# A Highly Active $Ir/WO_3$ Catalyst for the Selective Reduction of NO by CO in the Presence of $O_2$ or $O_2 + SO_2$

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$Ir/WO_3$ catalyst is highly active for the reduction of NO by CO even in the presence of either $O_2$ or $O_2 + SO_2$. However, the activity of $Ir/WO_3$ is fairly lowered by the presence of $SO_2$ alone. It is believed that the active sites lose their activity by the adsorption of $SO_2$ but $O_2$ promotes the desorption of $SO_2$ from these sites as suggested by TPD, thus the negative effect of $SO_2$ being suppressed by the coexistence of $O_2$.

The selective catalytic reduction of NO in oxygen-rich atmosphere has recently attracted extensive attention for removing NO*x* emitted from diesel and lean-burn engines. Under lean conditions, certain hydrocarbons have been proved to act as selective reductants,[1–3] while CO and $H_2$ have not been regarded as selective reductant since they are oxidized by $O_2$ rather than by NO. Furthermore, the catalysts are often deteriorated by the presence of $SO_2$ in diesel exhaust. Recently, it has been reported that Ir supported on silicate[4] and ZSM-5[5,6] can catalyze NO reduction by CO even in the presence of excess oxygen. Hamada et al.[7–9] have reported that $Ir/SiO_2$ showed no NO reduction activity in the absence of $SO_2$, while the presence of $SO_2$ drastically promotes NO reduction. This is quite a favorable characteristic for the treatment of diesel exhaust. Previously, the authors have studied the catalytic reduction of NO with CO in the presence of excess $O_2$ over various supported metal catalysts.[10] The pronounced activity was obtained with $Ir/WO_3$, Ir/ZnO, and $Rh/Al_2O_3$ catalysts, among which the first one is the most active. In the present study, the influence of $SO_2$ on the reduction of NO has further been investigated for the $Ir/WO_3$ catalyst.

$Ir/WO_3$ was prepared by an impregnation method. $WO_3$ support was prepared by a decomposition of $(NH_4)_{10}W_{12}O_{41} \cdot 5H_2O$ in air at 773 K for 3 h. $WO_3$ was impregnated with aqueous solution of $H_2IrCl_6$ in a rotary evaporator at 343 K. The catalyst was further calcined in air at 773 K for 2 h. Ir loading was 5.0 wt %.

The reaction was carried out in a conventional flow reactor at W/F of $0.06\ g\ s\ cm^{-3}$ and at 423–673 K. The reactor was made of 6 mm diameter Pyrex glass tubing in which the catalyst sample of 0.05 g was mounted on loosely packed quartz wool. Prior to the runs, the catalyst was treated in a stream of He at 773 K for 3 h and cooled to the reaction temperature. The reactant gases used were NO (1000 ppm), CO (1%) and $O_2$ (0–8%) and they were diluted with He. In order to investigate an effect of $SO_2$, 100 ppm of $SO_2$ was added to the reactant gas in the transient mode. Unless otherwise stated, all the experiments were carried out using 2% $O_2$. The concentrations of $N_2$, $N_2O$, $O_2$, CO, and $CO_2$ in the outflow gas were determined using gas chromatographs (Shimadzu 8A and 6A) with porapak Q and molecular sieve 5A columns. The concentration of $NO_2$ was monitored using a UV–vis spectrophotometer (Hitachi Model U-1100). TPD experiments of $SO_2$ adsorbed on $Ir/WO_3$ and $WO_3$ were carried out to investigate the desorption behavior of $SO_2$, using a BEL Japan, Inc., TPD-1-AT detected by Q-MASS detector.

The reactions were run at temperatures of 473–673 K and the reactions were slow at 523 K or below under the conditions used. Table 1 summarizes the values of conversion of NO to $N_2$ or $N_2O$, and CO over $Ir/WO_3$ measured at higher temperatures. The pronounced activity more than 60% NO conversion is observed above 573 K except in the presence of $SO_2$. The highest value of NO conversion is observed in the reaction of NO–CO without both $O_2$ and $SO_2$. CO conversion obtained in the presence of $O_2$ or $O_2 + SO_2$ reaches to 100% since the oxidation of CO proceeds very rapidly in the presence of excess $O_2$. It may be a reason for that the conversion of NO (to $N_2$ and $N_2O$) is saturated around 60% above 623 K in the presence of excess $O_2$. It is found that $SO_2$ remarkably inhibits the NO–CO reaction, while this reaction is not inhibited by the presence of $O_2$ or $SO_2 + O_2$. The values of total NO conversion for NO–CO–$O_2$ reaction in the presence and absence of $SO_2$ obtained at 573–673 K are almost identical, while the selectivity values for $N_2$ and $N_2O$ are different. The selectivity for $N_2O$ increases but that for $N_2$ decreases to almost the same extent by introducing $SO_2$. Namely, the coexisting $O_2$ was able to mask the negative effect of $SO_2$. Possible mechanisms for the formation of $N_2$ and $N_2O$ from NO is considered to be the recombination of N atoms adsorbed on adjacent Ir sites ($2N_{(a)} \rightarrow N_2$) and the reaction of an adsorbed N atom and an adsorbed (or gaseous) NO molecule, respectively. Introducing $SO_2$, which is adsorbed on Ir sites as proved by TPD (Figure 2), would reduce the couples of the adjacent N atoms, thus decreasing the conversion to $N_2$ but increas-

**Table 1.** The conversion[a] to $N_2$ and $N_2O$ and of CO in the reaction of NO and CO in the presence and absence of $O_2$ and/or $SO_2$ with a 5 wt % $Ir/WO_3$

| Temperature[b] | NO + CO | | | NO + CO + $O_2$ | | | NO + CO + $SO_2$ | | | NO + CO + $O_2$ + $SO_2$ | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| /K | $N_2$ | $N_2O$ | CO | $N_2$ | $N_2O$ | CO | $N_2$ | $N_2O$ | CO | $N_2$ | $N_2O$ | CO |
| 573 | 74 | 7 | 8 | 66 | 15 | 100 | 7 | 6 | 1 | 41 | 42 | 100 |
| 623 | 80 | 4 | 12 | 53 | 8 | 100 | 10 | 7 | 3 | 49 | 22 | 100 |
| 673 | 87 | 0 | 11 | 55 | 4 | 100 | 8 | 9 | 4 | 50 | 9 | 100 |

[a]In %. Conversion to $N_2$ (or $N_2O$) = ($N_2$ (or $N_2O$) at outlet)/(NO at inlet); conversion of CO = ($CO_2$ at outlet)/(CO at inlet) in the absence or presence of $O_2$. [b]Reaction temperature.

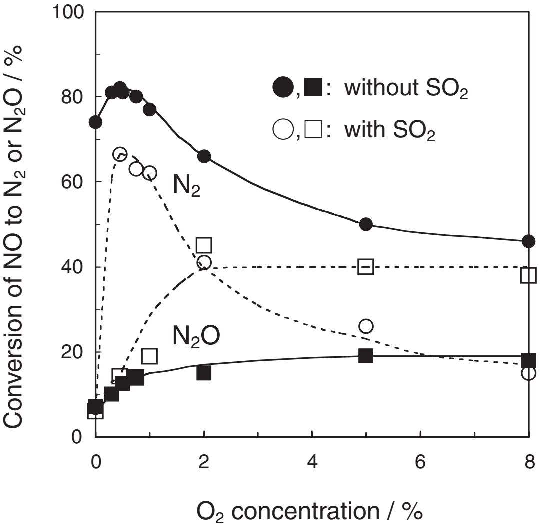

**Figure 1.** The relationship between $O_2$ concentration and the conversions of NO and CO in the reaction between NO and CO over $Ir/WO_3$ at 573 K in the presence and absence of $SO_2$.

ing the conversion to $N_2O$.

Figure 1 shows the relationship between the $O_2$ concentration and the conversion of NO to $N_2$ and $N_2O$ in the presence and absence of $SO_2$. The conversion to $N_2$ obtained in the NO–CO reaction without $O_2$ decrease drastically by introducing $SO_2$. When the reaction is carried out in the presence of $O_2$ between 0.3 and 1%, the conversion to $N_2$ increases up to 80% while the conversion to $N_2O$ shows less than 15%. When $SO_2$ is introduced in the NO–CO reaction in the presence of $O_2$ between 0.3 and 1%, the conversion to $N_2$ decreases and that to $N_2O$ increases inversely. It is found that the maximum conversion of NO in the absence of $SO_2$ is obtained at an $O_2$ concentration around 0.5%. When NO and CO are completely converted to $N_2$ and $CO_2$, respectively, according to an equation, $NO + 10CO + 9/2O_2 \rightarrow 1/2N_2 + 10CO_2$, 0.45% $O_2$ is the stoichiometric concentration under the present conditions (0.1% NO and 1% CO), which is close to the $O_2$ concentration for the maximum NO conversion observed. When more than 0.45% $O_2$ is added, the oxidation of CO may be promoted but this may decrease the NO reduction by CO. Certainly, when the reaction is carried out in the presence of $O_2$ above 1%, CO conversion steadily shows 100% and conversion to $N_2$ decreases with increase in $O_2$ concentration, while conversion to $N_2O$ increases inversely. The conversion to $N_2O$ is further increased by introducing $SO_2$. As well known in the literature,[1–4] 6–16% $O_2$ and 1–500 ppm $SO_2$ are usually contained in diesel exhaust. It is seen that $Ir/WO_3$ catalyst shows still high activity even in excess $O_2$ atmosphere, for example, 70% NO conversion for 5% $O_2$. It could be considered that the resistance of $Ir/WO_3$ to oxidation is very useful for SCR in oxygen-rich atmosphere.

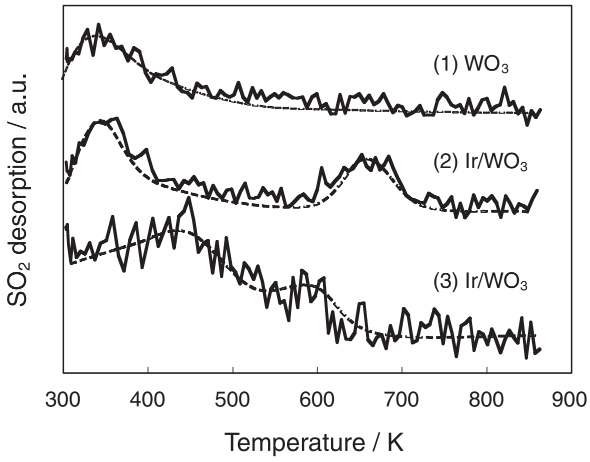

**Figure 2.** TPD curves of $SO_2$ adsorbed on $WO_3$ and $Ir/WO_3$ collected during heating in pure He (1 and 2) and in $O_2$ (2%) and He (3).

Figure 2 illustrates the TPD curves of $SO_2$ adsorbed on $WO_3$ and $Ir/WO_3$. For $SO_2$ adsorption, the samples were exposed to a stream of 1% $SO_2$ diluted with He at 50 $cm^3\,min^{-1}$ for 60 min at room temperature. They were flushed by flowing He for 60 min and heated in pure He (50 $cm^3\,min^{-1}$) at a rate of 10 $K\,min^{-1}$ (curves 1 and 2) or by flowing pure He for 45 min and further by 2% $O_2$ + He for 15 min, followed by TPD in the same $O_2$ + He stream (curve 3). A broad desorption peak is observed around 350 K for the support alone (curve 1). For curve (2), two peaks are seen around 350 and 650 K, which may correspond to desorption of $SO_2$ adsorbed on $WO_3$ and Ir species, respectively. When TPD was conducted in the presence of $O_2$, a different result was obtained (curve 3); the peak assigned to the desorption from Ir shifts to lower temperature by about 60 K. Namely $O_2$ can promote the desorption of $SO_2$ from surface Ir sites and this is a reason for $O_2$ to remove the negative effect of $SO_2$ deactivating those sites.

The influence of $O_2$ and $SO_2$ on the catalytic reduction of NO with CO has been investigated for an $Ir/WO_3$ catalyst, which is highly active for this reduction in the absence of those foreign gases. It is shown that NO can be reduced by CO even in the presence of either $O_2$ or $O_2 + SO_2$. It is also seen that the catalyst shows high activity even in excess $O_2$ atmosphere such as 5 to 8% $O_2$ in the presence and absence of $SO_2$. It could be considered that the resistance of $Ir/WO_3$ to oxidation is very useful for sulfur free lean-burn engines in addition to diesel exhaust.

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