

Activity Enhancement of WO₃-Promoted Ir/SiO₂ Catalysts by High-Temperature Calcination for the Selective Reduction of NO with CO

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The catalytic activity of WO₃-promoted Ir/SiO₂ for the selective reduction of NO with CO in the presence of excess O₂ is strongly dependent on the catalyst calcination conditions in the preparation process. WO₃/Ir/SiO₂ catalyst prepared by air calcination showed higher activity than that prepared by H₂ reduction. The activity of WO₃/Ir/SiO₂ catalyst prepared by air calcination was also found to increase with increasing calcination temperature up to 1073 K; however, a further increase in the temperature to 1173 K caused a decrease in the NO reduction activity, although very high selectivity was observed for this catalyst. The lack of a major difference in the apparent activation energy for NO reduction suggests that NO reduction occurs at the same reaction sites, irrespective of calcination temperature. On the other hand, the apparent activation energy for CO oxidation increased with increased calcination temperature, suggesting that the reaction sites for CO oxidation change according to calcination temperature. Catalyst characterizations revealed that iridium species interacting strongly with WO₃ are preferentially created by high-temperature air calcination. A combination of partially reduced iridium species (IrO_{2-x}) and WO₃ (IrO_{2-x}-WO₃) was concluded to act as catalytically active sites of WO₃/Ir/SiO₂ for NO reduction.

The selective catalytic reduction of NO in an oxidizing atmosphere is a promising technology for reducing NO_x emissions from diesel and lean-burn engines. A great number of studies have been made recently on the use of hydrocarbons as a reductant,¹ while until recently CO has not been regarded as an effective reductant. The use of CO as a reductant is, in practice, desirable, since vehicle exhaust generally contains CO. It is also known that CO can be relatively easily formed by controlling engine operation.

Various materials have been examined so far for catalytic activity for the selective reduction of NO with CO in the presence of O₂. To our knowledge, a paper by Tauster et al. is the first to report the selective reduction of NO with CO, which takes place over Ir/Al₂O₃.² Ogura et al. found that NO can successfully be reduced to N₂ with CO over Ir/silicalite catalyst and that the catalytic activity is not influenced by coexisting SO₂.³ Our group also discovered that Ir/SiO₂ is an effective catalyst for NO reduction with CO in the presence of O₂ and SO₂.⁴⁻⁶ The most interesting feature of this catalyst is the promotive effect of coexisting SO₂ on NO reduction, the role of which is considered to stabilize the catalytically active Ir⁰ site in oxidizing atmospheres.⁷ Ir/ZSM-5⁸ and Ir/WO₃^{9,10} have also been reported to effectively catalyze NO reduction with CO under lean conditions. Iridium thus seems to be the only active metal species to catalyze this reaction effectively.

Recently, Nanba et al. reported that the addition of W into Ir/SiO₂ drastically enhances NO reduction activity, even in the absence of SO₂.^{11,12} The Ir/WO₃-SiO₂ catalyst showed high

activity at a high space velocity (over 50000 h⁻¹). We also extensively studied the selective reduction of NO with CO over Ir/WO₃-SiO₂ catalyst and found that the catalytic activity of Ir/WO₃-SiO₂ catalyst strongly depends on the catalyst pre-treatment conditions.¹³ When Ir/WO₃-SiO₂ was treated in flowing 6% H₂O/He at 873 K after reduction in H₂ at 873 K, its activity was significantly enhanced. On the other hand, the activity of Ir/WO₃-SiO₂ oxidized at 873 K following reduction was quite low. On the basis of structural characterizations of the catalysts treated under different conditions, it was concluded that Ir metal species interacting strongly with W oxide (denoted as Ir-WO_x) are created by H₂O treatment as active sites for NO reduction with CO. This suggests that the dispersion of Ir and W oxide and their interactions are key factors in the catalytic activity of Ir/WO₃-SiO₂. In the present study, we investigated the influence of the state of Ir and W oxide on the catalytic activity of WO₃-added Ir/SiO₂ by using WO₃/Ir/SiO₂ catalysts prepared by changing the catalyst calcination conditions in the preparation process.

Experimental

Catalyst Preparation. Ir/SiO₂ was prepared by impregnation of SiO₂ (Fuji Silysia Chemicals, Cariat G-10, 300 m² g⁻¹) with an aqueous solution of [Ir(NH₃)₆](OH)₃ (Tanaka Kikinzoku Kogyo), followed by drying at 383 K overnight and then calcination at 873 K for 6 h in air. The loading of Ir metal was fixed at 0.5 wt % in this study. (NH₄)₁₀W₁₂O₄₁·5H₂O and citric acid were dissolved in distilled water to which the Ir/SiO₂ had been added. The loading

of WO₃ was fixed at 10 wt%. The solvent was evaporated at 363 K, and the resulting mixture was dried at 383 K overnight and calcined at 873 K for 6 h in air to obtain WO₃/Ir/SiO₂ powder. The reduced Ir/SiO₂ was also prepared by reducing at 873 K for 6 h in flowing 10% H₂/N₂ after impregnation with Ir precursor. The addition of W to the reduced Ir/SiO₂ was performed in the same manner as described above. The resulting W-added Ir/SiO₂ was again reduced at 873 K for 6 h in flowing 10% H₂/N₂. The catalysts calcined in air are abbreviated as Ir/SiO₂(Ox) and WO₃/Ir/SiO₂(Ox), while those reduced with H₂/N₂ are abbreviated as Ir/SiO₂(Rd) and WO₃/Ir/SiO₂(Rd).

As for the WO₃/Ir/SiO₂(Ox) catalysts, the WO₃/Ir/SiO₂ was further calcined at 973, 1073, and 1173 K for 6 h in air. In this case, the samples are expressed as WO₃/Ir/SiO₂(x), where x is the catalyst calcination temperature.

Catalytic Activity Measurement. Catalytic activity was evaluated using a fixed-bed continuous flow reactor. A reaction gas mixture containing NO (500 ppm), CO (3000 ppm), O₂ (5%), SO₂ (1 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 He at 873 K for 2 h, at a rate of 90 cm³ min⁻¹ (SV = ca. 75000 h⁻¹). The effluent gas was analyzed with the use of two online gas chromatographs equipped with a Molecular Sieve 5A column (for analyzing N₂ and CO) and a Porapak Q column (for analyzing CO₂ and N₂O). The reaction temperature was decreased from 873 to 473 K in steps of 20–50 K, and the steady-state catalytic activity was measured at each temperature. N₂ was mainly formed as the NO reduction products. The selectivity to N₂ (N₂/(N₂ + N₂O)) was more than 90% in most cases.

Catalyst Characterization. The crystal structure was identified by XRD (Mac Science M18XHF²²) measurements using Cu K α radiation at 40 kV and 150 mA. The BET surface area of the samples was determined using a volumetric adsorption apparatus (Quantachrome, Nova-4200e) by N₂ adsorption at 77 K. Elemental analysis for Ir and W was conducted using inductively coupled plasma (ICP) using a Shimadzu ICPS-1000IV.

The amount of chemisorbed CO was measured using a pulse method. The sample (100 mg) was first reduced with H₂ at 673 K for 1 h, then cooled to 323 K in flowing He. Several pulses of CO were introduced to the sample until no more adsorption was observed. Iridium dispersion was calculated by assuming a stoichiometry of 1.0 CO/Ir.¹⁴

Temperature-programmed reduction (TPR) measurements were carried out to estimate the reducibility of the WO₃/Ir/SiO₂ catalysts. Each catalyst sample (100 mg) was oxidized with 20% O₂/N₂ at 873 K for 1 h and then cooled to room temperature. The gas flow was then switched to 10% H₂/Ar and the temperature was raised to 973 K at a rate of 10 K min⁻¹. The consumption of H₂ was monitored using a thermal conductivity detector (TCD). Reduction of CuO to metallic copper was used to calibrate the TPR apparatus for H₂ consumption.

Results and Discussion

Influence of Calcination Atmosphere. Activity of Ir/SiO₂ Catalyst: Figure 1 shows the activity of Ir/SiO₂(Ox) and Ir/SiO₂(Rd) for NO reduction with CO in the presence of O₂ and SO₂. It is apparent that little NO reduction occurred on Ir/SiO₂(Rd) that had been reduced at 873 K. On the other hand, Ir/SiO₂(Ox) showed NO reduction activity in the temperature range of 523–623 K, with the maximum NO conversion as high as 40% at 553 K. In Table 1 are summarized the BET surface

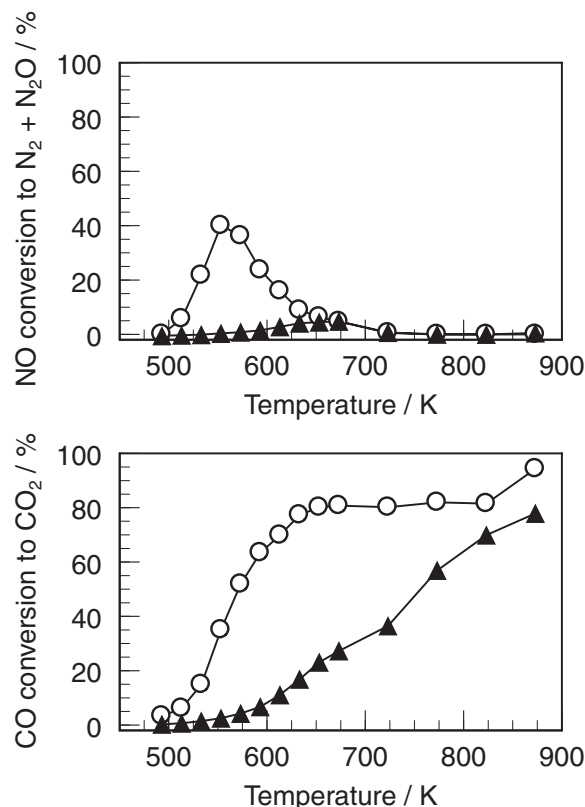


Figure 1. Activity of Ir/SiO₂ catalysts calcined under different conditions for NO reduction with CO in the presence of O₂ and SO₂. (○) Ir/SiO₂(Ox) calcined in air at 873 K, (▲) Ir/SiO₂(Rd) reduced in flowing 10% H₂/N₂ at 873 K. Conditions: NO, 500 ppm; CO, 3000 ppm; O₂, 5%; SO₂, 1 ppm; H₂O, 6%; and W/F = 0.0267 g s cm⁻³.

Table 1. Physical Properties of Ir/SiO₂ and WO₃/Ir/SiO₂

Catalyst	Calcination atmosphere	BET surface area /m ² g ⁻¹	Ir dispersion (Ir/CO)
Ir/SiO ₂ (Rd)	H ₂	261	0.61
Ir/SiO ₂ (Ox)	Air	267	0.10
WO ₃ /Ir/SiO ₂ (Rd)	H ₂	235	n.a. ^{a)}
WO ₃ /Ir/SiO ₂ (Ox)	Air	235	n.a. ^{a)}

a) n.a.: not available.

area of and Ir dispersion in Ir/SiO₂(Ox) and Ir/SiO₂(Rd). No difference in the BET surface was observed for both catalysts, while Ir dispersion was considerably higher for Ir/SiO₂(Rd) than for Ir/SiO₂(Ox). We have already reported that the catalytic activity of Ir/SiO₂ for the selective reduction of NO with CO is closely dependent on Ir dispersion:¹⁵ the turnover frequency (TOF) for NO reduction decreased with increasing Ir dispersion. This effect of Ir dispersion is explained by the stability of catalytically active Ir metal species: larger iridium crystallites show more resistance to oxidation and are much more easily reduced under reaction conditions, resulting in the formation of stable iridium metal sites on which NO reduction occurs. Consequently, the low activity of Ir/SiO₂(Rd) can be ascribed to the oxidation of Ir metal to IrO₂ under the reaction conditions due to its high Ir dispersion.

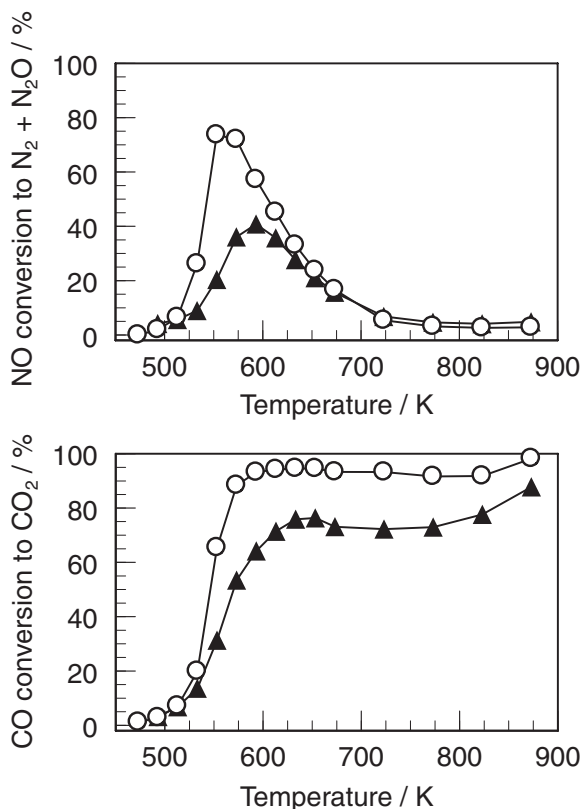


Figure 2. Activity of WO₃/Ir/SiO₂ catalysts calcined under different conditions for NO reduction with CO in the presence of O₂ and SO₂. (○) WO₃/Ir/SiO₂(Ox) calcined in air at 873 K, (▲) WO₃/Ir/SiO₂(Rd) reduced in flowing 10% H₂/N₂ at 873 K. The reaction conditions are the same as for Figure 1.

Activity of WO₃/Ir/SiO₂ Catalyst: Figure 2 shows the activity of WO₃/Ir/SiO₂(Ox) and WO₃/Ir/SiO₂(Rd) for NO reduction with CO in the presence of O₂ and SO₂. In contrast to the results of Ir/SiO₂ shown in Figure 1, WO₃/Ir/SiO₂(Rd) showed NO reduction activity. However, the activity of WO₃/Ir/SiO₂(Ox) was higher than that of WO₃/Ir/SiO₂(Rd). The same results were obtained for CO oxidation activity.

In order to estimate the Ir dispersion, CO adsorption measurements were also performed. However, no CO adsorption on WO₃/Ir/SiO₂ was observed. We have also observed in another set of experiments that Ir/WO₃/SiO₂, which was prepared by impregnating Ir precursor onto WO₃/SiO₂, does not adsorb CO.¹⁶ Therefore, the phenomenon that CO was not adsorbed on WO₃/Ir/SiO₂ is not due to covering of the Ir sites by WO₃. The inhibition of CO adsorption on supported Ir catalysts by WO₃ was also reported by Lecarpentier et al.¹⁷ They ascribed this phenomenon to the aggregation of Ir particles from the results of toluene hydrogenation, which is a structure-insensitive reaction, taking place over Ir metal sites. In order to clarify the possibility of the aggregation of Ir particles by WO₃ addition, XRD patterns of WO₃/Ir/SiO₂(Ox) and WO₃/Ir/SiO₂(Rd) were measured. As shown in Figure 3a, peaks due to IrO₂ (ICDD 15-870) and monoclinic WO₃ (ICDD 43-1035) were observed in the XRD pattern of WO₃/Ir/SiO₂(Ox). On the other hand, no distinct peaks were detected in

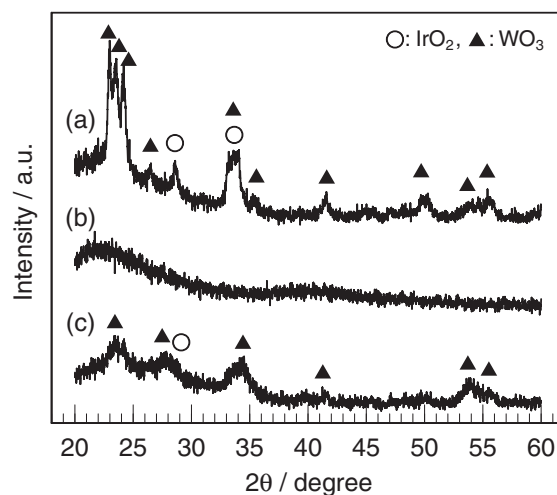


Figure 3. XRD patterns of (a) WO₃/Ir/SiO₂(Ox) calcined in air at 873 K, (b) WO₃/Ir/SiO₂(Rd) reduced in flowing 10% H₂/N₂ at 873 K, and (c) WO₃/Ir/SiO₂(Rd) after use in the reaction.

the XRD pattern of WO₃/Ir/SiO₂(Rd) (Figure 3b), suggesting that Ir and W species are highly dispersed in WO₃/Ir/SiO₂(Rd). This result indicates that Ir particles were not aggregated by the addition of WO₃ in the present study. We consider that the inhibition of CO adsorption on Ir by WO₃ is probably due to a strong interaction of Ir with WO₃. The details of the interaction between Ir and WO₃ will be discussed in the later part of this paper.

Since the selective reduction of NO with CO was carried out under oxidizing conditions, highly dispersed Ir and W species in WO₃/Ir/SiO₂(Rd) are likely to be easily oxidized to IrO₂ and WO₃ during the reaction, respectively. In fact, distinct but broad XRD peaks due to IrO₂ and WO₃ were observed in the XRD pattern of WO₃/Ir/SiO₂(Rd) after use in the reaction (Figure 3c). The formation of IrO₂ and WO₃ would result in low NO reduction activity. On the other hand, WO₃/Ir/SiO₂(Ox) showed high NO reduction activity (Figure 2), although the presence of IrO₂ and WO₃ was observed in the XRD pattern (Figure 3a). As described in the experimental section, the catalyst was pretreated in flowing He at 873 K prior to the reaction, leading to the formation of partially reduced iridium oxide (IrO_{2-x}) on which NO reduction with CO takes place.¹⁸ However, the IrO_{2-x} species thus formed would not be easily oxidized to IrO₂ under the reaction conditions, since larger iridium crystallites show more resistance to oxidation.¹⁵ In conclusion, the catalyst pretreatment conditions in the preparation process strongly affect the Ir species that are responsible for the NO reduction activity. The air calcination of supported Ir catalysts is an important procedure for obtaining stable catalytically active Ir species under these reaction conditions.

Influence of Calcination Temperature for WO₃/Ir/SiO₂(Ox) Catalysts. **Catalytic Activity of WO₃/Ir/SiO₂:** Figure 4 shows the catalytic activity of WO₃/Ir/SiO₂ calcined in air at different temperatures for NO reduction with CO in the presence of O₂ and SO₂. The catalytic activity strongly depends on the calcination temperature. NO conversions at temperatures

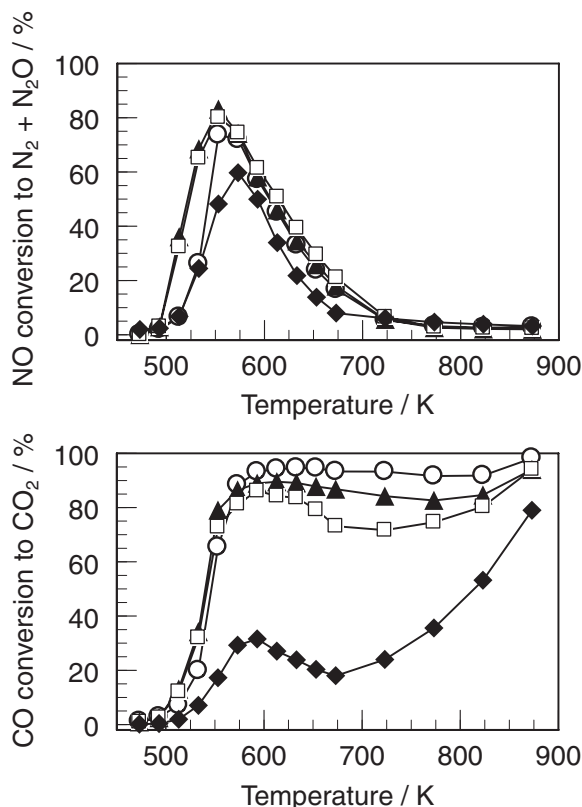
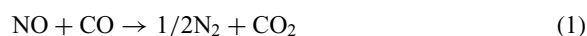


Figure 4. Activity of WO₃/Ir/SiO₂ catalysts calcined at different temperatures in air for NO reduction with CO in the presence of O₂ and SO₂. Calcination temperature: (○) 873, (▲) 973, (□) 1073, and (◆) 1173 K. The reaction conditions are the same as for Figure 1.

below 533 K were clearly enhanced when the calcination temperature was elevated from 873 to 1073 K. No great difference in the activity for NO reduction was observed between WO₃/Ir/SiO₂(973) and WO₃/Ir/SiO₂(1073), which showed the highest NO conversion. A further increase in the calcination temperature to 1173 K, however, caused depression of NO conversion. On the other hand, CO conversion monotonically decreased on increasing the calcination temperature to 1073 K at the reaction temperatures above 573 K, after which a significant drop in CO conversion was observed for WO₃/Ir/SiO₂(1173) in the entire temperature range. In order to get information on the practical performance of the most active WO₃/Ir/SiO₂(1073), the time on stream activity was measured at 553 K. As shown in Figure 5, no significant decrease in the NO conversion to N₂ + N₂O was observed during the reaction until 30 h. The selectivity for N₂ formation was almost constant at about 90%. CO oxidation activity was found to be clearly increased with time on stream.

Concerning the selective reduction of NO with CO in the presence of O₂, there are two unit reactions: NO reduction with CO (eq 1) and CO oxidation by O₂ (eq 2):



On the basis of eqs 1 and 2, the selectivity for NO reduction (S_{N_2}) can be defined as follows.

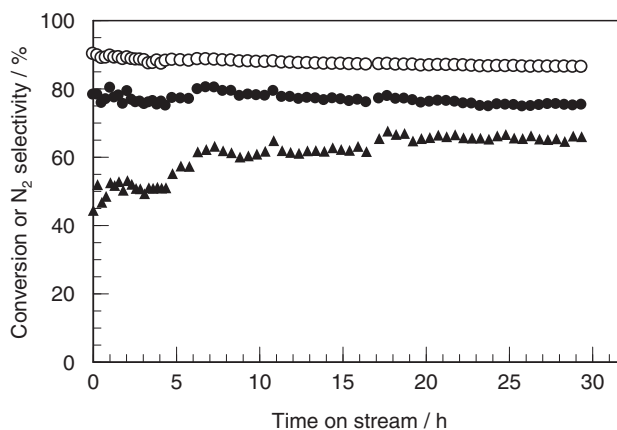


Figure 5. Time on stream conversion of NO to N₂ + N₂O (●) and CO to CO₂ (▲), and selectivity to N₂ (N₂/(N₂ + N₂O)) (○) over WO₃/Ir/SiO₂(1073) catalyst for NO reduction with CO in the presence of O₂ and SO₂ at 553 K. The reaction conditions are the same as for Figure 1.

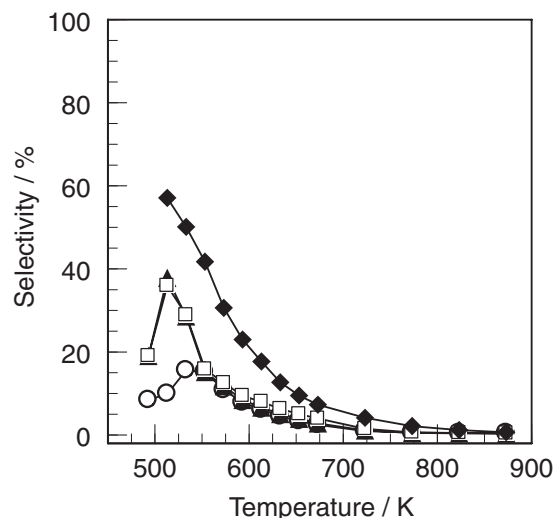


Figure 6. Selectivity for NO reduction on WO₃/Ir/SiO₂ catalysts calcined at different temperatures in air for NO reduction with CO in the presence of O₂ and SO₂. Calcination temperature: (○) 873, (▲) 973, (□) 1073, and (◆) 1173 K. The reaction conditions are the same as for Figure 1.

$$S_{\text{N}_2} = (4 \times \text{N}_2 \text{ yield (ppm)}) / (2 \times \text{CO}_2 \text{ yield (ppm)}) \times 100 \quad (3)$$

The selectivity for NO reduction over WO₃/Ir/SiO₂ thus estimated is shown in Figure 6. Clearly, selectivity was improved as the catalyst was calcined at higher temperatures. This result suggests that Ir species on which NO reduction selectively takes place are predominantly present in the WO₃/Ir/SiO₂(1173).

To obtain more information on the reaction sites, the apparent activation energies for N₂ and CO₂ formation over WO₃/Ir/SiO₂ were evaluated from the Arrhenius plots. Figure 7 shows the Arrhenius plots of the reaction rates for NO reduction to N₂ (r_{NO}) and CO oxidation to CO₂ (r_{CO}) measured under nearly differential reaction conditions giving NO conversions of less than 20% by varying the catalyst

weight. In Table 2 are summarized the apparent activation energies estimated from the slopes of the Arrhenius plots. It is of interest that almost the same apparent activation energies for NO reduction to N₂ ($E_{A,NO}$) were observed for all the WO₃/Ir/SiO₂ catalysts (153–161 kJ mol⁻¹), indicating that NO reduction to N₂ occurs at the same reaction sites, irrespective of calcination temperature. On the other hand, the apparent activation energies for CO oxidation to CO₂ ($E_{A,CO}$) varied according to calcination temperature: 122 kJ mol⁻¹ for WO₃/Ir/SiO₂(873), 148 kJ mol⁻¹ for WO₃/Ir/SiO₂(973) and WO₃/Ir/SiO₂(1073), and 170 kJ mol⁻¹ for WO₃/Ir/SiO₂(1173). This result is in good agreement with the selectivity shown in Figure 6. The number of reaction sites for CO oxidation by O₂ seems to be decreased by high-temperature calcination, resulting in an improvement of the reaction selectivity.

Catalyst Characterization: Since selective reduction of NO with CO does not take place over WO₃/SiO₂, iridium must be the catalytically active component. To obtain information on the reaction sites, catalyst characterizations were performed for WO₃/Ir/SiO₂ calcined at different temperatures.

Table 2. Apparent Activation Energies of NO Reduction to N₂ ($E_{A,NO}$) and CO Oxidation to CO₂ ($E_{A,CO}$)

Catalyst	Calcination temperature/K	$E_{A,NO}$ /kJ mol ⁻¹	$E_{A,CO}$ /kJ mol ⁻¹
WO ₃ /Ir/SiO ₂ (Ox)	873	157.9	121.9
	973	157.5	147.4
	1073	160.8	148.4
	1173	153.2	169.8

As given in Table 3, the surface area of WO₃/Ir/SiO₂ has considerably decreased from 235 m² g⁻¹ for WO₃/Ir/SiO₂(873) to 41 m² g⁻¹ for WO₃/Ir/SiO₂(1173). However, the depression of the activity of WO₃/Ir/SiO₂ by increasing the calcination temperature from 873 to 1173 K was not prominent (Figure 4). It is also noteworthy that WO₃/Ir/SiO₂(1073) showed the highest activity for NO reduction, in spite of its low surface area.

The crystallite structure of WO₃/Ir/SiO₂ was analyzed by XRD. Figure 8 shows the observed XRD patterns. Clear XRD peaks assignable to monoclinic WO₃ and IrO₂ were detected in all the samples. No difference in the crystallite structure of WO₃/Ir/SiO₂ was observed corresponding to calcination temperature. Their peak width decreased with increasing calcination temperature, indicating crystal growth. The crystallite size of IrO₂ and WO₃ calculated from the XRD peaks due to the (110) plane at $2\theta = \text{ca. } 28.1^\circ$ (ICDD 15-870) and the (222) plane at $2\theta = \text{ca. } 41.9^\circ$ (ICDD 43-1035), respectively, using Scherrer's equation. As summarized in Table 3, the crystallite size of IrO₂ and WO₃ increased with increasing the calcination temperature. This is in agreement with the results of BET surface area. These results suggest the presence of important factors, other than the number of reaction sites, which would be related to the crystallite size of IrO₂ and WO₃.

The reduction behavior of WO₃/Ir/SiO₂ was monitored by TPR. Normally, the reducibility of noble metals is considerably influenced by the metal-support interaction.^{19,20} Figure 9 shows the TPR profiles of WO₃/Ir/SiO₂ along with those of Ir/SiO₂ and WO₃/SiO₂ as the reference samples. Ir/SiO₂ and WO₃/SiO₂ gave reduction peaks at 508 and above 723 K,

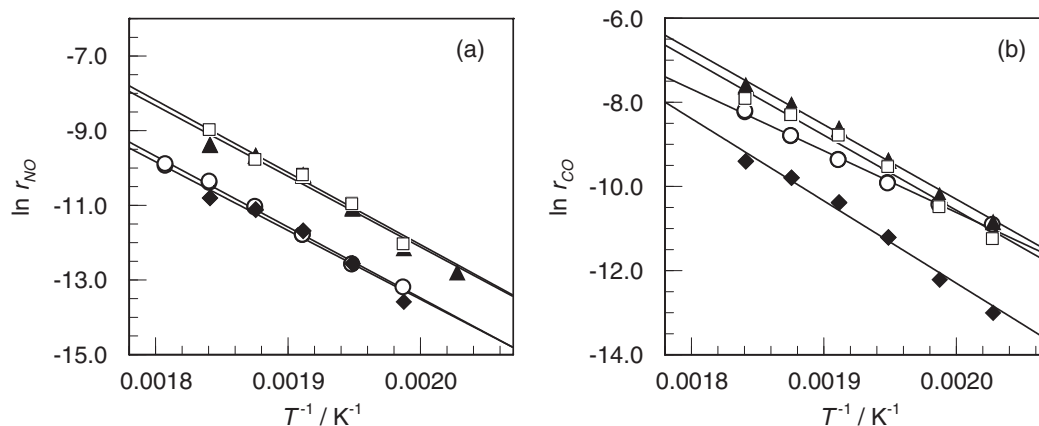


Figure 7. Arrhenius plots of (a) reaction rate for NO to N₂ and (b) reaction rate for CO to CO₂ over WO₃/Ir/SiO₂ catalysts calcined at different temperatures in air for NO reduction with CO in the presence of O₂ and SO₂. Calcination temperature: (○) 873, (▲) 973, (□) 1073, and (◆) 1173 K.

Table 3. Physical Properties of WO₃/Ir/SiO₂ Calcined at Different Temperatures Determined

Catalyst	Calcination temperature /K	BET surface area /m ² g ⁻¹	Crystallite size/nm		Composition/wt %	
			IrO ₂	WO ₃	Ir	W ^{a)}
WO ₃ /Ir/SiO ₂ (Ox)	873	235	21.8	14.1	0.36	10.2
	973	205	22.1	14.3	0.32	10.4
	1073	114	27.3	15.1	0.30	9.96
	1173	41	32.4	19.0	0.15	9.70

a) Composition of W was calculated as WO₃.

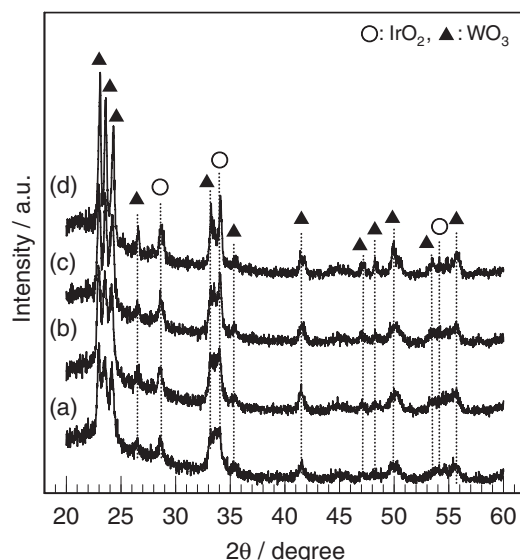


Figure 8. XRD patterns of WO₃/Ir/SiO₂ calcined at (a) 873, (b) 973, (c) 1073, and (d) 1173 K.

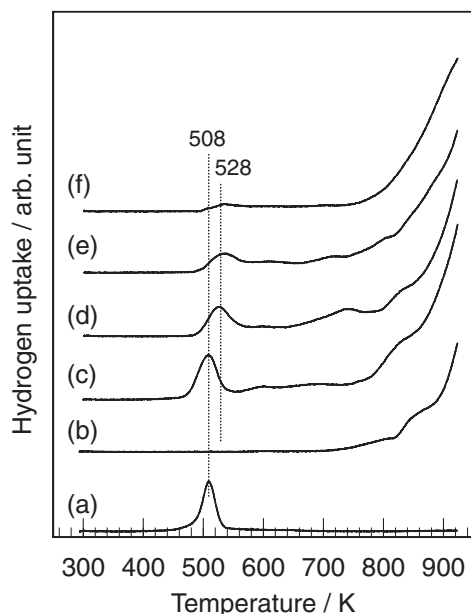


Figure 9. TPR profiles of (a) Ir/SiO₂, (b) WO₃/SiO₂ and WO₃/Ir/SiO₂ calcined at (c) 873, (d) 973, (e) 1073, and (f) 1173 K.

respectively, ascribed to the reduction of IrO₂ and WO₃. Although these two peaks were also observed for WO₃/Ir/SiO₂, the temperature of H₂ consumption peaks changed according to the calcination temperature. WO₃/Ir/SiO₂(873) gave the reduction peak of IrO₂ at 508 K (Figure 9c), which is the same as that for Ir/SiO₂, whereas the peak shifted to higher temperatures for the other WO₃/Ir/SiO₂ samples (Figures 9d–9f). The shift of this peak to a higher temperature suggests a strong interaction between Ir and W species, leading to the consideration that the Ir–WO₃ interaction can be created by high-temperature calcination. In the TPR profiles of WO₃/Ir/SiO₂(873), WO₃/Ir/SiO₂(973), and WO₃/Ir/SiO₂(1073), broad H₂ consumption peaks were also detected at around 573–773 K,

Table 4. Summary of H₂-TPR Measurements

Catalyst	Calcination temperature /K	Amount of H ₂ consumption / $\mu\text{mol-H}_2\text{ g-cat}^{-1}$	
		Peak around 508 K	Peaks in 573–773 K
Ir/SiO ₂ (Ox)	873	38.1	n.a. ^{a)}
WO ₃ /Ir/SiO ₂ (Ox)	873	36.1	41.7
	973	26.3	76.7
	1073	21.9	61.5
	1173	6.4	19.9

a) n.a.: not available.

which can be ascribed to the reduction of oxygen present at the Ir–WO₃ interface.¹⁸ The presence of a strong Ir–WO₃ interaction is also suggested by this result.

As can be seen in Figure 9, the amount of H₂ consumption for the reduction of IrO₂ and oxygen present at the Ir–WO₃ interface is different according to the calcination temperature. The quantitative results were summarized in Table 4. Obviously, the amount of H₂ consumption for the reduction of IrO₂ at around 508 K decreased with increasing calcination temperature. The decrease in the H₂ consumption would be due to a loss of iridium during high temperature calcination, which was confirmed by elemental analysis given in Table 3. The amount of H₂ consumption for the peaks between 573 and 773 K was also summarized in Table 4. It is apparent that higher H₂ consumption was obtained for WO₃/Ir/SiO₂(973) and WO₃/Ir/SiO₂(1073), suggesting that these catalysts contain a large number of Ir species interacting strongly with WO₃.

Reaction Sites of WO₃/Ir/SiO₂: As can be seen in Figure 4, the catalytic activity of WO₃/Ir/SiO₂ for NO reduction with CO strongly depended on the calcination temperature. Nevertheless, similar apparent activation energies for NO reduction to N₂ ($E_{A,\text{NO}}$) were obtained for all the WO₃/Ir/SiO₂ catalysts (153–161 kJ mol^{−1}) (Table 2). This clearly indicates that the reaction site for NO reduction on WO₃/Ir/SiO₂ is the same.

We reported that the active sites of Ir/WO₃/SiO₂ for NO reduction with CO are Ir–WO_x ($x = 2.92\text{--}3$) species in which Ir metal interacts strongly with W oxide.¹³ This means that the presence of reduced Ir sites is necessary for the NO reduction activity. In the present study, however, WO₃/Ir/SiO₂ catalyst was pretreated not in flowing H₂ but in flowing He at 873 K, under which conditions iridium oxide (IrO₂) is not completely reduced to Ir metal. As described before, a partially reduced iridium oxide (IrO_{2−x}) would be formed by He treatment at 873 K. Nevertheless, WO₃/Ir/SiO₂ effectively catalyzed the NO reduction with CO in the presence of O₂ and SO₂. This fact suggests that the IrO_{2−x} species thus formed acts as a catalytically active site for NO reduction. In addition, the presence of a strong interaction between Ir and WO₃ was indicated from the TPR profiles of WO₃/Ir/SiO₂(973) and WO₃/Ir/SiO₂(1073) (Figures 9d and 9e). The amount of H₂ consumption for the reduction of oxygen present at the Ir–WO₃ interface was also found to be higher for the both catalysts than for other catalysts (Table 4). Since these catalysts showed high NO reduction activity (Figure 4), it is suggested that a partially reduced IrO_{2−x} species interacting strongly with WO₃, abbrev-

viated as $\text{IrO}_{2-x}\text{-WO}_3$, is the catalytically active site for NO reduction.

The reaction site for CO oxidation by O_2 is probably different from that for NO reduction. As can be seen in Figure 6, $\text{WO}_3/\text{Ir}/\text{SiO}_2(873)$ was the least selective catalyst for NO reduction. In the TPR profiles of $\text{WO}_3/\text{Ir}/\text{SiO}_2(873)$, the H_2 consumption peak for IrO_2 was at the same temperature as that for Ir/SiO_2 . The ratio of H_2 consumption for the peaks between 573 and 773 K to that for the peak at 508 K was found to be 1.16, which is quite small compared with the other catalysts (2.81–3.11), suggesting the presence of less iridium species interacting strongly with WO_3 in $\text{WO}_3/\text{Ir}/\text{SiO}_2(873)$. Taking into account the fact that the apparent activation energy for CO oxidation ($E_{\text{A,CO}}$) on $\text{WO}_3/\text{Ir}/\text{SiO}_2(873)$ (122 kJ mol^{-1}) was different from that on other catalysts ($147\text{--}170 \text{ kJ mol}^{-1}$), CO oxidation by O_2 preferentially takes place over iridium species not interacting with WO_3 . Thus, the ratio of iridium species with or without an interaction with WO_3 determines the activity of $\text{WO}_3/\text{Ir}/\text{SiO}_2$ for NO reduction.

Since $\text{WO}_3/\text{Ir}/\text{SiO}_2(1173)$ showed good selectivity for NO reduction (Figure 6), most of the iridium species in $\text{WO}_3/\text{Ir}/\text{SiO}_2(1173)$ are believed to interact strongly with WO_3 . It is noteworthy that the H_2 consumption peak of IrO_2 for $\text{WO}_3/\text{Ir}/\text{SiO}_2(1173)$ is very weak compared with that for $\text{WO}_3/\text{Ir}/\text{SiO}_2(873)$, suggesting a loss of iridium during calcination at 1173 K, which was actually confirmed by the elemental analysis given in Table 3. While the weight composition of iridium in $\text{WO}_3/\text{Ir}/\text{SiO}_2(873)$ (0.36 wt %) was slightly lower than the expected value from the preparation conditions, the weight composition of iridium in $\text{WO}_3/\text{Ir}/\text{SiO}_2$ decreased on increasing the calcination temperature, resulting in a sharp drop to 0.15 wt % for $\text{WO}_3/\text{Ir}/\text{SiO}_2(1173)$. A loss of iridium after the calcination at 1173 K would be due to a vaporization of iridium oxide during the calcination, because it is known that IrO_2 is converted to IrO_3 under oxidizing conditions at the temperatures above 1173 K and IrO_3 thus formed is easily vaporized because of its high vapor pressure.²¹ In spite of such a low loading of Ir, it is of interest that $\text{WO}_3/\text{Ir}/\text{SiO}_2(1173)$ showed relatively high NO reduction activity (Figure 4), with a maximum NO conversion of 60% at 573 K. It can be concluded that iridium species strongly interacting with WO_3 are the only species encountered in the $\text{WO}_3/\text{Ir}/\text{SiO}_2(1173)$.

Conclusion

$\text{WO}_3/\text{Ir}/\text{SiO}_2$ catalyst prepared by air calcination showed higher activity for the selective reduction of NO with CO than that by H_2 reduction. Although the formation of highly dispersed Ir and W species in $\text{WO}_3/\text{Ir}/\text{SiO}_2$ by H_2 reduction was suggested from the XRD pattern, the Ir and W species were confirmed to be easily oxidized to IrO_2 and WO_3 during the reaction, resulting in a low NO reduction activity. On the other hand, as for the $\text{WO}_3/\text{Ir}/\text{SiO}_2$ catalyst prepared by air calcination, a partially reduced iridium oxide (IrO_{2-x}) formed by He treatment at 873 K as a pretreatment for the reaction was considered to be stable under the reaction conditions, leading to high NO reduction activity.

The catalytic activity of $\text{WO}_3/\text{Ir}/\text{SiO}_2$ prepared by air calcination was also found to strongly depend on the calcination temperature. NO conversion was clearly enhanced by elevating the calcination temperature from 873 to 1073 K. The highest NO conversion was achieved on $\text{WO}_3/\text{Ir}/\text{SiO}_2(1073)$. Iridium species interacting strongly with WO_3 were found to be selectively created by high-temperature calcination. The active site of $\text{WO}_3/\text{Ir}/\text{SiO}_2$ for NO reduction consisted of a combination of partially reduced IrO_{2-x} and WO_3 , i.e., $\text{IrO}_{2-x}\text{-WO}_3$ species, formed by He pretreatment at 873 K. Oxidation of CO by O_2 was believed to take place preferentially over iridium species not interacting with WO_3 .

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