



Redox chemistry of gold in a Au/FeO_x/CeO₂ CO oxidation catalyst

A. Penkova^{a,*}, K. Chakarova^b, O.H. Laguna^a, K. Hadjiivanov^{b,*}, F. Romero Saria^a,
M.A. Centeno^a, J.A. Odriozola^a

^aDepartamento de Química Inorgánica e Instituto de Ciencia de Materiales de Sevilla, Centro Mixto Universidad de Sevilla-CSIC, Avda, Américo Vespucio, 49. 41092, Sevilla, Spain

^bInstitute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria

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ABSTRACT

Calcination and evacuation of a Au/FeO_x/CeO₂ catalyst at 573 K leads to reduction of the deposited gold to metal. This metal state is stable under oxygen and only at 573 K some metal atoms are oxidized to Au^{δ+} sites (Au⁺ cations situated on metal gold particles). However, even at room temperature, gold is readily oxidized in a CO + O₂ mixture producing, in addition to the Au^{δ+} sites, some isolated Au⁺ cations.

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1. Introduction

Supported gold catalysts are one of the greatest recent challenges to the catalytic community. After the first report that highly dispersed gold was very active in low-temperature CO oxidation [1], there were numerous studies devoted to clarifying the reasons for this activity. However, even some basic questions remain disputable, for instance the oxidation state of the active gold species in the CO oxidation reaction. Many researches are of the opinion that metallic gold is catalytically active and provide sound arguments in support of this point of view [2–6]. However, strong evidence has also been provided that it is cationic gold that forms the catalytically active sites [7–9]. Since the reaction under consideration is a redox process, it seems also likely that Auⁿ⁺/Au⁰ redox couples would operate in the process [10]. That is why, the gold redox chemistry raises an increasing interest.

It is well established that calcination of supported gold catalysts leads to autoreduction of gold and formation of metal particles [11–17]. However, the surface of these particles is often covered by positively charged gold species (the so called Au^{δ+} sites) [10,15–21]. The latter are reduced to metallic gold under vacuum treatment at temperatures around 573 K [15]. Oxidation of these reduced samples results in back conversion of some metal surface atoms to Au^{δ+} sites [15]. However, the process depends on many factors. Among them, the most important seem to be (i) the nature of the oxidizing agent (ii) temperature, (iii) the nature of the support and (iv) the metal particle size [22–24].

Recently it was reported that CO₂ or a CO + O₂ mixture were much more efficient oxidizing agents for lanthana-supported Au⁰ than oxygen itself [10]. In this communication we report on the redox chemistry of gold in a Au/FeO_x/CeO₂ catalyst. Both iron oxide

and ceria are considered suitable supports for CO oxidation gold catalysts. We have found that a Au/FeO_x/CeO₂ catalyst is very active in CO oxidation at low-temperature and it was of interest to follow the gold redox chemistry with this sample. The experiments were performed using FTIR spectroscopy of CO as a probe molecule. We succeeded in detecting isolated Au⁺ species produced after interaction of the catalyst with a CO + O₂ gas mixture. In contrast, oxygen alone slightly affected metal gold sites.

2. Experimental

2.1. Catalyst preparation

The FeO_x/CeO₂ mixed oxide used as support was synthesized by modifying a reported pseudo sol–gel method that implied the thermal decomposition of the corresponding propionates [25]. The starting materials, Ce(III) acetate and Fe(III) acetyl acetonate, were dissolved separately on a 0.12 M solution of propionic acid. After that both solutions were mixed and homogenized by stirring and heated until evaporation of the propionic acid excess. The resulting resin was calcined in air for 2 h at 773 K at a 2 K min⁻¹ ramp. According to chemical analysis, the prepared solid had a 3.37% weight of Fe (Fe/Ce molar ratio of 15/85).

The gold-containing catalyst was prepared by deposition–precipitation [26]. An adequate amount of HAuCl₄ · 3H₂O (Alfa, 99.99% pure) to obtain 1% wt. of gold in the support, was dissolved in deionized water (6.0 × 10⁻⁴ M) and the pH of the solution adjusted to 8.0 by addition of 0.1 M solution of NaOH in an automatic system of measurement and titration (CRISON pH-Burette 24). The solution was heated to 343 K and then the support was added and kept under continuous stirring for 1 h. The solid obtained was washed with distilled water several times (until the disappearance of chlorine and sodium ions), then dried overnight at 333 K and finally calcined for 2 h at 573 K.

* Corresponding authors. Tel.: +3592 9793598; fax: +3592 8705024.

E-mail addresses: anna@cartuja.csic.es (A. Penkova), kih@svr.igic.bas.bg (K. Hadjiivanov).

2.2. Catalyst characterization

X-ray diffraction (XRD) patterns were recorded using an X'Pert Pro Philips diffractometer working with Cu K α radiation ($\lambda = 1.5404 \text{ \AA}$) in a continuous scan mode from 20° to 80° of 2θ using 0.05° sampling interval and 1.0 s.

The chemical composition of the catalyst was determined by X-ray fluorescence (XRF) with a Siemens SRS 3000 sequential spectrophotometer equipped with a rhodium tube. XRF measurements were performed onto pressed pellets (sample included 10% wt. of wax).

The BET surface area was measured by nitrogen adsorption at liquid nitrogen temperature in a Micromeritics ASAP 2000 apparatus. Before analysis, the sample was degassed for 2 h at 423 K in vacuum.

FTIR spectra were recorded in a transmission mode with a Nicolet Avatar 360 Spectrometer accumulating 64 scans at a spectral resolution of 2 cm^{-1} . The experiments were performed *in situ* using a purpose-made IR cell connected to a vacuum-adsorption apparatus with a residual pressure lower than 10^{-3} Pa . The cell allowed registering the spectra in the temperature interval between 100 K and ambient temperature. The sample powders were pressed into self-supporting wafers (density $10\text{--}12 \text{ mg cm}^{-2}$) under a pressure of $10^6\text{--}10^7 \text{ Pa}$. Prior to the experiments, the samples were activated *in situ* in the IR cell by heating for 1 h at 573 K under 2.67 kPa oxygen followed by 1 h evacuation at the same temperature. Carbon monoxide (>99.997 purity) was supplied by Linde AG. Before adsorption, it was purified by passing through a liquid nitrogen trap. CO adsorption was carried out at 100 K and at ambient temperature.

2.3. Catalytic activity

The catalytic tests of CO oxidation were carried out in a conventional continuous flow U-shape glass reactor working at atmospheric pressure where 80 mg of sample are placed over glass wools. A thermocouple in contact with the sample assures the right measure of temperature. The reactor was surrounded by an electrical furnace equipped with a temperature programmer. The feed mixtures were prepared using mass flow controllers (Bronkhorst). The reaction was followed by mass spectrometry, using a Balzers Thermostat benchtop mass spectrometer controlled by the software Balzers Quadstar 422 with capabilities for quantitative analysis.

The light-off curves of CO oxidation (573 K , 5 K min^{-1}) were obtained with a mixture of 3.4% CO and 21% O $_2$ balanced by He at a total flow rate of 42 ml min^{-1} . Empty reactor (without sample) shows no activity under such conditions. The catalysts were pre-activated *in situ* at 573 K during 60 min with 21% O $_2$ in He at a flow of 30 ml min^{-1} and then stabilized at room temperature before the light-off curved started.

3. Results and discussion

3.1. Initial characterization of the sample and background IR spectrum

The gold content of the sample, as measured by XRF was 0.95 wt%, i.e., very close to the nominal value of 1%, and its specific B.E.T. surface area was $49 \text{ m}^2 \text{ g}^{-1}$.

The XRD pattern of the calcined catalyst is presented in Fig. 1. Only diffraction peaks corresponding to the fluorite-type crystal-line structure of CeO $_2$ (cerianite phase) were observed. No peaks due to iron or gold species were detected. The lack of gold peaks could be due to its low content. The absence of peaks due to iron species could indicate introduction of iron in the cerianite structure or existence of iron in the form of amorphous particles.

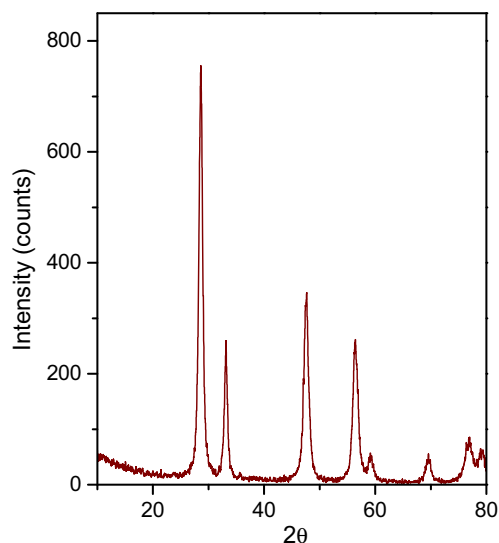


Fig. 1. XRD pattern of the Au/FeO $_x$ /CeO $_2$ sample calcined at 573 K.

The background spectrum of the activated support contains, in the OH region, a complex band with resolved maxima at 3675, 3650 and 3635 cm^{-1} corresponding to three kinds of isolated OH groups. In addition, bands at 1465 and 1390 cm^{-1} are registered in the low-frequency region and demonstrate the presence of some carbonates residual to evacuation at 573 K [27]. A weak band at 2341 cm^{-1} is also seen and assigned to occluded CO $_2$ molecules. The spectrum of the activated Au/FeO $_x$ /CeO $_2$ catalyst is very similar. Only the OH band at 3650 cm^{-1} is less intense and appears as a shoulder of the 3635 cm^{-1} band. Small alternation in the intensities of the bands in the carbonate region was also detected.

3.2. Catalytic activity

The results on the catalytic activity of the Au/FeO $_x$ /CeO $_2$ catalyst and the FeO $_x$ /CeO $_2$ support towards CO oxidation are shown as light-off curves on Fig. 2. The catalytic performance of a ceria sample prepared in similar conditions of those used for FeO $_x$ /CeO $_2$ support is also included for comparison.

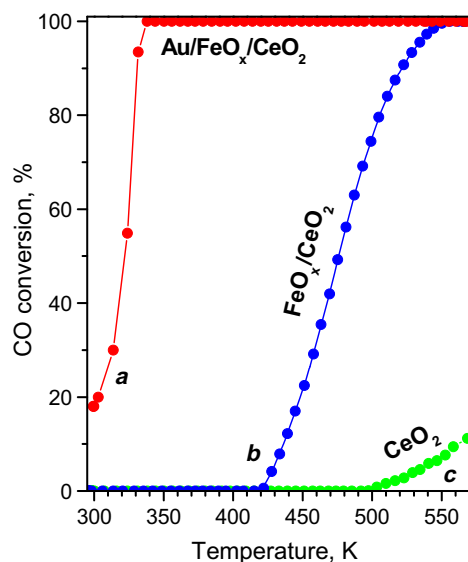


Fig. 2. Catalytic activity towards CO oxidation of: Au/FeO $_x$ /CeO $_2$ (a), FeO $_x$ /CeO $_2$ (b) and CeO $_2$ (c) shown as light-off curves.

The Au/FeO_x/CeO₂ sample is a very active catalyst. It has 18% CO conversion at room temperature and gets 100% conversion at 337 K (Fig. 2, curve a). The FeO_x/CeO₂ support is not active below 420 K (Fig. 2, curve b). With temperature the activity increases reaching total CO conversion at 550 K. Obviously, this activity is related with the presence of iron, which has been proved to be an active catalyst for CO oxidation [28]. Indeed, pure CeO₂ presents a very low activity starting at 500 K and reaching less than 15% CO conversion at 573 K. The results demonstrate that the activity of the Au/FeO_x/CeO₂ sample at temperatures below 420 K should be related to the presence of gold.

3.3. FTIR experiments: CO adsorption on the support

In order to be able to distinguish the carbonyl bands formed with the participation of gold sites, we have initially studied adsorption of CO on the support. The first set of experiments was performed with an oxidized sample: after standard activation it was heated for 1 h in oxygen at 473 K, then cooled to room temperature and oxygen evacuated.

Adsorption of CO (267 Pa equilibrium pressure) at 100 K on the FeO_x/CeO₂ sample thus treated results in the appearance of carbonyl bands with maxima at 2172 and 2152 cm⁻¹ (Fig. 3A, spectrum a). Evacuation at 100 K (Fig. 3A, spectra b–j) and at increasing temperatures up to ambient one (see the inset of Fig. 3A) provokes a decrease in intensity of all bands and finally they disappear.

The most intense band at 2152 cm⁻¹ is very sensitive to the equilibrium pressure and is the first carbonyl band disappearing after evacuation even at 100 K. It is blue shifted with the coverage decrease and at low coverages additional components become resolved. At least some components of the band are assigned to OH–CO interaction. Indeed, the OH bands are slightly eroded and a red shift to ca. 3580 cm⁻¹ is observed in parallel with the develop-

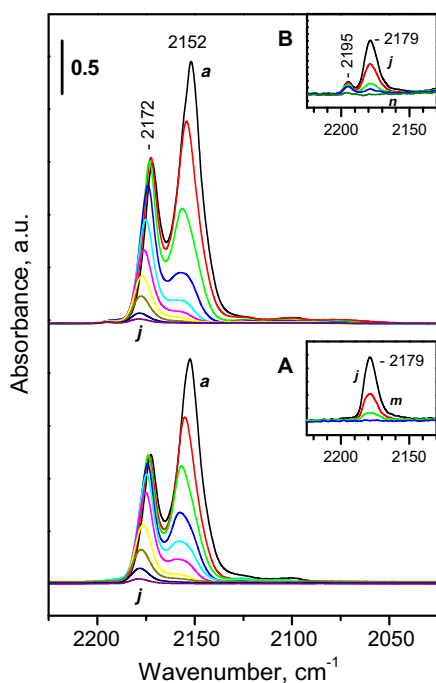


Fig. 3. FTIR spectra of CO adsorbed at 100 K on the FeO_x/CeO₂ support. The sample was heated for 1 h at 473 K in 2 kPa of oxygen and then evacuated at (A) ambient temperature and (B) at 573 K. Equilibrium CO pressure of 267 Pa (a) and evolution of the spectra in dynamic vacuum at 100 K (b–j) and at higher temperatures up to ambient one (k–n). The spectra are background corrected.

ment/disappearance of the 2153 cm⁻¹ band. The $\Delta\nu$ value for the band at 3675 cm⁻¹ is ca. –100 cm⁻¹ and for the bands at 3650–3635 cm⁻¹, ca. –60 cm⁻¹. Knözinger and Zaki [29] have reported that Ce–OH bands at 3664 and 3640 cm⁻¹ are not shifted upon CO adsorption due to the basic character of ceria. However, Binet et al. [30] and Bulanin et al. [31] have observed a small ill-defined shift together with the development of a band at 2153–2151 cm⁻¹. There are very scarce data in the literature on the acidity of Fe–OH groups [32]. A Fe³⁺–OH band at 3685 cm⁻¹ was reported for a Fe–BEA sample and this band was red shifted by 100 cm⁻¹ after CO adsorption (respective carbonyl band at 2158 cm⁻¹). Based on these observations, we tentatively assign the band at 3675 cm⁻¹ to Fe–OH species, and the bands at 3650–3635 cm⁻¹, to hydroxyls of Ce–OH type [22]. Consequently, the high frequency component around 2158 cm⁻¹ is attributed to CO interacting with Fe–OH groups, while the lower frequency one most probably reveals two types of interaction: CeOH–CO (unstable) and Ce³⁺–CO (more stable, around 2154 cm⁻¹), as also found by other authors [33].

The next band disappearing under evacuation (at temperatures higher than 100 K) is that at 2174 cm⁻¹ (see the inset in Fig. 3A). It is also blue shifted to 2183 cm⁻¹ with coverage decrease, which indicates that the respective adsorption sites are not isolated. Therefore, we assign this band to Fe²⁺–CO species formed with associated Fe²⁺ ions. Some arguments in favor of this assignment will be provided below.

When the sample was evacuated at 573 K after the oxidative treatment, adsorption of CO resulted in the appearance of the same bands, but somewhat more intense (Fig. 3B). This indicates that some Fe²⁺ and Ce³⁺ sites have been created during the vacuum treatment. In addition, another weak band at 2196 cm⁻¹ was observed. It is the most stable carbonyl band (see the inset of Fig. 3B). The band maximum remains hardly affected by coverage, suggesting the band is produced with isolated cationic sites. Based on literature data [34] and further experiments (see below), we assign the band to Fe²⁺–CO species produced with the participation of isolated Fe²⁺ ions. Evidently, these ions have been created by autoreduction of Fe³⁺ species.

3.4. FTIR experiments: CO adsorption on the activated Au/FeO_x/CeO₂ sample

Let us first briefly recall the principles of using CO as an IR probe for characterization of supported gold species [18]. The most stable carbonyls are formed with Au⁺ cations and they are observed around 2170–2160 cm⁻¹. The species are stabilized as a result of formation of both, σ - and π -bonds and the synergism between them. As a result, they resist evacuation at ambient temperature. Carbonyls of the Au⁰–CO type are usually observed around 2130–2080 cm⁻¹ and, due to weak σ -bond, are less stable than the Au⁺–CO species. These species are easily destroyed by evacuation. Bands between 2160 and 2130 cm⁻¹ characterize Au³⁺–CO species which, in addition to the frequency, are characterized by a stability intermediate between the stabilities of Au⁺–CO and Au⁰–CO. We believe that these species represent Au⁺ cations situated on metal gold particles and sharing their positive charge with the gold bulk [10,15–19].

Au³⁺–CO species are rarely observed because normally the Au³⁺ cations are blocked by water molecules and evacuation at elevated temperatures aimed at removing water leads to autoreduction of Au³⁺. The interaction between Au³⁺ and CO is essentially electrostatic and the Au³⁺–CO species can be easily destroyed even at a low-temperature. These species are observed in the 2210–2170 cm⁻¹ spectral region. Finally, carbonyls of negatively charged gold are observed below 2080 cm⁻¹ and, due to the enhanced π -bonding, are more stable than Au⁰–CO. For convenience, the

Table 1Assignment of the carbonyl bands observed with the Au/FeO_x/CeO₂ sample.

Assignment	Band position, cm ⁻¹	Comments
Fe ²⁺ –CO	2196	Formed with isolated Fe ²⁺ species. Coverage independent maximum. Not observed with a sample treated with oxygen at 473 K and above
Fe ²⁺ –CO	2174	Formed with associated Fe ²⁺ species. At low coverage shifted to 2183 cm ⁻¹ . Not observed with a sample treated with oxygen at 573 K
Fe ³⁺ –OH–CO	2158	OH modes shifted by ca. 100 cm ⁻¹
Ce ³⁺ –OH–CO	2153	OH modes shifted by ca. 60 cm ⁻¹
Ce ³⁺ –CO	2154	More stable than the Ce ³⁺ –OH–CO species
Au ⁺ –CO	2168	At high coverage observed at 2170 cm ⁻¹ . Sites produced after interaction of the sample with CO + O ₂ at ambient temperature. Disappears after evacuation at 373 K
Au ^{δ+} –CO	2136–2130	Negligible concentration on activated sample. Various sites produced after interaction of the sample with O ₂ at 573 K or with CO + O ₂ at ambient temperature
Au ^{δ+} –CO	2118	Shifted to 2127 cm ⁻¹ at low coverage. Sites produced after interaction of the sample with CO + O ₂ at ambient temperature
Au ⁰ –CO	2103	At low coverage shifted to 2118 cm ⁻¹

carbonyl bands observed in this study and their assignments are summarized in Table 1.

Adsorption of CO (100 K, 267 Pa equilibrium pressure) on the activated Au/FeO_x/CeO₂ sample results in the appearance of carbonyl bands with maxima at 2196, 2174, 2153 and 2103 cm⁻¹ (Fig. 4, spectrum a). Evacuation at 100 K (Fig. 4, spectra b–j) and at increasing temperatures (Fig. 5) provokes a decrease in intensity of all bands and finally they disappear.

All bands in the 2200–2150 cm⁻¹ region have also been registered with the pure support (see above) which indicates that they are not related to the presence of gold. The band at 2103 cm⁻¹ is assigned to Au⁰–CO species [2,7,10,11,13–19,35–37] and is progressively shifted during evacuation to 2118 cm⁻¹. This shift is opposite to the shift usually observed with CO on metals. However, it has been demonstrated by Boccuzzi et al. [35] that the shift is due to lateral interaction of the CO molecules adsorbed on gold with CO molecules on the support. At low coverages (see Fig. 5) a high frequency shoulder of the Au⁰–CO band, at 2136 cm⁻¹, becomes visible. This shoulder is assigned to small amounts of Au^{δ+}–CO species formed with positively charged gold residual to autoreduction [10,15–19,36,37]. Thus, the experiments revealed that gold on the 573 K evacuated sample was encountered in a metal form.

The band at 2196 cm⁻¹ is more intense than with the support. Thus, one can speculate some gold carbonyls participate in the absorbance. However, the frequency of the band at 2196 cm⁻¹ is too high, and the stability not high enough, to allow assignment of the band to Au⁺–CO type carbonyls. Bands at similar frequencies have been assigned to dicarbonyls of oxidized gold sites [22,38], but these latter species are easily destroyed by evacuation, which is not our case. Therefore, it appears, that the presence of gold somewhat facilitates reduction of Fe³⁺ species.

Another interesting phenomenon is that the band at 2174 cm⁻¹ is less intense with the gold-containing sample. This could be due to blocking of some iron sites by gold species and could indicate that part of the gold is located on the iron-containing part of the surface.

Many authors have detected a band around 2127 cm⁻¹ with ceria-based systems which is due to the forbidden electronic transition of surface Ce³⁺ ions [39,40]. Moreover, a band at 2110 cm⁻¹ has been proposed to be associated with Ce³⁺ surface sites adjacent to gold atoms [22]. However, due to their origin, these bands are not affected by evacuation. In our case all bands around this frequency disappeared upon outgassing. Therefore, no electronic transition of Ce³⁺ ions was observed with our sample after

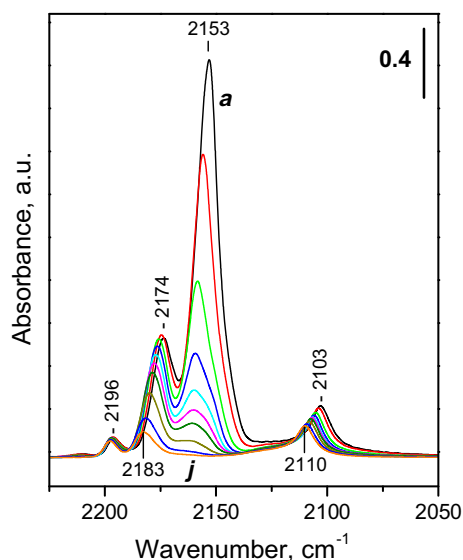


Fig. 4. FTIR spectra of CO (267 Pa equilibrium pressure) adsorbed at 100 K on an activated Au/FeO_x/CeO₂ sample (a) and evolution of the spectra in dynamic vacuum at 100 K (b–j). The spectra are background corrected.

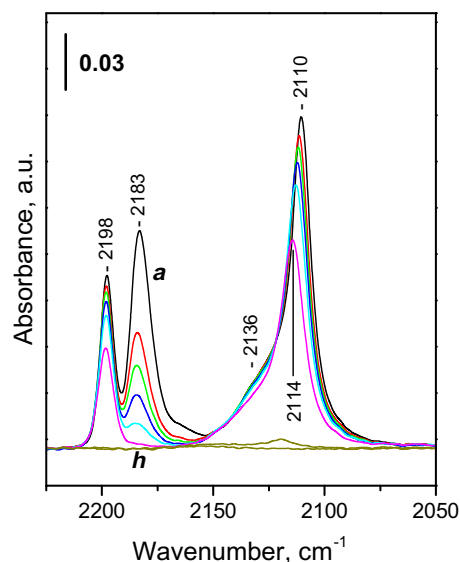


Fig. 5. (continuation from Fig. 4) FTIR spectra of CO (267 Pa equilibrium pressure) adsorbed at 100 K on an activated Au/FeO_x/CeO₂ sample: evolution of the spectra in dynamic vacuum at 100 K (a) and at increasing temperatures (b–h). The spectra are background corrected.

the described pretreatment which suggested that cerium ions were rather situated in bulk.

3.5. FTIR experiments: CO adsorption on the Au/FeO_x/CeO₂ sample reoxidized by oxygen

In order to obtain information on the ability of metallic gold to be reoxidized, we studied a sample after interaction with oxygen at different temperatures. The sample was heated for 1 h in the presence of O₂ at 373, 473 and 573 K, and then oxygen was evacuated at room temperature. The results of subsequent testing the sample with CO at 100 K are presented on Fig. 6.

It is seen, from the figure, that the band at 2196 cm⁻¹ is not produced with a sample treated with oxygen at temperatures of reoxidation higher than 473 K. Moreover, the band at 2172 cm⁻¹ is not registered with the sample oxidized at 573 K. These results confirm that the two bands (at 2196 and 2172 cm⁻¹) are due to two families of Fe²⁺–CO species, respectively (the Fe²⁺ ions have been converted to Fe³⁺ that are not able to form carbonyls [34]).

Let us now concentrate on the insets in Fig. 6, where the coverage is lower and allows a more detailed analysis of the spectra. It is seen that metallic gold is hardly affected by oxidation at 373 and 473 K. Only after oxidation at 573 K some Au^{δ+} sites appear, as evidenced by the band at 2130 cm⁻¹ (Fig. 6C, the inset). No isolated Au⁺ species were detected.

3.6. FTIR experiments: CO–O₂ interaction at ambient temperature

When CO (1.33 kPa equilibrium pressure) was adsorbed at room temperature on the activated sample, the bands at 2180 and 2157 cm⁻¹ appeared with a strongly reduced intensity due to the weak stability of the respective species (Fig. 7, spectrum a). A careful inspection of the spectrum also reveals that (i) the band at 2197 cm⁻¹ is somewhat less intense than expected and (ii) the shoulder at 2136 cm⁻¹ is not observable, i.e. the Au^{δ+} sites have

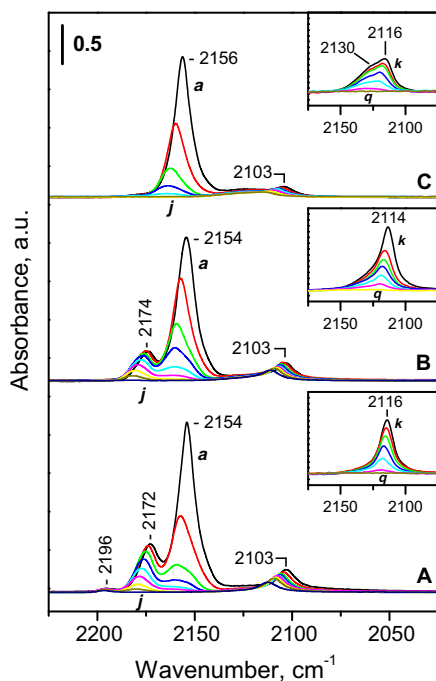


Fig. 6. FTIR spectra of CO adsorbed at 100 K on a Au/FeO_x/CeO₂ sample subjected to different pretreatments: oxidized with O₂ (2.67 kPa; 1 h; followed by evacuation at ambient temperature) at 373 (A), 473 (B) and 573 K (C). Equilibrium CO pressure of 267 Pa (a) and evolution of the spectra in dynamic vacuum at 100 K (b–j) and at increasing temperatures (k–q). The spectra are background corrected.

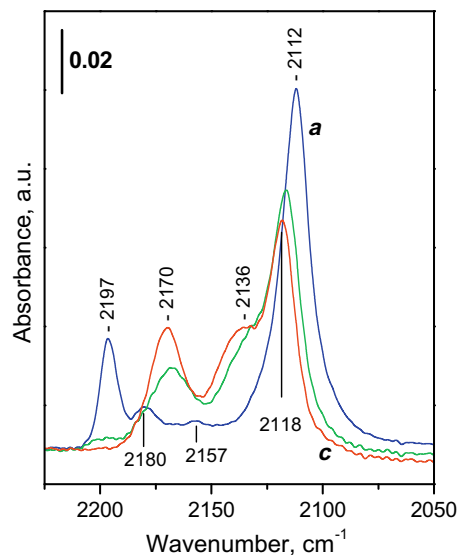


Fig. 7. FTIR spectra of CO (1.33 kPa equilibrium pressure) adsorbed at ambient temperature on an activated Au/FeO_x/CeO₂ sample (a), after addition to the system of 680 (b) and 800 Pa (c) O₂. The spectra are background and CO gas phase corrected.

been reduced by CO at ambient temperature. The principal carbonyl band in the spectrum is that at 2112 cm⁻¹. In addition, weak bands assigned to carbonate-like structures develop (Fig. 8, spectrum a). This may account for the reduced intensity of the 2197 cm⁻¹ band (blocking of the respective sites).

Introduction of oxygen to the sample put in equilibrium with CO provokes drastic changes in the IR spectra. First, the band at 2197 cm⁻¹ disappears (Fig. 7, spectra b, c). The band at 2112 cm⁻¹ decreases in intensity and is shifted to 2118 cm⁻¹, a well discernible shoulder at 2136 cm⁻¹ develops. A new band, at 2170 cm⁻¹ appears and rises in intensity. Although the band at 2180 cm⁻¹ is masked by the 2170 cm⁻¹ band, it seems that it slightly decreases in intensity. Simultaneously, strong bands in the carbonate region develop and a band at 2345 cm⁻¹, evidencing production of CO₂, grows (Fig. 8, spectra b–c).

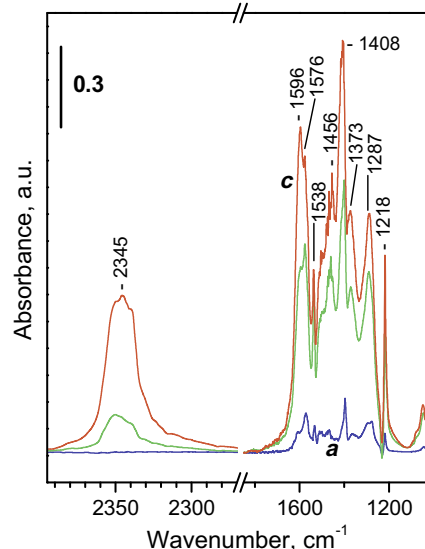


Fig. 8. FTIR spectra (CO₂ and carbonate spectral regions) registered after adsorption of CO (1.33 kPa equilibrium pressure) at ambient temperature on an activated Au/FeO_x/CeO₂ sample (a) after addition to the system of 680 (b) 800 Pa (c) O₂. The spectra are background corrected.

Then the system was evacuated. Fig. 9 shows the evolution of the spectra during evacuation. The first band to disappear is that at 2118 cm^{-1} with a simultaneous shifting to 2127 cm^{-1} . Since the singleton frequency of the $\text{Au}^0\text{--CO}$ species on the activated sample was at 2118 cm^{-1} , we conclude that the band at $2118\text{--}2127\text{ cm}^{-1}$ characterizes CO adsorbed on positively charged gold species ($\text{Au}^{\delta+}\text{--CO}$, to distinguish from $\text{Au}^{\delta+}\text{--CO}$). The next band to disappear is that at 2136 cm^{-1} . Analysis of the spectra indicates that this band is rather complex and consist of several components. We assign this band to $\text{Au}^{\delta+}\text{--CO}$ species. Indeed, the positively charged gold species could be very different, depending on their density on the gold particle and the counter anion (O^{2-} , O_2^- , etc.) [10].

The band at 2170 cm^{-1} is settled at 2168 cm^{-1} and slowly decreases in intensity during evacuation. However, it disappears from the spectra after evacuation at 373 K only. Bands around this frequency have been assigned to cerium carbonyls [22,24]. However, $\text{Ce}^{n+}\text{--CO}$ species are easily destroyed by evacuation. The only carbonyls with such a high stability in our system could be $\text{Au}^+\text{--CO}$ species. Indeed, carbonyls of isolated Au^+ cations have been reported to absorb around this frequency [13,15,19–21,41,42]. Note that here “isolated” means that there is no gold in the first coordination sphere. Therefore, our results indicate that, in a $\text{CO} + \text{O}_2$ atmosphere, some gold atoms are converted to isolated gold cations. Most probably these are atoms from the gold-support interface which can easily be separated from the mother gold particle. This is consistent with the ideas of reconstruction of the gold surface [22]. Evidently, the nature of the support is decisive for this process, since no formation of isolated Au^+ species has been reported with other gold-containing systems under analogous conditions. In addition, all gold centers detectable by CO become positively charged. Note that this state of the catalyst is under working catalytic conditions, as evidenced by the development of a CO_2 band at 2345 cm^{-1} .

Additional experiments (details not reported) showed that the $\text{Au}^+\text{--CO}$ band at 2168 cm^{-1} was stable in the reaction mixture at 373 K , but disappeared at 423 K , i.e., at higher temperatures the equilibrium was shifted towards metallic gold.

Let us now consider the disappearance of the bands at 2196 and 2174 cm^{-1} after interaction of the sample with oxygen at elevated

temperatures. At first sight, one could suggest conversion of the respective species into other ones. However, experiments with the support alone showed that the bands are sensitive to oxygen. Therefore, we infer that the bands at 2196 cm^{-1} and 2174 cm^{-1} , characterizing carbonyls of isolated and associated Fe^{2+} species, respectively, disappear because of the oxidation of Fe^{2+} ions to Fe^{3+} .

In summary, our results evidence that a $\text{CO} + \text{O}_2$ mixture is much more efficient for reoxidation of gold than oxygen itself. These results can be rationalized by the assumption that the real oxidizing agent is CO_2 produced by CO oxidation, as proposed earlier [10]. Reconstruction of gold in the presence of CO, as observed by some researches [21,43–45], can assist the process.

Also, the results indicate that, on our $\text{Au}/\text{FeO}_x/\text{CeO}_2$ catalyst (active in CO oxidation at room temperature) gold very easily changes its oxidation state. It appears that the nature of the support and the presence of $\text{Fe}^{3+}/\text{Fe}^{2+}$ and $\text{Ce}^{4+}/\text{Ce}^{3+}$ redox couples facilitate gold oxidation. In fact, no production of isolated Au^+ species was observed at room temperature with gold on other supports that are not so easily reduced and reoxidized (La_2O_3 [10], TiO_2 [15], MgO [17]). Finally, our findings endorse the hypothesis that Au^+/Au^0 redox couples operate in the CO catalytic oxidation.

4. Conclusions

A $\text{Au}/\text{FeO}_x/\text{CeO}_2$ catalyst, active in CO oxidation at room temperature, was investigated by means of IR spectroscopy of adsorbed CO. The results show that gold on 573 K evacuated sample is in metallic form and this state is hardly affected by interaction with oxygen up to 473 K . However, even at room temperature, gold is readily oxidized to Au^+ and $\text{Au}^{\delta+}$ species in the presence of a $\text{CO} + \text{O}_2$ mixture. The results favor the hypothesis that Au^+/Au^0 ($\text{Au}^{\delta+}/\text{Au}^0$) redox couples operate in low-temperature CO oxidation.

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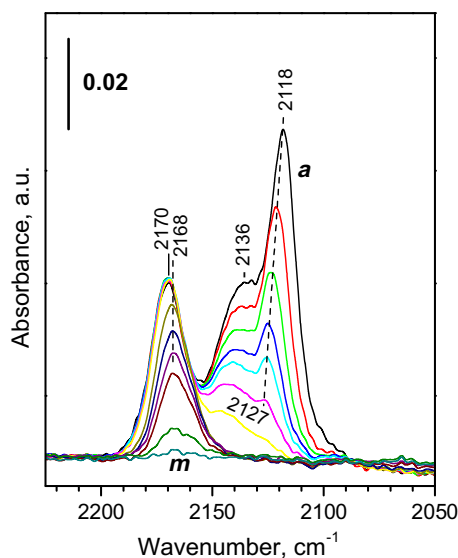


Fig. 9. FTIR spectra of CO (1.33 kPa equilibrium pressure) and O_2 (800 Pa equilibrium pressure) co-adsorbed at ambient temperature on an activated $\text{Au}/\text{FeO}_x/\text{CeO}_2$ sample (a), evolution of the spectra after evacuation at ambient temperature (b–i), 2 (j) and 7 min (k) at 323 K , 2 (l) and 7 min (m) at 373 K . The spectra are background and CO gas phase corrected.

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