Role of tungsten in promoting selective reduction of NO with CO over Ir/WO$_3$–SiO$_2$ catalysts

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The catalytic activity for the selective reduction of NO with CO over Ir/SiO$_2$ was greatly increased by the addition of a W species. The active site for reduction of NO over Ir/WO$_3$–SiO$_2$ was an Ir–WO$_x$ species ($2.92 \leq x \leq 3$). The role of the Ir–WO$_x$ active site was to promote the NO dissociation step.

KEY WORDS: selective reduction; carbon monoxide; nitrogen monoxide; iridium; tungsten.

1. Introduction

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. Many studies of various types of reductants for the selective catalytic reduction of NO have been carried out. Recently, H$_2$ and CO have begun to attract attention as effective reducing agents. Several researchers have investigated the selective reduction of NO with H$_2$ over Pt- and Pd-based catalysts [1–5]. Yokota et al. [1] reported that Pt/mordenite is catalytically active for the selective reduction of NO with H$_2$ in the presence of O$_2$ at around 423 K. They also found that the activity of Pt/mordenite was enhanced by the addition of Mo and Na. Recently, Yoshinari et al. discovered that Ir/SiO$_2$ and Rh/SiO$_2$ show marked catalytic activity for the reduction of NO with H$_2$ in the presence of O$_2$ and SO$_2$ [6, 7].

The selective catalytic reduction of NO with CO has been studied by several research groups [8–14]. Ogura et al. [8] reported that supported iridium catalysts such as Ir/silicalite exhibit a high NO conversion in the presence of O$_2$. Wang et al. [9] investigated Pt, Pd, Rh, and Ir catalysts and reported that an Ir/ZSM-5 catalyst exhibited a high activity for reduction of NO with CO in the presence of excess O$_2$. The selective catalytic reduction of NO with CO also takes place over supported metal oxide catalysts such as Cu/Al$_2$O$_3$ [10]. However, comparison of the activities of various supported metallic catalysts under identical conditions revealed that Cu/Al$_2$O$_3$ is not very active and that supported iridium catalysts are the most active for reduction of NO with CO [11]. The Ir/SiO$_2$ catalyst also shows excellent activity with respect to reduction of NO with CO in the presence of O$_2$ and SO$_2$ [12]. These results indicate that Ir metal is an effective species for the selective catalytic reduction of NO with CO. The promotional effect of added W on the activity of Ir catalysts was recently reported [11, 13, 14]. Shimokawabe et al. [11, 13] showed that the selective reduction of NO with CO proceeds effectively on Ir/WO$_3$ in the presence of O$_2$. Nanba et al. [14] found that the Ir/WO$_3$–SiO$_2$ catalyst shows a high activity even at a high space velocity (over 50,000 h^{-1}).

However, no detailed studies on the role of W in the selective reduction of NO over Ir catalysts with added W have been carried out. In this work, we studied the role of W in promoting the catalytic reduction of NO with CO over Ir/WO$_3$–SiO$_2$ and investigated the nature of the active sites of the catalyst.

2. Experimental

2.1. Catalyst preparation

(NH$_4$)$_{10}$W$_{12}$O$_{41}$·5H$_2$O and citric acid were dissolved in distilled water to which SiO$_2$ (Fuji Silysia Chemicals, Cariact G-10, 300 m^2 g^{-1}) was added. The WO$_3$:SiO$_2$ weight ratio was 1:9. The mixture was dried in air at 110 °C overnight and then calcined in air at 500 °C for 4 h to obtain the WO$_3$–SiO$_2$ support. Ir/WO$_3$–SiO$_2$ was

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prepared by impregnating the WO_3–SiO_2 support with an aqueous solution of H_2IrCl_6. The impregnated catalyst precursor was dried at 110 °C overnight and then calcined at 600 °C for 6 h in air. Ir loadings were 0.5, 2 and 5 wt%.

2.2. Catalytic activity measurements

The catalytic activity was measured using a fixed-bed flow reactor. Prior to each reaction, the catalyst was reduced in a flow of 10% H_2/He at 600 °C for 2 h. A reaction gas mixture consisting of 500 ppm NO, 3000 ppm CO, 5% O_2, 6% H_2O, 1 ppm SO_2, and He balance was passed through the catalyst at a gas flow rate of 90 cm^3 min^{-1} (SV = ca. 70,000 h^{-1}). The effluent gas was analyzed with the use of two on-line gas chromatographs equipped, respectively, with a Molecular Sieve 5A column (for analysis of N_2 and CO) and a Porapak Q column (for analysis of CO_2 and N_2O). The reaction temperature decreased from 600 to 400 °C and from 400 to 200 °C with a step of 50 and 20 °C, respectively, and the steady-state catalytic activity was measured at each temperature. NO conversion to N_2 + N_2O was defined as follows:

$$NO\, conversion\, to\, N_2 + N_2O\, (\%) = 2(y_{N_2,out} + y_{N_2O,out})/y_{NO,in}$$

(1)

where $y_{i,\,in}$ and $y_{i,\,out}$ are the mole fraction of compound i at inlet and outlet of reactor, respectively.

2.3. Catalyst characterization

X-ray diffraction patterns of the samples were obtained with an X-ray diffractometer (Mac Science M18XHF[22]) operated at 40 kV and 150 mA using Cu Kα monochromatized radiation (λ = 0.154178 nm). The diffraction patterns were taken in the 2θ range of 5–90° at a scan speed of 2.0°/min and a step width of 0.02°. The patterns were matched to JCPDS (Joint Committee on Powder Diffraction Standards) data, and corresponding phases were identified.

The pulse reaction experiments were conducted in a quartz fixed-bed reactor. NO/He (10% NO in He) was continually pulsed into the catalysts six times (0.54 ml of NO/He per repetition), using He as the carrier gas at 300 °C. The effluent gas from the reactor was continuously monitored for N_2 (m/e 28) by a quadrupole mass spectrometer.

3. Results and discussion

3.1. Effect of added W on NO reduction activity over Ir catalyst

Figure 1 shows conversion versus temperature plots for the selective reduction of NO with CO over Ir/SiO_2 and Ir/WO_3–SiO_2 with various Ir loadings. The NO conversion over Ir/WO_3–SiO_2 was higher than that over Ir/SiO_2 in the temperature range 260–320 °C. The maximum NO conversion over Ir/WO_3–SiO_2 was obtained at 0.5 wt% of Ir loading, which was about three times higher than that over 0.5 wt% Ir/SiO_2. No difference in N_2 selectivity between Ir/SiO_2 and Ir/WO_3–SiO_2 was observed. The activity for CO conversion was also enhanced by the addition of W in the temperature range 260–320 °C. The 5 wt% Ir/WO_3–SiO_2 catalyst exhibited a high CO oxidation activity at low reaction temperature. Thus, the enhancement of the NO reduction activity seems to be due to the activation of CO (the NO reductant) by the addition of W.

Figure 2 shows the effect of SO_2 on the catalytic activities of Ir/SiO_2 and Ir/WO_3–SiO_2 for the selective reduction of NO with CO. NO was selectively reduced over Ir/SiO_2 only in the presence of SO_2 over the entire range of reaction temperature. Haneda et al. [12] reported that Ir/SiO_2 exhibited no NO reduction activity in the absence of SO_2. They explained that Ir metal is the active site for reduction of NO with CO over Ir/SiO_2 and that SO_2 prevents deactivation of the Ir metal active site in the presence of O_2 during reaction.

In contrast, the NO reduction activity of Ir/WO_3–SiO_2 was not affected by SO_2, indicating that Ir/WO_3–SiO_2 catalysts do not require the co-presence of SO_2 to remain active. Thus, we conclude that the active site of Ir/WO_3–SiO_2 is not Ir metal.

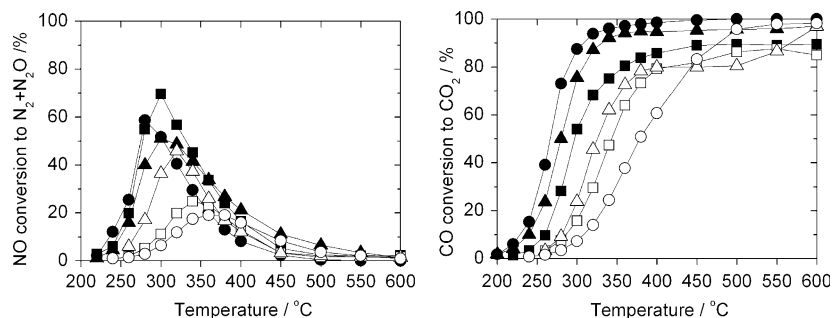To elucidate the catalytic properties of the active sites of Ir/SiO_2 and Ir/WO_3–SiO_2, we examined the effect of

Figure 1. Catalytic activities for the selective reduction of NO with CO over Ir/SiO_2 and Ir/WO_3–SiO_2. Reaction conditions: 500 ppm NO, 5% O_2, 3000 ppm CO, 6% H_2O, 1 ppm SO_2, Ir loading (wt%): 0.5 (□, ■), 2 (△, ▲), 5(○, ●), Open symbol: Ir/SiO_2, Closed symbol: Ir/WO_3–SiO_2.
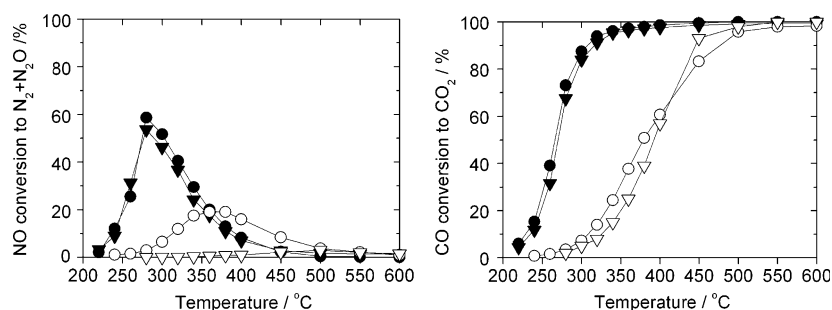
Figure 2. ffect of SO_2 on catalytic activities of Ir/SiO_2 and $Ir/WO_3–SiO_2$ for the selective reduction of NO with CO. Reaction conditions: 500 ppm NO, 5% O_2, 3000 ppm CO, 6% H_2O, 0 (∇, $\blacktriangledown$), 1($\bigcirc$, $\bullet$) ppm SO_2, Open symbol: Ir/SiO_2, Closed symbol: $Ir/WO_3–SiO_2$, Ir loading: 5 wt%.

Table 1
Comparison in the activities of H_2-reduced catalysts before pretreatment and after pretreatment with the reaction gas mixture

	Ir/SiO_2		$Ir/WO_3–SiO_2$	
	NO conv./%	CO conv./%	NO conv./%	CO conv./%
Reduction	53	100	28	92
Reaction gas treatment	4	3	58	73

Ir loading: 5 wt.%, Reduction condition: 10% H_2 in He at 600 °C. Reaction gas treatment condition: 500 ppm NO, 3000 ppm CO, 5% O_2, 6% H_2O, 1 ppm SO_2 in He at 600–280 °C,. Reaction condition: 500 ppm NO, 3000 ppm CO, 5% O_2, 6% H_2O, 1 ppm SO_2 in He at 280 °C, SV = ca. 70,000 h^{-1}.

pretreatment on the NO reduction activities. Table 1 compares the activities at 280 °C of H_2-reduced catalysts before pretreatment and after pretreatment with the reaction gas mixture (500 ppm NO, 3000 ppm CO, 5% O_2, 6% H_2O, 1 ppm SO_2). The reduced catalysts were treated as follows. H_2-reduced catalyst (no pretreatment with reaction gas mixture): after the catalyst was reduced with 10% H_2/He at 600 °C, the catalyst bed was cooled to 280 °C in flowing He, and the reaction gas mixture was introduced. Measurement of activity was started when the reaction temperature was constant at 280 °C. Pretreated catalyst: after reduction at 600 °C,

the catalyst was cooled from 600 to 280 °C under a flow of reaction gas mixture. Activities were measured at 280 °C.

For Ir/SiO_2, NO conversion was 53% and CO conversion was 100% on the untreated (no pretreatment) catalyst. In contrast, both the NO conversion and the CO conversion on the pretreated catalyst were significantly lower than those on the untreated catalyst, indicating that Ir metal was oxidized by the reaction gas during pretreatment. These results indicated that the active site of Ir/SiO_2 for NO reduction was Ir metal, which is consistent with the report of Haneda *et al.* [12].

For $Ir/WO_3–SiO_2$, NO conversion was 28% and CO conversion was 92% on the untreated catalyst. In contrast, the NO conversion on the pretreated catalyst was 58%, which is about two times as high as that on the untreated catalyst. CO conversion was 73%, which is lower than that on the untreated catalyst, indicating that the Ir in $Ir/WO_3–SiO_2$ was slightly oxidized by exposure to the reaction gas. It was thus clearly shown that the effective pretreatment for the catalytic activity was different between Ir/SiO_2 and $Ir/WO_3–SiO_2$.

Figure 3 shows Arrhenius plots of the reaction rates of NO and CO, r_{NO} and r_{CO}, for the selective reduction of NO with CO over Ir/SiO_2 and $Ir/WO_3–SiO_2$. Table 2 lists the apparent activation energies for conversion of NO to N_2, $E_{A,NO}$, and conversion of CO to CO_2, $E_{A,CO}$. The values of $E_{A,NO}$ and $E_{A,CO}$ were estimated from the
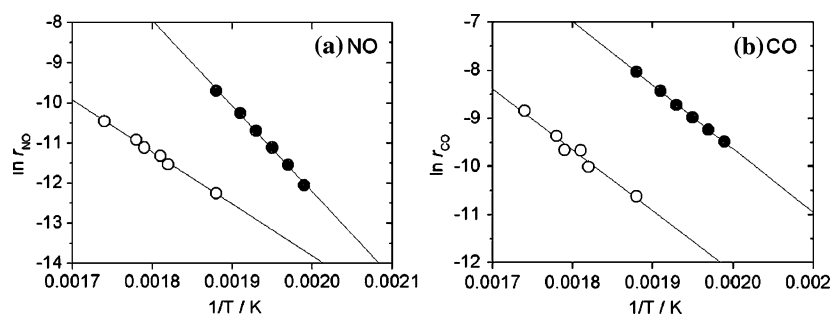

Figure 3. Arrhenius plots of (a) r_{NO} and (b) r_{CO} for the selective reduction of NO with CO over Ir/SiO_2 and $Ir/WO_3–SiO_2$: Open symbol: Ir/SiO_2, Closed symbol: $Ir/WO_3–SiO_2$, Ir loading: 5 wt%.

Table 2
Apparent activation energies of NO reaction to N_2 ($E_{A,NO}$) and CO reaction to CO_2 ($E_{A,CO}$)

	$E_{A,NO}$/kJ/mol	$E_{A,CO}$/kJ/mol
Ir/SiO$_2$	110.3	108.0
Ir/WO$_3$–SiO$_2$	172.6	107.3

Ir loading: 5 wt.%, Reaction condition: 500 ppm NO, 3000 ppm CO, 5% O$_2$, 6% H$_2$O, 1 ppm SO$_2$ in He at 300–230 °C, SV = ca. 70,000 h^{-1}.

slopes of the Arrhenius plots of r_{NO} and r_{CO} based on NO and CO conversions of less than 20%. Here, r_{NO} and r_{CO} are given as follows:

$$r_{NO} = F_{NO} \cdot X_{NO}/W_{Ir} \qquad (2)$$

$$r_{CO} = F_{CO} \cdot X_{CO}/W_{Ir} \qquad (3)$$

where F_i and X_i are the mole flow rate and conversion of compound i and W_{Ir} is the Ir content in the catalyst. The catalysts were treated as follows. After reduction at 600 °C, the catalyst was cooled from 600 °C to a given temperature under a flow of reaction gas mixture. The reaction temperature changed from 230 to 300 °C, and the steady-state catalytic activity was measured at each temperature.

The $E_{A,CO}$ of the Ir/WO$_3$–SiO$_2$ catalyst was almost the same as that of the Ir/SiO$_2$ catalyst (about 110 kJ/ mol), indicating that oxidation of CO occurs on the same sites over these catalysts. That is, oxidation of CO proceeds on Ir metal sites over the Ir catalysts. In contrast, the $E_{A,NO}$ of Ir/WO$_3$–SiO$_2$ was significantly different from that of Ir/SiO$_2$, indicating that the active site for reduction of NO on Ir/WO$_3$–SiO$_2$ is different from that on Ir/SiO$_2$. The Ir metal active sites on Ir/SiO$_2$ for reduction of NO were modified by the addition of W

Table 3
Effect of pretreatment on the catalytic activity for reduction of NO with CO over Ir/WO$_3$–SiO$_2$

	NO conv./% (N$_2$ selectivity/%)	CO conv./%
Without pretreatment	28 (90)	92
O$_2$ (5% in He)	0 (0)	3
H$_2$O (6% in He)	53 (91)	98
H$_2$O + CO (6% + 3000 ppm in He)	42 (89)	99
H$_2$O + O$_2$ (6% + 5% in He)	0 (0)	2
H$_2$O + O$_2$ + CO (6% + 5% + 3000 ppm in He)	50 (89)	35

Ir loading: 5 wt.%, Pretreatment temperature: 600 °C, Reaction condition: 500 ppm NO, 3000 ppm CO, 5% O$_2$, 6% H$_2$O, 1 ppm SO$_2$ in He at 280 °C, SV = ca. 70,000 h^{-1}

species. Thus, we conclude that the active sites for reduction of NO on Ir/SiO$_2$ and Ir/WO$_3$–SiO$_2$ are Ir metal and complexes with Ir and W species, respectively.

3.2. Nature of the active sites on Ir/WO$_3$–SiO$_2$

To elucidate the nature of the active sites on Ir/WO$_3$–SiO$_2$, we examined the effect of pretreatment on the catalytic activity for reduction of NO with CO over Ir/WO$_3$–SiO$_2$. The catalyst was pretreated for 30 min at 600 °C with flowing O$_2$, H$_2$O, H$_2$O + O$_2$, H$_2$O + CO, or H$_2$O + O$_2$ + CO and then cooled to 280 °C under a He flow. Activities were then measured at 280 °C (table 3). No NO reduction activity was observed after pretreatment with O$_2$ or H$_2$O + O$_2$. In contrast, pretreatment with H$_2$O, H$_2$O + CO, or H$_2$O + O$_2$ + CO enhanced NO reduction activities by about 1.5–2 times relative to the activity without pretreatment. Thus, we found that the catalytic activity on Ir/WO$_3$–SiO$_2$ for reduction of NO with CO strongly depends on the pretreatment condition. Treatment with H$_2$O plays an important role in the creation of active sites on Ir/WO$_3$–SiO$_2$.

Next, we examined the oxidation states of Ir and W in catalysts subjected to different pretreatment protocols. Figure 4 shows XRD patterns for the untreated Ir/WO$_3$–SiO$_2$ catalyst and the Ir/WO$_3$–SiO$_2$ catalysts subjected to pretreatment with O$_2$, H$_2$O, H$_2$O + CO, and H$_2$O + O$_2$ + CO. Peaks due to metallic Ir were present only in the XRD pattern of the untreated catalyst. Moreover, this pattern contained no peaks ascribable to W species, suggesting that W exists as a thin layer on the surface of the SiO$_2$ support [14]. The XRD pattern for the postreaction surface of the O$_2$-treated
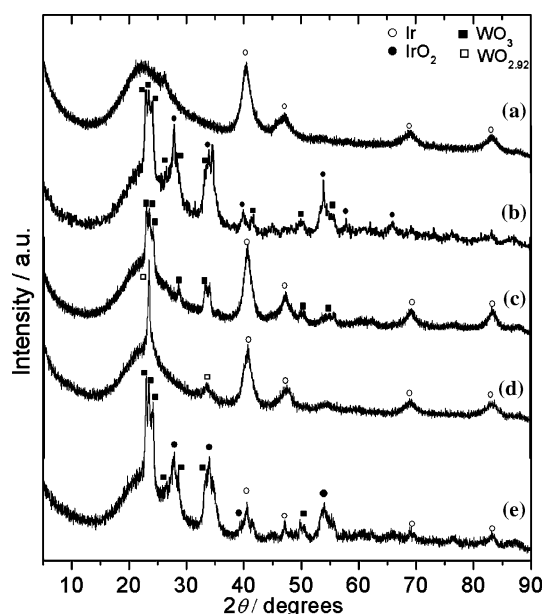

Figure 4. XRD patterns for (a) the untreated Ir/WO$_3$–SiO$_2$ catalyst and the Ir/WO$_3$–SiO$_2$ catalysts subjected to pretreatment with (b) O$_2$, (c) H$_2$O, (d) H$_2$O + CO, and (e) H$_2$O + O$_2$ + CO, Ir loading : 5 wt%.

catalyst shows that Ir and W existed as IrO_2 and WO_3, respectively. The oxidation states of Ir and W in the $(H_2O + O_2)$-treated catalyst were the same as those in the O_2-treated catalyst (XRD pattern not shown). In contrast, peaks due to Ir metal and WO_3 were present in the XRD pattern of the H_2O-treated catalyst, indicating that only W was oxidized by the H_2O treatment. The XRD pattern of the $(H_2O + CO)$-treated catalysts showed Ir metal and $WO_{2.92}$ peaks, suggesting that complete oxidation of W by H_2O was slightly inhibited by the presence of a reducing gas (CO). The oxidation of both Ir and W was observed for $(O_2 + H_2O + CO)$-treated catalysts.

Table 3 and the XRD results indicate that both Ir metal and W oxide are required for high NO reduction activities. Thus, we conclude that the active site of Ir/WO_3–SiO_2 consists of a combination of Ir metal and W oxide.

Regalbuto *et al.* [15] reported that W enhanced the catalytic activity of Pt/SiO_2 in NO + CO reactions. They suggested that Pt–WO_x adliniation sites, which are located on Pt particles decorated by partially oxidized W, have a high NO dissociation activity. Thus, we considered the possibility that the Ir–WO_x ($2.92 \leq x \leq 3$) site, which serves as an active site for NO reduction, was formed by the combination of Ir metal and W oxide on Ir/WO_3–SiO_2. Therefore, we examined the ability of NO to dissociate on Ir/WO_3–SiO_2. The NO dissociation activity was evaluated by measuring the amount of N_2 produced by the catalysts after exposure to NO in pulse reaction experiments. Figure 5 compares the NO dissociation activities of the H_2-reduced Ir/SiO_2 catalyst and the H_2O-pretreated Ir/WO_3–SiO_2 catalyst.

N_2 was detected at the first pulse on reduced Ir/SiO_2. However, no N_2 was detected in subsequent pulses, indicating that the Ir metal surface was oxidized by

oxygen from NO dissociation. In contrast, the amount of N_2 produced on H_2O-pretreated Ir/WO_3–SiO_2 was considerably larger than that produced on reduced Ir/SiO_2. The total amount of N_2 produced on Ir/WO_3–SiO_2 was about five times as large as that produced on Ir/SiO_2, indicating that Ir–WO_x has a high NO dissociation ability. Furthermore, N_2 was detected till the sixth pulse, suggesting that the Ir–WO_x species are highly resistant to oxidation.

We propose that the selective reduction of NO with CO mainly proceeds via three steps.

$$NO \rightarrow N_a + O_a \qquad (I)$$

$$CO_a + O_a \rightarrow CO_2 \qquad (II)$$

$$2N_a \rightarrow N_2 \qquad (III)$$
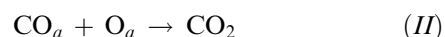
The Ir–WO_x sites promote the NO dissociation step (I), resulting in a significantly enhanced selective reduction of NO with CO over Ir/WO_3–SiO_2.

4. Conclusions

(1) The NO reduction activity of Ir/SiO_2 was promoted by the addition of W. The active site on Ir/WO_3–SiO_2 is different from that on Ir/SiO_2. That is, the Ir metal active sites on Ir/SiO_2 for NO reduction were modified by the addition of W species.

(2) The NO reduction activity on Ir/WO_3–SiO_2 was greatly promoted by pretreatment with H_2O. Peaks due to Ir metal and WO_3 were observed in the XRD pattern of the H_2O-treated catalyst, clearly indicating that the active site of Ir/WO_3–SiO_2 consists of a combination of Ir metal and W oxide, i.e., Ir–WO_x species ($2.92 \leq x \leq 3$).

(3) We found that the Ir–WO_x sites promote the NO dissociation step, resulting in a significantly enhanced selective reduction of NO with CO over Ir/WO_3–SiO_2.

Figure 5. NO dissociation activities of the H_2-reduced Ir/SiO_2 catalyst and the H_2O-pretreated Ir/WO_3–SiO_2 catalyst at 300 °C: Amount of pulse, 0.54 ml (10% NO in He), Ir loading: 5 wt%.

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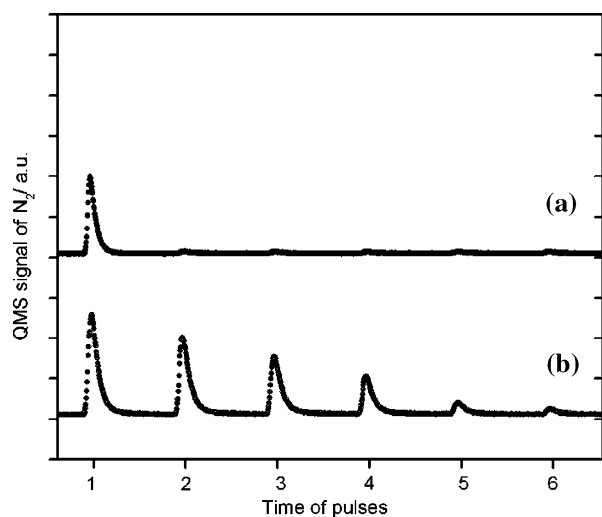[2] R. Burch, A.A. Shestov and A.J. Sullivan, J. Catal. 188 (1999) 69.

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