

Effect of iridium dispersion on the catalytic activity of Ir/SiO₂ for the selective reduction of NO with CO in the presence of O₂ and SO₂

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Abstract

The effect of iridium dispersion on the activity of Ir/SiO₂ for the selective reduction of NO with CO in the presence of O₂ and SO₂ 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/SiO₂ is a structure-sensitive reaction. Characterization of Ir/SiO₂ 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.

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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 H₂ is a promising approach to the efficient reduction of NO in the presence of O₂ at relatively low temperatures [4–7], the production and supply of H₂ is a difficult problem to solve from a practical point of view. On the other hand, CO is a more practical reductant than H₂, 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 O₂. 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 N₂ with CO over Ir/silicalite catalyst and that the catalytic

activity is not influenced by coexisting SO₂. We have recently discovered that Ir/SiO₂ is active for NO reduction with CO in the presence of both O₂ and SO₂ [7,12,13]. The most interesting feature of this reaction is that the presence of SO₂, which normally poisons catalytic reactions, actually promotes NO reduction in the presence of O₂. 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 ($\text{mol g}_{\text{cat}}^{-1}$)
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/SiO₂ for NO reduction with CO in the presence of O₂ and SO₂. 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/SiO₂ was prepared by impregnation of SiO₂ (Fuji Silysia Chemicals, Cariact G-10, 300 m² g⁻¹) with an aqueous solution of [Ir(NH₃)₆](OH)₃ (Tanaka Kikinzoku Kougyou), followed by drying at 110 °C overnight and then reduction in 10% H₂/N₂ at 400 °C for 4 h. Catalysts with varying metal dispersion were obtained by calcining 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), O₂ (10%), SO₂ (1 ppm) and H₂O (6%) diluted in He as the balance gas was fed through a catalyst (0.04 g) at a rate of 90 cm³ min⁻¹ (SV = ca. 75,000 h⁻¹). Prior to each reaction, the catalyst sample was pretreated in situ in a flow of 10% H₂/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 N₂ and CO) and a Porapak Q column (for the analysis of CO₂ and N₂O).

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 H₂ at 400 °C for 1 h. X-ray diffraction (XRD) patterns of the samples were recorded using a Mac Science M18XHF²² diffractometer with Cu K α radiation. For temperature-programmed oxidation (TPO), a catalyst sample was first reduced at 400 °C with 10% H₂/He for 1 h and cooled to room temperature in flowing He. Then the gas flow was switched to 5% O₂/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/SiO₂

3.1.1. Dispersion of iridium

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

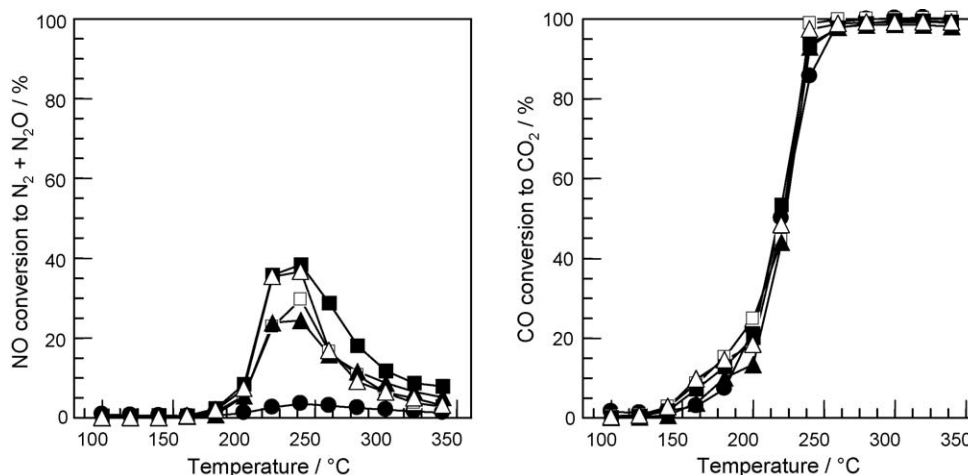


Fig. 1. Activity of 1 wt.% Ir/SiO₂ with different iridium dispersion for NO reduction with CO in the presence of O₂ and SO₂. Conditions: NO = 500 ppm; CO = 3000 ppm; O₂ = 10%; SO₂ = 1 ppm; H₂O = 6%; W/F = 0.0267 g s cm⁻³. (●) D_{Ir} = 86%, (□) D_{Ir} = 46%, (△) D_{Ir} = 22%, (■) D_{Ir} = 13%, (▲) D_{Ir} = 6.0%.

calcination temperature [15,17,20,21], heating rate [16] and calcination time [15]. In the present study, Ir/SiO₂ catalysts with varying iridium dispersion were prepared by calcining in air at different temperatures from 300 to 900 °C following reduction in 10% H₂/He at 400 °C. Table 1 summarizes the amount of CO chemisorption and iridium dispersion calculated by assuming a stoichiometry of 1.0 CO/Ir [22]. Obviously, the iridium dispersion in the catalyst decreased with increasing calcination temperature. In this way, Ir/SiO₂ catalysts with iridium dispersion ranging from 86 to 6.0% were obtained.

3.1.2. Relationship between activity and iridium dispersion

Fig. 1 shows the activity of Ir/SiO₂ with different iridium dispersion for NO reduction with CO in the presence of O₂ and SO₂. Ir/SiO₂ with the highest iridium dispersion, $D_{\text{Ir}} = 86\%$, showed little activity over the entire temperature range. Interestingly, NO conversion increased with decreasing iridium dispersion. The maximum NO conversion was attained for Ir/SiO₂ with iridium dispersion of 13%. Further decrease in iridium dispersion decreased the NO conversion. This tendency is best seen in Fig. 2 which shows the relationship between NO conversion and iridium dispersion. This result is in good agreement with the report of Nakatsuji [18,19], who revealed that Ir-based catalysts with 40–60 nm iridium crystallites showed the highest activity for NO reduction with propene. As can be seen in Fig. 1, no great difference in CO conversion was observed for all the Ir/SiO₂ catalysts, indicating that the selectivity for the reaction of NO with CO differs depending on the iridium dispersion.

In order to make more clear the effect of iridium dispersion, TOF, expressed as mole of NO reduced to N₂ and N₂O per mole of surface iridium atom and per minute, was calculated and illustrated as a function of iridium dispersion in Fig. 3. It appears that the TOF gradually increased with decreasing iridium dispersion, irrespective of the reaction temperature. Below 10% dispersion, the TOF at 220 °C increased rapidly, suggesting that very large crystallites have a high specific activity. However, it should be noted that the increased activity per surface atom at low dispersion is offset by the decrease in the number of surface atoms.

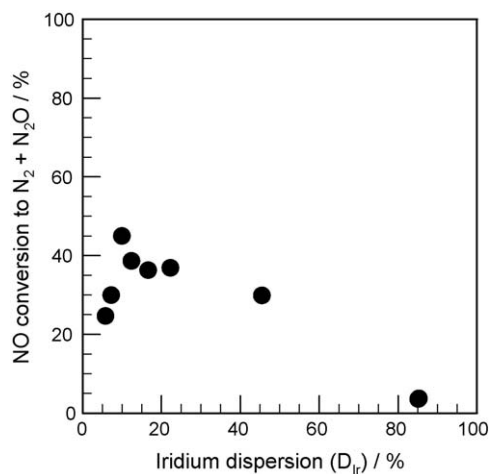


Fig. 2. NO conversion at 220 °C on 1 wt.% Ir/SiO₂ as a function of iridium dispersion.

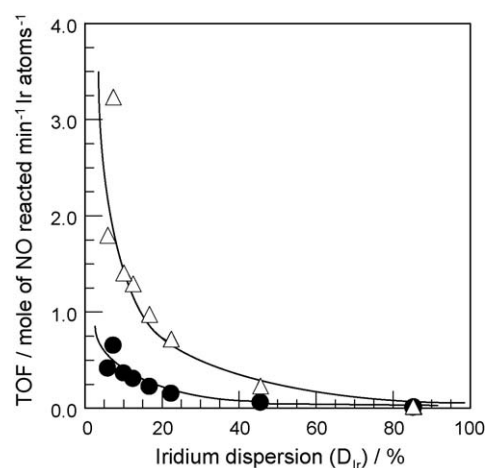


Fig. 3. TOF at 200 (●) and 220 °C (△) on 1 wt.% Ir/SiO₂ as a function of iridium dispersion.

This result clearly indicates that NO reduction with CO over Ir/SiO₂ seems to be a structure-sensitive reaction.

3.2. Oxidation behavior of iridium measured by TPO

Wögerbauer et al. [23–25] extensively studied the effect of structure properties on the catalytic activity of supported and unsupported iridium for NO reduction with hydrocarbons, and revealed that iridium is present as a mixture of Ir⁰ and IrO₂ under reaction conditions and that higher ratio of Ir⁰/Ir⁴⁺ is responsible for the catalytic activity. They also found that the oxidation state of iridium under the reaction conditions strongly depends on the crystallite size. In the present study, the oxidation behavior of iridium supported on SiO₂ can also be different depending on its dispersion. Accordingly, TPO of the pre-reduced Ir/SiO₂ with different iridium dispersion were performed.

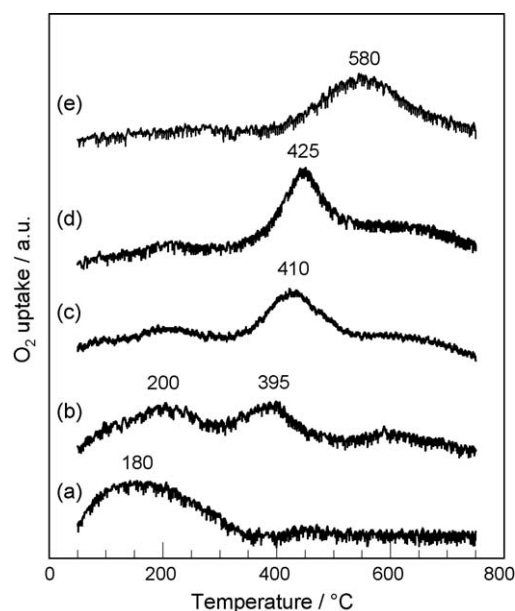


Fig. 4. TPO profiles of 1 wt.% Ir/SiO₂ with different iridium dispersion. (a) $D_{\text{Ir}} = 86\%$, (b) $D_{\text{Ir}} = 46\%$, (c) $D_{\text{Ir}} = 22\%$, (d) $D_{\text{Ir}} = 13\%$ and (e) $D_{\text{Ir}} = 6.0\%$.

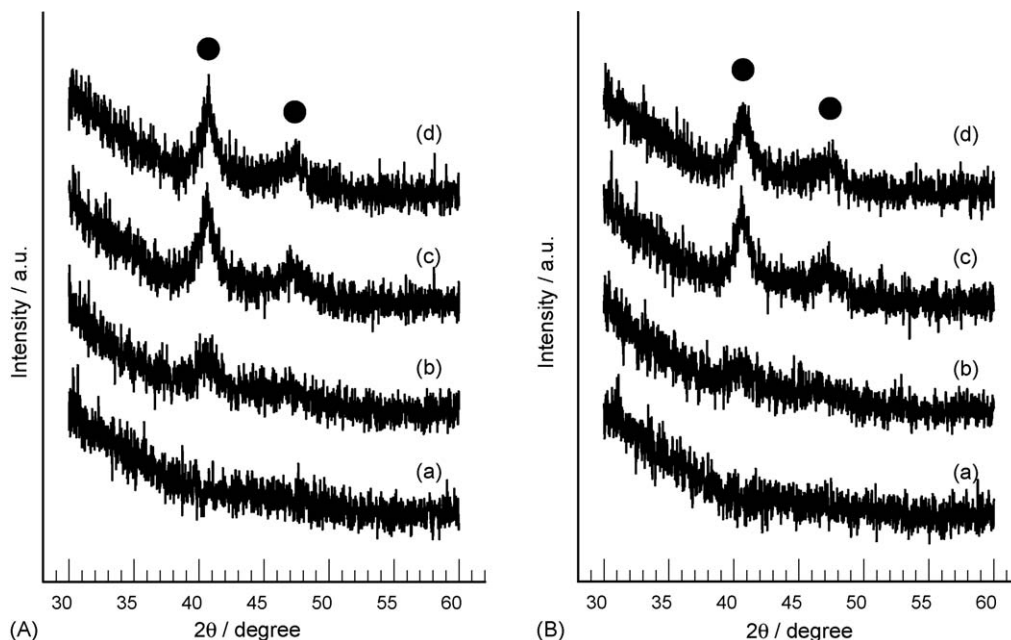


Fig. 5. XRD patterns of 1 wt.% Ir/SiO₂: (A) before and (B) after use in the reaction. (a) D_{Ir} = 86%, (b) D_{Ir} = 46%, (c) D_{Ir} = 13%, (d) D_{Ir} = 6.0%.

Fig. 4 shows the TPO profiles showing O₂ consumption with increasing temperature up to 750 °C. Highly dispersed iridium, with 86% iridium dispersion, was found to be easily oxidized in the low temperature region around 200 °C. This suggests that iridium in this catalyst is present predominantly as IrO₂ during the reaction. Obviously, O₂ consumption peak at around 200 °C decreased gradually with decreasing iridium dispersion, and a new peak appeared in the high temperature region above

400 °C. This O₂ consumption peak shifted to high temperature with decreasing iridium dispersion, indicating that larger crystallites contain predominantly Ir⁰ during the reaction.

In order to get more information on the crystallite structure of iridium, XRD measurements were performed for the fresh and used catalysts in the reaction. As shown in Fig. 5, no change in the XRD patterns was observed for Ir/SiO₂ with iridium dispersion below 13% before and after use (patterns (c) and (d),

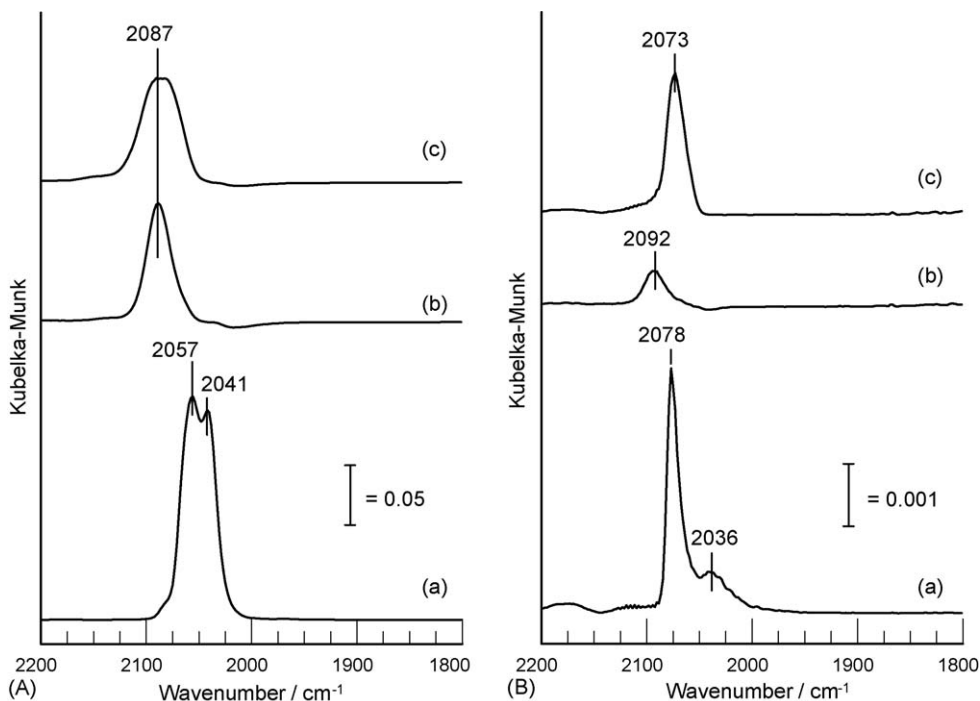


Fig. 6. FT-IR spectra of CO adsorbed on: (A) Ir/SiO₂($D_{86\%}$) and (B) Ir/SiO₂($D_{13\%}$), after the exposure of (a) 0.6% CO/He, (b) 0.6% CO–5% O₂/He and (c) 0.6% CO–5% O₂–20 ppm SO₂/He at 220 °C for 30 min.

respectively, assigned to Ir⁰). In contrast, the intensity of XRD peaks due to Ir⁰ for Ir/SiO₂ with 46% dispersion clearly weakened after use in the reaction, suggesting that a part of Ir⁰ was oxidized, although no distinct peaks of IrO₂ were observed (pattern (b)). This result is in good agreement with the results of TPO. We can conclude that crystallite size and oxidation state of iridium are crucial for the NO reduction behavior of Ir/SiO₂.

3.3. Study of iridium surface by FT-IR following CO adsorption

Because catalytic reactions take place on catalyst surface, the oxidation state of iridium surface must be an important factor. The oxidation state of iridium surface was investigated by FT-IR with CO as a probe molecule. Fig. 6 shows FT-IR spectra for CO species adsorbed on Ir/SiO₂ with high (86%) and low (13%) iridium dispersion, denoted as Ir/SiO₂ (D_{86%}) and Ir/SiO₂ (D_{13%}), respectively, recorded in different compositions of flowing gas at 220 °C. Solymosi et al. [26,27] measured the IR spectra of CO species adsorbed on Ir/Al₂O₃, and observed two IR bands at 2070–2060 and 2020 cm⁻¹. They assigned the IR bands to CO linearly bonded onto the metal atoms of larger iridium crystallites and of highly dispersed iridium crystallites, respectively. In agreement with this assignment, the exposure of 0.6% CO/He to Ir/SiO₂(D_{13%}) gave a strong IR band at 2078 cm⁻¹ (Fig. 6B-a), while for Ir/SiO₂(D_{86%}) the IR bands appeared at slightly lower wavenumber around 2050 cm⁻¹ (Fig. 6A-a). The strong intensity of the IR bands observed for Ir/SiO₂(D_{86%}) is due to a large number of iridium atoms exposed on the surface.

When Ir/SiO₂ was exposed to 0.6% CO/He with 5% O₂, a shift of IR band to higher wavenumber was observed, irrespective of iridium dispersion (Fig. 6A-b and B-b). Since a shift of the IR band to a higher wavenumber is often observed when CO is adsorbed onto an oxidized metal surface [28,29], the IR bands at around 2090 cm⁻¹ observed here can be ascribed to linearly bonded CO adsorbed onto Ir^{δ+} sites. This clearly indicates that the surface of iridium is oxidized in the presence of O₂.

Recently, we have reported that oxidized iridium surface can be reduced by introducing SO₂ into the reaction gas even in the presence of O₂ [13]. This was explained by the following model proposed based on the surface science study using a single-crystal model catalyst [30]: The disproportionation of SO₂ takes place on the Ir(1 1 1) surface, 3SO₂(a) → 2SO₃(a) + S(a). SO₃ is thermally desorbed, and the remaining atomic sulfur reacts with surface oxygen on iridium, S(a) + 2O(a) → 2SO₂(g). The iridium surface, thus, reverts to its initial metallic state. In the present study, as can be seen in Fig. 6A-c, no change in the IR spectrum for Ir/SiO₂(D_{86%}) was observed after the introduction of SO₂ into CO–O₂/He flowing gas, suggesting that the oxidized surface of highly dispersed iridium crystallites is very stable even in the presence of SO₂. On the other hand, an IR band at 2073 cm⁻¹ due to Ir⁰–CO was observed in the IR spectrum for Ir/SiO₂(D_{13%}) (Fig. 6B-c). This clearly indicates that the surface of larger iridium crystallites is stabilized in the metal state in the presence of O₂ and SO₂. Taking into account the results of TPO described before, it can be concluded that larger crystallites are more difficult to be oxidized and easier to be

reduced under reaction conditions, resulting in the formation of stable iridium metal sites on which NO reduction occurs.

4. Conclusions

Ir/SiO₂ catalysts with different metal dispersion from 86 to 6% were prepared by calcining the pre-reduced samples in air at different temperatures for 5 h. The activity of Ir/SiO₂ for NO reduction with CO in the presence of O₂ and SO₂ was strongly dependent on the iridium dispersion. Although the maximum NO conversion was attained at 10–20% dispersion, the intrinsic activity expressed as TOF increased with decreasing iridium dispersion. Larger iridium crystallites were found to be more difficult to be oxidized and much easier to be reduced under reaction conditions. This characteristic of iridium seems to be a key factor responsible for high NO reduction activity.

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