] suspected that it is necessary to oxidize the reduced Ir/WO_3–SiO_2 catalyst in order to obtain a high NO reduction activity, considering that Ir–WO_x-like ($x < 3$) sites are formed by the reduction–oxidation treatment, which act as active site for NO reduction.

The result of TPO measurement showed that Ba suppressed the oxidation of not only Ir but also W, suggesting that the partially reduced WO_x was prevent from deep-oxidation in the presence of Ba during the reaction. We thought that Ba plays an important role in stabilizing the active sites, Ir–WO_x species, during the reaction. Now, we are investigating the role of Ba and the active sites of the Ir/WO_3-based catalysts in further detail.

References

1 M. Ogura, A. Kawamura, M. Matsukata, E. Kikuchi, *Chem. Lett.* **2000**, *29*, 146.
2 M. Haneda, Pusparatu, 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 S. Shinohara, T. Nanba, J. Uchisawa, A. Ohi, A. Obuchi, 96th CATSJ Meeting, Kumamoto, Japan, September **2005**, Abstr., No. 3G16.
5 *Concepts of Modern Catalysis and Kinetics*, ed. by I. Chorkendorff, J. W. Niemantsverdriet, WILEY-VCH, Weinheim, **2003**.
6 A. Warren, A. Nylund, I. Olefjord, *Int. J. Refract. Met. Hard Mater.* **1996**, *14*, 345.
7 B. J. Kip, J. Van Grondelle, J. H. A. Martens, R. Prins, *Appl. Catal.* **1986**, *26*, 353.
8 A. Takahashi, T. Fujitani, I. Nakamura, Y. Katsuta, M. Haneda, H. Hamada, in preparation.
9 J. R. Regalbuto, E. E. Wolf, *J. Catal.* **1988**, *109*, 12.