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Strong Enhancement of CO-H_2-SCR of NO over Ir Catalyst Supported on Na-zeolite

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Introduction

A selective catalytic reduction of NO in the presence of excess oxygen is a potential method to remove NOx 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, but also CO and hydrogen. [1-4]. 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. In this study, we discover that Ir catalysts show high activity below 500 K by combination of co-presence of CO and H_2 and use of Na-zeolite supports. By means of Ir LIII-edge XANES, the reason for high activity is clarified to be low oxidation state and high dispersion of iridium species [5].

Experimental

Ir catalysts were prepared by impregnating supports with an aqueous solution of $IrCl_4$ 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%. The catalytic test was performed with a fixed-bed flow reactor by passing a mixture of 1000 ppm NO, 3000 ppm CO, 5000 ppm H_2 and 2% O_2 in He at a rate of 100 cm^3 min^{-1} over 0.05 g catalyst. 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 station [6] at KEK-PF with a Si(311) channel cut monochromator.

Results and discussion

The SCR under the co-presence of CO and H_2 was carried out with various supports at 448-673 K. 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 5wt% Ir/SiO_2 for the CO-SCR in the presence of SO_2 [5]. On the other hand, Ir/H-MOR showed NO reduction around 573 K, and little activity below 500 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/SiO_2 > Ir/SiO_2-Al_2O_3 > Ir/H-MOR > Ir/Al_2O_3 > Ir/MgO.

Figure 1A shows Ir LIII-edge XANES of Ir/H-MFI after the SCR by CO and H_2. XANES spectrum after the SCR by only CO (spectrum b) and only H_2 (spectrum c) had relatively large white line at 11220 eV and was similar to that of IrO_2, indicating Ir oxide was main species on H-MFI. On the other hand, XANES spectrum after the SCR under the co-presence of CO and H_2 had small white line at 11218 eV and was similar to Ir metal (spectrum d). Therefore, the co-presence of CO and H_2 leads to reduction of Ir oxide to metallic iridium.

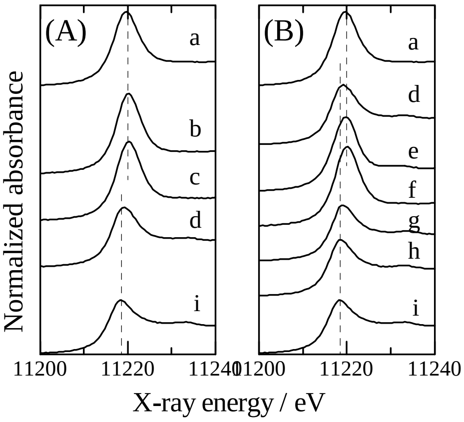

Figure 1. Ir L_{III}-edge XANES spectra of (a) IrO_2, (b–d) Ir/H-MFI, (e) Ir/Al_2O_3, (f) Ir/H-MOR, (g) Ir/Na-MOR, (h) Ir/SiO_2 and (i) Ir metal.

Figure 1B shows Ir L_{III}-edge XANES of various Ir catalysts after the SCR under the co-presence of CO and H_2. For Ir/Al_2O_3 (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/SiO_2 (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 indication for the oxidation state of iridium. Comparing with the catalytic tests, very high SCR activity of Ir catalysts Na-zeolite supports can be attributed to the remarkable formation of highly active metallic iridium species.

References

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