

# Reaction intermediates in the selective reduction of NO with propene over Ga<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> and In<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts

Masaaki Haneda<sup>a,b,c,\*</sup>, Emmanuel Joubert<sup>a</sup>, Jean-Christophe Ménézo<sup>a</sup>, Daniel Duprez<sup>a</sup>, Jacques Barbier<sup>a</sup>, Nicolas Bion<sup>b</sup>, Marco Daturi<sup>b</sup>, Jacques Saussey<sup>b</sup>, Jean-Claude Lavalley<sup>b</sup>, Hideaki Hamada<sup>c</sup>

<sup>a</sup> *Laboratoire de Catalyse en Chimie Organique (LACCO), UMR 6503, CNRS-Université de Poitiers, 40 Avenue du Recteur Pineau, 86022 Poitiers Cedex, France*

<sup>b</sup> *Laboratoire de Catalyse et Spectrochimie, UMR 6506, CNRS-ISMRA, 6 Bd du Maréchal Juin, F-14050 Caen Cedex, France*

<sup>c</sup> *National Institute of Advanced Industrial Science and Technology, AIST Tsukuba Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan*

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## Abstract

Minor products formed in the reaction of NO + C<sub>3</sub>H<sub>6</sub> + O<sub>2</sub> over Ga<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> and In<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> were identified by using GC-MS technique. A lot of minor products, such as oxygenated, nitrile, nitrite compounds and higher hydrocarbons were detected on both catalysts. The formation of surface nitrile species in the NO + C<sub>3</sub>H<sub>6</sub> + O<sub>2</sub> reaction was also recognized in the diffuse reflectance FT-IR spectra. FT-IR spectra showed that the reaction starts with the formation of adsorbed nitrate (NO<sub>3</sub><sup>-</sup>) species via NO oxidation by O<sub>2</sub>. From the comparison of the distribution of minor products in NO + C<sub>3</sub>H<sub>6</sub> + O<sub>2</sub> and 2-nitropropane oxidation, a reaction pathway in which NO reduction proceeds through the formation of organic nitro compounds and subsequent decomposition to some oxygenated and nitrile compounds was proposed. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** NO reduction by propene; Ga<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>; In<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>; GC-MS; Diffuse reflectance FT-IR spectroscopy

## 1. Introduction

Selective reduction of nitrogen oxide (NO<sub>x</sub>) with hydrocarbons is one of the most desirable control technologies for the abatement of NO<sub>x</sub> in diesel and lean burn engine exhausts. While a lot of in-

vestigations have focused on zeolite-based catalysts [1–3], metal oxide-based catalysts represented by alumina were also found to catalyze the selective reduction of NO [4,5]. Recently, we systematically investigated the catalytic activity of metal-supported alumina (In, Co, Ag, Sn, Ga, Mn/Al<sub>2</sub>O<sub>3</sub>) prepared by impregnation method [6]. Of these catalysts, In/Al<sub>2</sub>O<sub>3</sub> and Ga/Al<sub>2</sub>O<sub>3</sub> showed relatively high activity. It was also found that the catalysts prepared by sol-gel method are more effective than those

\* Corresponding author. Tel.: +81-298-61-9326;

fax: +81-298-61-4647.

E-mail address: m.haneda@aist.go.jp (M. Haneda).

prepared by impregnation method [7,8]. This was accounted for by the formation of highly dispersed catalytically active species strongly interacting with alumina.

A lot of reaction mechanisms, including intermediates, have been proposed so far for this reaction ([9] and references therein). They can be roughly classified into “decomposition mechanism” and “reduction mechanism” [4,10]. The latter mechanism in which NO is reduced into N<sub>2</sub> via certain nitrogen- and oxygen-containing intermediates has been supported by many researchers [11–15]. However, some disagreements still exist in the literature.

In many cases, infrared spectroscopic technique is employed to clarify the reaction mechanism ([16] and references therein) because in situ observation of surface species formed during NO reduction is possible. On the other hand, identification of minor products in NO reduction has also been made by some researchers [17–19]. Since minor products possess useful information concerning the reaction steps, analysis of them would lead to the proposal of reaction mechanism.

The present paper is devoted to the study of the reaction mechanism of the selective reduction of NO with propene over Ga<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> and In<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>. In situ diffuse reflectance FT-IR spectroscopy and GC-MS analysis were employed to identify the surface species and the minor products in the gas phase, respectively, produced during the reactions.

## 2. Experimental

### 2.1. Catalyst preparation

Ga<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> and In<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> were prepared by sol-gel method. The aluminium boehmite sol was first prepared by hydrolysis of aluminium(III) tri-isopropoxide in a hot water (363 K) with a small amount of nitric acid. Then, a solution of gallium(III) nitrate or indium(III) nitrate dissolved in ethylene glycol was added into the aluminium boehmite sol solution. After the sol solution was stirred at room temperature for 1 day, the solvents were removed by heating them under reduced pressure. The catalyst precursor thus obtained was dried at 383 K in an oven, followed by calcination at 873 K for 5 h in flowing

air. The loading of Ga<sub>2</sub>O<sub>3</sub> and In<sub>2</sub>O<sub>3</sub> was fixed at 30 and 5 wt.%, respectively. BET surface area, which was determined by the standard nitrogen adsorption at 77 K (Micromeritics Flowsorb II), of the catalysts was found to be as follows: Ga<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> 191 m<sup>2</sup> g<sup>-1</sup> and In<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> 227 m<sup>2</sup> g<sup>-1</sup>.

### 2.2. Analysis of minor products

Attempts to detect oxygen- and/or nitrogen-containing compounds have been carried out by using GC-MS in the same manner as described elsewhere [19]. Products from NO + C<sub>3</sub>H<sub>6</sub> + O<sub>2</sub> reaction were trapped at the temperature of liquid nitrogen for 3 h, separated on a Chrompack capillary column AT-1 and detected on Incos 500 Finnigan quadrupole mass spectrometer. The composition of the inlet gas mixture was 800 ppm NO, 460 ppm C<sub>3</sub>H<sub>6</sub>, 4.5% O<sub>2</sub> and helium as the balance gas. The total gas flow rate was set at 130 cm<sup>3</sup> min<sup>-1</sup>. In order to examine the reactivity of organic nitro compounds as possible intermediates, 2-nitropropane instead of NO was introduced to the reactor with a concentration of 250 ppm via a saturated condenser.

### 2.3. FT-IR spectroscopy

The diffuse reflectance FT-IR spectra were recorded with a Nicolet 550 FT-IR spectrometer, accumulating 64 scans at a resolution of 4 cm<sup>-1</sup>. Prior to each experiment, 20 mg of a catalyst placed in a diffuse reflectance high-temperature cell (Spectra Tech) fitted with KBr windows was activated in situ by heating in a flow of 10% O<sub>2</sub>/Ar at 873 K, followed by cooling to the desired temperatures. The background spectrum of the clean surface was measured for spectra correction. A reaction gas mixture containing 1000 ppm NO, 1000 ppm C<sub>3</sub>H<sub>6</sub>, 10% O<sub>2</sub> and Ar as the balance gas was fed to the catalyst at a flow rate of 25 cm<sup>3</sup> min<sup>-1</sup>.

Observation of surface species was carried out under steady-state conditions as the reaction temperature was changed from 523 to 623 K in steps of 50 K. The IR spectra were taken in 45 min at a given temperature. In addition to the steady-state reaction, transient reaction technique was employed to clarify the role and the reactivity of surface NO<sub>x</sub> adspecies. The catalyst was first exposed to NO + O<sub>2</sub> at 623 K

for 90 min to form and accumulate the surface  $\text{NO}_x$  adspecies. After purging with Ar for 10 min, the reaction gas was switched to  $\text{C}_3\text{H}_6$  diluted in Ar, and then changes in the intensity of IR bands were measured with time on stream.

### 3. Results

#### 3.1. Identification of minor products by GC–MS

##### 3.1.1. $\text{NO} + \text{C}_3\text{H}_6 + \text{O}_2$ reaction

Various oxygen- and/or nitrogen-containing compounds are produced during the selective reduction of NO with hydrocarbons [19,20]. It is often possible to speculate the reaction pathway by following the origin of minor products. Hence, identification of minor products in NO reduction by  $\text{C}_3\text{H}_6$  over  $\text{Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$  and  $\text{In}_2\text{O}_3\text{-Al}_2\text{O}_3$  at four different temperatures (648, 673, 698 and 723 K) was made by GC–MS measurements.

Figs. 1 and 2 show the GC–MS chromatogram of minor products in the reaction of  $\text{NO} + \text{C}_3\text{H}_6 + \text{O}_2$  on  $\text{Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$  and  $\text{In}_2\text{O}_3\text{-Al}_2\text{O}_3$  at 673 K, respectively. Obviously, both catalysts gave very similar distribution of minor products. Following the first peak containing light gases not separated in the chromatograph column, traces of oxygenated products (acetone ( $\text{CH}_3)_2\text{CO}$ , acetic acid  $\text{CH}_3\text{COOH}$ ), nitrile products

(acetonitrile  $\text{CH}_3\text{CN}$ , acrylonitrile  $\text{CH}_2=\text{CHCN}$ , butenenitrile  $\text{CH}_3\text{CH}=\text{CHCN}$ ), nitrite products (methyl-nitrite  $\text{CH}_3\text{ONO}$ ), nitrate products (ethyl nitrate  $\text{CH}_3\text{CH}_2\text{ONO}_2$ ) and higher hydrocarbons (benzene) were detected. An unknown peak, which consists of six mass fragments,  $M/e = 16, 17, 28, 30$  (main fragment) and 47, was also detected on both catalysts at a retention time of 124 s. This peak could be assigned to nitrous acid ( $\text{HNO}_2$ ), because this compound gives the fragment of NO ( $M/e = 30$ ) by decomposition inside the ionization chamber. Only the difference between  $\text{Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$  and  $\text{In}_2\text{O}_3\text{-Al}_2\text{O}_3$  is that the formation of acrylonitrile was observed on the latter catalyst while not on the former one. These results suggest that NO reduction by propene over  $\text{Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$  and  $\text{In}_2\text{O}_3\text{-Al}_2\text{O}_3$  proceeds via the formation of similar intermediates.

Table 1 summarizes the results of quantification analysis of the minor products formed on  $\text{Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$  and  $\text{In}_2\text{O}_3\text{-Al}_2\text{O}_3$ . A continuous decrease in the concentration with the reaction temperature was observed for both catalysts. It appears that a relatively large amount of benzene was formed on  $\text{Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$  in the temperature range between 648 and 698 K. This could be due to high aromatization activity of  $\text{Ga}_2\text{O}_3$  [21]. Interestingly, on  $\text{In}_2\text{O}_3\text{-Al}_2\text{O}_3$ , the concentration of nitrile compounds was much higher than that of the other compounds over the entire temperature range.

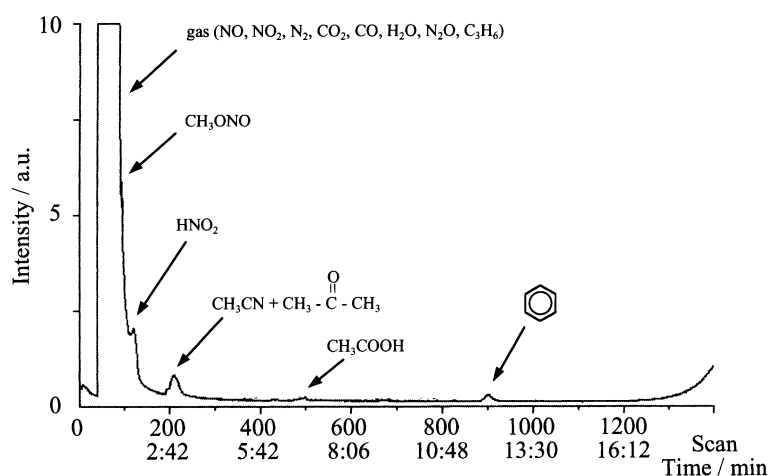


Fig. 1. GC–MS chromatogram of minor products in the reaction of  $\text{NO} + \text{C}_3\text{H}_6 + \text{O}_2$  over  $\text{Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$  at 673 K. Conditions:  $\text{NO} = 800$  ppm,  $\text{C}_3\text{H}_6 = 460$  ppm,  $\text{O}_2 = 4.5\%$ ,  $\text{W/F} = 0.09$   $\text{g s cm}^{-3}$ .

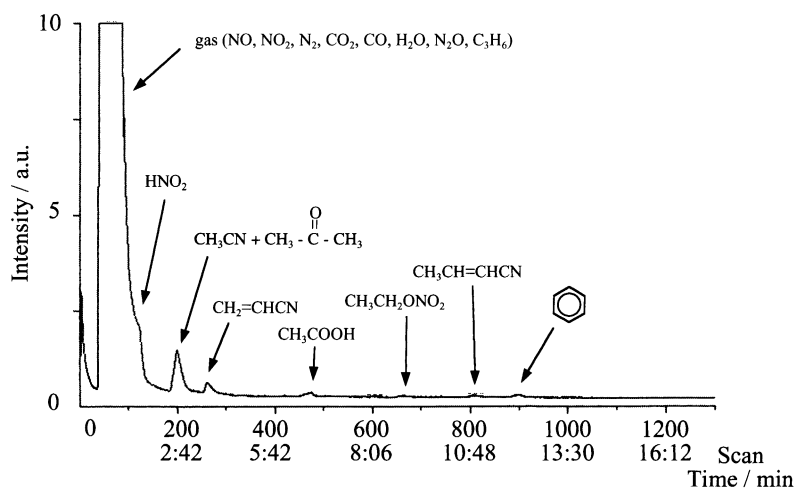


Fig. 2. GC–MS chromatogram of minor products in the reaction of  $\text{NO} + \text{C}_3\text{H}_6 + \text{O}_2$  over  $\text{In}_2\text{O}_3\text{-Al}_2\text{O}_3$  at 673 K. Conditions:  $\text{NO} = 800$  ppm,  $\text{C}_3\text{H}_6 = 460$  ppm,  $\text{O}_2 = 4.5\%$ ,  $\text{W/F} = 0.07$   $\text{g s cm}^{-3}$ .

### 3.1.2. 2-Nitropropane oxidation

The formation of organic nitro compounds has been proposed so far in the mechanism of this reaction [11,15,22–25]. As a typical organic nitro compound, Chen et al. [15] studied the decomposition of 2-nitropropane and revealed that some species containing “CN” groups are formed by this reaction. Since we also observed the formation of nitrile compounds as minor products in the present reaction (Figs. 1 and 2), minor products produced by 2-nitropropane

oxidation over  $\text{Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$  and  $\text{In}_2\text{O}_3\text{-Al}_2\text{O}_3$  at 673 K were investigated by using GC–MS.

A typical GC–MS chromatogram of minor products formed by 2-nitropropane/ $\text{C}_3\text{H}_6/\text{O}_2$  reaction over  $\text{Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$  is shown in Fig. 3. No great difference in the distribution of minor products was observed between  $\text{Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$  and  $\text{In}_2\text{O}_3\text{-Al}_2\text{O}_3$ . In addition to higher hydrocarbons, such as butene, butadiene and benzene, the formation of oxygenated compounds, such as acetone and acetic acid was observed. Also,

Table 1

Summary of quantification analysis of minor products in  $\text{NO} + \text{C}_3\text{H}_6 + \text{O}_2$  reaction over  $\text{Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$  and  $\text{In}_2\text{O}_3\text{-Al}_2\text{O}_3^a$

	$\text{Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$				$\text{In}_2\text{O}_3\text{-Al}_2\text{O}_3$			
	723 K	698 K	673 K	648 K	723 K	698 K	673 K	648 K
NO conversion (%)	40	24	19	11	54	38	22	18
$\text{C}_3\text{H}_6$ conversion (%)	89	55	33	22	98	68	38	21
Compounds	Concentration (ppm)				Concentration (ppm)			
–CHO <sup>b</sup>	0.4	0.7	0.9	5.0	0.1	0.9	0.7	3.3
R–CN <sup>c</sup>	2.1	5.6	2.6	11	2.4	8.4	9.0	10
R′–NO <sub>x</sub> <sup>d</sup>	0.9	2.3	3.7	8.5	–	0.1	0.1	–
$\text{C}_6\text{H}_6$	0.5	6.8	3.5	5.3	0.1	1.0	0.6	0.3

<sup>a</sup> Reaction conditions:  $\text{NO} = 800$  ppm,  $\text{C}_3\text{H}_6 = 460$  ppm,  $\text{O}_2 = 4.5\%$ ,  $\text{W/F} = 0.09$   $\text{g s cm}^{-3}$  ( $\text{Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$ ) or  $0.07$   $\text{g s cm}^{-3}$  ( $\text{In}_2\text{O}_3\text{-Al}_2\text{O}_3$ ).

<sup>b</sup> CHO for aldehyde and ketone compounds and acetic acid.

<sup>c</sup> R–CN for nitrile compounds.

<sup>d</sup> R′–NO<sub>x</sub> for nitrite compounds.

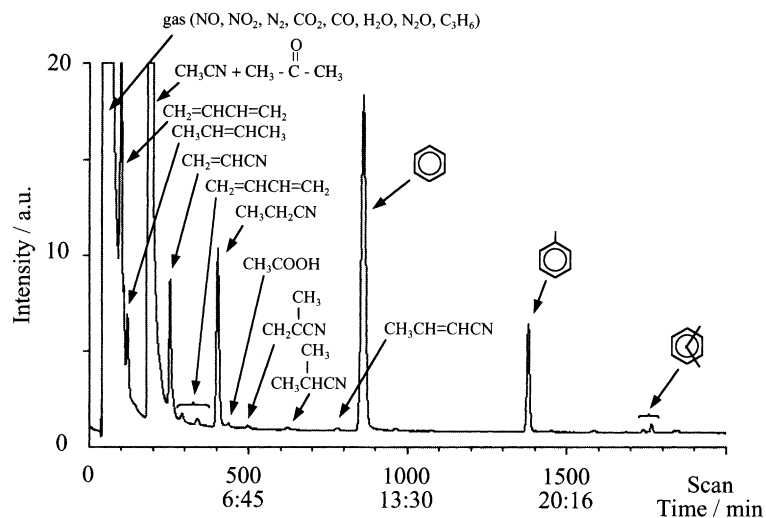


Fig. 3. GC-MS chromatogram of minor products in the reaction of 2-nitropropane/ $C_3H_6/O_2$  over  $Ga_2O_3-Al_2O_3$  at 673 K. Conditions: 2-nitropropane = 250 ppm,  $C_3H_6$  = 200 ppm,  $O_2$  = 4.5%, W/F =  $0.09 \text{ g s cm}^{-3}$ .

several nitrile compounds were detected, among which the formation of acetonitrile ( $CH_3CN$ ) is remarkable. Since only 2-nitropropane serves as the source of “nitrogen” atom, nitrile compounds should be formed by 2-nitropropane oxidation. It should be noted that the formation of acetonitrile as a major by-product was observed in  $NO + C_3H_6 + O_2$  reaction (Fig. 1).

### 3.2. In situ diffuse reflectance FT-IR measurements

#### 3.2.1. Steady-state reaction

The IR spectra recorded during the  $NO + C_3H_6 + O_2$  reaction over  $Ga_2O_3-Al_2O_3$  and  $In_2O_3-Al_2O_3$  in the temperature range between 523 and 623 K are shown Fig. 4. In the spectral range below  $1800 \text{ cm}^{-1}$ , almost the same IR spectra were obtained for the two catalysts, where six distinct bands at 1300, 1376, 1393, 1463, 1574 and  $1587 \text{ cm}^{-1}$  and two broad bands at 1665 and  $1715 \text{ cm}^{-1}$  were detected. Since the bands at 1376, 1393, 1463, 1574, 1587 and  $1715 \text{ cm}^{-1}$  were also observed in the reaction of  $C_3H_6 + O_2$  [26], these are due to nitrogen-free species. They can be assigned to formate ( $1376$ ,  $1393$  and  $1587 \text{ cm}^{-1}$ ) [27], acetate ( $1463$  and  $1574 \text{ cm}^{-1}$ ) [28] and carbonyl ( $1715 \text{ cm}^{-1}$ ) [29] species. A band at  $1300 \text{ cm}^{-1}$  would be due to unidentate nitrate ( $NO_3^-$ ) species [30]. A broad band at  $1665 \text{ cm}^{-1}$  was not detected in  $NO + O_2$

and  $C_3H_6 + O_2$ , suggesting that the species responsible for this peak contains “N” and “C” atoms. In the literature [31–33], IR absorption band ascribed to organic nitrito ( $R-ONO$ ) compound appears at around  $1655 \text{ cm}^{-1}$ . Taking into account the bands around  $3371 \text{ cm}^{-1}$ , which evolve in the same way, this feature is also likely due to acrylamide species [34]. It is apparent that the intensity of IR bands except for those due to acetate decreased as the reaction temperature increases.

When the reaction was carried out at 523 K, two IR bands appeared on  $Ga_2O_3-Al_2O_3$  at 2186 and  $2232 \text{ cm}^{-1}$  in the spectral range above  $2000 \text{ cm}^{-1}$ . On  $In_2O_3-Al_2O_3$ , a broad IR band at  $2231 \text{ cm}^{-1}$  was observed. According to the literature [35], the  $2186 \text{ cm}^{-1}$  band can be assigned to surface cyanide ( $-CN$ ) species coordinated to  $Ga^{3+}$  ions. The  $2232 \text{ cm}^{-1}$  band would be assigned to surface isocyanate ( $-NCO$ ) species formed on  $Al^{3+}$ ,  $Ga^{3+}$  and/or  $In^{3+}$  cations, because the frequency of the band closely resembles to that of the band observed on  $Al_2O_3$  by Ukisu et al. [36]. It is noteworthy that these bands diminished completely at the temperatures above 573 K at which NO reduction was initiated [7,8].

#### 3.2.2. Transient reaction

$NO_x$  adspecies, probably  $NO_3^-$ , formed on the catalyst surface is known to play an important role in

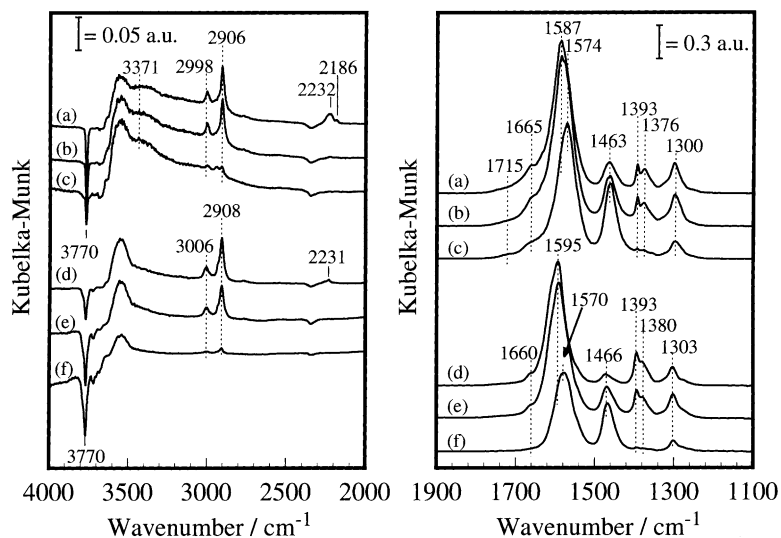


Fig. 4. Diffuse reflectance FT-IR spectra of adsorbed species formed during the reaction of  $\text{NO} + \text{C}_3\text{H}_6 + \text{O}_2$  over  $\text{Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$  (a–c) and  $\text{In}_2\text{O}_3\text{-Al}_2\text{O}_3$  (d–f) at (a and d) 523, (b and e) 573 and (c and f) 623 K for 45 min. Conditions:  $\text{NO} = 1000$  ppm,  $\text{C}_3\text{H}_6 = 1000$  ppm,  $\text{O}_2 = 10\%$ , catalyst = 20 mg, gas flow rate =  $25 \text{ cm}^3 \text{ min}^{-1}$ .

$\text{NO}$  reduction [16,37]. As described above, the formation of  $\text{NO}_3^-$  species was observed during the  $\text{NO} + \text{C}_3\text{H}_6 + \text{O}_2$  reaction (Fig. 4). Hence, the reactivity of surface  $\text{NO}_3^-$  species toward  $\text{C}_3\text{H}_6$  was evaluated at 623 K. Fig. 5 shows the time course of the integrated area of the bands assignable to  $\text{NO}_3^-$  species in the region of  $1175\text{--}1335 \text{ cm}^{-1}$ . Obviously, the exposure of the catalysts to  $\text{NO} + \text{O}_2$  caused the formation of

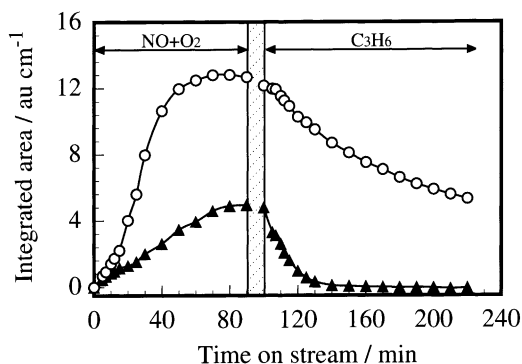


Fig. 5. Time dependence of the integrated area of the bands due to  $\text{NO}_3^-$  species ( $1175\text{--}1335 \text{ cm}^{-1}$ ) formed by exposure of  $\text{NO} + \text{O}_2$  to  $\text{Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$  ( $\circ$ ), and  $\text{In}_2\text{O}_3\text{-Al}_2\text{O}_3$  ( $\blacktriangle$ ) at 623 K, followed by Ar purge for 10 min and switching flowing gas to  $\text{C}_3\text{H}_6$ . The reaction conditions are the same as for Fig. 4.

surface  $\text{NO}_3^-$  species (given in the 1st region). The surface concentration seems to be about three times larger for  $\text{Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$  than for  $\text{In}_2\text{O}_3\text{-Al}_2\text{O}_3$ . When the reaction gas was switched to  $\text{C}_3\text{H}_6$  (given in the 2nd region), the consumption of  $\text{NO}_3^-$  species by the reaction with  $\text{C}_3\text{H}_6$  was observed for both catalysts. The nitrate bands on  $\text{In}_2\text{O}_3\text{-Al}_2\text{O}_3$  diminished almost completely in 45 min, while those on  $\text{Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$  still remained even after the reaction for 2 h. This suggests that  $\text{NO}_3^-$  species on  $\text{In}_2\text{O}_3\text{-Al}_2\text{O}_3$  is more reactive toward  $\text{C}_3\text{H}_6$  than that on  $\text{Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$ .

Fig. 6 shows the change of the IR spectra as a function of time after the reaction gas was switched to  $\text{C}_3\text{H}_6$ . No great difference in the IR spectra below  $1800 \text{ cm}^{-1}$  was observed between  $\text{Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$  and  $\text{In}_2\text{O}_3\text{-Al}_2\text{O}_3$ . A consumption of  $\text{NO}_3^-$  species ( $1175\text{--}1335 \text{ cm}^{-1}$ ) and an evolution of acetate ( $1473 \text{ cm}^{-1}$ ) as well as formate ( $1392 \text{ cm}^{-1}$ ) species take place simultaneously, suggesting the reaction of  $\text{NO}_3^-$  species and  $\text{C}_3\text{H}_6$  leading to the formation of acetate and formate species. In the spectral range above  $2000 \text{ cm}^{-1}$ , additional IR bands assignable to  $-\text{CN}$  ( $2146 \text{ cm}^{-1}$ ) and  $-\text{NCO}$  ( $2246 \text{ cm}^{-1}$ ) species were detected on  $\text{Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$  immediately after the introduction of  $\text{C}_3\text{H}_6$ , while the formation of  $-\text{CN}$  and  $-\text{NCO}$  species was not evidenced on  $\text{In}_2\text{O}_3\text{-Al}_2\text{O}_3$ .

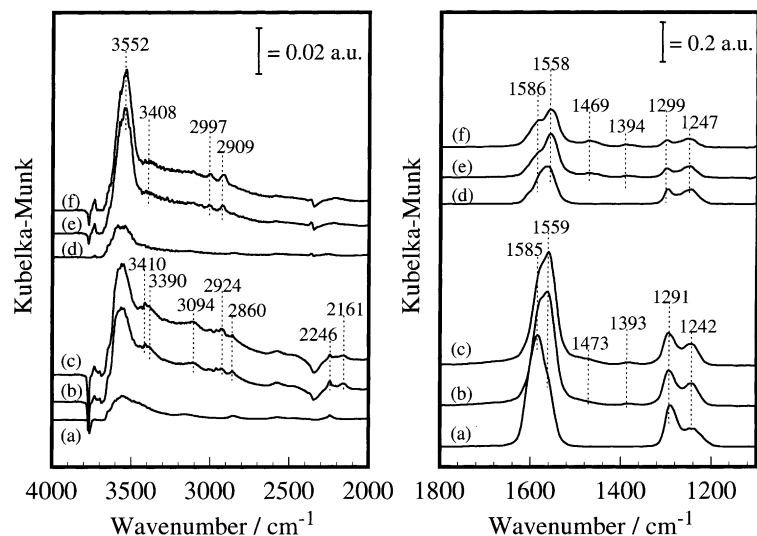


Fig. 6. Diffuse reflectance FT-IR spectra of adsorbed species on  $\text{Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$  (a–c) and  $\text{In}_2\text{O}_3\text{-Al}_2\text{O}_3$  (d–f) at 623 K. The spectra were taken in flowing  $\text{NO} + \text{O}_2$  for 90 min, followed by Ar purge for 10 min and switching flowing gas to  $\text{C}_3\text{H}_6$  for (a and d) 0, (b and e) 5 and (c and f) 10 min. The reaction conditions are the same as for Fig. 4.

Possibly,  $\text{NO}_3^-$  species formed on  $\text{In}_2\text{O}_3\text{-Al}_2\text{O}_3$  serves as a strong oxidant for  $\text{C}_3\text{H}_6$ . It is noteworthy that two characteristic IR bands at 3390 and 3410  $\text{cm}^{-1}$ , assigned to the  $\nu(\text{NH})$  of amines [30,38], was observed for  $\text{Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$  simultaneously with a disappearance of the  $-\text{NCO}$  band.

#### 4. Discussion

It is well known that the selective reduction of NO with hydrocarbons is a very complex reaction comprising several parallel and/or consecutive reaction steps of NO and hydrocarbons. In the present work, the obtained experimental results suggest that NO reduction over  $\text{Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$  and  $\text{In}_2\text{O}_3\text{-Al}_2\text{O}_3$  proceeds through a similar reaction pathway, although the rate of each step may be different. Our view of the reaction pathway proposed is illustrated in Fig. 7.

The reaction seems to begin with the formation of adsorbed nitrate ( $\text{NO}_3^-$ ) species via NO oxidation by  $\text{O}_2$ . As can be seen in Fig. 5, this step was catalyzed effectively on  $\text{Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$  than on  $\text{In}_2\text{O}_3\text{-Al}_2\text{O}_3$ . It was also found that the surface  $\text{NO}_3^-$  species can react with  $\text{C}_3\text{H}_6$ , leading to the formation of some surface species. Radtke et al. [17] have proposed that

the formation of allyl species by hydrogen abstraction from propene is an important step at the initial stage of this reaction. In the present work, the reaction between  $\text{NO}_3^-$  species and  $\text{C}_3\text{H}_6$  may also cause the formation of allyl species. If this reaction takes place, nitrous acid ( $\text{HNO}_2$ ) should be produced. In fact, the formation of  $\text{HNO}_2$  as a by-product was recognized in the GC-MS chromatogram of minor products formed from the reaction of  $\text{NO} + \text{C}_3\text{H}_6 + \text{O}_2$  over  $\text{Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$  and  $\text{In}_2\text{O}_3\text{-Al}_2\text{O}_3$  (Figs. 1 and 2). It should be noted that  $\text{In}_2\text{O}_3\text{-Al}_2\text{O}_3$  catalyzed effectively the reaction between  $\text{NO}_3^-$  species and  $\text{C}_3\text{H}_6$  compared with  $\text{Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$ .

The possibility of the formation of organic nitro compounds, such as nitromethane ( $\text{CH}_3\text{NO}_2$ ) [11], nitroethene ( $\text{C}_2\text{H}_3\text{NO}_2$ ) [25] and nitropropane ( $\text{C}_3\text{H}_7\text{NO}_2$ ) [15,23,24] has been proposed. In the present work, organic nitro compounds may be formed by the reaction of allyl species and  $\text{NO}_x$ . Organic nitro compounds are, however, thermally unstable, so that the detection of these compounds by GC-MS and FT-IR is very difficult. Chen et al. [15] reported that decomposition of 2-nitropropane over  $\text{Fe/ZSM-5}$  at 473 K forms a deposit including “CN” groups on the catalyst. Joubert et al. [23,39] also emphasized that hydrolysis of 2-nitropropane over  $\text{Pt/Al}_2\text{O}_3$  occurs

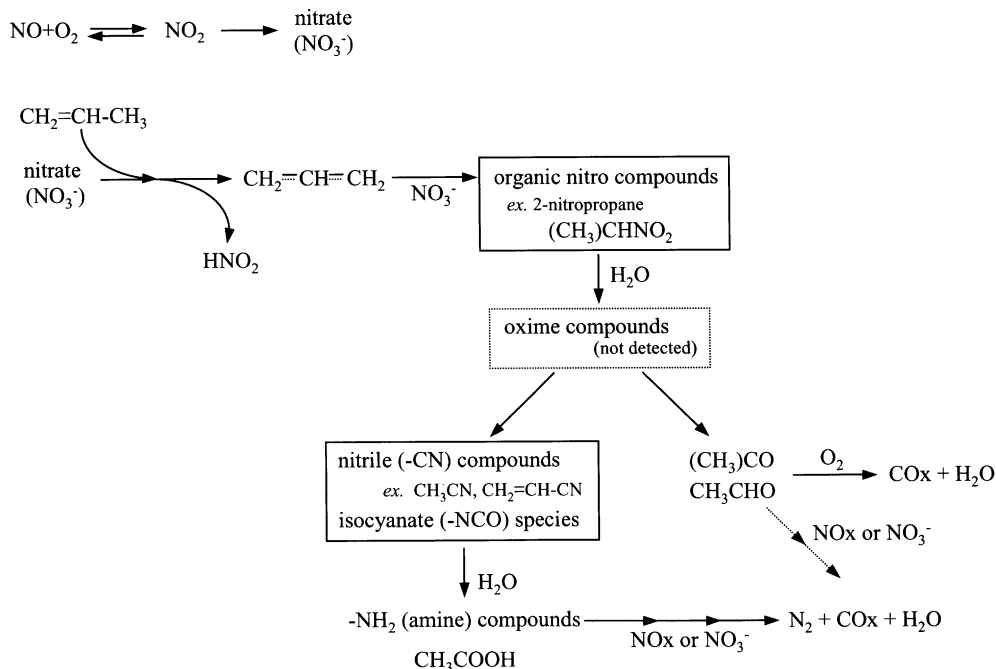


Fig. 7. Mechanistic scheme proposed for the selective reduction of NO with propene over Ga<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> and In<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts.

even at 423 K and then leads to the formation of N<sub>2</sub>O and acetone via acetone oxime. The formation of acetone oxime from nitrosopropane was also proposed by Sachtler et al. [40,41]. The resulting acetone oxime is easily dehydrated to nitrile compound on acid sites [42].

As can be summarized in Table 1, relatively large amounts of acetone and nitrile compounds, such as acetonitrile (CH<sub>3</sub>CN) and acrylonitrile (CH<sub>2</sub>=CHCN) were formed as the minor products in the NO + C<sub>3</sub>H<sub>6</sub> + O<sub>2</sub> reaction. The primary minor products in 2-nitropropane oxidation were also nitrile compounds (Fig. 3). Probably, the formation of acetone and nitrile compounds in NO + C<sub>3</sub>H<sub>6</sub> + O<sub>2</sub> may be due to 2-nitropropane oxidation. Oxime compounds, the formation of which was not evidenced, would easily be hydrated to nitrile compounds, because relatively large amounts of Lewis acid sites are present on the surface of Ga<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> and In<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> [43].

The concentration of oxygenated and nitrile compounds decreased continuously as the reaction temperature increases (Table 1). An increase of N<sub>2</sub> and CO<sub>x</sub> yields in NO reduction by propene with reaction

temperature was also observed in the same temperature region [7,8]. These facts suggest that oxygenated and nitrile compounds act as the intermediates leading to the formation of N<sub>2</sub>. Recently, Gerlach et al. [44] reported that the formation of acrylonitrile and subsequently hydrolysis into acrylic acid and ammonia (NH<sub>3</sub>) take place in NO<sub>2</sub> reduction by propene over H-MOR. The resulting NH<sub>3</sub> seems to serve as a reductant for NO<sub>2</sub> reduction. Poignant et al. [38] proposed that isocyanate (-NCO) species formed on Cu/ZSM-5 is easily hydrolyzed to NH<sub>3</sub> in the presence of H<sub>2</sub>O traces. In the present work, although the compounds including "-NCO" groups were not detected as by-product in the gas phase, the formation of the -NCO species on the catalyst surface was recognized by FT-IR measurements (Fig. 4). Probably, the hydrolysis of isocyanate compounds is very fast step. This idea is also supported by the fact that the formation of acetic acid, which is a probable by-product of its hydrolysis, was observed by GC-MS analysis (Figs. 1 and 2). In addition, a broad IR band at around 3400 cm<sup>-1</sup>, which can be ascribed to the ν(NH) stretching mode of adsorbed acrylamide



and/or amines, was detected in the FT-IR spectra taken in the steady-state reaction (Fig. 4).  $\text{NH}_3$  is known to serve as a very effective reducing agent for the selective removal of NO. Therefore, resulting  $\text{NH}_3$  (including ammines) would react with  $\text{NO}_x$  to form  $\text{N}_2$ . This step may be very fast, because  $\text{NH}_3$  was not recognized in minor products.

The reaction mechanism proposed here is very similar to those by Nanba et al. [25] and Gerlach et al. [44], even though they studied on H-type zeolites (mordenite and ferrierite). The present mechanism may widely be applicable on a lot of solid acid catalysts, irrespective of catalyst supports (zeolite, metal oxide).

## 5. Conclusions

Investigation of the reaction mechanism by measuring the surface species and minor products formed during NO reduction by propene over  $\text{Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$  and  $\text{In}_2\text{O}_3\text{-Al}_2\text{O}_3$  revealed that organic nitro compounds are the initial important intermediates, which are then hydrolyzed to several oxygen- and nitrogen-containing compounds. Among them, nitrile and isocyanate compounds were presumed to play an important role, and these are hydrolyzed to the surface species including amine group as the final important intermediate. Finally,  $\text{NO}_x$  is effectively reduced to  $\text{N}_2$  by reaction with amines.

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