

Ir/SiO₂ as a highly active catalyst for the selective reduction of NO with CO in the presence of O₂ and SO₂

Masaaki Haneda,^{*a} Tomohiro Yoshinari,^b Kazuhito Sato,^b Yoshiaki Kintaichi^a and Hideaki Hamada^a

^a Research Institute for Green Technology, National Institute of Advanced Industrial Science and Technology (AIST), AIST Tsukuba Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan

^b Petroleum Energy Center, Tsukuba Laboratory, AIST Tsukuba Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan

Received (in Cambridge, UK) 19th August 2003, Accepted 26th September 2003

First published as an Advance Article on the web 15th October 2003

Coexisting SO₂ considerably enhanced the catalytic activity of Ir/SiO₂ for NO reduction with CO in the presence of O₂ because of the formation of a *cis*-type coordinated species of NO and CO to one iridium atom ($Ir < \frac{NO}{CO}$), a possible reaction intermediate leading to N₂ formation.

Selective reduction of NO in oxidizing atmospheres is an increasing focus of research attention, since it has potential as a practical measure for removing NO_x emitted from diesel engines, lean-burn engines and combustors. In this regard, a great number of studies have been made recently to use hydrocarbons as reductant for the selective reduction of NO.¹ On the other hand, H₂ and CO have not until recently been regarded as effective reductants. In 1997, Yokota *et al.*² reported the activity of Pt/mordenite for NO reduction with H₂ in the presence of O₂ at around 423 K. Several researchers then studied the selective reduction of NO with H₂ over Pt and Pd-based catalysts.^{3–4} As for NO reduction with CO, Ogura *et al.*⁵ investigated the activity of supported iridium catalysts and found that NO can successfully be reduced to N₂ with CO over Ir/silicalite catalyst and that the catalytic activity is minimally influenced by coexisting SO₂. We have recently discovered that Ir/SiO₂ and Rh/SiO₂ show marked catalytic activity with respect to NO reduction with H₂ in the presence of O₂ and SO₂.⁶ The most significant feature of this reaction is that the presence of SO₂, which normally poisons catalytic reactions, promotes NO reduction in the presence of O₂. However, no evidence has been obtained up to now that explains this promoting effect of SO₂. In this communication, we report that CO, which is a more practical reductant than H₂, also serves as an effective reductant for NO reduction over Ir/SiO₂ catalyst in the presence of O₂ and SO₂. A mechanistic role for SO₂ is also proposed based on *in situ* IR measurements.

Silica-supported noble metal (Pt, Rh, Pd, Ir) catalysts were prepared by impregnating SiO₂ (Fuji Silysia Chemicals, Cariact G-10, 300 m² g⁻¹) with aqueous solutions of [Pt(NH₃)₄](NO₃)₂,

Rh(NO₃)₂, [Pd(NH₃)₄](NO₃)₂ or H₂IrCl₆·6H₂O. For comparison, Ir/Al₂O₃ was also prepared by impregnating Al₂O₃ (Mizusawa Chemicals, GB-45, 190 m² g⁻¹) with an aqueous solution of H₂IrCl₆·6H₂O. The impregnated catalyst precursors were dried at 383 K and finally calcined at 873 K for 8 h in air. The loading of noble metals was fixed at 5 wt%. Their catalytic activity was evaluated using a fixed-bed continuous flow reactor. A reaction gas mixture containing NO (1000 ppm), CO (6000 ppm), O₂ (0 or 5%), SO₂ (0 or 20 ppm) and H₂O (6%) diluted in He as the balance gas was fed through a catalyst (0.04 g), pretreated *in situ* in a flow of 0.6% H₂/6% H₂O/He at 873 K for 1 h, at a rate of 90 cm³ min⁻¹ (SV = *ca.* 75000 h⁻¹). The effluent gas was analyzed by two on-line gas chromatographs equipped with a Molecular Sieve 5A column (for the analysis of N₂ and CO) and a Porapak Q column (for analysis of CO₂ and N₂O). The reaction temperature was changed from 873 to 473 K in 50 K steps and the steady-state catalytic activity was measured at each temperature. *In situ* IR spectra were recorded with a Nicolet NEXUS 670 FT-IR spectrometer equipped with a diffuse reflectance high-temperature cell (Spectra Tech) connected to a gas flow system.⁶ Various gas mixtures were fed to the catalyst (15 mg), which was pretreated *in situ* in a flow of 1% H₂/6% H₂O/He at 873 K for 1 h, at a flow rate of 30 cm³ min⁻¹.

Table 1 summarizes the catalytic activity of the silica-supported noble metal catalysts for NO reduction by CO in the presence of O₂ either with or without 20 ppm SO₂. The reproducibility of the catalytic activity data was found to be quite good in this study. Pt/SiO₂, Rh/SiO₂ and Pd/SiO₂ showed little catalytic activity with respect to NO reduction to N₂/N₂O over the entire temperature range, irrespective of coexisting SO₂. The performance of Ir/SiO₂, on the other hand, was quite different. Although Ir/SiO₂ showed no NO reduction activity over the entire temperature range in the absence of SO₂, the presence of SO₂ was found to promote NO reduction drastically. At 623 K, for instance, the presence of 20 ppm SO₂ increased NO conversion to N₂/N₂O from 0% to 51%. The

Table 1 NO reduction with CO over supported noble metal (5 wt%) catalysts

	O ₂ (%)	SO ₂ (ppm)	NO conversion to N ₂ (N ₂ O) (%)					
			473 K	573 K	623 K	673 K	723 K	773 K
Pt/SiO ₂	5	0	0 (1.2)	0 (1.3)	0 (0.3)	0 (0.2)	0 (0)	0 (0)
	5	20	0 (1.0)	0 (0.7)	0 (0.4)	0 (0.6)	0 (0.3)	0 (0.2)
Rh/SiO ₂	5	0	0 (0.7)	0 (0.2)	0 (0.2)	0 (0)	0 (0)	0 (0)
	5	20	0 (0.6)	0 (1.1)	0 (1.7)	0 (1.3)	0 (0.6)	0 (0.2)
Pd/SiO ₂	5	0	0 (0.2)	0 (0.2)	0 (0)	0 (0)	0 (0)	0 (0)
	5	20	0 (0.7)	0 (1.2)	0 (0.7)	0 (0.5)	0 (0.2)	0 (0)
Ir/SiO ₂	0	0	7.4 (2.2)	54 (3.6)	61 (2.0)	43 (1.5)	44 (0)	79 (0)
	5	0	0 (0)	0 (0)	0 (0)	0.7 (0.2)	0 (0)	0 (0)
	5	20	0 (1.1)	17 (4.9)	45 (6.3)	16 (2.2)	6.9 (0.7)	1.4 (0.4)
Ir/Al ₂ O ₃	0	0	0.8 (0.9)	35 (4.6)	30 (2.8)	83 (4.8)	84 (1.2)	42 (0)
	5	0	0 (0)	0 (0)	1.4 (0.2)	5.7 (0.4)	12 (0.7)	7.3 (0.6)
	5	20	0 (0.6)	0 (0.6)	2.8 (1.1)	15 (1.9)	6.1 (1.1)	2.4 (0.3)

Conditions: NO = 1000 ppm, CO = 6000 ppm, O₂ = 0 or 5%, SO₂ = 0 or 20 ppm, H₂O = 6%, catalyst weight = 0.04 g, gas flow rate = 90 cm³ min⁻¹.

notable difference between NO reduction with CO and that with H₂, which we have reported before, is that Rh/SiO₂ does not work as an effective catalyst for NO reduction with CO in the presence of O₂ and SO₂. In Table 1 is also given the activity of Ir/Al₂O₃ catalyst. It is noteworthy that the catalytic activity of Ir/Al₂O₃ was only minimally affected by the presence of SO₂, although a slight downward shift of the effective temperature window was observed. Thus, SiO₂ appears to be a more effective support than Al₂O₃ for NO reduction with CO in the presence of O₂ and SO₂.

Since the promotional effect of SO₂ may be related to the change in the supported iridium species, the response of the NO conversion to N₂/N₂O over Ir/SiO₂ to intermittent feed of 20 ppm SO₂ was examined at 623 K. The results are given in Fig. 1. It is clear that the conversion of NO was rapidly increased after introduction of SO₂. The subsequent removal of SO₂ caused a gradual decrease in the conversion of NO, after which the activity returned to its initial steady state in 4 h. This means that the effect of coexisting SO₂ was almost completely lost after removal of SO₂ from the reaction gas, suggesting that the catalytically active sites for NO reduction are created by interaction with coexisting SO₂ on the catalyst surface.

To investigate the effect of SO₂ on the behavior of surface-adsorbed species formed during NO reduction with CO on the supported iridium catalysts, *in situ* IR spectra were measured at 473 K, at which the catalytic activity is low enough to observe surface intermediates due to their low reactivity. Fig. 2

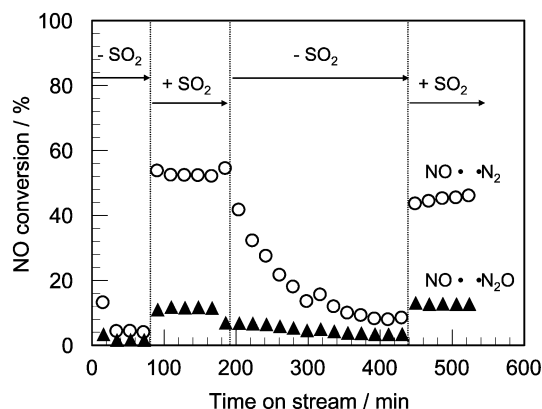


Fig. 1 Response of NO conversion to intermittent feed of 20 ppm SO₂ over 5 wt% Ir/SiO₂ at 623 K. Conditions: NO = 1000 ppm, CO = 6000 ppm, O₂ = 5%, SO₂ = 0 or 20 ppm, H₂O = 6%, catalyst weight = 0.04 g, gas flow rate = 90 cm³min⁻¹.

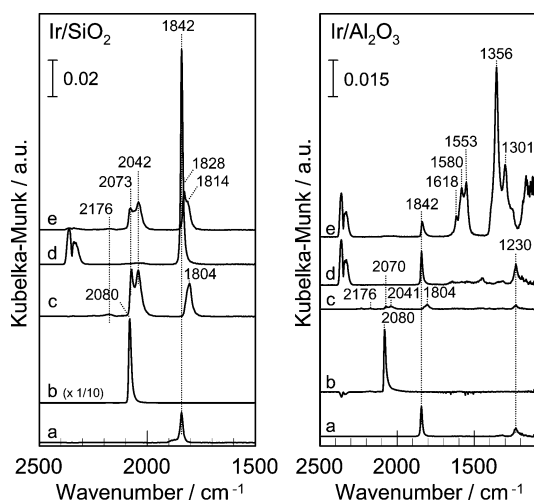


Fig. 2 *In situ* IR spectra of adsorbed species on 5 wt% Ir/SiO₂ and 5 wt% Ir/Al₂O₃ in a flow of (a) NO, (b) CO, (c) NO + CO, (d) NO + CO + O₂ and (e) NO + CO + O₂ + SO₂ at 473 K for 0.5 h.

illustrates *in situ* IR spectra of adsorbed species on Ir/SiO₂ and Ir/Al₂O₃ contacted with a series of gas flows containing some of the selected gas components. In flowing NO/He (spectrum a), an IR band assignable to NO linearly adsorbed onto iridium (Ir–NO^{δ+})⁷ was detected at 1842 cm⁻¹ in both catalysts. Exposure to CO also gave an IR band at 2080 cm⁻¹ due to CO species being adsorbed onto iridium (Ir–CO)⁷ (spectrum b). When a mixture of NO + CO was introduced (spectrum c), a shift of the 1842 cm⁻¹ band to 1804 cm⁻¹ as well as the appearance of a new IR band at 2042 cm⁻¹ was observed. The shift of the NO band to a lower wavenumber due to surface interaction with CO was reported for Rh/Al₂O₃⁸ and Ir/Al₂O₃.⁹ This shift is explained by the perturbing effect of adsorbed CO, suggesting the formation of *cis*-type coordinated species of NO and CO with one metal atom. ($M < \begin{smallmatrix} NO \\ CO \end{smallmatrix}$)^{8,9} Accordingly, the IR bands at 1804 and 2042 cm⁻¹ observed here can be attributed to the formation of $Ir < \begin{smallmatrix} NO \\ CO \end{smallmatrix}$ species.

The $M < \begin{smallmatrix} NO \\ CO \end{smallmatrix}$ species would be decomposed to give CO₂ and nitride (M–N), which can react with NO and CO to produce N₂O and NCO, respectively.⁹ In fact, as can be seen in Fig. 2 (spectrum c), a weak IR band due to the NCO species adsorbed onto iridium (Ir–NCO)¹⁰ was detected at 2176 cm⁻¹ for both catalysts. It is noteworthy that Ir/SiO₂ and Ir/Al₂O₃ showed high activity for NO reduction by CO in the absence of O₂ and SO₂ (Table 1). This suggests that the $Ir < \begin{smallmatrix} NO \\ CO \end{smallmatrix}$ species is a possible intermediate for NO reduction by CO. The fact that the bands at 1804 and 2042 cm⁻¹ disappeared completely on the addition of O₂ to the NO + CO mixture (spectrum d) also supports this idea, since NO reduction by CO did not take place over Ir/SiO₂ and Ir/Al₂O₃ in the presence of O₂ (Table 1).

Although almost the same surface species were detected for Ir/SiO₂ and Ir/Al₂O₃ catalysts in NO reduction by CO in the absence of SO₂, addition of SO₂ to the reaction gas caused different features to appear in the IR spectra (spectrum e). For Ir/SiO₂ catalyst, the presence of coexisting SO₂ caused a shift of the 1842 cm⁻¹ band to lower wavenumbers as well as the appearance of IR bands at 2042 and 2073 cm⁻¹. These band features are consistent with those obtained in the flow of NO + CO (spectrum c). Namely, the $Ir < \begin{smallmatrix} NO \\ CO \end{smallmatrix}$ surface species can be produced during NO reduction by CO in the presence of O₂ and SO₂. Therefore, the coexisting SO₂ is likely to play an important role in the formation of the $Ir < \begin{smallmatrix} NO \\ CO \end{smallmatrix}$ surface species, resulting in the significant activity enhancement described above (Table 1). On the other hand, no change in the frequency of the 1842 cm⁻¹ band was observed for Ir/Al₂O₃ in the presence of coexisting SO₂, nor the absorption band of the $Ir < \begin{smallmatrix} NO \\ CO \end{smallmatrix}$ species. Instead, the presence of SO₂ gave rise to SO₄²⁻ species (1356 cm⁻¹) and NO₃⁻ species (1301, 1553, 1580 and 1618 cm⁻¹) on Al₂O₃.

In summary, Ir/SiO₂ shows excellent activity with respect to NO reduction with CO in the presence of O₂ and SO₂. Although the details of the reaction mechanism are not yet known, coexisting SO₂ appears to play an important role in creating the sites for formation of the $Ir < \begin{smallmatrix} NO \\ CO \end{smallmatrix}$ surface species as a reaction intermediate.

Notes and references

- H. Hamada, *Catal. Today*, 1994, **22**, 21.
- K. Yokota, M. Fukui and T. Tanaka, *Appl. Surf. Sci.*, 1997, **121/122**, 273.
- R. Burch, A. A. Shestov and J. A. Sullivan, *J. Catal.*, 1999, **188**, 69.
- A. Ueda, T. Nakao, M. Azuma and T. Kobayashi, *Catal. Today*, 1998, **45**, 135.
- M. Ogura, A. Kawamura, M. Matsukata and E. Kikuchi, *Chem. Lett.*, 2000, 146.
- T. Yoshinari, K. Sato, M. Haneda, Y. Kintaichi and H. Hamada, *Appl. Catal. B*, 2003, **41**, 157.
- F. Solymosi and J. Raskó, *J. Catal.*, 1980, **62**, 253.
- H. Arai and H. Tominaga, *J. Catal.*, 1976, **43**, 131.
- F. Solymosi and J. Raskó, *J. Catal.*, 1980, **63**, 217.
- J. Raskó and F. Solymosi, *J. Catal.*, 1981, **71**, 219.