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Enhancing Effect of H_2 on the Selective Reduction of NO with CO over Ba-doped $Ir/WO_3/SiO_2$ Catalyst

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Abstract In order to improve the catalytic performance of supported-Ir catalysts for the selective reduction of NO with CO, the effect of H_2 was investigated. While adding H_2 showed no or negative effect on NO conversion on Ir/SiO_2, $Ba/Ir/SiO_2$ and $Ir/WO_3/SiO_2$ catalysts, the activity of Ba-doped $Ir/WO_3/SiO_2$ catalyst for NO reduction was significantly increased by H_2 addition. The role of H_2 was found to stabilize the catalytically active Ir-WO_x sites during the reaction.

Keywords Selective reduction · Carbon monoxide · Hydrogen · Ba-doped $Ir/WO_3/SiO_2$

1 Introduction

The selective reduction of NO in oxidizing atmospheres has recently received extensive attention, since it has potential as a practical strategy for removing NO_x emitted from diesel engines, lean-burn engines and combustors. In addition to hydrocarbons [1–3], hydrogen and CO have been proved to act as effective reductant for NO reduction under lean conditions. Among a number of catalysts reported so far, supported-Ir catalysts showed specific activity for the selective reduction of NO with not only hydrocarbons [4–6] but also hydrogen and CO [7–10].

We have discovered that Ir/SiO_2 is active for NO reduction with CO in the presence of both O_2 and SO_2 [8, 11, 12]. The most interesting feature of this reaction is that the presence of SO_2, which normally poisons catalytic reactions, promotes NO reduction in the presence of O_2. In other words, the coexistence of O_2 and SO_2 is essential for NO reduction to occur. Recently, Nanba et al. [13] reported that the addition of W into Ir/SiO_2 drastically enhances NO reduction activity even in the absence of SO_2. We also found that the catalytic performance of Ir/SiO_2 and $Ir/WO_3/SiO_2$ is effectively improved by addition of Ba [14, 15]. However, the activity of these catalysts at lower temperatures is insufficient from a practical point of view, focusing on the after treatment of diesel NO_x emission.

Hydrogen, on the other hand, is a promising reductant to reduce NO efficiently in the presence of O_2 at relatively low temperatures [16–18]. Such a characteristic of hydrogen would lead us to the expectation that the use of H_2 + CO mixture brings the low-temperature NO reduction activity. In the present paper, we want to report the promoting effect of hydrogen on the activity of Ba-doped $Ir/WO_3/SiO_2$ catalyst for the selective reduction of NO with CO at lower temperatures.

2 Experimental

$(NH_4)_{10}W_{12}O_{41} \cdot 5H_2O$ and citric acid was dissolved in distilled water to which SiO_2 (Fuji Silysia Chemicals, Cariact G-10, 300 m^2g^{-1}) was added. The solvent was evaporated at 90 °C, and the resulting mixture was dried at 110 °C overnight and calcined at 500 °C for 5 h in flowing

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air to obtain WO_3/SiO_2 powder. The loading of WO_3 was fixed at 10 wt%. SiO_2 and WO_3/SiO_2 thus obtained were used as the support for iridium.

Ir/SiO_2 and $Ir/WO_3/SiO_2$ were prepared by impregnation method using an aqueous solution of $H_2IrCl_6 \cdot 6H_2O$, followed by drying at 110 °C overnight and calcination at 600 °C for 6 h in air. The loading of Ir metal was fixed at 5 wt% in this study. Then, Ba was doped to Ir/SiO_2 and $Ir/WO_3/SiO_2$ using $Ba(NO_3)_2$ solution, followed by drying at 110 °C overnight and calcination at 600 °C for 6 h in air. The loading of Ba was varied from 1/20 to 2/1 (molar ratio of Ba/Ir) for $Ba/Ir/WO_3/SiO_2$, while the molar Ba/Ir ratio was fixed at 1/10 for $Ba/Ir/SiO_2$ [14].

Catalytic activity was evaluated using a fixed-bed continuous flow reactor. The standard reaction gas, containing 500 ppm NO, 5,000 ppm reductant (CO, H_2 or CO + H_2 with the ratio of unity), 5% O_2, 6% H_2O and 1 ppm SO_2 diluted in He, was fed through a catalyst (0.04 g), pretreated in situ in a flow of 10% H_2/He at 600 °C for 2 h, at a rate of 90 cm^3 min^{-1}. In some experiments, the concentration of each component gas was changed. The effluent gas was analyzed with the use of two on-line gas chromatographs equipped with a Molecular Sieve 5A column (for the analysis of N_2 and CO) and a Porapak Q column (for analysis of CO_2 and N_2O). The reaction temperature was decreased from 600 to 200 °C in steps of 20–50 °C, and the steady-state catalytic activity was measured at each temperature. In some cases, the activity was measured while the temperature was raised from 150 to 600 °C in steps of 20–50 °C.

X-ray diffraction measurements (Mac Science M18 XHF^{22}) were performed to get information on the crystal structure of the catalyst samples by using CuKα radiation at 40 kV and 150 mA. The scanning was done from 2θ = 20–60° at a speed of 5 deg min^{-1}. Diffuse reflectance FT-IR spectra of adsorbed CO, as a probe molecule, were taken with a Nicolet Nexus 670 FT-IR spectrometer at a resolution of 4 cm^{-1}.

3 Results and Discussion

3.1 Comparison of the activity for NO reduction with CO, H_2 and CO + H_2

Figure 1 shows the activity of the four supported-Ir catalysts for the selective catalytic reduction of NO with CO (CO-SCR), H_2 (H_2-SCR) or CO + H_2 ((CO + H_2)-SCR) in the presence of O_2 and SO_2. As given in Fig. 1A and B, the use of CO + H_2 mixture reductant caused a significant decrease in the activity of Ir/SiO_2 and $Ir/WO_3/SiO_2$ compared with CO-SCR. This indicates that H_2 inhibits NO reduction. On the other hand, the activity of $Ba/Ir/SiO_2$ (Ba/Ir = 1/10) for CO-SCR reaction was clearly enhanced by addition of H_2 in the temperature range below 250 °C (Fig. 1C). However, no difference in the NO conversion was observed between H_2-SCR and (CO + H_2)-SCR. In case of $Ba/Ir/WO_3/SiO_2$ with a molar Ba/Ir ratio of 3/2, as given in Fig. 1D, the activity for (CO + H_2)-SCR was very high in the temperature range below 280 °C, compared with that for CO-SCR and H_2-SCR. This clearly indicates that the presence of both H_2 and CO is necessary to reduce effectively NO at lower temperatures. Since the

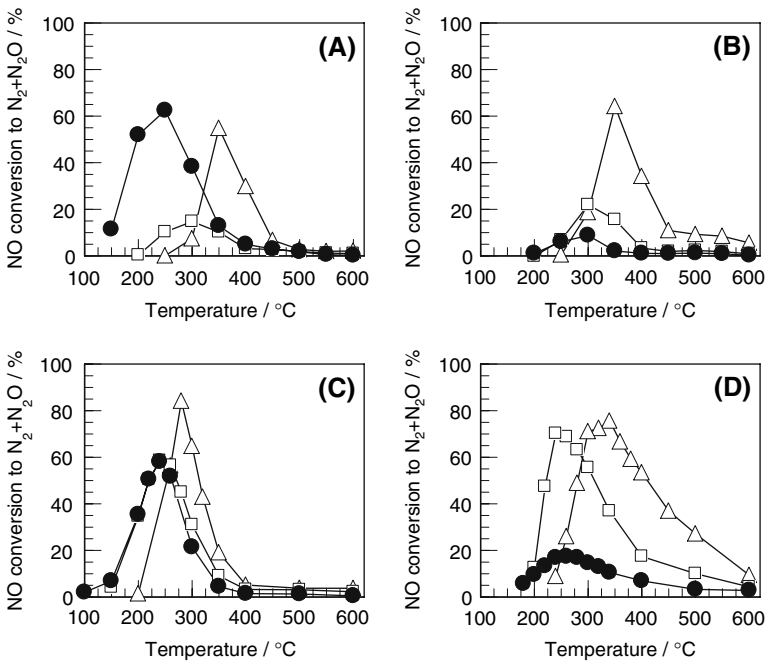

Fig. 1 Activity of (**A**) Ir/SiO_2, (**B**) $Ir/WO_3/SiO_2$, (**C**) $Ba/Ir/SiO_2$ (Ba/Ir = 1/10) and (**D**) $Ba/Ir/WO_3/SiO_2$ (Ba/Ir = 3/2) for the selective reduction of NO with CO, H_2, or CO + H_2 in the presence of O_2 and SO_2. Reaction conditions; 500 ppm NO, 5% O_2, 5,000 ppm reductant (5,000 ppm CO, 5,000 ppm H_2 or 2,500 ppm CO + 2,500 ppm H_2), 6% H_2O, 1 ppm SO_2, W/F = 0.0267 gscm^{-3}. (Δ) CO-SCR, (●) H_2-SCR, (□) (CO + H_2)-SCR

NO conversion for H_2-SCR was less than 20%, H_2 does not act as reductant but contributes as a promoter for CO-SCR reaction. Since Ba/Ir/WO_3/SiO_2 was the only catalyst showing the promotional effect of H_2, the rest of this paper deals mainly with Ba/Ir/WO_3/SiO_2.

3.2 Catalytic Performance of Ba/Ir/WO_3/SiO_2 for NO Reduction with CO + H_2

3.2.1 Effect of Ba Loading

Figure 2 shows the effect of Ba loading on the catalytic activity of Ba/Ir/WO_3/SiO_2 for NO reduction with CO + H_2. It is apparent that the activity of Ba/Ir/WO_3/SiO_2 at the temperatures around 220–300 °C was significantly high when the Ba loading was increased up to Ba/Ir = 3/2. However, an excess of Ba additive (Ba/Ir = 2/1) decreased NO conversion. Thus, the most effective molar ratio was found to be Ba/Ir = 3/2. CO conversion also increased by Ba addition up to 3/2 but decreased by excess addition.

3.2.2 Effect of O_2 Concentration

Since the selective reduction of NO with CO or H_2 is very sensitive to the presence of O_2 [12, 18], the effect of O_2 concentration on the catalytic activity was examined by changing O_2 concentration from 0 to 10%. Figure 3 shows the activity of Ba/Ir/WO_3/SiO_2 (Ba/Ir = 3/2) for NO reduction with CO or CO + H_2 in the presence of various concentration of O_2. In the absence of O_2, the activity for (CO + H_2)-SCR was very low at the temperatures below 500 °C (Fig. 3B). We have recently reported that the disproportionation of SO_2 to atomic sulfur and SO_3 takes place on the surface of iridium [19]. If O_2 is absent in the reaction gas, the atomic sulfur thus formed is accumulated on the surface of iridium and poisons the active sites. The low activity in the absence of O_2 observed here is probably due to the formation and accumulation of atomic sulfur. The formation of atomic sulfur would be promoted by presence of H_2 via the reduction of SO_2, because the activity for CO-SCR was higher than that for (CO + H_2)-SCR.

When 1% O_2 was introduced into the reaction gas, NO conversion was significantly increased. In accordance with previous results [8, 11, 12], O_2 is necessary for NO reduction to occur. It is apparent that coexistence of CO and H_2 widened the active temperature window to lower temperature region. The promoting effect of H_2 is noticed particularly at higher O_2 concentrations, especially 10%, although increased O_2 concentration caused a decrease of NO conversion. Maximum NO conversion for (CO + H_2)-SCR was still as high as 40% at 260 °C, while that for CO-SCR less than 5%.

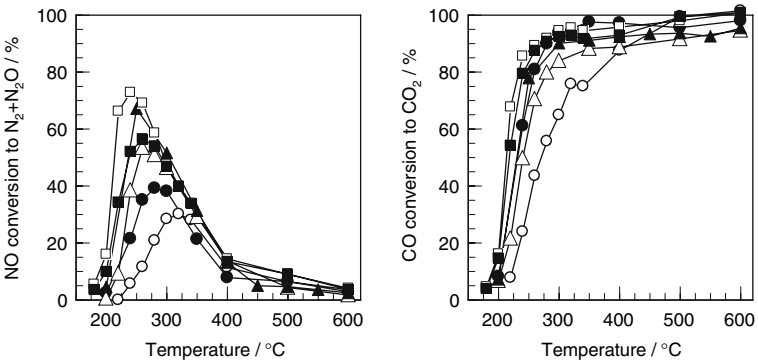

Fig. 2 Effect of Ba loading on the activity of Ba/Ir/WO_3/SiO_2 for NO reduction by CO + H_2 in the presence of O_2 and SO_2. Reaction conditions; 500 ppm NO, 5% O_2, 2,500 ppm CO + 2,500 ppm H_2, 6% H_2O, 1 ppm SO_2, W/F = 0.0267 gscm^{-3}. (◯) Ba/Ir = 0 (Ir/WO_3/SiO_2), (●) Ba/Ir = 1/20, (Δ) Ba/Ir = 1/5, (▲) Ba/Ir = 1/1, (□) Ba/Ir = 3/2, (◯) Ba/Ir = 2/1

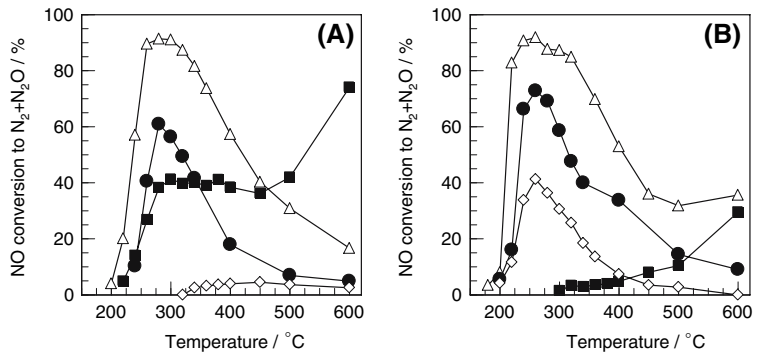

Fig. 3 Effect of O_2 concentration on the activity of Ba/Ir/WO_3/SiO_2 (Ba/Ir = 3/2) for (**A**) CO-SCR and (**B**) (CO + H_2)-SCR. Reaction conditions: 500 ppm NO, 0–10% O_2, 2,500 ppm CO or 2,500 ppm CO + 2,500 ppm H_2, 6% H_2O, 1 ppm SO_2, W/F = 0.0267 gscm^{-3}. (■) O_2 = 0%, (Δ) O_2 = 1%, (●) O_2 = 5%, (◇) O_2 = 10%

3.2.3 Effect of H_2 Concentration

The effect of H_2 concentration was examined. Figure 4 shows the change in the activity of $Ba/Ir/WO_3/SiO_2$ (Ba/Ir = 3/2) when H_2 concentration was varied from 500 ppm to 1% with maintaining CO concentration at 2,500 ppm. It is apparent that NO reduction at lower temperatures around 260–280 °C was significantly promoted by addition of 1,000 ppm H_2. Further increase in H_2 concentration caused an increase in the maximum NO conversion and a shift of effective temperature window to low temperature region. It is of interest that the temperature window was widened to not only low temperature but also high temperature in the presence of 1% H_2. As can be seen in Fig. 4, CO conversion was also increased with increasing H_2 concentration. Iridium is supposed to be more effectively reduced as H_2 concentration is increased, because metallic iridium is highly active for CO oxidation. The role of adding hydrogen will be discussed in the next section.

3.3 Role of Adding Hydrogen

3.3.1 Response of Activity to H_2 Addition

The response of NO and CO conversion over $Ba/Ir/WO_3/SiO_2$ (Ba/Ir = 3/2) to an intermittent feed of 2,500 ppm H_2 was examined at 240 °C to get information on the role of adding H_2. Here, NO reduction with CO + H_2 was started from 600 to 240 °C, and then the removal and introduction of H_2 was carried out at 240 °C. The results are given in Fig. 5.

During the reaction in the presence of CO and H_2 at 240 °C, almost stable activity was obtained. When H_2 was removed from the reaction gas, no significant decrease in NO conversion was observed, while CO conversion was clearly decreased from 80 to 65%. It should be noted that the NO conversion level was quite high as compared with that obtained in CO-SCR reaction (Fig. 1D). The subsequent introduction of H_2 caused a slight increase in NO conversion to the initial value. CO conversion was also

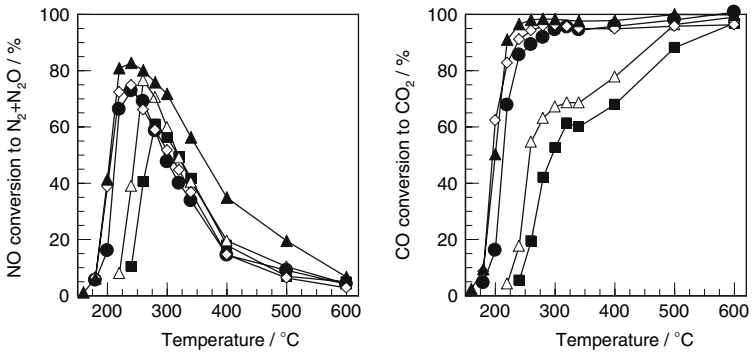

Fig. 4 Effect of H_2 concentration on the activity of $Ba/Ir/WO_3/SiO_2$ (Ba/Ir = 3/2) for NO reduction with CO + H_2 in the presence of O_2 and SO_2. Reaction conditions; 500 ppm NO, 5% O_2, 2500 ppm CO, 0–10,000 ppm H_2, 6% H_2O, 1 ppm SO_2, W/F = 0.0267 $gscm^{-3}$. (■) H_2 = 0 ppm, (Δ) H_2 = 1,000 ppm, (●) H_2 = 2,500 ppm, (◇) H_2 = 5,000 ppm, (▲) H_2 = 10,000 ppm

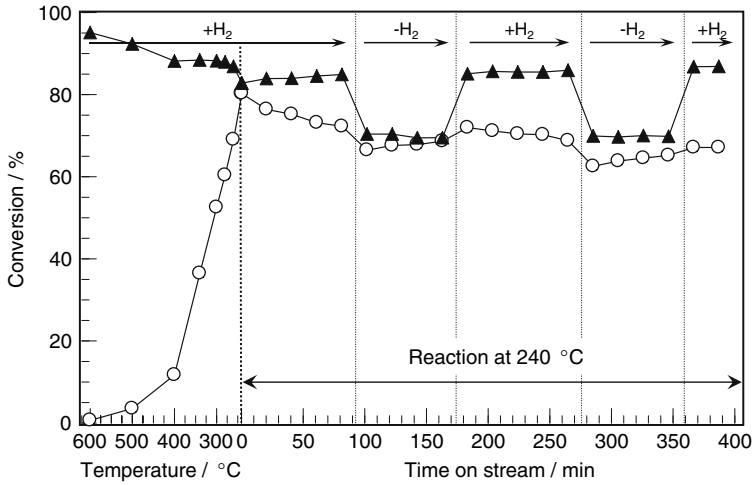

Fig. 5 Response of NO conversion to N_2 + N_2O (◯) and CO conversion to CO_2 (▲) to intermittent feed of 2,500 ppm H_2 over $Ba/Ir/WO_3/SiO_2$ (Ba/Ir = 3/2) at 240 °C. Reaction conditions; 500 ppm NO, 5% O_2, 2,500 ppm CO, 0 or 2,500 ppm H_2, 6% H_2O, 1 ppm SO_2, W/F = 0.0267 $gscm^{-3}$

completely recovered to the initial value. These results suggest that H_2 doe not directly participate in the reaction as reductant. Adding H_2 would possibly contribute to stabilize the catalytically active sites during the reaction.

In order to confirm this idea, the activity of $Ba/Ir/WO_3/SiO_2$ (Ba/Ir = 3/2) for CO-SCR was measured from 150 °C, where the catalyst was first reduced with 10% H_2/He at 600 °C and then cooled to 150 °C in flowing He. Figure 6 compares the results of CO-SCR measured under the conditions of decreasing and increasing reaction temperature and (CO + H_2)-SCR. Obviously, the NO conversion for CO-SCR under the latter condition (indicated as a symbol of Δ) is higher at lower temperature than that for CO-SCR under the former condition (as a symbol of ▲). In addition, the active temperature window for CO-SCR measured at increasing reaction temperature is well consistent with that for (CO + H_2)-SCR (as a symbol of ●), although the maximum NO conversion was slightly higher for the latter one. No great difference in CO conversion was also observed for CO-SCR measured at increasing reaction temperature and (CO + H_2)-SCR. These results suggest that the role of adding H_2 is to keep the catalytically active reduced species during the reaction as described above.

3.3.2 *Structure of Iridium after Use in the Reaction*

The crystal structure of the catalysts after use in the CO-SCR and (CO + H_2)-SCR was then measured. As shown in Fig. 7A, XRD peaks due to Ir metal as well as those due to $BaWO_4$ were observed for fresh $Ba/Ir/WO_3/SiO_2$ (Ba/Ir = 3/2) before use in the reaction. After use in the reaction, the intensity of XRD peak due to Ir metal significantly decreased, and distinct ones to IrO_2 were observed, indicating that Ir metal is oxidized to IrO_2 during the reaction. Since no clear difference in the crystal structure was observed for the catalysts after use in the CO-SCR and (CO + H_2)-SCR, adding H_2 does not affect the bulk structure of the catalyst.

Because catalytic reactions take place on catalyst surface, the oxidation state of iridium surface of $Ba/Ir/WO_3/SiO_2$ (Ba/Ir = 3/2) was investigated by FT-IR with CO as a probe molecule. The catalyst was first reduced at 600 °C, and then the temperature was decreased from 600 to 240 °C in 5 h after changing the gas flow to the reaction gas with the same composition as employed for CO-SCR and (CO + H_2)-SCR. Figure 8 shows FT-IR spectra for CO species adsorbed on $Ba/Ir/WO_3/SiO_2$ (Ba/Ir = 3/2) recorded in flowing 0.3% CO/He gas at 240 °C. No difference in the characteristic of IR band, which appeared at around 2060 cm^{-1} assignable to CO linearly bonded to Ir^0 sites [20], was observed for all the samples. However, the band intensity is quite different depending on the history of catalyst samples. Apparently, more intense peak was observed for the sample after use in the (CO + H_2)-SCR (Fig. 8C) than that in the CO-SCR (Fig. 8B). This suggests that the surface of iridium is stabilized in the reduced state during the (CO + H_2)-SCR reaction.

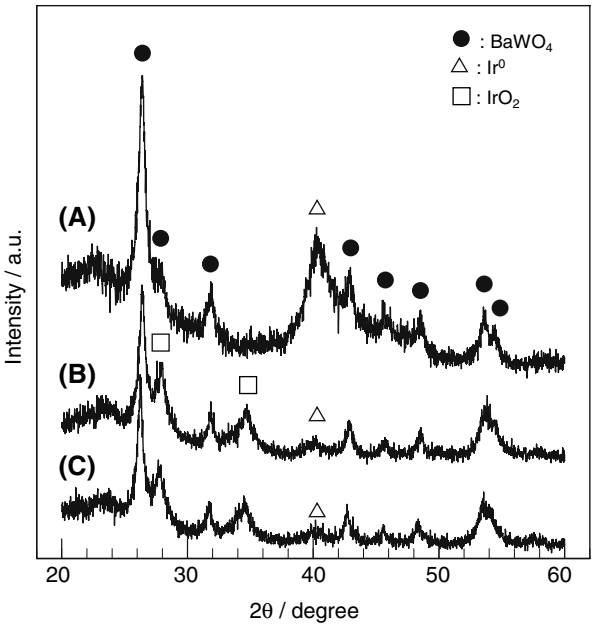

Fig. 7 XRD patterns of $Ba/Ir/WO_3/SiO_2$ (Ba/Ir = 3/2): (**A**) after the reduction at 600 °C (before use in the reaction), (**B**) after use in the CO-SCR and (**C**) (CO + H_2)-SCR

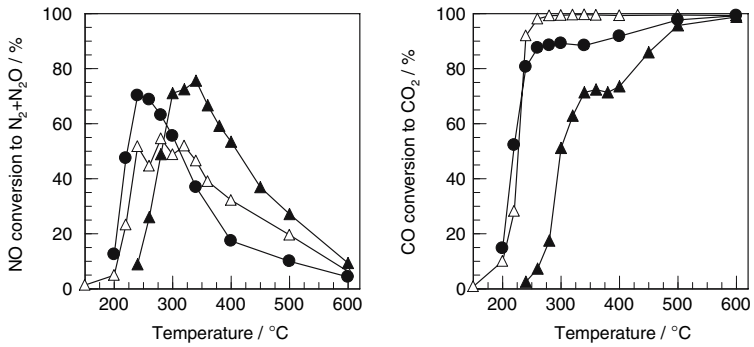

Fig. 6 Comparison of the activity for CO-SCR measured under the conditions of decreasing (▲) and increasing reaction temperature (Δ) and (CO + H_2)-SCR (●) over $Ba/Ir/WO_3/SiO_2$ (Ba/Ir = 3/2). Reaction conditions; 500 ppm NO, 5% O_2, 2,500 ppm CO or 2,500 ppm CO + 2,500 ppm H_2, 6% H_2O, 1 ppm SO_2, W/F = 0.0267 $gscm^{-3}$

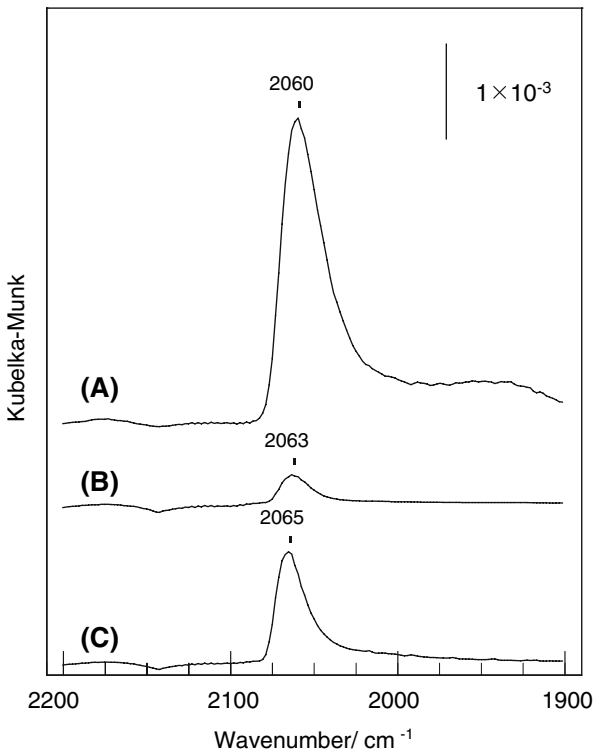

Fig. 8 FT-IR spectra of CO adsorbed on $Ba/Ir/WO_3/SiO_2$ (Ba/Ir = 3/2): (**A**) after the reduction at 600 °C (before use in the reaction), (**B**) after use in the CO-SCR and (**C**) (CO + H_2)-SCR. FT-IR spectra were recorded after the exposure of 0.3% CO/He at 240 °C for 30 min

3.3.3 Catalytically Active Sites

Recently, we found that the active site for CO-SCR over $Ir/WO_3/SiO_2$ catalyst is Ir metal interacted strongly with W oxide, which was denoted as Ir-WO_x (x = 2.92–3) [21]. We also proposed the reaction mechanism in which the selective reduction of NO with CO over this catalyst proceeds via NO dissociation and removal of oxygen thus formed by CO. The Ir-WO_x sites promote the dissociation of NO. The selective reduction of NO with CO over $Ba/Ir/WO_3/SiO_2$ would also take place according to the same mechanism. The results of FT-IR measurements following CO adsorption (Fig. 8) lead us to the conclusion that adding H_2 stabilizes the catalytically active Ir-WO_x sites in more active reduced state during the reaction, and then the NO dissociation as the first step in this reaction is promoted, resulting in an increase in NO and CO conversion (see in Fig. 4).

4 Conclusions

(1) The catalytic performance of $Ba/WO_3/Ir/SiO_2$ for CO-SCR was promoted by the addition of H_2, while either no or negative effect of H_2 was observed for Ir/SiO_2, $Ir/WO_3/SiO_2$ and $Ba/Ir/SiO_2$ catalysts.
(2) The promoting effect of H_2 on the activity of $Ba/WO_3/Ir/SiO_2$ for CO-SCR was especially remarkable at higher O_2 concentrations.
(3) The role of adding H_2 is suggested to keep the catalytically active Ir-WO_x sites in more active state during the reaction.

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