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.

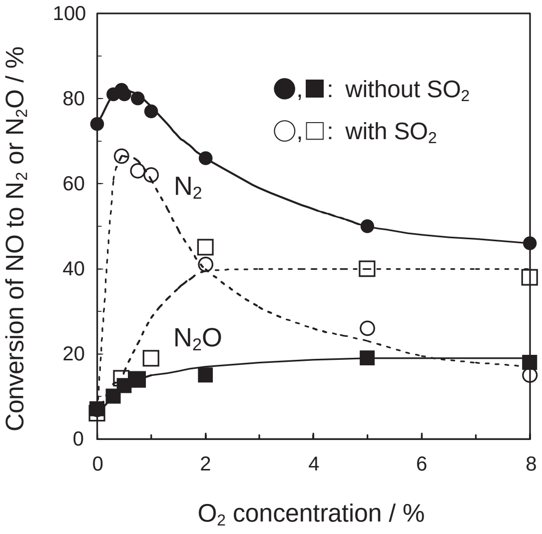

Figure 1. The relationship between O_2 concentration and the conversions of NO and CO in the reaction between NO and CO over Ir/WO_3 at 573 K in the presence and absence of SO_2.

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 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.

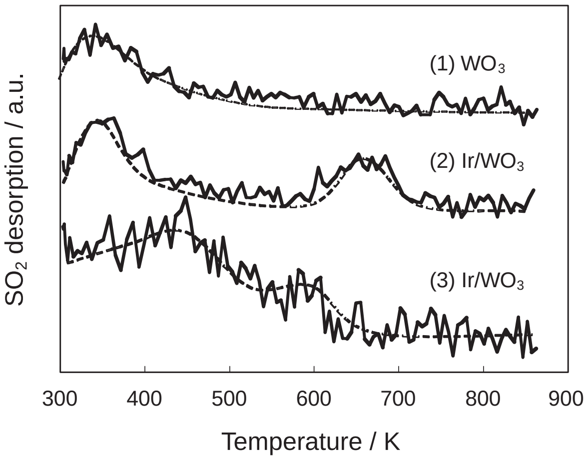

Figure 2. TPD curves of SO_2 adsorbed on WO_3 and Ir/WO_3 collected during heating in pure He (1 and 2) and in O_2 (2%) and He (3).

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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