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Infrared study of catalytic reduction of nitrogen monoxide by propene over Ag/TiO_2–ZrO_2

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Abstract

The reaction mechanism of NO reduction by propene over silver-supported TiO_2–ZrO_2 catalyst was studied by means of in situ FT-IR, combined with catalytic activity studies. The catalytic activity studies suggested that silver plays an important role as the active species. In FT-IR measurements under a static condition, organic nitro (R-NO_2), nitrite (R-ONO), inorganic NO_3^-, carbonate, formate and acetate species were detected when TiO_2–ZrO_2 or Ag/TiO_2–ZrO_2 was exposed to a gas mixture of $NO+C_3H_6+O_2$ at room temperature. In the case of Ag/TiO_2–ZrO_2, an intense IR band assigned to isocyanate (–NCO) species was observed by evacuation at temperatures above 300°C after being exposed to $NO+C_3H_6+O_2$. Under a dynamic condition, the isocyanate band was not detected on Ag/TiO_2–ZrO_2, but observed on TiO_2–ZrO_2. The isocyanate species was found to be highly reactive toward NO_2. A reaction mechanism has been proposed that organic nitro and nitrite compounds formed initially on TiO_2–ZrO_2 are converted on Ag sites to isocyanate, which is then reduced to N_2 by the reaction with NO_2 on Ag sites. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Nitrogen monoxide; Selective reduction; Fourier transform infrared; Ag/TiO_2–ZrO_2; Isocyanate

1. Introduction

Air pollution by nitrogen oxides (NO_x) emitted from mobile and stationary sources is a serious environmental problem to be solved because NO_x cause acid rain destroying the environment. In this connection, the selective catalytic reduction of NO with hydrocarbons or oxygenated hydrocarbons (HC-SCR) in the presence of oxygen has attracted much attention recently. For this reaction, zeolite-based catalysts such as Cu-ZSM-5 [1], alumina-based catalysts such as Co/Al_2O_3 [2–4,7] and supported noble metals [5,6] have been reported. However, the activities of these catalysts differ remarkably depending upon the kind of support, the supported metal and the hydrocarbon used as reductant.

A lot of different reaction mechanisms have been proposed so far concerning HC-SCR. They can be roughly classified into ‘‘decomposition mechanism’’ and ‘‘reduction mechanism’’ [8]. The latter mechanism in which NO is reduced into N_2 via some nitrogen and oxygen containing intermediates has been supported by many researchers [9–13]. In the recent infrared (IR) studies on HC-SCR, several surface species such as inorganic NO_3^- [14,17], –$(N_xO_y)_z$ [16], nitro (–NO_2) [15,18,19], nitrite (–ONO) [14,18,19], nitrile (cyanide) (–CN) [14,15,18–20] and isocyanate (–NCO) [16,20–22] have been observed. However, the majority of these investiga-

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tions were made either under reduced pressures or in the flow of reaction gases. In the former case, it is hard to reveal which of many species observed in IR absorption spectra is the true intermediate for NO reduction into N_2. In the latter case, it is often difficult to discuss the exact reaction mechanism because the adsorbed species having high reactivity cannot be observed.

In this study, we made IR measurements of adsorbed species formed over Ag/TiO_2–ZrO_2 in the reaction gas of NO–C_3H_6–O_2 to investigate the reaction mechanism of the selective reduction of NO with propene in the presence of oxygen. In order to examine in detail the behavior of adsorbed species, two conditions were employed: one is a static condition at a low pressure and the other is a dynamic condition in the reaction gas at atmospheric pressure. Ag/TiO_2–ZrO_2 was selected as the catalyst because Ag/TiO_2–ZrO_2 showed the highest catalytic activity for NO reduction by propene of several transition metal-supported TiO_2–ZrO_2 catalysts [23]. We will discuss the reaction mechanism based on this in situ FT-IR study.

2. Experimental

2.1. Materials

TiO_2–ZrO_2 was prepared by a coprecipitation method. A mixture of titanium(IV) tetraisopropoxide ($Ti(OC_3H_7)_4$) and zirconium(IV) tetrapropoxide ($Zr(OC_3H_7)_4$) was added into 2-propanol at 60°C and stirred at the same temperature for 2 h. The resulting solution was hydrolyzed by adding it dropwise into an excess amount of distilled water at room temperature. The precipitate thus formed was separated by centrifuging and was dried at 110°C. The sample was finally calcined at 500°C for 5 h in flowing air. The molar ratio of TiO_2/ZrO_2 in the binary oxide was fixed at unity. BET surface area of TiO_2–ZrO_2 was found to be 284 $m^2\ g^{-1}$. Ag/TiO_2–ZrO_2 catalyst was prepared by immersing TiO_2–ZrO_2 powder in an aqueous solution of $Ag(NO_3)$, followed by drying and calcination at 500°C for 5 h in flowing air. Since we found previously that the maximum NO conversion on Ag/TiO_2–ZrO_2 was attained at a silver loading of 5 wt% [23], silver loading was fixed at 5 wt% as Ag metal. The observed surface area of 5 wt% Ag/TiO_2–ZrO_2 was 152 $m^2\ g^{-1}$.

The gases ^{14}NO, C_3H_6, O_2, 0.3% NO/He, 30% O_2/He and 1% C_3H_6/He supplied from Takachiho Kagaku Kogyo and ^{15}NO (isotopic purity, 99.5 at.%) supplied from Shoko were used without further purification.

2.2. Catalytic activity measurements

The catalytic activity was measured with a fixed-bed flow reactor by passing a reactant gas containing 900 ppm NO, 10% O_2, 860 ppm C_3H_6 and helium as the balance gas at a rate of 66 $cm^3\ min^{-1}$ over 0.2 g of catalyst. NO_2 (930 ppm) reduction and propene (860 ppm) oxidation by O_2 (10%) were also carried out. The analysis of the effluent gas was made by gas chromatographs equipped with a Molecular Sieve 5A column (for the analysis of N_2 and CO) and a Porapak Q column (for that of CO_2, N_2O, and C_3H_6). The reaction temperature was changed with a step of 50°C from 500°C to 200°C.

2.3. FT-IR measurements

Fourier transform infrared (FT-IR) spectra were recorded by using an FT-IR spectrometer (Shimadzu FT-IR 8600) equipped with an MCT detector at a resolution of 4 cm^{-1}. A self-supporting sample disk (20 mm diameter, about 50 mg) prepared by pressing the catalyst powder of TiO_2–ZrO_2 or Ag/TiO_2–ZrO_2 was placed in an IR cell with NaCl windows. All the IR measurements were carried out at room temperature.

As for the IR measurements under the static condition, the sample disk was pretreated according to the following procedure: evacuation at 500°C for 1 h, oxidation at 500°C for 1 h with oxygen at 100 T (1 T=133.3 Pa), cooled either to room temperature or to 300°C in the same atmosphere and evacuation at the same temperature for 30 min. After the sample was exposed to a reaction gas composed of NO (5 T), C_3H_6 (5 T) and O_2 (50 T) either at room temperature or at 300°C for 2 h, outgassed for 30 min, FT-IR spectra of adsorbed species formed on the catalyst were recorded. IR spectra were also taken after being heated up to a desired temperature. In order to clarify the contribution of nitrogen atom to the IR absorption, the isotopic shift of the IR peaks was checked by using ^{15}NO.

As for the IR measurements under the dynamic condition, the sample disk was heated in He flow at 500°C for 1 h, oxidized in a flow of 10% O_2/He at 500°C for 1 h, and then a reaction gas mixture containing 900 ppm NO, 900 ppm C_3H_6, 10% O_2 and He as the balance gas was introduced at a rate of 60 cm^3 min^{-1}. After that, FT-IR spectra were taken, as the reaction gas was flown steadily and then the temperature was decreased from 500°C to 200°C in steps of 100°C.

The IR spectra taken here were displayed in absorbance units, and the background spectra were monitored each time before the observation of adsorbed species.

3. Results and discussion

3.1. *Catalytic activity of* Ag/TiO_2–ZrO_2 *for* NO *reduction by propene*

Table 1 summarizes the catalytic activity of TiO_2–ZrO_2 and Ag/TiO_2–ZrO_2 for NO+C_3H_6+O_2, NO_2+C_3H_6+O_2 and C_3H_6+O_2 reactions. Obviously, the addition of silver into TiO_2–ZrO_2 enhanced drastically NO conversion to N_2 as well as C_3H_6 conversion to CO_x for NO+C_3H_6+O_2 reaction, suggesting that the supported silver plays an important role for this reaction.

It has been reported that one of the roles of the supported metal is to promote NO oxidation to NO_2, as in the case of Co in Co/Al_2O_3 [24] and Ce in Ce-ZSM-5 [25]. However, Table 1 shows that NO_2 conversion to N_2 on TiO_2–ZrO_2 was much lower than NO conversion to N_2 on Ag/TiO_2–ZrO_2, indicating that the role of silver on Ag/TiO_2–ZrO_2 is not to accelerate NO oxidation. It was suggested in our previous study [26] that the first reaction step is the NO oxidation to NO_2 on acid sites of TiO_2–ZrO_2.

In Table 1 are also presented the conversions of propene into CO_x for the reaction systems of NO+C_3H_6+O_2, NO_2+C_3H_6+O_2 and C_3H_6+O_2. Apparently, silver did not affect the activity of TiO_2–ZrO_2 for simple oxidation of propene by oxygen. However, the addition of nitrogen oxides (NO or NO_2) into the reaction gas caused a difference in the catalytic performance between TiO_2–ZrO_2 and Ag/TiO_2–ZrO_2, namely, the conversion of propene to CO_x on Ag/TiO_2–ZrO_2 was increased by the presence of nitrogen oxides, while that on TiO_2–ZrO_2 was depressed, meaning that silver accelerates the reduction of nitrogen oxides with propene.

On the basis of our experimental results, we speculated that NO reduction over Ag/TiO_2–ZrO_2 proceeds mainly through the following pathway. NO_2 formed on acid sites of TiO_2–ZrO_2 is reduced to N_2 via the formation of several intermediates by the reaction with propene on silver sites. IR studies were performed next to investigate possible reaction intermediates on the catalysts.

3.2. *IR spectra obtained under the static condition*

3.2.1. *Behavior of adsorbed species formed on* TiO_2–ZrO_2 *and* Ag/TiO_2–ZrO_2 *at room temperature*

TiO_2–ZrO_2 and Ag/TiO_2–ZrO_2 catalysts were exposed to a gas mixture of NO+C_3H_6+O_2 at room

Table 1
Comparison of the conversions of NO_x to N_2 and C_3H_6 to CO_x on TiO_2–ZrO_2 and 5% Ag/TiO_2–ZrO_2 for several reaction systems

Catalyst	Reaction	NO_x conversion to N_2 (%) (C_3H_6 conversion to CO_x (%))				
		300°C	350°C	400°C	450°C	500°C
TiO_2–ZrO_2	NO+C_3H_6+O_2	10 (5.7)	13 (12)	24 (30)	35 (60)	27 (82)
	NO_2+C_3H_6+O_2	27 (16)	33 (25)	42 (40)	49 (68)	35 (89)
	C_3H_6+O_2	(34)	(58)	(69)	(76)	(81)
5% Ag/TiO_2–ZrO_2	NO+C_3H_6+O_2	18 (16)	52 (55)	70 (84)	66 (93)	55 (95)
	NO_2+C_3H_6+O_2	32 (35)	60 (70)	66 (86)	58 (94)	45 (96)
	C_3H_6+O_2	(33)	(51)	(66)	(78)	(87)

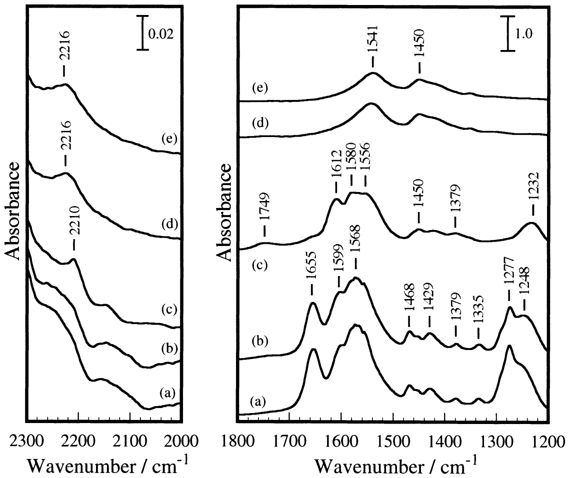


Fig. 1. FT-IR spectra of adsorbed species formed on TiO_2–ZrO_2 after exposure to a gas mixture of NO (5 T)+C_3H_6 (5 T)+O_2 (50 T) at room temperature for 2 h and subsequent heating in vacuum for 30 min at temperature: (a) room temperature, (b) 100°C, (c) 200°C, (d) 300°C and (e) 350°C.

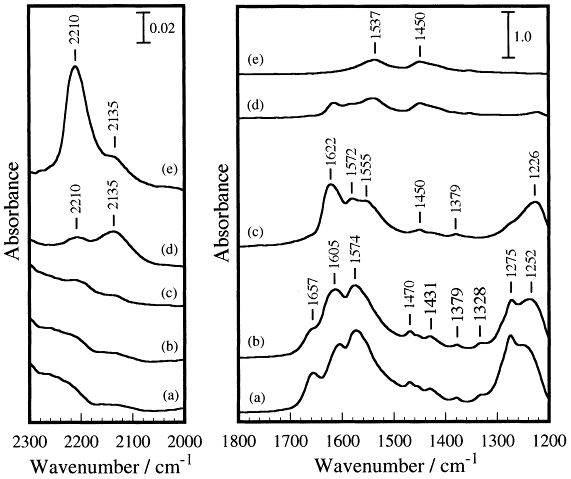


Fig. 2. FT-IR spectra of adsorbed species formed on 5% Ag/TiO_2–ZrO_2 after exposure to a gas mixture of NO+C_3H_6+O_2 at room temperature for 2 h and subsequent heating in vacuum for 30 min at temperature: (a) room temperature, (b) 100°C, (c) 200°C, (d) 300°C, (e) 350°C. The composition of the gas mixture is the same as for Fig. 1.

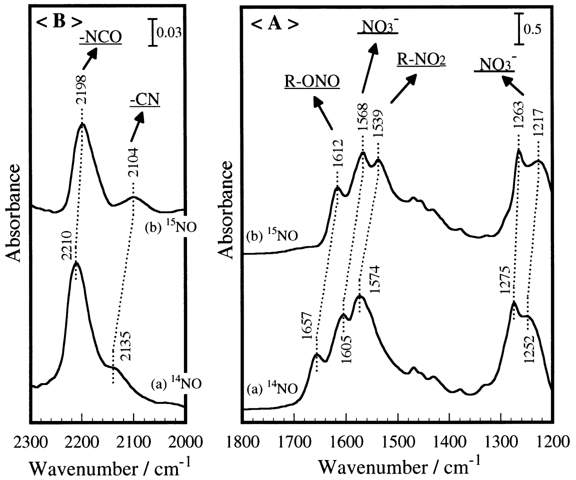


Fig. 3. Isotopic shift of FT-IR spectra of adsorbed species formed on 5% Ag/TiO_2–ZrO_2 after exposure to a gas mixture of (a) $^{14}NO + C_3H_6 + O_2$ and (b) $^{15}NO + C_3H_6 + O_2$ at room temperature for 2 h and subsequent heating in vacuum for 30 min at temperature: (A) room temperature and (B) 350°C. The composition of the gas mixture is the same as for Fig. 1.

temperature for 2 h and were heated up to 350°C after evacuation for 30 min. Fig. 1 and 2 show the change in the IR spectra of adsorbed species on TiO_2–ZrO_2 and Ag/TiO_2–ZrO_2 with increasing temperature in vacuum, respectively. In the IR spectra obtained after the evacuation at room temperature, no remarkable difference in the IR spectra between TiO_2–ZrO_2 and Ag/TiO_2–ZrO_2 was observed, although many IR peaks appeared in the region below 1800 cm^{-1}. The only difference was that the relative intensity of the 1655 cm^{-1} band on TiO_2–ZrO_2 was slightly stronger than that on Ag/TiO_2–ZrO_2, suggesting that TiO_2–ZrO_2 participates in the formation of this species. Of these peaks, five intense peaks at 1250, 1275, 1575, 1600 and 1657 cm^{-1} shifted to lower wave numbers when ^{15}NO was used instead of ^{14}NO, as shown in Fig. 3(A). This indicates that the species responsible for these peaks contain nitrogen atoms.

Among the five peaks for which the isotopic shift by ^{15}NO was observed, the 1250, 1275 and 1600 cm^{-1} bands were also observed when the catalysts were exposed to a mixture of NO and O_2. Accordingly, they can be assigned to surface inorganic NO_x species derived from NO and O_2. Hoost et al. [27] assigned tentatively an IR band at 1233 cm^{-1}, which appeared upon adsorption of NO on the oxidized Pd/Al_2O_3, to nitrate complexes associated with alumina. According to the IR observations during NO_2 adsorption on TiO_2 by Hadjiivanov et al. [28], the IR absorption peaks attributable to NO_3^- monodentate and NO_3^- bidentate compounds seem to appear in the regions of 1600–

1500 cm^{-1} and 1300–1200 cm^{-1}. Therefore, the three IR bands at 1250, 1275 and 1600 cm^{-1} observed here can be assigned to inorganic NO_3^- species adsorbed on TiO_2–ZrO_2 support.

On the other hand, the other two IR peaks at 1575 and 1657 cm^{-1} appeared only in the presence of all the three components of NO, C_3H_6 and O_2. This means that they are organic NO_x species containing carbon and nitrogen. Misono et al. [18,19] observed intense IR absorption peaks at 1555 and 1655 cm^{-1} during NO-C_3H_6-O_2 reaction at temperatures around 100°C on Ce-ZSM-5 and Pt/SiO_2. They assigned the 1555 cm^{-1} band to ν(–NO_2) of an organic nitro compound (R-NO_2) and the 1655 cm^{-1} band to ν(–ONO) of an organic nitrite compound (R-ONO). Tabata et al. [14] also suggested that a 1670 cm^{-1} band on Cu-ZSM-5 can be assigned to an organic NO_x species (–ONO or –ONO_2). Therefore, the IR absorption peaks at 1575 and 1657 cm^{-1} observed here would be assigned to ν(–NO_2) and ν(–ONO) of an organic nitro and nitrite compound, respectively.

The weak IR bands between 1300 and 1500 cm^{-1} were also observed when both catalysts were exposed to a mixture of propene and oxygen. Although the accurate assignment of these bands is considerably difficult, these peaks would be due to carbonate, formate and/or acetate species formed by the reaction of propene with oxygen, judging from their band positions [29].

When the temperature was elevated to above 100°C in vacuum, a pronounced difference in the IR spectra between TiO_2–ZrO_2 and Ag/TiO_2–ZrO_2 was observed. For TiO_2–ZrO_2 catalyst (Fig. 1), the intensity of almost all the peaks was hardly changed, when the sample was heated at 100°C in vacuum. On the other hand, the intensity of the 1275 (NO_3^-), 1574 (–NO_2) and 1657 cm^{-1} (-ONO) bands on Ag/TiO_2–ZrO_2 was weakened evidently at 100°C (Fig. 2(b)), meaning that the supported silver seems to promote the reaction or decomposition of these species. Further heating up to 200°C in vacuum caused an appearance of two broad bands at 2135 and 2210 cm^{-1} along with a complete disappearance of the 1657 and 1275 cm^{-1} bands on Ag/TiO_2–ZrO_2 (Fig. 2(c)). The new bands above 2000 cm^{-1}, particularly 2210 cm^{-1} band, grew up considerably with increasing temperature. Since many IR peaks below 2000 cm^{-1} observed at 200°C disappeared at the same time at the temperatures above 300°C, the 2135 and 2210 cm^{-1} bands would be due to the decomposition and/or the reaction of these species. Evidently, the supported silver plays an important role for the conversion of these species, because the intensity of the 2216 cm^{-1} band on TiO_2–ZrO_2 did not change even at elevated temperatures above 300°C (Fig. 1).

Ukisu et al. [22] observed two intense IR bands at 2262 and 2232 cm^{-1} on Ag/Al_2O_3 by NO-ethanol-O_2 reaction. They assigned the former IR band to the –NCO species coordinated to silver supported on alumina and the other band to that coordinated to alumina. The same assignment was also made for NO–CO reaction over noble metal catalysts by Unland [30]. Bamwenda et al. [20] observed IR bands at 2125 and 2232 cm^{-1} on Rh/Al_2O_3 and assigned them to a cyanide (–CN) species associated with Rh and an –NCO species coordinated to alumina, respectively. The isotopic shift of the 2135 and 2210 cm^{-1} bands by using ^{15}NO instead of ^{14}NO was observed (Fig. 3(B)), meaning that these species contain nitrogen. Taking into account these facts, the IR band at 2135 cm^{-1} on Ag/TiO_2–ZrO_2 in Fig. 2(d) would be ascribed to a surface cyanide (–CN) species coordinated to Ag. The 2210 cm^{-1} band on Ag/TiO_2–ZrO_2 would be assigned to a surface isocyanate (–NCO) species formed on Ag sites, because its peak position was at a slightly lower wave number compared with that on TiO_2–ZrO_2 (2216 cm^{-1}).

3.2.2. *Behavior of adsorbed species formed on* Ag/TiO_2–ZrO_2 *at* 300°C

Fig. 4 shows the IR spectra of adsorbed species formed on Ag/TiO_2–ZrO_2 after exposure to a gas mixture of NO+C_3H_6+O_2 at 300°C. Three intense IR bands at 1242, 1580 and 1612 cm^{-1} as well as three weak bands at 1454, 1547 and 2123 cm^{-1} were observed immediately after exposure to the gas mixture. Of these peaks, the 1242, 1580 and 1612 cm^{-1} bands would be assigned to weakly adsorbed inorganic NO_3^- species on TiO_2–ZrO_2 and/or silver, because these peaks were weakened by evacuation at 300°C (Fig. 4(c)). The formation of –CN species at 2123 cm^{-1} was recognized and its peak intensity increased with exposure time. The other peaks would be due to carbonate or carboxylate species.

After evacuation at 300°C, interesting change was observed in the IR spectra in the region above

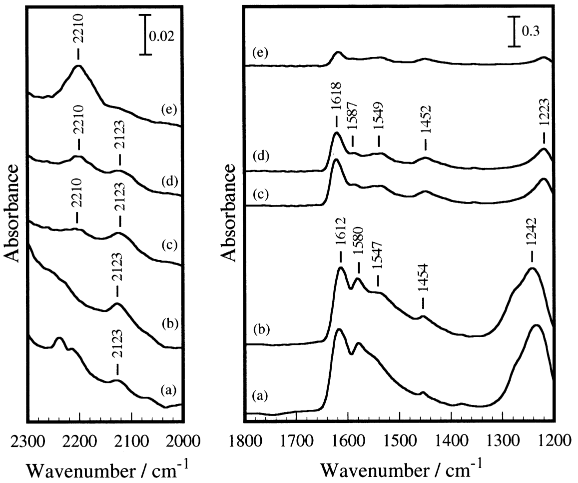


Fig. 4. FT-IR spectra of adsorbed species formed on 5% Ag/TiO_2–ZrO_2 after exposure to a gas mixture of NO+C_3H_6+O_2 at 300°C for (a) 1 min and (b) 2 h, and then evacuation at 300°C for (c) 30 min and (d) 90 min, and (e) at 350°C for 30 min. The composition of the gas mixture is the same as for Fig. 1.

2000 cm^{-1}, namely, the IR band assigned to –NCO species at 2210 cm^{-1} appeared immediately after evacuation. It is noteworthy that the peak intensity of –NCO species increased with evacuation time, while that of –CN species decreased slightly. A part of –CN species is likely to be converted to –NCO species, although its rate seems to be slow. Bamwenda et al. [20] investigated in detail the reactivity of several adsorbed species and revealed that the –NCO species formed on Rh/Al_2O_3 possesses the highest reactivity toward NO_x (NO or NO_2), C_3H_6 and O_2. Yasuda et al. [18] and Okuhara et al. [31] also reported that the –NCO species on Ce-ZSM-5 and Pt/SiO_2 was highly reactive toward NO_2 and O_2 to form N_2 and N_2O. They presumed the –NCO species as the active intermediate in the selective reduction of NO with hydrocarbons. In this study, the –NCO species formed on Ag/TiO_2–ZrO_2 might be the active intermediate leading to the formation of N_2. Because of its high reactivity, the –NCO band would not be observed in the presence of a gas mixture of NO+C_3H_6+O_2. On the other hand, the reactivity of the –CN species seems to be low. Because the intensity of the –NCO band at 2210 cm^{-1} increased by outgassing at 350°C, it is suggested that the –NCO species is formed by the reaction of several adsorbed species.

3.3. IR spectra obtained under the dynamic condition

Fig. 5 and 6 show the IR spectra observed on TiO_2–ZrO_2 and Ag/TiO_2–ZrO_2, respectively, in the flow of a reaction gas containing 900 ppm NO, 900 ppm C_3H_6 and 10% O_2. For TiO_2–ZrO_2 catalyst (Fig. 5), two IR

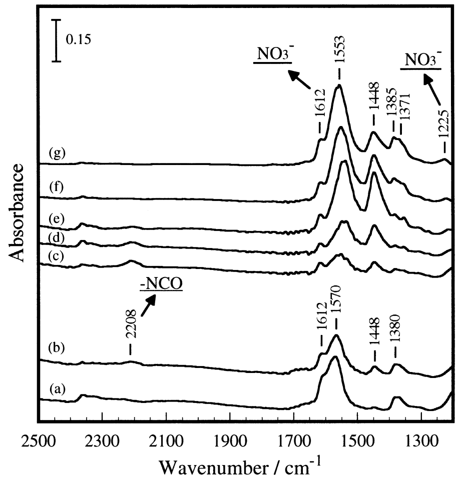


Fig. 5. FT-IR spectra of adsorbed species formed during NO reduction by propene over TiO_2–ZrO_2 at (a) 500°C, (b) 450°C, (c) 400°C, (d) 350°C, (e) 300°C, (f) 250°C and (g) 200°C. Conditions: NO=900 ppm, C_3H_6=900 ppm, O_2=10%, gas flow rate=60 cm^3 min^{-1}.

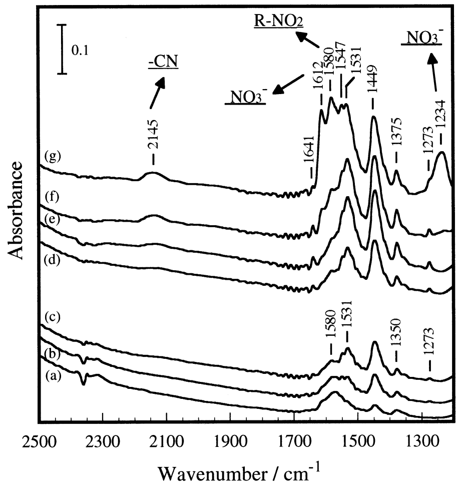


Fig. 6. FT-IR spectra of adsorbed species formed during NO reduction by propene over 5% Ag/TiO_2–ZrO_2 at (a) 500°C, (b) 450°C, (c) 400°C, (d) 350°C, (e) 300°C, (f) 250°C and (g) 200°C. The reaction conditions are the same as for Fig. 5.

bands at 1570 and 1612 cm^{-1} were observed above 1500 cm^{-1} at the temperatures over 350°C. They are assigned to an organic nitro species (–NO_2) and an inorganic NO_3^- species, respectively. The former peak might also be assigned to formate species, because the IR bands ascribed to the stretching mode of formate species appear usually at 1380 and 1560 cm^{-1} [29]. The intensity of the peaks at 1380 and 1570 cm^{-1} declined gradually with decreasing temperature and showed a minimum at 400°C. This means that the formation rate of these species decreased with decreasing temperature and the decomposition rate was faster than the formation rate at 400°C. It should be noted that the –NCO band at 2208 cm^{-1} was observed at the temperatures between 300°C and 450°C. Its peak intensity showed a maximum at 400°C. Since there is a good correlation between the appearance of the –NCO species and the disappearance of –NO_2, formate and/or NO_3^- species, the –NCO species would be formed by the decomposition of –NO_2 species and/or by the reaction of formate species with NO_3^-. However, the reaction rate of the –NCO species on TiO_2–ZrO_2 might be very slow, because the –NCO band was observed in IR spectra.

Ag/TiO_2–ZrO_2 catalyst showed a quite different behavior from TiO_2–ZrO_2 catalyst. As shown in Fig. 6, an IR band at 2145 cm^{-1} was observed below 300°C. This is assigned not to –NCO species but to cyanide (–CN) species. Since the formation of the –NCO species was recognized in the IR measurements under the static condition (Fig. 2), the –NCO species should also be formed in the reaction under the dynamic condition. It is considered that the reaction rate of the –NCO species is very fast over Ag/TiO_2–ZrO_2 and that the supported silver promotes this reaction step. Probably, this step is not rate-determining. IR bands assigned to –NO_2 species and NO_3^- species were observed at 1580 and 1612 cm^{-1} at the temperatures below 350°C, and their peak intensities decreased with increasing temperature. It is also noteworthy that the peak intensity of the IR bands ascribed to the carbon-containing species (1547, 1531, 1449 and 1375 cm^{-1}) on Ag/TiO_2–ZrO_2 was weak compared with that on TiO_2–ZrO_2 and declined with increasing temperature, suggesting that those species formed on Ag/TiO_2–ZrO_2 possess high reactivity and the supported silver accelerates the reaction of these adsorbed species to form the –NCO and –CN species.

3.4. Reaction mechanism on Ag/TiO_2–ZrO_2

On the basis of the present experimental results, the following reaction mechanism of the selective reduction of NO with propene over Ag/TiO_2–ZrO_2 is suggested, namely, NO_2 formed on acid sites of TiO_2–ZrO_2 is reduced to N_2 via several intermediates by the reaction with propene on silver sites. Similar reaction mechanisms have been proposed by many researchers. Recently, Smits and Iwasasa [12] suggested a reaction mechanism, based on some organic chemistry literature, that NO is reduced to N_2 via dispropotionation of nitroso-intermediates formed by the reaction of NO_2 with oxygenated hydrocarbons (e.g. C_3H_6O). The oxygenated hydrocarbons were considered to be formed from the reaction between NO_2 and hydrocarbon (e.g. C_3H_6). According to their mechanism, there may be a lot of adsorbed species formed on the catalyst surface during NO reduction.

In the present study, we made IR measurements to observe the adsorbed species formed during NO reduction by propene. In the IR spectra obtained under the static condition, organic nitro (–NO_2), nitrite (–ONO), inorganic NO_3^- and the carbon containing species such as carbonate, formate and/or acetate were observed on Ag/TiO_2–ZrO_2 as possible precursors for N_2 formation (Fig. 2). Since these species were also formed on TiO_2–ZrO_2 (Fig. 1), it is considered that the supported silver does not play an important role on the formation of these species. The role of silver seems to catalyze the reaction of these species to form isocyanate (–NCO) and cyanide (–CN) species, because the –NO_2 and –ONO bands on Ag/TiO_2–ZrO_2 vanished with the formation of the –NCO and the –CN species at lower temperatures than on TiO_2–ZrO_2.

Concerning the IR measurements under the dynamic condition, the –NCO band was observed on TiO_2–ZrO_2 (Fig. 5), whereas the band was not observed on Ag/TiO_2–ZrO_2 and the –CN band appeared instead (Fig. 6). Since the IR spectra obtained under the static condition shows the presence of –NCO species on Ag/TiO_2–ZrO_2 (Fig. 2), the reactivity of the –NCO species on Ag sites should be very high compared with that on TiO_2–ZrO_2, namely, the supported silver catalyzes the reaction of the –NCO species with the reaction gases and/or the adsorbed species.

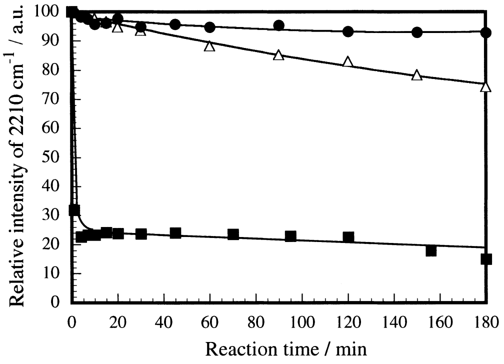
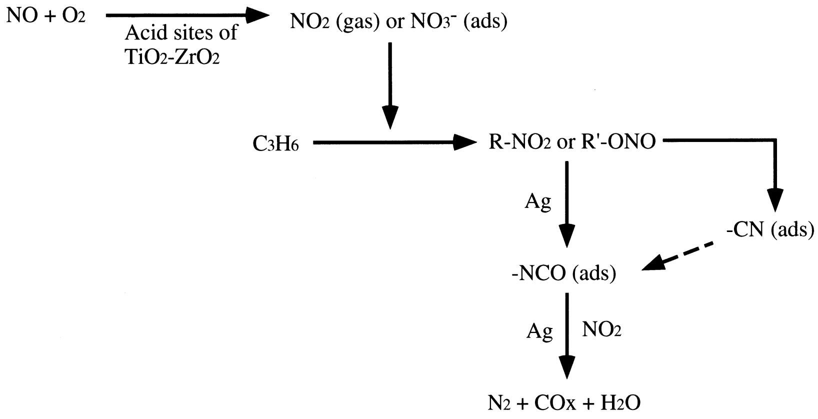


Fig. 7. Changes of the intensity of 2210 cm^{-1} band assigned to –NCO species formed on 5% Ag/TiO_2–ZrO_2 upon the exposure to (●) O_2 (100 T), (△) NO (20 T) and (■) NO (20 T)+O_2 (100 T) at room temperature. The –NCO species was formed under the same conditions as for Fig. 2.

Iwamoto and Takeda [13] reported that the isocyanate species is the final intermediate leading to the formation of N_2 and CO_2 in the selective reduction of NO with hydrocarbon over Cu-ZSM-5. They presumed that the –NCO species reacts with NO. Okuhara et al. [31] reported recently that the isocyanate species formed on Pt/SiO_2 was highly reactive toward NO_2 and O_2 to form N_2 and N_2O. Accordingly, the reactivity of the –NCO species toward NO, NO+O_2 (NO_x) and O_2 was investigated on Ag/TiO_2–ZrO_2 catalyst at room temperature under the static condition. In this experiment, the –NCO species was first produced by heating up to 350°C in vacuum after exposing to NO+C_3H_6+O_2 at room temperature. After cooling the sample disk to room temperature in vacuum, a reaction gas of O_2 (100 T), NO (20 T) or NO (20 T)+O_2 (100 T) was introduced into the IR cell at the same temperature. Fig. 7 shows the change of the intensity of the –NCO band (2210 cm^{-1}). When only O_2 or NO was introduced, the peak intensity of the –NCO species decreased gradually with time. However, its rate was very slow. In contrast, the peak intensity of the –NCO species decreased immediately upon the addition of NO+O_2 and became nearly constant after about 5 min. Since NO was mostly oxidized to NO_2 by coexisting oxygen, the gas mixture of NO+O_2 actually consisted of NO+NO_2+O_2. Therefore, it is evident that the isocyanate species was highly reactive toward NO_2 compared with NO or O_2, probably resulting in the formation of N_2. We also examined the reactivity of –CN species toward NO, NO+O_2 (NO_x) and O_2 in the same manner as in the case of –NCO species. As a result, the peak intensity of the –CN decreased slightly when NO+O_2 was introduced, meaning that the reactivity of –CN species is very low (not shown). Consequently, the final intermediate for N_2 formation would not be the –CN species but the –NCO species.

The proposed reaction pathway based on the IR study is illustrated in Scheme 1. First, propene reacts with NO_2 and/or NO_3^-, which are formed from NO and O_2 on the acid sites of TiO_2–ZrO_2, resulting in the formation of organic nitro and nitrite compounds. The organic nitro and nitrite compounds are converted to the isocyanate and the cyanide species on Ag sites. Finally, the isocyanate species is reduced to N_2 by the reaction with NO_2 on Ag sites.



Scheme 1. A proposed reaction mechanism for the selective reduction of NO with propene over Ag/TiO_2–ZrO_2.

4. Conclusions

The reaction mechanism of NO reduction by propene in the presence of oxygen over silver-supported TiO_2–ZrO_2 catalyst was studied by means of in-situ FT-IR, combined with catalytic activity studies. The catalytic activity studies suggested an important role of silver as the catalytically active species. In FT-IR measurements under a static condition, organic nitro (–NO_2), nitrite (–ONO), inorganic NO_3^-, carbonate, formate and/or acetate were detected when TiO_2–ZrO_2 and Ag/TiO_2–ZrO_2 were exposed to a gas mixture of $NO+C_3H_6+O_2$ at room temperature. An intense IR band assigned to isocyanate (–NCO) species was observed, along with disappearance of –ONO and NO_3^- species, on Ag/TiO_2–ZrO_2 by evacuation at the temperatures above 300°C after the reaction of $NO+C_3H_6+O_2$. It was also found that the reactivity of –NCO species was much higher than that of cyanide (–CN) species. The –NCO band was detected on TiO_2–ZrO_2, but not on Ag/TiO_2–ZrO_2 under the dynamic condition. From these results, it was concluded that the role of silver is to promote the formation and the reaction of –NCO species. N_2 was considered to be formed from –NCO and NO_2.

References

[1] M. Iwamoto, H. Yahiro, S. Shundo, Y. Yu-u, N. Mizuno, Appl. Catal. 69 (1991) L15; W. Held, A. Koening, T. Richter, L. Puppe, SAE Paper, 900496 (1990).
[2] Y. Kintaichi, H. Hamada, M. Tabata, M. Sasaki, T. Ito, Catal. Lett. 6 (1990) 239.
[3] H. Hamada, Y. Kintaichi, M. Sasaki, T. Ito, M. Tabata, Appl. Catal. 75 (1991) L1.
[4] H. Hamada, Y. Kintaichi, M. Sasaki, T. Ito, T. Yoshinari, M. Tabat, F. Suganuma, H. Tsichida, in: R. Yamamoto (Ed.), Advanced Materials'93, V/A: Ecomaterials, vol. 18A, Elsevier, Amsterdam, 1994, pp. 421–424.
[5] R. Burch, P.J. Millington, A.P. Walker, Appl. Catal. B 4 (1994) 65.
[6] A. Obuchi, A. Ohi, M. Nakamura, A. Ogata, K. Mizuno, H. Ohuchi, Appl. Catal. B 2 (1993) 71.
[7] T. Miyadera, Appl. Catal. B 2 (1993) 199.
[8] H. Hamada, Catal. Today 22 (1994) 21.
[9] C. Yokoyama, M. Misino, J. Catal. 150 (1994) 9.
[10] K.A. Bethke, C. Li, M.C. Kung, B. Yang, H.H. Kung, Catal. Lett. 31 (1995) 287.
[11] C.N. Montreuil, M. Schelf, Appl. Catal. B 1 (1992) L1.
[12] R.H. Smits, Y. Iwasawa, Appl. Catal. B 6 (1995) L201.
[13] M. Iwamoto, H. Takeda, Catal. Today 27 (1996) 71.
[14] T. Tabata, H. Ohtsuka, M. Kokitsu, O. Okada, Bull. Chem. Soc. Jpn. 68 (1995) 1905.
[15] G. Centi, A. Galli, S. Perathoner, J. Chem. Soc. Faraday. Trans. 92 (1996) 5129.
[16] V.A. Bell, J.S. Feeley, M. Deeba, R.J. Farrauto, Catal. Lett. 29 (1994) 15.
[17] T.E. Hoost, K.A. Laframboise, K. Otto, Catal. Lett. 37 (1996) 153.
[18] H. Yasuda, T. Miyamoto, M. Misono, Prepr. Pap. ACS, Div. Petr. Chem. 39 (1994) 99.
[19] T. Tanaka, T. Okuhara, M. Misono, Appl. Catal. B 4 (1994) L1.
[20] G.R. Bamwenda, A. Ogata, A. Obuchi, J. Oi, K. Mizuno, J. Skrzypek, Appl. Catal. B 6 (1995) 311; G.R. Bamwenda, A. Obuchi, A. Ogata, K. Mizuno, Chem. Lett. (1994) 2109; G.R. Bamwenda, A. Ogata, A. Obuchi, H. Takahashi, K. Mizuno, React. Kinet. Catal. Lett. 56 (1995) 311.
[21] Y. Ukisu, S. Sato, G. Muramatsu, K. Yoshida, Catal. Lett. 11 (1991) 177; Y. Ukisu, S. Sato, G. Muramatsu, K. Yoshida, Catal. Lett. 16 (1992) 11; Y. Ukisu, S. Sato, A. Abe, K. Yoshida, Appl. Catal. B 2 (1993) 147.
[22] Y. Ukisu , T. Miyadera, A. Abe, K. Yoshida, Catal. Lett. 39 (1996) 265.
[23] M. Haneda, Y. Kintaichi, M. Inaba, H. Hamada, Bull. Chem. Soc. Jpn. 70 (1997) 499.
[24] H. Hamada, Y. Kintaichi, M. Inaba, M. Tabata, T. Yoshinari, H. Tsuchida, Catal. Today 29 (1996) 53.
[25] C. Yokoyama, M. Misono, Catal. Lett. 29 (1994) 1.
[26] Y. Kintaichi, M. Haneda, M. Inaba, H. Hamada, Catal. Lett. 48 (1997) 121.
[27] T.E. Hoost, K. Otto, K.A. Laframbois, J. Catal. 155 (1995) 303.
[28] K. Hadjiivanov, V. Bushev, M. Kantcheva, D. Klissurski, Langmuir 10 (1994) 464.
[29] A.A. Davydov, in: C.H. Rochester (Ed.), Infrared Spectroscopy of Adsorbed Species on the Surface of Transition Metal Oxides, Wiley, Chichester, 1990.
[30] M.L. Unland, J. Catal. 31 (1973) 459; M.L. Unland, J. Phys. Chem. 77 (1973) 1952.
[31] T. Okuhara, Y. Hasada, M. Misono, Catal. Today 35 (1997) 83.