In situ FT-IR investigation of the reduction of NO with CO over Au/CeO$_2$-Al$_2$O$_3$ catalyst in the presence and absence of H$_2$

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ABSTRACT

The NO + CO + H$_2$ reaction over CeO$_2$, Au/CeO$_2$ (3 wt% Au), Au/CeO$_2$-Al$_2$O$_3$ (2.9 wt% Au, 20 wt% Al$_2$O$_3$) and CeO$_2$-Al$_2$O$_3$ mixed support prepared by co-precipitation has been studied by FT-IR spectroscopy at elevated temperatures. Formation of NCO species has been detected on all of the samples. The presence of metallic gold is not necessary for the generation of the isocyanates on ceria and the mixed ceria-alumina support. The NCO species are produced by a process involving the dissociation of NO on the oxygen vacancies of the support, followed by the reaction between N atoms lying on the surface and CO molecules. Gold plays an important role in the modification of ceria leading to Ce^{3+} and oxygen vacancies formation, and causes significant lowering of the reduction temperature of CeO$_2$ and CeO$_2$-Al$_2$O$_3$ enhancing the reducibility of ceria surface layers. The role of H$_2$ is to keep the surface reduced during the course of the reaction. The onset temperature, at which the interaction between the surface isocyanates and NO begins, is low (100 °C). This explains the high activity of the Au/CeO$_2$-Al$_2$O$_3$ catalyst with 100% selectivity in the reduction of NO by CO at low temperature (200 °C) and in the presence of H$_2$.

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1. Introduction

Nanosized gold clusters have attracted a great deal of interest as a new type of catalysts for reduction of NO with H$_2$, CO or hydrocarbons [1–8]. These materials possess high activity at low temperatures, which is preserved in the presence of steam [3,6–8]. This makes the performance of gold catalysts suitable for application during the cold start of the vehicles.

Recently, some of us reported results on the reduction of NO with CO over gold deposited on ceria and mixed ceria-alumina supports prepared by co-precipitation (CP) [6] or mechanochemical activation (MA) [7]. The highest conversion of NO and CO was observed in the presence of 3% Au/CeO$_2$ catalyst. The modification of ceria with alumina decreased the activity, but increased the stability of the gold catalysts by hindering the agglomeration of gold and ceria particles. It has been established that the catalysts prepared by CP exhibited higher catalytic activity in the reduction of NO by CO than those obtained using the MA method. For both methods of synthesis, the CeO$_2$-Al$_2$O$_3$-based catalysts with higher amount of Al$_2$O$_3$ showed higher catalytic activity. The addition of hydrogen to the feed led to the enhancement of both NO and CO

conversions [6,8]. The Au/CeO$_2$-Al$_2$O$_3$ catalyst containing 2.9 wt% Au and 20 wt% Al$_2$O$_3$ exhibited high and stable activity with 100% selectivity toward N$_2$ at 200 °C.

The IR spectroscopic studies performed on the NO + CO reaction on supported noble metals revealed the formation of NCO species [1,9–18]. It is believed that their generation takes place on the metal sites by reaction between adsorbed CO and N atoms that are formed as a result of NO dissociation [1,9–16]. It has been also proposed that after their formation, the NCO species migrate from the metal sites on the support, where they are stabilized [11–19]. The results of the IR studies on supported gold catalysts are controversial. Salama et al. [1] observed NCO species over Au(I)/NaY catalyst only when hydrogen was present in the CO + NO reaction mixture. They concluded that the hydrogen promotes the NO dissociation. No isocyanate species were detected in the reaction of pre-adsorbed CO with gaseous NO on Au/SiO$_2$, Au/MgO [20] and Au/TiO$_2$ [21]. Debeila et al. [21] concluded that the high NO pressure and the low temperature used in the investigation of Au/TiO$_2$ did not favor the NO dissociation. This conclusion agreed with the results of Solymosi et al. [12]. They found that in the range of 300–500 °C the extent of NO decomposition on supported gold catalysts (Au/Al$_2$O$_3$, Au/TiO$_2$, Au/MgO and Au/SiO$_2$) was very small, ca. 0.4–0.7%. However, Solymosi et al. assumed that CO accelerated greatly this process by removing the adsorbed atomic oxygen. The formation of NCO species upon NO + CO adsorption on these

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catalysts was observed at 300–350 °C. The positions of the absorption bands indicated that the isocyanates were formed on metallic Au followed by migration on the support, where they accumulated. This has been confirmed by the fact that no NCO species were produced during the NO + CO adsorption on the Au-free oxides. Solymosi et al. [12,15] concluded that the behavior of Au-supported catalysts in the NO + CO reaction is similar to that of supported platinum-group metals.

Regarding the NO + CO adsorption on reduced CeO_2, no NCO species were observed at temperatures between 100 and 300 °C [13]. On the other hand, the exposure of γ-Al_2O_3 modified by 20% of CeO_2 to NO + CO mixture at 400 °C led to the appearance of surface isocyanate species [16]. However, the mechanism of their formation was not provided.

To the best of our knowledge there are no reports dealing with the mechanism of NO + CO reaction over Au-promoted CeO_2-Al_2O_3 catalysts. In the present paper, we describe the results of in situ FT-IR experiments performed at elevated temperatures using NO + CO and NO + CO + H_2 mixtures. Subjects of the investigations were Au-free and Au-promoted CeO_2 and CeO_2-Al_2O_3. As mentioned above, the CeO_2-based catalyst containing 20 wt% of Al_2O_3 and 2.9 wt% of Au showed 100% selectivity towards N_2 at 200 °C [6]. Moreover, the catalytic activity of the sample was higher when the hydrogen content in the feed was higher. This fact is particularly interesting taking into account that the hydrogen is not a very effective reducing agent of NO at low temperatures over supported gold catalysts [1,3,4,22]. The same conclusion has been reached while studying the reduction of NO with CO in the presence of H_2 over gold supported on ceria-alumina [7]. The aim of this investigation was to obtain information about the role of each component of the catalytic system in the reduction of NO by CO and to clarify the effect of H_2 on the enhancement of the reduction process by gaining insights into the NO + CO reaction mechanism.

2. Experimental

CeO_2 was synthesized by precipitation from aqueous solutions of $Ce(NO_3)_3 \cdot 6H_2O$ and K_2CO_3 at 60 °C and pH 9.0. The obtained precipitate was washed thoroughly with deionized water and after drying, was calcined at 400 °C for 2 h. Mixed ceria-alumina support was prepared by co-precipitation. Gold was loaded on CeO_2 and CeO_2-Al_2O_3 by deposition-precipitation method. Details on the synthesis are given elsewhere [6]. The analytical gold content in CeO_2 is 3.0 wt% (sample notation AuCe). The CeO_2-Al_2O_3 mixed oxide support contains 20 wt% of alumina (the sample is denoted as CeAl20) and the analytical content of gold in the Au-promoted sample is 2.9 wt% (sample notation AuCeAl20). The results of sample characterization by means of XRD, TPR, XPS, Raman spectroscopy and catalytic activity measurements of the reduction of NO with CO have been reported previously [6].

The FT-IR spectra were recorded on a Bomem MB 102 FT-IR spectrometer equipped with a liquid-nitrogen cooled MCT detector at a resolution of 4 cm^{-1} (128 scans). The self-supporting discs (0.02 g/cm^2) were activated in situ. Since before the catalytic activity measurements [6], the AuCeAl sample was pretreated using 5% H_2 in helium for 30 min at 120 °C, we choose an activation procedure consisting of two steps: (i) treatment of the sample in atmosphere of 100 mbar of oxygen at 400 °C for 1 h, followed by evacuation of the oxygen for 30 min at 120 °C and cooling to room temperature (O_2-pretreated sample) and (ii) subsequent exposure of the sample to 10 mbar of hydrogen for 30 min at 120 °C followed by evacuation at the same temperature and cooling to room temperature (H_2-pretreated sample). The spectrum taken at room temperature after the first step of activation has been used as a background reference. The sample holder of the IR cell can be moved up and down relative to the light beam for detection of the gas phase spectra. The FT-IR spectra of the samples (except those shown in Fig. 1) are obtained by subtracting the spectra of the O_2-
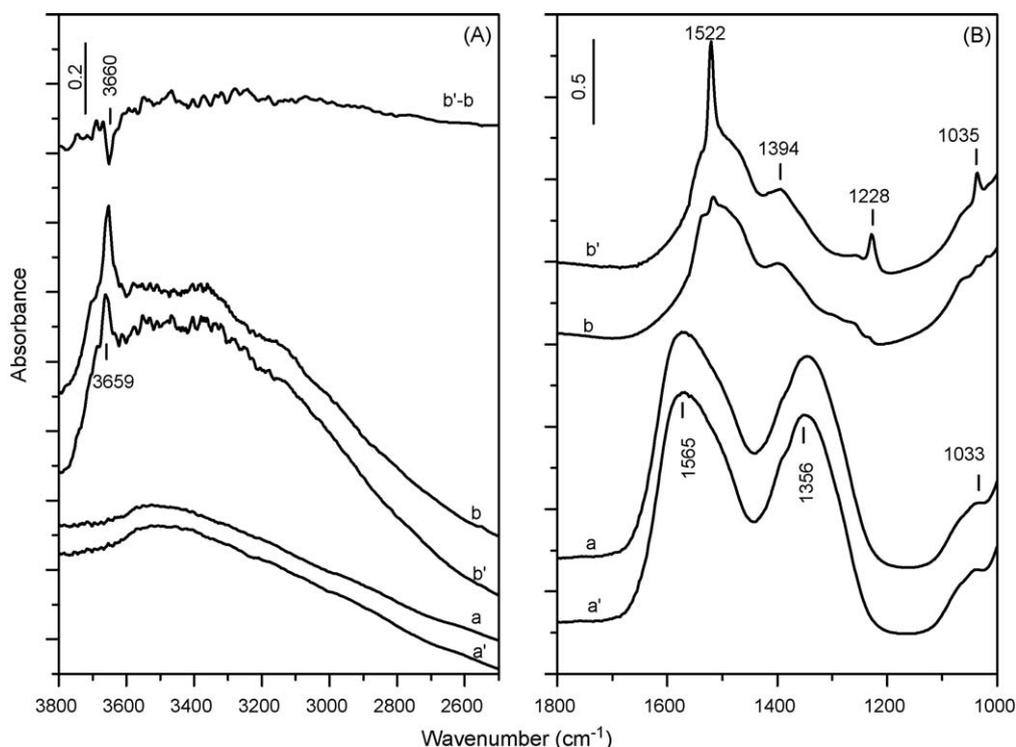
Fig. 1. FT-IR spectra of the activated CeAl20 and AuCeAl20 samples in the OH stretching (Panel A) and carbonate-nitrate regions (Panel B): O_2-pretreated CeAl20 (a), H_2-pretreated CeAl20 (a′), O_2-pretreated AuCeAl20 (b) and H_2-pretreated AuCeAl20 (b′).

activated samples taken at room temperature from the spectra recorded. The sample spectra are also gas-phase corrected.

The NO gas (99.9%) was supplied by Air Products. The purities of H_2 and CO were 99.9% and 99.95% (BOS, Istanbul), respectively. Both gases were passed through a trap cooled in liquid nitrogen before admission to the IR cell. The ^{13}CO supplied by CIL contained 99% ^{13}C.

3. Results and discussion

3.1. FT-IR spectroscopic characterization of the activated samples

The spectra of the CeAl20 and AuCeAl20 samples obtained after steps 1 and 2 of the activation procedure are shown in Fig. 1. The broad band in the 3800–3000 cm^{-1} region observed on the O_2-activated CeAl20 sample corresponds to H-bonded OH groups (Fig. 1A, spectrum a). The treatment with H_2 at 120 °C does not affect considerably the intensity of this absorption (Fig. 1A, spectrum a′). After the introduction of gold, the hydroxyl coverage increases (compare spectra a and b in Fig. 1A). The reason for this could be associated with the presence of larger amount of defects in the Au-containing sample [6], which serve as coordination sites of surface OH groups. Higher surface hydroxylation caused by gold particles as compared with the pure support, has been already reported for Au/Fe_2O_3 catalysts used in the low-temperature WGS reaction [23,24]. The spectrum of the AuCeAl20 sample after the activation with oxygen (Fig. 1A, spectrum b) displays a sharp band at 3659 cm^{-1} characteristic of OH species bridging two Ce^{4+} ions [25]. The treatment of the sample with H_2 at 120 °C results in noticeable increase in the absorption due to H-bonded hydroxyls and decrease in the intensity of the bridged OH groups (Fig. 1A, spectra b′ and b′–b). The observed changes suggest that some reduction of the surface took place during step 2 of the activation procedure. The bands in the 1800–1000 cm^{-1} region (Fig. 1B) indicate the presence of residual nitro-nitrate and carbonate-carboxylate structures originating from the precursors used for sample preparation. The amount of these species in the CeAl20 sample is not affected by the reductive activation at 120 °C. In contrast, this treatment leads to strong decrease in the intensities of the bands at 1522, 1228 and 1035 cm^{-1} on the AuCeAl20 sample (Fig. 1B, spectra b and b′) indicating that the residual impurities characterized by these absorptions undergo reduction.

The presence of a very weak band at 2132 cm^{-1} in the spectrum of the AuCeAl20 sample detected at room temperature after the pre-treatment with H_2 at 120 °C (Fig. 2, spectrum a) confirms that some reduction occurred during step 2 of the activation procedure. This band corresponds to the forbidden $^2F_{5/2} \rightarrow {}^2F_{7/2}$ electronic transition of surface and subsurface Ce^{3+} ions [26]. The absorption increases in intensity and shifts to lower frequency (2126 cm^{-1}) after the reduction of the AuCeAl20 sample at 350 °C with 10 mbar of H_2 for 60 min (Fig. 2, spectrum b), which supports the assignment of the band at 2132–2126 cm^{-1} to reduced Ce^{3+} sites.

3.2. High-temperature adsorption of CO + H_2

Heating the CeAl20 and AuCeAl20 samples for 15 min in the isolated IR cell in the 200–350 °C temperature range in the atmosphere of CO and H_2 causes the appearance of growing positive bands in the 1600–1000 cm^{-1} region (Fig. 3, panels A and B). Simultaneously, formation of gaseous CO_2 is detected at the expense of CO, as illustrated with the spectra of the gas phase over the AuCeAl20 sample (Fig. 3C). This indicates that the samples promote the oxidation of CO to CO_2, which leads to the formation of various surface carbonate-carboxylate structures. The amount of
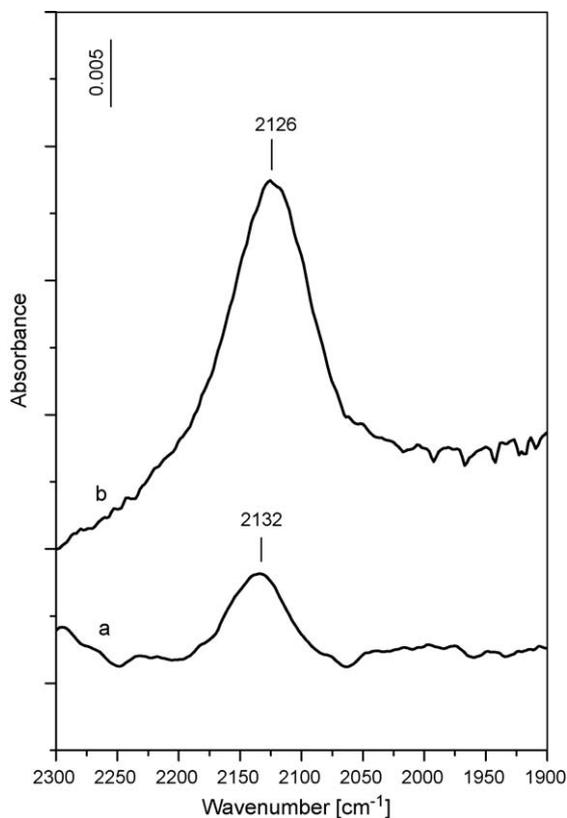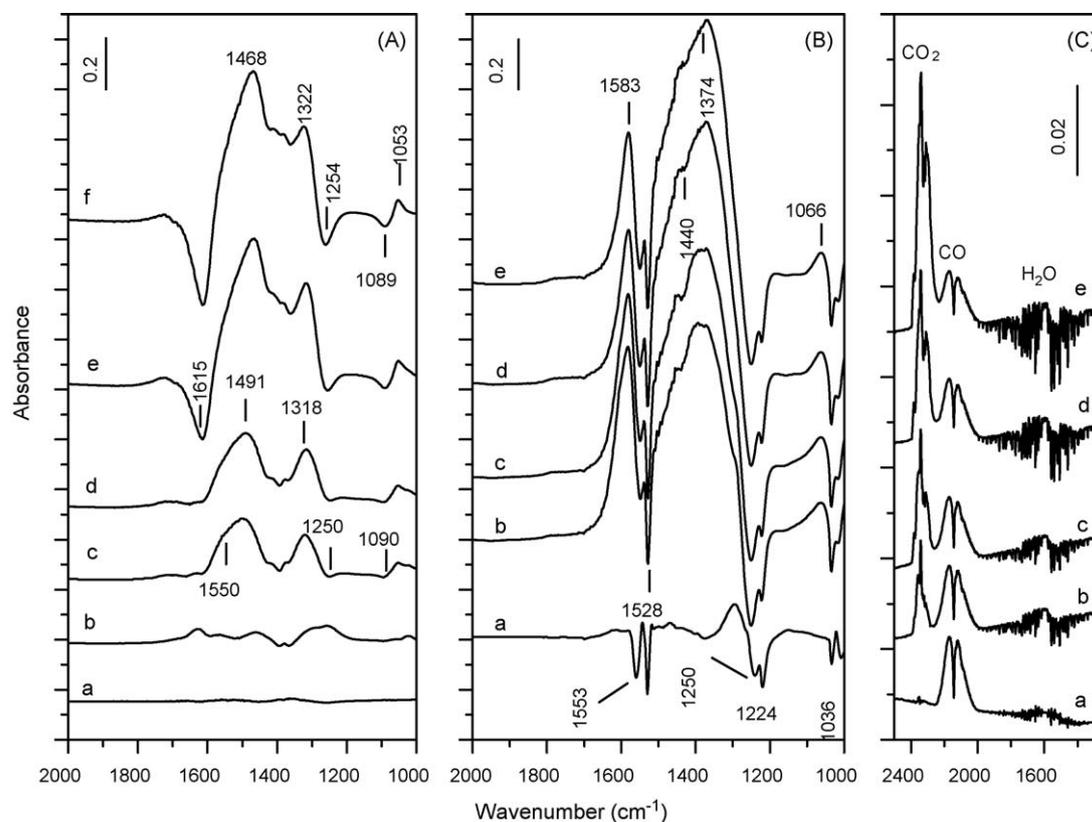

Fig. 2. FT-IR spectra of the AuCeAl20 sample in the 2300–1900 cm^{-1} region detected at room temperature after step 2 of the activation procedure, the pre-treatment with H_2 at 120 °C, (a) and after reduction at 350 °C with 10 mbar of H_2 for 60 min (b). The spectrum taken at room temperature after the first step of activation has been used as a background reference.

the carbonate-carboxylate species is larger on the Au-containing sample than on the Au-free one.

The presence of negative bands at 1615, 1254 and 1089 cm^{-1} in the spectrum of the CeAl20 sample taken at 350 °C (Fig. 3A, spectrum e) indicates that at this temperature the CO + H_2 mixture reduces the species associated with these absorptions. This process begins at 250 °C, which is evident by the appearance of weak negative bands at 1250 and 1090 cm^{-1} (Fig. 3A, spectrum c). As mentioned above, the reductive activation of the AuCeAl20 sample at 120 °C causes decrease in the concentration of residual species giving rise to the absorption bands in the 1800–1000 cm^{-1} region. The spectrum obtained at room temperature upon CO + H_2 atmosphere (Fig. 3B, spectrum a) shows that the altered species exhibit negative bands at 1553, 1528, 1250, 1224 and 1036 cm^{-1}. The subtraction spectra (not shown) reveal that the reduction of the residual impurities in the presence of gaseous mixture containing 10 mbar of CO and 3 mbar of H_2 is completed at 200 °C. The negative absorptions at 1615, 1254 and 1089 cm^{-1} (CeAl20) and at 1553, 1528, 1250, 1224 and 1036 cm^{-1} (AuCeAl20) are assigned to residual nitrates originating from the precursor nitrate compounds used for the catalyst preparation. Arguments for assignment of these bands to nitrate species are given below. It should be noted that the positions of the bands in the 1800–1000 cm^{-1} region do not correspond to the actual band positions of the corresponding species due to overlap of the positive and negative bands. The gas phase spectra (Fig. 3C) show also that the amount of water vapor detected in the 200–350 °C temperature range has increased which indicates that oxidation of the hydrogen takes place as well.

Fig. 3. FT-IR spectra in the 2000–1000 cm^{-1} region collected during exposure of the CeAl20 (Panel A) and AuCeAl20 samples (Panel B) to a (10 mbar CO + 3 mbar H$_2$) mixture at 25 °C (a), 200 °C (b), 250 °C (c), 300 °C (d), 350 °C (e) and under dynamic evacuation at 350 °C (f). Panel C: Spectra of the gas phase detected in the presence of the AuCeAl20 sample at various temperatures.

It should be noted that the extent of reduction of the residual nitrates increases with the pressure of hydrogen. We were not able to eliminate completely the impurities after three consecutive reduction/oxidation cycles at 400 °C using 50 mbar of H$_2$ and 100 mbar of O$_2$. Because this extensive activation procedure lowered the dispersion of gold (which was evident from the intensity of Au^0–CO band), we adopted the activation procedure described above that resembles the pretreatment of the samples made before the catalytic activity measurements as reported in reference [6].

The spectra of the samples in the 2300–2000 cm^{-1} region are shown in Fig. 4. In the case of the Au-free CeO$_2$-Al$_2$O$_3$ (Fig. 4A), no absorption bands are detected at temperatures below 250 °C. The spectrum taken at 250 °C shows the appearance of a weak absorption at 2165 cm^{-1} with shoulder at approximately 2130 cm^{-1} (Fig. 4A, spectrum c). The latter band corresponds to the Ce^{3+} electronic transition [26]. A noticeable increase in the intensities of the bands at 2165 and 2130 cm^{-1} and appearance of weak absorption at approximately 2230 cm^{-1} are detected at 350 °C (Fig. 4A, spectrum e). The evacuation at the same temperature does not change the intensities of the bands at 2165 and 2130 cm^{-1}, whereas the absorption at ~2230 cm^{-1} almost disappears (Fig. 4A, spectrum f).

The weak band at 2112 cm^{-1}, observed in the spectrum of the Au-containing sample taken at room temperature (Fig. 4B, spectrum a), is characteristic of CO adsorbed on Au^0 [27–29]. Under these conditions, we did not detect absorptions corresponding to CO adsorbed on Ce$^{4+/3+}$ and Al^{3+} sites which are expected to be positioned at 2170–2150 cm^{-1} [28–32] and 2240–2000 cm^{-1} [32], respectively. The poorly resolved shoulder at approximately 2130 cm^{-1} of the Au^0–CO band corresponds to the Ce^{3+} electronic

transition. It is important to note that this transition on pure ceria is observed after the reduction with hydrogen at temperatures higher than 350 °C [26]. The fact that the absorption at 2130 cm^{-1} in the case of the CeAl20 sample is detected at 250 °C indicates that the modification of ceria with alumina increases the reducibility of CeO$_2$. The promotion of CeAl20 by gold further decreases the reduction temperature of Ce^{4+} ions and the electronic absorption band is detected after the pretreatment of the AuCeAl20 sample at 120 °C with hydrogen (see also Fig. 2). It should be noted that gold exerts strong modifying effect on ceria, which is manifested by the formation of oxygen vacancies and Ce^{3+} ions [33]. The observed lowering of the reduction temperature of both CeAl20 and AuCeAl20 is in agreement with the results of TPR published earlier [6].

The interaction of the AuCeAl20 sample with CO + H$_2$ mixture in the 150–300 °C temperature range (Fig. 4B) leads to the formation of absorptions at 2236 and 2168 cm^{-1} analogous to those observed on the CeAl20 sample, however, with higher intensities. Alexeev et al. [16] detected similar band at 2230 cm^{-1} during the adsorption of CO/He mixture on Pd^{n+}/Ce^{n+}/Na$^+$/γ-Al$_2$O$_3$ at 400 °C. They attributed this band to CO adsorbed on coordinatively unsaturated Al^{3+} cations. Because under the same conditions the band at 2230 cm^{-1} was absent on the Pd-free samples, the authors concluded that Pd plays an important role for the formation of the Al^{3+}–CO species. However, the interaction of CO with Al^{3+} and Ce$^{4+/}$$^{3+}$ is fully reversible and the corresponding carbonyls are stabilized by CO adsorption at low temperature [28,30–32]. Therefore, we are of the opinion that the bands at 2236–2230 and 2168–2165 cm^{-1} formed in the 150–350 °C temperature range (Fig. 4) cannot be attributed to adsorbed CO. By referring to the spectra in the low-frequency region (Fig. 3), it can be proposed that the formation of
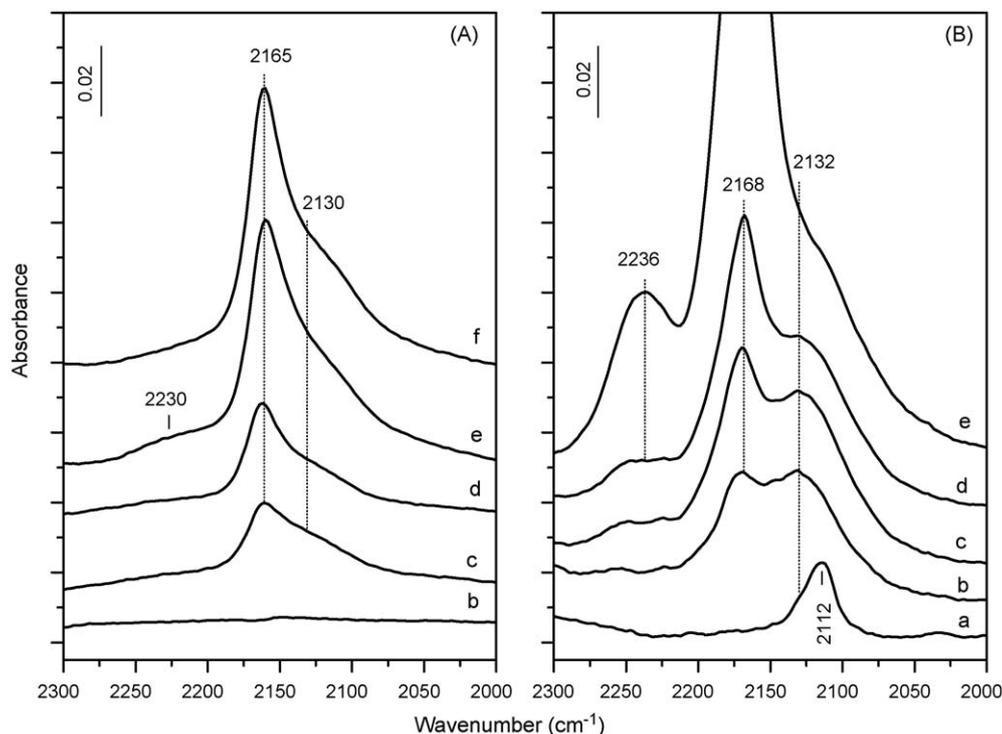
Fig. 4. FT-IR spectra in the 2300–2000 cm^{-1} region collected during exposure of the CeAl20 (Panel A) and AuCeAl20 samples (Panel B) for 15 min to a (10 mbar CO + 3 mbar H$_2$) mixture at 25 °C (a), 200 °C (b), 250 °C (c), 300 °C (d), 350 °C (e) and under dynamic evacuation at 350 °C (f).

the species, giving rise to the absorptions at 2236–2230 and 2168–2165 cm^{-1}, is associated with the transformation of residual impurities that undergo reduction in the presence of CO + H$_2$ mixture. Based on the fact that bands at the same positions are detected during the co-adsorption of NO + CO (see below) and in agreement with the literature data [1,9–16,18,19], the absorptions at 2236 and 2168 cm^{-1} are assigned to surface isocyanate species. The heating in the CO + H$_2$ atmosphere causes the reduction of the residual nitrates leading to the formation of small amount of NCO species. Most probably this process occurs in two steps: reduction of the NO$_3^-$ species with H$_2$ to NO followed by NO + CO interaction to NCO. This assumption is supported by the fact that the NCO bands on the AuCeAl20 sample grow in intensities at temperatures exceeding the temperature at which the reduction of the nitrate species under the partial pressure of hydrogen of 3 mbar is completed (200 °C). Because the reduction temperature of the residual nitrates on the AuCeAl20 is lower than that on the Au-free sample, it can be concluded that the promotion of CeAl20 with gold destabilizes these species. The surface concentration of the NCO groups decreased considerably after the activation using three consecutive reduction/oxidation cycles but as already mentioned, the dispersion of gold has decreased.

In order to ascertain the assignment of the absorptions at 2236–2230 and 2168–2161 cm^{-1} to NCO species (Fig. 4), we performed ^{13}CO + H$_2$ co-adsorption experiment (Fig. 5). This allowed also monitoring the behavior of the Au^0–CO species at high temperatures, which were masked by the growing complex absorption in the 2300–2000 cm^{-1} region. Upon exposure of the AuCeAl20 sample to the ^{13}CO + H$_2$ mixture at room temperature, the Au^0–CO band shifts from 2112 to 2060 cm^{-1} (Fig. 5, spectrum a). In agreement with the literature [34], the $\Delta\nu$ value of 52 cm^{-1} corresponds to that predicted by using the isotopic factor of 0.98. The weak signal at 2130 cm^{-1} is due to the Ce^{3+} electronic transition and clearly shows that the treatment with H$_2$ at 120 °C reduces the surface. The heating at 150 °C causes vanishing of the

Au^0–^{13}CO band (Fig. 5, spectrum b), which indicates that CO adsorbs weakly on reduced gold. The two bands at 2236 and 2168 cm^{-1}, which develop with the increase in the temperature (Fig. 4B), are shifted down by 59 and 58 cm^{-1}, respectively, and are
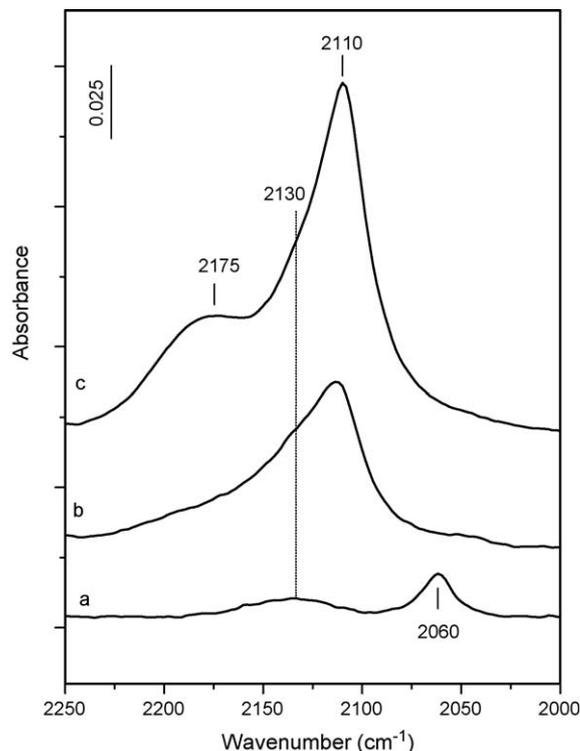
Fig. 5. FT-IR spectra collected during exposure of the AuCeAl20 sample to a (10 mbar ^{13}CO + 3 mbar H$_2$) mixture for 15 min at 25 °C (a), 150 °C (b) and 250 °C (c).

positioned at 2175 and 2110 cm^{-1} on ^{13}C substitution (Fig. 5, spectrum c). The observed $\Delta\nu$ value is consistent with that reported in the literature for the isotopic shift expected on substituting ^{13}C for ^{12}C in NCO species [9,18,35]. The low-frequency region is not shown, but the negative bands attributed to residual nitrates appear exactly at the same positions during both CO + H$_2$ and ^{13}CO + H$_2$ co-adsorption experiments. These results confirm the assignment of the bands at 2236 and 2168 cm^{-1} to adsorbed NCO species formed by the reaction between the residual nitrates and CO + H$_2$ mixture at elevated temperatures. The low-frequency shift of the isocyanate bands observed in ^{13}CO + H$_2$ atmosphere cover the absorption at 2130 cm^{-1} and it appears as a poorly resolved shoulder.

3.3. Adsorption of NO in the presence and absence of H$_2$

The spectra in 2300–2000 cm^{-1} region obtained during the co-adsorption of NO + H$_2$ on the AuCeAl20 sample heated in the isolated IR cell between 25 and 350 °C are shown in Fig. 6A. No NCO species originating from the residual nitrates are produced under these conditions. This allows monitoring the behavior of the Ce^{3+} sites initially formed by the pre-treatment of the sample with H$_2$ at 120 °C. The band at 2132 cm^{-1} characteristic of the Ce^{3+} electronic transition is present in the spectrum taken at room temperature after the admission of the NO + H$_2$ mixture (Fig. 6, spectrum a). Raising the temperature to 150 °C causes increase in the amount of Ce^{3+} sites (Fig. 6, spectrum b). This is in excellent agreement with the TPR results published earlier [6], according to which the peak corresponding to the reduction of CeO$_2$ surface layers is located at 150 °C. However, further increase in the temperature leads to lowering of the intensity of the band at 2130 cm^{-1} and at 350 °C this band is no longer observed (Fig. 5, spectrum e). The disappearance of the electronic absorption of Ce^{3+} at 350 °C suggests that NO re-oxidizes the reduced surface of AuCeAl20.

Daturi et al. [36] and Haneda et al. [37] reported that NO decomposes at 400–500 °C on partially reduced ceria. According to Daturi et al. [36], in the mechanism of NO dissociation at high temperatures, two oxygen atoms from two NO molecules fill two neighboring oxygen vacancies re-oxidizing the pre-reduced ceria surface, while the nitrogen atoms recombine giving rise to a N$_2$ molecule. This reaction scheme rules out the possibility for formation of N$_2$O at the beginning of the re-oxidation process. However, the spectrum taken at room temperature immediately after the admission of NO + H$_2$ mixture contains a signal corresponding to N$_2$O (Fig. 6B, spectrum a). The precursor of N$_2$O under these conditions could be the dimmer of NO$^-$, the cis-hyponitrite (N$_2$O$_2^{2-}$) ion [38]. The former species is identified by the absorption band at 1176 cm^{-1} (see the inset in Fig. 6A), whereas the latter gives rise to the weak band at 1300 cm^{-1} [38–40]. Both species are located on the CeO$_2$-Al$_2$O$_3$ surface and they disappear at 150 °C (see the inset in Fig. 6A) with simultaneous increase in the amount of N$_2$O (Fig. 6B, spectrum b). The highest concentration of N$_2$O is observed at 150–200 °C (Fig. 6B, spectra b and c). With further increase in the temperature, the amount of N$_2$O decreases. This suggests that at 250–300 °C the nitrogen protoxide either undergoes reduction by the hydrogen or it may act as re-oxidizing agent for the reduced surface by trapping the oxygen atom of the molecule in a vacancy [36–38]. The results of this experiment do not allow distinguishing between these two possibilities and do not provide unequivocal evidence that in the re-oxidation of Ce^{3+} the dissociation of NO to atomic nitrogen and oxygen could be involved. An attempt to avoid the presence of N$_2$O has been made by studying the adsorption of NO at 350 °C. The AuCeAl20 sample was reduced at 350 °C with 10 mbar of H$_2$ for 60 min followed by evacuation for 30 min at the same temperature. Prior the reduction, the sample was treated in O$_2$ (100 mbar) for 1 h at 400 °C and then the oxygen was evacuated at 120 °C. The spectrum of the reduced AuCeAl20 catalyst recorded at 350 °C
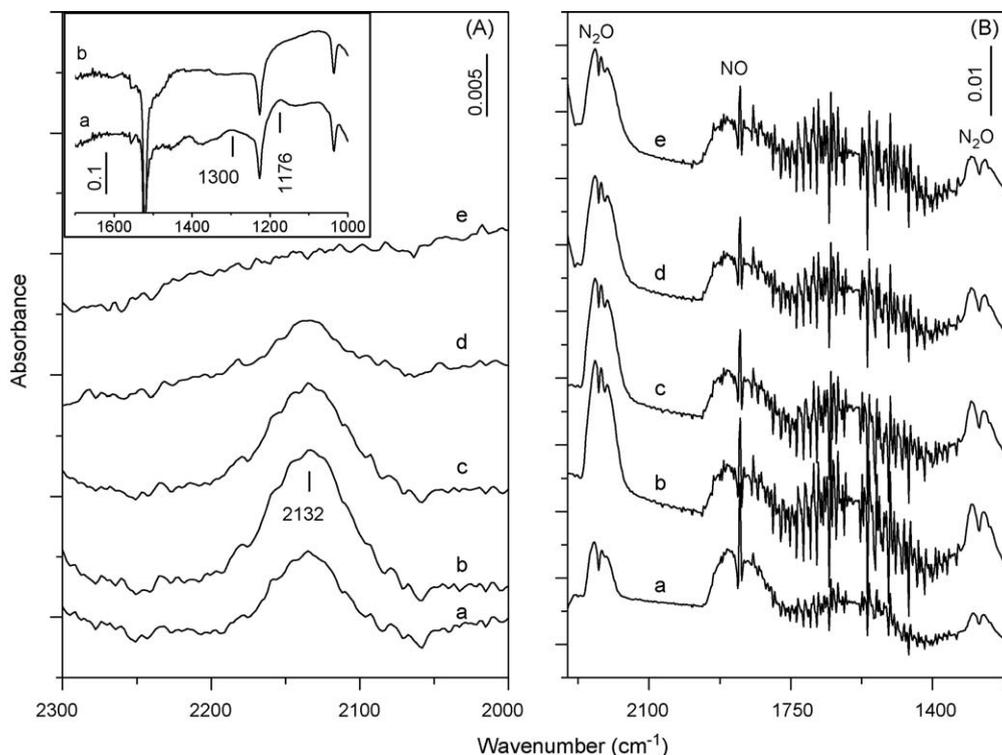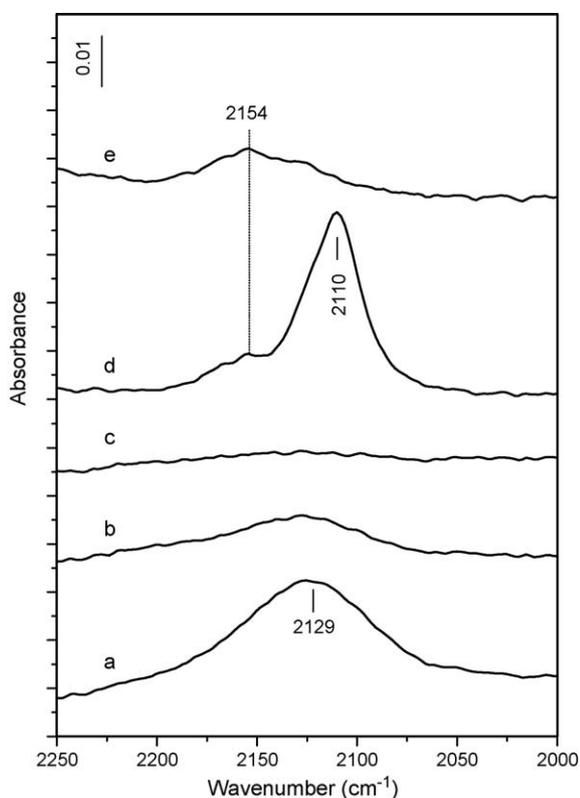

Fig. 6. FT-IR spectra collected during exposure of the AuCeAl20 sample to a (5 mbar NO + 3 mbar H$_2$) mixture (Panel A) for 15 min and spectra of the gas phase over the AuCeAl20 sample (Panel B) at 25 °C (a), 150 °C (b), 200 °C (c), 250 °C (d) and 350 °C (e). Inset in Panel A: FT-IR spectra in nitro-nitrato region.
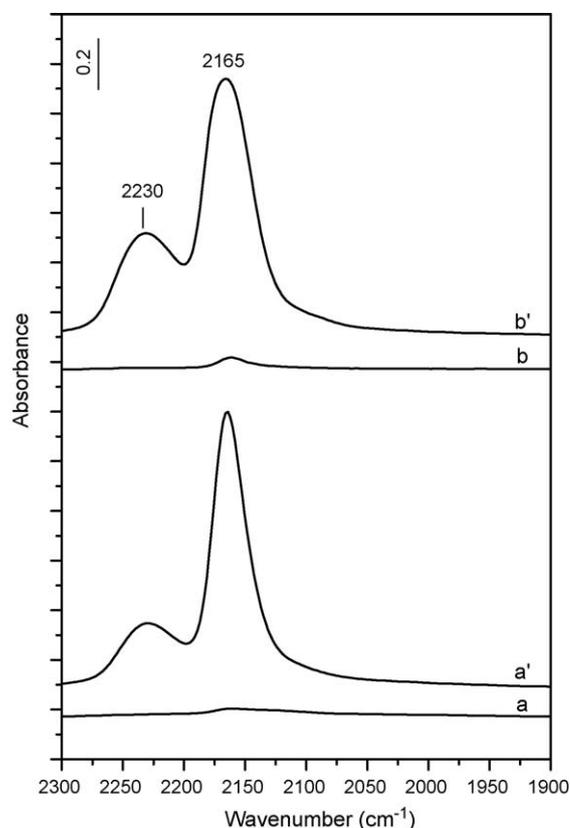
Fig. 7. FT-IR spectra of the AuCeAl20 sample reduced at 350 °C with 10 mbar of H_2 for 60 min followed by evacuation for 30 min at the same temperature (a) and after exposure at 350 °C to 5 mbar of NO for 3 min (b) and 40 min (c) followed by evacuation of NO at 200 °C, cooling to room temperature and admission of 10 mbar of CO (d), and under dynamic evacuation (e).
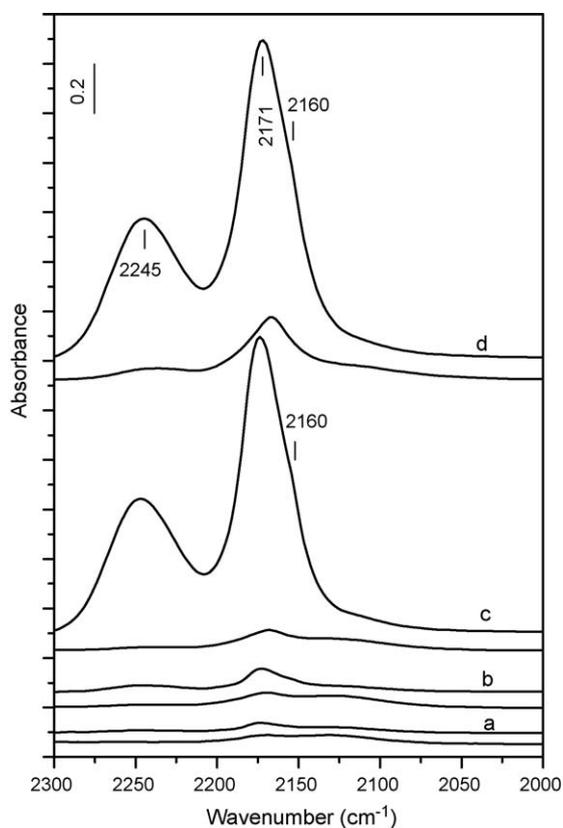

Fig. 8. FT-IR spectra collected during exposure of CeAl20 sample to a (5 mbar NO + 10 mbar CO) mixture for 15 min at 300 °C (a) and 350 °C (a'), and to a (5 mbar NO + 10 mbar CO + 3 mbar H_2) mixture for 15 min at 300 °C (b) and 350 °C (b').

exhibits the band at 2129 cm^{-1} characteristic of the electronic transition of Ce^{3+} (Fig. 7, spectrum a). The exposure to 5 mbar of NO at the same temperature causes decrease in the intensity of the band at 2129 cm^{-1} (Fig. 7, spectrum b) indicating that the re-oxidation of the reduced surface by NO starts immediately. Keeping the sample in contact with NO for 40 min removes completely the signal associated with the Ce^{3+} ions (Fig. 7, spectrum c). Formation of NO^-, $N_2O_2^{2-}$ species and N_2O, has not been observed under these conditions. These results show that the dissociation of NO on the reduced AuCeAl20 catalyst occurs already at 200 °C (see Fig. 6A) re-oxidizing the surface by filling the vacancies with oxygen of the molecule as proposed for reduced ceria [36]. The reason for the decrease in the N_2O concentration, observed during the NO + H_2 adsorption in the 25–350 °C temperature range (Fig. 6B), is the reduction of N_2O with hydrogen, which is found to take place at 250–350 °C.

After the evacuation of NO at 200 °C and reaching room temperature, 10 mbar of CO was added to the IR cell. The spectrum is shown in Fig. 7, spectrum d. The band at 2110 cm^{-1} corresponding to CO adsorbed on Au^0 has a high-frequency shoulder. The evacuation of CO removes the former band and leaves a weak absorption with maximum at 2154 cm^{-1} assigned to $Au^{\delta+}$–CO carbonyl [27]. Migration of O atoms produced by the dissociation of NO to Au^0 sites gives rise to $Au^{\delta+}$. It could be assumed that the gold species that acquire a positive charge are in the vicinity of the oxygen vacancies on the CeAl20 support.

3.4. Adsorption of NO + CO in the presence and absence of H_2

Fig. 8 compares the spectra of the CeAl20 sample obtained by co-adsorption of NO + CO at 300 and 350 °C (spectra a–b and a'–b',

respectively) in the absence (spectra a–a') and presence of H_2 (spectra b–b'). The interaction between NO and CO over the CeAl20 sample occurs at 350 °C (Fig. 7, spectra a' and b'), which is evident by the appearance of strong bands at 2230 and 2165 cm^{-1} assigned to isocyanate species [1,9–19].

Fig. 9 shows the spectra in the 2300–2000 cm^{-1} region detected between 150 and 300 °C during the exposure of the AuCeAl20 sample to NO + CO + H_2 (thick line) and CO + H_2 mixtures (thin line). The promotion of CeAl20 by gold lowers the temperature of formation of the NCO species and they appear in considerable amount already at 150–200 °C (Fig. 9, spectra a and b, thick lines) exceeding the amount of the NCO species formed by transformation of the residual nitrates during the CO + H_2 adsorption (Fig. 9, spectra a and b, thin lines). Significant increase in the intensities of the NCO bands is observed at 250 °C regardless of the presence (Fig. 9, spectrum c, thick line) or absence of H_2 (the spectra are not shown). At this temperature, the contribution of the NCO species formed by the transformation of the residual nitrates to the intensity of the band at 2171 cm^{-1} is negligible.

In order to determine the location of the surface isocyanates, we performed co-adsorption of NO + CO + H_2 on CeO_2 and AuCe samples. The CeO_2 sample for these measurements was prepared by calcination of Ce(III) acetate at 450 °C for 4 h and does not contain residual nitrates. The XRD patterns of the sample correspond to the characteristic peaks of CeO_2. Prior the adsorption experiments, the ceria specimen was activated following steps 1 and 2 of the activation procedure. After cooling to room temperature, the NO + CO + H_2 mixture was admitted to the IR cell. No adsorbed species in the 2300–1900 cm^{-1} region were detected up to 350 °C (Fig. 10A, spectrum a). The absence of the band of Ce^{3+} electronic transition suggests that the sample does
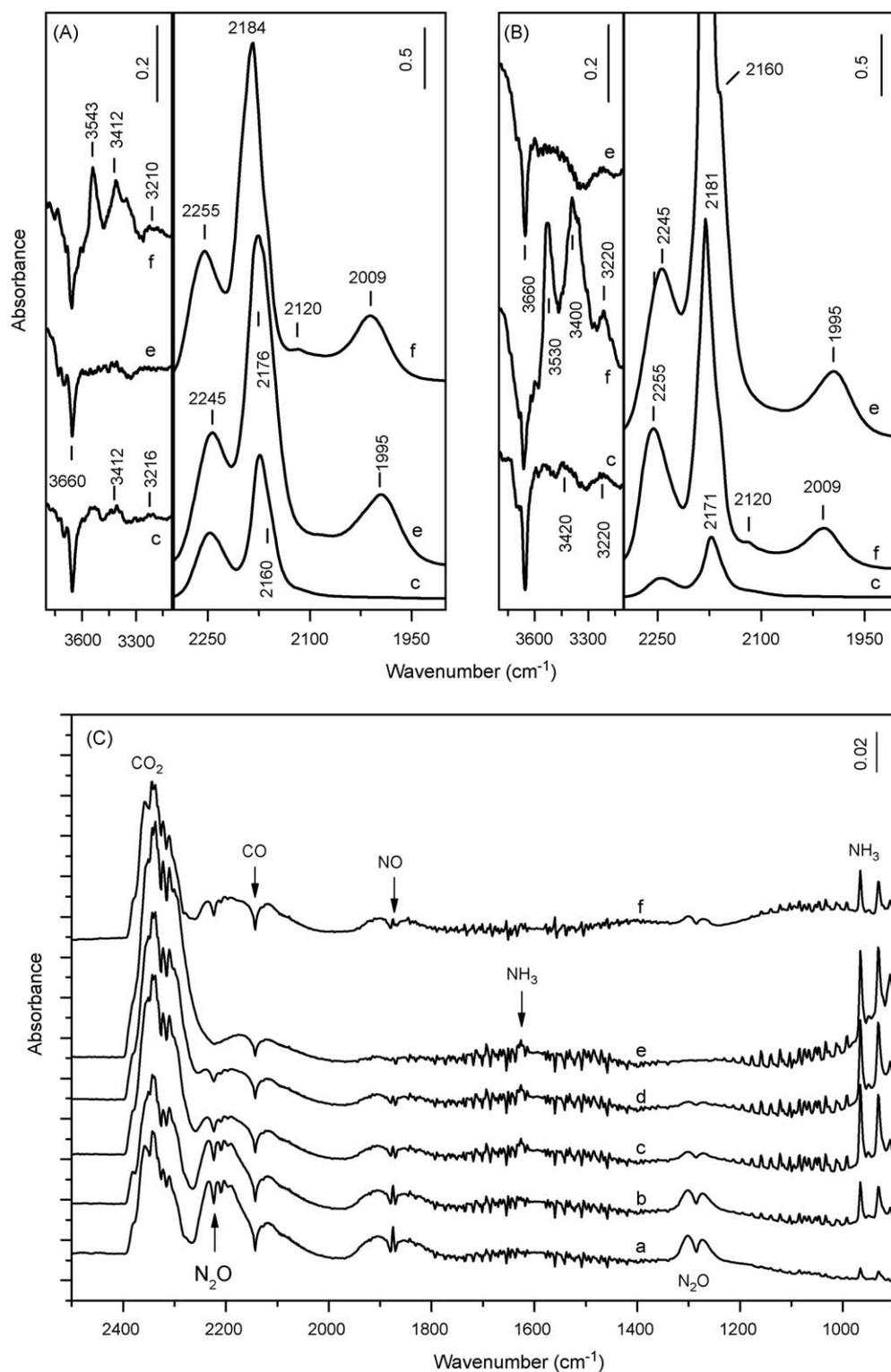
Fig. 9. Comparison between the spectra collected during exposure of the AuCeAl20 sample for 15 min to a (10 mbar CO + 3 mbar H_2) mixture (thin line) and to a (5 mbar NO + 10 mbar CO + 3 mbar H_2) mixture (bold line) at 150 °C (a), 200 °C (b), 250 °C (c) and 300 °C (d).

not contain reduced cerium ions. At 400 °C (Fig. 10A, spectrum b), two strong absorptions appear at 2173 cm^{-1} with a shoulder at ~2160 cm^{-1} and at 1985 cm^{-1}. Bánsági et al. [13] reported bands at 2210 and 2184 cm^{-1} observed upon adsorption of HNCO on reduced CeO_2 and attributed them to NCO species coordinated to Ce^{4+} and Ce^{3+} sites, respectively. Based on these observations, the absorptions at 2173 and 2160 cm^{-1} (Fig. 10A, spectrum b) are assigned to NCO species attached to two Ce^{3+} sites differing in their coordinative saturation. The different oxygen environment should affect the strength of the Ce^{3+}–NCO bond. The cationic center with higher oxygen deficiency should form stronger Ce^{3+}–NCO bond and consequently, the ν_{as}(NCO) vibration should appear at lower frequency. The assignment of the absorptions at 2173 and 2160 cm^{-1} in the spectrum taken at 400 °C to Ce^{3+}–NCO species is supported also by the fact that reduction of ceria with hydrogen occurs at temperatures higher than 350 °C [26]. The band at 1985 cm^{-1} is attributed tentatively to surface CN species. All of the absorption bands resist the evacuation at 400 °C for 15 min.

Fig. 10B shows the spectrum of the H_2-pretreated AuCe sample (step 2 of the activation procedure) taken at room temperature (spectrum a) and the spectra obtained in the 150–350 °C temperature range after the addition of the NO + CO + H_2 mixture to the IR cell. The weak, broad absorption at 2128 cm^{-1} (Fig. 10B, spectrum a) indicates the presence of Ce^{3+} ions [26]. As in the case of the CeAl20 sample, the promotion of ceria by gold lowers significantly the temperature of formation of NCO (2176 cm^{-1}) and CN species (2000 cm^{-1}) and they appear at 200 and 350 °C, respectively (Fig. 10B, spectra c and e). In addition, the shoulder at ~2160 cm^{-1} of the NCO band is practically absent and the absorption at 2173 cm^{-1} displays only a low-frequency tail. The absence of absorption above 2200 cm^{-1} in the spectra shown in Fig. 10 indicates that CeO_2 and AuCe samples do not contain exposed Ce^{4+} ions. This allows the assignment of the bands at 2245–2230 cm^{-1} in the spectra of the CeAl20 (Fig. 8) and AuCeAl20 samples (Fig. 9) obtained during the NO + CO adsorption in the
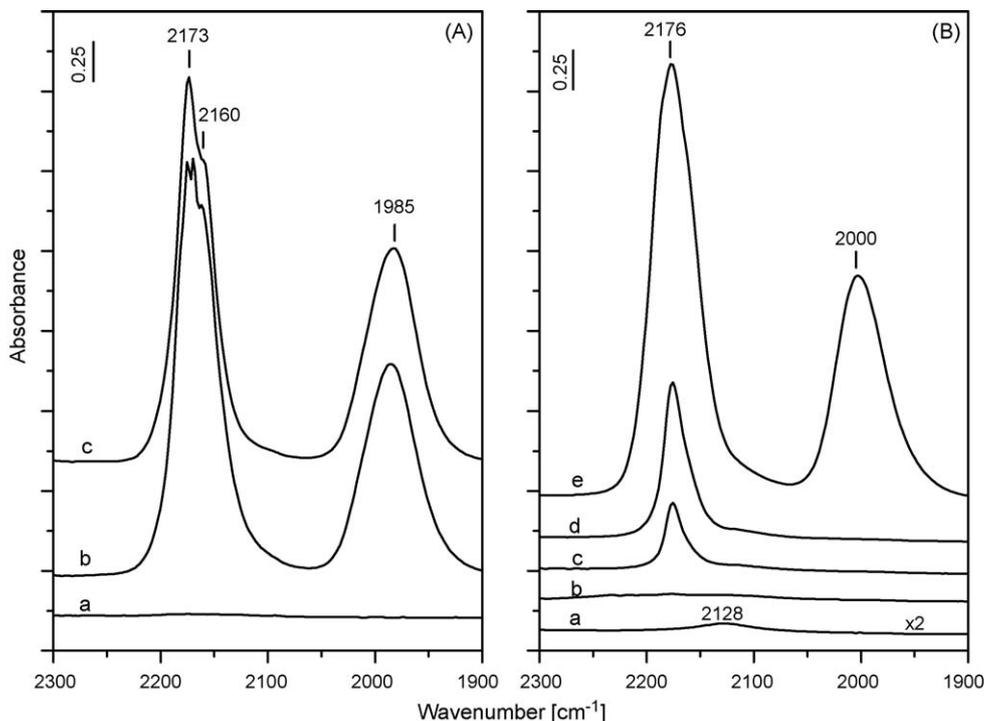
Fig. 10. Panel A: FT-IR spectra of activated CeO_2 collected during exposure of the sample for 15 min to a (5 mbar NO + 10 mbar CO + 3 mbar H_2) mixture at 350 °C (a), 400 °C (b) and after dynamic evacuation at 400 °C for 15 min (c). Panel B: FT-IR spectrum of the activated AuCe sample in the 2300–1900 cm^{-1} region (a) and FT-IR spectra collected during exposure of the sample for 15 min to a (5 mbar NO + 10 mbar CO + 3 mbar H_2) mixture at 150 °C (b), 200 °C (c), 250 °C (d) and 350 °C (e).

Fig. 11. FT-IR spectra collected during exposure of the AuCeAl20 sample for 15 min to a (5 mbar NO + 10 mbar CO) mixture (Panel A) and to a (5 mbar NO + 10 mbar CO + 3 mbar H$_2$) mixture (Panel B), and development of the gas phase with the temperature (Panel C) during the contact of the sample with a (5 mbar NO + 10 mbar CO + 3 mbar H$_2$) mixture at 150 °C (a), 200 °C (b), 250 °C (c), 300 °C (d), 350 °C (e), and after cooling to room temperature (f).

presence and absence of hydrogen to NCO species coordinated to Al^{3+} sites. The spectra in Fig. 8 shows that the presence of H$_2$ causes broadening of the band at 2165 cm^{-1} suggesting an increase in the heterogeneity of the Ce^{3+} adsorption sites. In addition, the intensity of the band at 2230 cm^{-1} detected upon NO + CO + H$_2$ co-adsorption is higher than that observed in the absence of H$_2$ in

the NO + CO mixture (compare spectra a′ and b′). This can be explained by assuming that the NCO species migrate from the Ce^{3+} to Al^{3+} sites. The presence of hydrogen in the NO + CO mixture increases the concentration of the Ce^{3+} ions and consequently, the amount of NCO species coordinated to Al^{3+} sites increases as well. The assignment of the bands at 2245–2230 cm^{-1} in the spectra of

Table 1
The position of the ν_{as}(NCO) mode of the NCO species formed in the NO + CO + H$_2$ reaction over the samples studied and the lowest temperature of their detection.

Sample	ν_{as}(NCO) (cm^{-1})	Coordination site	Temperature of detection (°C)
CeO$_2$	2173, ~2160	Ce^{3+} (two types)	400
AuCe	2176	Ce^{3+}, Au^0	200
CeAl20	2165	Ce^{3+}	300–350
	2230	Al^{3+}	
AuCeAl20	~2165	Ce^{3+}	150–200
	2171	Ce^{3+}, Au^0	
	2245	Al^{3+}	

the CeAl20 (Fig. 8) and AuCeAl20 samples (Fig. 9) to Al^{3+}–NCO species is in agreement with the literature [12,17–19] and the XPS results [6], according to which the modification of ceria by alumina causes the enrichment of the surface by (3+) ions. It seems that the CeAl20 sample, in addition to the Al^{3+}–NCO species, contains mainly NCO groups coordinated to the Ce^{3+} sites with higher coordinative unsaturation giving rise to the low-frequency Ce^{3+}– NCO band at 2165 cm^{-1}. This agrees well with the fact that the modification of ceria by alumina increases the concentration of the oxygen vacancies [6]. Analogous to ceria, the promotion of CeAl20 sample with gold makes the feature at 2171 cm^{-1} predominant in the spectra taken during the NO + CO + H$_2$ co-adsorption at 250 and 300 °C (Fig. 9, spectra c and d) and the low-frequency isocyanate band is observed as a poorly resolved shoulder at approximately 2160 cm^{-1}. This behavior could be associated with the formation of Au^0–NCO groups having their ν_{as}(NCO) mode superimposed to that of the Ce^{3+}–NCO species that give rise to the high-frequency NCO band. From these experimental results it is difficult to deduce if the absorption at 2171 cm^{-1} (Fig. 9, spectra c and d) is due only to Au^0–NCO or to NCO species adsorbed on both Ce^{3+} and Au^0 sites. At room temperature the absorption band at 2176–2171 cm^{-1} shifts to 2184–2181 cm^{-1} (see Fig. 11, spectra f). Solymosi et al. [12,15] attributed a band at 2185–2190 cm^{-1} to Au^0–NCO species formed during the high-temperature adsorption of HNCO on SiO$_2$- and TiO$_2$-supported gold. They found also that the thermal stability of NCO group coordinated to Au^0 is significantly higher than that when bonded to Pt [12] or Rh [13]. Table 1 summarizes the position of the ν_{as}(NCO) mode of the NCO species formed in the NO + CO + H$_2$ reaction over the samples studied and gives the lowest temperature at which they appear.

The addition of H$_2$ to the NO + CO mixture affects the surface concentrations of the isocyanates formed on the AuCeAl20 sample. As shown by the spectra taken at 250 °C (Fig. 11), the amount of the NCO species produced upon H$_2$-containing NO + CO mixture (Fig. 11B, spectrum c) is lower than that formed in the absence of H$_2$ (Fig. 11A, spectrum c). At 350 °C there is an enhancement in the absorption corresponding to the surface isocyanates, which is particularly strong for the H$_2$-containing mixture and the absorption peak at 2171 cm^{-1} is off scale (Fig. 11B, spectrum e).

As shown above, NO dissociates over the reduced AuCeAl20 sample. Judging from the intensity of the Ce^{3+} electronic transition band, this process becomes observable at 200 °C (Fig. 6A). The amount of the NCO species that are formed upon the NO + CO + H$_2$ co-adsorption is considerable at this temperature (see Fig. 9). The highest amount of isocyanate species on the AuCeAl20 sample is obtained at 350 °C and their concentration increases drastically upon addition of H$_2$ to the reaction mixture. At the same temperature, the adsorption of NO over the pre-reduced AuCeAl20 catalysts causes complete re-oxidation of Ce^{3+} by filling the vacancies by oxygen from the molecule (see Fig. 7). The decomposition of NO on reduced ceria takes place at 400–500 °C

[36,37] and the NCO species appear at higher temperature (400 °C). These facts lead to the conclusion that metallic gold is not necessary for the formation of NCO species. The latter are generated by a process involving the dissociation of NO on the oxygen vacancies of the CeO$_2$ and CeO$_2$-Al$_2$O$_3$ supports, followed by the reaction between N atoms lying on the surface and CO molecules. Dissociation of NO may take place also on gold particles as proposed by Solymosi et al. [12,15] but the main role of gold is to lower the reduction temperature of CeO$_2$ and CeO$_2$-Al$_2$O$_3$. The absorption bands at 2000–1985 cm^{-1} that appear during the NO + CO + H$_2$ reaction at 400 °C on CeO$_2$ (Fig. 10A, spectrum c) and at 350 °C on the AuCe (Fig. 10B, spectrum e) and AuCeAl20 samples (Fig. 11, spectra e) have been attributed to CN species. The probable formation of these species should occur through dissociation of CO. Most likely the C atom remains attached to Ce^{3+} site and combines with a nitrogen atom produced by the dissociation of NO, whereas the O atom fills a vacancy on the surface. Similar mechanism has been proposed by Unland [9] in the case of NO + CO reaction over Pt/Al$_2$O$_3$ and confirmed by Bion et al. [18] using C^{18}O + N^{16}O isotopic substitution experiment with Ag/Al$_2$O$_3$. It is interesting to note that there is no difference in the intensities of the bands corresponding to the CN species generated at 350 °C on the AuCeAl20 sample during the NO + CO co-adsorption without (Fig. 11A, spectrum e) or with H$_2$ (Fig. 10B, spectrum e).

The weak bands at 3412–3420 and 3216–3220 cm^{-1} detected between 250 and 350 °C point to the appearance of adsorbed ammonia (Fig. 11, spectra c and e in panels A and B). They correspond to the ν_{as}(NH) and ν_s(NH) modes, respectively [41]. When coordinated to Lewis acid site, ammonia exhibits δ_{as}(NH$_3$) and δ_s(NH$_3$) modes at 1630–1600 and 1300–1150 cm^{-1}, respectively. However, it is difficult to locate these features because of the significant overlapping of the bands in the 1700–1000 cm^{-1} region. The gas phase spectra taken during the exposure of the AuCeAl20 sample to the NO + CO + H$_2$ mixture at various temperatures confirm the formation of ammonia (Fig. 11C). The characteristic bands of δ_s(NH$_3$) modes of gaseous ammonia are detected at 964 and 932 cm^{-1}. The process of ammonia formation begins at 150 °C (Fig. 11C, spectrum a). The amount of gaseous ammonia increases up to 250 °C and remains practically unchanged at higher temperatures. This indicates that ammonia does not act as reducing agent of NO under the conditions of the experiment. Formation of ammonia at 250 °C and higher temperatures has been detected also by MS analysis during the catalytic test with the AuCeAl20 sample in the reduction of NO with CO [6].

The NCO groups formed on various oxides easily hydrolyze to ammonia in the presence of water [19,35,42]. Adsorbed water molecules are produced during the reductive activation of the AuCeAl20 sample with hydrogen at 120 °C (step 2). This causes enhancement of the absorption due to H-bonded hydroxyls and perturbation of the band corresponding to the bridged OH groups (negative band at 3660 cm^{-1}, see Fig. 1). The amount of adsorbed water is sufficient to cause some hydrolysis of the NCO species produced during the NO + CO co-adsorption in the absence of hydrogen. According to the TPR data [6], the reduction of surface layers of the AuCeAl20 sample is completed at about 250 °C. Heating the activated sample in the isolated IR cell between 150 and 350 °C in the presence of NO + CO + H$_2$ gas mixture, leads to further reduction of the catalyst and formation of larger amount of adsorbed water than in the absence of H$_2$. The higher degree of hydration of the surface under the conditions of CO + NO + H$_2$ compared to that of the NO + CO co-adsorption results in more extensive hydrolysis of the isocyanate species, respectively, higher production of ammonia. This is reflected by the somewhat higher intensities of the bands corresponding to the N–H stretching
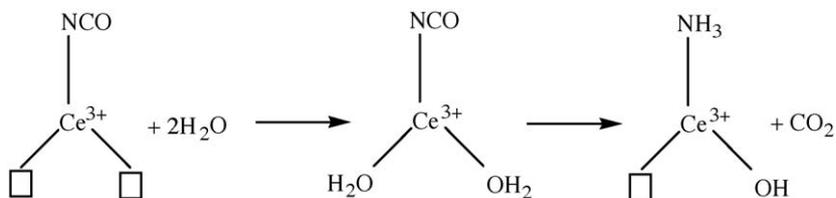
Scheme 1.

vibrations of ammonia adsorbed at 250 °C and lower intensities of the NCO bands detected in the CO + NO + H$_2$ (Fig. 11B, spectrum c) versus the NO + CO experiment (Fig. 11A, spectrum c). The fact that the amount of ammonia in the gas phase remains unchanged between 250 and 350 °C indicates that the process of NCO hydrolysis is favored at temperatures below 250 °C. This is associated with the degree of hydration of the surface. At 350 °C, the surface is dehydrated and the amount of surface isocyanates formed in the presence of NO + CO + H$_2$ mixture increases drastically (Fig. 11B, spectrum b). Cooling the isolated IR cell from 350 °C to room temperature (Fig. 11B, spectrum f) causes strong decrease in the intensity of the band at 2171 cm^{-1} (shifted to 2181 cm^{-1}). In contrast, the lowering of the temperature to 25 °C in CO + NO atmosphere (Fig. 11A, spectrum f) has a little effect on the isocyanate band at 2176 cm^{-1} (shifted to 2184 cm^{-1}). This rules out the possibility that in the former case the strong decrease in the intensity of the NCO band at 2181 cm^{-1} (spectrum f in Fig. 11B) is caused by the interaction of the isocyanate species with NO. While cooling to room temperature, the surface becomes rehydrated and NCO groups produced at 350 °C in the presence of the three-component gas mixture are consumed in the hydrolysis process. The produced ammonia adsorbs on the surface giving rise to relatively strong bands at 3400 and 3220 cm^{-1} in the spectrum taken at room temperature (Fig. 11B, spectrum f). This is evident also by the decrease of its concentration in the gas phase (Fig. 11C, spectrum f). The extent of hydrolysis of the isocyanate species at 2176 cm^{-1} obtained in the NO + CO experiment is limited by the amount of water produced during step 2 of the sample activation and the decrease in the temperature does not have effect on the NCO concentration (Fig. 11A, spectrum f).

In both cases (in the presence or absence of H$_2$ in the NO + CO mixture), the intensities of the bands at 2245 and 1995 cm^{-1} (shifted to 2255 and 2009 cm^{-1}) do not change significantly while reaching room temperature (Fig. 11, spectra f in panels A and B). These two bands have been assigned to isocyanates bound to Al^{3+} ions and to surface CN species, respectively. It can be proposed that the hydrolysis of the Ce^{3+}-NCO groups requires two neighboring oxygen vacancies for dissociative adsorption of two water molecules (Scheme 1).

The absorption at 3543–3530 cm^{-1} detected after cooling the isolated IR cell to room temperature (Fig. 11, spectra f in panels A and B) is attributed to a surface OH group, which is formed during the hydrolysis of the isocyanates attached to the Ce^{3+} ion and which completes an oxygen vacancy. This band is observed in the spectra at high temperatures as a weak feature. The weak signal at approximately 2120 cm^{-1} detected at 25 °C corresponds to the electronic transition of Ce^{3+}. At high temperatures, the strong isocyanate bands cover this absorption. All of the bands resist the evacuation at room temperature (the spectra are not shown).

As in the case of the NO + H$_2$ co-adsorption, the amount of N$_2$O formed upon exposure of the AuCeAl20 sample to the NO + CO and NO + CO + H$_2$ mixtures at room temperature increases at 150 °C (Fig. 11C, spectrum a). This species disappears completely at 350 °C (Fig. 11C, spectrum e) during the interaction between the AuCeAl20 catalyst and NO + CO mixture regardless of the presence

or absence of H$_2$. The reappearance of N$_2$O at room temperature (Fig. 11C, spectrum f) is due to the interaction of NO with the catalyst surface by a mechanism which has been discussed above (Section 3.3). Over the Au-free sample, the nitrogen protoxide is present at 350 °C. This suggests that the gold particles promote the reduction of N$_2$O with H$_2$ and/or CO.

The NCO and CN species formed on the surface of the AuCeAl20 catalyst possess high thermal stability. The Ce^{3+}–NCO and CN bands obtained during the NO + CO + H$_2$ co-adsorption at 300 °C (Fig. 12, spectrum a) stay intact upon dynamic evacuation at the same temperature for 15 min (Fig. 12, spectrum b), whereas there is a little loss in the intensity of the Al^{3+}–NCO band.

3.5. Reactivity of the adsorbed NCO and CN species

The experimental results described so far do not present evidence for the reaction of the surface NCO species and NO, which should lead to the products of NO reduction, N$_2$ and CO$_2$. The reason for this could be that the rate of formation of the isocyanates exceeds the rate of their reaction with NO. In order to verify this assumption, we studied the interaction between
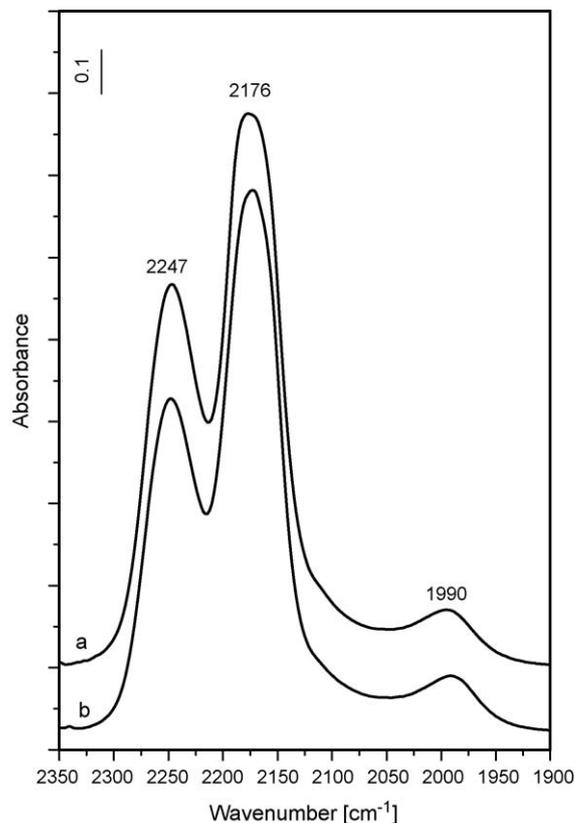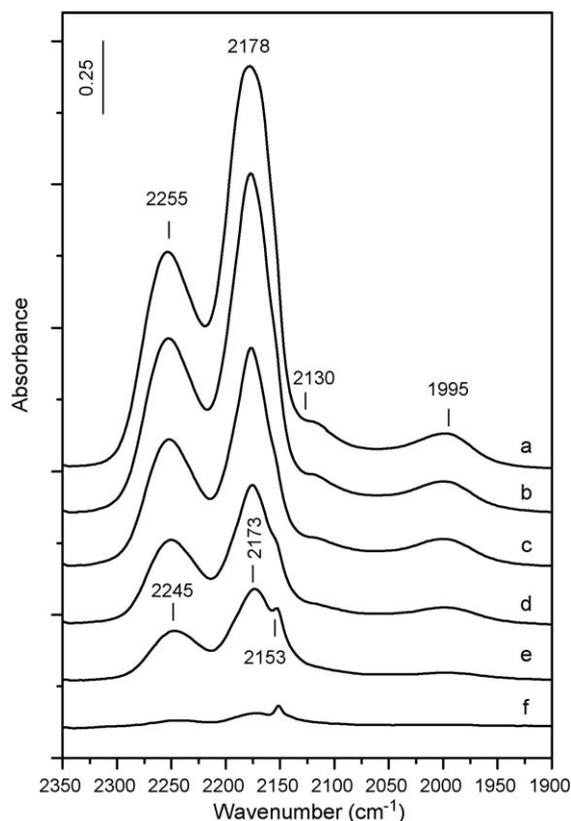

Fig. 12. FT-IR spectra collected during exposure of the AuCeAl20 sample for 15 min to a (5 mbar NO + 10 mbar CO + 3 mbar H$_2$) mixture at 300 °C (a) followed by dynamic evacuation for 15 min at 300 °C (b).

NCO-precovered AuCeAl20 catalyst and NO at various temperatures. The absence of CO in the gas phase will prevent the formation of the NCO species and will allow monitoring of the NCO + NO reaction.

The NCO species were created on the surface of the activated AuCeAl20 catalyst by co-adsorption of NO + CO + H_2 mixture at 300 °C followed by evacuation at the same temperature. Then, after cooling to room temperature, 5 mbar of NO were added and the isolated IR cell was heated at temperatures between 100 and 300 °C for 15 min at each temperature. The spectra are shown in Fig. 13. The exposure of the sample to NO at room temperature does not affect the amount of the isocyanate (bands at 2255 and 2178 cm^{-1}) and cyanide species at 1995 cm^{-1} (Fig. 13, spectrum a). The weak absorption at 2130 cm^{-1} corresponds to the electronic transition of Ce^{3+} ions. Noticeable decrease in the intensity of this band is observed at 150 °C (Fig. 13, spectrum b) caused by the re-oxidation of the surface upon NO atmosphere. At 250 °C the absorption at 2130 cm^{-1} is no longer present (Fig. 13, spectrum e). The onset temperature of the reaction between the isocyanates and NO is at 100 °C (Fig. 13, spectrum b). The surface concentration of the NCO species decreases rapidly with the increase in temperature allowing the detection of a low-frequency shoulder of the NCO band at 2178 cm^{-1}. At 200–250 °C (Fig. 13, spectra d and e), this shoulder gives rise to clearly resolved absorption with maximum at 2153 cm^{-1}. The latter band appeared as poorly resolved shoulder at 2160 cm^{-1} in the spectra detected at 300 °C upon NO + CO + H_2 co-adsorption (Fig. 9) and was attributed to NCO species coordinated to more defective Ce^{3+} sites. Noticeable decrease in the intensity of the CN band at 1995 cm^{-1} is observed at 200 °C (Fig. 13, spectrum d), which
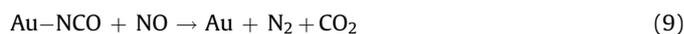
indicates that the reactivity of these species with respect to NO is lower than that of the isocyanates. The NCO species disappear almost completely at 300 °C (Fig. 13, spectrum f). As shown above, the NCO and CN species have high thermal stability and they do not leave the surface upon dynamic evacuation at 300 °C (Fig. 12). These results indicate that the surface isocyanates and cyanides react with gaseous NO. The gas phase spectra (not shown) contain CO_2 (whose concentration increases with the temperature) and NO that has been taken in excess.

In similar experiments, we studied the reactivity of the surface isocyanates and cyanides of the AuCeAl20 catalyst toward CO and H_2. The NCO and CN species do not react with CO. Fig. 14A illustrates the changes in the surface concentration of the NCO and CN species observed during the heating of the catalyst in the isolated IR cell between room temperature and 300 °C in the presence of 3 mbar of H_2. Panel B of the same figure represents the spectra of the gas phase taken at various temperatures. Strong decrease in the concentration of the NCO groups is observed at 150 °C (Fig. 14A, spectrum c). The spectra in Fig. 14A clearly show that with increase in the temperature, the Ce^{3+}/Au^0–NCO species disappear faster than the Al^{3+}–NCO. The gas phase spectra obtained between 100 and 300 °C contain H_2O, NH_3 and HNCO (ν_{as}(NCO) at 2282 cm^{-1} and ν_s(NCO) at 1250 cm^{-1} [43]). Most likely, the NCO species undergo hydrolysis to ammonia. The water molecules involved in this process are produced by reduction of the catalyst surface that has been re-oxidized during the NCO formation. The presence of some amount of gaseous HNCO suggests that dissociative chemisorption of hydrogen takes place on the catalyst surface followed by transfer of atomic hydrogen to the NCO species. It is possible that HCN can be formed by the same mechanism, which accounts for the disappearance of the CN species.

These experimental results lead to the conclusion that the intermediates in the reduction of NO with CO in the presence of H_2 are the surface NCO and CN species. Taking into account that the promotion of ceria by gold causes strong modification of the support by forming Ce^{3+} and oxygen vacancies [33], the mechanism of NO reduction with CO and H_2 over the AuCeAl20 catalyst can be represented by the following reactions:

$$Au + CeO_2 \rightarrow Au^{\delta+} \square CeO_{2-x} \tag{1}$$

$$CeO_{2-x} + yH_2 \rightarrow CeO_{2-y} + y\square + yH_2O \tag{2}$$

$$NO + \square \rightarrow N_s + O_s \tag{3}$$

$$NO + 2Au \rightarrow Au\text{-}N + Au\text{-}O \tag{4}$$

$$N_s + CO \rightarrow NCO_s \tag{5}$$

$$Au\text{-}N + CO \rightarrow Au\text{–}NCO \tag{6}$$

$$2N_s \rightarrow N_2 \tag{7}$$

$$NCO_s + NO \rightarrow N_2 + CO_2 \tag{8}$$

$$Au\text{–}NCO + NO \rightarrow Au + N_2 + CO_2 \tag{9}$$

$$CO + \square \rightarrow C_s + O_s \tag{10}$$

$$C_s + N_s \rightarrow CN_s \tag{11}$$

$$CN_s + NO \rightarrow N_2 + CO \tag{12}$$

$$Au\text{-}O + CO \rightarrow Au + CO_2 \tag{13}$$

$$Au\text{-}O + H_2 \rightarrow Au + H_2O \tag{14}$$

$$O_s + CO \rightarrow CO_2 + \square \tag{15}$$
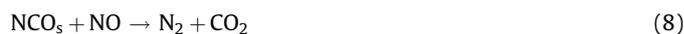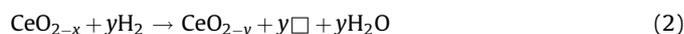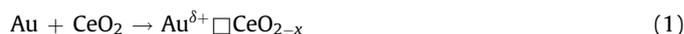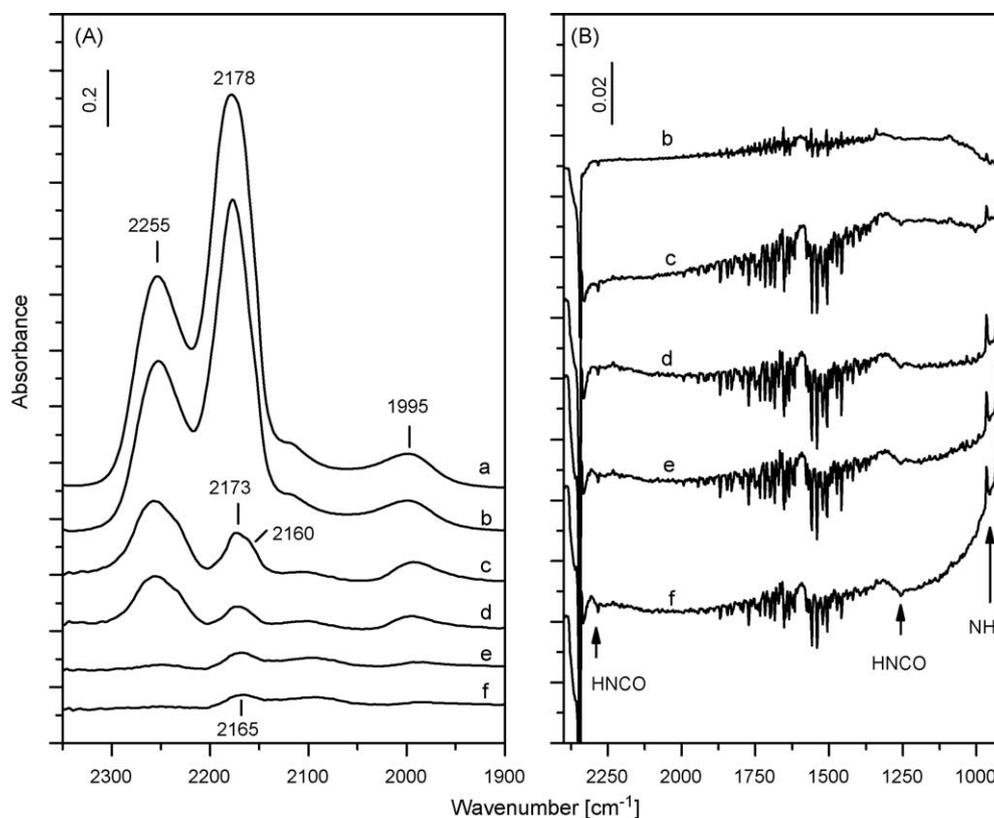
$$O_s + H_2 \rightarrow H_2O + \square \tag{16}$$

Fig. 13. FT-IR spectra collected during exposure of the AuCeAl20 sample for 15 min to a (5 mbar NO + 10 mbar CO + 3 mbar H_2) mixture at 300 °C followed by evacuation for 15 min at the same temperature and cooling to room temperature with subsequent addition of 5 mbar of NO (a) and heating for 15 min at 100 °C (b), 150 °C (c), 200 °C (d), 250 °C (e) and 300 °C (f).

Fig. 14. FT-IR spectra collected during exposure of the AuCeAl20 sample for 15 min to a (5 mbar NO + 10 mbar CO + 3 mbar H_2) mixture at 300 °C followed by evacuation for 15 min at the same temperature and cooling to room temperature with subsequent addition of 3 mbar of H_2 (a) and heating for 15 min at 100 °C (b), 150 °C (c), 200 °C (d), 250 °C (e) and 300 °C (f).

where $\square$ stands for oxygen anion vacancy, NCO_s and CN_s are isocyanate and cyanide species coordinated to surface M^{3+} ion, O_s are surface or subsurface oxygen, N_s is surface nitrogen and C_s is surface carbon. Steps 4, 6, 9 and 13 are suggested in references [12,15]. We do not have direct evidence for the dissociation of NO on the supported gold particles. The proposed mechanism is in agreement with the results of the catalytic activity tests [6,8]. The high reactivity of the isocyanates formed on the surface of the AuCeAl20 sample ensures, under steady-state conditions, high and stable activity (66% conversion of NO) and 100% selectivity toward N_2 at temperature as low as 200 °C [6]. It has been already shown that the AuCeAl20 catalyst is also active in the WGS reaction [33]. The fact that the activity of the AuCeAl20 sample is influenced positively under moist feed [8] suggests that this reaction may contribute to the mechanism by promoting the H_2 production.

The formation of N_2O and the hydrolysis of the NCO species are not shown in the proposed reaction steps. The former compound is observed during the interaction of NO with the catalyst surface at room temperature and does not form when the adsorption of NO is performed at high temperature (see Section 3.3). Ammonia appears to be undesirable product of the NO + CO + H_2 reaction over the AuCeAl20 catalyst because it does not act as reducing agent for NO. However, the generation of ammonia in situ can offer possibilities to combine the Au/CeO$_2$-Al$_2$O$_3$ with a SCR catalyst in DeNO$_x$ technologies using rich and lean cycles.

4. Conclusions

The NO + CO + H_2 reaction over CeO_2, Au/CeO$_2$, Au/CeO$_2$-Al$_2$O$_3$ and CeO$_2$-Al$_2$O$_3$ mixed support at elevated temperatures leads to the formation of NCO species on all of the samples. The presence of

oxygen vacancies in CeO_2 and ceria-alumina support helps in the dissociation of NO to nitrogen and oxygen species. The oxygen species, originating from the NO dissociation, fill the oxygen vacancies, while the nitrogen atoms lying on the surface react with CO to produce NCO species. The presence of metallic gold is not necessary for the generation of isocyanates on ceria and the mixed ceria-alumina support. Gold plays an important role in the modification of ceria leading to Ce^{3+} and oxygen vacancies formation, and causes significant lowering of the reduction temperature of CeO_2 and CeO_2-Al$_2$O$_3$ enhancing the reducibility of ceria surface layers.

The results of this investigation indicate that the CeO_2-Al$_2$O$_3$ phase in the Au/CeO$_2$-Al$_2$O$_3$ system participates directly in the catalytic reduction of NO with CO. The catalytic activity is associated with the formation of Ce^{3+} ions, respectively, oxygen vacancies, during the contact of the reacting gases, NO, CO and H_2, with the catalyst surface. The onset temperature, at which the interaction between the isocyanates on AuCeAl20 and NO begins, is low (100 °C). This explains the observed high activity of the AuCeAl20 catalyst with 100% selectivity in the reduction of NO by CO at low temperatures (200 °C) and in the presence of H_2. The role of hydrogen is to keep the surface reduced during the course of the reaction.

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