

Drastic Enhancement of SCR of NO over Ir Catalyst through Formation of Metallic Iridium on Na-zeolite

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The co-existence of both CO and H₂ and the use of Na-zeolite supports leads to effective NO reduction below 500 K for the SCR of NO over low loaded (0.5 wt %) Ir catalyst, which was attributed to the formation of metallic iridium species.

A selective catalytic reduction of NO in the presence of excess oxygen is a potential method to remove NO_x from lean-burn and diesel exhausts. Among a number of catalysts, Ir catalysts are effective in the reduction of NO by not only unsaturated hydrocarbon,¹⁻³ but also CO^{3,4} and hydrogen³ under lean-burn exhaust conditions. Moreover, Ir catalysts have been reported to have moderate tolerance to water and SO₂,^{1,4} and exhibit high NO reduction activity rather in the presence of SO₂.³ However, Ir catalysts show lower NO reduction activity at lower temperatures below ca. 500 K. Hence, the extension of active window of Ir catalysts to lower temperatures is strongly desired. Recently, Haneda et al. have reported that Ir/SiO₂ exhibits about 10% of NO conversion at 473 K for the SCR by CO in the presence of SO₂.⁵ However, loaded amount of Ir (5 wt %) was high. In this study, we discover that Ir catalysts with low loaded amount (0.5 wt %) show high activity below 500 K by co-existence of CO and H₂ and use of Na-zeolite supports. Moreover, by means of Ir L_{III}-edge XANES and CO-H₂ titration, the reason for high activity is clarified to be low oxidation state and high dispersion of iridium species.

Ir catalysts were prepared by impregnating supports with an aqueous solution of IrCl₄ followed by evaporation to dryness at 303 K and by calcination in air at 773 K for 4 h. Loaded Ir amount was 0.5 wt %. Na-MOR, SiO₂-Al₂O₃, SiO₂, and MgO were supplied by the Committee of Reference Catalysts, Catalysis Society of Japan (JRC-Z-M15, JRC-SAL-2, JRC-SIO-8 and JRC-MGO-4 100A). H-MOR (Si/Al = 7.9), H-MFI (Si/Al = 20) and Na-MFI (Si/Al = 13) were supplied by Tosoh Corporation. Boehmite was employed as starting materials of Ir/

Al₂O₃. The catalytic test was performed with a fixed-bed flow reactor by passing a mixture of 1000-ppm NO, 3000-ppm CO, 5000-ppm H₂, and 2% O₂ in He at a rate of 100 cm³ min⁻¹ over 0.05-g catalyst. Prior to the experiment the catalyst was heated in 6.7% O₂/He at 773 K for 1 h. After reaching a steady-state, the effluent gas was analysed by a gas chromatograph and a chemiluminescence NO_x analyser (Best BCL-100uH). Dispersion of Ir catalysts before and after the SCR was measured with CO-H₂ titration method.⁶ Ir L_{III}-edge XANES spectra of the samples treated with exposing reaction gas mixtures were recorded in fluorescence mode by using Lytle detector at the BL-10B station⁷ at KEK-PF with a Si(311) channel cut monochromator.

SCR of NO by CO and H₂ was examined over Ir/H-MFI. As shown in Table 1, NO conversions were very low for the SCR by sole reductant. Maximum NO conversions at 673 K were 3% for CO-SCR and 10% for H₂-SCR, respectively. On the other hand, the co-existence of CO and H₂ increased NO conversion remarkably. Maximum NO conversion was 78% at 523 K, and NO was also reduced effectively even below 500 K. Under the co-presence of CO and H₂, NO conversion was remarkably higher than the sum of those by individual reductants. In separate experiments, NO conversion in CO (2000 ppm)-H₂ (3000 ppm)-SCR over Ir/H-MFI was 7% at 498 K, while those in H₂ (5000 ppm)-SCR and CO (5000 ppm)-SCR were 4% and 0%, respectively. These results indicate that there is a synergistic effect of co-existence of CO and H₂.

Ir dispersion on Ir/H-MFI estimated from CO-H₂ titration was 7, 13, and 12% after SCR by CO (3000 ppm), H₂ (5000 ppm) and CO (3000 ppm) + H₂ (5000 ppm), respectively. This result indicates that the co-presence of two reducing agents does not cause a change in Ir dispersion. Figure 1A shows Ir L_{III}-edge XANES of Ir/H-MFI after the SCR by CO and H₂. XANES spectrum after the SCR by only CO (spectrum b) and only H₂ (spectrum c) had relatively large white line at 11220 eV and was similar to that of IrO₂, indicating Ir oxide was main species

Table 1. NO conversion and N₂ selectivity over Ir catalysts for the SCR by CO and H₂

Catalysts	[CO] / ppm	[H ₂] / ppm	Ir dispersion / % ^a	NO conversion (N ₂ selectivity) / %						
				448 K	473 K	498 K	523 K	573 K	623 K	673 K
Ir/H-MFI	3000	0	7		0 (— ^b)	0 (—)	0 (—)	2 (100)	3 (100)	3 (100)
	0	5000	13		3 (100)	3 (100)	4 (85)	8 (89)	6 (100)	10 (100)
	3000	5000	12		14 (81)	40 (79)	78 (83)	71 (88)	52 (89)	30 (86)
Ir/Na-MFI	3000	5000	30	6 (82)	25 (75)	50 (74)	41 (73)	22 (72)	12 (75)	7 (68)
Ir/Na-MOR	3000	5000	26	12 (61)	38 (62)	64 (64)	57 (67)	44 (76)	29 (76)	9 (61)
Ir/SiO ₂	3000	5000	8.9		11 (69)	63 (45)	75 (70)	70 (78)	62 (83)	45 (87)
Ir/SiO ₂ -Al ₂ O ₃	3000	5000	9.1		5 (67)	13 (50)	36 (59)	35 (77)	17 (79)	12 (82)
Ir/H-MOR	3000	5000	17		2 (100)	8 (83)	22 (65)	38 (81)	24 (80)	12 (79)
Ir/Al ₂ O ₃	3000	5000	20		0 (—)	2 (100)	23 (74)	38 (85)	26 (100)	17 (100)
Ir/MgO	3000	5000	25		0 (—)	0 (—)	0 (—)	0 (—)	1 (100)	1 (100)

^a measured with CO-H₂ titration⁶ after SCR reaction. ^b neither N₂ nor N₂O was detected.

on H-MFI. On the other hand, XANES spectrum after the SCR under the co-existence of CO and H₂ had small white line at 11218 eV and was similar to Ir metal (spectrum d). Therefore, the co-presence of CO and H₂ leads to reduction of Ir oxide to metallic iridium.

In order to design more active Ir catalyst, the SCR under the co-existence of CO and H₂ was carried out with various supports. Table 1 also shows NO conversion for the SCR by co-existence of CO and H₂ at various temperatures. For all the catalysts except for Ir/MgO, NO conversion increased with reaction temperature, reached the maximum at 498–573 K, and then decreased with further increase of temperature. Clearly, NO conversion differed by support materials. Among Ir/zeolites, Ir/Na-zeolites exhibited higher NO reduction activity than Ir/H-MFI below 500 K. Particularly, NO conversion on Ir/Na-MOR was 38% at 473 K. This low temperature catalytic activity is much higher than that of 5 wt % Ir/SiO₂ for the CO-SCR in the presence of SO₂ (NO conversion: 9.6%).⁵ On the other hand, Ir/H-MOR showed NO reduction around 573 K, and little activity below 500 K. Among Ir/metal oxides, Ir/SiO₂ showed comparable activity to Ir/H-MFI. Ir/SiO₂-Al₂O₃ and Ir/Al₂O₃ had NO reduction activity around 550 K. NO reduction activity of Ir/MgO was very low over the whole reaction temperatures. The order of NO reduction activity at 473 K was Ir/Na-MOR > Ir/Na-MFI > Ir/H-MFI = Ir/SiO₂ > Ir/SiO₂-Al₂O₃ > Ir/H-MOR > Ir/Al₂O₃ > Ir/MgO. N₂ selectivity (N₂ yield/(N₂ yield + N₂O yield)) on all catalysts was above 60% in the active temperature range.

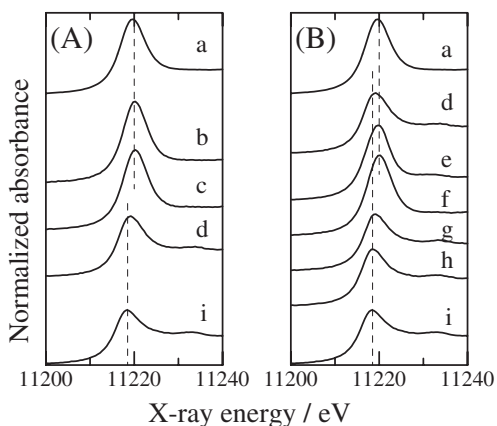


Figure 1. Ir L_{III}-edge XANES spectra of (a) IrO₂, (b–d) Ir/H-MFI, (e) Ir/Al₂O₃, (f) Ir/H-MOR, (g) Ir/Na-MOR, (h) Ir/SiO₂, and (i) Ir metal. The spectra b and c were measured after SCR reaction by only CO and only H₂, respectively. The spectra d–h were measured after SCR reaction under co-existence of CO and H₂.

Figure 1B shows Ir L_{III}-edge XANES of various Ir catalysts after the SCR under the co-existence of CO and H₂. For Ir/Al₂O₃ (spectrum e) and Ir/H-MOR (spectrum f), XANES spectra showed white line at 11220 eV, which indicates that Ir oxide is main Ir species on these supports. On the other hand, XANES spectra of Ir/Na-MOR (spectrum g) and Ir/SiO₂ (spectrum h) as well as Ir/H-MFI, showed white line at 11218 eV, which is similar to a spectrum of Ir metal.

Since the white line of Ir L_{III}-edge XANES spectrum is assigned to the electron transition to 5d_{3/2} and 5d_{5/2} orbitals, it is supposed that the white line intensity is an informative indica-

tion for the oxidation state of iridium. Therefore, electronic state of Ir catalysts after the SCR was estimated by integrated intensity of white line at Ir L_{III}-edge XANES spectra, obtained by curve-fitting analysis with an arctangent and a Gaussian function.⁸ Figure 2 shows the relationship between integrated intensity of the white line and TOF of NO (NO reaction rate per surface iridium atom). TOF of NO increased roughly with a decrease in the white line intensity, that is, extent of oxidation of Ir species. This relationship strongly supports that metallic iridium is highly active species for NO reduction. Nakatsuji¹ and Nojima et al.² have reported the high NO reduction activity of metallic iridium for the SCR by unsaturated hydrocarbons. Our present result reveals quantitatively the high NO reduction activity of metallic iridium for the SCR by CO and H₂. Higher NO conversions on Ir/Na-zeolites than Ir/SiO₂ and Ir/H-MFI can be ascribed mainly to higher dispersion of iridium.

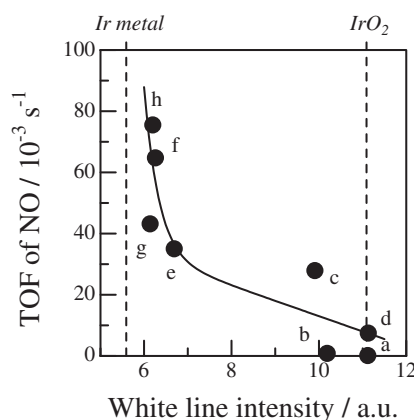


Figure 2. NO TOF for SCR under co-existence of CO and H₂ over Ir catalysts at 473 K, as a function of white line intensity estimated from Ir L_{III}-edge XANES. Catalysts: (a) Ir/MgO, (b) Ir/Al₂O₃, (c) Ir/SiO₂-Al₂O₃, (d) Ir/H-MOR, (e) Ir/H-MFI, (f) Ir/SiO₂, (g) Ir/Na-MFI and (h) Ir/Na-MOR.

In summary, Ir/Na-zeolites, particularly Ir/Na-MOR, exhibits excellent activity at 500 K for the SCR under the co-existence of CO and H₂. This effect is attributed to the remarkable formation of highly active metallic iridium species and high dispersion of iridium species.

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