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In situ diffuse reflectance IR of catalytic reduction of nitrogen oxides by propene in the presence of oxygen over silica-supported platinum

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Abstract

The reaction mechanism of catalytic reduction of nitrogen oxides (NO or NO_2) by propene in the presence of O_2 has been studied by means of in situ diffuse reflectance IR, combined with transient response analysis. Three surface species, organic nitro (**I**) (1565 cm^{-1}), carbonyl (**II**) (1740 cm^{-1}), and isocyanate species (**III**) (2174 cm^{-1}) were the main species detected during the reaction. Organic nitro (**I**) and isocyanate species (**III**) were highly reactive toward NO_2 and O_2 to form N_2 and N_2O, suggesting that these are the intermediates.

Keywords: Reduction; NO_x; Diffuse reflectance IR; Silica-supported platinum; Isocyanate

1. Introduction

Selective catalytic reduction of NOx with hydrocarbons in the presence of excess oxygen is a promising method for the removal of NOx in the exhaust gases from diesel and lean-burn gasoline engines. Iwamoto [1] and Held et al. [2] reported independently, following earlier patents, that catalytic reduction of NOx by hydrocarbons was promoted by excess oxygen over Cu–ZSM-5. Afterwards, H-form zeolite [3], Al_2O_3 [4], Ce–ZSM-5 [5,6], Ga–ZSM-5 [7], etc. were reported to be effective. In addition, Pt–ZSM-5 [2,8], supported platinum catalysts [9], and Pt–Rh/Al_2O_3 [10] were also active for the selective reduction of NO with hydrocarbons at low temperatures. It has been emphasized that the activities of the Pt catalysts were little diminished by the introductions of SO_2 [9] or water [10]. Interestingly, it was found that methane was an effective reductant for this reaction over Co–ZSM-5 [11], Ga–ZSM-5 [12], and Pd–ZSM-5 [13].

Several reaction mechanisms have been proposed for this reaction [14]. Iwamoto and Mizuno [15] suggest that oxygen reacts first with hydrocarbon to form partially oxidized hydrocarbons, and then they react with NO over Cu–ZSM-5. On the other hand, it was shown that the reaction between NO_2 and hydrocarbon was crucial over Al_2O_3 [4], Ce–ZSM-5 [16,17] and Pt/SiO_2 [18]. Organic nitro species was proposed as a possible intermediate by IR stud-

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ies [16–18]. Isocyanate (–NCO) and nitrile (–CN) species formed on the surface have been claimed as possible intermediates [19–21]. However, the reactivities of these species are not yet fully elucidated. Here we wish to report that isocyanate species as well as organic nitro species are key surface species for this reaction.

2. Experimental

Pt/SiO_2 (Pt, 5.5 wt%) was prepared by an impregnation method with SiO_2 (Reference Catalyst of Catalysis Society of Japan, JRC-SIO-4; 347 $m^2\ g^{-1}$) and an aqueous solution (0.1 mol dm^{-3}) of $Pt(NH_3)_4(OH)_2$ (Strem Chem.) [18]. After the sample was calcined at 500°C for 5 h in air, it was reduced at 450°C for 3 h in a flow of H_2 (50 ml min^{-1}). The dispersion of Pt was determined to be 15% by CO adsorption [18]. The reaction was carried out in a continuous flow reactor (12 mm Pyrex tube) under atmospheric pressure in the temperature range from 50 to 300°C. Prior to the reaction, the catalyst (0.3 g) was pretreated with a flow of H_2 at 350°C for 1 h and then with a flow of He (0.5 h). The feed gas (100 ml min^{-1}) consists of NO or NO_2 (1000 ppm), C_3H_6 (500 ppm) and O_2 (2%) with He balance. The products were analyzed with a gas chromatograph (Nippon Tylan, M-200) equipped with Molecular sieve 5A for O_2, N_2 and CO, and Porapak Q for CO_2, N_2O and C_3H_6. An NOx meter (Yanaco, ELC-77A) was used for the analysis of NO and NO_2. Infrared spectra of the adsorbed species on the catalyst were recorded on an IR spectrometer (Shimadzu 8500). As shown in Fig. 1, a diffuse reflectance infrared cell (Spectra Tech Inc., 0030-033) is directly connected with the flow system, where the feed gas passes first through the cell and then the reactor. About 30 mg of the catalyst was set in the IR cell. Transient responses upon the change of the feed gas were followed by using the IR and GC. For assignment of the surface species, isotopes of ^{15}NO (^{15}N, 95%), $^{18}O_2$ (^{18}O, 99%), and $N^{18}O$ (^{18}O, 45%) were used. An IR cell made of Pyrex has been used to measure the isotope shift [18].

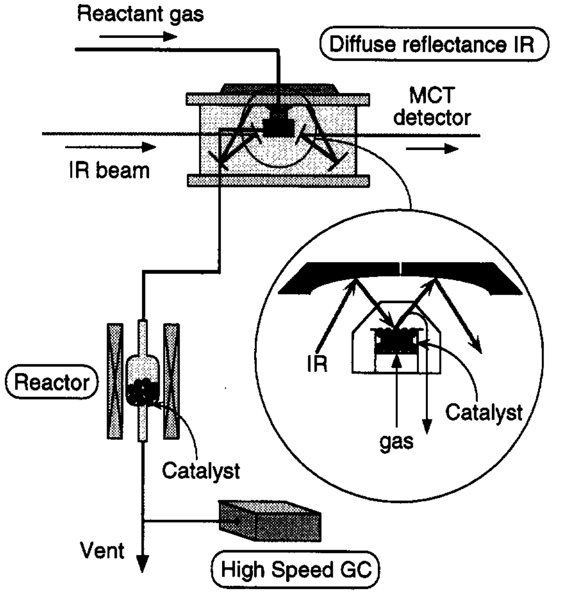


Fig. 1. Apparatus of the flow system.

3. Results and discussion

3.1. Selective reduction of NOx and IR spectroscopy

Fig. 2 shows the temperature dependencies of NOx conversion to $N_2 + N_2O$ and C_3H_6 conversion to CO_2 for $NO + C_3H_6 + O_2$ or $NO_2 + C_3H_6 + O_2$. The temperature was raised stepwise after the reaction reached a stationary state at each temperature. In the absence of O_2

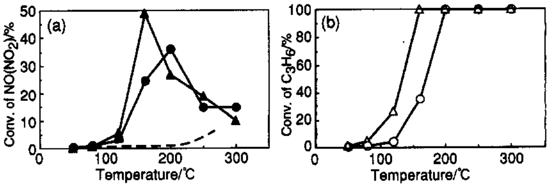


Fig. 2. Temperature dependencies of conversion of NOx to $N_2 + N_2O$ (a) and of C_3H_6 to CO_2 (b) over Pt/SiO_2. △ and ▲, $NO+C_3H_6+O_2$; ○ and ●, $NO_2+C_3H_6+O_2$; ---, $NO+C_3H_6$; NO or NO_2, 1000 ppm, C_3H_6, 500 ppm, O_2, 2%; total flow rate, 100 $cm^3\ min^{-1}$; and Pt/SiO_2, 0.3 g.

(broken line in Fig. 2), the reaction of NO with propene was slow below 250°C. On the other hand, in the presence of O_2, the reaction took place, and the NO conversions showed a maximum for each reaction system. The reaction rate of $NO_2 + C_3H_6 + O_2$ was higher than that of $NO + C_3H_6 + O_2$ below 150°C, but no large difference between them was observed at higher temperatures. The oxidation of propene started at about 80 and 120°C for $NO_2 + C_3H_6 + O_2$ and $NO + C_3H_6 + O_2$, respectively (Fig. 2b).

Oxidation of NO (1000 ppm) with O_2 (2%) to NO_2 reached the equilibrium at 250°C over Pt/SiO_2, showing that Pt/SiO_2 is more active than Cu–ZSM-5 for the NO oxidation [16].

The infrared spectra of the adsorbed species on Pt/SiO_2 during the reaction of $NO_2 + C_3H_6 + O_2$ is given in Fig. 3, where the temperature was also elevated stepwise. The data were taken after 1 h at each temperature. At 50°C, two main peaks appeared at 1565 and 1656 cm^{-1}. As the temperature increased, the intensities of both peaks decreased. The peak intensity of the 1740 cm^{-1} band increased and showed a maximum at 210°C. In the range of higher wave number (2000–3000 cm^{-1}), a small peak at 2174 cm^{-1} was detected above 200°C (note that the absorbance expanded 10 times).

As reported previously [18], the bands at 1565 and 1656 cm^{-1} can be assigned to $\nu(NO_2)$ and $\nu(ONO)$ of the surface organic nitro and nitrite compounds, respectively, on the basis of the isotope shift for ^{15}NO and the comparison with the spectra of standard nitro and nitrite compounds adsorbed on the surface. In addition, the band at 1740 cm^{-1} is assignable to $\nu(CO)$ of organic carbonyl species, since no isotope shift was observed when ^{15}NO was used in place of ^{14}NO. The assignment of the peak at 2174 cm^{-1} was attempted. When ^{15}NO (^{15}N, 95%) was used instead of NO for $NO + C_3H_6 + O_2$ system, the peak shifted to a lower wave number, 2160 cm^{-1}, as shown in Fig. 4. Furthermore, the peak also shifted to a lower wave number, 2151 cm^{-1} in the case of $N^{18}O$ (^{18}O, 45%) $+ C_3H_6 + {}^{18}O_2$. These results show that the peak at 2174 cm^{-1} is due to the species containing both N and O atoms. Thus the species can be assigned to isocyanate (–NCO) species.

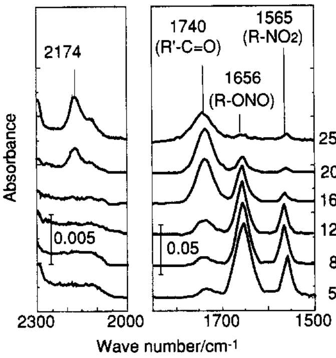


Fig. 3. IR spectra of the surface species during $NO_2 + C_3H_6 + O_2$ reaction at elevated temperatures. The reaction conditions are the same as in Fig. 2.

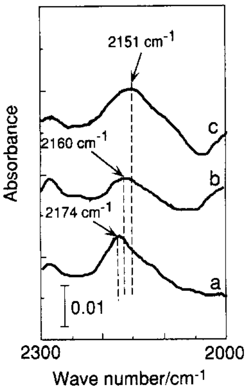


Fig. 4. IR spectra of the adsorbed species formed on Pt/SiO_2 at 180°C after exposure to (a) $NO + C_3H_6 + O_2$; (b) $^{15}NO + C_3H_6 + O_2$; and (c) $N^{18}O + C_3H_6 + {}^{18}O_2$. NO_2, 3 torr; C_3H_6, 3 torr; O_2, 30 torr; and Pt/SiO_2, 0.05 g.

3.2. *Reactivities of the surface species*

Fig. 5 shows the transient responses upon the switching of gas from He to O_2 after the reaction of $NO_2 + C_3H_6 + O_2$ reached the stationary state at 120°C. The intensity of the peak at 1565 cm^{-1} due to organic nitro species (**I**) decreased rapidly just after the switching and then decreased gradually with time (Fig. 5a). In the case of the organic nitrite species, the re-

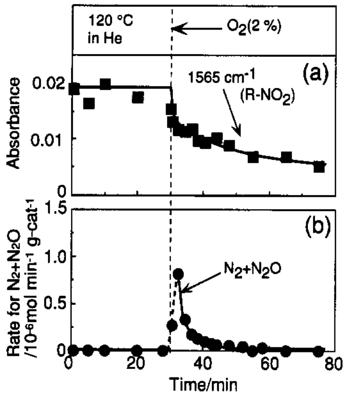


Fig. 5. Responses of the absorbance of the band at 1565 cm^{-1} (a) and the rate of the formation of N_2+N_2O (b) upon addition of O_2 to the surface species on Pt/SiO_2. Pt/SiO_2 was first exposed to $NO_2+C_3H_6+O_2$ stream at 50°C for 2 h, and the gas phase was purged by He at 120°C for 0.5 h. Then O_2 was introduced at 120°C. IR spectra were measured continuously after the introduction of He.

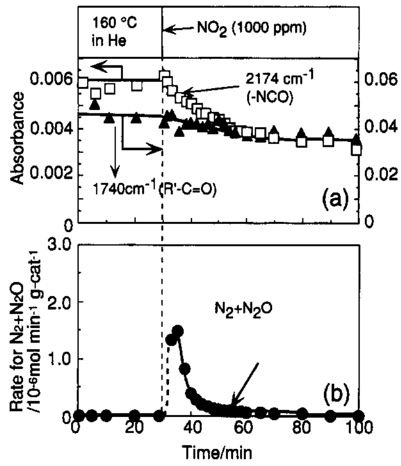


Fig. 6. Responses of the peaks at 1740 and 2174 cm^{-1} (a) and the rate of the formation of N_2+N_2O (b) upon the addition of NO_2 on Pt/SiO_2. Pt/SiO_2 was first exposed to $NO+C_3H_6+O_2$ stream at 160°C for 2 h, and then the gas phase was purged by He for 0.5 h. Then NO_2 was introduced at 160°C as shown in the figure.

sponse of IR band intensity was not reliable (rather scattered), probably because the water adsorbed on the surface disturbed the measurement. N_2 and N_2O were formed after the addition of O_2. The rate of the formation of N_2 and N_2O decreased greatly with time (Fig. 5b). The addition of NO_2 gave a result similar to that of O_2, but NO and C_3H_6 did not react with the organic nitro species (I).

In order to examine the reactivities of carbonyl (II) and isocyanate species (III), the responses upon the addition of NO_2 were followed. The responses at 160°C are given in Fig. 6, where these surface species were preformed by the reaction of $NO+C_3H_6+O_2$ at 160°C. The peak intensity of the isocyanate species (III) decreased upon the addition of NO_2 and became nearly constant after about 20 min. On the other hand, the change in the intensity of carbonyl species (II) was small upon the addition of NO_2. In the gas phase, N_2 and N_2O as nitrogen containing products were produced after the addition of NO_2 (Fig. 6b). These results indicate that the reaction occurred between isocyanate species (III) and NO_2, but not between carbonyl species (II) and NO_2, resulting in the formation of N_2 and N_2O.

In order to elucidate the reactivity of the surface isocyanate species (III) in situ, the responses of IR intensity and the gas phase were measured upon the switching of the feed gas from $NO+C_3H_6+O_2$ to one gas only. The result for the switching to NO is shown in Fig. 7; here the feed gas was switched after the reaction reached a stationary state at 180°C. It is clear that the peak intensity was almost un-

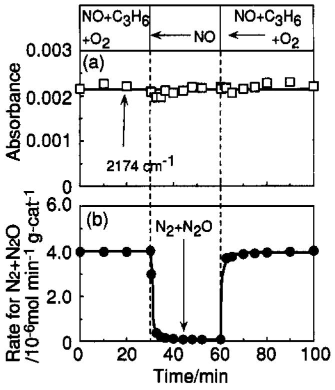


Fig. 7. Responses of the intensities of IR peaks at 2174 cm^{-1} (a) and the rate for the formation of N_2+N_2O (b) upon switching the feed gas from $NO+C_3H_6+O_2$ to NO at 180°C. NO, 1000 ppm; C_3H_6, 500 ppm; O_2, 2%; total flow rate, 100 cm^3 min^{-1}; and Pt/SiO_2, 0.3 g.

changed upon the switching of the feed gas. Furthermore, changes in the formation of $N_2 + N_2O$ were rapid and reversible (Fig. 7) and were consistent with those for the switching to He (blank test). It is presumed that the contribution of the reaction between the isocyanate species (III) and NO is negligibly small.

The reactivity of the isocyanate species (III) to NO_2 is demonstrated in Fig. 8. The decrease in the peak intensity was rapid at the initial stage after the addition of NO_2 and then became slower. It was confirmed that the peak intensity recovered when the feed gas was returned to the reaction mixture. At the same time, an appreciable delay of the response of the rate for the formation of N_2 and N_2O was detected (the response in the blank test is shown by the dotted line in Fig. 8b). The result demonstrates that, contrary to NO, NO_2 reacts with the isocyanate species (III) to form N_2 and N_2O. It should be noted that the changes of the intensity of the IR peak were slow as compared to those of the rate of the product formation. It is probable that there are several isocyanate species and a part of the surface isocyanate species (III) is involved in the catalytic reaction, but the remaining has little reactivity toward NO_2. It is presumed that the species adsorbed on the SiO_2 surface of Pt/SiO_2 did not react and hardly changed upon the addition of NO_2 or O_2.

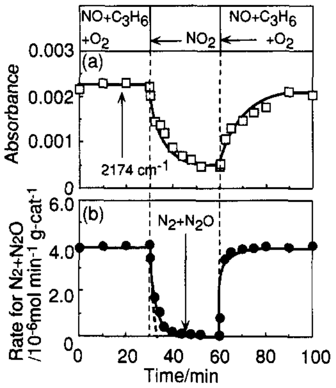


Fig. 8. Responses of the intensities of the IR peaks at 2174 cm^{-1} (a) and the rate for the formation of $N_2 + N_2O$ (b) upon switching the feed gas from $NO + C_3H_6 + O_2$ to NO_2 or NO at 180°C on Pt/SiO_2. NO or NO_2, 1000 ppm; C_3H_6, 500 ppm; O_2, 2%; total flow rate, 100 cm^3 min^{-1}; and Pt/SiO_2, 0.3 g.

Table 1

Reactivities of the surface species toward each reactant gas

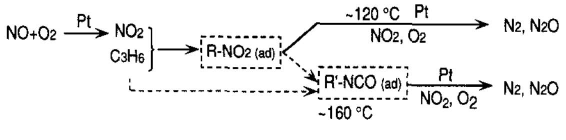
	NO_2	NO	O_2	C_3H_6
$R-NO_2$ (1565 cm^{-1})	+	−	+	−
$R'-C=O$ (1740 cm^{-1})	−	−	−	−
−NCO (2174 cm^{-1})	+	−	+	−

+, reactive; −, non-reactive.

When the O_2 was added instead of NO_2 under the same conditions as in Fig. 8, the responses of the IR peak intensity and the rate were similar to those in Fig. 8, indicating that the reaction between the isocyanate species (III) and O_2 is also the key reaction.

In Table 1, the reactivities of these three surface species toward each reactant gas examined as described above are summarized. The organic nitro (I) and isocyanate species (III) reacted with NO_2 and O_2 to form N_2 and N_2O, while the organic nitro (I) and isocyanate species (III) were inactive to propene and NO. On the other hand, carbonyl species (II) were inactive to all of these gases.

From these results, we conclude that the main reactions for the formation of N_2 and N_2O are those between organic nitro species (I) and NO_2 and/or O_2 at low temperature conditions, and between isocyanate species (III) and NO_2 and/or O_2 at high temperature conditions. We propose the reaction scheme illustrated in Scheme 1 for the selective reduction of NO. First, propene reacts with NO_2 which is formed from NO and O_2, resulting in the formation of organic nitro species (I). The oxidation step of NO is accelerated by Pt, since SiO_2 was inactive for this reaction. The organic nitro species (I) behaves as a reaction intermediate around 120°C. The isocyanate species (III) formed at higher temperatures also contributes to the catalytic formation of N_2 and N_2O. Whether iso-



Scheme 1. A proposed reaction mechanism.

cyanate species (**III**) is formed from the organic nitro species (**I**) or not is still unclear at present.

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