Promoting Effect of Coexisting H_2O on the Activity of $Ir/WO_3/SiO_2$ Catalyst for the Selective Reduction of NO with CO

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The catalytic activity of $Ir/WO_3/SiO_2$ for the selective reduction of NO with CO (CO-SCR) in the presence of excess O_2 was significantly increased by the presence of coexisting H_2O, whereas NO reduction hardly occurred in the absence of H_2O. Coexisting H_2O plays an important role preventing catalyst deactivation caused by oxidation of the catalytically active Ir sites at high temperatures.

The selective reduction of NO in oxidizing atmosphere currently attracts great interest both in applied and fundamental research. Recently, we reported that CO acts as an effective reductant for NO reduction over Ir/SiO_2 catalyst in the presence of O_2 and SO_2.[1] The most outstanding feature of this catalytic reaction is that the coexistence of O_2 and SO_2 is essential for NO reduction to occur. By combining surface science techniques using single-crystal model catalyst and real catalyst,[2] it was found that the coexisting SO_2 stabilizes the catalytically active reduced Ir site.

In addition to SO_2, H_2O is another important coexisting constituent in diesel exhaust. The influence of H_2O on the selective reduction of NO with hydrocarbons (HC-SCR) has been extensively studied, and activity enhancement by H_2O has been reported.[3–5] In this case, the role of H_2O is considered to remove carbonaceous materials deposited on the catalyst surface and/or to improve the reaction selectivity by suppression of undesirable hydrocarbon oxidation. Therefore, it is of interest to study how coexisting H_2O influences the catalytic activity for the CO-SCR reaction from not only fundamental but also practical points of view. In the present work, we have investigated in detail the effect of coexisting H_2O on the catalytic activity of $Ir/WO_3/SiO_2$, which, as we already found, shows high activity for CO-SCR.[6]

$Ir/WO_3/SiO_2$ was prepared by consecutive impregnation method. $(NH_4)_{10}W_{12}O_{41}\cdot 5H_2O$ and citric acid were dissolved in distilled water, to which commercial SiO_2 (Fuji Silysia Chemicals, Cariact G-10) was added. The mixture was dried in air at 110 °C overnight and calcined in flowing air at 500 °C for 5 h. The resulting WO_3/SiO_2 powder was then impregnated with a solution of $Ir(NO_3)_3$ (Ishifuku Metal Industry Co., Ltd.), followed by drying at 110 °C overnight and calcination at 600 °C for 6 h in air. The loading of Ir and WO_3 was fixed at 0.5 and 10 wt %, respectively. The catalytic activity test was carried out using a flow reactor system by passing a reaction gas mixture containing NO (500 ppm), CO (3000 ppm), O_2 (5%), SO_2 (1 ppm), and H_2O (0–10%) diluted in He at a rate of 90 $cm^3\,min^{-1}$ over 0.04 g of catalyst, which had been pretreated in situ in a flow of He at 600 °C for 2 h. The effluent gas was analyzed by gas chromatography. The reaction temperature was changed from 600 to 200 °C in steps of 20–50 °C, and the steady-state activity was measured at each temperature. N_2 was mainly formed as the NO reduction products. The selectivity to N_2 ($N_2/(N_2 + N_2O)$) was more than 90% in most cases. Temperature-programmed reduction (TPR) measurements were performed to investigate the reducibility of the catalysts.

Figure 1 shows the activity of $Ir/WO_3/SiO_2$ for CO-SCR when H_2O concentration was varied from 0 to 10%. When H_2O was not present in the reaction gas, NO reduction hardly occurred in the entire temperature range, and CO conversion to CO_2 was low. On the other hand, the presence of 0.75% H_2O caused a significant increase in NO conversion as well as CO conversion. It was also found that the catalytic activity of $Ir/WO_3/SiO_2$ increased with increasing H_2O concentration up to 6%. This indicates that coexisting H_2O plays an important role for the catalytic activity.

The response of NO conversion to the intermittent feed of H_2O was examined at 300 °C. As shown in Figure 2, when H_2O was removed from the reaction gas, NO conversion slightly decreased with time but did not reach the value given in Figure 1 (4%). The subsequent introduction of H_2O did not recover the NO conversion to the initial level. This result suggests that

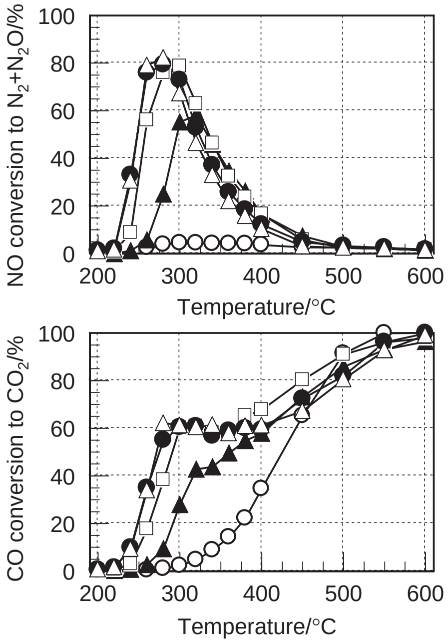

Figure 1. Effect of H_2O concentration on the activity of $Ir/WO_3/SiO_2$ for NO reduction with CO. Conditions: 500 ppm NO, 5% O_2, 3000 ppm CO, 1 ppm SO_2, 0–10% H_2O, $W/F = 0.027\,g\,s\,cm^{-3}$. (○) 0% H_2O, (▲) 0.75% H_2O, (□) 1.5% H_2O, (●) 6% H_2O, (△) 10% H_2O.

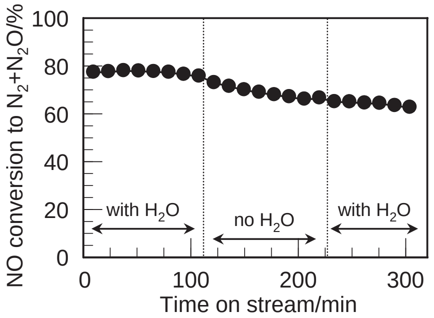

Figure 2. Response of NO conversion to $N_2 + N_2O$ over $Ir/WO_3/SiO_2$ to the intermittent feed of H_2O at 300 °C. Conditions: 500 ppm NO, 5% O_2, 3000 ppm CO, 1 ppm SO_2, 0 or 6% H_2O, $W/F = 0.027\,g\,s\,cm^{-3}$.

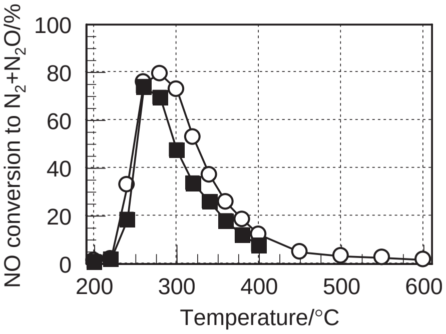

Figure 3. Comparison of NO conversion measured in the presence of H_2O from 600 °C (○) and in the absence of H_2O from 400 °C (■). Conditions are the same as for Figure 2.

H_2O does not directly participate in the reaction as a reactant. In order to get information on the role of H_2O, the NO reduction activity in the absence of H_2O was measured from 400 °C after pretreatment in He at 600 °C. As shown in Figure 3, in this case, the NO conversions were very similar to those in the presence of H_2O. We recently reported that the active sites of $Ir/WO_3/SiO_2$ for NO reduction with CO are Ir–WO_x ($x = 2.92$–3) species in which Ir metal interacts strongly with tungsten oxide.[6] This means that the presence of reduced Ir sites is necessary for the NO reduction activity. On the other hand, reduced Ir is oxidized in the presence of O_2 at temperatures above 500 °C.[7] Therefore, coexisting H_2O can be considered to prevent catalyst deactivation caused by oxidation of the catalytically active Ir sites at the temperatures above 400 °C.

In order to confirm this idea, the oxidation state of Ir in $Ir/WO_3/SiO_2$ was examined by TPR, the results of which are shown in Figure 4. Ir/SiO_2 and WO_3/SiO_2 as the reference samples, which were oxidized in flowing 20% O_2/N_2 at 600 °C before measurement, gave a peak at 236 °C and above 450 °C, respectively. These peaks are due to the reduction of IrO_2 and WO_3. In the TPR profile of $Ir/WO_3/SiO_2$ oxidized at 600 °C (profile-c), broad H_2 consumption peaks were detected at 379 and 444 °C in addition to these two peaks. These peaks would be ascribed to the reduction of oxygen present at the Ir–WO_3 interface, because no such peaks were observed for Ir/SiO_2 and WO_3/SiO_2. It is apparent that a significant decrease in the area of the low-temperature peak and a shift of the middle-temperature peaks to lower temperature (329 and 386 °C) were observed for $Ir/WO_3/SiO_2$ treated with He (profile-d). This suggests the slight reduction of Ir sites and the creation of strong interaction between Ir and WO_3 by He treatment. As given in profile-e, an increase in the area of the low-temperature peak and a shift of the middle-temperature peaks to high temperature were observed for $Ir/WO_3/SiO_2$ after use in the reaction in the absence of H_2O. This TPR profile is very similar to that for $Ir/WO_3/SiO_2$ oxidized at 600 °C (profile-c). The surface of $Ir/WO_3/SiO_2$ seems to be oxidized under the reaction conditions in the absence of H_2O. On the other hand, $Ir/WO_3/SiO_2$ after use in the presence of H_2O (profile-f) gave very similar TPR profile with that for He treated sample. Namely, the TPR profile with a small low-temperature peak and middle-temperature peaks shifted to low-temperature was obtained. These results lead us to the consideration that coexisting H_2O plays a role to keep a portion of the Ir sites in the reduced state and in the strong Ir–W interaction during the reaction.

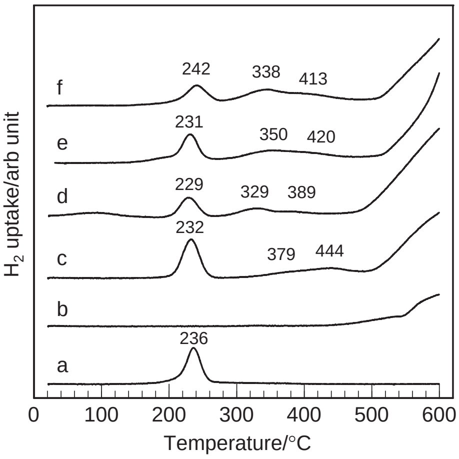

Figure 4. TPR profiles of (a) Ir/SiO_2, (b) WO_3/SiO_2, (c) $Ir/WO_3/SiO_2$, (d) $Ir/WO_3/SiO_2$ after He treatment, (e) $Ir/WO_3/SiO_2$ after the reaction in the absence of H_2O, (f) in its presence.

Since the reaction gas employed in this study contains CO and H_2O, the formation of H_2 by water gas shift (WGS) reaction can be expected. In fact, a certain amount of CO_2 was formed when a gas mixture of CO and H_2O was exposed to $Ir/WO_3/SiO_2$ catalyst at temperatures above 400 °C, suggesting the possibility of WGS reaction. We also observed that the activity of $Ir/WO_3/SiO_2$ for NO reduction with CO in the absence of H_2O is increased by addition of H_2. In conclusion, coexisting H_2O plays an essential role for NO reduction to occur over $Ir/WO_3/SiO_2$ catalyst through stabilization of the catalytically active Ir sites in reduced state by H_2 produced on-site via WGS reaction.

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