

FTIR spectroscopic study of the nature and reactivity of NO_x compounds formed on Cu/Al₂O₃ after coadsorption of NO and O₂

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Abstract

Copper cations present on alumina surface even in low concentrations (0.75 wt %) are characterized by a high heterogeneity. Thus, two kinds of Cu⁺ sites have monitored by CO adsorption and three kinds of Cu²⁺ cations by NO adsorption. Adsorption of NO also leads to development of bands due to small amounts of nitro/nitrito and nitrato compounds. Introduction of oxygen to the Cu/Al₂O₃–NO system causes initial concentration rise of the NO₂[−] compounds followed by oxidation of these complexes to nitrates. The nitrates thus obtained are stable up to 723 K. Surface copper nitrates begin to react with C₂H₄ at 573 K, as a result of which isocyanate and cyanide species are formed. Simultaneously, oxidation of C₂H₄ on the catalyst surface proceeds, leading ultimately to the appearance of carboxylates. The mechanism of SCR by ethene on Cu/Al₂O₃ has been discussed.

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1. Introduction

Selective catalytic reduction of nitrogen oxides with hydrocarbons (HC-SCR) is of great interest since it permits controlling nitrogen oxide emissions from internal combustion engines [1–4]. One of the most studied catalysts for this process is Cu-ZSM-5 [3–12]. However, zeolites have some disadvantages such as a low hydrothermal stability leading to catalyst deactivation [1,9,13]. This is the reason for developing [13–17] metal oxides-based SCR catalysts, which are more stable. In particular, Cu/Al₂O₃ has demonstrated activity in various reactions of NO_x conversion such as HC-SCR [18] and N₂O decomposition [19]. That is why it is of interest to study the nature and reactivity of the adsorption forms appearing after adsorption of nitrogen oxides on the surface of Cu/Al₂O₃ [20–22]. In the literature, there are different opinions concerning the mechanism of SCR of nitrogen oxides with hydrocarbons. Some authors [11,23] believe that in presence of oxygen the hydrocarbons are partly oxidized forming H_xC_yO_z complexes which subsequently

reduce the nitrogen oxides. Other authors assume that the first stage of the process is oxidation of NO [7,24–29], this leads to the formation of NO₂ [7,29] or nitro and nitrato complexes [24–28]. These surface NO_x compounds react with the hydrocarbons from the gas phase, which results in the formation of the so-called C–H–N–O deposit [26–28]. The decomposition of the latter is associated with formation of intermediate CN[−] and NCO[−] compounds on the surface [26–28,30]. Analysis of the literature data [20,21] concerning the mechanism of selective catalytic reduction of nitrogen oxides with hydrocarbons on Cu/Al₂O₃ shows that the nature of intermediate compounds being formed during the reaction has not yet been well established. The purpose of the present work is to study carefully, by FTIR spectroscopy, the nature of surface compounds formed on the Cu/Al₂O₃ surface during adsorption of NO and coadsorption of NO and O₂ as well as to obtain data on the interaction between the species formed and ethene. In order to achieve more detailed information on the state of the copper ions in the supported phase, the samples were also characterized by thermoprogrammed reduction, X-ray photoelectron spectroscopy and FTIR spectroscopy of adsorbed CO. On the basis of summarized results from these experiments, some new data on the mechanism of selective catalytic reduction of NO_x with ethene over Cu/Al₂O₃ were obtained.

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2. Experimental

2.1. Reagents and materials

Alumina, which was used for the experiments, was a commercially available Degussa product with a specific surface area of $98 \text{ m}^2 \text{ g}^{-1}$.

The $\text{Cu}/\text{Al}_2\text{O}_3$ sample was prepared by impregnating Al_2O_3 with a $0.05 \text{ mL}^{-1} \text{ Cu}^{2+}$ solution. The latter was obtained by dissolving $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in distilled H_2O followed by addition of concentrated NH_3 to attain pH 9. After the synthesis, the sample was calcined in air for 1 h at 673 K. The nominal concentration of copper in the sample was 0.75 wt.%.

2.2. Instrumental methods

2.2.1. FTIR spectroscopy

The FTIR measurements were carried out using a Nicolet Avatar 360 spectrophotometer with a resolution of 2 cm^{-1} and accumulating 128 scans. Self-supporting pellets were obtained by pressing the powdery sample under a pressure of 10^4 kPa . The sample was treated directly in the IR cell connected to a vacuum apparatus with a residual pressure of about 10^{-4} Pa . Prior to the adsorption measurements, the sample was activated by heating for 1 h at 673 K under oxygen and evacuation for 1 h at the same temperature.

2.2.2. TPR–TGA measurements

The TPR–TGA (temperature-programmed reduction–thermogravimetric analysis) experiments were performed with a Setaram TG92 instrument. Fifty milligrams of the sample were placed in a microbalance crucible and heated in a flow of 10 vol.% H_2 in Ar ($50 \text{ cm}^3 \text{ min}^{-1}$) up to 873 K at 10 K/min and a final hold-up of 20 min. Prior to the TPR experiments, the sample was treated in situ in a flow of air up to 673 K at a rate of 10 K/min followed by a hold-up of 2 h.

2.2.3. X-ray photoelectron spectroscopy

The XPS measurements were made on an ESCALAB MkII (VG Scientific) apparatus using a radiation source with a magnesium anode ($h\nu = 1254.6 \text{ eV}$). The binding energy values were corrected with respect to the C1s level (284.8 eV) of the carbon impurities on the surface.

3. Results

3.1. Sample characterization

3.1.1. TPR–TGA measurements

Fig. 1 shows the TPR-pattern of $\text{Cu}/\text{Al}_2\text{O}_3$. The reduction of the copper species proceeds in the interval of 560–870 K. The TPR-profile of the sample is characterized by several redox processes which could be ascribed to the reduction of copper oxide species with different reducibility. The observed results suggest the presence of certain heterogeneity in the state of the copper species. The reduction maximum at 790 K characterizes the presence of isolated copper ions strongly interacting with

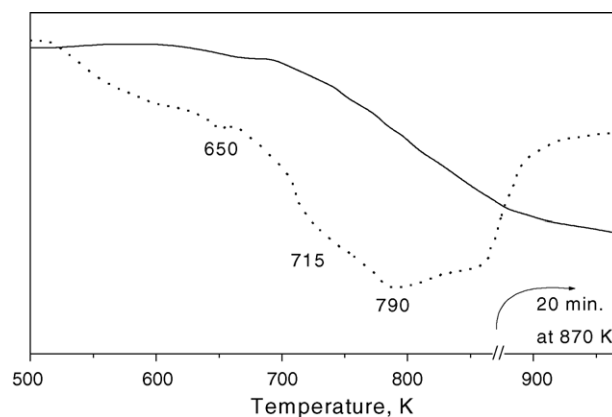


Fig. 1. TPR (dotted line)–TGA (solid line) curves of $\text{Cu}/\text{Al}_2\text{O}_3$ (10% H_2 in Ar with $50 \text{ cm}^3 \text{ min}^{-1}$; heating rate of 10 K/min).

the support while the registered processes at lower temperatures (650 K and about 715 K) could be ascribed to the reduction of more readily reducible copper species [31]. We could not assign the observed shoulder in the DTG profile at about 860 K to an additional redox process because it is most probably due to the change of the dynamic temperature programmed regime into static heating at 870 K.

3.1.2. X-ray photoelectron spectroscopy

In order to obtain information on the initial state of the copper ions on the $\text{Cu}/\text{Al}_2\text{O}_3$ surface, we studied the sample with X-ray photoelectron spectroscopy. The XP spectrum of $\text{Cu}/\text{Al}_2\text{O}_3$ demonstrated the presence of an intense signal ($\text{Cu}2p_{3/2}$) at 935 eV along with one more lower-intensity satellite at 944 eV (Fig. 2). A possible criterion on the basis of which one may estimate whether the signals observed are due to the presence of Cu^+ or Cu^{2+} ions is the ratio between the intensities of the $\text{Cu}2p_{3/2}$ signal and its satellite observed at higher energies [32]. The Cu^{2+} ions are characterized by a clearly visible satellite whose intensity is about twice as low as the intensity of the $\text{Cu}2p_{3/2}$ signal. In contrast to them, the satellite of the $\text{Cu}2p_{3/2}$ signal of the Cu^+ ions is characterized by a negligible intensity. On this basis, we attribute the peaks appearing at 935 and 944 eV to Cu^{2+} ions on the Al_2O_3 surface. More careful analysis of the $\text{Cu}2p_{3/2}$ signal indicates that probably the peaks of several kinds of Cu^{2+} ions

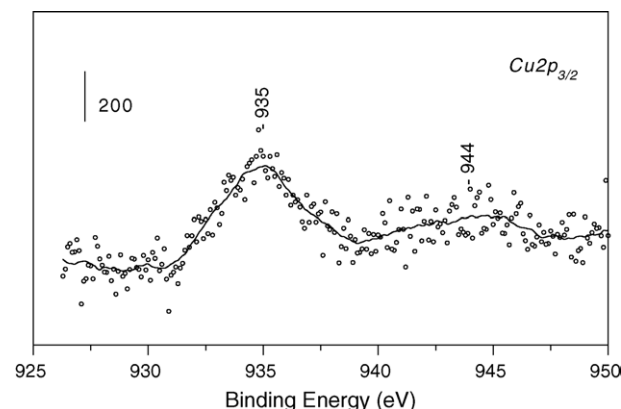


Fig. 2. Photoelectron spectrum of $\text{Cu}/\text{Al}_2\text{O}_3$.

overlap. This is also confirmed by the results from TPR of the sample which again evidence heterogeneity of the copper ions on the Al_2O_3 surface. It should also be noted that due to the width of the two signals the probability for the appearance of peaks produced by Cu^+ ions is not to be excluded.

3.2. FTIR spectroscopic studies

3.2.1. Background spectrum

The IR spectrum of activated Al_2O_3 in the region of O–H stretching modes exhibits four bands with maxima at 3790, 3773, 3734 and 3675 cm^{-1} (spectra not shown) characterizing different OH groups [33–37]. The band at 3733 cm^{-1} is absent from the spectrum of the activated $\text{Cu}/\text{Al}_2\text{O}_3$ sample and the bands at 3790 and 3734 cm^{-1} are much less intense than are those of the support. This is an indication that during the synthesis the copper ions have displaced the protons and have been localized on the oxygen atoms from the hydroxyl groups on the support surface. These observations are in line with the already noted heterogeneity of the copper ions on the sample surface.

3.2.2. Low temperature CO adsorption

To avoid eventual reduction of Cu^{2+} ions by CO, adsorption has at first been carried out at a low temperature. Introduction of CO at 100 K (260 Pa equilibrium pressure) to the activated sample produces four bands with maxima at 2186, 2155, 2120 and 2105 cm^{-1} (Fig. 3, spectrum a). The band at 2155 is assigned to H-bonded CO [38]. Indeed, it changes in concert with a red shift of the initial OH bands to ca. 3570 cm^{-1} (spectra not shown). With the increase of temperature, the remaining bands at 2200–2100 cm^{-1} also display an intensity drop (Fig. 3, spectra b–f). When room temperature is reached, the

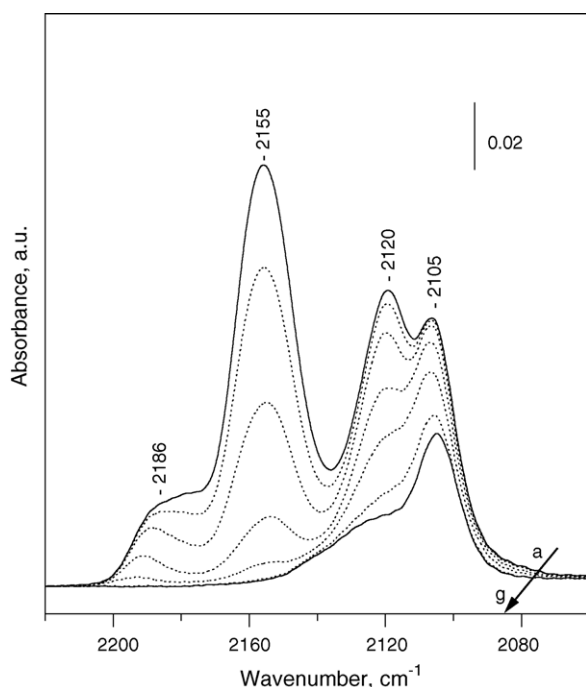


Fig. 3. FTIR spectra of CO adsorbed at 100 K on $\text{Cu}/\text{Al}_2\text{O}_3$. Equilibrium pressure of 670 Pa (a), after gradual heating in presence of CO up to 293 K (b–g).

band at 2186 cm^{-1} vanishes and only the band with a maximum at 2105 cm^{-1} remains along with a low-intensity shoulder at 2120 cm^{-1} (Fig. 3, spectrum g).

The bands at 2120 and 2105 cm^{-1} are assigned to two kinds of $\text{Cu}^+ - \text{CO}$ species [36–38]. In fact, $\text{Cu}^0 - \text{CO}$ species could also be observed at these frequencies, but they are characterized by a very low stability [34,38,39].

The band at 2186 cm^{-1} is characterized by a low stability and disappears from the spectrum at temperatures close to the ambient. This band may be due to both $\text{Al}^{3+} - \text{CO}$ and $\text{Cu}^{2+} - \text{CO}$ carbonyls. The two types of complexes are observed in the same spectral region and are characterized by a low stability, which makes their spectral differentiation difficult. According to the literature [34,38], one might expect partial reduction of the Cu^{2+} ions to Cu^+ in a CO atmosphere. In order to establish the nature of the band at 2186 cm^{-1} , the sample was cooled again under CO. The results obtained (spectra not shown here) evidenced reappearance of the band at 2186 cm^{-1} , this indicating it to be due to $\text{Al}^{3+} - \text{CO}$ carbonyl complexes. A similar band at 2186 cm^{-1} was also observed after CO adsorption on pure Al_2O_3 , which confirmed the above hypothesis. The absence of bands for $\text{Cu}^{2+} - \text{CO}$ carbonyls indicated the activation of the sample to result in autoreduction of the Cu^{2+} ions to Cu^+ . However, it is also probable that the Cu^{2+} ions from the surface to be coordinatively saturated or to possess too low electrophilicity to form carbonyl species.

3.2.3. Adsorption of NO

Adsorption of NO (570 Pa equilibrium pressure) on the sample under investigation leads to the appearance of a series of bands with maxima at 1915, 1895, 1877, 1591, 1467, 1319, 1227 and 1073 cm^{-1} (Fig. 4, spectrum a). The intensity of the bands at 1591, 1467, 1319, 1227 and 1073 cm^{-1} increases with time whereas the bands at 1915, 1895 and 1877 cm^{-1} show almost no change (Fig. 4, spectra b–i).

The bands with maxima at 1467, 1227 and 1073 cm^{-1} can in general be attributed to nitro and/or nitrito compounds while the bands at 1591 and 1319 cm^{-1} are most probably due to surface nitrates [40]. The corresponding ν_1 vibration of the NO_3^- complexes is probably masked by the band at 1073 cm^{-1} .

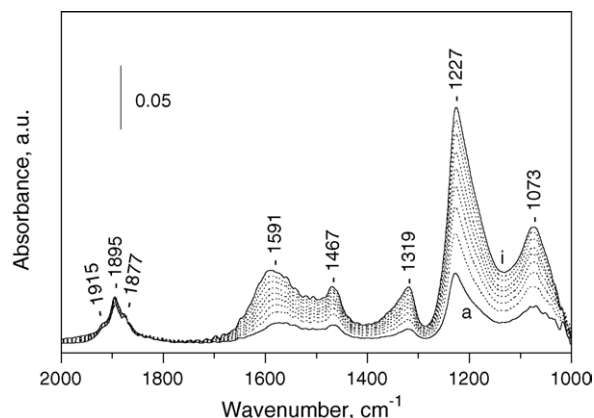


Fig. 4. FTIR spectra of NO (670 Pa equilibrium pressure) adsorbed on $\text{Cu}/\text{Al}_2\text{O}_3$ (a) and development of the spectra with time (b–i).

The bands in the region $1920\text{--}1870\text{ cm}^{-1}$ are typical of nitrosyls [40,42]. It is known that Al^{3+} ions on alumina do not form nitrosyl species [35]. Nitrosyls on alumina are only detected after formation of surface nitrates enhancing the Lewis acidity of adjacent Al^{3+} cation. However, in our case after NO adsorption the sample surface is covered with negligible amounts of anionic nitrogen–oxo compounds due to which it is not likely that the above complexes have modified the surface. In addition, none of the nitrosyl bands change in concert with band(s) characterizing nitro–nitrite compounds. This indicates that the bands in the $1920\text{--}1870\text{ cm}^{-1}$ region are produced by nitrosyls formed with the participation of copper ions from the deposited phase [41–48]. We exclude the probability for them to arise from $\text{Cu}^+\text{--NO}$ species since the latter are observed at lower frequencies ($1820\text{--}1740\text{ cm}^{-1}$) and have been usually registered at low temperatures [47,49]. In addition, it is known that in presence of NO, the Cu^+ ions are oxidized to Cu^{2+} , which should be accompanied by disappearance of the $\text{Cu}^+\text{--NO}$ nitrosyls and appearance of bands produced by $\text{Cu}^{2+}\text{--NO}$ complexes [40,47]. This allows us to conclude that on the surface of the sample under consideration there are three types of Cu^{2+} ions. These results are also supported by the data obtained in the TPR and XPS studies of the sample where again a certain heterogeneity of the Cu^{2+} has been assumed.

3.2.4. Coadsorption of NO and O_2

After the introduction of small amounts of O_2 (133 Pa initial equilibrium pressure) to the cell containing NO (1.3 Pa), the bands in the region $1600\text{--}1000\text{ cm}^{-1}$ increase in intensity (Fig. 5, spectrum b). After a prolonged contact of the sample with the gas mixture, the band at 1550 cm^{-1} splits into three components with maxima at 1630, 1590 and 1565 cm^{-1} (Fig. 5, spectrum f). On reaching maximum intensity, the band at 1227 cm^{-1} begins to decrease in intensity and is converted into a band with a maximum at 1266 cm^{-1} (Fig. 5, spectra c and d). These facts indicate oxidation of the NO_2^- complexes (1227 cm^{-1}) to compounds containing nitrogen of an oxidation degree higher than +3. Simultaneously with the formation of the band at 1266 cm^{-1} , an intensity increase of the 1298 cm^{-1} band

is observed. Similarly to the band at 1227 cm^{-1} , the 1071 cm^{-1} band shows an initial intensity rise up to a maximum value followed by a drop (Fig. 5, spectra a–c). The bands at 1227 and 1071 cm^{-1} have an analogous behaviour, which indicates that they belong to the same compound. Simultaneously, two more bands are distinguished at 1044 and 1014 cm^{-1} and found to develop with time. With increasing amount of introduced oxygen up to 400 and 930 Pa, respectively, the intensities of the bands at 1630, 1590, 1565, 1298, 1266, 1044 and 1014 cm^{-1} also increase (Fig. 5, spectra f–h), a maximum saturation degree of the bands being achieved on introducing 3.3 kPa oxygen (Fig. 5, spectrum i).

In the presence of NO and excess oxygen one can expect formation of nitrates. Due to lowered symmetry, the ν_3 modes of surface nitrates splits into two components: ν_3 and ν_3'' . On this basis and according to literature data [40], we ascribe the bands with maxima at 1630, 1590 and 1565 cm^{-1} to ν_3' vibrations, and those at 1298 and 1266 cm^{-1} , to ν_3'' vibrations of surface nitrates. The average ν_3 frequency is higher than ν_3 of symmetric nitrates (1380 cm^{-1}) which is indicative of the change of the N–O bond order during the coordination of nitrates. The bands with maxima at 1044 and 1014 cm^{-1} are due to the corresponding ν_1 modes [40].

In the $2000\text{--}1800\text{ cm}^{-1}$ region, with the introduction of O_2 the bands at 1915, 1895 and 1877 cm^{-1} display a slight intensity increase (Fig. 5, spectra b–e). With increasing amount of introduced oxygen the bands overlap, as a result of which a broad band with a maximum at 1890 and a shoulder at 1880 cm^{-1} (Fig. 5, spectra h and i) are formed. Bands characterizing the $\nu(\text{N=O})$ vibration of adsorbed N_2O_3 (formed after oxidation of NO) can appear in this region [40]. On this basis and in agreement with literature data [35,40] the bands at 1890 and 1880 cm^{-1} are attributed to the $\nu(\text{N=O})$ vibration of N_2O_3 adsorbed on the surface of the sample investigated.

Additional data facilitating the interpretation of separate bands as due to nitrate or nitro–nitrite compounds can be obtained by analysis of the overtones and the combination modes [35,40]. After the introduction of small oxygen amounts to the system, three low-intensity bands with maxima at 2877, 2629 and 2552 cm^{-1} are formed (Fig. 5, spectrum f). With increasing oxygen amount, the above bands gain somewhat in intensity and two other bands with maxima at 2918 and 2893 cm^{-1} (Fig. 5, spectra h and i) appear. The nature of the complexes which are responsible for these bands will be discussed in what follows.

In the $3900\text{--}3000\text{ cm}^{-1}$ region, three bands characterizing $\nu(\text{O–H})$ vibrations of isolated surface hydroxyl groups of Al_2O_3 (with maxima at 3700, 3770 and 3730 cm^{-1}) decrease in intensity, while a broad band with a maximum at 3543 cm^{-1} and an intensity increasing with time (spectra not shown here) becomes visible. The band at 3543 cm^{-1} characterizes hydrogen-bonded hydroxyl groups and may be due to both interaction of $\text{Al}^{3+}\text{--OH}$ groups with adsorbed compounds and water being evolved during the processes.

3.2.5. Interaction of the surface NO_x compounds with NO

The differentiation between the NO_2^- and NO_3^- complexes on the basis of their spectra is a complex problem. One of

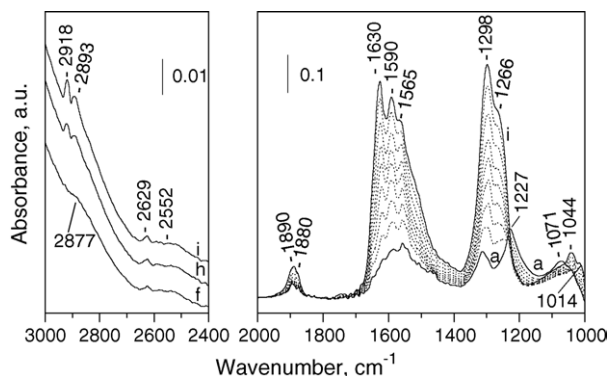


Fig. 5. FTIR spectra of NO (1.3 kPa equilibrium pressure) adsorbed on $\text{Cu}/\text{Al}_2\text{O}_3$ (a), after addition of O_2 (133 Pa initial equilibrium pressure) (b), and development of the spectra with time (c–e), addition of O_2 (400 Pa initial equilibrium pressure) (f and g), addition of O_2 (930 Pa initial equilibrium pressure) (h), addition of O_2 (3.3 kPa initial equilibrium pressure) (i).

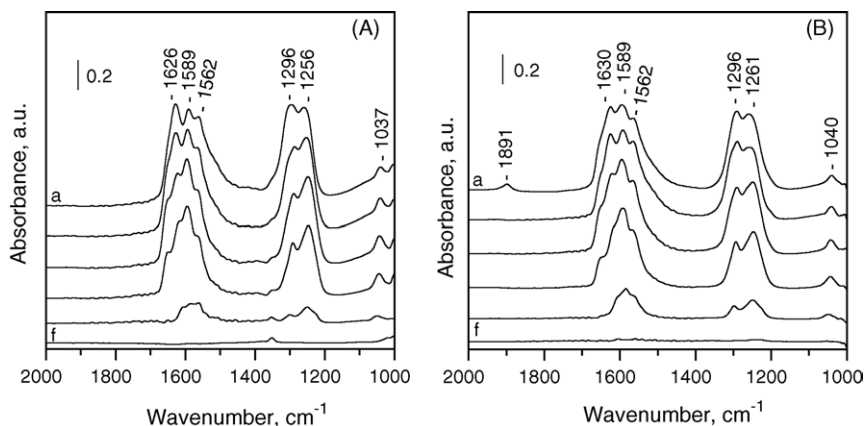
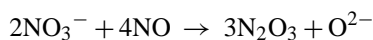


Fig. 6. Stability of the nitrates formed on Al_2O_3 (A) and $\text{Cu}/\text{Al}_2\text{O}_3$ (B). Coadsorption of NO (2 kPa equilibrium pressure) and O_2 (2 kPa initial equilibrium pressure) followed by evacuation for 10 min at room temperature (a), 373 K (b), 473 K (c), 573 K (d), 673 K (e) and 723 K (f).

the methods proposed for that purpose is their interaction with NO [40]. Reactive surface nitrates can be reduced by nitrogen oxide, which lowers the intensity of their characteristic band. In contrast to them, surface compounds in which nitrogen is of oxidation degree +3 do not react with nitrogen oxide [40]. However, it should be noted that nitrates of a low reactivity can show no trend to react with NO either. Adsorption of NO (930 Pa equilibrium pressure) on a sample pre-treated under NO and O_2 causes a slight intensity decrease of the bands at 1630, 1589, 1562, 1296 and 1261 cm^{-1} (spectra not shown here). Simultaneously, the spectrum exhibits a new band at 1891 cm^{-1} . The latter characterizes N_2O_3 which is formed as a result of interaction between the nitrates adsorbed on the sample surface and NO from the gas phase:



The results obtained indicate that (i) the bands with maxima at 1636, 1589, 1562, 1296, 1261 and 1040 cm^{-1} are due to surface nitrates and (ii) the nitrates appearing on the surface are reactive towards nitrogen oxide.

3.2.6. Stability of the NO_x compounds formed

Comparison of the spectra registered with maximum nitrate coverages on Al_2O_3 and $\text{Cu}/\text{Al}_2\text{O}_3$, reveals no special differences. The bands characterizing NO_3^- compounds appear in both cases at analogous frequencies and have the same shape, this indicating that on the $\text{Cu}/\text{Al}_2\text{O}_3$ surface mainly nitrates coordinated to Al^{3+} ions on the support are formed. Eventual copper nitrates are masked by the strong bands due to nitrates formed on alumina. We studied the thermal stability of the nitrates hoping to use it as a criterion for discriminating between copper and aluminum nitrates.

Fig. 6 presents the spectra registered during the study of the thermal stability of surface nitrates on Al_2O_3 (panel A) and $\text{Cu}/\text{Al}_2\text{O}_3$ (panel B). With rising evacuation temperature, the bands of the surface nitrates decrease in intensity, to disappear completely at 723 K (Fig. 6). A more careful analysis of the bands behaviour at $1296\text{--}1256\text{ cm}^{-1}$ shows that after evacuation of $\text{Cu}/\text{Al}_2\text{O}_3$ at 373 K, the band at 1296 cm^{-1} is characterized by

a higher intensity as compared to the same band registered in the spectrum of Al_2O_3 . Hence, it can be assumed that at 1296 cm^{-1} in the spectrum of $\text{Cu}/\text{Al}_2\text{O}_3$ there is overlapping of the bands of bidentate nitrates coordinated to (i) Cu^{2+} ions from the supported phase and (ii) Al^{3+} ions from the support surface. Probably the corresponding ν_3 vibration of the copper nitrates is masked by the intense bands of $\text{Al}^{3+}\text{--}(\text{NO}_3)_x$ complexes.

3.2.7. Adsorption of ethene

In order to identify the nature of the compounds formed during interaction of surface nitrates and ethene, adsorption of C_2H_4 on the clean sample was first studied. Ethene was introduced into the IR cell and, as a result, additional bands due to gaseous C_2H_4 were only seen: at 3125, 3089, 3010 and 2963 cm^{-1} , due to $\nu(\text{C--H})$ stretching modes (Fig. 7, spectrum a). With rising temperature of heat-treatment up to 573 K, a series of bands with maxima at 1593, 1470, 1386 and 1351 cm^{-1} appeared (Fig. 7, spectrum b). After evacuation of the sample at room temperature, the bands at $1600\text{--}1350\text{ cm}^{-1}$ were present in the spectrum, which evidenced them to be due to compounds strongly bound to the surface (Fig. 7, spectrum c). The bands at

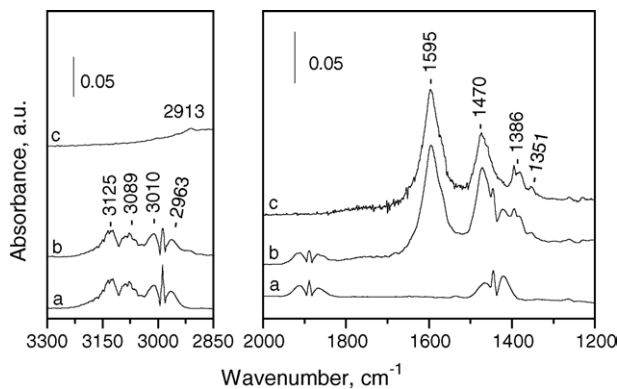


Fig. 7. FTIR spectra of $\text{Cu}/\text{Al}_2\text{O}_3$ after introduction of C_2H_4 (5.3 kPa equilibrium pressure) (a), heating under ethene at 623 K (b) and evacuation at room temperature (c).

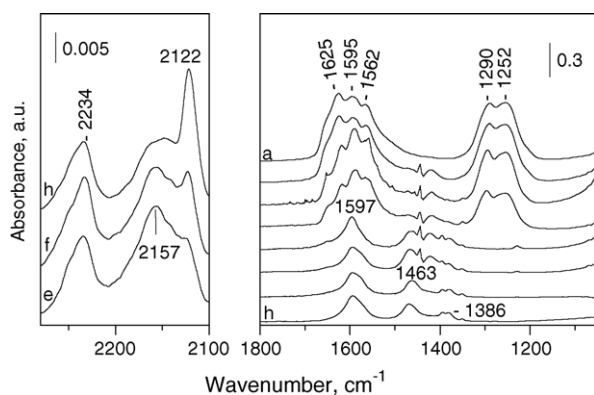


Fig. 8. Interaction of the surface nitrates with ethene: coadsorption of NO (2 kPa equilibrium pressure) and O₂ (2 kPa initial equilibrium pressure) followed by evacuation at room temperature (a), adsorption of ethene (6.7 kPa initial equilibrium pressure) (b), heating under ethene at 423 K (c), 473 K (d), 573 K (e), 623 K (f), evacuation at room temperature (g) and at 573 K (h).

1595 and 1470 cm⁻¹ can be attributed to $\nu_{as}(\text{COO})$ and $\nu_s(\text{COO})$ vibrations of surface carboxylates [21] obtained during ethene oxidation.

3.2.8. Interaction of the NO_x surface compounds with ethene

Coadsorption of NO (2 kPa equilibrium pressure) and O₂ (2 kPa initial equilibrium pressure) on the sample followed by evacuation at room temperature produces a series of bands with maxima at 1625, 1595, 1562, 1290 and 1252 cm⁻¹ due to surface nitrates (Fig. 8, spectrum a). Introduction of ethene into the system causes practically no intensity change of the bands at 1700–1000 cm⁻¹ (Fig. 8, spectrum b). Four low-intensity bands with maxima at 3125, 3089, 3010 and 2963 cm⁻¹ characterizing $\nu(\text{C-H})$ vibrations of ethene in the gas phase appear at 3200–2900 cm⁻¹. To identify possible intermediate compounds appearing during the interaction between the surface nitrates and ethene, we heated the sample at various temperatures in the presence of C₂H₄. With increasing temperature of interaction up to 423 and 473 K, respectively, the bands at 1625, 1595, 1562, 1290 and 1252 cm⁻¹ displayed a slight intensity drop. At 573 K the bands characterizing surface nitrates disappeared, and new bands at 1597, 1463, 1386 and 1351 cm⁻¹ (Fig. 8, spectrum e) became visible. Simultaneously, two bands with maxima at 2234 and 2157 cm⁻¹ as well as a low-intensity shoulder at 2122 cm⁻¹ (Fig. 8, spectrum e) were observed. With temperature rise up to 623 K, the intensity of the 2122 cm⁻¹ band slightly increased while the remaining bands did not change their intensity (Fig. 8, spectrum f). After sample evacuation at 573 K, the 2122 cm⁻¹ band intensity showed a significant increase whereas the band at 2157 cm⁻¹ slightly decreased in intensity (Fig. 8, spectrum g).

The new bands at 1597, 1463, 1386 and 1351 were already registered after ethene adsorption on a sample not covered by nitrates. In contrast to these bands, however, the bands at 2300–2100 cm⁻¹ are new, which indicates they correspond to products of the interaction of the surface nitrates with ethene. These results indicate that ethene interacts preferably with sur-

face nitrates and, only after their consumption, with Cu²⁺ ions on the sample.

3.2.9. Reactivity of nitriles and isocyanates

The bands at 2234, 2157 and 2122 cm⁻¹ however, are absent from the spectra registered after adsorption of ethene alone, which means that they are formed due to the presence of nitrates and probably arise from species containing nitrogen. The band at 2122 cm⁻¹ could be assigned to Cu⁺–CO carbonyls. However, it possesses a much higher stability than do the Cu⁺–CO species. We assign the bands at 2157 and 2122 cm⁻¹ to Cu⁺–CN species [40]. The band at 2234 cm⁻¹ is associated with NCO⁻ species coordinated to Al³⁺ sites [50]. The results show that the bands in the 2250–2100 cm⁻¹ region are stable after evacuation of the sample at 573 K, which indicates a bond strength between the Cu⁺ (Al³⁺) ions and the CN⁻ and NCO⁻ ligands coordinated to them. In order to study the reactivity of the CN⁻ and NCO⁻ complexes, we followed the behaviour of the bands at 2234, 2157 and 2122 cm⁻¹ in presence of NO and NO + O₂, respectively (spectra not shown here). The results showed that the intensities of these bands did not change in a NO atmosphere whereas the introduction of small amounts of oxygen to the Cu/Al₂O₃–NO system led to an intensity drop of the bands followed by their disappearance.

4. Discussion

Since a lot of bands were registered during the experiments, for the sake of facility their interpretation was summarized in Table 1.

4.1. Localization and coordination state of the copper ions on Cu/Al₂O₃

Comparison of the spectra of Al₂O₃ and Cu/Al₂O₃ in the region of $\nu(\text{O-H})$ stretching modes shows a reduced intensity of three of the hydroxyl groups (3790, 3773 and 3734 cm⁻¹) on the copper-containing sample. This indicates that the copper ions form bonds with coordinatively unsaturated oxygen ions by replacing the proton from the corresponding hydroxyl groups of Al₂O₃. In this case, the copper ions will be characterized by different surroundings which may be one of the reasons for their heterogeneity. These results are in agreement with the data from the TPR–TGA characterization of the sample where again three signals due to reduction of three kinds of Cu²⁺ ions to Cu⁰ are observed. The heterogeneity of the copper sites on the Cu/Al₂O₃ surface is also confirmed by the formation of three types of Cu²⁺–NO nitrosyls characterized by bands at 1915, 1893 and 1877 cm⁻¹ after the adsorption of nitrogen oxide on the sample (Fig. 4).

The results on CO adsorption on Cu/Al₂O₃ are rather controversial. Thus, some authors have reported a nitrosyl band around 1876–1873 cm⁻¹ only [43,44]. Fu et al. [41] have observed two bands at 1888 and 1862 cm⁻¹. Similar to our results have been obtained by Lokhov and Davydov [51,52]. The authors have detected the presence of three types of sites on the surface of Cu/Al₂O₃ and have ascribed them to (i) isolated copper ions

Table 1

Assignment of the bands observed after adsorption of CO and NO and after coadsorption of NO + O₂ as well as of on NO + O₂ + C₂H₄ on Cu/Al₂O₃

Band (cm ⁻¹)	Formation conditions	Species	Assignment	Site	Note
Assignment of bands observed after adsorption of CO					
2186	CO	Al ³⁺ -CO	$\nu(\text{C-O})$	Al ³⁺	Low stability
2156	CO	H-bounded CO	$\nu(\text{C-O})$	H ⁺	Low stability
2120	CO	Cu ⁺ -CO	$\nu(\text{C=O})$	Cu ⁺	Decomposes at $T = 373$ K
2105	CO	Cu ⁺ -CO	$\nu(\text{C=O})$	Cu ⁺	Decomposes at $T = 373$ K
Assignment of bands observed after adsorption of NO					
1915	NO	Cu ²⁺ -NO	$\nu(\text{N-O})$	Cu ²⁺	Low intensity
1895	NO	Cu ²⁺ -NO	$\nu(\text{N-O})$	Cu ²⁺	Low intensity
1877	NO	Cu ²⁺ -NO	$\nu(\text{N-O})$	Cu ²⁺	Low intensity
1591	NO	Bidentate nitrates	ν'_3	Al ³⁺ or Cu ²⁺	Increases in intensity in the presence of O ₂
1467	NO	Nitro compounds	$\nu_{\text{as}}(\text{NO}_2)$	Cu ²⁺	Disappears at excess of O ₂
1319	NO	Bidentate nitrates	ν''_3	Al ³⁺ or Cu ²⁺	Increases in intensity in the presence of O ₂
1227	NO	Bridging nitrito compounds	$\nu_s(\text{NO}_2)$	Al ³⁺	Disappears at excess O ₂
1073	NO	Nitro compounds	$\nu_s(\text{NO}_2)$	Cu ²⁺	Disappears at excess O ₂
Assignment of bands observed after coadsorption of NO and O ₂					
2918	NO + O ₂	Bridging or bidentate nitrates	$(\nu'_3 + \nu''_3)$	Cu ²⁺ or Al ³⁺	Also observed with Al ₂ O ₃
2893	NO + O ₂	Bridging or bidentate nitrates	$(\nu'_3 + \nu''_3)$	Cu ²⁺ or Al ³⁺	Also observed with Al ₂ O ₃
2629	NO + O ₂	Bridging nitrates	$(\nu'_3 + \nu_1)$	Cu ²⁺ or Al ³⁺	Also observed with Al ₂ O ₃
2552	NO + O ₂	Bidentate nitrates	$(\nu'_3 + \nu_1)$	Cu ²⁺ or Al ³⁺	Also observed with Al ₂ O ₃
1890	NO + O ₂	N ₂ O ₃	$\nu(\text{N=O})$	Cu ²⁺ or Al ³⁺	Disappears after evacuation
1880	NO + O ₂	N ₂ O ₃	$\nu(\text{N=O})$	Cu ²⁺ or Al ³⁺	Disappears after evacuation
1630	NO + O ₂	Bridging nitrates	ν'_3	Cu ²⁺ or Al ³⁺	Decomposes at $T = 723$ K
1590	NO + O ₂	Bidentate nitrates	ν'_3	Cu ²⁺	Decomposes at $T = 723$ K
1565	NO + O ₂	Monodentate nitrates	ν'_3	Cu ²⁺ or Al ³⁺	Decomposes at $T = 723$ K
1298	NO + O ₂	Bidentate nitrates and N ₂ O ₃	ν''_3 and $\nu_{\text{as}}(\text{NO}_2)$	Cu ²⁺	Decomposes at $T = 723$ K
1266	NO + O ₂	Bridging nitrates	ν''_3	Cu ²⁺ or Al ³⁺	Decomposes at $T = 723$ K
1044	NO + O ₂	Bidentate nitrates	ν_1	Cu ²⁺ or Al ³⁺	Decomposes at $T = 723$ K
1014	NO + O ₂	Bridging nitrates	ν_1	Cu ²⁺ or Al ³⁺	Decomposes at $T = 723$ K
Assignment of bands observed after coadsorption of NO, O ₂ and C ₂ H ₄					
2234	NO + O ₂ + C ₂ H ₄	Al ³⁺ -NCO	$\nu(\text{C-N})$	Al ³⁺	Appears after interaction at 573 K
2157	NO + O ₂ + C ₂ H ₄	Cu ⁺ -CN	$\nu(\text{C-N})$	Cu ⁺	Appears after interaction at 573 K
2122	NO + O ₂ + C ₂ H ₄	Cu ⁺ -CN	$\nu(\text{C-N})$	Cu ⁺	Appears after interaction at 573 K
1597	NO + O ₂ + C ₂ H ₄	Carboxylates	$\nu_{\text{as}}(\text{COO}^-)$	Cu ⁺	High stability
1463	NO + O ₂ + C ₂ H ₄	Carboxylates	$\nu_s(\text{COO}^-)$	Cu ⁺	High stability
1386	NO + O ₂ + C ₂ H ₄	Organic nitro compounds	$\nu_s(\text{NO}_2)$	Cu ²⁺	High stability

(1920 cm⁻¹), (ii) copper ions localized on a segment of the surface characterized by a CuAl₂O₄ spinel structure (1900 cm⁻¹) and (iii) CuO clusters (1875 cm⁻¹). However, adsorption of NO on a CuAl₂O₄ sample has revealed appearance of a band at 1876 cm⁻¹ only [45]. Based on this observation, we assign the band at 1877 cm⁻¹ (observed by us) to NO attached to copper ions from a CuAl₂O₄ phase. The bands at 1915 and 1895 cm⁻¹ are assigned to NO adsorbed on two kinds of isolated Cu²⁺ sites, respectively. Indeed, similar frequencies are typical of NO adsorbed on isolated Cu²⁺ cations in zeolites [40,47,48].

It is well known that, while NO is selectively adsorbed on the Cu²⁺ sites, the Cu⁺ sites form a strong bond with CO [41]. In addition, the Cu²⁺ ions are partially reduced to Cu⁺ in the presence of CO. Our results indicate that the Cu⁺ ions thus formed can coordinate one CO molecule only, as a result of which the corresponding linear Cu⁺-CO carbonyls (2120 and 2105 cm⁻¹) appear. Analysis of the literature data [34,38] shows that the Cu⁺ ions situated on other supports are characterized by a lower coordination number as compared to the copper ions of Cu/Al₂O₃. Thus, Zecchina et al. [53] have found that the Cu⁺ ions of Cu-ZSM-5 can coordinate three CO molecules at

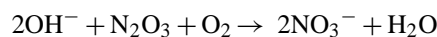
low temperatures, which results in the corresponding Cu⁺(CO)₃ complexes. Similar results have also been observed with other copper-containing zeolites such as Cu-Y [54], Cu-MOR [55] etc. In contrast to them, the Cu⁺ ions on the surface of some oxides possess one less coordination vacancy, which is an indication that they are coordinated to more oxygen atoms from the support surface [56,57]. Recently Scarano et al. [56] suggested that the Cu⁺ ions in Cu/SiO₂ can coordinate two CO molecules at low temperatures, which shows them to possess two effective coordination vacancies. Studying low-temperature CO adsorption on Cu/TiO₂ we have also established formation of Cu⁺(CO)₂ dicarbonyls, which evidences that the copper ions in this sample are also characterized by two coordinative vacancies [57]. In contrast to Cu/SiO₂ and Cu/TiO₂, the Cu⁺ ions on the surface of Cu/Al₂O₃ can coordinate only one CO molecule. This evidences a low coordinative unsaturation of Cu⁺ on alumina.

4.2. Formation of surface nitrates

Nitrogen oxide adsorption on Cu/Al₂O₃ leads to the formation of negligible amounts of nitro and/or nitrito surface

compounds (1467, 1319, 1227 and 1073 cm^{-1}), nitrate compounds (1591 cm^{-1}) and Cu^{2+} -NO nitrosyls characterized by bands at 1920–1875 cm^{-1} (Fig. 4). The introduction of small amounts of oxygen to the $\text{Cu}/\text{Al}_2\text{O}_3$ -NO system results in an initial increase in concentration of the nitro/nitrito and nitrate surface compounds, the bands at 1591, 1467, 1319, 1227 and 1073 cm^{-1} increasing in intensity (Fig. 5, spectra b,c). With rising oxygen amount, the NO_2^- compounds are oxidized to nitrates which are identified by bands at 1636, 1590, 1565, 1298, 1266, 1044 and 1014 cm^{-1} (Fig. 5). For the sake of facility, in the discussion of these bands we will denote by ν_3' the band characterizing the nitrates in the 1650–1550 cm^{-1} region, while ν_3'' will be used for the band of nitrates in the 1300–1250 cm^{-1} region. The two bands (ν_3' and ν_3'') are due to splitting of the ν_3 vibration of the free nitrate ion as a result of a decrease of its symmetry during its coordination to surface cations [40]. Depending on the way of coordination of the nitrate ion to the active sites, the nitrates can be classified as bridged, bidentate and monodentate [40]. On this basis and in agreement with previous studies [35], we attributed the bands at 1630 and 1266 cm^{-1} to bridged, and those at 1590 and 1298 cm^{-1} , to bidentate nitrates. The band at 1565 cm^{-1} characterizes the ν_3' vibration of monodentate nitrates, the corresponding ν_3'' probably overlapping with the bands at 1298 and 1266 cm^{-1} . The three types of surface nitrates are characterized by bands at 1045–1014 cm^{-1} due to ν_1 modes [35,40]. With a view to a more precise interpretation of the nature of NO_3^- compounds, some authors proposed using the analysis of the bands at 3000–2400 cm^{-1} where overtones or combination frequencies of the anionic nitrogen-oxo compounds may appear [36]. In a previous work [35], on the coadsorption of nitrogen oxide and oxygen upon Al_2O_3 we observed bands with maxima at 2918, 2893, 2624 and 2546 cm^{-1} and ascribed them to combination frequencies of nitrates coordinated to Al^{3+} sites. On this basis and in agreement with literature data [58,59], the bands at 2624 cm^{-1} observed in the present paper can be defined as combination frequencies ($\nu_3' + \nu_1$) of bridged and bidentate nitrates, respectively, while the bands at 2918 and 2893 cm^{-1} probably correspond to the ($\nu_3' + \nu_3''$) vibrations of bridged or bidentate nitrates.

The possibility of formation of surface nitrates during coadsorption of NO and O_2 are three: (i) oxidation of a surface cation; (ii) disproportionation of N_2O_4 or (iii) displacement of another anion, usually a hydroxyl group. Our results permit rejecting the first possibility because even in a NO atmosphere the Cu^+ cations are oxidized to Cu^{2+} . Analysis of the spectra in the region of O–H stretching modes permits the assumption that the major part of the nitrates are formed after interaction with the surface hydroxyl groups, e.g.



The water formed is registered by a broad band in the region of O–H stretching modes and a $\delta(\text{H}_2\text{O})$ band overlapping with the ν_3' vibration of the nitrates. The nitrates formed in this way on the sample surface are decomposed at 723 K (Fig. 6).

4.3. Interaction of the surface nitrates with ethene

Investigations of ethene adsorption on $\text{Cu}/\text{Al}_2\text{O}_3$ show that C_2H_4 is adsorbed very weakly on the sample surface. With rising temperature, however, the spectra display new bands due to $\nu_{\text{as}}(\text{COO})$ and $\nu_{\text{s}}(\text{COO})$ vibrations, respectively, of carboxylates, this indicating ethene oxidation by the Cu^{2+} cations on the surface of $\text{Cu}/\text{Al}_2\text{O}_3$. However, in contrast to the case of ethene, the surface nitrates are tightly bonded to the active sites of the surface and are stable up to 723 K (Fig. 6). On this basis, it may be assumed that under $\text{NO} + \text{O}_2 + \text{C}_2\text{H}_4$ at first nitrates appear on the sample surface and, under suitable conditions, they would interact with the ethene from the gas phase producing nitriles and isocyanate species.

The CN and NCO species are considered as important SCR intermediates. It is generally believed that these species are produced after decomposition of the so-called H–N–C–O deposit formed during the interaction of surface nitrates with hydrocarbons. In our case, we have detected no H–C–N–O deposit, which indicates that it is very easily decomposed on the surface of $\text{Cu}/\text{Al}_2\text{O}_3$. Studying the mechanism of SCR of nitrogen oxides with C_2H_6 and $\text{C}_2\text{H}_5\text{OH}$ over Cu/ZrO_2 , Li et al. [30] observed the appearance of two bands with maxima at 2190 and 2140 cm^{-1} . Using isotope exchange, the authors proved these bands to be due to NCO^- and CN^- compounds, respectively. Similar results were obtained by Shimizu et al. [21] who observed a band at 2150 cm^{-1} and ascribed it to CN^- complexes.

These results confirm the opinion existing in the literature [26–28,30] about CN^- and NCO^- as intermediate compounds appearing after interaction of the surface nitrates with ethene and decomposing to the final reaction products in a NO_2 atmosphere.

5. Conclusions

- Copper cations on a $\text{Cu}/\text{Al}_2\text{O}_3$ sample prepared by impregnation with $\text{Cu}(\text{NH}_3)_x(\text{NO}_3)_2$ solution are heterogeneous. At least some of them have exchanged protons from the original Al–OH groups. Evidences of isolated cations and cations from a CuAl_2O_4 phase are found.
- Adsorption of NO on $\text{Cu}/\text{Al}_2\text{O}_3$ leads to formation of small amounts of NO_2^- surface compounds which are oxidized to nitrates in the presence of oxygen. The surface nitrates thus obtained are characterized by a high stability and decompose after evacuation of the sample at 723 K.
- During reduction of the nitrogen oxides with ethene over $\text{Cu}/\text{Al}_2\text{O}_3$, NCO^- and CN^- complexes are formed as intermediate compounds, while the deeper reduction of the support results in carboxylates. The nitriles and isocyanate complexes are inert with respect to NO but readily interact with a $\text{NO} + \text{O}_2$ mixture.

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