

# In situ diffuse reflectance infrared Fourier transform spectroscopy study of surface species involved in NO<sub>x</sub> reduction by ethanol over alumina-supported silver catalyst

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Received 1 October 1997; accepted 17 January 1998

## Abstract

In situ diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy has been used to investigate the surface species involved in NO<sub>x</sub> reduction by ethanol over alumina-supported silver catalyst. The experiments were carried out in dynamic conditions (under reaction mixture flow and reaction temperature) at atmospheric pressure. The DRIFT measurements were combined with gas chromatography (GC) analysis to monitor the N<sub>2</sub> formation under reaction mixture and when the reaction mixture flow was switched to He followed by heating the catalyst under He flow (mixture, 250°C → He, 250°C → heating under He). A parallelism has been observed between the isocyanate band change and N<sub>2</sub> formation during the step change experiment using an initial C<sub>2</sub>H<sub>5</sub>OH/NO/O<sub>2</sub>/He reaction mixture. Furthermore, the isocyanate species (NCO) were found to be generated from the decomposition of adsorbed organic nitro compounds formed under both ethanol/NO/O<sub>2</sub>/He and ethanol/NO/He and reaction mixtures. The role of oxygen in NO<sub>x</sub> reduction process was determined by comparing the result of different step-change experiment using an initial reaction mixture containing oxygen and without oxygen. © 1998 Elsevier Science B.V. All rights reserved.

**Keywords:** In situ DRIFT; NO<sub>x</sub> reduction; Ethanol; Silver; Alumina

## 1. Introduction

Since the past few years, there has been a great attention paid to environmental issues. One of the main concerns is related to nitrogen oxides (NO<sub>x</sub>) which represent a serious menace to air quality. Removal of NO<sub>x</sub> contained in automotive exhaust is achieved with the 'three way' catalytic converters containing Pt, Pd and Rh supported on alumina and ceria. As for NO<sub>x</sub>

elimination from stationary installation emissions (e.g., power station), selective catalytic reduction (SCR) using ammonia as a reducing agent is the most common method used commercially. However, several inconvenient aspects are associated with this technology mainly because of ammonia toxicity, transportation, and storage equipment corrosion. One of the promising process up to date is based on NO<sub>x</sub> reduction by hydrocarbons in excess of oxygen. However, the Cu-ZSM-5 catalyst generally used is still not quite effective yet for reducing NO<sub>x</sub>

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with hydrocarbon under oxidizing atmosphere in presence of water [1]. The challenge facing catalyst technologists is to design an efficient system capable of reducing  $\text{NO}_x$  from the heavily oxidizing exhaust-gas (e.g., diesel engine).

Miyadera et al. [2] recently reported an interesting finding related to the use of oxygen-containing organic compounds (such as ethanol) for reducing effectively  $\text{NO}_x$  over  $\text{Ag}/\text{Al}_2\text{O}_3$  even in the presence of water and excess of oxygen. At present, this system has been practically used to achieve around 80% of  $\text{NO}_x$  removal from diesel engine emissions [3]. Therefore, further information must still be provided for elucidating the mechanism of  $\text{NO}_x$  reduction process. In an attempt to address this issue, Ukisu et al. [4] recently reported the formation of adsorbed isocyanate species on  $\text{Ag}/\text{Al}_2\text{O}_3$  catalyst on the basis of static FTIR experiment of  $\text{C}_2\text{H}_5\text{-OH}/\text{NO}/\text{O}_2$  adsorption at low temperature and heating in vacuum to  $350^\circ\text{C}$ . However, the role of these species as reaction intermediate has not been fully established since the experiments were carried out under different lean  $\text{NO}_x$  reduction reaction conditions. In fact, most of the mechanistic studies reported in literature were performed under such conditions and various surface species containing carbon and nitrogen have been observed on different lean  $\text{NO}_x$  catalysts. Yasuda et al. [5] observed the formation of nitro, nitrite compounds and isocyanate species over  $\text{Ce-ZSM-5}$  catalyst under  $\text{C}_3\text{-H}_6/\text{O}_2/\text{NO}$ . The same mixture was used by Hayes et al. [6] to generate organic nitrile species over  $\text{Cu-ZSM-5}$  catalyst. Bell et al. [7] observed  $\text{Cu-(N}_x\text{O}_y)_z$ , organic NCO and  $\text{Cu-NCO}$  species on  $\text{Cu-ZSM-5}$  catalyst. All these species were proposed to take part into  $\text{NO}_x$  reduction process, but definitive data explaining the mechanism of  $\text{NO}_x$  reduction with hydrocarbons or oxygen-containing organic compounds in excess of oxygen are still expected.

The in-situ characterization of catalyst surface (under reactant flow and at reaction temperature) using FTIR spectroscopy has proven to be a powerful tool for investigating the dy-

namics of surface reaction process and to identify surface adsorbed intermediate. Combining FTIR spectroscopy with a gas phase product analysis (such as GC) is an effective approach permitting the monitoring of gas phase product composition as well as catalyst surface species evolution. As a result, more details on surface intermediates species are provided. This has a major advantage of distinguishing between adsorbed reaction intermediate and spectator species, which is extremely important for heterogeneously catalyzed reaction mechanistic study.

In this paper, in-situ diffuse reflectance IR spectroscopy has been used to study the behavior of surface species formed on  $\text{Ag}/\text{Al}_2\text{O}_3$  under  $\text{C}_2\text{H}_5\text{OH}/\text{NO}/\text{O}_2/\text{He}$  and  $\text{C}_2\text{H}_5\text{OH}/\text{NO}/\text{He}$  mixtures as well as upon switch to He flow and during heating under He process. The in-situ diffuse reflectance infrared Fourier transform (DRIFT) measurements has been combined with GC analysis to monitor  $\text{N}_2$  formation during different steps of experiment. Particular attention was given to emphasize the effect of oxygen on the behavior of surface species and its role in  $\text{NO}_x$  reduction process.

## 2. Experimental

The catalyst used in this work was an alumina-supported silver catalyst ( $\text{Ag}/\text{Al}_2\text{O}_3$ ) prepared by an ordinary impregnation method according to the previously outlined procedure [2]. The silver content in the catalyst was 2% by weight corresponding to the reported highest activity catalyst composition [2].

The infrared spectrometer used is a NICOLET MAGNA 550 equipped with a MCT detector and a KBr beamsplitter. The instrument was operated using a specific macro elaborated to perform automatic spectra acquisition at resolution of  $4\text{ cm}^{-1}$  by averaging sets of 16 scans. The catalyst pretreatment and in-situ DRIFT experiments were conducted in DRIFT cell (Spectra Tech) permitting measurements in a

controlled gas atmosphere and temperature. Prior to the reaction, the catalyst was treated in-situ under 10% O<sub>2</sub>/Ar flow at 500°C for 3 h followed by He purging for 30 min. A clean catalyst surface spectrum was then recorded at reaction temperature to be used as a background to which experiment spectra were corrected, and the final spectra was presented in Kubelka–Munk form. All the gases used to make a simulated exhaust stream were of ultra high purity. A reaction mixture flow of 500 ppm ethanol/800 ppm NO/10%O<sub>2</sub> and He balance was directly introduced to the DRIFT cell at a flowing rate of 60 cm<sup>3</sup> min<sup>-1</sup>. As for N<sub>2</sub> formation analysis, the same mixture was flowed at 200 cm<sup>3</sup> min<sup>-1</sup> through a quartz continuous flow reactor connected to a gas chromatograph equipped with a molecular sieve 5A column and TC detector. A linear heating rate of 10°C min<sup>-1</sup> was applied to the quartz reactor for heating under He experiment. As for the DRIFT cell, the sample holder heating was manually controlled to perform an approximate heating rate of 10°C min<sup>-1</sup>.

### 3. Results and discussion

#### 3.1. Surface species formed during C<sub>2</sub>H<sub>5</sub>OH/NO/O<sub>2</sub>/He reaction at various temperatures

Fig. 1 shows the DRIFT spectra recorded at different temperatures on Ag/Al<sub>2</sub>O<sub>3</sub> after 30 min under C<sub>2</sub>H<sub>5</sub>OH/NO/O<sub>2</sub>/He flow. For the spectra (a) and (b) recorded at 150 and 250°C, respectively, there are no differences in the spectral region between 1300 and 1750 cm<sup>-1</sup>. The IR bands identification at this region requires a short overview of the assignment reported in the literature; one attribute the observed bands to several surface species such as formate, formyl, aldehyde or carbonyl resulting from the partial oxidation of ethanol which produce IR bands at spectral region between 1300 and 1750 cm<sup>-1</sup>. In fact, the shoulder at 1750 cm<sup>-1</sup> observed in spectra (a) only was

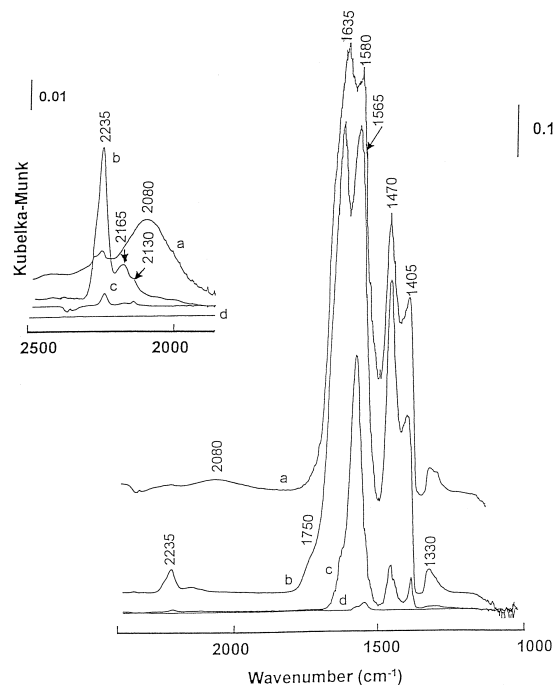


Fig. 1. In-situ FTIR spectra of Ag/Al<sub>2</sub>O<sub>3</sub> catalyst after 30 min under C<sub>2</sub>H<sub>5</sub>OH/NO/O<sub>2</sub>/He at different temperatures. (a) 150°C, (b) 250°C, (c) 350°C, (d) 470°C.

tentatively assigned by Tanaka et al. [8] to an organic carbonyl species considering the absence of isotope shift when <sup>15</sup>NO was used in their experiment. The band at 1635 cm<sup>-1</sup> was attributed to C=O mode of formyl species [9] or OH deformation of adsorbed water as suggested by Hayes et al. [6]. According to Nakamoto [10], the IR band at 1635 cm<sup>-1</sup> is characteristic of C=O vibration of an aldehyde, whereas the band at 1580 cm<sup>-1</sup> is attributed to C–O asymmetric stretching mode of a carboxylic group which has also a symmetric stretching vibration at 1470 cm<sup>-1</sup>. Moreover, the IR band at 1580 cm<sup>-1</sup> could also be associated with OCO asymmetric stretching of a formate species which has also a symmetric stretching band at 1330 cm<sup>-1</sup> and a CH bending around 1405 cm<sup>-1</sup> [11,12]. As a consequence, it could be generally admitted that the IR bands observed in the region 1300–1750 cm<sup>-1</sup> indicate the formation of C<sub>x</sub>H<sub>y</sub>O<sub>z</sub> species resulting from the partial oxi-

dation of ethanol on Ag/Al<sub>2</sub>O<sub>3</sub>. In support of this, the recent TPO study of ethanol on Ag/Al<sub>2</sub>O<sub>3</sub> conducted by Cordi and Falconer [13] indicated acetaldehyde as a main product of the partial oxidation of ethanol on Ag/Al<sub>2</sub>O<sub>3</sub> which gives rise also to CO<sub>2</sub>, CO, H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub>. Therefore, the high intensity of the IR bands at 1580 and 1635 cm<sup>-1</sup> may generate an overlapping of other surface species IR bands such as nitrogen-containing species which also gives IR bands at the spectral range between 1300–1750 cm<sup>-1</sup>. Tanaka et al. [8] observed IR bands at 1565 and 1405 cm<sup>-1</sup> assigned to adsorbed organic nitro compounds on the basis of isotope shift for <sup>15</sup>NO and comparison with the spectra of standard organic nitro compound. Similar results were also reported by Hayes et al. [6]. Additionally, studies of nitromethane adsorption on Ag/Al<sub>2</sub>O<sub>3</sub> catalyst performed recently in our laboratory [14] revealed the formation of the same IR bands at 1565 and 1405 cm<sup>-1</sup>. Accordingly, the shoulder at 1565 cm<sup>-1</sup> and the band at 1405 cm<sup>-1</sup> of spectra (a) are associated, respectively, with  $\nu_{as}(\text{NO}_2)$  asymmetric and  $\nu_s(\text{NO}_2)$  symmetric stretching mode of an organic nitro group. It could be concluded that the IR features observed in the spectra (a) and (b) at 1300–1750 cm<sup>-1</sup> region are attributed to some C<sub>x</sub>H<sub>y</sub>O<sub>z</sub> and adsorbed nitrogen-containing species.

The main differences between the spectra (a) and (b) are observed at 2000–2500 cm<sup>-1</sup> spectral range, where a large band centered at 2080 cm<sup>-1</sup> due to a linear adsorbed CO [15] is formed at 150°C (spectrum (a)). The CO required for the formation of the band at 2080 cm<sup>-1</sup> is provided by the partial oxidation of ethanol. The aforementioned CO band at 2080 cm<sup>-1</sup> was not detected in the spectrum (b) obtained during the exposure of Ag/Al<sub>2</sub>O<sub>3</sub> catalyst to ethanol/NO/O<sub>2</sub> mixture at 250°C. However, the intensity of the small band located at 2235 cm<sup>-1</sup> in the spectrum (a) drastically increased at 250°C (spectrum (b)) and was formed together with IR bands at 2130 and 2165 cm<sup>-1</sup> in the spectral range between 2000–

2500 cm<sup>-1</sup>. According to the static IR study of ethanol/NO/O<sub>2</sub> adsorption on Ag/Al<sub>2</sub>O<sub>3</sub> conducted recently in our laboratory by Ukisu et al. [4], two IR bands at 2262 and 2232 cm<sup>-1</sup> were attributed to two different NCO on Al<sub>2</sub>O<sub>3</sub> and Ag–NCO, respectively, because the higher frequency band was observed on Al<sub>2</sub>O<sub>3</sub> alone. Note that the experiment of the present study performed in dynamic conditions led to the detection of one IR band at 2235 cm<sup>-1</sup>. The assignment of isocyanate species reported in the literature was a matter of debate. Unland [16,17] pointed out that isocyanate species coordinated to the metal have an absorption band in the region between 2180 and 2000 cm<sup>-1</sup> and isocyanate coordinated to the support (e.g., alumina) have an absorption band in the region between 2230 and 2260 cm<sup>-1</sup>. A similar conclusion was reported by Arai and Tominaga [15], Solymosi and Bansagi [18] as well as by the recent work of Bamwenda et al. [19]. Moreover, Li et al. [20] and Yang et al. [21] reported that the reduction of NO on Cu–ZrO<sub>2</sub> in excess of O<sub>2</sub> by C<sub>3</sub>H<sub>6</sub>, as well as when ethanol was used in place of C<sub>3</sub>H<sub>6</sub>, led to the formation of two IR band at 2140 and 2190 cm<sup>-1</sup> assigned to CN and NCO species, respectively, on the basis of isotopic shift. Taking these facts into consideration, the IR bands of spectrum (b) at 2130, 2165 and 2235 cm<sup>-1</sup> are tentatively assigned to two different CN and NCO species. In order to provide direct evidence for the assignment of the IR band at 2235 cm<sup>-1</sup> to Ag–NCO species, isocyanic acid has been adsorbed on Ag/Al<sub>2</sub>O<sub>3</sub> catalyst at 250°C. In the present work, the isocyanic acid vapor adsorption leading to surface active adsorbate on Ag/Al<sub>2</sub>O<sub>3</sub> catalyst, have been carried out by performing an in-situ depolymerization of cyanuric acid ((HOCN)<sub>3</sub>) at 450°C according to the procedure outlined by Herzberg and Reid [22]. The FTIR spectrum recorded in static conditions following a prolonged HNCO gas phase evacuation (Fig. 2) clearly indicated the formation of an intense NCO IR band at 2235 cm<sup>-1</sup>, accompanied with an NCO stretching vibration at 1372 cm<sup>-1</sup> [22].

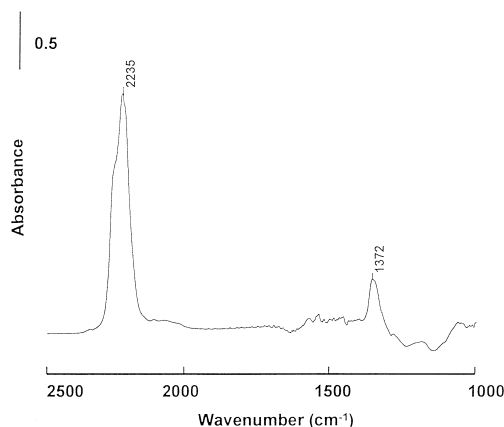


Fig. 2. FTIR spectra recorded after adsorption and evacuation of isocyanic acid (HNCO) on Ag/Al<sub>2</sub>O<sub>3</sub> catalyst at 250°C.

When the catalyst is exposed to the NO/ethanol/O<sub>2</sub> reaction mixture at 350°C (spectrum (c), Fig. 1), the band intensities of NCO and CN species decreased and disappeared completely at reaction temperature of 470°C (spectrum (d), Fig. 1). The same behavior is observed for the IR bands at 1300–1750 cm<sup>-1</sup> spectral range where less IR bands were detected by increasing reaction temperature. This fact may be related to the thermal stability and/or an increased reactivity of the adsorbed species with the temperature as well as an augmentation of reaction kinetic which shortens the lifetime of adsorbed species on the catalyst surface. On the other hand, the activity of Ag/Al<sub>2</sub>O<sub>3</sub> catalyst for NO<sub>x</sub> reduction with ethanol was found to depend strongly on the reaction temperature and exhibit a maximum between 350 and 400°C [2]. Nevertheless, the NO<sub>x</sub> reduction by ethanol at 250°C was reported to proceed with a reasonable activity [2], moreover, the most interesting IR features as well as the better detection of surface species resulting from C<sub>2</sub>H<sub>5</sub>OH/NO/O<sub>2</sub>/He reaction were provided by the in-situ studies at 250°C. These reasons justify the choice of the 250°C temperature to investigate the reactivity of surface species involved in NO<sub>x</sub> reduction by ethanol.

### 3.2. Surface species formed under different reaction mixtures at 250°C

Fig. 3 shows IR spectra of surface species on Ag/Al<sub>2</sub>O<sub>3</sub> catalyst at 250°C after 30 min exposure to three different mixtures; ethanol/NO/O<sub>2</sub>/He, ethanol/NO/He and NO/O<sub>2</sub>/He corresponding to the spectra (a), (b) and (c), respectively. For the spectrum (a) discussed previously, it was pointed out that the contact of catalyst with ethanol/NO/O<sub>2</sub>/He mixture gave rise to several surface species namely isocyanates, cyanides, nitro-organic compounds and some C<sub>x</sub>H<sub>y</sub>O<sub>z</sub> species resulting from the partial oxidation of ethanol. As for the spectrum (b) obtained under ethanol/NO mixture, although the formed IR bands present lower intensity, the absence of oxygen in the mixture did not generate any change in the position of the IR band at 1300–1750 cm<sup>-1</sup> region and therefore the same assignment may be applied also to this spectrum, indicating the formation

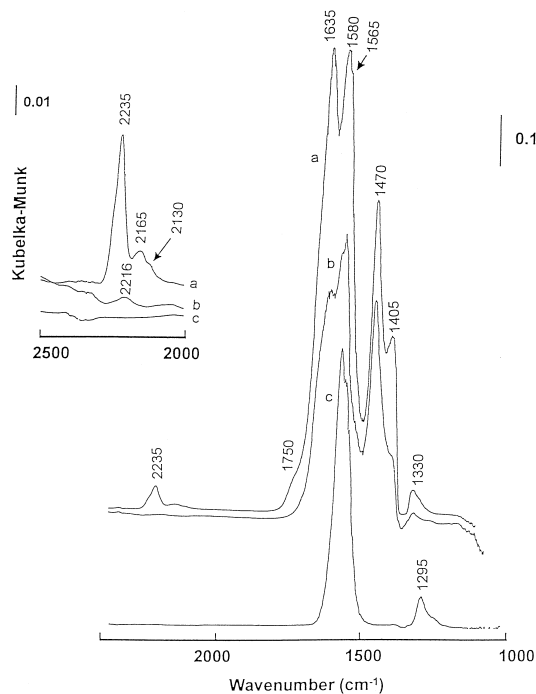


Fig. 3. In-situ FTIR spectra of surface species on Ag/Al<sub>2</sub>O<sub>3</sub> catalyst at 250°C after 30 min under different reactions mixtures. (a) C<sub>2</sub>H<sub>5</sub>OH/NO/O<sub>2</sub>/He, (b) C<sub>2</sub>H<sub>5</sub>OH/NO/He, (c) NO/O<sub>2</sub>/He.

of  $C_xH_yO_z$  species and nitrogen-containing organic compounds. Similar results were obtained by Gaudin et al. [23] from GC–MS study of  $NO/C_3H_6$  reaction on Cu–MFI catalyst. The same observations were also reported by Hayes et al. [6] who explained the nitro species formation in the absence of oxygen in propene/NO mixture by an interaction with the extra-lattice oxygen of the zeolite. However, it should be noted that the intensity of NCO band observed in spectrum (b) is very small and hardly detected at  $2216\text{ cm}^{-1}$ , this position indicated that the nature of the NCO adsorption silver site has been affected by the absence of oxygen in the mixture.

The spectrum (c) recorded under  $NO/O_2/He$  mixture showed the formation of intense bands at  $1580$  and  $1295\text{ cm}^{-1}$  assigned according to literature to surface nitrates ( $NO_3^-$ ) species resulting from the oxidation of NO by oxygen [24,25]. The presence of IR bands at the same position in the spectra (a) and (b) suggest also the formation of  $NO_3^-$  species when the catalyst is exposed to ethanol/NO/ $O_2/He$ , ethanol/NO/He mixtures.

### 3.3. Surface species evolution during step change experiment at $250^\circ\text{C}$ (mixture $\rightarrow$ He)

The in-situ FTIR spectra recorded at  $250^\circ\text{C}$  under  $C_2H_5OH/NO/O_2/He$  and  $C_2H_5OH/NO/He$  mixtures implies the presence of adsorbed nitrates, isocyanate and organic nitro compounds as well as some  $C_xH_yO_z$  species resulting from the partial oxidation of ethanol. It is of interest to investigate the dynamic behavior and the reactivity of the observed adsorbates simultaneously with  $N_2$  formation under reaction mixture and during step change experiment such as a switch followed by heating under He flow.

#### 3.3.1. ( $C_2H_5OH/NO/O_2/He$ at $250^\circ\text{C}$ ) $\rightarrow$ He at $250^\circ\text{C}$ $\rightarrow$ heating under He flow

Fig. 4 shows the spectra change upon the switching of gas from reactant mixture (after

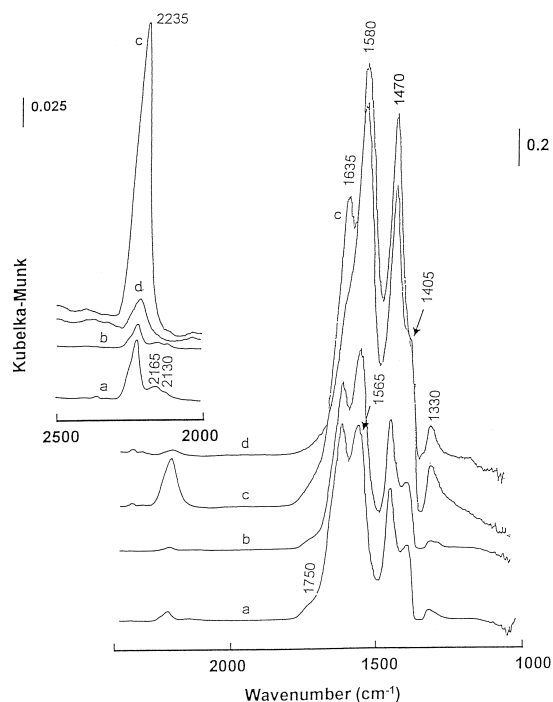


Fig. 4. FTIR spectra change upon the switching from reactant mixture to He flow after 30 min exposition ( $C_2H_5OH/NO/O_2/He$ ,  $250^\circ\text{C}$   $\rightarrow$  He,  $250^\circ\text{C}$   $\rightarrow$  Heating under He). (a) After 30 min under  $C_2H_5OH/NO/O_2/He$  at  $250^\circ\text{C}$ , (b) after 15 min under He at  $250^\circ\text{C}$ , (c) during heating under He flow at  $400^\circ\text{C}$ , (d) during heating under He flow at  $500^\circ\text{C}$ .

exposure at  $250^\circ\text{C}$  for 30 min) to He followed by heating under He flow. The isothermal exposure of the catalyst to the He flow leads to a decrease in NCO band intensity, meanwhile the IR band at the  $1300\text{--}1750\text{ cm}^{-1}$  spectral region seems to be hardly affected. However, the heating under He generates a drastic change in the recorded spectra; the increase of the NCO band is accompanied with a clear decrease in the IR bands at  $1405$  and  $1565\text{ cm}^{-1}$  corresponding to the organic nitro species. These features are clearly showed by the spectrum (c) recorded at  $400^\circ\text{C}$  where the NCO band reached its maximum. The spectrum (d) recorded at  $500^\circ\text{C}$  showed only a presence of the two intense IR bands at  $1580\text{ cm}^{-1}$  and  $1470\text{ cm}^{-1}$  as well as the band at  $1330\text{ cm}^{-1}$  which disappeared later on during the heating process (spectra not shown). These bands may be assigned to some

$\text{NO}_3^-$  and/or carboxylates and formates species considered as spectator species according to their behavior. From these results, correlation between the adsorbed NCO formation and the decomposition of organic nitro species can be made, indicating that the regeneration of surface NCO species observed during the heating under He process is apparently originated from the decomposition of adsorbed organic nitro compounds. Thus, the importance of the two aforementioned species in the process of  $\text{NO}_x$  reduction by ethanol has to be taken into consideration.

Further confirmation of the role of NCO species in  $\text{NO}_x$  reduction is demonstrated in Fig. 5 showing the evolution of the IR band area at  $2235\text{ cm}^{-1}$  and  $\text{N}_2$  production during the step change experiment ( $\text{C}_2\text{H}_5\text{OH}/\text{NO}/\text{O}_2/\text{He}$ ,  $250^\circ\text{C} \rightarrow \text{He}$ ,  $250^\circ\text{C} \rightarrow$  heating under He flow). The clear detection of the NCO band at  $2100\text{--}2350\text{ cm}^{-1}$  region made it easier to integrate rather than the complex  $\text{R-NO}_2$  bands

located in the  $1300\text{--}1750\text{ cm}^{-1}$  region. The shape of  $\text{N}_2$  formation monitoring showed in Fig. 5A is similar to the NCO band area curve (Fig. 5B). Under reaction mixture flow, the detected  $\text{N}_2$  is originated from  $\text{NO}_x$  reduction by ethanol. The switch from the reaction mixture to He ( $\text{C}_2\text{H}_5\text{OH}/\text{NO}/\text{O}_2/\text{He}$ ,  $250^\circ\text{C} \rightarrow \text{He}$ ,  $250^\circ\text{C}$ ) led to a decrease in the intensity of NCO band accompanied with a diminution of  $\text{N}_2$  formation. Heating under He flow led to a detection of  $\text{N}_2$  and a regeneration of NCO species which seems to be resulting from the decomposition of adsorbed organic nitro compounds occurring at temperatures higher than  $250^\circ\text{C}$ . The curves of  $\text{N}_2$  formation and NCO peak area obtained during the heating step exhibited the same maximum around  $400^\circ\text{C}$ .

The parallelism between the  $\text{N}_2$  formation and the NCO band area change indicated by Fig. 5A and B strongly support the participation of NCO species (formed by organic nitro compounds decomposition) into the  $\text{NO}_x$  reduction process.

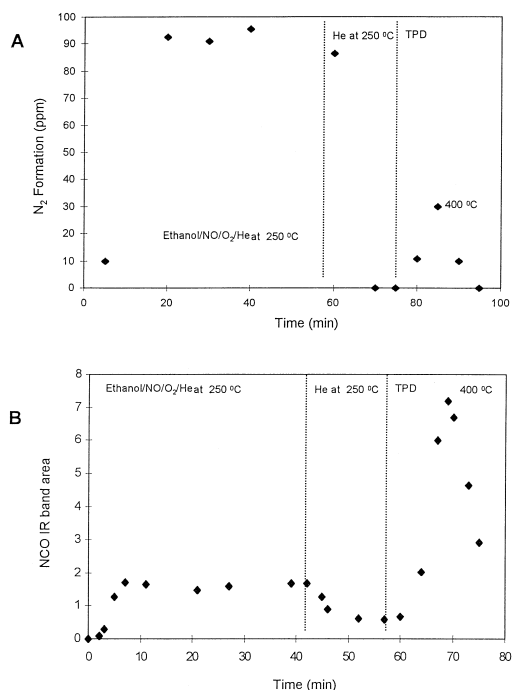


Fig. 5. Evolution of the  $\text{N}_2$  production (A) and NCO band area at  $2235\text{ cm}^{-1}$  (B) during the step change experiment ( $\text{C}_2\text{H}_5\text{OH}/\text{NO}/\text{O}_2/\text{He}$ ,  $250^\circ\text{C} \rightarrow \text{He}$ ,  $250^\circ\text{C} \rightarrow$  Heating under He flow).

### 3.3.2. ( $\text{C}_2\text{H}_5\text{OH}/\text{NO}/\text{He}$ at $250^\circ\text{C}$ ) $\rightarrow$ He at $250^\circ\text{C} \rightarrow$ heating under He flow

In order to investigate the role of oxygen in  $\text{NO}_x$  reduction by ethanol, similar in-situ step change experiments were performed in the absence of  $\text{O}_2$  in (Fig. 6). It was previously indicated that under  $\text{C}_2\text{H}_5\text{OH}/\text{NO}/\text{He}$  mixture, the IR bands observed in the spectral region between  $1300$  and  $1750\text{ cm}^{-1}$  (spectrum (a), Fig. 6) are almost similar to those of spectrum (a) of Fig. 4. It should be noted that the NCO band produced by  $\text{C}_2\text{H}_5\text{OH}/\text{NO}/\text{He}$  reaction was located at  $2216\text{ cm}^{-1}$  (Fig. 6). The switch to He led to an increase of NCO band intensity which might arise from the same decomposition profile of the nitro organic compounds. The NCO band intensity after switching to He at  $250^\circ\text{C}$  and during heating under He was smaller as compared with the one formed in the case of step change experiment performed with  $\text{C}_2\text{H}_5\text{OH}/\text{NO}/\text{O}_2/\text{He}$  mixture. Furthermore, the GC analysis of  $\text{N}_2$  formation during

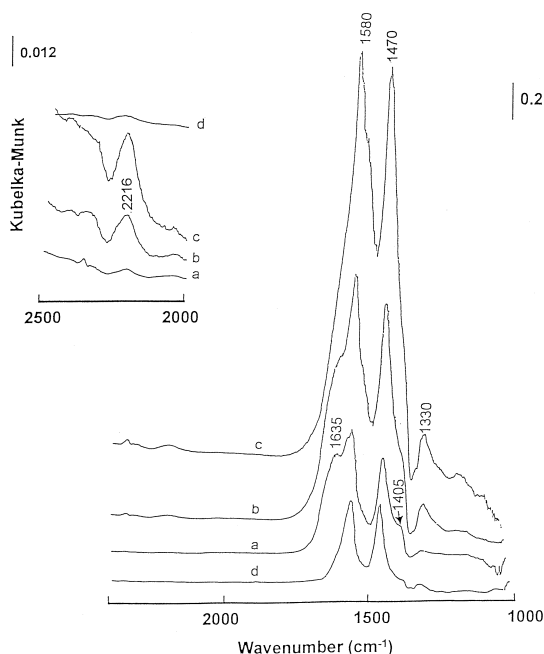


Fig. 6. FTIR spectra change upon the switching from reactant mixture without  $O_2$  to He flow ( $C_2H_5OH/NO/He$ ,  $250^\circ C \rightarrow He$ ,  $250^\circ C \rightarrow$  Heating under He flow). (a) After 30 min under  $C_2H_5OH/NO/He$  at  $250^\circ C$ , (b) after 10 min under He at  $250^\circ C$ , (c) during heating under He flow at  $400^\circ C$ , (d) during heating under He flow at  $500^\circ C$ .

step change experiment with  $C_2H_5OH/NO/He$  mixture showed the absence of  $N_2$  formation neither under reaction mixture nor during the heating process. This result may be related to fact that the quantities of  $N_2$  formed were very small to be detected by our analytical apparatus. From the above experiments, it could be concluded that the absence of oxygen in the reaction mixture did not affect the nature of the nitrogen-containing surface species formation as well as their thermal decomposition. Therefore, the presence of oxygen in the reaction mixture strongly enhanced  $N_2$  production during  $C_2H_5OH/NO/O_2/He$  reaction on  $Ag/Al_2O_3$ . The way in which nitro compounds decompose to form dinitrogen and adsorbed NCO species in our experiment remains unclear. Certainly, gas phase and/or adsorbed oxygen is needed to decompose the adsorbed nitrogen-containing species and to contribute to their formation from NO reaction with ethanol. The fact that the

latter processes took place in the absence of oxygen in gas phase mixture strongly justify the implication of adsorbed oxygen on silver stored during the oxidative pretreatment of the catalyst. In support of this, the recent result of Aoyama et al. [26] where the oxidized  $Ag/Al_2O_3$  was reported to be highly active for  $NO_x$  reduction with ethanol and propene rather than the reduced catalyst. The authors explained this result in terms of specific oxygen silver interaction. This issue has been addressed by many works in the literature where the presence of diatomic oxygen on catalyst surface was a matter of argue, but the dissociation of  $O_2$  on silver above room temperature was also reported to give rise to adsorbed  $O^-$  species which were the most active adsorbed oxygen forms [27–29]. The highest reactivity of this species was related to the relatively weak oxygen bond with silver. Furthermore, silver surface was also found to present another interesting aspect related to its strong ability to adsorb other gases once the surface contains adsorbed oxygen [30].

Considering silver oxygen affinity in  $Ag/Al_2O_3$  catalyst, it seems to be clear that the role of oxygen in  $NO_x$  reduction process is not limited only (i) to convert NO to  $NO_2$  [31,32] and/or (ii) to clean the catalyst surface from carbonaceous deposit [33] and/or (iii) to keep the metal particles in high oxidation state [31,34], but also to participate in the process of  $NO_x$  reduction by ethanol on  $Ag/Al_2O_3$  by enhancing the decomposition of organic nitro

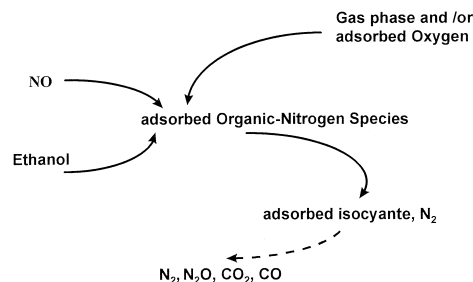


Fig. 7. Possible mechanistic scheme of  $NO_x$  reduction by ethanol on  $Ag/Al_2O_3$ .



compounds and the formation of  $N_2$  and NCO surface species. Accordingly, a possible mechanistic scheme of  $NO_x$  reduction by ethanol on  $Ag/Al_2O_3$  is summarized on Fig. 7. It has been suggested that the adsorbed NCO species gives  $N_2$ ,  $CO_2$  and CO in the presence of NO and/or  $O_2$  [35]. Kinetic studies on the reactivity of NCO species are under investigation in our laboratory.

#### 4. Conclusion

In-situ DRIFT monitoring of surface species combined with gas phase analysis by gas chromatography revealed a parallelism between the  $N_2$  production and the NCO band behavior during  $NO_x$  reduction by ethanol over alumina-supported silver catalyst as well as upon switching from reaction mixture to He flow.

The decomposition under He flow of organic nitro compounds formed with  $C_2H_5OH/NO/He$  in the absence of  $O_2$  as well as in presence of  $O_2$  in the mixture leads to the generation of adsorbed isocyanate and  $N_2$  production. However, it should be pointed out that the presence of oxygen in the reaction mixture is necessary to enhance drastically the  $N_2$  formation and to decompose the nitrogen-containing species to adsorbed NCO species.

#### Acknowledgements

T.C. gratefully acknowledges the Science and Technology Agency of Japan (S.T.A.) for the financial support.

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