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Study by in situ FTIR spectroscopy of the SCR of NO_x by ethanol on Ag/Al_2O_3—Evidence of the role of isocyanate species

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Abstract

The selective catalytic reduction (SCR) of NO_x in excess of oxygen using ethanol as reducing agent on silver/alumina was studied by coupling in situ FTIR spectroscopy and mass spectrometry. A comparison with the same reaction on bare alumina permitted us to show the connection between the presence of silver and isocyanate species on a catalyst. Then, a detailed investigation concerning these groups was undertaken to understand their formation, their localization, and their reactivity in order to propose the pathway of the NO_x SCR into N_2. Three elemental sequences are suggested explaining, first, the formation of silver cyanide and its transformation into $Al^{3+}NCO$, then isocyanates hydrolysis into ammonia, and finally the reaction of the latter species with NO in the presence of oxygen giving rise to nitrogen.
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1. Introduction

Since the elimination of soot particulates emitted from diesel has been resolved using a filter associated to a cerium-based additive [1], diesel engines are considered to be less polluting than gasoline engines thanks to their lower fuel consumption, which involves lower CO_2 rejects. However, a new generation of cars using gasoline, with a large excess of oxygen (called lean-burn motorization) is commercialized because of its weak CO_2 pollution as well. Nevertheless, the drawback of these two kinds of engines is the large excess of oxygen making the NO_x removal difficult. This problem is still the subject of much research on the selective catalytic reduction (SCR) reaction, particularly on alumina-based oxide catalysts, which seem to be the best candidates for applications under real conditions [2–14].

Among the mechanisms proposed by the different authors, isocyanate species have often been proposed as reaction intermediates. However, in many cases, the demonstration of their role is often made without real proof. The model reaction commonly used is the SCR of NO_x by propene. Results obtained from this reaction studied by in situ FTIR have been verified in those species [15]. But the weak concentration of isocyanates obtained and detected by IR in the reaction has caused some controversy.

The goal of the present report, using ideal conditions, is to definitively demonstrate that isocyanates are really intermediate species and then to understand how these species react. Thus we decided to undertake the analysis of the $C_2H_5OH + NO + O_2$ reaction on Ag/Al_2O_3 and Al_2O_3 in a steady state and pulse regime, the choice of ethanol as reducing agent being dictated by the necessity to increase the NCO concentration. A specific study of isocyanate species has allowed us to determine a possible mechanism for the $DeNO_x$ reaction.

2. Experimental

Al_2O_3 and Ag/Al_2O_3 catalysts, prepared by RHODIA, present respectively a specific surface area of 112 and 103 m^2/g. The silver catalyst contains 2wt% of metal that

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is usually proposed as the optimum percentage for the SCR of NO using ethanol as reducing agent [16].

Our in situ system allows the analysis of the reactives and of the reaction products by mass spectrometry and FTIR spectroscopy. The catalyst is placed in a DRIFTS reactor cell commercialized by Spectratech, which permits the observation of adsorbed species present on its surface under reaction conditions. IR spectra are collected with a Nicolet 550 FT-IR spectrometer, accumulating 64 scans at a resolution of 4 cm^{-1}. Gas products are analyzed by quadrupole mass spectrometer QMS, Balzers TCP 121, and by FTIR via a gas microcell of 0.088 cm^3 volume.

Twenty milligrams of catalyst is pretreated for 2 h at 873 K under a flow (25 ml/min) of 10% O_2 in Ar. The sample is then taken to the reaction temperature. For steady-state analysis, the gas mixture is composed of 1000 ppm C_2H_5OH, 500 ppm NO, and 10% O_2 with Ar balance (total flow 25 ml/min). For the pulse regime, the catalyst is exposed to NO + O_2 mixtures in Ar flow and then pulses of C_2H_5OH are introduced into the stationary stream. After optimization of the experiments, the following parameters were chosen. Ethanol containing saturator placed at ambient temperature, purged by 10 cm^3/min argon flow (saturation vapor pressure of ethanol at 298 K: about 56 Torr). Use of a 0.02 cm^3 injection loop. One-tenth of the carrier flow purges the injection loop circuit.

To achieve the aim of this study, we have undertaken a panel of different experiments. Thus, gas compositions are given in detail along with the results. However, all these experiments were realized at atmospheric pressure and the W/F ratio has been kept at 0.048 $g\,s\,cm^{-3}$.

3. Results

3.1. Study of the $C_2H_5OH + NO + O_2$ steady-state reaction

Our in situ technique gives us the possibility of detecting, during the reaction, the surface adsorbed species and the gas products simultaneously. In the $C_2H_5OH + NO + O_2$ reaction study spectra were collected on the catalyst surface by the DRIFTS cell and in the gas phase by the FTIR gas cell for each temperature after 20 min of steady-state reaction (under isotherm conditions).

3.1.1. DeNO$_x$ activity: comparison between Al_2O_3 and Ag/Al_2O_3 versus temperature

Fig. 1 compares the DeNO$_x$ activity of alumina and silver/alumina catalysts versus reaction temperature. The gas flow consists of 1000 ppm of C_2H_5OH, 500 ppm of NO, and 10% of O_2. From 623 to 773 K, silver-containing catalysts present higher activity than Al_2O_3: almost 30% of NO_x conversion under our conditions for Ag/Al_2O_3 compared to 10% for bare alumina. In the $C_2H_5OH +$ NO + O_2 reaction, the support does not seem to be a major element. However the same experiment realized on
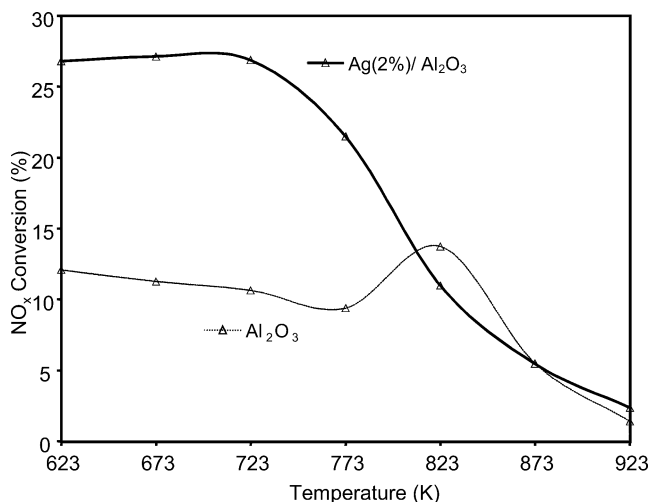

Fig. 1. Conversion of NO_x versus reaction temperature. Reaction flow: NO (500 ppm), C_2H_5OH (1000 ppm), O_2 (10%); W/F = 0.048 $g\,s\,cm^{-3}$.

silver/silica catalysts has not shown any activity. Thus, we think that support as well as silver content plays an important role in the SCR of NO_x by ethanol in excess of oxygen.

3.1.2. Gas-phase analysis

Thanks to the coupling of a IR gas microcell with our analysis system, gas spectra presented in Fig. 2 are obtained for each temperature corresponding to the adsorbed phase spectra. In a first experience, the $C_2H_5OH + NO + O_2$ reaction was realized by replacing the catalyst with carburondum to determine the specific products of the thermal reaction (Fig. 2A). The mixture NO (1875 cm^{-1}) + O_2 causes the formation of small amounts of NO_2 (1617 cm^{-1}). Ethanol addition (1394, 1241, 1066, and 879 cm^{-1}) produces (already starting from 623 K) acetaldehyde (1745 cm^{-1}), CO_2 (667 cm^{-1}), and, above 673 K, CO (2143 cm^{-1}) and ethylene (949 cm^{-1}). The characteristic band of acetaldehyde is situated at the same wavenumber as formaldehyde, but it is possible to differentiate the two species observing the distance between the P and R rotation-vibration components maxima: 35 cm^{-1} for CH_3CHO and about 50 cm^{-1} for HCHO, which has a lighter mass. When the flow goes through the Ag/Al_2O_3 catalyst, NO as well as ethanol conversions are much more important than during the thermal reaction. Other differences appear, such as CO and C_2H_4 formation, at lower temperatures; we also detect new catalytic conversion products at 623 K (HCN, 713 cm^{-1}) and between 623 and 723 K (NH_3, 932 and 964 cm^{-1}). The last compound is the only gas product not present on bare alumina, because either it is not produced or its reaction is too fast to allow detection.

However, the presence of this molecule near the temperature of maximal conversion and on silver-containing catalyst leads us to consider a mechanism of selective reduction of NO_x detected on Cu–ZSM-5, in which isocyanate groups were proposed as possible reaction intermediates. In
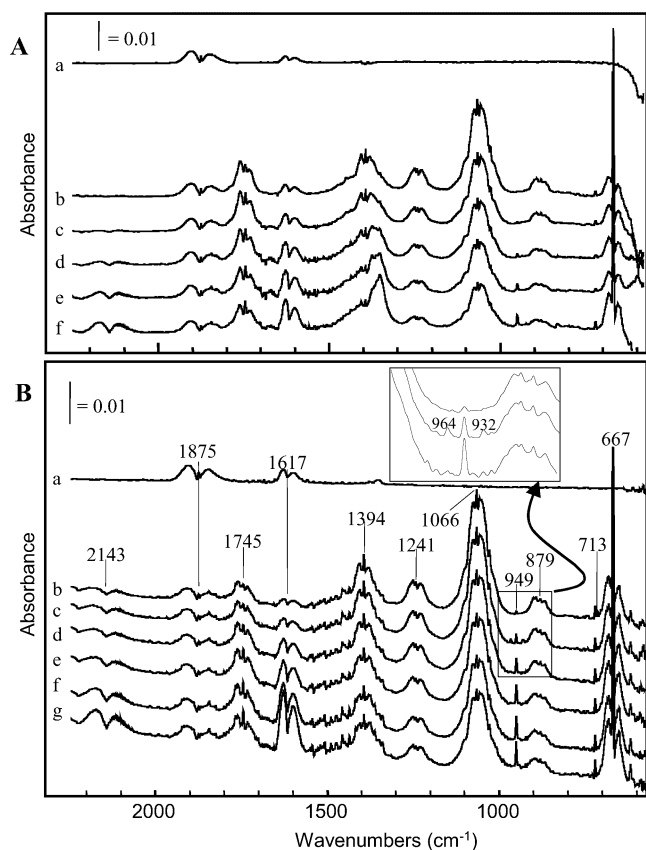
Fig. 2. FTIR spectra of gas products after NO (500 ppm) + O$_2$ (10%) flow introduction on (A) SiC and (B) Ag/Al$_2$O$_3$ at (a) 623 K and then C$_2$H$_5$OH (1000 ppm) addition at (b) 623, (c) 673, (d) 723, (e) 773, (f) 823, and (g) 873 K.

that mechanism NCO species hydrolyze leading to N$_2$ production [17,18]. Under our conditions silver would play a role similar as copper and would explain the good activity of Ag/Al$_2$O$_3$; the presence of ammonia would confirm the specific reaction for isocyanate species on these catalysts. We will reconsider this possibility later.

3.1.3. Catalyst surface adsorbed species

In Fig. 3, spectra of adsorbed species at 623 K are reported when ethanol is added into the initial flow composed by Ar, NO, and O$_2$. Spectra corresponding to silver-containing catalysts (Fig. 3b) are remarkable by bands situated in the 2260–2125 cm^{-1} region, as well as for features at 1630, 1412, and 1340 cm^{-1}. We attribute bands at 2255 and 2228 cm^{-1} to Al$_{VI}$NCO and to Al$_{IV}$NCO species, respectively. However, controversial opinions exist about these assignments, and the authors have already clarified this point in a previous report [19]. Therefore isocyanate species will be assigned as in the above-noted reference. We also find in the literature attributions concerning the other less intense and well-defined bands at 2155 and 2127 cm^{-1}: they seem be due to the presence of cyanide groups on alumina and/or silver (ν(C≡N) of AgCN complex absorbs at 2146 cm^{-1}) [20]. Bands observed in the region below 2000 cm^{-1} contain vibrations characteristic of ethyl carbonate species [21] on alumina (1630, 1412, and 1340 cm^{-1}) and whose formation is favored by the presence of the metal. Other features exist and are common for both catalysts. Four minutes after C$_2$H$_5$OH introduction, the first spectrum (full line) presents the bands of vibration of formate species (ν(COO$^-$) at 1593 and 1375 cm^{-1}; ν(CH) at about 3000 cm^{-1}—zone not reported here; δ(CH) at 1390 cm^{-1}). Two intense bands at 1578 and 1466 cm^{-1} are also visible on all the spectra: they are due to acetate species. A study of surface species formed during the C$_2$H$_5$OH + O$_2$ reaction showed that all theses bands detected in the 1700–1100 cm^{-1} range appear, which confirms that they are not nitrogen-containing species. Dotted lines spectra were collected about 15 min later. A comparison between these spectra and the others previously interpreted shows that species characterized by bands in the 1650–1200 cm^{-1} area have the tendency to accumulate on catalyst surfaces (bands intensities increased with time). So, acetate and carbonate species produced by the decomposition or by the oxidation of ethanol do not seem to act as intermediate compounds in the SCR of NO$_x$. On the contrary,
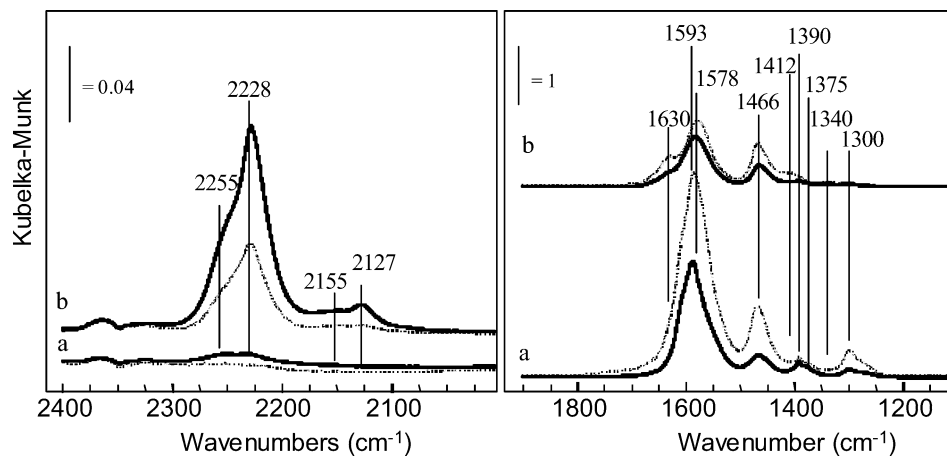

Fig. 3. FTIR spectra of surface adsorbed species on (a) Al$_2$O$_3$, and (b) Ag/Al$_2$O$_3$ under C$_2$H$_5$OH (1000 ppm) + NO (500 ppm) + O$_2$ (10%) flow at 623 K; (full line) 4 min and (dotted line) 20 min after ethanol introduction.
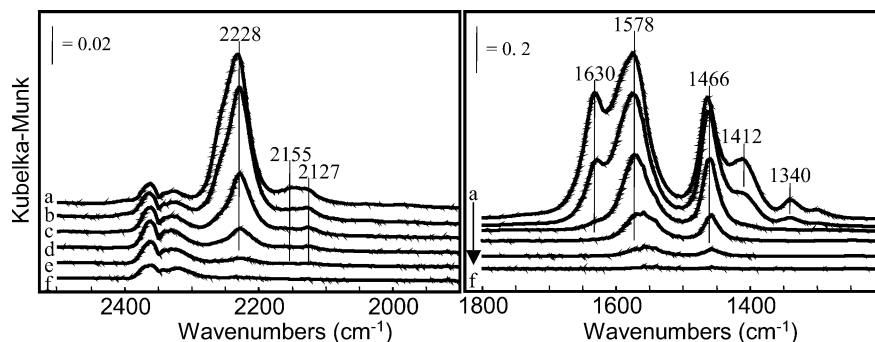
Fig. 4. FTIR spectra of surface adsorbed species on Ag/Al$_2$O$_3$ under C$_2$H$_5$OH (1000 ppm) + NO (500 ppm) + O$_2$ (10%) flow at (a) 623, (b) 673, (c) 723, (d) 773, (e) 823, and (f) 873 K.

isocyanate and cyanide species are in major part consumed: indeed, the intensities of the bands supposed to characterize them decrease.

Fig. 4 shows the evolution with temperature of Ag/Al$_2$O$_3$ catalyst surface adsorbed species. The reaction is studied between 623 and 873 K; spectra are collected every 50 K after about 20 min of steady state. The intensities of NCO bands decrease quite strongly with a temperature increase up to 773 K, a temperature at which these bands almost completely disappear. Features at lower wavenumbers (around 1500 cm^{-1}) follow the same evolution. The spectrum collected at 823 K (Fig. 4e) clearly shows two bands at 1550 and 1450 cm^{-1} that characterize acetate species, which are more stable with respect to other compounds. Similar phenomena are observed on Al$_2$O$_3$ (spectra not shown). We have observed that bare alumina catalysts do not present NCO groups on their surface. Thus, increasing the temperature, we observe only the decrease of acetate and carbonate corresponding bands intensities. The simultaneous analysis of catalytic surface and catalytic activity curves informs us about the eventual role of isocyanate species in the SCR of NO$_x$. These species do not accumulate at 823 K, at temperature at which the NO$_x$ conversion is still relatively important, but follow the activity evolution, disappearing above 773 K, a temperature where the conversion begins to heavily decrease. In this temperature domain, –CN and –NCO groups are mainly present on silver-containing catalysts, which possess the most important DeNO$_x$ activity.

3.2. Study of pulse reaction: NO reduction by ethanol pulses in oxygen excess

3.2.1. Gas-phase observations

We have analyzed the gas phase by FT-IR, collecting a spectrum every 4 s during the introduction of four successive ethanol pulses on Ag/Al$_2$O$_3$ at 698 K. The resulting waterfall of spectra (not presented in the figures) shows the same gas products observed during the study of the stationary reaction: (from higher to lower wavenumbers) CO$_2$, CO, NO, CH$_3$CHO, NO$_2$, C$_2$H$_5$OH, C$_2$H$_4$, and HCN. Only NH$_3$ is absent or it is in too small amount to be detected.
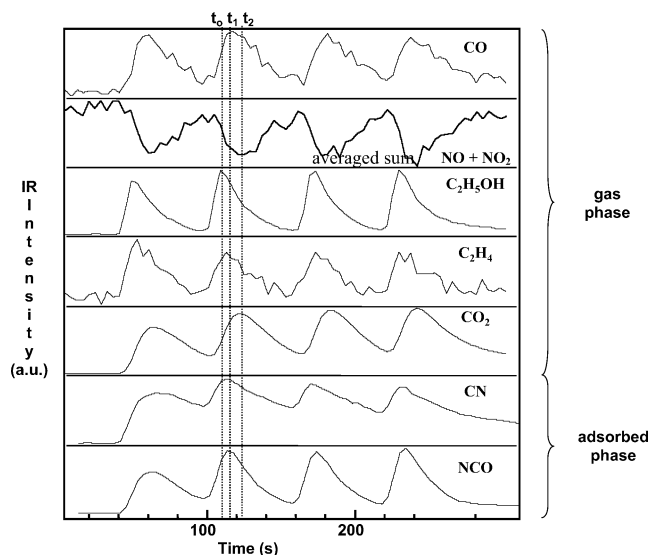

Fig. 5. Correlation of FTIR analysis of gas and adsorbed species during the introduction of 4 ethanol pulses at 698 K on Ag/Al$_2$O$_3$ catalysts under NO (1000 ppm) + O$_2$ (10%) flow.

Fig. 5 shows the trend of the integrated area of the characteristic bands for each gaseous compound noted above. These curves called chemigrams make the analysis of the results obtained during these pulse experiments easier and can be directly correlated to those presented in Fig. 6, which correspond to the evolutions of the different gases detected by mass spectrometry. Comparing the data belonging to the two analysis systems is very important: mass spectrometry alone would not have permitted us to distinguish CO$_2$ from N$_2$O if the last had been present in the gas phase, to detect ethylene, acetaldehyde, and hydrogen cyanide; on the other hand IR spectroscopy is not sensitive to centro-symmetric molecules, such as O$_2$ and N$_2$.

Alcohol detection is concomitant with the start of CO (in a small amount), CO$_2$, C$_2$H$_4$ (weak), CH$_3$CHO (not shown), and HCN (very weak and not represented) production and with NO and NO$_2$ consumption. This double consumption shows either NO$_x$ reduction into N$_2$ (because N$_2$O and NH$_3$ are not detected) or NO$_x$ transformation into adsorbed surface species, or both phenomena. If C$_2$H$_5$OH, C$_2$H$_4$,
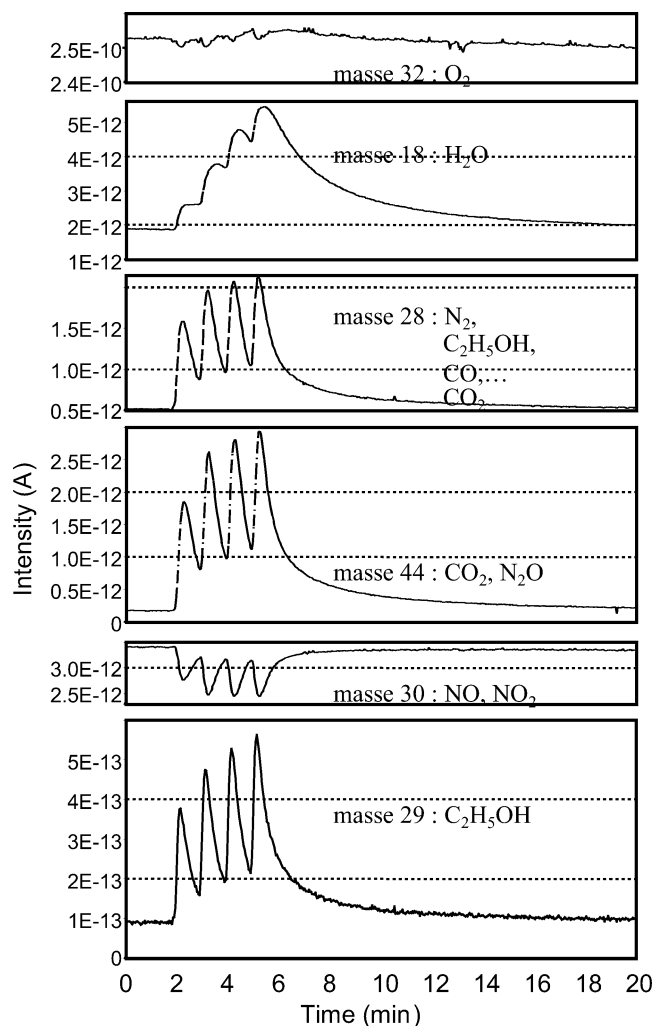
Fig. 6. Analysis by mass spectrometry of the gas phase during the introduction of 4 ethanol pulses at 698 K on Ag/Al$_2$O$_3$ catalysts under NO (1000 ppm) + O$_2$ (10%) flow.

Fig. 7. FTIR spectra of adsorbed species during the introduction of 4 ethanol pulses at 698 K on Ag/Al$_2$O$_3$ catalysts under NO (1000 ppm) + O$_2$ (10%) flow. Part (b) represents a magnification of part (a) in the 2500–1900 cm^{-1} spectral region. The third axis reports time in seconds.

and CH$_3$CHO present the same evolution, their maxima shortly precedes those of CO and CO$_2$. These features are reproducible for each pulse.

3.2.2. Catalytic surface observation

The species detected in the adsorbed phase (Fig. 7) are in major part due to the presence of gas-phase species as formates, acetates, carbonates, cyanide, and isocyanates. However, a scrupulous observation of the different spectra (1 spectrum/4 seconds) gives the following added information:

– Before the appearance of the first ethanol pulse, the catalyst is under NO + O$_2$ flow and nitrate species are present on its surface (ν_3(NO$_3^-$) at 1650–1500 and 1300–1170 cm^{-1} [22]). They disappear when ethanol arrives, while a weak peak appears in the NO$_2$ gas evolution.

– The synchronism between gas and adsorbed species evolution (possibly thanks to the knowledge of the
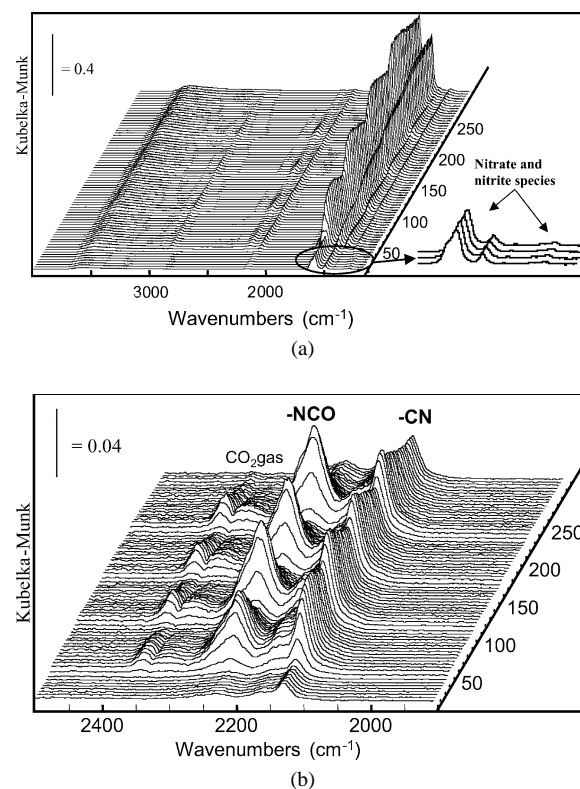
collecting time as well as to CO$_2$ detection, which can be made in both phases) shows that formate and acetate species are detected on the catalyst surface before ethanol appears in the gas phase. This observation shows that, first of all, ethanol is oxidized into these compounds.

– Almost at the same time cyanides characteristic bands increase in intensity, followed by isocyanates (Fig. 7b).

– The integrations of the different bands versus time show that the evolution of formate, cyanide, and isocyanate species is similar to ethanol evolution (presence of a maximum) whereas acetate species (integration of 1460 cm^{-1} band) accumulate.

3.2.3. Correlation between surface and gas phases

The juxtaposition, on a same time scale, of gas and adsorbed phases analysis (Fig. 5) is a very interesting approach to the intermediary role of cyanide and isocyanate species:

– First we note the importance of NO consumption during ethanol pulse sending. Each pulse induces the disappearance of some NO amount, but in particular the NO consumption persists continuously between 2 minima. Indeed, for 300 s (corresponding to the efficiency of the 4 ethanol pulses), the average conversion is 20%.

– Second, we note that time resolution in the formation and disappearance of the different gas and adsorbed species (measured in FTIR as well as in mass spectrometry) gives information on the NO_x SCR pathway on Ag/Al_2O_3 catalysts. We are able to establish the following time scale according to the observations of maxima and minima for the evolution of each species:

t_0: $C_2H_5OH_{gas}$ maximum,

$t_1 (t_0 + 7 \text{ s})$: $-NCO_{ads}$ maximum,

$t_2 (t_0 + 15 \text{ s})$: NO_{gas} minimum and CO_{2gas} maximum.

t_0 could correspond to the maximum ethanol concentration, followed by the fast formation of cyanide species probably by the reaction of NO with ethylene, nitroso species formation, and then isomerization into intermediate oximes, which transform themselves into nitrile (acetonitrile). The last one would be cut to give silver cyanide as it has been shown on Cu–ZSM-5 [17]. In this first step, experimental proof is lacking to support all these elemental reactions (probably because of the short lifetime of intermediate compounds), the only evidence being the presence of ethylene in the gas phase.

t_1 would match with the slower transformation of cyanides into isocyanates, which probably needs an intermediate isomerisation $-CN \rightarrow -NC$ before oxidation into isocyanate. The isomerization step is also much slower than oxidation on Cu–ZSM-5 [17]; on the contrary, here, the oxidation is much faster since we do not detect the intermediate isocyanide. In this second sequence, the experimental evidence supports our statements, although we have not been able to show (as in the case of Cu–ZSM-5) isocyanide species expected at 2060 cm^{-1} (about 100 cm^{-1} lower than the cyanide species wavenumber).

t_2 would correspond to the isocyanate hydrolysis using water due to the alcohol combustion (Fig. 2) to give, as usually seen, ammonia and carbon dioxide. Ammonia has been detected in the gas phase but its concentration is never high enough to allow integration: its activity as reducing agent in NO_x SCR is too important. NH_3 formed by isocyanate hydrolysis classically reacts with another NO molecule, that could partially explain the concomitance between NO minimum and CO_2 maximum observed in Fig. 5.

The presence of carbon monoxide and ethanol in the gas phase does not allow us to follow the nitrogen formation by mass spectrometry analysis, these 3 compounds giving a response in 28 mass; it would be interesting to localize the N_2 maximum in our relative time scale.

In the interpretation of this experiment, several surface intermediate species are evoked; among them, only cyanide and isocyanate species have been detected on the catalyst surface. Their intermediate nature in the SCR of NO_x seems very reasonable, so that a deeper investigation is necessary.

3.3. Investigation about isocyanate species

The species characterized by the bands localized at 2258 and 2235 cm^{-1} seem to play an important role in the $C_2H_5OH + NO + O_2$ reaction on Ag/Al_2O_3 catalysts. Thus accurate information about them is necessary. To eliminate the ambiguity caused by the large amount of literature and to give a reliable interpretation of our results, a complete characterization has been undertaken on these groups [19, and refs. therein]. The EtNCO adsorption as well as the isotopic substitution experiments and other experiments have allowed us to conclude on the nature and the coordination of the species produced in the $C_2H_5OH + NO + O_2$ reaction. The band observed at 2255 cm^{-1} characterizes the adsorption of the $-NCO$ group on octahedrally coordinated Al^{3+} ions, while the band at 2228 cm^{-1} corresponds to the same species coordinated on tetrahedral Al^{3+} ions. We think that silver enhances the formation of isocyanate species but that this molecule rapidly spills over Al_2O_3 support [19].

To understand this mechanism further, we propose a NCO formation pathway and we will investigate the reactivity of these groups toward molecules that may be present among the reaction compounds.

3.3.1. NCO formation

Studies in the literature for the past 30 years ago explain the formation schemes of isocyanate species by the $CO + NO$ reaction on different metals supported on oxides [23–31]. Several authors agree that on oxide-based catalysts such as SiO_2, Al_2O_3, MgO, and TiO_2 supporting noble metals as Pt, Pd, Ru, Rh, isocyanate species are never observed on the metal. These elements would play an indirect role dissociating NO molecules. Then, adsorbed nitrogen atoms would migrate on the support by spillover. All these authors propose or show that after migration, the nitrogen atom preferentially reacts by insertion of a CO molecule in the gas phase more than with adsorbed CO to form the isocyanate group on the support. Almost all these results have been obtained using FTIR spectroscopy with or without isotopic exchange reactions.

In an additional isotopic substitution experiment using $C^{18}O + N^{16}O$, we have observed $C^{16}O$ formed by reaction of $C^{18}O$ with surface oxygen atoms or with oxygen atoms from NO molecules. This phenomenon explains why when the reaction is performed on oxidized Ag/Al_2O_3 we observed the same band as for the reaction with unlabeled molecules. To obtain the expected isotopic shift [19], we must undertake the same experiment on reduced catalysts to inhibit the transformation $C^{18}O \rightarrow C^{16}O$ due to surface oxygen atoms. Therefore, we have introduced a $C^{18}O$ probe alone on the catalyst. After heating at 873 K, the temperature is decreased to 473 K and CO is evacuated. At this temperature NO (15 Torr) is introduced. Very quickly, we have detected $N^{18}O$ in the gas phase. That means that NO is dissociated very easily on the catalyst surface and that $C^{18}O$ was dissociated previously, leaving ^{18}O and carbon on the
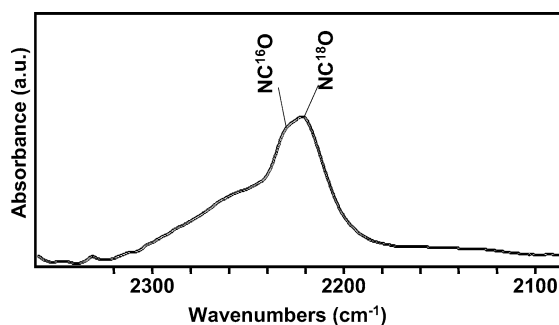
Fig. 8. Magnification on FTIR spectrum of the adsorbed phase recorded during the $^{12}C\,^{18}O$ (4 Torr) + $^{14}N\,^{16}O$ (2.2 Torr) reaction on Ag/Al$_2$O$_3$ prereduced by H$_2$ at room temperature for 10 min and then increasing the temperature to 873 K for 90 min.

surface (explaining the black color of the pellet at this moment). Nevertheless no isocyanate species are observed on the surface at this temperature. This also shows that it is necessary that both reactive molecules be present to form the isocyanate group. Thus, it seems that contrarily to previous results reported on noble metal supported catalysts, on Ag/Al$_2$O$_3$ isocyanate species are not formed by linkage of CO molecules to N$_{ads}$ due to the dissociation of NO. According to our results, the following reactions occur during the C^{18}O + N^{16}O experiment:

$$C\,^{18}O \rightarrow C_{ads} + {}^{18}O_{ads},$$

$$N\,^{16}O \rightarrow N_{ads} + {}^{16}O_{ads},$$

$$N_{ads} + {}^{18}O_{ads} \rightarrow N\,^{18}O,$$

$$C_{ads} + {}^{16}O_{ads} \rightarrow C\,^{16}O.$$

Fig. 8 confirms the above-reported reactions: a spectrum with both NC^{16}O and NC^{18}O species is recorded after the C^{18}O + N^{16}O reaction experiment. If we follow the idea developed in the literature that CO reacts with adsorbed nitrogen atoms, the band attributed to NC^{18}O should be much more important than the NC^{16}O corresponding band. On the contrary, according to our dissociation hypothesis, the statistic presence of O from CO and NO explains the equivalent mixture of both isotope groups. A fortiori, when CO reduced the catalyst, the presence of C^{16}O was favored and so NC^{16}O became predominant.

The isocyanate species are formed at temperatures higher than those of the NO dissociation reaction, which is thus the initial step in the NCO formation mechanism. That explains, on the one hand, the need to work at high temperatures (isocyanates species do not appear before 773 K under these conditions) and, on the other hand, the predominant role of silver. Bare alumina is unable to break the CO bond.

We can suppose that cyanide species is one of the recombination products. On the different adsorbed phase spectra, a broad and weak band is detected at 2150 cm^{-1} and is only shifted for nitrogen 15 and carbon 13 substitutions [19].

It is certainly the signature of aluminum cyanide or silver cyanide (although ν(CN) on Ag is usually given at 2165 cm^{-1}).

3.3.2. Reactivity of NCO species

The first step in the study of isocyanate reactivity consists in isolating it on Ag/Al$_2$O$_3$ at a temperature in the domain of activity of this catalyst. However, to prevent a too fast decomposition of the adsorbed species under argon flow, we have undertaken these experiments at 573 K. Indeed, at this temperature, the intensities of the 2255 and 2228 cm^{-1} bands do not decrease very quickly.

3.3.2.1. Experimental data. Both CO + NO reaction and adsorption of EtNCO have been used to isolate NCO groups on the silver/alumina catalyst surface. The sample is placed in the crucible of the DRIFTS cell and is first activated at 873 K under Ar + O$_2$ (10%). Then, NCO species have been isolated by:

– Sending NO + CO reactive molecule, heating at 873 K, then decreasing the temperature to 573 K before stopping the NO + CO flow and purging the catalyst under argon;
– Adsorbing ethyl isocyanate at 573 K; this technique allows us to obtain much more adsorbed isocyanate species but it involves the appearance on the surface of secondary species as carbonates, formates, urethane, etc.

Concerning the first technique, the reactive molecules (O$_2$, NO, H$_2$O) are introduced 2 min after NO + CO flows cutting because they are very quickly evacuated, whereas for the second experimental protocol we let more time for the evacuation of EtNCO, to be sure that this molecule is absent from the system lines. The different molecules sent to the catalyst so impregnated of isocyanates are:

(i) O$_2$, because this molecule is in large excess in the reactive SCR flow;
(ii) NO, because it is the molecule we want to reduce;
(iii) H$_2$O, because this molecule seems to play a role in the mechanism proposed after the preliminary study. All these compounds are introduced by pulses.

3.3.2.2. Reactivity toward O$_2$. In Fig. 9 are grouped the series of spectra collected into the gas cell and the corresponding series collected on the adsorbed phase. NCO groups are produced by NO + CO reaction; 2 min after the Ar purge, O$_2$ pulses are sent every minute (30 s for injecting; 30 s for recharging the loop). On adsorbed phase spectra, we discover that each O$_2$ pulse corresponds to a period when intensities of 2255 and 2228 cm^{-1} bands decrease, a sign of decomposition or consumption.

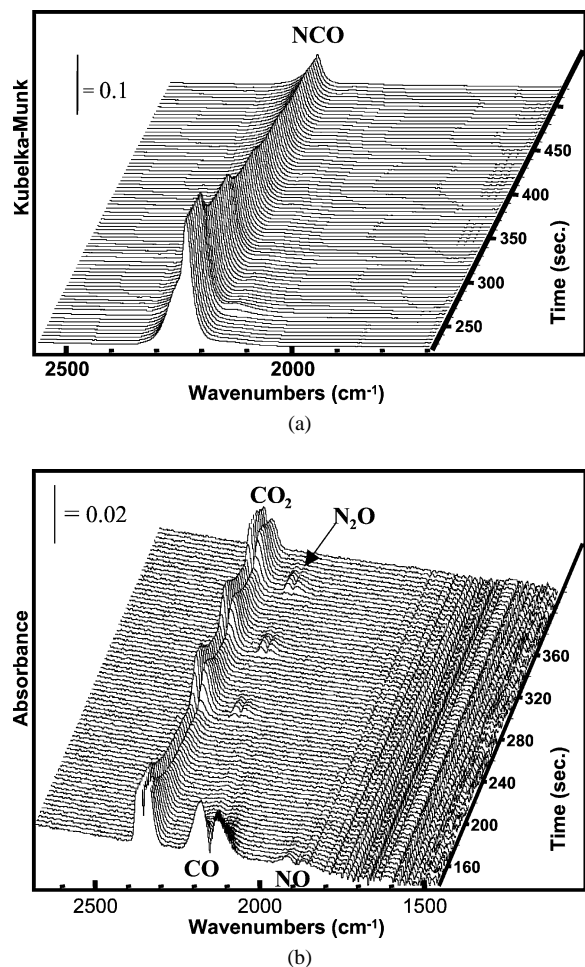From IR gas spectra, we detect that the decrease of NCO bands is concomitant with the production of a small amount

(a)

(b)

Fig. 9. FTIR spectra of (a) adsorbed phase and (b) gas phase, collected at 573 K during the introduction of 10 µl O_2 pulses on Ag/Al_2O_3 previously treated under $CO + NO$ at 873 K.

of N_2O as well as with a more important production of CO_2. The NO band localized at 1875 cm^{-1}, which disappears after the argon purge and does not reappear later. NO_2 is no longer detected on these spectra. Thus NCO groups are not decomposed into NO or NO_2 and O_2. However, the amount of N_2O being weak (taking into account its molar absorption coefficient), other nitrogen species, which are not detectable by FTIR, must be produced. To confirm this deduction, the mass spectrometry analysis is very useful. Indeed, we have represented it in Fig. 10b, where we observe by this technique that for each O_2 pulse (32 mass peak), some 28 mass peaks appear. Given the absence of CO in the IR gas spectra and after subtraction of the contribution due to CO_2, these peaks can only be due to N_2 formation. If we correlate the adsorbed species and gas product evolution (Fig. 10a), we clearly note that sending O_2 pulses involves the transformation of NCO groups into N_2 and N_2O according to the following reactions:
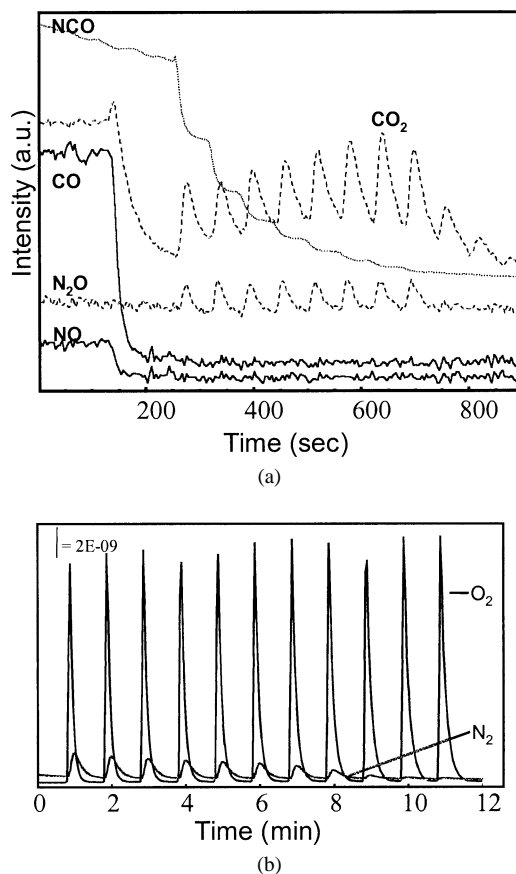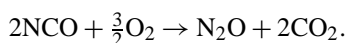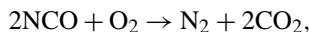
$$2NCO + O_2 \rightarrow N_2 + 2CO_2,$$

$$2NCO + \tfrac{3}{2}O_2 \rightarrow N_2O + 2CO_2.$$

(a)

(b)

Fig. 10. (a) FTIR chemigrams of adsorbed species (NCO) correlated to gas species produced during the introduction of O_2 pulses on Ag/Al_2O_3 previously treated under $CO + NO$ at 873 K. (b) Analysis by mass spectrometry of O_2 (mass 32) and N_2 (mass 28) during this experiment.
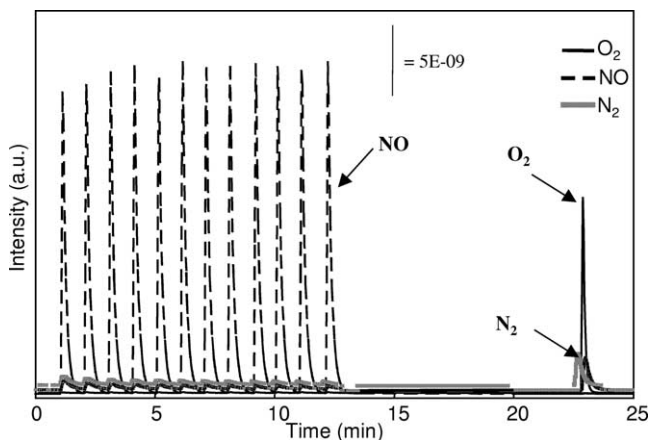

Fig. 11. Analysis by mass spectrometry of NO (mass 30), O_2 (mass 32), and N_2 (mass 28) during the introduction of 12 NO (10 µl) pulses followed by 1 O_2 (10 µl) pulse on Ag/Al_2O_3 previously treated under $CO + NO$ at 873 K.

3.3.2.3. Reactivity toward NO. Under the same conditions as those of previous experiment, we have analyzed the reactivity of NCO groups when NO pulses are introduced on Ag/Al_2O_3 catalysts. The result of this experiment obtained by mass spectrometry is shown in Fig. 11 where we could
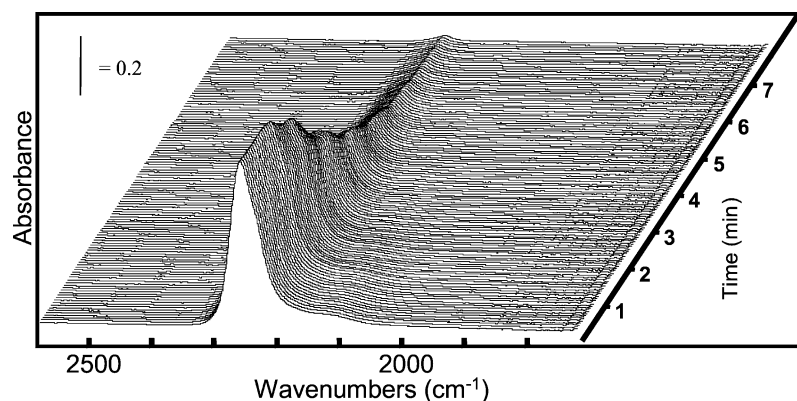
Fig. 12. FTIR spectra of adsorbed species, collected at 573 K during the introduction of 1.5 µl H_2O pulses on Ag/Al_2O_3 previously treated under CO + NO at 873 K.

not detect N_2 production peaks concomitant with the NO peaks. This observation matches with the FTIR spectra corresponding to the adsorbed phase (not shown), where we have only remarked that the introduction of NO pulses does not modify the NCO bands at all. Indeed a weak and continuous decrease in the NCO evolution curve has been verified to be caused by the small decomposition of NCO groups under argon flow at the temperature of the study. The rate of this decrease is not increased when NO is sent through the catalytic bed. To support these results we have sent O_2 pulses after the NO pulses. We have observed the same N_2 production as reported above, due to the reactivity of isocyanates (Fig. 10b).

3.3.2.4. Reactivity toward H_2O. To conclude this study, we have analyzed the behavior of adsorbed isocyanates species on Ag/Al_2O_3 catalyst toward H_2O. Because of the technique, we have introduced 1.5 µl H_2O pulses instead of 10 µl for the other reacting agents.

Isocyanate species were adsorbed introducing EtNCO. As in the case of reactivity toward oxygen, we can clearly distinguish several decreasing levels in the Al–NCO evolution curve, while no other new species appear on the catalyst surface (Fig. 12). However by observing mass spectrometry results (not shown), we have noted that H_2O pulses are well consumed by reaction with –NCO groups and that the product formed by this reaction is neither N_2 nor N_2O. Mass results are also confirmed by IR spectra:

– production of CO_2,
– production of neither N_2O nor NO_2.

Furthermore, the characteristic bending bands δ_s(N–H) of gaseous NH_3 are detected at 964 and 932 cm^{-1} (the 17 mass perturbed by the H_2O presence cannot permit us to observe this NH_3 production). For each pulse, the evolution of the gas products curves (CO_2 and NH_3), reported in Fig. 13, is concomitant with the consumption of isocyanate species. Thus, we can conclude that this experimental result corresponds to the hydrolysis of –NCO groups into NH_3.

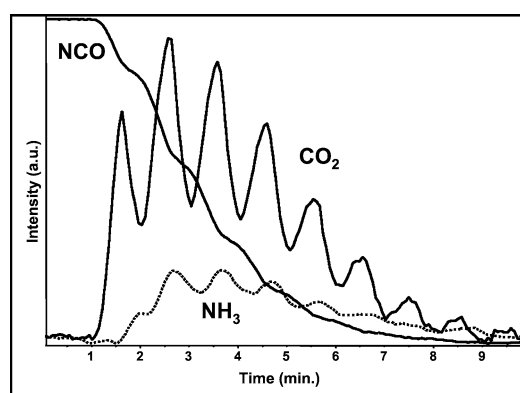Fig. 13. FTIR chemigrams of NCO consumption and of CO_2 and NH_3 gas species produced during the introduction of H_2O pulses on Ag/Al_2O_3 previously treated under CO + NO at 873 K.

4. Discussion and conclusion

First, to draw a mechanism for DeNO$_x$ reaction via isocyanate intermediates, it appears useful to summarize the reactivity experiments reported above. We can establish a classification of the molecules reacting with isocyanate species:

– H_2O is the most reactive molecule because, despite the low amount sent in the injection loop, it is with this molecule that the isocyanates have disappeared the most rapidly. This reaction is a hydrolysis, whose products are NH_3 and CO_2.
– O_2 is also reactive and completely selective into N_2. Nevertheless a large proportion of the oxygen pulses is not consumed. And we can suppose that if isocyanates were very reactive toward O_2, the first pulses would be completely consumed.
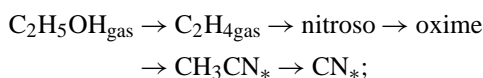– NO alone does not react with isocyanates.

The reactivity of isocyanate species toward oxygen must be minimized in the case of competitiveness with water, as shown by the small amount of oxygen pulses consumed. Moreover, the strong reactivity of isocyanates species toward

water as well as the formation of ammonia is in good agreement with the results obtained during the $C_2H_5OH + NO + O_2$ reaction studied in steady state (Figs. 1, 2, and 4). Indeed, we had noted at the maximum conversion temperatures (623 and 673 K) a decrease of NCO characteristic bands intensities and simultaneously appearance of NH_3 in the gas phase.
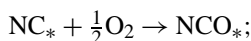
Thus, we think that this reaction way may be privileged rather than the direct reactivity toward O_2, even if the presence of this molecule is necessary to inhibit the NO_x reduction to NH_3.

In Section 3.2 the time-resolved analysis permitted us to hypothesize a NO_x SCR mechanism on silver/alumina catalyst developed in three sequences (the asterisk indicates an adsorption site):
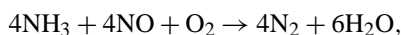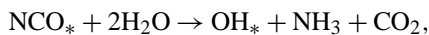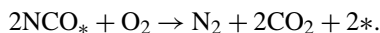
First sequence (hypothetical),

$$C_2H_5OH_{gas} \rightarrow C_2H_{4gas} \rightarrow nitroso \rightarrow oxime$$
$$\rightarrow CH_3CN_* \rightarrow CN_*;$$

Second sequence,

$$CN_* \rightarrow NC_*,$$

$$NC_* + \tfrac{1}{2}O_2 \rightarrow NCO_*;$$

Third sequence,

$$NCO_* + 2H_2O \rightarrow OH_* + NH_3 + CO_2,$$

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O,$$

or alternatively

$$2NCO_* + O_2 \rightarrow N_2 + 2CO_2 + 2*.$$

The experiments on the nature, the localization, and the reactivity of cyanide and isocyanate species have given us complementary information, which allow us to define several steps of the pathway.
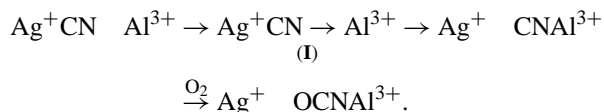
The study undertaken by isotopic substitution experiments on the nature of the species detected during the $C_2H_5OH + NO + O_2$ reaction supports their assignment to cyanides and isocyanates. This study also reveals the probable formation of cyanide and isocyanate species from $NO + CO$ reactions. In particular, the use of $N^{16}O$ and $C^{18}O$ on Ag/Al_2O_3 catalysts showed that NO dissociation would occur at 474 K and CO dissociation at about 673 K. The first intermediate formed would be the adsorbed cyanide species contrary to what was expected (the bond of a CO molecule with an adsorbed nitrogen atom). The cyanide due to the reaction between N and C atoms is probably initially formed on Ag^+. Cyanide species are not directly detected in the $NO + CO$ reaction but the characteristic wavenumbers of these groups have been observed under transitory conditions during ethanol pulses experiments (2155 and 2127 cm^{-1} at 673 K under dynamic conditions) or in the EtNCO decomposition experiments (2165 cm^{-1} at 573 K under static conditions) [19], proving that their evanescence is likely due to their high reactivity. The latter bands (2165 and 2155 cm^{-1}),

visible on Ag/Al_2O_3 catalysts as well as on bare alumina, could be attributed to aluminum cyanide ($Al^{3+}CN$). Thus the 2127 cm^{-1} feature is likely assigned to Ag^+CN. Silver as well as copper can complex from one to four –CN radicals, which present stretches appearing between 2146 cm^{-1} for one radical to 2092 cm^{-1} for four radicals [20].

This conclusion on the formation of cyanide by $CO + NO$ reaction does not disagree with the hypothesis proposed in Section 3.2, because the conditions are completely different: oxidizing conditions in the case of ethanol pulses, and reducing conditions in the $CO + NO$ reaction case. In the SCR of NO_x by ethanol in steady state, the gas phase contains CO from 623 K and the amount of this molecule increases with the temperature. Then, CO and NO being present, we cannot exclude that in a C_2H_5OH molecule decomposition environment the atmosphere could be temporarily and locally reducing and that the cyanide formation by $NO + CO$ reaction might occur.

The study, performed on cyanide and isocyanate localization, shows that if –CN groups are linked to Ag^+ and Al^{3+} ions, –NCO groups are only detected on Al^{3+} ions. The $-CN \rightarrow -NCO$ transformation, which seems to be the slow step of the mechanism, is more complex than expected since we observe Ag^+CN to finally obtain $Al^{3+}NCO$. Therefore two hypotheses can be formulated:

(a) Ag^+CN can isomerize into isocyanide species (Ag^+NC), and can oxidize into silver isocyanate (Ag^+NCO), and then would give $Al^{3+}NCO$ by spillover;

(b) (a more interesting hypothesis that needs less elementary steps) a transformation by intermediate complexation between silver and aluminum ions can take place:

$$Ag^+CN \quad Al^{3+} \rightarrow Ag^+CN \rightarrow Al^{3+} \rightarrow Ag^+ \quad CNAl^{3+}$$
$$\underset{(\mathbf{I})}{}$$

$$\overset{O_2}{\rightarrow} Ag^+ \quad OCNAl^{3+}.$$

This bridged complex (**I**) has already been identified in the case of nickel cyanide linked to BF_3 [31]. Nakamoto [20] explains that the cyanide group $M-C\equiv N$ can be bridged to form $M-C\equiv N-M'$ involving a blue shift of the vibration $\nu(CN)$. For example, this vibration in $K_2[Ni(CN)_4]$ complex absorbs at 2130 cm^{-1} and the band is shifted to 2250 cm^{-1} in $K_2[Ni(CN)_4] \cdot 4BF_3$ due to the complexation $Ni-C\equiv N-BF_3$ [32]. The existence of this bridged species let us consider a reversal of the CN group: a cyanide linked to a silver atom or to an aluminum atom could give an isocyanide linked to a neighboring aluminum ion acceptor of the nitrogen free doublet. The absence of bridged species characteristic vibration bands on our spectra can be explained by their instability (that would involve the reversal as soon as formed) and by the quick oxidation of isocyanide species as described in the Scheme 1. Al^{3+} ions are also, as well as BF_3, strong Lewis acid sites and we can imagine that an unstable bridged complex $Ag^+CN \rightarrow Al^{3+}$ could be formed and provoke a $Ag^+ \rightarrow Al^{3+}$ reversal of the group. In this
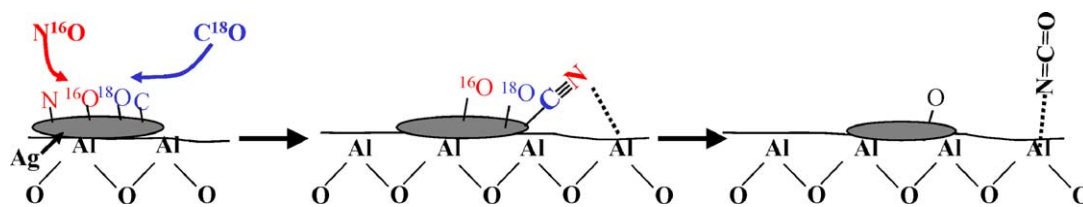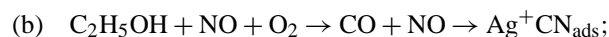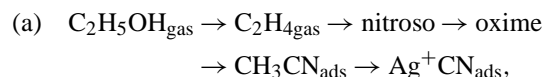
Scheme 1. Proposed formation mechanism of NCO groups in a CO + NO reaction on Ag/Al_2O_3 catalysts.
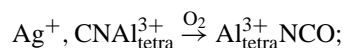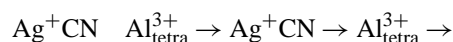
case, the oxidation would happen on the aluminum iso-cyanide. One argument, which matches with this hypothesis is the fact that the formation and the distribution of –NCO groups are different between EtNCO decomposition and CO + NO or $C_2H_5OH + NO + O_2$ reactions; in the first case, the main Al^{3+}NCO band is situated at about 2260 cm^{-1}, whereas in the other cases the most intense Al^{3+}NCO band is at 2230 cm^{-1}. The formation of bridged species can only be possible in the CO + NO and $C_3H_6 + NO + O_2$ reactions where cyanide species are intermediate. To form the bridged complex, the nitrogen atom can choose between two aluminum sites in γ-Al_2O_3. The tetrahedrally coordinated Al^{3+} site (more acidic by Lewis considerations than the octahedrally coordinated Al^{3+} site) is privileged to host the free doublet of nitrogen, which explains the band at 2230 cm^{-1}.

To conclude, all these results allow us to propose the following mechanism for SCR of NO_x by ethanol on silver/alumina catalysts:
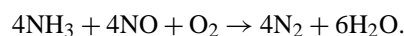
First sequence (2 hypotheses),

(a) $C_2H_5OH_{gas} \rightarrow C_2H_{4gas} \rightarrow$ nitroso $\rightarrow$ oxime
$$\rightarrow CH_3CN_{ads} \rightarrow Ag^+CN_{ads},$$

(b) $C_2H_5OH + NO + O_2 \rightarrow CO + NO \rightarrow Ag^+CN_{ads}$;

Second sequence,

$Ag^+CN \quad Al_{tetra}^{3+} \rightarrow Ag^+CN \rightarrow Al_{tetra}^{3+} \rightarrow$

$Ag^+, CNAl_{tetra}^{3+} \xrightarrow{O_2} Al_{tetra}^{3+}NCO$;

Third sequence,

$Al_{tetra}^{3+}NCO + 2H_2O \rightarrow Al_{tetra}^{3+}-OH + NH_3 + CO_2$,

$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O$.

This mechanism is proposed on Ag/Al_2O_3 catalysts and the reducing agent used is C_2H_5OH. Nevertheless, the results obtained on Ga_2O_3/Al_2O_3 catalysts with propene as reducing agent allow us to consider that the mechanism could be generalized to other alumina-based catalysts and to different hydrocarbons [15]. Indeed, Haneda et al. [15] have shown that in the $C_3H_6 + NO + O_2$ reaction, isocyanate species are formed on Ga_2O_3/Al_2O_3 surfaces. Moreover, on the same catalyst, the $NH_3 + NO + O_2$ reaction has shown that ammonia selectively reduces NO into N_2, in oxygen excess. In this case, gallium will operate as silver does. For these reasons we can hypothesize that the mechanism of NO_x SCR by hydrocarbon on alumina-based catalysts can follow the same steps as those for Ag/Al_2O_3.

References

[1] http://www.rhodia-ec.com/site_ec_us/catalysis/index_automotive.htm.
[2] A. Ueno, H. Suzuki, Y. Kotera, J. Chem. Soc., Faraday Trans. I 79 (1983) 127, and references therein.
[3] Y. Kintaichi, H. Hamada, M. Tabata, M. Sasaki, T. Ito, Catal. Lett. 6 (1990) 239.
[4] Y. Torikai, H. Yahiro, N. Mizuno, M. Iwamoto, Catal. Lett. 9 (1991) 91.
[5] H. Hamada, Y. Kintaichi, M. Sasaki, T. Ito, M. Tabata, Appl. Catal. 75 (1991) L1.
[6] T. Miyadera, Appl. Catal. B 2 (1993) 199.
[7] R. Burch, P.J. Millington, A.P. Walker, Appl. Catal. B 4 (1994) 65.
[8] K.A. Bethke, M.C. Kung, B. Yang, M. Slah, D. Alt, C. Li, H.H. Kung, Catal. Today 26 (1995) 169.
[9] H. Hamada, Y. Kintaichi, M. Inaba, M. Tabata, T. Yoshinari, H. Tsuchida, Catal. Today 29 (1996) 53.
[10] M. Haneda, Y. Kintaichi, H. Shimada, H. Hamada, Chem. Lett. (1998) 181.
[11] T. Maunula, Y. Kintaichi, M. Inaba, M. Haneda, K. Sato, H. Hamada, Appl. Catal. B 15 (1998) 291.
[12] T. Nanba, A. Uemura, A. Ueno, M. Haneda, H. Hamada, N. Kakuta, H. Miura, H. Ohfune, Y. Udagawa, Bull. Chem. Soc. Jpn. 71 (1998) 2331.
[13] K. Takagi, T. Kobayashi, H. Ohkita, T. Mizushima, A. Kakuta, N. Abe, K. Yoshida, Catal. Today 45 (1998) 123.
[14] T. Maunula, Y. Kintaichi, M. Haneda, H. Hamada, Catal. Lett. 61 (1999) 121.
[15] M. Haneda, N. Bion, M. Daturi, J. Saussey, J.-C. Lavalley, D. Duprez, H. Hamada, J. Catal. 206 (2002) 114.
[16] K.A. Bethke, H.H. Kung, J. Catal. 172 (1997) 93.
[17] F. Poignant, PhD thesis, Caen, 1997.
[18] F. Poignant, J.-L. Freysz, M. Daturi, J. Saussey, J.-C. Lavalley, in: A. Corma, F.V. Melo, S. Mendioroz, J.L.G. Fierro (Eds.), 12th International Congress on Catalysis, in: Stud. Surf. Sci. Catal., Vol. 130, Elsevier, 2000, pp. 1487–1492.
[19] N. Bion, J. Saussey, C. Hedouin, T. Seguelong, M. Daturi, Phys. Chem. Chem. Phys. 3 (2001) 4811.
[20] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Wiley–Interscience, New York, 1986.
[21] C. Morterra, G. Magnacca, Catal. Today 27 (1996) 497.
[22] K.I. Hadjiivanov, Catal. Rev.-Sci. Eng. 42 (2000) 71.
[23] J. Raskó, F. Solymosi, J. Chem. Ser. Faraday Trans. 1 76 (1980) 2383.
[24] Y. Ukisu, T. Miyadera, A. Abe, K. Yoshida, Catal. Lett. 39 (1996) 265.
[25] S. Sumiya, A. Abe, N. Takesawa, K. Yoshida, J. Chem. Soc. 94 (1998) 2217.

[26] S. Kameoka, T. Chafik, Y. Ukisu, T. Miyadera, Catal. Lett. 55 (1998) 211.

[27] S. Kameoka, Y. Ukisu, T. Miyadera, Phys. Chem. Chem. Phys. 2 (2000) 367.

[28] F. Solymosi, L. Völgyesi, J. Sárkány, J. Catal. 54 (1978) 336.

[29] F. Solymosi, L. Völgyesi, J. Raskó, Z. Phys. Chem. Neue Folge 120 (1980) 79.

[30] W.C. Hecker, A.T. Bell, J. Catal. 85 (1984) 389.

[31] F. Solymosi, J. Raskó, Appl. Catal. 10 (1984) 19.

[32] D.F. Shriver, J. Am. Chem. Soc. 84 (1962) 4610.