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Effect of iridium dispersion on the catalytic activity of Ir/SiO_2 for the selective reduction of NO with CO in the presence of O_2 and SO_2

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Abstract

The effect of iridium dispersion on the activity of Ir/SiO_2 for the selective reduction of NO with CO in the presence of O_2 and SO_2 has been investigated. The intrinsic activity, expressed in terms of turnover frequency (TOF), increases with decreasing iridium dispersion, indicating that NO reduction with CO over Ir/SiO_2 is a structure-sensitive reaction. Characterization of Ir/SiO_2 using TPO, XRD and FT-IR spectroscopy following CO adsorption shows that larger iridium crystallites are more difficult to be oxidized and much easier to be reduced under reaction conditions, resulting in the formation of stable iridium metal sites on which NO reduction occurs.

Keywords: Selective reduction; Carbon monoxide; Nitrogen monoxide; Ir/SiO_2; Iridium dispersion; Structure-sensitive

1. Introduction

The selective reduction of NO in an oxidizing atmosphere has recently received extensive attention, since it has potential as a practical strategy for removing NO_x emitted from diesel engines, lean-burn engines and combustors. In addition to hydrocarbons [1–3], hydrogen and CO have been proved to act as effective reductant for NO reduction under lean conditions. Although selective reduction with H_2 is a promising approach to the efficient reduction of NO in the presence of O_2 at relatively low temperatures [4–7], the production and supply of H_2 is a difficult problem to solve from a practical point of view. On the other hand, CO is a more practical reductant than H_2, since it can be easily produced by controlling engine operation.

Various materials have been tested so far for catalytic activity for the selective reduction of NO with CO (CO-SCR) in the presence of O_2. Interestingly, iridium was found to be the only active metal to catalyze this reaction effectively [7–10]. For example, Ogura et al. [11] reported that NO can successfully be reduced to N_2 with CO over Ir/silicalite catalyst and that the catalytic activity is not influenced by coexisting SO_2. We have recently discovered that Ir/SiO_2 is active for NO reduction with CO in the presence of both O_2 and SO_2 [7,12,13]. The most interesting feature of this reaction is that the presence of SO_2, which normally poisons catalytic reactions, actually promotes NO reduction in the presence of O_2. This is a quite favorable characteristic for the treatment of diesel exhaust.

The selective reduction of NO with hydrocarbons (HC-SCR) over supported noble metal catalysts was reported to be a structure-sensitive reaction [14,15]. Denton et al. [16] investigated the influence of various parameters such as nature of support and platinum dispersion on the activity of supported platinum catalysts for NO reduction with propene, and concluded that only the platinum dispersion is of key importance. The intrinsic activity increased with decreasing platinum dispersion. García-Cortés et al. [17] also reported a similar experimental result that the turnover frequency (TOF) for NO reduction with propene over Pt-beta catalysts linearly increased with increasing particle size of platinum. Nakatsuji [18,19] investigated the relationship between the catalytic activity of iridium on various metal oxide supports and the crystallite size of iridium for NO reduction by propene, and found that iridium metal with 40–60 nm of nanocrystal size showed a high NO conversion. However, no detailed discussion was made on the effect of iridium crystallite size.

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Table 1
Dispersion of iridium on catalysts

Catalyst	Calcination condition	Dispersion (D_{Ir}) (%)	Amount of CO adsorption (mol g_{cat}^{-1})
1 wt.% Ir/SiO_2	Reduction at 400 °C	86	4.45×10^{-5}
	→ Calcination at 300 °C	46	2.38×10^{-5}
	→ Calcination at 400 °C	22	1.17×10^{-5}
	→ Calcination at 500 °C	17	8.77×10^{-6}
	→ Calcination at 600 °C	13	6.57×10^{-6}
	→ Calcination at 700 °C	10	5.31×10^{-6}
	→ Calcination at 800 °C	9.1	4.72×10^{-6}
	→ Calcination at 900 °C	6.0	3.14×10^{-6}

Thus, structure–activity relationship, which is useful information for development and implementation of highly active catalysts, was investigated mainly on HC-SCR, and no one has reported on CO-SCR. In this study, we have investigated the effect of iridium dispersion on the activity of Ir/SiO_2 for NO reduction with CO in the presence of O_2 and SO_2. As larger crystallites (catalysts with lower metal dispersion) were found to exhibit higher TOF, several characterizations, mainly on the behavior of iridium under CO-SCR conditions, were performed to clarify the effect of iridium dispersion.

2. Experimental

Ir/SiO_2 was prepared by impregnation of SiO_2 (Fuji Silysia Chemicals, Cariact G-10, 300 $m^2 g^{-1}$) with an aqueous solution of $[Ir(NH_3)_6](OH)_3$ (Tanaka Kikinzoku Kougyou), followed by drying at 110 °C overnight and then reduction in 10% H_2/N_2 at 400 °C for 4 h. Catalysts with varying metal dispersion were obtained by calcinig the pre-reduced samples in air at different temperatures for 5 h. The loading of Ir metal was fixed at 1 wt.% in this study.

Catalytic activity was evaluated using a fixed-bed continuous flow reactor. A reaction gas mixture containing NO (500 ppm), CO (3000 ppm), O_2 (10%), SO_2 (1 ppm) and H_2O (6%) diluted in He as the balance gas was fed through a catalyst (0.04 g) at a rate of 90 $cm^3 min^{-1}$ (SV = ca. 75,000 h^{-1}). Prior to each reaction, the catalyst sample was pretreated in situ in a flow of 10% H_2/He at 400 °C for 2 h, and then cooled to 100 °C without changing the gas flow. The reaction temperature was increased from 100 to 340 °C by 20 °C at every step, and the steady-state catalytic activity was measured at each temperature. The effluent gas was analyzed with the use of two on-line gas chromatographs equipped with a Molecular Sieve 5A column (for the analysis of N_2 and CO) and a Porapak Q column (for the analysis of CO_2 and N_2O).

Iridium dispersion (D_{Ir}) was calculated from the amount of CO chemisorption measured by the pulse method at room temperature after the samples were reduced with H_2 at 400 °C for 1 h. X-ray diffraction (XRD) patterns of the samples were recorded using a Mac Science M18XHF^{22} diffractometer with Cu Kα radiation. For temperature-programmed oxidation (TPO), a catalyst sample was first reduced at 400 °C with 10% H_2/He for 1 h and cooled to room temperature in flowing He. Then the gas flow was switched to 5% O_2/He and the temperature was raised to 750 °C at a rate of 10 °C min^{-1}. Diffuse reflectance FT-IR spectra of adsorbed CO, as a probe molecule, were taken with a Nicolet Nexus 670 FT-IR spectrometer at a resolution of 4 cm^{-1}.

3. Results and discussion

3.1. Dispersion of iridium and activity of Ir/SiO_2

3.1.1. Dispersion of iridium

Supported noble metal catalysts with different metal dispersion can be prepared by controlling various parameters such as

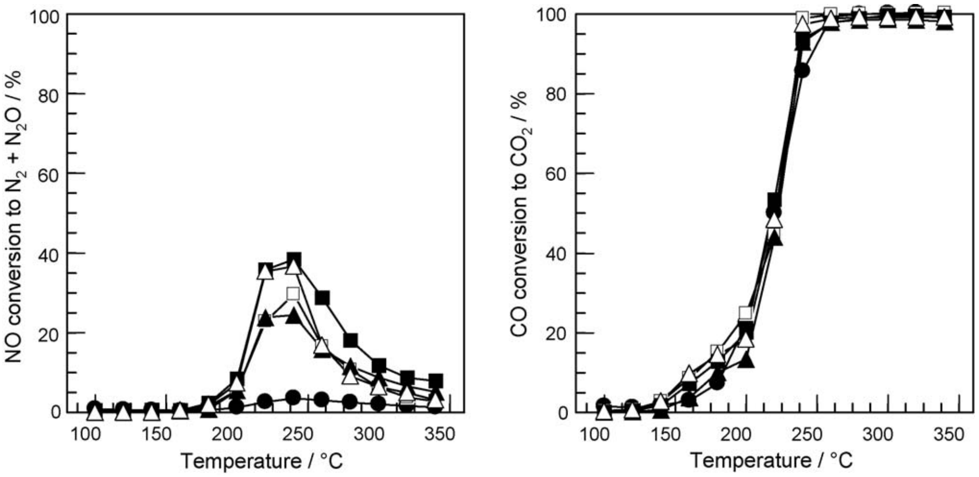

Fig. 1. Activity of 1 wt.% Ir/SiO_2 with different iridium dispersion for NO reduction with CO in the presence of O_2 and SO_2. Conditions: NO = 500 ppm; CO = 3000 ppm; O_2 = 10%; SO_2 = 1 ppm; H_2O = 6%; W/F = 0.0267 g s cm^{-3}. (●) D_{Ir} = 86%, (□) D_{Ir} = 46%, (△) D_{Ir} = 22%, (■) D_{Ir} = 13%, (▲) D_{Ir} = 6.0%.