



FT-IR spectroscopic investigation of the reactivity of NO_x species adsorbed on Cu²⁺/ZrO₂ and CuSO₄/ZrO₂ catalysts toward decane

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Abstract

The nature of the NO_x species produced on NO adsorption and its co-adsorption with O₂ at room temperature on zirconia-supported copper(II) catalysts has been studied by means of in situ FT-IR spectroscopy. The samples were prepared by impregnation of zirconia with aqueous solutions of copper(II) nitrate and sulfate. The structural identification of the surface NO_x complexes exhibiting absorptions in the fundamental nitro–nitrate region was performed by analyzing the combination bands of the nitrate species. In order to understand which factors control the selectivity of the catalysts in the catalytic reduction of NO by longer chain hydrocarbons, the stability of surface nitro–nitrate species and their reactivity toward adsorbed decane at various temperatures was investigated. The nitrates on the CuSO₄/ZrO₂ catalyst are characterized by significantly lower thermal stability than the nitro–nitrate species on the Cu²⁺/ZrO₂ sample. The difference in the thermal stability of the NO_x[−] species (x is 2 and 3) parallels their reactivity toward the adsorbed decane. The sulfate-free catalyst contains bidentate nitro species that are inert toward the hydrocarbon. The bidentate nitro species start to decompose to NO at temperatures higher than 523 K. In contrast, the nitrate species formed on the CuSO₄/ZrO₂ catalyst are able to oxidize the adsorbed decane completely at 523 K producing acetates, formates, adsorbed CO and isocyanate species. It is proposed that the presence of stable nitro species on the sulfate-free copper(II)-zirconia catalyst is associated with its non-selective behavior above 573 K in the reduction of NO with decane in an excess of oxygen reported in the literature.

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1. Introduction

Recent reports have shown that oxide catalysts based on copper-supported on zirconia or sulfated zirconia are promising in the selective catalytic reduction of NO_x with hydrocarbons (CH-SCR) and ammonia in an excess of oxygen [1–10]. In addition, zirconia-supported copper oxide catalysts possess very high activity for NO reduction with CO at low tempera-

tures [11–17] and comparable catalytic behavior with Cu-ZSM5 in the decomposition of N₂O [18–20].

The results of the structural investigations combined with the performance of the CuO/ZrO₂ catalysts show that isolated copper ions or small 3D clusters are the active sites for the reactions of N₂O decomposition [18–20], reduction of NO by CO [16,17] and SCR of NO with hydrocarbons [1–3,5–7,9,21] or ammonia [10,21].

The performance of the CuO/ZrO₂ catalysts in the SCR of NO with propene is comparable to that of Cu-ZSM5 [1,2,7]. This catalytic system has a lower

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activity when propane is used as the reducing agent [1,2]. However, in the presence of silver-promoted CuO supported on mesoporous cubic zirconia (stabilized by BaO), a high level of NO conversion has been observed with both short- and long-chain saturated hydrocarbons [9]. This oxide system approaches the performance of the zirconia-based copper catalyst containing sulfate ions in an amount corresponding to monolayer coverage. The latter material exhibits high activity and 100% selectivity in the reduction of NO with decane up to 773 K [4–6]. In contrast, sulfate-free CuO/ZrO₂ catalysts are active and selective at lower temperatures (up to 600 K), but oxidize NO to NO₂ at higher temperatures [4–6]. The observed dependence of selectivity on the temperature suggests that SCR on a CuO/ZrO₂-SO₄²⁻ catalyst with decane follows a bi-functional mechanism: in the low-temperature range the rate-determining step is controlled by the copper, whereas, above 600 K the rate-determining step is an acid-catalyzed reaction [5,6].

In order to understand which factors control the selectivity of the catalysts in the CH-SCR of NO on a molecular level, it is necessary to characterize the surface intermediates and to study the elementary steps they follow. The results of TPD of adsorbed NO_x species [22,23] and the IR data on the mechanism of SCR of NO by hydrocarbons on various oxide catalysts [24–31] reveal a reaction scheme that involves interaction of strongly adsorbed NO_x⁻ species (x is 2 or 3) with the hydrocarbon. However, only a few studies using in situ FT-IR spectroscopy have appeared on the identification of surface NO_x species produced during the adsorption of NO on copper(II)-zirconia catalysts, whereas, many reports have been published dealing, for example, with copper-supported on zeolites and alumina [31]. Delahay et al. [32] studied the adsorption of NO on CuO/ZrO₂ catalysts. At room temperature, they observed formation of mononitrosyls coordinated to copper(II) ions and nitrate and nitrito species. The nitrito species transform into nitrates during high-temperature desorption. The sulfatation of zirconia suppresses the formation of nitrito and nitrate complexes and leads to stabilization of copper(II) mononitrosyls [10,32]. Formation of Cu⁺-NO species has been reported on sulfate-modified samples with high copper content [10]. To the best of our knowledge, no IR data on co-adsorption of NO and O₂ on copper(II)-zirconia catalysts are available [31].

The aim of this study is to identify the surface complexes formed on CuO/ZrO₂ and CuSO₄/ZrO₂ catalysts upon NO adsorption and its co-adsorption with oxygen by means of FT-IR spectroscopy and to investigate the stability and chemical reactivity of the adsorbed NO_x species toward decane.

2. Experimental

2.1. Sample preparation

The zirconia support was prepared by hydrolysis of ZrCl₄ (Merck, for synthesis) with a concentrated (25%) solution of ammonia according to a procedure described earlier [33]. After drying the precipitate was calcined for 4 h at 773 K. The BET surface area was 69 m² g⁻¹ and according to XRD, the substance was predominantly monoclinic (94%).

The impregnated Cu²⁺/ZrO₂ catalyst was obtained by grinding ZrO₂ (5 g) with Cu(NO₃)₂·3H₂O (nominal content of copper 2.5 wt.%). Addition of deionized water (maximum 5 ml) yielded a dense suspension, which was dried at 393 K, calcined for 2 h at 573 K and then for 1 h at 673 K. This material is denoted by CuZ and it contained 85% monoclinic and 15% tetragonal phases. The BET surface area was 75 m² g⁻¹.

The impregnated CuSO₄/ZrO₂ catalyst was synthesized in a similar fashion as to the catalyst CuZ keeping the same nominal content of copper (2.5 wt.%), but using CuSO₄·5H₂O instead the nitrate salt. The content of sulfate ions was 3.8 wt.% corresponding to 3.6 SO₄²⁻ nm⁻², i.e. close to the theoretical monolayer of 4 SO₄²⁻ nm⁻² [34]. According to XRD, the phase composition of the substance was a mixture of monoclinic (68%) and tetragonal (32%) structures. The BET surface area was 73 m² g⁻¹. This material is denoted by CuZS.

2.2. Experimental methods

The BET surface areas of the samples (dehydrated at 523 K) were measured by nitrogen adsorption at 77 K using a MONOSORP apparatus from Quantochrome. XRD analysis was performed on a Rigaku Miniflex diffractometer with Ni-filtered Cu K α radiation under ambient conditions. The crystallographic phase

composition was calculated using the method of Toraya et al. [35].

The FT-IR spectra were recorded on a Bomem MB 102 FT-IR (Hartman and Braun) equipped with a liquid-nitrogen cooled MCT detector at a resolution of 4 cm^{-1} (128 scans). A specially designed IR cell allowed recording of the spectra at ambient temperature and catalyst activation at higher temperatures. The cell was connected to a vacuum/adsorption apparatus. Self-supporting discs (0.046 g cm^{-2}) were used for the FT-IR studies. These specimens were activated by heating for 1 h in vacuum at 673 K and in oxygen (13.3 kPa, passed through a trap cooled in liquid nitrogen) at the same temperature followed by evacuation for 1 h at room temperature. The spectra of the activated samples (taken at ambient temperature) were used as a background reference. The spectra of the samples that had been subjected to elevated temperatures were recorded after the IR cell had been cooled to room temperature. All of the spectra presented (except those as shown in Fig. 1) were obtained by subtraction of the corresponding background reference. The purity of NO gas was 99.9% (air products).

3. Results and discussion

3.1. FT-IR spectra of the activated samples

Fig. 1 shows the FT-IR spectra of the catalysts CuZ and CuZS together with the spectrum of pure zirconia. The spectrum of the support in the OH-stretching region displays a weak band at 3744 cm^{-1} , a sharp, strong band at 3650 cm^{-1} , and a broad absorption with maximum at 3475 cm^{-1} . According to the literature data [36–38] the former two bands are assigned to terminal (3744 cm^{-1}) and bridged (3650 cm^{-1}) OH groups coordinated to three Zr atoms. The broad band centered at 3475 cm^{-1} is attributed to H-bonded tribridged hydroxyls [33].

The impregnation of zirconia with a concentrated solution of copper(II) sulfate (catalyst CuZS) results in disappearance of the terminal $\text{Zr}^{4+}\text{-OH}$ groups. This accounts for their participation in the deposition process. In addition, the copper-containing samples are characterized by an absorption in the $3500\text{--}3300\text{ cm}^{-1}$ region (better resolved in the case of the CuZS sample), which can be attributed to

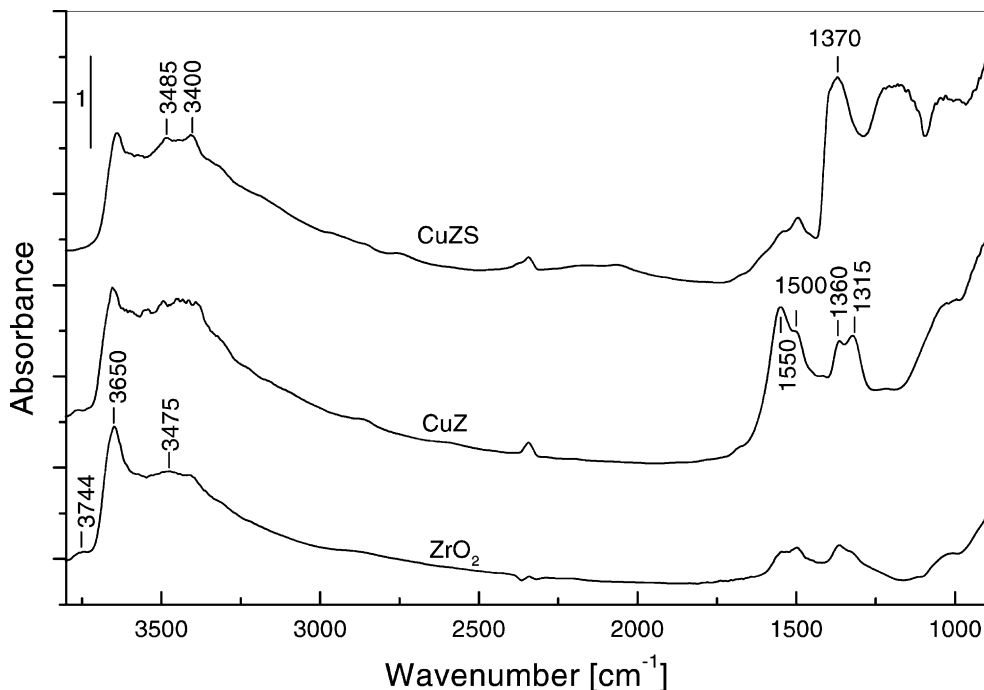


Fig. 1. FT-IR spectra of the activated catalysts and zirconia support.

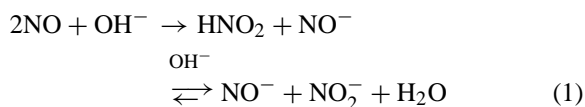
Cu^{2+} -OH groups. The band at 1370 cm^{-1} observed on the sulfated sample corresponds to the $\nu(\text{S}=\text{O})$ vibration of highly covalent sulfates coordinated to Zr^{4+} ions, whereas, the poorly resolved absorption between 1100 and 950 cm^{-1} is assigned to the $\nu(\text{S}-\text{O})$ vibrations [39,40]. The broad absorption between 1250 and 1100 cm^{-1} (absent in the spectrum of sulfated zirconia [33]) reveals the presence of sulfate ions attached to copper sites [40].

The bands in the 1600 – 1300 cm^{-1} region, detected with variable intensities for all of the samples studied, are assigned to split ν_3 modes of surface carbonates. Such residual species are often observed on zirconia and copper oxide surfaces and cannot be removed by high-temperature activation of the catalyst [19].

3.2. Adsorption of NO on CuZ catalyst

The spectra of adsorbed NO (0.67 kPa) at room temperature taken after 40 min of contact with the activated CuZ sample are as shown in Fig. 2. Under equilibrium pressure of NO, a strong band

at 1878 cm^{-1} is observed which is attributed to Cu^{2+} -NO species [32]. Bands of moderate intensity at 2280 , 2244 and 1180 cm^{-1} with a shoulder at approximately 1220 cm^{-1} are detected as well. In the 1700 – 1300 cm^{-1} region a series of weak bands appears. The majority of these bands have been observed upon NO adsorption on pure zirconia [33]. The bands at 2280 , 2244 and the shoulder at 1220 cm^{-1} are assigned to N_2O [41] probably adsorbed on two different surface sites. The absorption at 1180 cm^{-1} is due to anionic nitrosyl, NO^- , which is produced by disproportionation of NO with the participation of the surface hydroxyls according to the equation [33]:



Indeed, a negative band at 3637 cm^{-1} and positive absorption in the region of the H-bonded OH groups are detected. The other products of reaction (1) are identified as follows: *cis*- HNO_2 (1670 cm^{-1} , $\nu(\text{N}=\text{O})$),

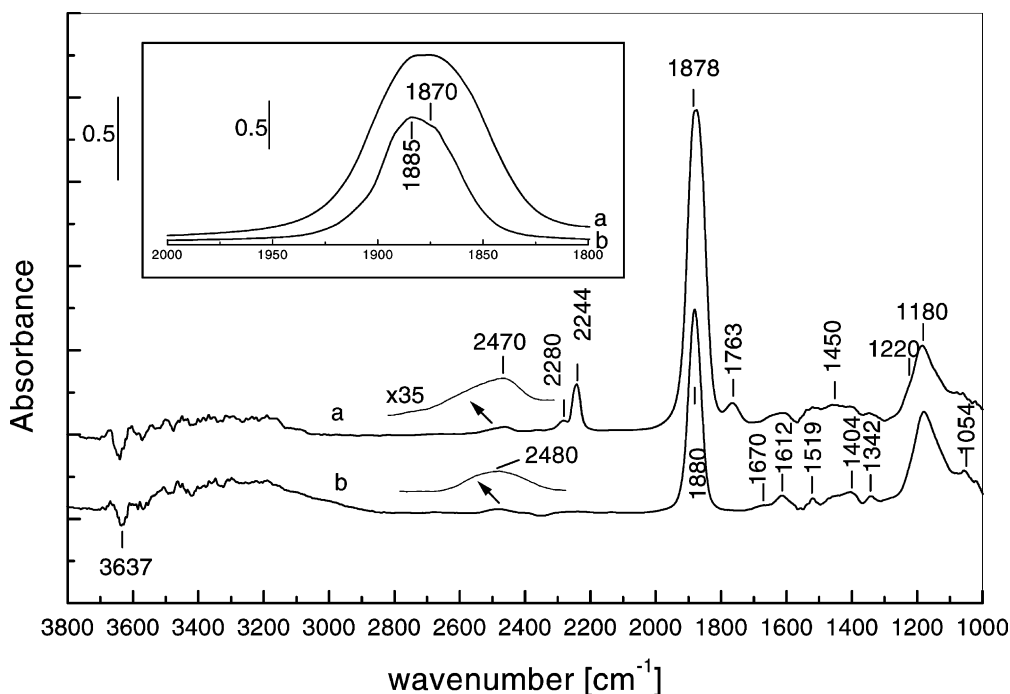


Fig. 2. FT-IR spectra of NO (0.67 kPa) adsorbed at room temperature for a period of 40 min on the sample CuZ (a) and after evacuation at room temperature for 10 min (b). The spectrum of the activated sample is used as a background reference.

H₂O (1612 cm⁻¹, δ (H₂O)), chelated nitro (1519 cm⁻¹, $\nu_{\text{as}}(\text{NO}_2)$) and 1342 cm⁻¹, $\nu_{\text{s}}(\text{NO}_2)$) and nitrito (1450, 1404 cm⁻¹, $\nu(\text{N}=\text{O})$) and 1054 cm⁻¹, $\nu(\text{NO})$) species [31,33,42].

Evacuation at room temperature for 10 min causes an approximately two-fold decrease in the intensity of the band due to Cu²⁺-NO. The inset in Fig. 2 shows that this band has a shoulder at about 1870 cm⁻¹, which indicates the existence of a second Cu²⁺-NO species. The weak absorption at 1763 cm⁻¹, which disappears after evacuation, is assigned to Cu⁺-NO mononitrosyl [43]. Probably, the Cu⁺ sites are produced during the first step of activation of the sample consisting of evacuation at 673 K. This reduction process has been found to occur with samples containing hydrated Cu²⁺ ions during dynamic evacuation at temperatures higher than 473 K [43,44]. According to Centi et al. [20], the Cu⁺ species formed on zirconia are stable and are not readily re-oxidized during the second step of the activation procedure by heating the sample in oxygen at 673 K. Bordiga et al. [43] observed Cu⁺-NO nitrosyls that are stable at room temperature. These species are formed on Cu₂O nanoparticles dispersed on Cu-ETS10 and silica. An alternative assignment of the absorption at 1763 cm⁻¹ is to adsorbed N₂O₄ [31]. However, this possibility should be ruled out because this species is observed usually upon NO and O₂ co-adsorption or during adsorption of NO₂.

The presence of exposed coordinatively unsaturated (cus) Zr⁴⁺ ions could be detected by the appearance of a band at 1912 cm⁻¹ due to formation of Zr⁴⁺-NO species [33]. However, no such absorption has been observed on the CuZ sample. This indicates that the Cu²⁺-O²⁻ fragments are located in the vicinity of the cus Zr⁴⁺ sites and complete their coordination sphere. Finally, the weak absorption with a maximum at about 2470–2480 cm⁻¹ should be mentioned. At the equilibrium pressure of NO, the shape of this band is asymmetric, with a maximum at 2470 cm⁻¹ and a shoulder at about 2480 cm⁻¹ (Fig. 2, spectrum a). After evacuation at room temperature (spectrum b) the absorption at 2470 cm⁻¹ disappears together with the bands due to adsorbed N₂O and only the band at 2480 cm⁻¹ is observed. According to the literature data [45], the band at 2470 cm⁻¹ is assigned to the first overtone of the $\nu(\text{NO})$ mode of N₂O. The latter appears in the spectrum as a shoulder at about 1220 cm⁻¹ of the band at

1180 cm⁻¹. The absorption at 2480 cm⁻¹ is attributed to combination between the $\nu(\text{NO})$ mode of the anionic nitrosyl at 1180 cm⁻¹ and the band at 1342 cm⁻¹ due to the $\nu_{\text{s}}(\text{NO}_2)$ mode of the nitro species.

3.3. Co-adsorption of NO and O₂ on CuZ catalyst

Fig. 3 shows the FT-IR spectra obtained as a function of time during the room-temperature adsorption of a gas mixture containing 1.07 kPa of NO and 4.26 kPa of O₂ on the CuZ sample. The sharp bands at 1896 and 1865 cm⁻¹ fall in the nitrosyl region and can be attributed to two types of Cu²⁺-NO species. The position of the former band (compared to that of the high-frequency nitrosyl observed upon NO adsorption only (Fig. 2)) is blue shifted by approximately 20 cm⁻¹. This shift probably is due to an induction effect from the NO_x species formed in the presence of oxygen. The position of the low-frequency nitrosyl does not change. However, the intensity of this band decreases with time, which indicates conversion of the corresponding Cu²⁺-NO species to other NO_x adsorption forms. Early in the process of NO/O₂ co-adsorption (spectra 0'–15'), the bands in the 1300–1000 cm⁻¹ region display a considerable growth. This spectral region is typical of NO_x species containing nitrogen in lower oxidation state, e.g. NO⁻ and NO₂⁻ [31,33,42]. Indeed, the broad and unresolved absorption in the 1300–1050 cm⁻¹ region (detected immediately after the introduction of the gases into the IR cell (spectrum 0') corresponds to overlapping bands that belong to the anionic nitrosyl at 1178 cm⁻¹ ($\nu(\text{NO})$) [33] and most probably to chelated nitrito species at about 1200 ($\nu_{\text{as}}(\text{NO}_2)$) and 1120 cm⁻¹ ($\nu_{\text{s}}(\text{NO}_2)$) [31,42]. The appearance of the anionic nitrosyl implies that a process analogous to that described by reaction (1) takes place leading to the formation of water molecules (band at 1612 cm⁻¹), NO₂⁻ (nitro, with bands at 1510 and 1337 cm⁻¹), and nitrito species.

The weak band at 2480 cm⁻¹ observed upon NO adsorption appears also during the NO/O₂ co-adsorption.

Keeping the CuZ sample in the NO/O₂ atmosphere for a longer time (30–40 min) results in the appearance of strong absorption in the 1650–1400 cm⁻¹ region (Fig. 3, spectra 30' and 40'). At the same time, a series of weak bands between 2900 and 2000 cm⁻¹ region is detected. The former bands are typical of

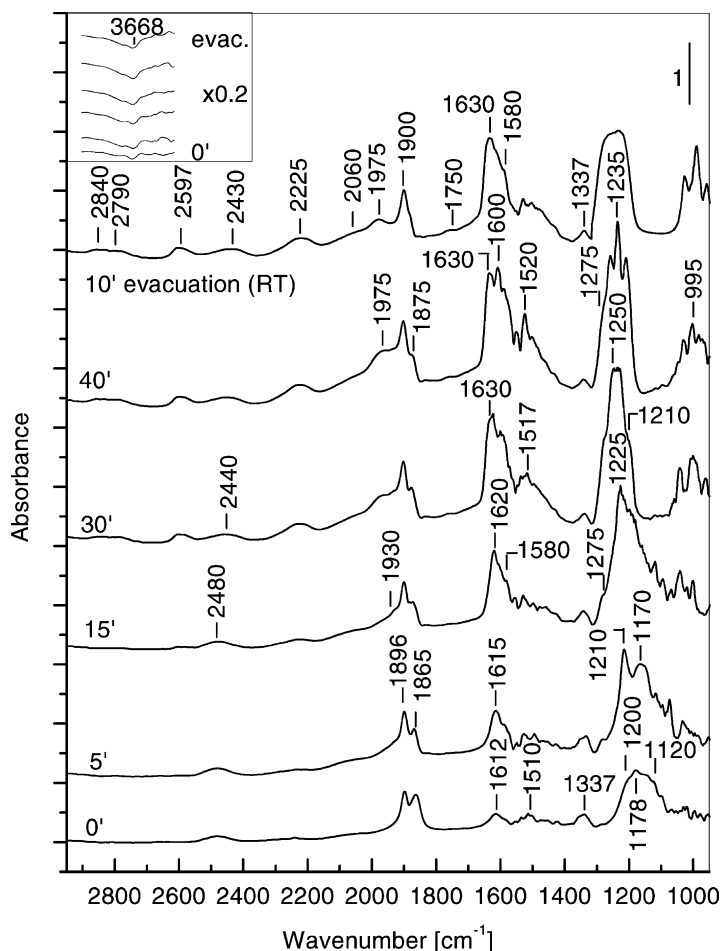
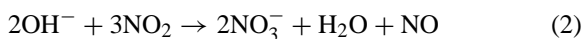


Fig. 3. FT-IR spectra of adsorbed NO/O₂ mixture (5.33 kPa; NO:O₂, 1:4) on the catalyst CuZ at room temperature for various times. The spectrum of the activated sample is used as a background reference. Spectrum 0' corresponds to the spectrum taken immediately after introduction of the gas mixture into the IR cell.

different kinds of surface nitrate (NO₃⁻) species [31,33,42,46,47], whereas, the latter are due to combination modes of the NO₃⁻ fundamental bands [33]. The nitrate species can form by disproportionation of NO₂ (produced by oxidation of NO with O₂) according to the equations [33,46,47]:



The latter process occurs on surface Lewis acid–base pairs. Another possibility for the formation of surface nitrates involves oxidation of the NO⁻ and NO₂⁻

species produced early in the co-adsorption of NO and O₂.

The inset in Fig. 3 shows the involvement of the isolated OH groups of the CuZ catalyst in the process of formation of surface NO_x. The appearance of the negative band at 3668 cm⁻¹ is accompanied by the development of a strong positive absorption between 3600 and 2900 cm⁻¹ (not shown) due to H-bonded hydroxyls. The broad absorption at 2060 cm⁻¹, which grows with time and resists evacuation at room temperature, could be assigned to NO⁺ ion. Consumption of the isolated OH groups and formation of NO⁺ species indicate that surface nitrates are formed

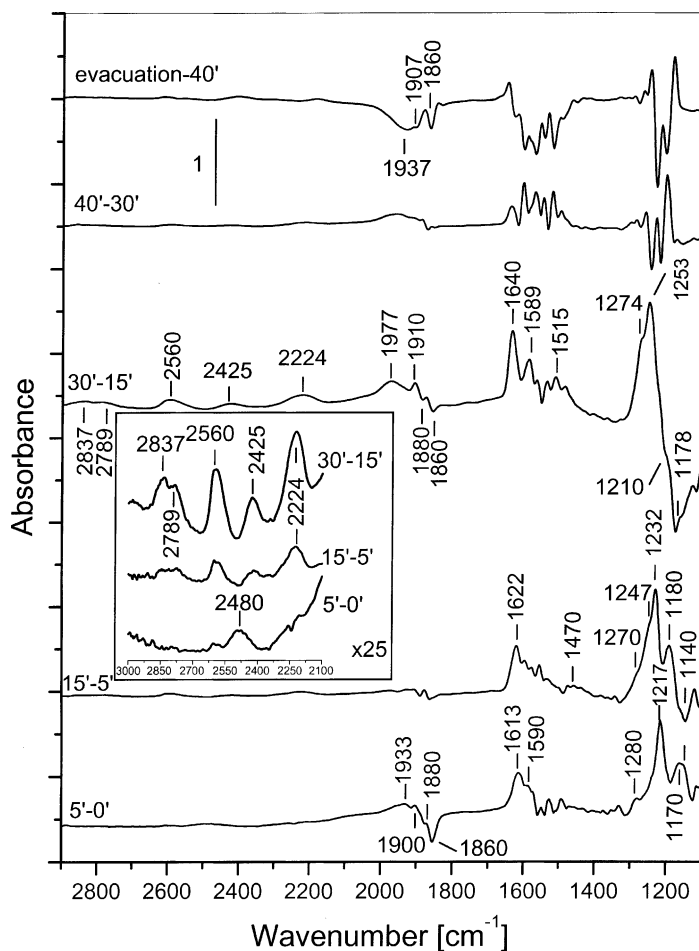


Fig. 4. FT-IR subtraction spectra of the catalyst CuZ obtained from the spectra as shown in Fig. 3.

following Eqs. (2) and (3). A similar process has been observed to occur with pure zirconia [33].

In order to understand the dynamic behavior of the NO_x species produced during NO/O_2 co-adsorption, the subtraction spectra were considered. Each spectrum in Fig. 4 was obtained by subtraction of the preceding spectrum from the spectrum taken at a given time of NO/O_2 co-adsorption. The spectra below 1100 cm^{-1} were of poor quality so, this region is not shown.

Contact of the CuZ sample with the NO/O_2 gas mixture for 5 min (spectrum 5'-0') leads to an increase in intensity of the bands corresponding to anionic nitrosyl (at 1170 cm^{-1}) and chelated nitrito species (at 1217 and about 1140 cm^{-1}). The band at 2480 cm^{-1}

appears also with enhanced intensity (the inset as shown in Fig. 4). At the same time, a considerable increase in the intensity of the band at 1613 cm^{-1} is observed. A shoulder at about 1590 cm^{-1} and a weaker band at 1280 cm^{-1} are detected. All these bands are typical of nitrate species [31,33,42,46,47] and their appearance in the spectrum indicates that oxidation of NO starts to take place simultaneously with NO disproportionation. The Cu^{2+} -NO nitrosyls at 1860 cm^{-1} are involved in formation of surface NO_x species and they appear as negative bands. The weak positive band at 1933 cm^{-1} falls in the spectral region typical of coordination of NO on strong Lewis acid sites and it is attributed to nitrosyl most probably bonded to a zirconium(IV) site that has NO_x

species (NO^- or NO_2^-) in its coordination sphere. Similar mixed $\text{NO}_x^- - \text{M}^{n+} - \text{NO}$ complexes (x is 1 or 3) have been observed on zirconia [33], titania [29] and $\text{MnO}_x/\text{TiO}_2$ [29].

The subtraction spectrum obtained after 10 min of NO/O_2 adsorption (Fig. 4, spectrum 15'–5') contains a negative band at 1140 cm^{-1} due to $\nu_s(\text{NO}_2)$ of chelated NO_2^- species. The contaminant $\nu_{\text{as}}(\text{NO}_2)$ band is overlapped by the strong positive absorption in the $1300\text{--}1200\text{ cm}^{-1}$ region. The decrease in intensity of the band at 1140 cm^{-1} shows that the nitrito species are not stable in the NO/O_2 atmosphere and they undergo oxidation to nitrates. The anionic nitrosyl, however, displays higher stability and the intensity of its $\nu(\text{NO})$ band at 1180 cm^{-1} increases correspondingly.

The absorption between 1622 and 1400 cm^{-1} and the bands in the $1300\text{--}1200\text{ cm}^{-1}$ region are characteristic of both nitrate and nitro species [31,42]. In the high-frequency region (the inset as shown in Fig. 4, spectrum 15'–5') three weak bands at $2600\text{--}2580$, 2425 and 2224 cm^{-1} appear. These bands correspond to $(\nu(\text{N}=\text{O}) + \nu_{\text{as}}(\text{NO}_2))$, $2\nu_{\text{as}}(\text{NO}_2)$ and $(\nu_{\text{as}}(\text{NO}_2) + \nu_s(\text{NO}_2))$ combination modes of bidentate NO_3^- species [33]. This allows assignment of the most intense, positive bands at 1622 and 1232 cm^{-1} to $\nu(\text{N}=\text{O})$ and $\nu_{\text{as}}(\text{NO}_2)$ fundamental modes of bidentate nitrate species [33]. The very weak absorption in $2850\text{--}2700\text{ cm}^{-1}$ is due to combination modes $(\nu(\text{N}=\text{O}) + \nu_{\text{as}}(\text{NO}_2))$ of bridged NO_3^- species [33]. The corresponding fundamental bands are not resolved in the low-frequency region. The bridged nitrates make a contribution to the intensity of the combination band at 2224 cm^{-1} [33].

The spectrum 30'–15' in Fig. 4 shows that extending the contact of the catalyst with the adsorbates for 15 min leads to disappearance of the NO^- and the nitrito species (negative bands at 1178 and about 1210 cm^{-1}). In the NO/O_2 atmosphere, the anionic nitrosyl is unstable and can convert into nitrates [33]. Nitrates can be produced by oxidation of the nitrito species as well. As a result, the intensities of the positive bands at 1640 , 1589 , 1515 , 1274 and 1253 cm^{-1} increase considerably. The bands in the combination region indicate that bridged and bidentate nitrates are present on the catalyst surface. The fundamental band at 1640 cm^{-1} due to $\nu(\text{N}=\text{O})$ mode is assigned to bridged nitrates. The bridged nitrates are of two

types producing combination bands at 2837 and 2789 cm^{-1} . Taking this into account, the position of the corresponding $\nu_{\text{as}}(\text{NO}_2)$ modes should be at $1230\text{--}1200\text{ cm}^{-1}$. However, the positive absorption expected in this region is offset by the negative band due to oxidation of the NO^- and NO_2^- species. There are also two types of bidentate nitrates (at 1620 and $1590\text{--}1580\text{ cm}^{-1}$) because the corresponding combination band at 2560 cm^{-1} has a low-frequency shoulder at about 2540 cm^{-1} (as shown also in Figs. 3 and 5). Since the existence of monodentate nitrates cannot be revealed from the combination region [33], they cannot be distinguished from the chelated nitro species by using the corresponding fundamental bands because of their overlap. In other words, the positive absorption at about 1515 cm^{-1} in Fig. 4, spectrum 30'–15' can be due either to monodentate nitrates and/or nitro species. Finally, the band at 1977 cm^{-1} appears when large amounts of surface nitrates are formed and by analogy with the pure zirconia [33], this absorption corresponds to a $\text{ON-Zr}^{4+}\text{-NO}_3^-$ complex.

The disappearance of the NO^- species from the spectrum 30'–15' should be accompanied by a negative band at 2480 cm^{-1} to which the ionic nitrosyl makes a contribution. It can be assumed that the expected negative band is cancelled by the broad, positive absorption between 2530 and 2350 cm^{-1} (due to the $(\nu(\text{N}=\text{O}) + \nu_{\text{as}}(\text{NO}_2))$ modes of the bidentate nitrate species), which appears in very close proximity (as shown in Fig. 3).

Further increase of the adsorption time by 10 min (Fig. 4, spectrum 40'–30') causes some changes in the envelope of the nitrate bands (as shown in also Fig. 3) and it seems that the catalyst surface is close to saturation. Evacuation for 10 min at room temperature (Fig. 4, spectrum evacuation: 40') results in a loss of nitrate and nitrosyl species.

The spectra in Fig. 4 shows that with time, the intensity of the band at 1860 cm^{-1} due to $\text{Cu}^{2+}\text{-NO}$ species decreases, whereas, the band at 1880 cm^{-1} shifts to $1900\text{--}1910\text{ cm}^{-1}$. This behavior can be explained by assuming that the former absorption belongs to NO coordinated on associated copper(II) sites and the latter to NO adsorbed on isolated copper(II) sites. It can be proposed that the nitrosyls on the associated copper(II) sites are involved in formation of surface NO_x^- species (x is 2 or 3) as well.

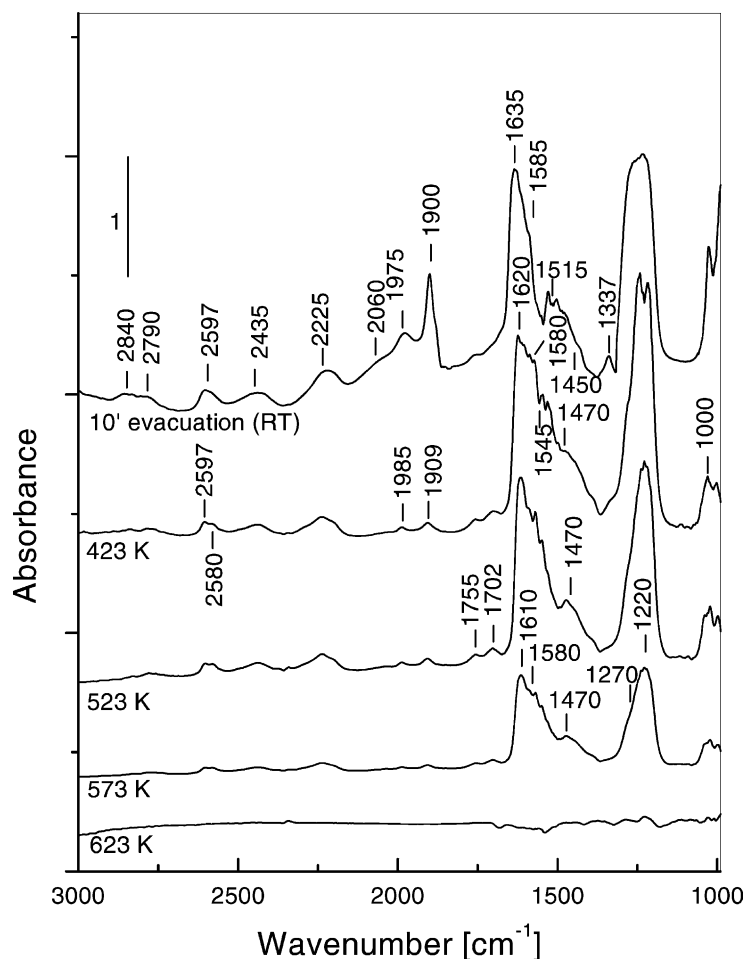


Fig. 5. FT-IR spectra obtained after heating the catalyst CuZ containing adsorbed NO_x species for 10 min in vacuum. The spectra are recorded after cooling the IR cell to room temperature. The spectrum of the activated sample is used as a background reference.

There is a great resemblance between the spectral features of the nitrates produced on pure zirconia [33] and CuZ catalyst. A noticeable difference between the two samples is that the concentration of the surface nitrates on CuZ catalyst is much higher. This implies that a larger amount of NO_2 is produced and indicates that Cu^{2+} ions catalyze the formation of NO_2 from NO and O_2 . A high concentration of surface nitrates on CuO/ZrO_2 catalysts compared to pure zirconia has been observed also by others [32].

The evacuation of catalyst CuZ at 423 K for 10 min (Fig. 5) leads to disappearance of the nitrosyl bands at 1975 and 1900 cm^{-1} and the absorption due to the NO^+ ion. The pair of weak bands at 1985 and

1755 cm^{-1} and 1702 cm^{-1} are due to the split ($\nu_s(\text{NO}_2) + \delta(\text{ONO})$) modes of the bridged and bidentate nitrates [33], respectively. Compared with the spectrum taken at room temperature, the shapes and the relative intensities of the bands in the fundamental nitrate region have changed. The absorption between 1600 and 1400 cm^{-1} increased in intensity leading to the appearance of clearly distinguishable shoulders at 1580, 1545 and 1470 cm^{-1} . The former band could be interpreted as the $\nu_{\text{as}}(\text{NO}_2)$ mode of bidentate nitrate [31,33,42,46,47]. However, the spectrum in the combination region shows a decrease, instead of an increase, in the intensities of the characteristic combination bands of the bridged (2840

and 2790 cm^{-1}) and bidentate (2597 and 2580 cm^{-1}) nitrates and no new bands are observed. It can be concluded that the new species formed exhibits a vibration that coincides with the $\nu(\text{N}=\text{O})$ mode of the bidentate nitrate at $1580\text{--}1590\text{ cm}^{-1}$, but does not produce combination bands. The bands at 1545 and 1470 cm^{-1} fall in the region typical of monodentate nitrate species [31,33,42,46,47]. However, it is well known that the monodentate nitrates have low thermal stability and the increase in the temperature of dynamic evacuation cannot favor their formation. These considerations lead to the conclusion that the bands at 1580 , 1545 and 1470 cm^{-1} are due to $\nu_{\text{as}}(\text{NO}_2)$ modes of chelated nitro species [31,42]. The corresponding $\nu_{\text{s}}(\text{NO}_2)$ vibrations should fall between 1260 and 1180 cm^{-1} and are superimposed to the $\nu_{\text{as}}(\text{NO}_2)$ modes of the nitrate bands. The nitro species can appear during NO/O_2 co-adsorption at room temperature, but their concentration increases significantly after evacuation at 423 K . Obviously, the formation of the nitro species takes place at the expense of bridged and bidentate nitrates. In this process, the type of coordination of the parent nitrate species is preserved.

The weak bands in the combination region at 1985 , 1909 , 1755 and 1702 cm^{-1} , and the absorptions at 1580 and 1470 cm^{-1} in the fundamental region reveal that the nitrates (bridged and bidentate) and the nitro species are still present after evacuation for 10 min at 573 K . However, increase in the temperature to 623 K causes their complete desorption. The thermal stability of the NO_x^- species (x is 2 and 3) obtained on the surface of CuZ catalyst is lower than that of the NO_3^- species on zirconia [33]. In the latter case, the bidentate nitrates resist the evacuation at 673 K . In addition, no formation of nitro species has been observed during room temperature NO/O_2 co-adsorption on zirconia, or during evacuation at higher temperatures [33].

The absorption bands observed on CuZ catalyst after exposure to either NO or a NO/O_2 mixture are summarized in Table 1.

3.4. Adsorption of NO on CuZS catalyst

The adsorption of NO (0.67 kPa) for 40 min at room temperature on the CuZS catalyst leads to the formation of a complex band in the nitrosyl region with

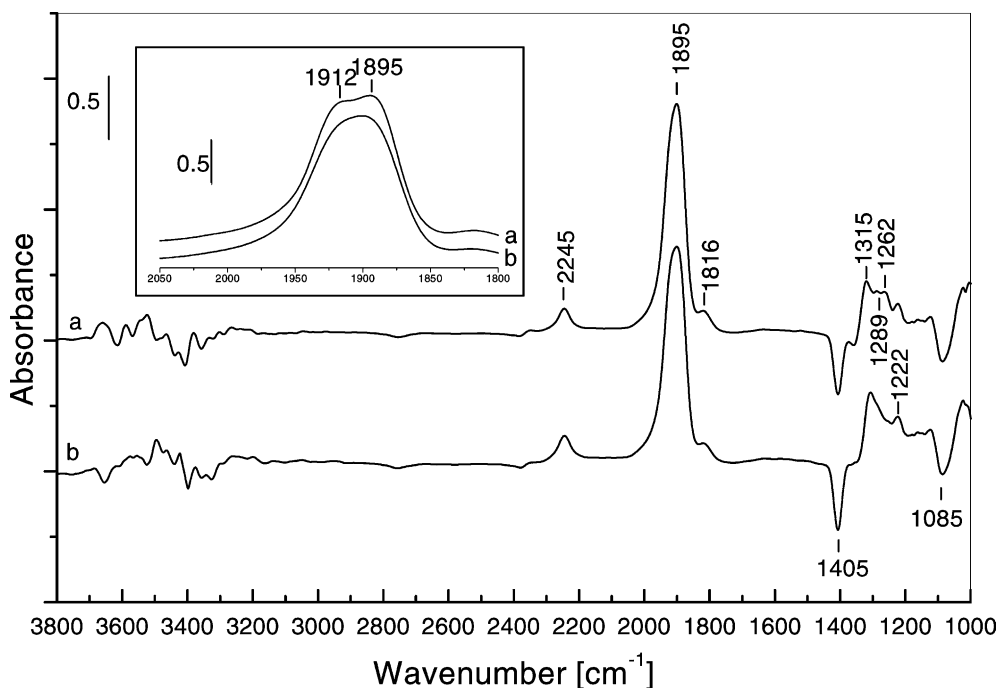


Fig. 6. FT-IR spectra of NO (0.67 kPa) adsorbed at room temperature for a period of 40 min on the sample CuZS (a) and after evacuation at room temperature for 10 min (b). The spectrum of the activated sample is used as a background reference.

Table 1

Assignments of the FT-IR bands observed during adsorption of 0.67 kPa NO and its co-adsorption with O₂ (NO:O₂, 1:4) at room temperature on the CuZ sample

NO _x species	Band positions (cm ⁻¹)	Modes
N ₂ O (ads)	2280, 2244	ν(NN)
	1220	ν(NO)
	2470	2ν(NO)
NO ⁺	2060	ν(NO)
ON–Zr ⁴⁺ –NO _x ⁻ (x = 1 or 3)	1977–1933	ν(NO)
Cu ²⁺ –NO (two types)	1885–1880	ν(NO)
	1870–1865	
Cu ⁺ –NO	1763	ν(NO)
<i>cis</i> -HNO ₂	1670	ν(N=O)
H ₂ O (ads)	1612	δ(HOH)
	3600–3000	ν(OH)
NO ₂ ⁻ (chelated nitro)	1519–1510	ν _{as} (NO ₂)
	1342–1337	ν _s (NO ₂)
NO ₂ ⁻ (monodentate nitrito) (two types)	1450, 1404	ν(N=O)
	1054	ν(NO)
NO ⁻	1180–1170	ν(NO)
	2480	1180 + 1342
NO ₂ ⁻ (chelated nitrito)	~1210–1200	ν _{as} (NO ₂)
	~1140–1120	ν _s (NO ₂)
NO ₃ ⁻ (bidentate)	1620–1622, 1590–1580	ν(N=O)
	1235–1232	ν _{as} (NO ₂)
	2600–2500	ν(N=O) + ν _{as} (NO ₂)
	2425	2ν _{as} (NO ₂)
	2224	ν _{as} (NO ₂) + ν _s (NO ₂)
	1755, 1702	ν _s (NO ₂) + δ(ONO)
NO ₃ ⁻ (bridged)	1640–1630	ν(N=O)
	1230–1200	ν _{as} (NO ₂)
	2850–2700	ν(N=O) + ν _{as} (NO ₂)
	1985, 1909	ν _s (NO ₂) + δ(ONO)
NO ₂ ⁻ (chelated nitro) (three types)	1580, 1545, 1470	ν _{as} (NO ₂)
	1260–1180	ν _s (NO ₂)

maxima at 1912 and 1895 cm⁻¹ (inset as shown in Fig. 6, spectrum a). As in the case of the CuZ catalyst, this reveals the presence of two kinds of Cu²⁺ ions giving rise to two types of nitrosyl species. However, compared to the sulfate-free sample these bands are blue-shifted by approximately 25 cm⁻¹ and the intensity ratio between the high- and low-frequency nitrosyls is reverse. This confirms the existence of sulfate ions bonded to copper(II) sites, thus completing their coordination sphere (Section 3.1; Fig. 1). This makes

the latter inaccessible to NO adsorption. In addition, the intensities of the nitrosyl bands on the CuZS catalyst are not affected significantly by evacuation for 10 min at room temperature (Fig. 6, spectrum b). The higher frequency and the higher stability of the Cu²⁺–NO species on the sulfated catalyst is consistent with the increased positive charge of the copper ions caused by the SO₄²⁻ ions located in their vicinity. A similar effect of sulfate ions on the position of the Cu²⁺–NO band is reported also in [10,32].

By analogy with the CuZ catalyst, the bands at 2245 and 1222 cm^{-1} are assigned to adsorbed N_2O and the absorption at 1816 cm^{-1} is attributed to Cu^+-NO nitrosyl [10]. The latter band is positioned at higher frequency compared to that on the sulfate-free sample (weak absorption at 1763 cm^{-1} , as shown in Fig. 2) and like the $\text{Cu}^{2+}-\text{NO}$ species, the copper(I) mononitrosyls display higher stability. The negative bands at 1405 and 1085 cm^{-1} indicate that the sulfate groups coordinated to Zr^{4+} sites are altered by the adsorbed NO. Probably these are the topmost SO_4^{2-} ions, which appear in the spectrum of adsorbed NO with reduced order of the S=O bond, giving rise to the band at 1315 cm^{-1} . The absence of negative absorption between 1200 and 1100 cm^{-1} (Fig. 1) indicates that the sulfate groups coordinated to the copper(II) sites are not affected by adsorbed NO and probably the CuZS sample contains a CuSO_4 -like phase.

The weak bands at 1289 and 1262 cm^{-1} can be assigned to nitrito species [31,42]. These bands are not observed after evacuation at room temperature indicating that the corresponding species are weakly bonded. Contrary to the CuZ sample, the adsorbed N_2O is held strongly on the sulfated catalyst and no alteration of the surface OH groups is observed. This fact shows that the process described by Eq. (1) does not take place in the case of the CuZS sample. The reason for this is the absence of terminal $\text{Zr}^{4+}-\text{OH}$ groups in the CuZS sample (Fig. 1). The results of NO adsorption on sulfated zirconia [33] demonstrated that these types of surface hydroxyls are involved in reaction (1).

3.5. Adsorption of NO and O_2 on CuZS catalyst

The saturation of the surface of the CuZS catalyst with NO_x species upon adsorption of a gas mixture (5.33 kPa) of NO and O_2 (NO: O_2 , 1:4) was reached after 30 min. The spectrum taken after evacuation for 10 min at room temperature is as shown in Fig. 7 (spectrum 10' evacuation (room temperature)). The appearance of weak absorption between 2900 and 2750 cm^{-1} and the band at 2600 cm^{-1} are indicative of the presence of bridged and bidentate nitrates. The band at 1284 cm^{-1} has a high-frequency shoulder at about 1325 cm^{-1} due to perturbation of the sulfate groups (negative band at 1398 cm^{-1}) caused by the nitrate species. Analogous shift of the $\nu(\text{S}=\text{O})$ mode to lower frequency due to adsorbed nitrates has been

observed on sulfated zirconia [33]. In contrast to the CuZ sample, the surface OH groups of the CuZS catalyst do not participate in the formation of nitrate species and adsorbed water molecules are not produced. Since the spectra of the OH groups are noisy, they are not shown and this conclusion is made based on the fact [33] that no absorption in the 1120–1145 cm^{-1} region due to water-perturbed sulfate groups is detected. The absence of terminal $\text{Zr}^{4+}-\text{OH}$ groups in the CuZS catalyst makes the occurrence of reaction (3) (in which surface Lewis acid–base pairs are involved) as the only possible route for formation of nitrate species. This conclusion is supported by the appearance of a broad, poorly resolved band at approximately 2140 cm^{-1} due to NO^+ ions [31,46,47]. This absorption is superimposed on the band at 2248 cm^{-1} corresponding to adsorbed N_2O [41]. The single band at 1912 cm^{-1} is attributed to $\text{Cu}^{2+}-\text{NO}$ nitrosyl. Compared to the spectra of adsorbed NO (Fig. 6), this band is positioned at higher frequency. Analogous to the CuZ catalyst, this shift is due to an induction effect from the NO_3^- species formed.

It was shown previously that study of the thermal stability of the adsorption forms produced during interaction of the catalyst with the NO/ O_2 mixture can help in distinguishing between nitro and nitrate species. Dynamic evacuation in the temperature range of 363–553 K causes a gradual decrease in the intensities of the bands in the 1650–1200 cm^{-1} region (Fig. 7). This behavior is in strong contrast to that observed for the sulfate-free copper catalyst: there is no enhancement in the absorption between 1580 and 1400 cm^{-1} after evacuation at 363 and 423 K (compare with Fig. 5), which indicates that there is no transformation of the bridged and bidentate nitrates into nitro species. If the latter species could form during the room temperature NO/ O_2 co-adsorption, their thermal stability should be low. Indeed, the shoulder at approximately 1540 cm^{-1} disappears after evacuation at 423 K (Fig. 7). This band could be assigned either to chelated nitro or monodentate nitrate species [31,42]. Evacuation at 423 K causes also almost complete decomposition of the bridged nitrates: the absorption between 2900 and 2700 cm^{-1} nearly vanishes. The bidentate nitrates at 1620, 1580 ($\nu(\text{N}=\text{O})$) and 1280, 1220–1255 cm^{-1} ($\nu_{\text{as}}(\text{NO}_2)$) and combination bands at 2600–2615 cm^{-1} disappear

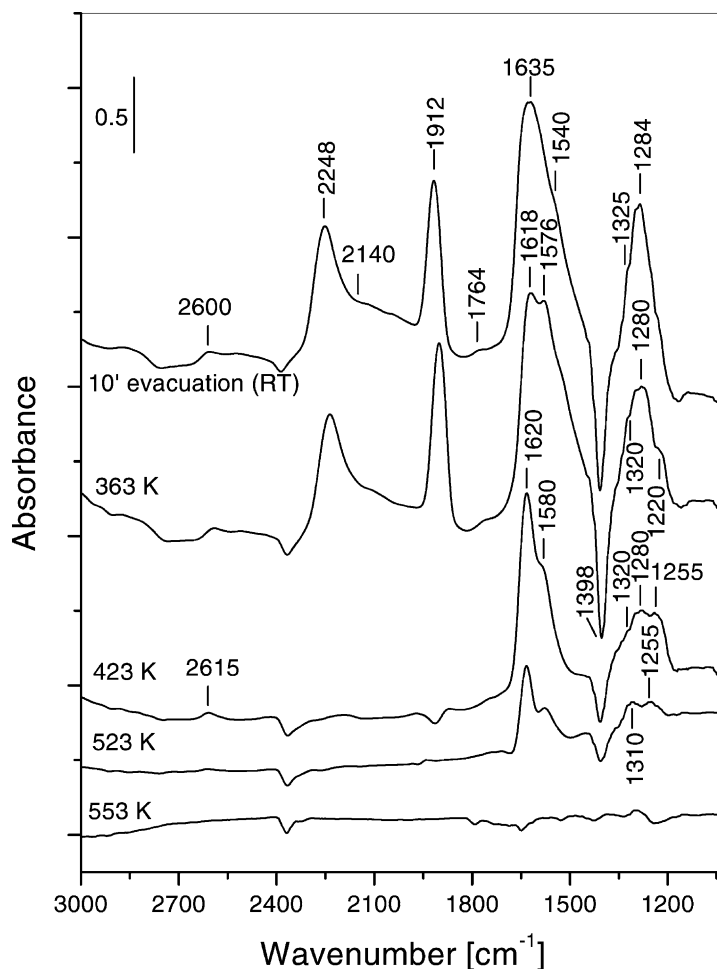


Fig. 7. FT-IR spectra obtained after heating the catalyst CuZS containing adsorbed NO_x species for 10 min in vacuum. The spectra are recorded after cooling the IR cell to room temperature. Spectrum 10' evacuation (at room temperature) is obtained after adsorption of NO/O_2 mixture (5.33 kPa; $\text{NO}:\text{O}_2$, 1:4) for 30 min followed by evacuation for 10 min at room temperature. The spectrum of the activated sample is used as a background reference.

after evacuation at 553 K. This leads to restoration of the original coordination of the sulfate groups: the negative band at 1398 cm^{-1} is no longer present in the spectrum. The adsorbed N_2O , NO^+ and $\text{Cu}^{2+}\text{-NO}$ nitrosyls display higher stability and they survive the evacuation at 363 K (Fig. 7). In conclusion, the thermal stability of the nitro–nitrate species on CuZS catalyst is lower than that of the NO_2^- and NO_3^- groups on the CuZ sample and the nitrates on the sulfated zirconia—in the latter case, they decomposed after heating at 673 K [33]. In contrast to the CuZ catalyst, the amount of the NO_x^- species (x is 2

and 3) is lower on the CuZS sample. These results are in agreement with the NO-TPD measurements of Delahay et al. [32].

Table 2 illustrates the absorption bands observed during NO adsorption and its co-adsorption with O_2 on catalyst CuZS.

3.6. Interaction of the NO_x species with decane

3.6.1. Catalyst CuZ

Fig. 8A shows the spectrum of adsorbed NO/O_2 (5.33 kPa; $\text{NO}:\text{O}_2$, 1:4) on the catalyst CuZ after

Table 2

Assignments of the FT-IR bands observed during adsorption of 0.67 kPa NO and its co-adsorption with O₂ (NO:O₂, 1:4) at room temperature on the CuZS sample

NO _x species	Band positions (cm ⁻¹)	Modes
N ₂ O (ads)	2245	ν(NN)
	1222	ν(NO)
NO ⁺	2140	ν(NO)
Cu ²⁺ -NO (two types)	1912	ν(NO)
	1895	
Cu ⁺ -NO	1816	ν(NO)
NO ₂ ⁻ (chelated nitrito)	1289	ν _{as} (NO ₂)
	1262	ν _s (NO ₂)
NO ₃ ⁻ (bidentate)	1620–1618, 1580–1576	ν(N=O)
	1284–1280, 1255–1220	ν _{as} (NO ₂)
	2600–2615	ν(N=O) + ν _{as} (NO ₂)
NO ₃ ⁻ (bridged)	1635	ν(N=O)
	1284	ν _{as} (NO ₂)
	2900–2750	ν(N=O) + ν _{as} (NO ₂)
NO ₃ ⁻ (monodentate) or NO ₂ ⁻ (chelated nitro)	1540	ν _{as} (NO ₂)
	1284	ν _s (NO ₂)

subsequent evacuation at room temperature for 30 min (spectrum a). To the catalyst treated in this way, decane vapor (0.07 kPa) is added and then evacuated at room temperature for 10 min. The spectrum obtained (spectrum b) contains bands in the ν(CH) stretching region due to adsorbed decane corresponding to ν_{as}(CH₃) at 2955, ν_{as}(CH₂) at 2930 and ν_s(CH₂) at 2853 cm⁻¹ [48]. The CH₂ scissors (observed at 1453 cm⁻¹ in gas phase) fall in the region of strong nitrate bands. The bending modes of the CH₃ groups (at 1373 cm⁻¹) are weaker and difficult to detect. The adsorption of the hydrocarbon does not cause considerable changes in the spectrum of the adsorbed NO_x species. However, heating (spectrum c) the closed cell for 40 min at 453 K (without evacuation) leads to the following changes (see also spectrum c–b in Fig. 8B): (i) slight decrease in the intensities of the hydrocarbon bands in the ν(CH) stretching region; (ii) decrease in the intensities of the bands at 1640 and 1210 cm⁻¹ corresponding to the bridged nitrates (characteristic combination bands at 1980 and 1908 cm⁻¹ [33]); (iii) decrease in the intensities of the bands at 1520, 1489, 1280 and 1264 cm⁻¹ assigned mainly to nitro species (Section 3.3); (iv) appearance of a positive band at 1875 cm⁻¹ attributed to Cu²⁺-NO species (Fig. 2);

(vi) appearance of a weak, positive absorption in the 2800–2700 cm⁻¹ region typical of formate moieties and a band at 1715 cm⁻¹ due to ν(C=O) modes most probably of formic acid bonded to surface hydroxyl groups [29,49,50]. This indicates that partial oxidation of the adsorbed hydrocarbon takes place. The negative bands between 1650 and 1200 cm⁻¹ suggest that in this process bridged nitrate and nitro species are involved, although they undergo some decomposition leading to formation of copper(II) nitrosyls.

Heating for 15 min at 523 K (Fig. 8 A and B, spectra d and d–c) causes additional decrease in the intensity of the decane bands with simultaneous disappearance of the bidentate nitrates at 1613 and 1238 cm⁻¹ (combination bands at 2240 and 1760 cm⁻¹) and the nitro species at 1530, 1500 and 1275 cm⁻¹ (shoulder). As a result of the interaction of the adsorbed hydrocarbon and nitro–nitrate species, the amount of formic acid increased giving rise to the band at 1666 cm⁻¹ due to the ν(C=O) mode [29,49,50]. The shift in the stretching frequency of the carbonyl group from 1715 cm⁻¹ (spectrum c–b) to 1666 cm⁻¹ (spectrum d–c) suggests that, in the latter case, the formic acid is coordinated to a Lewis acid site [29,49,50]. The intense positive band at 1385 cm⁻¹ and the shoulder

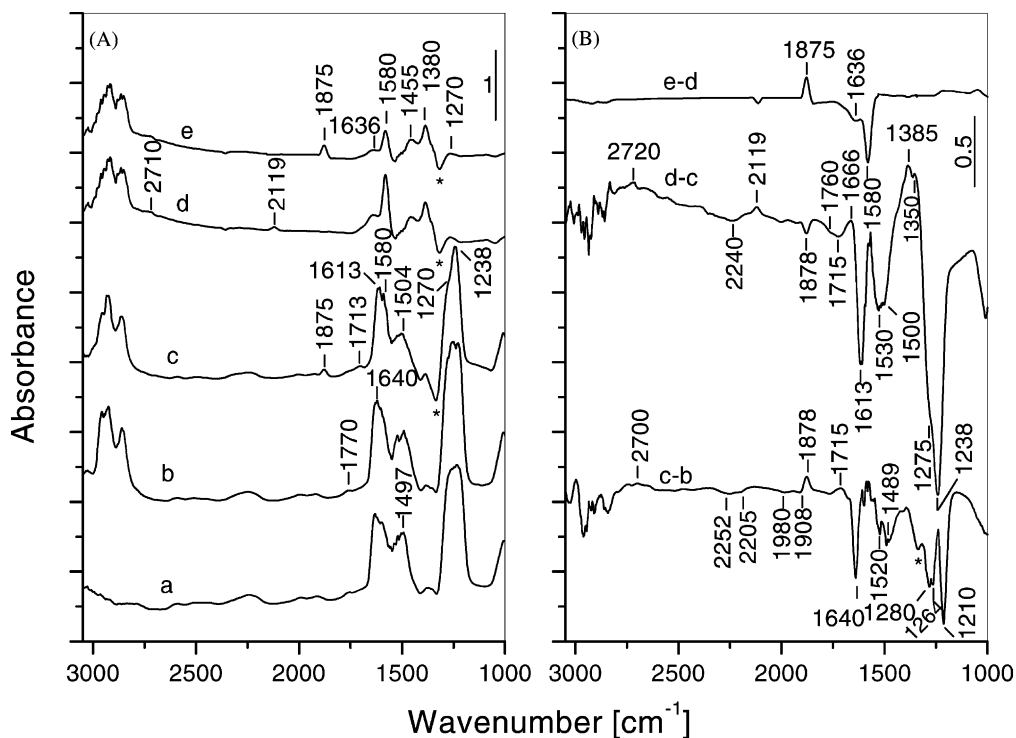


Fig. 8. (A) FT-IR spectra of the catalyst CuZ taken after adsorption of a NO/O₂ mixture (5.33 kPa; NO:O₂, 1:4) at room temperature followed by evacuation for 10 min (a), after adsorption of decane (0.07 kPa) on the NO_x pre-covered catalyst followed by evacuation for 10 min at room temperature (b), and after heating the closed IR cell for 40 min at 453 K (c), for 15 min at 523 K (d) and for 15 min at 623 K (e). The spectra are recorded after cooling the IR cell to room temperature. The spectrum of the activated sample is used as a background reference. (B) FT-IR subtraction spectra of the catalyst CuZ obtained from the spectra as shown in Fig. 8A. The negative band at 1335 cm⁻¹ marked by an asterisk is due to nitrate species adsorbed on the window of the IR cell.

at 1350 cm⁻¹ are typical of $\delta(\text{CH})$ and $\nu_s(\text{CO}_2^-)$ modes, respectively, of formate species [26–30,49,50]. The $\nu_{\text{as}}(\text{CO}_2^-)$ stretching vibration usually falls in the 1600–1550 cm⁻¹ region and probably is covered by the band at 1580 cm⁻¹ (Fig. 8, spectrum d) and does not appear in the subtraction spectrum d–c. The latter band corresponds to $\nu_{\text{as}}(\text{NO}_2)$ mode of chelated nitro species, whereas, the $\nu_s(\text{NO}_2)$ mode is positioned at 1270 cm⁻¹ (spectrum d). The band at 1580 cm⁻¹ is absent in the subtraction spectra c–b and d–c as shown in Fig. 8B. This behavior indicates that this type of nitro species (probably bidentate) does not interact with the hydrocarbon under the experimental conditions. Finally, the appearance of the weak band at 2119 cm⁻¹ characteristic of Cu⁺–CO carbonyl [7,18–22,43,51] shows that the heating at 523 K leads to the formation of CO. Carbon monoxide can arise from partial

oxidation of the adsorbed decane and decomposition of the formate species and formic acid. The absorption at 1636 cm⁻¹ belongs to adsorbed water molecules (Fig. 8A, spectrum d). The band at 1455 cm⁻¹ is attributed to CH₂ scissors vibrations of the unconverted hydrocarbon.

Increase of the temperature to 598 K for 15 min (Fig. 8, spectra e and e–d) does not lead to any significant change in the intensity of the bands in the $\nu(\text{CH})$ stretching region indicating that no further oxidation of the hydrocarbon takes place. However, a significant decrease in the intensity of the bands at 1580 and 1270 cm⁻¹ is observed with simultaneous appearance of the band at 1875 cm⁻¹ corresponding to Cu²⁺–NO species (Fig. 2). Obviously, the bridged nitro species (at 1580 and 1270 cm⁻¹) do not react with the adsorbed decane and under these conditions, they start to

decompose producing NO. The latter, on lowering the temperature to 298 K, forms nitrosyls bonded to the Cu^{2+} sites. The band at 2119 cm^{-1} due to Cu^+-CO species disappears. Decrease in the intensity of the band at 1636 cm^{-1} is due to loss of molecularly adsorbed water. No change in the intensity of the band at 1380 cm^{-1} , assigned to formate species, is detected.

3.6.2. Catalyst CuZS

The reactivity of the NO_x species that are strongly bonded to the surface of the CuZS catalyst toward adsorbed decane was followed by a similar experiment to that described previously. The results are as shown in Fig. 9. The adsorption of decane (0.07 kPa) on the NO_x pre-covered catalyst followed by evacuation for 10 min at room temperature Fig. 9A, spectrum b) causes slight decrease in the intensity of the bands at 2242 and 1900 cm^{-1} due to adsorbed N_2O and NO, respectively. The weak absorption at 1460 cm^{-1} is

attributed to the CH_2 scissoring vibrations of the adsorbed hydrocarbon. The band at 1232 cm^{-1} is due to sulfate groups perturbed by a small amount of water contained in the decane (as shown later). Heating the closed IR cell for 40 min at 453 K Fig. 9A, spectrum c) leads to a strong decrease in the intensities of the bands corresponding to the adsorbed hydrocarbon and the NO_3^- species (see also the subtraction spectrum c–b as shown in Fig. 9B). New bands at 2140 , 1718 , 1667 and 1424 cm^{-1} are detected. The band at 2140 cm^{-1} is attributed to Cu^+-CO carbonyls. Here again, the absorption at 1718 cm^{-1} is typical of a carboxylic acid coordinated to surface hydroxyl groups, whereas, the band at 1667 cm^{-1} is assigned to a carboxylic acid coordinately bonded through the carbonyl oxygen to a Lewis acid site. The band at 1424 cm^{-1} is characteristic of acetate moiety and corresponds to the $\nu_s(\text{CO}_2^-)$ mode [26–30]. These facts show that the nitrate species oxidize the adsorbed decane, which

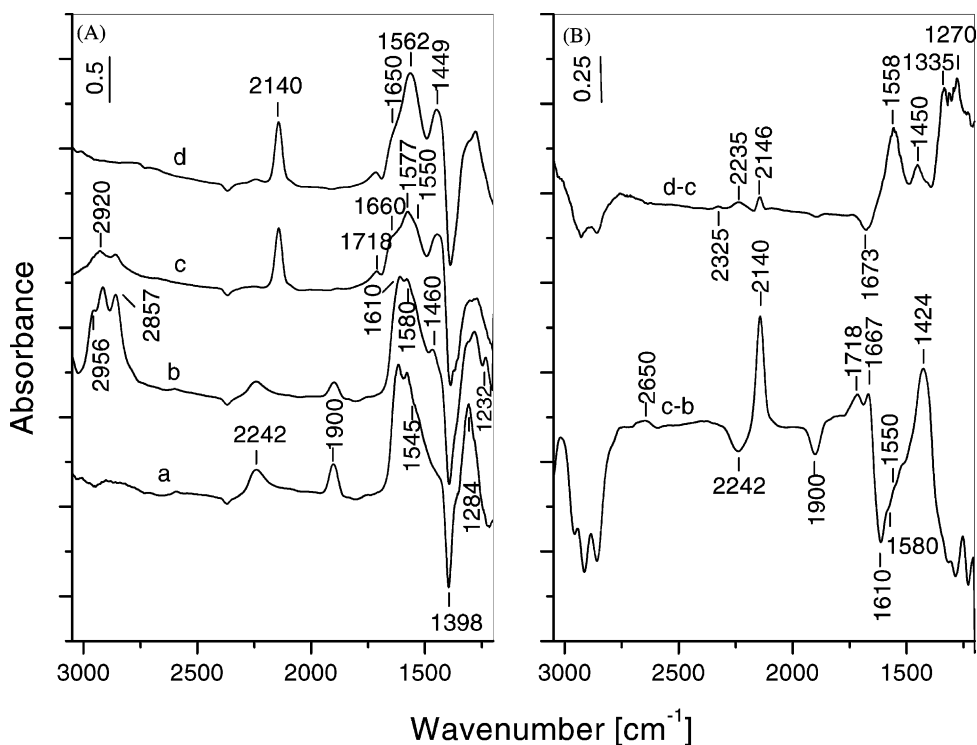


Fig. 9. (A) FT-IR spectra of the catalyst CuZS taken after adsorption of a NO/O_2 mixture (5.33 kPa; $\text{NO}:\text{O}_2$, 1:4) at room temperature followed by evacuation for 10 min (a), after adsorption of decane (0.07 kPa) on the NO_x pre-covered catalyst followed by evacuation for 10 min at room temperature (b), and after heating the closed IR cell for 40 min at 453 K (c) and for 15 min at 523 K (d). The spectra are recorded after cooling the IR cell to room temperature. The spectrum of the activated sample is used as a background reference. (B) FT-IR subtraction spectra of the catalyst CuZS obtained from the spectra as shown in Fig. 9A.

results in formation of acetic acid and CO. The existence of a weak band at 2650 cm^{-1} suggests that formic acid is formed as well. Under these conditions, the most reactive NO_x species in the oxidation of the hydrocarbon are the bridged nitrates characterized by the band at 1610 cm^{-1} . This absorption is not observed after heating at 453 K (Fig. 9, spectrum c) and appears as a negative band in the subtraction spectrum c–b. The bidentate nitrates at 1577 cm^{-1} and the monodentate nitrates or nitro species at 1550 cm^{-1} display lower reactivity and they are present in the spectrum with reduced concentration (Fig. 9, spectrum c). Under these conditions, the adsorbed N_2O and NO disappear (negative bands at 2242 and 1900 cm^{-1} , spectrum c–b as shown in Fig. 9). Probably they are replaced by the products of hydrocarbon oxidation.

Increasing the temperature to 523 K leads to complete disappearance of the adsorbed decane (Fig. 9, spectrum d). The bands at 1577 and 1550 cm^{-1} corresponding to the less reactive nitro–nitrate species are not observed and an intense absorption at 1562 cm^{-1} appears instead. The subtraction spectrum d–c shows that the amount of carboxylic acids coordinated to the Lewis acid sites decreases (negative band at 1673 cm^{-1}), whereas, the concentration of the H-bonded acids does not change. The positive bands at 1558 and 1450 cm^{-1} attributed to $\nu_{\text{as}}(\text{CO}_2^-)$ and $\nu_{\text{s}}(\text{CO}_2^-)$ modes of adsorbed acetate ion increase in intensity. The bands at 1335 and 1270 cm^{-1} are assigned to $\nu_{\text{s}}(\text{CO}_2^-)$ stretching vibrations of formate species coordinated to two different Lewis acid sites [49]. The latter give rise to the broad, weak absorption between 2800 and 2600 cm^{-1} corresponding to the $(\nu_{\text{s}}(\text{CO}_2^-) + \delta(\text{CH}))$ modes. The formate ions should contribute to the intensity of the band at 1558 cm^{-1} assigned to the $\nu_{\text{as}}(\text{CO}_2^-)$ stretching vibrations of the acetate ion. The appearance of formate and acetate species indicates that heating at 523 K causes dissociation of the carboxylic acids formed. It can be assumed that a process of recombination of the dissociated acids takes place as the temperature is lowered to ambient for recording of the FT-IR spectrum. This results in a constant concentration of the molecularly adsorbed acids ($\nu(\text{C}=\text{O})$ band at 1718 cm^{-1} as shown in Fig. 9, spectra c and d).

It has been noted that in the formation of partially oxidized hydrocarbon compounds from decane at 523 K the nitrate species at 1577 and 1550 cm^{-1}

are involved. These bands do not appear as negative bands in the subtraction spectrum d–c in Fig. 9 due to superimposition on the positive absorption with a maximum at 1558 cm^{-1} . There is a slight increase in the amount of adsorbed CO relative to that formed at 453 K. The band at 2325 cm^{-1} of low intensity reveals the presence of adsorbed CO_2 . According to the literature data [27,31], the weak absorption at 2235 cm^{-1} is associated with isocyanate ion, NCO^- , coordinated to a copper site. These species can form by direct oxidation of the decane with nitrates (or more reactive nitro species) or by reduction of the nitrates with the acetate and formate species [26,27,29]. It has been suggested that the NCO^- species are the final intermediates in the SCR of NO by decane, leading to dinitrogen formation by interaction with the surface nitrates [29]. The spectra in Fig. 9 shows also that under the experimental conditions the sulfate groups are not altered.

The fact that the surface nitro–nitrate species disappear as the temperature of interaction with decane increases and that no other adsorbed NO_x species (e.g. nitrosyls) are detected in the spectra can be used as evidence that the nitro–nitrate species are reduced to dinitrogen. Homogeneous interaction between the decane and NO_2 (which could arise from thermal decomposition of the nitrates) should be excluded because the interaction of this hydrocarbon and $\text{NO} + \text{O}_2$, respectively NO_2 in the gas phase, occurs at about 673 – 713 K [52]. This, together with the facts reported, presents evidence that the decane adsorbed on the CuZS catalyst is oxidized by the surface nitro–nitrate species.

3.7. Interaction of the adsorbed decane with the surfaces of CuZ and CuZS catalysts

The ability of the NO_x -free surfaces of CuZ and CuZS catalysts to oxidize the adsorbed decane has been investigated as well. After adsorption of 0.07 kPa of decane on the activated catalysts (followed by evacuation at room temperature for 10 min), the closed IR cell was heated at 453 and 523 K. Both catalysts displayed activity toward the oxidation of the hydrocarbon. However, the maximum conversion of the adsorbed decane is shifted to higher temperatures compared to the NO_x pre-covered catalysts. This is illustrated by the spectra obtained for the CuZS catalyst (Fig. 10). The absorption in the 3700 – 3500 cm^{-1}

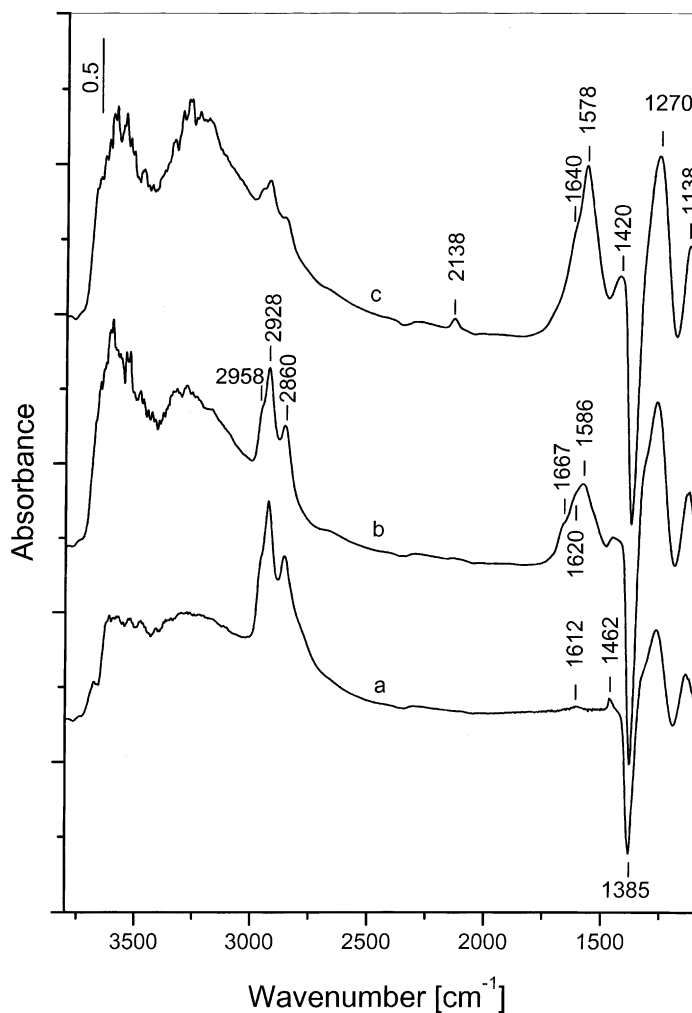


Fig. 10. FT-IR spectra of the CuZS catalyst taken after adsorption of decane (0.07 kPa) at room temperature followed by evacuation for 10 min at room temperature (a), and after heating the closed IR cell for 40 min at 453 K (b) and for 15 min at 523 K (c). The spectra are recorded after cooling the IR cell to room temperature. The spectrum of the activated sample is used as a background reference.

region and the band at 1612 cm^{-1} observed after contact of the catalyst with decane at room temperature (spectrum a) are associated with water contained in the hydrocarbon. The latter affects the symmetry of the sulfate groups (negative band at 1385 cm^{-1}) leading to the appearance of positive bands at 1270 and 1138 cm^{-1} . A similar set of bands has been observed upon adsorption of water on sulfated zirconia [39] and is assigned to the split ν_3 mode of a bidentate sulfato complex of C_{2v} symmetry. Heating of the closed IR cell first at 453 K for 40 min (spectrum b) and then

at 523 K for 15 min (spectrum c) leads to decrease in the intensities of the absorption bands corresponding to the adsorbed hydrocarbon. This decrease is more pronounced after the treatment at 523 K. In the carboxylate region bands with growing intensities are detected. The band at 1667 cm^{-1} observed after heating at 453 K corresponds to $\nu(\text{C}=\text{O})$ stretching vibration of the carboxylic acid [49,50]. This, combined with the fact that there is an enhancement in the absorption in the $\nu(\text{OH})$ stretching region, leads to the conclusion that under these conditions, partial

oxidation of the adsorbed decane has occurred. Increasing the temperature to 523 K causes a noticeable increase of the intensity of the band at 1558 cm^{-1} (shifted to 1578 cm^{-1}) and appearance of a band at 1420 cm^{-1} . The latter is partially masked by the negative absorption at 1385 cm^{-1} due to sulfate groups perturbed by the water molecules produced (absorption at approximately 1640 cm^{-1}). The bands at 1578 and 1420 cm^{-1} are typical of acetate species [26–30]. However, formation of HCOO^- ions, which usually display their $\nu_{\text{as}}(\text{CO}_2^-)$ modes between 1600 and 1550 cm^{-1} [26–30,49,50], cannot be excluded. The $\nu_{\text{s}}(\text{CO}_2^-)$ modes could be offset by the negative band at 1385 cm^{-1} . The weak absorption at 2138 cm^{-1} reveals formation of CO adsorbed on copper(I) sites [7,18–22,43,51]. Since the experiment is performed in the absence of gaseous oxygen, the observed oxidation of the hydrocarbon is caused by surface oxide ions coordinated to Cu^{2+} ions. The spectrum in the carboxylate region obtained after heating at 523 K (Fig. 10, spectrum c) has a great similarity to that detected after interaction of decane at the same temperature with the NO_x pre-covered catalyst (Fig. 9). However, the NO_x -modified catalyst displays higher activity at 453 K (by comparing Fig. 9, spectrum c and Fig. 10, spectrum b) and, after heating at 523 K, oxidation of the adsorbed hydrocarbon is complete. The activity of the CuZ sample toward the oxidation of decane is somewhat lower than that of the CuZS catalyst and comparable to that of the NO_x -modified CuZ sample. These experimental facts demonstrate the role of the surface nitro–nitrate species as key intermediates in the reduction of NO by decane and the importance of their nature in the activation of the hydrocarbon.

4. Summary

The results of the present investigation show that the reactivity of the nitro–nitrate species formed on the surface of the CuZ and CuZS catalysts upon NO/O_2 adsorption toward the adsorbed decane is different. The nitro–nitrate species on the sulfated catalyst are able to interact completely with the hydrocarbon at temperatures up to 523 K, whereas, the sulfate-free catalyst contains quite stable bidentate nitro species, which are inert toward the adsorbed decane even after heating at 623 K. The latter species are formed

most probably by transformation of the bidentate nitrates upon heating of the NO_x pre-covered CuZ sample. Such a process is not observed to occur with the CuZS catalyst. This difference in the behavior of the surface nitrates can be associated with the different history of the formation of the nitro–nitrate structures on each catalyst. In the case of the CuZ sample, there are nitrates that are obtained by disproportionation of NO_2 (produced by oxidation of NO) with participation of the surface OH groups, whereas, this process does not take place on the sulfate-modified catalyst. Instead, only the surface acid–base pairs are involved. This results in different localization, which in conjunction with the enhanced acidity of the adsorption sites on the CuZS catalyst (due to presence of sulfate ions) decreases the stability and increases the reactivity of the NO_3^- species.

It should be noted that despite the different methods of catalyst preparation, the thermal stability of the nitro–nitrate species formed on the surfaces of pure and sulfated zirconia [33] and on the copper-containing catalysts studied parallels their activity in the SCR of NO with decane reported in the literature [5,6]. No activity below 773 K was detected on ZrO_2 and sulfated zirconia. In the case of the Cu/ ZrO_2 catalyst two temperature ranges have been distinguished: below 573 K, where N_2 was selectively formed and, above 673 K, where the main product was NO_2 . In contrast, the conversion of NO by reduction with decane in the presence of oxygen on Cu/ SO_4^{2-} - ZrO_2 is selective toward N_2 in the temperature range of 523–773 K [5,6]. The results of the present investigation show that at temperatures up to 523 K the nitrates and bridged nitro species formed on the surface of the CuZ catalyst are involved in oxidation of decane. Above this temperature, the bidentate nitro species start to decompose without the interaction with the hydrocarbon producing NO. The latter, in presence of oxygen, can be oxidized to NO_2 . This experimental fact can be related to the observed temperature dependence of the selectivity toward dinitrogen in the case of the sulfate-free copper-zirconia catalyst. It is suggested that the absence of stable nitro species on the surface of the sulfate-modified catalyst and the formation of highly reactive nitrates coordinated to Lewis acid sites with enhanced acidity ensure good activity and selectivity in a broader temperature range.

5. Conclusions

The nature of the NO_x species produced on NO adsorption and its co-adsorption with O_2 at room temperature on catalysts obtained by impregnation of zirconia with aqueous solutions of copper(II) nitrate and sulfate has been studied by means of in situ FT-IR spectroscopy. The adsorption of NO on both catalysts leads to formation of copper(II) nitrosyls. These species are stabilized on the surface of the CuZS catalyst through an induction effect from the sulfate ions coordinated in the vicinity of the adsorption sites. In addition, in the presence of the CuZ sample, disproportionation of NO with participation of the surface hydroxyl groups is observed to occur, leading to the formation of adsorbed nitrous acid, water molecules, nitro and nitrito species and anionic nitrosyls, NO^- . Due to the absence of terminal $\text{Zr}^{4+}\text{-OH}$ groups, this process does not take place on the CuZS catalyst.

On co-adsorption of NO and O_2 at room temperature, various kinds of surface nitrates are observed differing in the mode of their coordination. The NO_3^- species on the CuZ sample are obtained by disproportionation of NO_2 (produced by oxidation of NO) with participation of both surface hydroxyls and Lewis acid–base pairs, whereas, in the case of the CuZS catalyst only the latter sites are involved. This results in different localization, and in conjunction with the enhanced acidity of the adsorption sites on the CuZS catalyst, affects the stability and reactivity of the nitrates. Upon dynamic evacuation at higher temperatures, part of the bidentate and bridged nitrates on the CuZ catalyst transform into chelated nitro species. This process does not occur with the sulfate-containing catalyst. The nitrates on the CuZS catalyst are characterized by significantly lower thermal stability than the nitro–nitrate species on the CuZ sample. The difference in the thermal stability of the NO_x^- species (x is 2 and 3) parallels their reactivity toward the adsorbed decane. The sulfate-free catalyst contains bidentate nitro species that are inert toward the hydrocarbon. They start to decompose to NO at temperatures higher than 523 K. In contrast, the nitrate species formed on the CuZS catalyst are able to oxidize the adsorbed decane completely at 523 K producing acetates, formates, adsorbed CO and isocyanate species. It is proposed that the presence of stable nitro species on the sulfate-free copper(II)-zirconia

catalyst is associated with its non-selective behavior above 573 K in the reduction of NO with decane in an excess of oxygen reported in the literature.

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References

- [1] K.A. Bethke, D. Alt, M.C. Kung, *Catal. Lett.* 25 (1994) 37.
- [2] K.A. Bethke, M.C. Kung, B. Yang, M. Shah, D. Alt, C. Li, H.H. Kung, *Catal. Today* 26 (1995) 169.
- [3] H.H. Kung, M.C. Kung, *Catal. Today* 30 (1996) 5.
- [4] G. Delahay, B. Coq, E. Ensuque, F. Figueras, *Catal. Lett.* 39 (1996) 105.
- [5] F. Figueras, B. Coq, E. Ensuque, D. Tachon, G. Delahay, *Catal. Today* 42 (1998) 117.
- [6] G. Delahay, E. Ensuque, B. Coq, F. Figueras, *J. Catal.* 175 (1998) 7.
- [7] D. Pietrogiacomini, D. Sannino, S. Tuti, P. Ciambelli, V. Indovina, M. Occhiuzzi, F. Pepe, *Appl. Catal. B* 21 (1999) 141.
- [8] J. Pasel, V. Speer, C. Albrecht, F. Richter, H. Papp, *Appl. Catal. B* 25 (2000) 105.
- [9] V.A. Sadykov, R.V. Bunina, G.M. Alikina, A.S. Ivanova, T.G. Kuznetsova, S.A. Beloshapkin, V.A. Matyshak, G.A. Konin, A.Ya. Rozovskii, V.F. Tretyakov, T.N. Burdeynaya, M.N. Davydova, J.R.H. Ross, J.P. Breen, *J. Catal.* 200 (2001) 131.
- [10] D. Pietrogiacomini, D. Sannino, A. Magliano, P. Ciambelli, S. Tuti, V. Indovina, *Appl. Catal. B* 36 (2002) 217.
- [11] N. Mizuno, M. Yamamoto, M. Tanaka, M. Misono, *Bull. Chem. Soc. Jpn.* 64 (1991) 1383.
- [12] N. Mizuno, M. Yamamoto, M. Tanaka, M. Misono, *J. Catal.* 132 (1991) 560.
- [13] W.P. Dow, T.J. Huang, *J. Catal.* 147 (1994) 322.
- [14] W.P. Dow, T.J. Huang, *J. Catal.* 160 (1996) 171.
- [15] Y. Okamoto, H. Gotoh, *Catal. Today* 36 (1997) 71.
- [16] Y. Okamoto, H. Gotoh, H. Aritani, T. Tanaka, S. Yoshida, *J. Chem. Soc., Faraday Trans.* 93 (1997) 3879.
- [17] Y. Okamoto, T. Kubota, H. Gotoh, Y. Ohto, H. Aritani, T. Tanaka, S. Yoshida, *J. Chem. Soc., Faraday Trans.* 94 (1998) 3743.
- [18] G. Centi, G. Cerrato, S. D'Angelo, U. Finardi, E. Giamello, C. Morterra, S. Perathoner, *Catal. Today* 27 (1996) 265.
- [19] C. Morterra, E. Giamello, G. Cerrato, G. Centi, S. Perathoner, *J. Catal.* 179 (1998) 111.
- [20] G. Centi, G. Cerrato, S. D'Angelo, U. Finardi, E. Giamello, C. Morterra, S. Perathoner, *Catal. Today* 27 (1996) 265.

- [21] V. Indovina, M. Occhiuzzi, D. Petrogiacomì, S. Tuti, *J. Phys. Chem. B* 103 (1999) 9967.
- [22] V.A. Sadykov, R.V. Bunina, G.M. Alikina, A.S. Ivanova, D.I. Kochubei, B.N. Novgorodov, E.A. Paukshtis, V.B. Fenelonov, V.I. Zaikovskii, T.G. Kuznetsova, S.A. Beloshapkin, V.N. Kolomichuk, E.M. Moroz, V.A. Matyshak, G.A. Konin, A.Y. Rozovskii, J.R.H. Ross, J.P. Breen, *J. Catal.* 200 (2001) 117.
- [23] V.A. Sadykov, S.L. Baron, V.A. Matyshak, G.M. Alikina, R.V. Bunina, A.Y. Rozovskii, V.V. Lunin, E.V. Lunina, A.N. Kharlanov, A.S. Ivanova, S.A. Veniaminov, *Catal. Lett.* 37 (1996) 157.
- [24] B. Adelman, T. Beutel, G. Lei, W.M.H. Sachtler, *J. Catal.* 158 (1996) 327.
- [25] K. Hadjiivanov, D. Klissurski, G. Ramis, G. Busca, *Appl. Catal. B* 7 (1996) 251.
- [26] K. Shimizu, H. Kawabata, A. Satsuma, T. Hattori, *J. Phys. Chem. B* 103 (1999) 5240.
- [27] K. Shimizu, H. Kawabata, H. Maehima, A. Satsuma, T. Hattori, *J. Phys. Chem. B* 104 (2000) 2885.
- [28] F.C. Meunier, V. Zuzaniuk, J.P. Breen, M. Olsson, J.R.H. Ross, *Catal. Today* 59 (2000) 287.
- [29] M. Kantcheva, *J. Catal.* 204 (2001) 479.
- [30] M. Haneda, E. Joubert, J.-C. Menezes, D. Duprez, J. Barbier, N. Bion, M. Daturi, J. Saussey, J.-C. Lavalley, H. Hamada, *J. Mol. Catal. A* 175 (2001) 179.
- [31] K.I. Hadjiivanov, *Catal. Rev.-Sci. Eng.* 42 (2000) 71.
- [32] G. Delahay, B. Coq, E. Ensuque, F. Figueras, *Langmuir* 13 (1997) 5588.
- [33] M. Kantcheva, E.Z. Ciftlikli, *J. Phys. Chem. B* 106 (2002) 3941.
- [34] C. Morterra, G. Cerrato, *Phys. Chem. Chem. Phys.* 1 (1999) 2825.
- [35] H. Toraya, M. Yashmura, S. Simiyama, *J. Am. Ceram. Soc.* 67 (1984) C119.
- [36] C. Morterra, R. Aschieri, M. Volante, *Mat. Chem. Phys.* 20 (1988) 539.
- [37] G. Cerrato, S. Bordiga, S. Barbera, C. Morterra, *Appl. Surf. Sci.* 115 (1997) 53.
- [38] K.T. Jung, A.T. Bell, *J. Mol. Catal. A* 163 (2000) 27.
- [39] C. Morterra, G. Cerrato, F. Pinna, M. Signoretto, *J. Phys. Chem.* 98 (1994) 12373.
- [40] E. Laperdix, A. Sahibed-dine, G. Costentin, O. Saur, M. Bensitel, C. Nedež, A.B. Mohamed Saad, J.-C. Lavalley, *Appl. Catal. B* 26 (2000) 71.
- [41] T.M. Miller, V.H. Grassian, *Catal. Lett.* 46 (1997) 213.
- [42] S.-H. Huang, A.B. Walters, M.A. Vannice, *J. Catal.* 192 (2000) 29.
- [43] S. Bordiga, C. Pază, G. Berlier, D. Scarano, G. Spoto, A. Zecchina, C. Lamberti, *Catal. Today* 70 (2001) 91.
- [44] G.T. Palomiro, P. Fiscaro, S. Bordiga, A. Zecchina, E. Giamello, C. Lamberti, *J. Phys. Chem. B* 104 (2000) 4064.
- [45] J. Laane, J.R. Ohlsen, *Prog. Inorg. Chem.* 28 (1986) 465.
- [46] M.M. Kantcheva, V.P. Bushev, K.I. Hadjiivanov, *J. Chem. Soc., Faraday Trans.* 88 (1992) 3087.
- [47] K. Hadjiivanov, V. Bushev, M. Kantcheva, D. Klissurski, *Langmuir* 10 (1994) 464.
- [48] S. Holly, P. Sohar, in: L. Lang, W.H. Prichard (Eds.), *Absorption Spectra in the Infrared Region*, Akademiai Kiado, Budapest, 1975, p. 123.
- [49] G. Busca, J. Lamotte, J.-C. Lavalley, V. Lorenzelli, *J. Am. Chem. Soc.* 109 (1987) 5197.
- [50] M. Kantcheva, M.U. Kucukkal, S. Suzer, *J. Catal.* 190 (2000) 144.
- [51] M.M. Kantcheva, K.I. Hadjiivanov, A.A. Davydov, A.A. Budneva, *Appl. Surf. Sci.* 55 (1992) 49.
- [52] C.C. Cheung, M.C. Kung, *Catal. Lett.* 61 (1999) 131.