

Study of the surface evolution of nitrogen species on CuO/CeZrO₂ catalysts

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Abstract A series of CuO/CZ catalysts with different amounts of copper oxide were synthesized from copper nitrates by incipient wetness impregnation of the ceria–zirconia support. The structural, redox, acidic and adsorption properties were investigated using X-ray diffraction (XRD), BET, H₂ temperature programmed reduction (H₂-TPR), temperature programmed desorption of NO in the presence of oxygen (NO-TPD) and in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). The results have shown good catalytic activity for CuO/Ce_{0.62}Zr_{0.38}O₂ in NO oxidation to NO₂. Species such as nitrites and nitrates were formed on the surface. The transformation of nitrite compounds into nitrate was observed above 200 °C. From 300 up to 400 °C, decomposition of the surface nitrate to nitrite was discerned. Ammonia was adsorbed on the Lewis and Brønsted acid sites on Cu/CZ catalyst surface during temperature programmed reactions. The evolution of adsorbed NH₃ species to NH₂ surface group was confirmed by formation specific band of absorption at 1528 cm⁻¹.

Keywords TPD · TPR · DRIFTS · Cu/CZ · deNO_x · Ammonia

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Introduction

The exhaust gases from stationary and mobile combustion sources containing, among others, nitrogen oxides, i.e. NO and NO₂, are a major source of air pollution. These nitrogen oxides lead to photochemical smog, acid rain and ozone depletion [1, 2]. In order to decrease the NO_x emissions according to the environmental emission standards, a various catalytic methods have been developed, e.g. the three-way catalysts for gasoline fuelled vehicles, NO_x storage-reduction systems for lean burn engines or the selective catalytic reduction (SCR) processes for the large-scale combustion facilities [3–5]. The selective catalytic reduction of NO_x has been widely studied. The key roles in this process are played by both the catalyst and the reducing agent, which can be ammonia, urea or hydrocarbons. Ammonia is considered to be the most active in the selective catalytic reduction of NO_x (SCR-NH₃) [10].

Various catalysts such as zeolites, metal oxides and noble metal catalysts have been widely investigated in the deNO_x process [1, 4, 5]. These catalysts should be active in the interaction with NO and have properties to oxidize NO to NO₂, which is more favored to NO_x conversion under oxidizing conditions, such as the technique of the selective catalytic reduction of NO_x, especially with some N-containing as agents like ammonia or urea (NH₃-SCR) [6]. Unfortunately, all these catalysts exhibit a lot of disadvantages. For example commonly used commercial catalysts, e.g. V₂O₅-WO₃/MnO₃ or V₂O₅-WO₃/TiO₂, at high temperatures oxidize SO₂ to SO₃, which can give sulfuric acid and, as a consequence, result in corrosion and deposition of solid by-products downstream from the reactor, where the temperature is lower. Another disadvantage of V₂O₅ is its toxicity. The metal oxides, such as unsupported MnO_x or MnO_x/Al₂O₃ have low deNO_x selectivity to N₂ and produce great amounts of the N₂O. The noble metals, on the other hand, are expensive, suffer due to deactivation by poisoning with the sulfur compounds and have weak thermal stability, which leads to active phase aggregation. Other catalysts like zeolites have low hydrothermal stability [6–11]. A very promising alternative for the above mentioned catalysts is ceria–zirconia mixed oxide (CZ), which has attracted much attention of the researchers working on the NO_x reduction in the last 20 years. The main advantages of CZ are good stability and unique redox properties. The labile oxygen vacancies and bulk oxygen species with relatively high mobility are easily formed during the redox shift between Ce³⁺ and Ce⁴⁺ under oxidizing and reducing conditions, respectively. The pure CeO₂ is rarely used as a catalyst or support for NO_x reduction because it has poor thermal stability. The addition of ZrO₂ improves not only thermal stability but also the oxygen storage capacity and redox properties of ceria, upgrading the same its catalytic activity at lower temperatures. Furthermore, the addition of noble or transition metals (or their oxides) has a promotional effect on the redox properties and oxygen storage capacity of CZ [5, 12–14]. The catalytic activity of ceria–zirconia mixed oxides depends on the Ce/Zr ratio. Among a few Ce_xZr_(1-x)O₂ supports, the Ce_{0.62}Zr_{0.38}O₂ has been found to be the most active [15], and such support has been chosen as a support for the copper catalysts used in our studies.

The aim of our work is to prepare and characterize catalysts, which can be potentially used for NO_x removal via NH_3 -SCR. The ceria–zirconia supported copper catalyst ($\text{CuO}/\text{Ce}_{0.62}\text{Zr}_{0.38}\text{O}_2$) was synthesized with different copper loadings and characterized using the BET method and powder X-ray diffraction (XRD). The temperature programmed reduction of the catalysts with hydrogen (H_2 -TPR) was conducted in order to evaluate the variation of their redox properties. Acidic properties have been examined by the NH_3 adsorption. The catalysts have also been investigated for their ability to oxidize NO to NO_2 . According to the literature, NO_2 particles are preferentially reduced when the reaction is carried out in the presence of a reductant such as ammonia. For this purpose, the experiments of temperature programmed desorption of NO (NO-TPD) and NO oxidation to NO_2 were conducted. Additionally, for better understanding the structure and evolutions of species adsorbed on the catalyst surface, both experiments, i.e. NO-TPD and NO oxidation, were carried out in the DRIFT cell in controlled atmosphere.

Experimental

Catalysts preparation

The ceria–zirconia supported copper catalysts were prepared by the incipient wetness impregnation of the commercial $\text{Ce}_{0.62}\text{Zr}_{0.38}\text{O}_2$ (CZ), provided by Rhodia Electronics & Catalysts, with aqueous solutions of copper nitrate. After impregnation, the samples were dried at 120 °C for 12 h and then calcined at 550 °C for 2. The loading of copper was 2, 4 and 10 wt%. The obtained catalysts $\text{CuO}/\text{Ce}_{0.62}\text{Zr}_{0.38}\text{O}_2$ were denoted as $\text{Cu}(x)/\text{CZ}$, where x was the loading of Cu.

Characterization of the catalysts

The specific surface area (S_{sp}) of the support and studied catalysts was determined using the BET method. The S_{sp} was measured by nitrogen adsorption at 77.35 K on the ASAP 2010 apparatus. Prior to each measurement, the samples were degassed at 105 °C until the stable vacuum of 10^{-3} Pa was reached. The chemical compositions of the studied catalysts were obtained by ICP.

The X-ray diffraction (XRD) measurements were performed on the Siemens D5005 apparatus (Bruker-AXS) with CuK_α radiation, operating at 30 kV and 50 mA. The data were collected in the 2θ range of 10° – 90° . The phase identification was made using the JCPDS cards.

The experiments of temperature-programmed reduction (H_2 -TPR) were performed using 50 mg samples of the support and studied catalysts. The samples were reduced in hydrogen 5 % (v/v) H_2/Ar (flow 20 ml min^{-1}) from room temperature to 900 °C with the heating rate of 7.5 °C min^{-1} . The consumption of hydrogen was monitored by the thermal conductive detector.

The experiments of temperature-programmed desorption of NO (NO-TPD) were performed using a BELCAT-M apparatus. First, NO was adsorbed at room temperature in the presence of oxygen (500 ppm NO and 5 % (v/v) O_2/Ar) for

60 min. The NO-TPD experiment was carried out in flowing 5 % (v/v) O₂/Ar from RT to 500 °C with a heating rate of 4 °C min⁻¹. In all experiments, the total flow rate was 250 ml min⁻¹ and the gas hourly space velocity was 10,000 h⁻¹. The concentration of NO and NO₂ gas at the detector outlet was analyzed using NDIR detector.

The evolution of surface species on Cu/CZ catalysts during their interaction with 500 ppm of NO + 5 % vol. O₂/Ar at programmed temperature was studied. The in situ FTIR spectra of adsorbed species were recorded in the range of 4000–500 cm⁻¹ using a BIORAD FTS 165 spectrometer equipped with the high temperature environmental DRIFT cell. The total gas flow was 20 ml min⁻¹. In the first step, the samples were pretreated in flowing Ar at 400 °C for 0.5 h in order to remove water and other impurities from the catalysts surface. Then, the sample was cooled in Ar to the room temperature. The background spectra were collected from RT to 400 °C in flowing Ar. The spectra of catalyst surface in NO+O₂/Ar were also collected from RT to 400 °C after 20 min of isotherm in given temperature. The same procedure was performed during interaction catalyst surface with 500 ppm NH₃/Ar.

The DRIFTS spectra during the temperature programmed desorption of NO (NO-TPD) were recorded as follows: first, the reaction mixture (500 ppm of NO + 5 vol. % of O₂/Ar) was adsorbed on the catalyst surface at 20 °C for 60 min; then, the surface was purged with Ar for 30 min; and finally, the temperature was increased from RT up to 400 °C in flowing Ar. The spectra of catalyst surface were collected after 10 min of remaining at each temperature.

Before the experiments, each sample was calcined in air for 2 h at 500 °C with the rate of heating 10 °C min⁻¹ and cooled down to room temperature.

Results and discussion

Catalyst composition and specific surface area

The chemical composition and SSA of the support and obtained catalysts are presented in Table 1. It is observed that the specific surface area decreases with increasing copper content, which can be due to the sintering of ceria–zirconia, as a consequence of impregnation process and further calcination.

Table 1 Results of the textural analysis by N₂ adsorption/desorption and composition for CZ and catalyst

Catalysts reference	Composition (wt%)				S _{BET} (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)
	Ce	Zr	O	Cu		
CZ	53.3	21.27	25.43	0	138	0.32
Cu(2)/CZ	51.5	20.56	25.95	1.99	113	0.26
Cu(4)/CZ	49.5	19.76	26.85	3.89	109	0.25
Cu(10)/CZ	45.9	18.39	25.93	9.78	101	0.23

X-ray diffraction (XRD)

The ceria–zirconia solid solutions $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ exist in the three stable phases: monoclinic, tetragonal, cubic and two metastable phases [16]. Fig. 1 presents the XRD pattern of the studied support and catalysts. All the diffractograms show the main reflexes typical to a fluorite cubic structure. The reflections corresponding to (111), (200), (220), (311), (222), (400) and (420) planes are observed [17]. In addition, no segregation of the individual phases such as CeO_2 or ZrO_2 was detected, which can be due to the incorporation the Zr^{4+} cations into the ceria lattice. The radius of Zr is 0.084 nm and is smaller than the radius of Ce (0.097 nm). Such incorporation leads to formation of homogenous solid solutions [16, 18]. The XRD pattern of Cu(2)/CZ and Cu(4)/CZ (Fig. 1b and c) do not show any typical reflections of the CuO phase. It can be caused by the detection limits of this technique or due to high dispersion of the metal oxide phase. When the CuO content was increased to 10 wt% (Fig. 1d), the CuO crystallites formed agglomerates and the reflexes corresponding to (200), (111), (013), (022) and (222) planes of CuO were observed [19].

Temperature programmed reduction (H_2 -TPR)

Fig. 2 shows the H_2 -TPR profiles of the support and studied catalysts. The positions of the reduction peaks (T_{max}) and values of H_2 consumption are presented in

Fig. 1 XRD patterns of the support CZ (a) and catalysts: Cu(2)/CZ (b), Cu(4)/CZ (c) and Cu(10)/CZ (d)

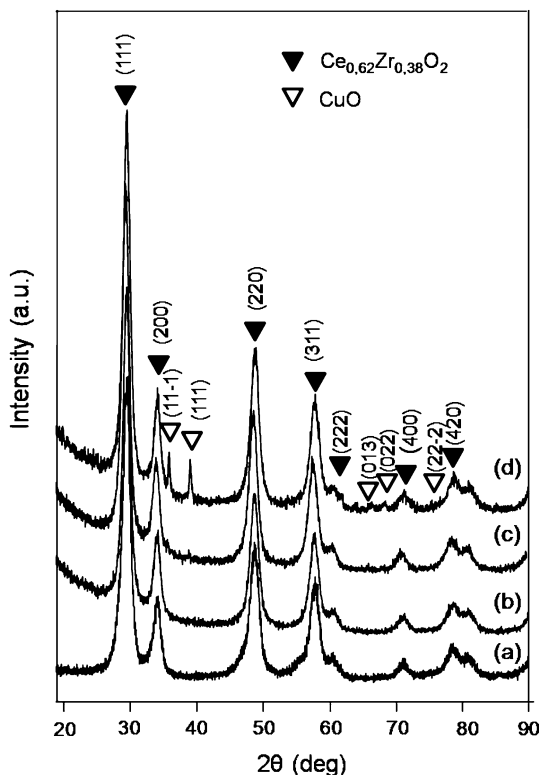
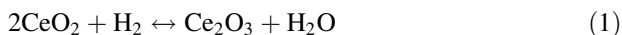


Table 2. The H₂-TPR profile of pure ceria–zirconia revealed the presence of two peaks at a temperature of 377 and 557 °C. These peaks suggest that the reduction of CZ occurs in two steps. At lower temperature, the surface ceria is reduced, whereas the reduction of bulk ceria occurs at higher temperature [12, 20]. The reduction of ceria Ce⁴⁺ occurs according to the following equation Eq. (1) [21]:



The oxygen anions are eliminated as water molecules and oxygen vacancies are formed, which promotes the mobility of oxygen from the bulk to the surface, according to Eq. 2, where V_o it is oxygen vacancy [22] The H₂ consumption arises only from the reduction of Ce⁴⁺ to Ce³⁺ because Zr⁴⁺ is the non-reducible cation [23].

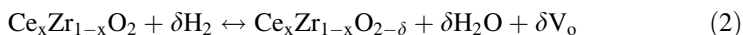


Fig. 2 shows the H₂-TPR profiles for the Cu/CZ catalysts. Each TPR profile can be divided into two reduction areas. The first area from 100 to 180 °C can be ascribed to the reduction of surface ceria or highly dispersed CuO. Moreover, the presence of copper oxide changes the shape of the support reduction curve and shifts the reduction into lower temperature. The second reduction area from 200 to 220 °C can be attributed to the reduction of copper oxide [21, 24], which occurs according to Eq. 3:



Additionally, the reduction of copper oxide requires the presence of a starting point such as an oxygen vacancy on the surface, which can be formed by the reduction of surface ceria [20]. Table 2 presents temperature of the reduction peaks (*T*_{max}) and values of H₂ consumption. The H₂ consumption is the smallest for the

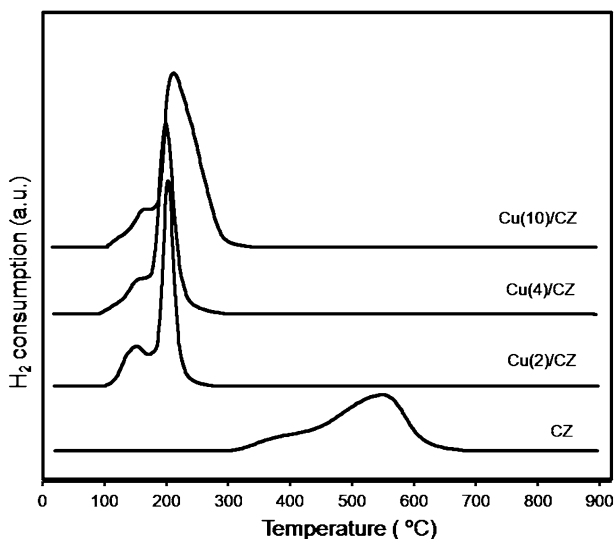


Fig. 2 H₂-TPR profiles of the support and Cu(2)/CZ, Cu(4)/CZ, Cu(10)/CZ catalysts

Table 2 H₂ consumption during H₂-TPR experiments

Catalyst	T_{\max} (°C)	H ₂ consumption (mmol g _{cat} ⁻¹)
CZ	557	0.76
Cu(2)/CZ	206	0.99
Cu(4)/CZ	203	1.34
Cu(10)/CZ	217	2.16

support, and addition of CuO leads to an increase in hydrogen consumption from Cu(2)/CZ to Cu(10)/CZ. Increasing redox properties with the increasing loading of Cu can be explained not only by the reducibility of CuO but also by the strong interaction between the copper and support. Copper is responsible for the increase of oxygen mobility. Therefore, the support is reduced at lower temperature and value of hydrogen consumption for catalysts is higher [23, 25].

Temperature programmed desorption of NO (NO-TPD) and in situ DRIFTS

The temperature programmed desorption of NO (NO-TPD) has been used for characterizing the support and catalysts from the point of view of NO activation on their surfaces. The NO-TPD experiments have been complemented by the in situ DRIFTS, which is extremely useful method for studying the binding states of adsorbed species. Fig. 3 and Table 3 show the NO-TPD curves and amounts of adsorbed and desorbed NO_x species for the studied catalysts. As shown in Fig. 3a, two peaks of NO₂ desorption occur for both the support and copper catalysts. The low temperature peaks may be ascribed to desorption of the weakly physisorbed NO₂ species. The high temperature desorption peaks may be attributed to the strongly adsorbed NO₂ species [26–28]. Analogously, two peaks of desorption are observed for the NO curve (Fig. 3b). It can be observed that the introduction of CuO to ceria–zirconia shifts the desorption peaks both for NO and NO₂ into lower temperature. The addition of the metal phase (CuO) shift a peaks of desorption to the lower temperature.

The amount of the adsorbed NO_x species per 1 g of catalyst increase with the addition of active phase and is the highest for Cu(4)/CZ. The lowest amount adsorbed NO_x species is for Cu(10)/CZ, which can be explained by the blocking of active sites in the CuO phase and, thus, the difficulty in the adsorption of NO_x species. Another reason can be explained by the formation of agglomerates by CuO, while for the catalyst with 2 and 4 % amount of copper CuO can be well dispersed and the active sites are more available for NO_x adsorption. It is interesting that the amount of adsorbed NO and desorbed NO_x species on the studied catalysts is different. These phenomena can be explained by strong chemical adsorption of NO on the catalyst surface. Therefore, completely desorption of adsorbed NO species is difficult to observing in studied region of the temperature.

The results of in situ DRIFTS spectra Cu(10)/CZ during NO by O₂ at the catalyst surface at the temperatures ranging from RT to 400 °C are shown in Fig 4. According to Hadjiivanov [29] and other authors [30–32], nitrogen oxides can be

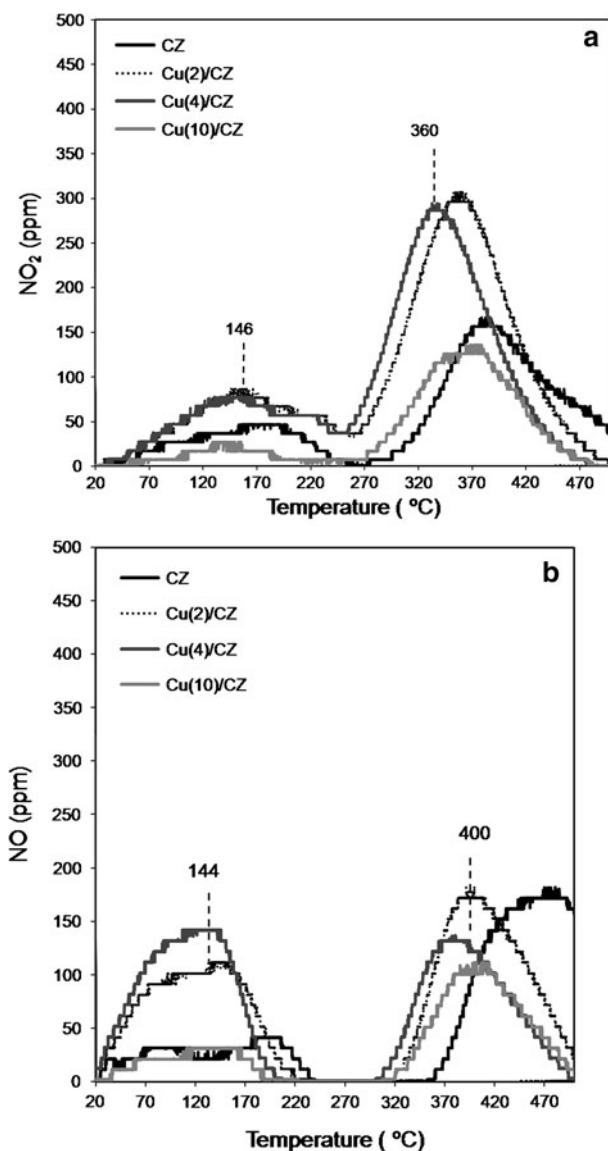


Fig. 3 NO₂ (a) and NO (b) evolution during NO-TPD carried out in the presence of 500 ppm NO, 5 % O₂ on CZ and Cu(2)/CZ, Cu(4)/CZ, Cu(10)/CZ catalysts

adsorbed on the catalyst surface forming nitrite (NO₂⁻) or nitrate (NO₃⁻) anions. When NO₂⁻ and NO₃⁻ ions are coordinated with cations by one or two of its oxygen atoms, the corresponding species are called nitrito and nitrato species, respectively. Nitrite (NO₂⁻) and nitrate (NO₃⁻) species can be monodentate, bidentate or bridging. Generally, the presence of bands at 1470–1375 cm⁻¹ (ν N=O) and 1206–1065 cm⁻¹ (ν N–O) corresponds to monodentate nitrito species.

Table 3 The amount of adsorbed at RT and desorbed NO per 1 g of catalyst

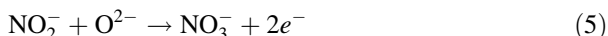
Catalyst	Amount of adsorbed NO species ($\mu\text{mol g}_{\text{cat}}^{-1}$)	Amount of desorbed NO_x species ($\mu\text{mol g}_{\text{cat}}^{-1}$)	Percent of desorbed NO_x species (%)
CZ	252	223	88.5
Cu(2)/CZ	304	290	95.5
Cu(4)/CZ	365	329	90.1
Cu(10)/CZ	211	178	84.2

Consequently, the bands at 1378 and 1453 cm^{-1} , which are observed in Fig. 4, can be attributed to nitrite species. These bands are observed up to 200 °C, and they decrease at higher temperatures. Simultaneously, absorptions at 1528, 1609 cm^{-1} (ν_3 (N–O)), indicate formation of monodentate and bridging nitrato species. The bands at 1239 and 1196 cm^{-1} can be attributed to the nitrate or nitrite species. Hence, nitrites and nitrates are formed at low temperatures.

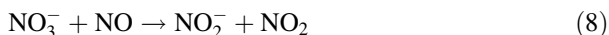
The surface oxygen interacts with NO from the gas phase to yield nitrite, which is related to electron transfer to the surface of catalyst [30]:



The formation of some NO_3^- species at lower temperature may involve the surface reaction between the nitrite species with oxygen from the surface, Eq. 5, or as the result of the disproportionation of nitrite species, Eq. 6:



The electrons in Eqs. 4 and 5 participate in the reduction of the active phase. When the temperature is increased, nitrites are transformed to nitrates. Consequently, nitrates can be decomposed to NO_2 , Eq. 7, or can react with NO from the gas phase, which results in nitrite and NO_2 species, Eq. 8.



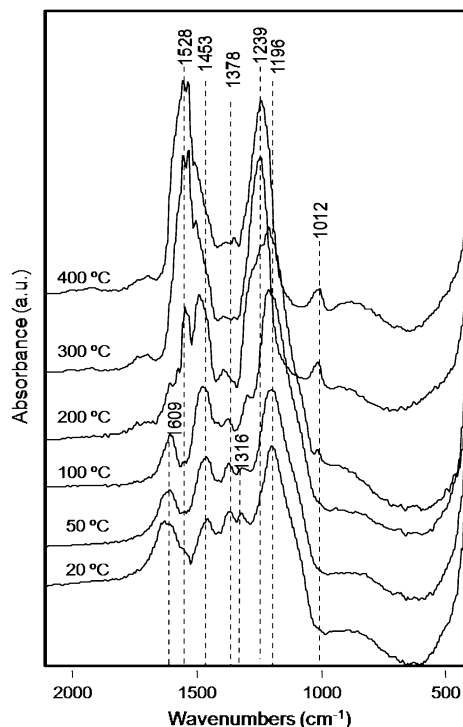
At high temperature, the NO_2 species are decomposed to NO according to thermodynamic equilibrium, Eq. 9.



This can explain the presence of bands coming from NO_2^- and NO_3^- surface species (Figs. 4, 5) and the presence of NO and NO_2 on NO-TPD profile (Fig. 3) [30, 32].

The above results were confirmed by DRIFTS studies of Cu/CZ catalysts during NO-TPD. The NO-TPD experiments were preceded by the adsorption of $\text{NO} + \text{O}_2/\text{Ar}$. The DRIFTS spectra during NO-TPD (Fig. 5) revealed the presence of bands at 1475 cm^{-1} , which can be assigned to stretching vibrations of N–O bond in

Fig. 4 DRIFTS spectra of Cu(10)/CZ surface during adsorption of the 500 ppm NO, 5 % O₂



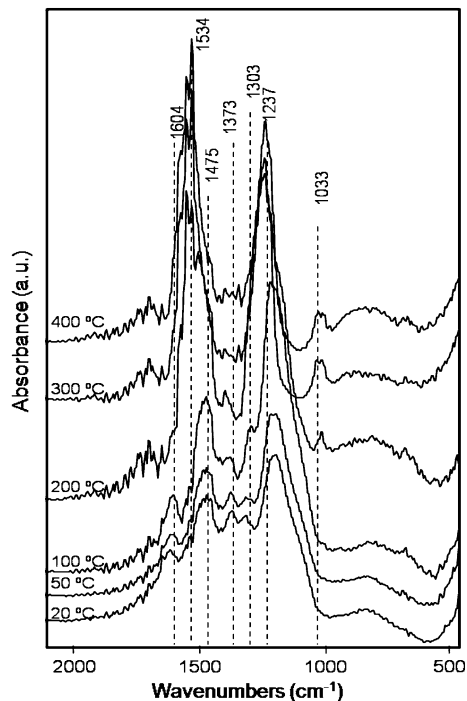
NO₂⁻ structure. The intensity of these bands increases with temperature up to 200 °C and then decreases. Simultaneously, three bands at 1534, 1237 and 1033 cm⁻¹ are shown. Their intensities are low below 200 °C but they increase significantly above this temperature. The DRIFTS spectra of Cu(10)/CZ during NO-TPD have shown that nitrites transform into nitrates when temperature increases. Moreover, the highest rate of the formation of surface nitrates is observed from 200 to 300 °C. It is due to thermodynamic limitation, because simultaneously nitrates decompose into nitrites above 300 °C. Hence, further increase of absorptions up to 400 °C for bands at 1534, 1237 cm⁻¹ is practically not observed.

DRIFTS of NH₃ adsorption

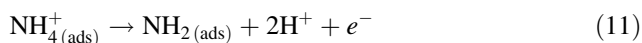
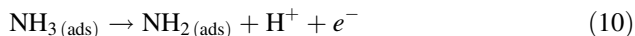
Because ammonia is considered as an active reductant in process of NO_x reduction, it is important to know in which way ammonia interacts with the catalyst surface. It is well known that one of the methods for determined adsorption ammonia and surface acidity is DRIFT [31].

The DRIFT spectra of adsorbed species on the Cu/CZ surface resulting from ammonia adsorption at different temperatures are shown in Fig. 6. According to many authors, adsorption of ammonia can proceed at the Brønsted or Lewis acid sites, forming NH₄⁺ or adsorbed NH₃ [33, 34]. When ammonia is adsorbed on the Brønsted acid sites, the bands in the 1480–1395 cm⁻¹ region of absorption can be

Fig. 5 DRIFT spectra of Cu(10)/CZ surface after adsorption of the 500 ppm NO, 5 % O₂



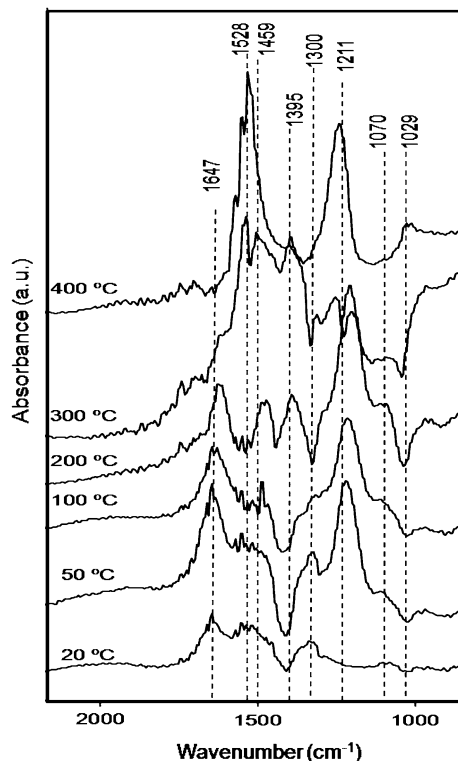
observed [2, 10, 34]. Thus, the bands at 1459 and 1395 cm⁻¹ for Cu(10)/CZ are attributed to these ammonia species. The absorption bands assigned to the ammonia adsorbed on the Lewis acid sites are observed at 1211 and 1647 cm⁻¹ [2, 10, 33]. For the Cu(10)/CZ catalyst, the bands at 1647 cm⁻¹ disappear at 200 °C, whereas absorptions band at 1211 cm⁻¹ increase up to 400 °C. During the temperature programmed surface reaction of the Cu(10)/CZ catalyst with ammonia, the bands corresponding to NH₃ adsorbed on the Lewis and Brønsted acid strength decrease. Therefore, new bands at 1528 cm⁻¹ are observed and they can be attributed to the NH₂ species. We proposed the formation of NH₂ species on the catalysts surface as the results of H or 2H abstraction from coordinated NH₃ or NH₄⁺ on the catalyst surface, respectively, Eqs. 10 and 11 [2, 10, 33].



The electrons forming in the above reactions are transfer to the surface of catalyst. The absorption assigned to the coordinated NH₃ species are observed at 1300 cm⁻¹ and other bands, appearing at 1070–1020 cm⁻¹ region and can be assigned to the adsorption of ammonia on the surface oxygen atoms via hydrogen bonding [33].

The surface acidity was confirmed by the adsorption of ammonia both on the Lewis and Brønsted acid sites. Moreover, during temperature programmed surface

Fig. 6 DRIFT spectra of Cu(γ10)/CZ surface during adsorption of the 500 ppm NH₃



reaction these acid sites have been disappeared and the band new absorptions of NH₂ species are formed.

Conclusions

The CuO/CZ catalysts with different amounts of copper oxide were synthesized. The structural, redox, acidic and adsorption properties were investigated. Surface acidity was studied by DRIFT spectra of the adsorbed NH₃ species. The ammonia was adsorbed on the Lewis and Brønsted acid sites and it was transformed into the NH₂ species when temperature was increased. From the NO-TPD results, it was calculated that the amount of adsorbed NO species increased after addition of the copper. It was the highest for Cu(4)/CZ. The CuO could be well dispersed in the case of Cu(4)/CZ catalyst. For this metal loading, the active sites are more available for NO adsorption than for Cu(10)/CZ catalyst, in which CuO can form agglomerates, and consequently it is difficult to adsorb NO species. The presented work has shown that the ceria–zirconia supported copper catalysts are able to oxidize NO to NO₂ even at low temperature. It can be explained by the strong oxidizing properties of the surface oxygen of ceria–zirconia. From the DRIFT spectra, it was observed that NO can adsorb on the catalysts surface to form

nitrate and nitrite species. Nitrites are formed by electron transfer from NO to the catalyst and they are transformed to nitrate species via oxygen transfer promoted later in presence of NO₂. The nitrite species are subsequently transformed into nitrates when temperature increases up to 300 °C. The rate of surface nitrate formation also increases with temperature. Above 300 °C, the absorption bands of the nitrates disappear because of their decomposition to nitrites which are due to thermodynamic limitations. The results of DRIFT spectroscopy were consistent with the results of NO-TPD experiments. By the observation of the functional groups evolution, several surface reactions have been proposed.

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