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An Ir/WO$_3$ catalyst for selective reduction of NO with CO in the presence of O$_2$ and/or SO$_2$

Hironori Inomata, Masahide Shimokawabe and Masahiko Arai *

Division of Chemical Process Engineering, Graduate School of Engineering, Hokkaido University, Sapporo 060-8628, Japan

* E-mail: marai@eng.hokudai.ac.jp; Fax: +81-11-7066594

Abstract

The catalytic performance of Ir/WO$_3$ catalyst has been studied in the reduction of NO with CO in the presence of O$_2$ and/or SO$_2$. The catalyst was active for the selective reduction of NO to N$_2$ without foreign gases. The conversion of NO to N$_2$ was further enhanced by the addition of a small amount of O$_2$ while that to N$_2$O was reduced. The N$_2$ conversion went through a maximum, which depended on the composition of the reacting gaseous mixture (NO and CO). The catalyst was still active at higher O$_2$ concentrations up to 5%, so this Ir/WO$_3$ catalyst can be used effectively under lean-burn conditions. The presence of SO$_2$ (100 ppm) caused a significant deactivation but this negative effect was completely removed by co-existing O$_2$. The reaction mechanisms and the effects of co-existing O$_2$ and SO$_2$ gases are discussed on the bases of those reaction results, those of the reduction of NO$_2$ instead of NO, and FTIR measurements of the catalysts after the reactions under various conditions. Possible reaction pathways are proposed, which depend on the concentration of O$_2$ added in the reaction mixture.

Keywords: Selective catalytic reduction; Nitrogen monoxide; Iridium catalyst; Tungsten oxide support; Lean-burn condition

1. Introduction

Nitrogen oxides (NO, NO$_2$, and N$_2$O) are major sources of air pollutants, which bring about acid rain and snow, photochemical smog, ozone destruction, and green house effects. Recently, the selective catalytic reduction (SCR) of NO in oxygen-rich atmosphere has been attracting extensive attention for removing NOx emitted from various engines and combustors. Under lean conditions, hydrocarbons have been proved to act as effective reductants in SCR of NO [1, 2]. Carbon monoxide is also one of the effective reducing agents involved in engine exhaust. It has recently been reported that Ir supported on silicate [3] and

ZSM-5 [4] can catalyze NO reduction by CO even in the presence of excess oxygen. Hamada et al. [5-8] have reported that catalysts made from Ir/SiO_2 alone or doped with various metals are active for NO reduction with CO in the presence of both O_2 and SO_2. It is interesting that the reduction of NO in the presence of O_2 is promoted by SO_2, which normally poisons the active sites and significantly decreases the activity of catalysts, although the activity of those catalysts becomes lower in the presence of O_2 alone. The present authors have studied the activity of Ir/WO_3 catalyst for the reduction of NO with CO [9, 10]. It is noteworthy that this catalyst is highly active even in the presence of excess O_2 or O_2 + SO_2; such resistance to oxidation is very useful for sulfur-free lean-burn engines. Tamai et al. have recently reported that a catalyst of Ir/SiO_2 modified with Nb_2O_5 is also active for the SCR of NO by CO under excess O_2 and SO_2-free conditions [11]. They explain that the high observed activity of this $Nb_2O_5/Ir/SiO_2$ catalyst can be attributed to strong interaction of Ir with Nb_2O_5 as well as to high Ir dispersion.

The present work has been undertaken as a follow-up work of our previous communication [10] to study in more detail the SCR of NO by CO with Ir/WO_3 catalyst in the presence or absence of O_2 and/or SO_2. The SCR runs have been conducted under various conditions to examine the effects of these foreign gases on the total conversion of NO and the product selectivity. In addition, FTIR spectroscopy has been used to study surface species formed on the catalyst during the SCR runs. Possible reaction mechanisms have been discussed on the basis of the results of those kinetics and FTIR measurements.

2. Experimental

2.1. Catalyst preparation

An impregnation method was used to prepare 5.0 wt.-% Ir/WO_3 catalysts [9, 10]. WO_3 supports were prepared by thermal decomposition of H_2WO_4 at 673 K in air for 3 h. WO_3 (4 g) was impregnated with 100 cm^3 of H_2IrCl_6 aqueous solution in a rotary evaporator at 343 K. The sample so obtained was dried in air at 383 K for 12 h and further calcined in air at 673 K for 2 h.

2.2. NO reduction

The reaction runs were carried out in a conventional flow reactor at a W/F of 0.06 g s cm^{-3} and at 573 K. Prior to the runs, the catalyst sample was treated in a stream of He at 673 K for 2 h and cooled to the reaction temperature. The reactor was made of 9 mm diameter Pyrex glass tubing in which a catalyst sample of 0.05 g was mounted on loosely packed quartz wool. The reactant gases used under standard experimental conditions were NO (1000 ppm), CO (1%), O_2 (0.45%), and SO_2 (100 ppm) diluted with He. For elucidation of the effect of O_2 on the reduction of NO, O_2 (0, 0.3, 0.45, 1, 2, and 5) was introduced in the feed gas. 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 and that of NO_2 was monitored using a UV-VIS spectrophotometer (Hitachi Model U-1100). For comparison, the reduction of NO_2 with CO was also examined under the same reaction conditions. Because of the low concentrations of NO and hydrocarbons in the outflow, the total flow rate was practically constant throughout the catalyst bed.

2.3. FTIR measurements

A Fourier transform-infrared spectrophotometer (Nihon Bunko FT-IR5M) with a diffuse reflectance attachment (Nihon Bunko DG-500/H) was used to examine the surface species on the catalyst. After the catalyst sample was subjected to the reaction between NO (5000 ppm) and CO (2%) in the presence and absence of O_2 (0.75%) and/or SO_2 (100 ppm) diluted with He at 573 K for 1 h, it was cooled down to room temperature and the FTIR measurements were made using diffuse reflection mode under ambient conditions. The reaction was conducted at higher concentrations of NO and CO compared with those used in reaction runs to obtain clearer, stronger absorption peaks due to NO- and CO-containing surface species. The catalyst that had been used for the reduction of NO_2, instead of NO, with CO was also subjected to the FTIR measurement.

3. Results and discussion

3.1. Reduction of NO by CO under various conditions

The reduction of NO with CO was carried out by a transient mode using various gas mixtures to examine the influence of coexisting gaseous components. Figure 1 shows the conversions of NO to N_2 and N_2O in the absence or presence of O_2 and/or SO_2. The catalyst indicates a stable activity after about 60 min in region I for the run with NO and CO; the stable values of conversion of NO to N_2 and N_2O are about 70% and 15%, respectively. The addition of SO_2 decreases the conversion of NO to either N_2 or N_2O, more markedly for N_2 (region II). That is, SO_2 has a negative effect on the catalytic activity in the present case as well. When O_2 is also added, however, the catalyst recovers its initial activity (region III), the conversion levels being very similar to those in region I. The conversion of NO is reduced again by stopping the addition of O_2 (region IV) and this lowered catalytic activity remains unchanged after stopping the addition of SO_2 as well (region V). When O_2 is again introduced, the high catalytic activity can be recovered (region VI); namely, O_2 removes the inhibiting effect of SO_2. Our previous TPD results indicate that the coexistence of O_2 facilitates the desorption of SO_2 species adsorbed on the catalyst of Ir/WO_3, which occurs at lower temperatures [10]. When O_2 was stopped (region VII), the catalytic activity decreased to a level comparable to that observed in region I. That is, the addition of O_2 promoted the reduction of NO by CO.

Figure 1

Then the influence of O_2 on the SCR of NO with CO was examined by using stable conversion data collected in 1.5 - 3.0 h on stream. Figure 2 shows the conversion of NO to N_2 and N_2O at different O_2 partial pressures in the presence and absence of SO_2. In the absence of O_2, the conversion of NO to N_2 drastically decreased from 75% to 20% on the addition of SO_2, while that to N_2O did not change so much. When a small quantity of O_2 was added, NO conversion was significantly promoted even in the presence of SO_2 and the conversion to N_2 reached more than 70%, but that to N_2O decreased to a level of 10%. Similar positive and negative effects of O_2 on the conversion of NO to N_2 and N_2O, respectively, were also observed for the reactions in the absence of SO_2 at lower O_2 concentrations up to 1%. In these reactions, the conversion to N_2 observed in the absence of SO_2 was larger than that in the presence of SO_2 while, oppositely, that to N_2O was smaller. At about 1% O_2, the reductant, CO, was completely converted to CO_2. When more O_2 was added, the conversion of NO to N_2 decreased and that to N_2O increased with O_2 concentration irrespective of the presence or absence of SO_2. That is, a maximum conversion of NO to N_2 (about 95%) appeared at an O_2 concentration of about 0.45% in the absence of SO_2. As discussed previously [10], 0.45% O_2 is the stoichiometric concentration for the conversion of NO (1000 ppm) to N_2 and of CO (1%) to CO_2 under the present conditions according to $NO + 10CO + 9/2O_2 \rightarrow 1/2N_2 + 10CO_2$. When O_2 is added at a larger concentration than 0.45%, the oxidation of CO is promoted and this may decrease the conversion of NO by CO, as observed in Fig. 2.

Figure 2

FTIR results will be presented next to discuss the surface species formed and adsorbed on the catalyst of Ir/WO_3 during the reduction of NO by CO. To obtain strong and clear absorption of those species, we conducted the reaction at higher concentrations of NO (5000 ppm) and CO (2 %). The influence of O_2 on the NO reduction was also examined at these concentrations under the same conditions as those used in the runs for Fig. 1. Figure 3 shows the very similar effects of O_2 and SO_2 on the conversion of NO to N_2 and N_2O. In the absence of SO_2, a maximum conversion was observed at an O_2 concentration of 0.75%, corresponding again to the stoichiometric concentration for the complete conversion of 5000 ppm NO and 2% CO_2 to N_2 and CO_2, respectively. The reaction results are also given in Table 1.

Figure 3

Table 1

4

A positive feature of our Ir/WO$_3$ catalyst is that it is active at an O$_2$ concentration of 5% in the presence of 100 ppm SO$_2$, showing as high a NO conversion level as 40%. According to the literature [1-4], diesel exhaust gases usually contain 6 - 16% O$_2$ and 1 - 500 ppm SO$_2$. Such resistance of Ir/WO$_3$ catalyst to oxidation is useful for lean-burn engines.

3.2. Reduction of NO$_2$ by CO

As detailed in the following, such an adsorbed species as Ir NO$_2$ has been detected for the catalyst after the reduction of NO with CO by FTIR measurements. So, the reaction of NO$_2$ and CO has been examined under conditions similar to those used for the above-mentioned NO CO reaction. Figure 4 compares the results of the reduction of NO$_2$ and NO by CO at different O$_2$ concentrations in the absence of SO$_2$. At an O$_2$ concentration of 0.5% or below, the conversion of NO$_2$ to N$_2$ is more than 90%, being larger than that of NO to N$_2$, and the conversion of NO$_2$ to N$_2$O is smaller than that of NO to N$_2$O. The conversion levels in the NO$_2$ CO reaction show little dependence on the O$_2$ concentration. At larger O$_2$ concentrations, however, the results are very similar for the NO$_2$ CO and the NO CO reactions. At any O$_2$ concentration examined, the total conversion of NO$_2$ is similar to that of NO and the conversion of CO with NO$_2$ is also similar to that with NO. Researchers have suggested that NO$_2$ plays an important role in the overall selective reduction of NO by hydrocarbons [12-14], which can react selectively on the catalyst with NO$_2$ formed by the oxidation of NO. Furthermore, Ogura et al. [15] have reported that Ir-loaded In/H-ZSM-5 is effective for the reduction of low concentration NO and the effects of Ir are not only to promote NO oxidation but also probably to strengthen NOx adsorption. Those results suggest a possible reaction pathway for the reduction of NO with CO that goes through an adsorbed NO$_2$ species.

Figure 4

3.3. Surface species detected by FTIR measurements

Figure 5 shows FTIR spectra obtained after passing various gas mixtures containing O$_2$ at a low concentration of 0.75% over the catalyst of Ir/WO$_3$ (see Table 1). When NO and CO were passed, strong IR bands at 2048 and 1823 cm^{-1} were observed (Fig. 5 (a)). These should be assigned to *cis*-type coordinated species of NO and CO with one metal atom according to Haneda et al. [6]. These authors have suggested that such a *cis*-type coordinated species of NO and CO is a possible intermediate for NO reduction by CO. When the reaction mixture included 100 ppm SO$_2$, no IR absorption was seen (Fig. 5 (b)) and the conversion of NO was very small (Table 1). When O$_2$ coexisted along with SO$_2$, the bands of the *cis*-type coordinated species of NO and CO were observed again and a new band at 1619 cm^{-1}

assignable to NO_2 species appeared (Fig. 5 (c)). The conversion levels of NO to N_2 and N_2O are comparable to those in the reaction of NO and CO. When only O_2 was added to the mixture of NO and CO, the bands at 2048, 1823 and 1619 cm^{-1} were also observed (Fig. 5 (d)). Haneda et al. reported that the *cis*-type coordinated species completely disappeared in the presence of O_2 and that the reduction of NO with CO did not take place over Ir/SiO$_2$ [6]. In our results with the catalyst of Ir/WO$_3$, however, the addition of O_2 promoted the conversion to N_2 but decreased the conversion to N_2O (Table 1).

Figure 5(e) shows an IR spectrum obtained after the reaction of 5000 ppm NO_2 and 2% CO. IR bands were observed at 2048, 1823 and 1619 cm^{-1}. When NO_2 was reduced with CO, a maximum conversion of NO_2 around 94% was obtained in the absence of O_2, and a similar high conversion was also obtained in the NO reduction with CO in the presence of a stoichiometric O_2 concentration of about 0.5%. This also suggests that the reduction of NO with CO goes through the same reaction pathways with an adsorbed NO_2 species as in the reduction of NO_2.

Figure 5

Figure 6 shows the spectra collected after the reduction of NO with CO at higher O_2 concentrations such as 3% and 5%. These spectra show shoulder peaks at 2048 and 1828 cm^{-1}, which are assignable to the *cis*-type coordinated species of NO and CO on a single Ir site, along with a peak at 1619 cm^{-1} due to NO_2 species. For those spectra, however, new stronger bands can be seen at 2112 and 1885 cm^{-1} and these bands may be assigned, respectively, to CO and NO each adsorbed on an $Ir^{\delta+}$ site [5-8]. Table 1 shows the addition of a larger quantity of O_2 to have a significant negative effect on the conversion of NO to N_2; the conversion to N_2 decreased from 65% to 35% at an O_2 concentration of 3%, but that to N_2O increased from 9% to 30%.

3.4. Reaction mechanisms consideration

On the basis of the present reaction and FTIR results and previous considerations in the literature [5-8], we will discuss possible reaction pathways for SCR of NO with CO over Ir/WO$_3$ catalyst, including the effects of coexisting O_2 and SO_2. Note again that the species of NO and CO co-adsorbed and NO_2 adsorbed on exposed Ir sites have been confirmed by FTIR measurements; the latter was not detected in the absence of O_2. Furthermore, the species of either adsorbed CO or NO have also been indicated to exist at a high O_2 concentration of 3% or 5%. Different reaction pathways may be assumed depending on the O_2 concentration, which modifies the nature of supported Ir particles, affects the adsorption mode of reactive species, as illustrated in Scheme 1 (and 2), and changes the relative amounts of the adsorbed species formed. In addition to those adsorbed species such as Ir - NO(CO) (co-adsorbed), Ir -

NO$_2$, Ir - NO, Ir - CO, we suppose that Ir - N and Ir - O species may be produced from the other surface reactive species and will be involved in the reaction pathways. The surface Ir - O species may also be formed via dissociative adsorption of O$_2$ at a higher O$_2$ concentration. Oh et al. previously indicated that dissociatively adsorbed O species participated in CO - O$_2$ and CO - NO reactions on Rh catalysts [16]. Other authors studied the kinetics of the adsorption of O$_2$ on Pt [17, 18]; the O$_2$ dissociation barrier is non-zero and the O$_2$ binding energy is not high, as compared with Ni for example. The present authors have suggested the action of surface O species in SCR of N$_2$O by various hydrocarbons over Fe-ZSM-5 catalysts and have concluded that these adsorbed O species are produced from interactions of N$_2$O and O$_2$ [19, 20]. Nobukawa et al. have recently studied the role of active O species formed through dissociation of N$_2$O in SCR of N$_2$O by CH$_4$ over similar Fe-zeolite catalysts [21]. According to the previous results [22], an -NCO species is a common intermediate for the reduction of NO by CO. However, our FTIR results did not indicate the presence of such an adsorbed species on the surface of Ir/WO$_3$ catalyst. In the following the authors will propose and discuss possible reaction mechanism in which -NCO species are not included although the possibility of formation of these intermediate species is not ruled out for the present SCR of NO by CO.

Scheme 1

In the absence of O$_2$, the reactions occur on reduced Ir particles. As depicted in Scheme 1(a), the reaction may start with the co-adsorption of two NO and CO molecules on a single Ir adsorption site, followed by reaction between these adsorbed species, releasing a CO$_2$ gas molecule and leaving an N species on the Ir site. The adsorbed N species would interact with either (2) one another, giving an N$_2$ gas molecule and free Ir sites, or (3) gaseous or adsorbed NO, releasing N$_2$O gas. The rate of the reaction (3) is likely to be slower compared with the other one (2), judging from the high selectivity to N$_2$ observed in the absence of O$_2$.

When O$_2$ is present in such a small quantity as 0.75%, the reaction atmosphere still retains the reducing nature and so the reactions occur on the reduced Ir particles through the same reaction pathways as described above. However, the Ir - NO$_2$ species are formed from NO and O$_2$. An adsorbed NO$_2$ species reacts with two CO molecules in the reactions (8) through (9), giving CO$_2$ gas and an Ir - NO(CO) species, and the latter goes through the reactions of (a). That is, the presence of O$_2$ opens the new process (c) and the reactions (7) - (9) should go faster than (1) - (2) do. Thus, the contribution of the reaction (3) giving N$_2$O is reduced, and the addition of O$_2$ should increase the total conversion of NO and the selectivity to N$_2$, but decrease the selectivity to N$_2$O (Table 1). The Ir - O species formed via (7) may interact with NO giving Ir - NO$_2$, which goes through (8) and (9), or with CO releasing CO$_2$.

The latter is an undesired wasteful reaction for the SCR of NO by CO to N_2, but it may be insignificant at a low O_2 concentration.

When a larger quantity of O_2, such as 3% or 5%, co-exists, the reaction atmosphere changes to the oxidizing nature and this causes a change in the properties of supported Ir particles, affecting the adsorption of reactive species. Either an N species or a CO species adsorbed on an Ir site is formed on the surface of partially oxidized Ir particles (as confirmed by FTIR). It is assumed that one adsorbed NO species can interact with (4) another one, giving off a N_2O gas molecule and leaving an adsorbed O species, and with (5) an adsorbed CO species, giving an adsorbed N species along with a CO_2 gas molecule; (6) the former N species then reacts with the adsorbed or gaseous NO species, producing a N_2O gas (similar to reaction (3)). The reactions occurring at low O_2 concentration as given in Scheme 1(a) may also be possible, but those of (4) - (6) should be more significant at higher O_2 concentration and should proceed at comparable rates to those of (a). The reactions of (c) also take place under the oxidizing conditions but the Ir - NO formed in the reaction (8) may go through (b), since the quantity of CO to be expected for the NO reduction would become lower through useless consumption of CO via direct oxidation by O_2. Thus, the addition of O_2 in a large concentration affects the total conversion of NO but not so much, similar to the case of a smaller concentration of 0.75%, but, in contrast, causes the significant change in the product selectivity, in which the selectivity to N_2O increases while that to N_2 decreases (Table 1). The dissociative adsorption of O_2 may occur and the dissociatively adsorbed O species (Ir - O) may participate in the undesired oxidation of CO. However, these species should not be so large as to hinder the desired adsorption of other reacting species such as NO and CO.

Process (c) of Scheme 1 via the formation of Ir - NO_2 is assumed to occur under the present reaction conditions, but the rate of the formation of this adsorbed species from NO and O_2 including the dissociative adsorption of O_2 is unknown and so it is difficult at present to evaluate the relative importance (contribution) of this process in the conversion of NO with respect to those of (a) and (b). Further work is in progress in our laboratory to study the features of kinetics of the SCR of NO with Ir/WO_3 catalyst using temperature programmed desorption and reaction methods.

Finally, the influence of SO_2 and O_2 will be discussed. In the presence of SO_2, the surface Ir sites may be occupied by SO_2 species (Scheme 2) and this preferential adsorption of SO_2 decreases the number of free Ir sites to be used for the adsorption of NO and CO, decreasing the catalytic activity significantly. When O_2 coexists, the mode of SO_2 adsorption would change; this releases free Ir sites and so the coexistence of O_2 suppresses the negative effect of SO_2. The difference in the adsorption of SO_2 on the surface of Ir/WO_3 catalyst in the presence and in the absence of O_2 was previously indicated by TPD measurements [10]. It

was shown that SO_2 desorbed at lower temperatures in the presence of O_2 compared with the case in the absence of O_2.

Scheme 2

4. Conclusion

In the present work, the catalytic performance Ir/WO_3 was tested for the reduction of NO by CO in the presence and absence of O_2 and/or SO_2 under various conditions, similar to those used in industrial applications of lean-burn engines and others. In addition, the surface species adsorbed on the catalyst was also examined by FTIR measurements. The addition of a small amount of O_2 increases the activity for the conversion of NO to N_2 while it decreases that to N_2O. The N_2 conversion is maximal at a certain O_2 concentration depending on the concentration of either NO or CO, which corresponds to the complete conversion of NO to N_2 and of CO to CO_2. The catalyst is also active at higher O_2 concentration up to 5%, which is helpful under lean-burn conditions. The catalytic activity decreases in the presence of a small amount of SO_2 (100 ppm) but this inhibition effect does not appear when O_2 co-exists in the reaction mixture, which should modify the adsorption behavior of SO_2 on the catalyst. Some possible reaction mechanisms are proposed, which depend on the O_2 concentration used, and the effects of co-existing O_2 and SO_2 are discussed. At low O_2 concentration (under reducing conditions), the reduction of NO may go through either Ir - NO(CO co-adsorbed) or Ir - NO_2 species formed and adsorbed on the catalyst. At high O_2 concentration, however, another pathway involving Ir - NO and Ir - CO may be possible rather than that with the Ir - NO(CO), and so the reduction of NO proceeds via the formation of Ir - NO, Ir - CO, and Ir - NO_2.

References

[1]   Y. Li, J. N. Armor, Appl. Catal. B Environ. 1 (1992) L31-L40.
[2]   M. Iwamato, H. Hamada, Catal. Today 10 (1991) 57-71.
[3]   M. Ogura, A. Kawamura, M. Matsukata, E. Kikuchi, Chem. Lett. 29 (2000) 146-147.
[4]   A. Wang, D. Liang, C. Xu, X. Sun, T. Zhang, Appl. Catal. B Environ. 32 (2001) 205-212.
[5]   T. Yoshinari, K Sato, M. Haneda, Y. Kintaichi, H. Hamada, Catal. Commun. 2 (2001) 155-158.
[6]   M. Haneda, Pusparatu, Y. Kintaichi, I. Nakamura, M. Sasaki, H. Hamada, J. Catal. 229 (2005) 197-205.
[7]   M. Haneda, T. Fujitani, H. Hamada, J. Mol. Catal. A Chem. 256 (2006) 143-148.
[8]   M. Haneda, H. Kudo, Y. Nagao, T. Fujitani, H. Hamada, Catal. Commun. 7 (2006)

423-426.

[9]   M. Shimokawabe, N. Umeda, Chem. Lett. 33 (2004) 534-535.

[10]   M. Shimokawabe, M. Niitsu, H. Inomata, N. Iwasa, M. Arai, Chem. Lett. 34 (2005) 1426-1427.

[11]   T. Tamai, M. Haneda, T. Fujitani, H. Hamada, Catal. Commun. 8 (2007) 885-888.

[12]   H. Hamada, Catal. Today 22 (1994) 21-40.

[13]   C. Yokoyama, M. Misono, Catal. Lett. 29 (1994) 1-6.

[14]   N. Okazaki, Y. Shiina, H. Itoh, A. Tada, M. Iwamoto, Catal. Lett. 49 (1997) 169-174.

[15]   M. Ogura, S. Hiromoto, E. Kikuchi, Chem. Lett. 24 (1995) 1135-1136.

[16]   S. H. Oh, G. B. Fisher, J. E. Carpenter, D. W. Goodman, J. Catal. 100 (1986) 360-376.

[17]   L. A. Abramova, A. V. Zeigarnik, S. P. Baranov, E. Shustorovich, Surf. Sci. 565 (2004) 45-56.

[18]   B. C. Stipe, M. A. Rezaei, W. Ho, J. Chem. Phys. 107 (1997) 6443-6447.

[19]   T. Chaki, M. Arai, T. Ebina, M. Shimokawabe, J. Mol. Catal. A Chem. 227 (2005) 187-196.

[20]   M. Shimokawabe, T. Chaki, S. Ozawa, M. Arai, React. Kinet. Catal. Lett., 86 (2005) 363-370.

[21]   T. Nobukawa, K. Sugawara, K. Okumura, K. Tomishige, K. Kunimori, Appl. Catal. B Environ. 70 (2007) 342-352.

[22]   V. A. Matyshak, O. V. Krylov, Catal. Today 25 (1995) 1-88.

Figure 1
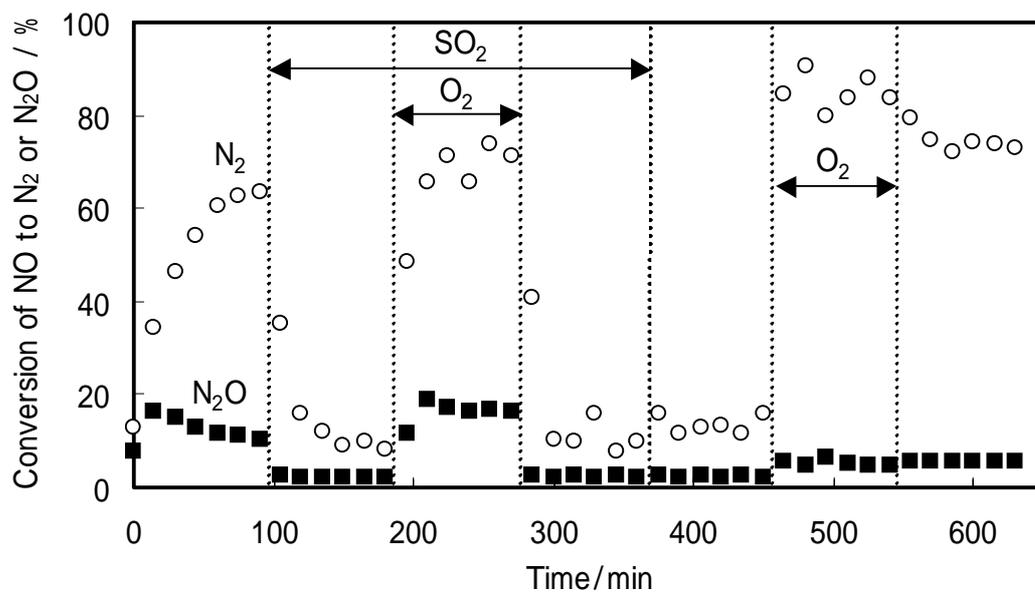
Figure 1　　　　　The transient reduction of NO (5000 ppm) with CO (2%) to N_2 and N_2O over Ir/WO$_3$ catalyst at 573 K in the absence and presence of SO$_2$ (100 ppm) and/or O$_2$ (0.75%)
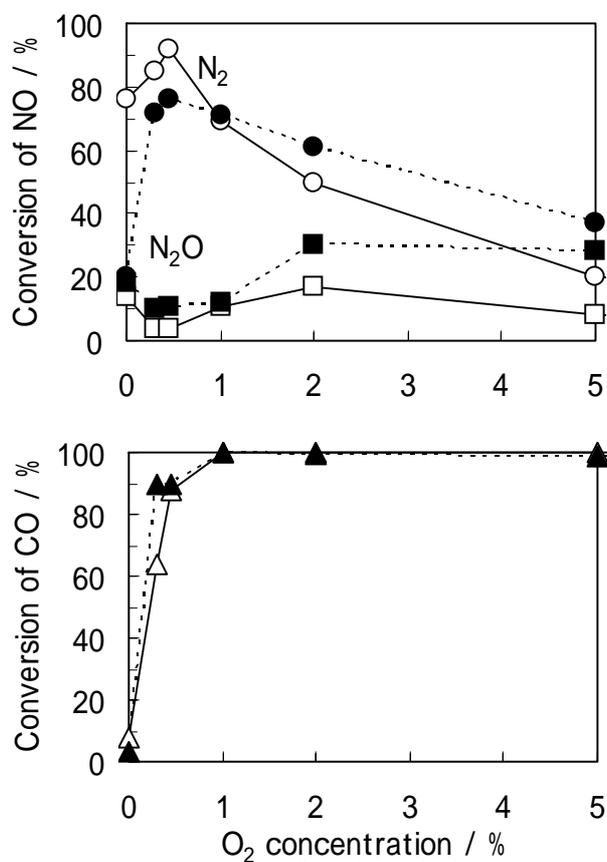
Figure 2

Figure 2   Influence of O_2 concentration on the reduction of NO (1000 ppm) with CO (1%) in the absence (open marks) and presence (closed marks) of SO_2 (100 ppm).   ,   : Conversion to N_2;   ,   : Conversion to N_2O;   ,   : Conversion of CO to CO_2.
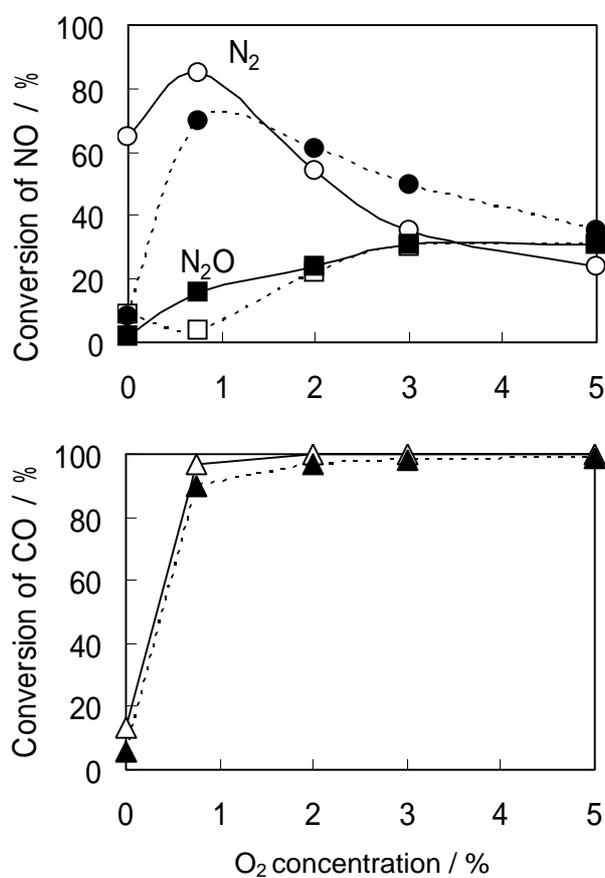
Figure 3

Figure 3　　　　　Influence of O_2 concentration on the reduction of NO (5000 ppm) with CO (2%) in the absence (open marks) and presence (closed marks) of SO_2 (100 ppm).　　,　: Conversion to N_2;　　,　: Conversion to N_2O;　　,　: Conversion of CO to CO_2. Larger concentrations of NO and CO were used in these runs, compared with those for Fig. 2.

Table 1

Table 1   Conversion of NO to N_2 and N_2O in various gaseous mixtures [a]

| Entry | Reactant gases | Conversion to | | FTIR spectra [b] |
		N_2 (%)	N_2O (%)	
At a low O_2 concentration of 0.75% (under reducing atmosphere)				
1	NO + CO	65	9	a in Fig. 5
2	NO + CO +SO_2	8	2	b
3	NO + CO + O_2 + SO_2	70	16	c
4	NO + CO + O_2	85	4	d
5	NO_2 + CO	86	8	e
At a high O_2 concentration of 3% or 5% (under oxidizing atmosphere)				
6	NO + CO + O_2 (3%)	35	30	a in Fig. 6
7	NO + CO + O_2 (3%) +SO_2	50	31	b
8	NO + CO + O_2 (5%)	24	31	c
9	NO + CO + O_2 (5%) + SO_2	35	31	d

a. Reaction conditions: NO or NO_2 5000 ppm, CO 2%, SO_2 100 ppm,

   temperature 573 K, VHSV 60000 cm^3 g^{-1} h^{-1}.

b. Collected after the conversion of NO under these conditions and given in Fig. 5 or

   Fig. 6.

Figure 4
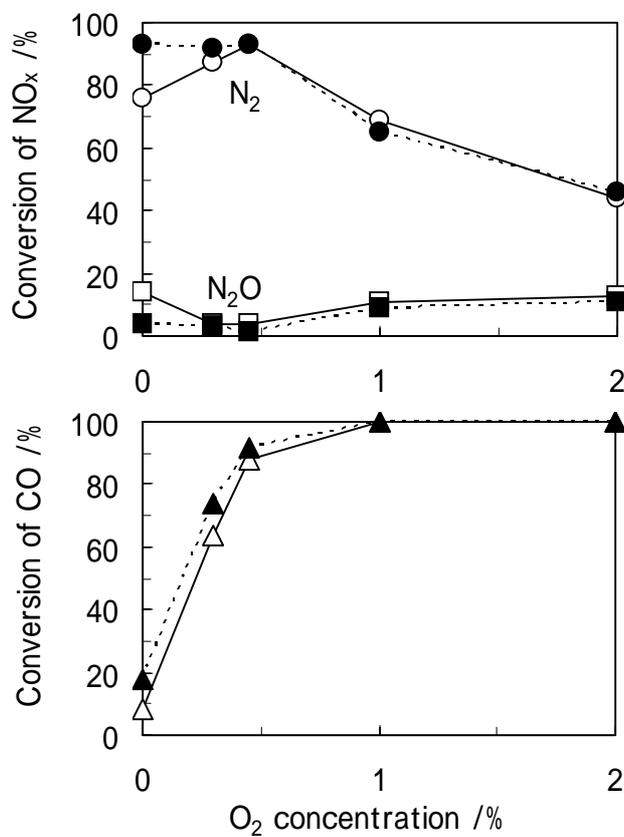
Figure 4　　　　Influence of O_2 concentration on the reduction of NO_2 (1000 ppm) with CO (closed marks) under the same conditions as for the reduction of NO in the absence of SO_2. For comparison, the data with NO are also plotted (open marks).　，　: Conversion to N_2;　，　: Conversion to N_2O;　，　: Conversion of CO to CO_2.
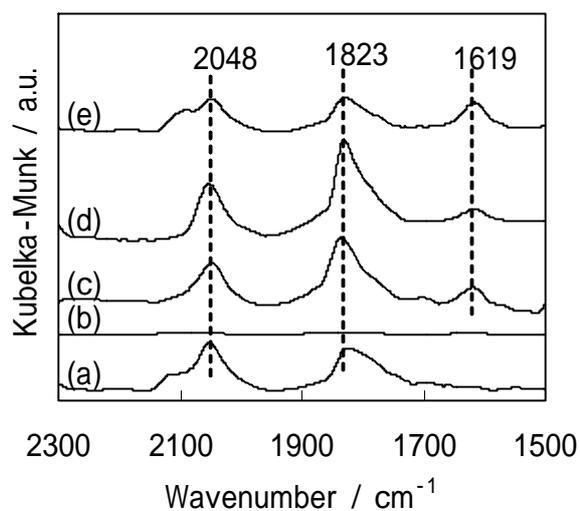
Figure 5

Figure 5   FTIR spectra for Ir/WO$_3$ catalyst after the reaction of NO and CO under various conditions as given in Table 1 (Entries 1 - 5). In these reaction runs, a small O$_2$ concentration of 0.75% was used.

Figure 6

Figure 6   FTIR spectra for Ir/WO$_3$ catalyst after the reaction of NO and CO under various conditions as given in Table 1 (Entries 6 - 9). In these reaction runs, a larger O$_2$ concentration of 3% or 5% was used, as compared with the runs (Entries 1 - 5) for Fig. 5.

Scheme 1

a. Conversion of NO on reduced Ir particles at low O_2 concentration

$$Ir\underset{CO}{\overset{NO}{\diagup}} \quad \xrightarrow[\text{(1)}]{-\ CO_2} \quad Ir\ \ N \quad \xrightarrow[\text{(2)}]{+\ Ir\ \ N} \quad N_2$$

$$\xrightarrow[\text{(3)}]{+\ NO}\ N_2O$$

b. Conversion of NO on partially oxidized Ir particles at high O_2 concentration

$$Ir\ \ NO \quad \xrightarrow[\text{(4)}]{+\ Ir\ \ NO} \quad Ir\ \ O\ +\ N_2O$$

$$\xrightarrow[\text{(5)}]{+\ Ir\ \ CO}$$

$$Ir\ \ N\ +\ CO_2 \qquad Ir\ \ N\underset{O}{\overset{O}{\diagup}}$$

$$\xrightarrow[\substack{\text{(6)}\\[(3)]}]{+\ NO}\ N_2O \qquad \xrightarrow{\text{via (c) 8}}\ N_2 \uparrow \text{ or } N_2O \uparrow$$

$$\xrightarrow{+\ NO}$$

c. Conversion of NO via Ir NO_2 species

$$Ir \quad \xrightarrow[\text{(7)}]{+\ NO,\ O_2} \quad Ir\ \ N\underset{O}{\overset{O}{\diagup}} \quad \xrightarrow[\text{(8)}]{+\ CO} \quad Ir\ \ NO\ +\ CO_2$$

$$+$$

$$Ir\ \ O$$

$$\xrightarrow[\text{via (b)}]{}\ N_2O \qquad \xrightarrow[\substack{\text{(9)}\\+\ CO}]{}\ Ir\underset{CO}{\overset{NO}{\diagup}}$$

$$\xrightarrow{\text{via (a)}}\ N_2$$

Scheme 1   Possible reaction pathways for the conversion of NO with CO under reducing atmosphere (a), under oxidizing atmosphere (b), and through the formation of adsorbed NO_2 species (c). The surface of supported Ir particles may be partially oxidized in the case of (b) but this is not indicated here. "+ CO" and "+ NO" mean the interactions with adsorbed and/or gaseous CO and NO species. Ir   O may react with CO, in addition to NO (as illustrated here), producing CO_2. The paths for Ir - O formed via (7) are omitted.
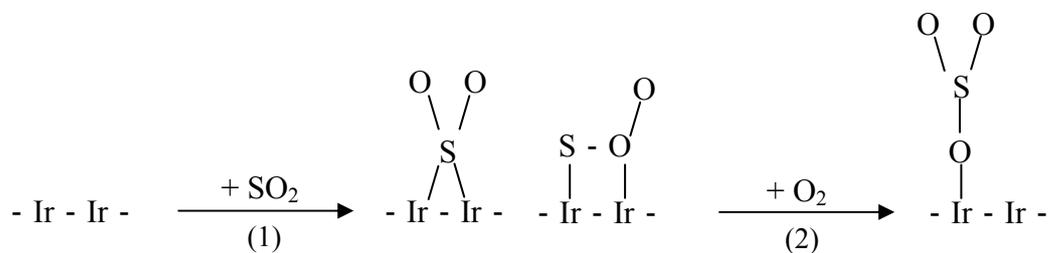
Scheme 2

Scheme 2   Possible effects of co-existing SO_2 and O_2 on the activity of Ir catalyst: (1) the exposed Ir sites are preferentially occupied with SO_2 species but (2) the addition of O_2 modifies the adsorption mode of SO_2 species, releasing free Ir sites. In addition, O_2 may promote the desorption of the adsorbed SO_2 species [10].

Captions to Figures and Schemes

Figure 1   The transient reduction of NO (5000 ppm) with CO (2%) to N_2 and N_2O over Ir/WO_3 catalyst at 573 K in the absence and presence of SO_2 (100 ppm) and/or O_2 (0.75%)

Figure 2   Influence of O_2 concentration on the reduction of NO (1000 ppm) with CO (1%) in the absence (open marks) and presence (closed marks) of SO_2 (100 ppm).   ,   : Conversion to N_2;   ,   : Conversion to N_2O;   ,   : Conversion of CO to CO_2.

Figure 3   Influence of O_2 concentration on the reduction of NO (5000 ppm) with CO (2%) in the absence (open marks) and presence (closed marks) of SO_2 (100 ppm).   ,   : Conversion to N_2;   ,   : Conversion to N_2O;   ,   : Conversion of CO to CO_2. Larger concentrations of NO and CO were used in these runs, compared with those for Fig. 2.

Figure 4   Influence of O_2 concentration on the reduction of NO_2 (1000 ppm) with CO (closed marks) under the same conditions as for the reduction of NO in the absence of SO_2. For comparison, the data with NO are also plotted (open marks).   ,   : Conversion to N_2;   ,   : Conversion to N_2O;   ,   : Conversion of CO to CO_2.

Figure 5   FTIR spectra for Ir/WO_3 catalyst after the reaction of NO and CO under various conditions as given in Table 1 (Entries 1 - 5). In these reaction runs, a small O_2 concentration of 0.75% was used.

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Scheme 1   Possible reaction pathways for the conversion of NO with CO under reducing atmosphere (a), under oxidizing atmosphere (b), and through the formation of adsorbed NO_2 species (c). The surface of supported Ir particles may be partially oxidized in the case of (b) but this is not indicated here. "+ CO" and "+ NO" mean the interactions with adsorbed and/or gaseous CO and NO species. Ir   O may react with CO, in addition to NO (as illustrated here), producing CO_2. The paths for Ir - O formed via (7) are omitted.

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