

## CO selective oxidation on ceria-supported Au catalysts for fuel cell application

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### Abstract

Ceria-supported Au catalysts for selective oxidation of CO under simulated fuel processing conditions for polymer electrolyte membrane fuel cell (PEMFC) application were investigated. Fresh and used catalysts were characterized by X-ray diffraction, X-ray fluorescence and transmission electron microscopy (TEM). The influence of catalyst heat treatment, reaction temperature, gas composition and space velocity on CO conversion and CO<sub>2</sub> selectivity has been evaluated. Air calcination at 500 °C resulted in the establishment of adequate interfacial metal oxide properties which are essential to promote the selective CO oxidation. CO conversion close to 100% was obtained at 120 °C, whereas CO<sub>2</sub> selectivities not higher than 40% were obtained in the entire temperature range investigated (80–120 °C). The presence of CO<sub>2</sub> in the inlet stream negatively affected both CO conversion and CO<sub>2</sub> selectivity. Both calcined and uncalcined Au/CeO<sub>2</sub> catalysts resulted to be very stable, as demonstrated by 120 h endurance tests. TEM investigation of the used catalysts revealed that a surface Au particles reconstruction occurred during reaction.

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### 1. Introduction

Great R&D efforts are currently being made for polymer electrolyte membrane fuel cells (PEMFC) owing to its advantageous potentialities in automotive applications, such as high efficiency, low emissions and low operating temperature [1–3]. On-board hydrogen production should be the most practical way to feed the cell, as no infrastructure for handling and distribution of this fuel is currently available; thus, fuels such as methane, methanol or gasoline must be reformed to obtain a hydrogen-rich gas mixture via a fuel processor. Yet, the as-obtained reformat contains carbon monoxide at concentration levels near 1 vol.%, which irreversibly poisons the Pt-based anode catalyst of the fuel cell. As a consequence, the CO concentration in the reformat must be reduced to <20 ppm; this could be achieved through its selective oxidation in a preferable oxidation (PROX) process. In order to avoid the presence of heat exchangers, the most convenient temperature for PROX is the fuel cell op-

erating temperature (around 80 °C), although higher values (up to 130 °C) are currently taken into consideration due to the superior CO tolerance of the anode catalyst under this condition. In this temperature range, oxide-supported Au catalysts have demonstrated to be very promising candidates [4–11] for CO selective oxidation; some of these (such as Au/Fe<sub>2</sub>O<sub>3</sub>, Au/MnOx and Au/Co<sub>3</sub>O<sub>4</sub>) are active at very low temperature, well below the range of interest for fuel cell applications.

Several papers on the Au-catalyzed CO oxidation, often contradictory in their conclusions, have been produced in the last few years. Most debated arguments are, in particular, the identification of active species, the role played by the support and, more generally, the mechanism that governs the reaction. In this respect, most of the authors agree with a synergistic mechanism that would occur at the gold–oxide support interface; the nature of this latter plays a well defined role in the catalytic process [12–14]. Accordingly, CO oxidation appears to occur with high reaction rates if CO, adsorbed on a gold particle, interacts with oxygen adsorbed on a highly reducible metal oxide support, with subsequent dissociation at the metal–support interface. In this view, the role of the substrate (such as Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, NiO, Co<sub>3</sub>O<sub>4</sub>) is

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not only to stabilize the small supported Au particles, but even to promote the adsorption and activation of oxygen. For non-reducible supports, such as SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, the catalytic activity is much more strongly dependent on Au dispersion; in fact, the oxygen adsorption occurs only on the metal site [6].

Among the metal oxides used as support for gold, ceria has not been widely investigated; on the other hand, ceria-containing materials have been widely studied for a number of heterogeneous catalytic reactions such as, for example, the treatment of exhaust gases from automobiles [15].

Gardner et al. [16] reported high catalytic activity in CO oxidation at 75 °C for coprecipitated 20% Au/CeOx, with negligible activity decay over 160 h. Lyn and Flytzani-Stephanopoulos [17] demonstrated the complete CO oxidation in air at room temperature on a Au<sub>0.05</sub>[Ce(La)]<sub>0.95</sub>Ox catalyst calcined in air at 500–600 °C. Dekkers et al. [18] showed an increased catalytic activity in CO oxidation on silica- and alumina-supported Au samples when a 10% CeOx was subsequently impregnated on the parent catalysts. More recently, Bera and Hegde [19] reported complete CO oxidation below 200 °C over thermally treated Au/CeOx prepared by the solution-combustion method. Moreover, the activity and selectivity of Au/CeOx for low temperature (40–80 °C) CO oxidation in hydrogen-rich reformer gas were found by Han et al. [7] to be higher than those of conventional Pt/Al<sub>2</sub>O<sub>3</sub> catalysts.

In this study, the results of selective CO oxidation over Au/CeOx catalysts are presented. Varying amounts of CO<sub>2</sub> have been added to the inlet gas stream to allow a first evaluation of the Au/CeOx system for fuel cell applications.

## 2. Experimental

### 2.1. Catalysts preparation and characterization

Au/CeOx catalysts were prepared by coprecipitation. Two aqueous solutions, one containing HAuCl<sub>4</sub> (Aldrich) and the other containing (NH<sub>4</sub>)<sub>2</sub>Ce(NO<sub>3</sub>)<sub>6</sub> (Aldrich) were mixed under continuous stirring and subsequently added to an 1 M Na<sub>2</sub>CO<sub>3</sub> solution kept at 10 °C, carefully maintaining the pH of the solution within the range 9–10. The yellow precipitate was digested for 24 h and washed with water to remove chlorine. Then, the catalyst was dried at 80 °C under vacuum (10<sup>-2</sup> mbar) for 48 h. An aliquot of the as-obtained catalyst was calcined at 500 °C in static air for 4 h. The Au content was determined by X-ray Fluorescence (Bruker AXS S4 Explorer). The average crystallite size of the calcined catalyst was determined by X-ray diffraction (Philips X'Pert).

The morphology of fresh and used catalysts was investigated by transmission electron microscopy (TEM) using a Philips CM12 instrument provided with a high resolution camera which allows acquisition and elaboration of TEM images. Specimens were prepared by ultrasonic dispersion

of the catalysts in isopropyl alcohol depositing a drop of suspension on carbon-supported films.

### 2.2. Activity measurements

Oxidation measurements were carried out at atmospheric pressure in a quartz microreactor ( $d = 4$  mm) placed in a ceramic tube furnace; the weight and length of the catalyst bed were 170 mg and 6 mm, respectively. The pure catalyst mass was varied between 12 and 50 mg about, corresponding to gas hourly space velocity (GHSV) values ranging from 100,000 to 450,000 h<sup>-1</sup>, assuming that the catalyst density was roughly 1 g/cc. SiC was used as a diluent; the catalyst/diluent volume ratio was varied in the range 10–40 vol.%. The temperature of the catalyst bed was monitored with a thermocouple sheathed in a quartz thermowell inserted into the reactor bed. The reaction was conducted at temperatures ranging from 80 to 120 °C. The composition of the gas mixture was: H<sub>2</sub>: 48 cc/min; CO: 1 cc/min; O<sub>2</sub>: 1.5 cc/min, rest He; total flow 100 cc/min. The influence of CO<sub>2</sub> was investigated by adding to the mixture up to 24 cc/min CO<sub>2</sub>; the He flow rate was correspondingly decreased in order to maintain constant the total flow (100 cc/min). So doing, the H<sub>2</sub>, CO and O<sub>2</sub> concentrations were maintained constant (48, 1 and 1.5%, respectively) while CO<sub>2</sub> concentration was varied from 0 to 24%. Gases were fed with properly calibrated mass flow controllers (Brooks 5850S) after purification by De-oxo Gas Clean Filters (Chrompack) and molecular sieve trap to remove contaminants and water. Reaction streams were analyzed by gas-chromatography (Chrompack 9001 instrument) equipped with a two columns system (13X molecular sieve and Porapack sh 172 columns) and TCD. The GC analysis was performed in isothermal conditions (oven temperature = 80 °C). The detection limit for CO<sub>2</sub>, CO and O<sub>2</sub> was 5 ppm.

CO conversion is defined as:  $([CO]_{inlet} - [CO]_{outlet}) / [CO]_{inlet} \times 100$ . Selectivity to CO<sub>2</sub> is defined as the moles of CO converted to CO<sub>2</sub> divided by the total moles of oxygen reacted multiplied by 100: % selectivity =  $0.5 \text{ [moles CO converted to CO}_2\text{] / [total moles O}_2\text{ reacted]} \times 100$ .

## 3. Results and discussion

XRD patterns of the AuCeOx (dried at 80 °C) and AuCeOx500 (calcined at 500 °C) catalysts are shown in Fig. 1. Some of the characteristic peaks of CeO<sub>2</sub> ( $2\theta = 28.38, 47.58$  and  $56.64$ , attributed to (1 1 1), (2 2 0) and (3 1 1) crystal planes, respectively) appear, for the AuCeOx sample, in a very broad shape on account of the small crystallite size (2.2 nm, as calculated by the Debye–Scherrer method). No peaks related to gold are visible, as a consequence of its very poor crystallinity. On the other hand, the diffractogram of the calcined sample denotes, besides a more marked crystallinity, the presence of very low

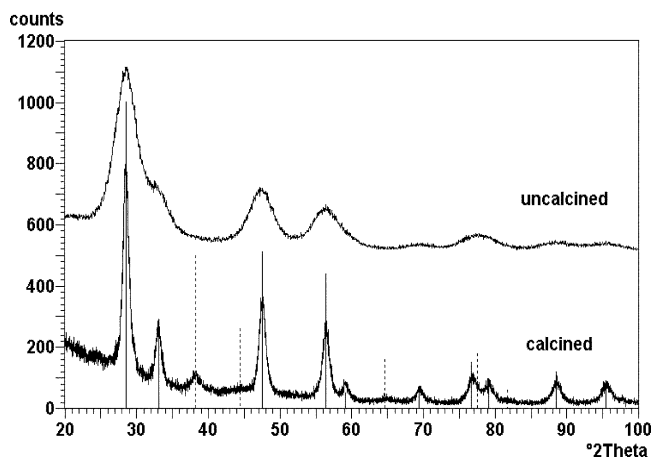


Fig. 1. X-ray diffraction pattern of calcined and uncalcined Au/CeO<sub>2</sub> catalysts: solid line CeO<sub>2</sub>; dashed line Au.

prominent peaks related to gold at  $2\theta = 38.2$  and  $64.7$ , corresponding to the (111) and (220) planes. The particle size for CeO<sub>2</sub> has been calculated to be 9.4 nm.

TEM micrographs of both samples (Fig. 2a and b) show a very irregular shape of gold particles dispersed on ceria. However, Au particles appear to be more aggregated in the calcined sample as denoted by the presence of well defined and intense dark zones. No exact estimation of Au particle size can be made, in view of the complicated morphology of the ensemble, although an average dimension of 10 nm for gold could be roughly envisaged from the high resolution image shown in Fig. 3.

In order to determine the reaction orders with respect to CO and O<sub>2</sub>, experiments were performed following the standard procedure, consisting in varying the partial pressure of one of the reactants while keeping the other ones constant. On the AuCeO<sub>2</sub> catalyst, at constant oxygen partial pressure (1 kPa O<sub>2</sub>), a weak dependence of  $P_{CO}$  (reaction order = 0.2) on CO oxidation rate was observed. A slightly

higher value (0.40) was found for the calcined sample. Even a weaker dependence of the reaction rate, for both catalysts, on  $P_{O_2}$  was observed (reaction orders: 0.11 and 0.18 for AuCeO<sub>2</sub> and AuCeO<sub>2</sub>500, respectively).

Literature data on supported gold catalysts show a large divergence of results, likely due to the variety of experimental conditions and catalysts. For ceria-supported gold, to our knowledge, the few results reported in literature are somewhat contradictory. Liu and Flytzani-Stephanopoulos [17] reported, for Au<sub>0.05</sub>[Ce(La)<sub>0.95</sub>O<sub>x</sub> calcined in air at 500 and 600 °C, a weak dependence on both CO and O<sub>2</sub> partial pressures (0.3 and 0.18, respectively). Han et al. [7], in a more recent investigation on the CO oxidation in H<sub>2</sub>-rich reformer gas, reported reaction orders of 0.7 for CO and 0.02 for oxygen. According to Kahlich et al. [4], the discrepancies may derive from several factors, such as metal particle size, temperature dependence of reaction order and the presence of hydrogen in the reaction stream.

As for the value of apparent activation energy, measured in the temperature range 80–120 °C, similar results for both as prepared and heat treated catalysts (20.1 and 22.2 kJ/mol, respectively) were obtained. These values are significantly lower than those previously reported for ceria-supported gold in the CO oxidation reaction [7,17,19], but they are rather in line with those obtained for other oxide-supported gold catalysts, such as coprecipitated FeOx [4], deposited-precipitated Co<sub>3</sub>O<sub>4</sub> [10] and TiO<sub>2</sub> obtained by the Iwasawa's preparation procedure [22]. In this respect, a dependence of activation energy on the temperature range investigated has been previously envisaged [21].

The influence of CO<sub>2</sub> content in the feed gas on CO conversion and selectivity is shown in Fig. 4a and b. CO<sub>2</sub> negatively affects the activity of both uncalcined and calcined catalysts. CO conversion linearly decreases as the CO<sub>2</sub> concentration increases. However, for CO<sub>2</sub> concentration higher than 12%, where CO conversion is lower than 20%, CO<sub>2</sub> slightly affects the CO conversion. Likewise, selectivity to

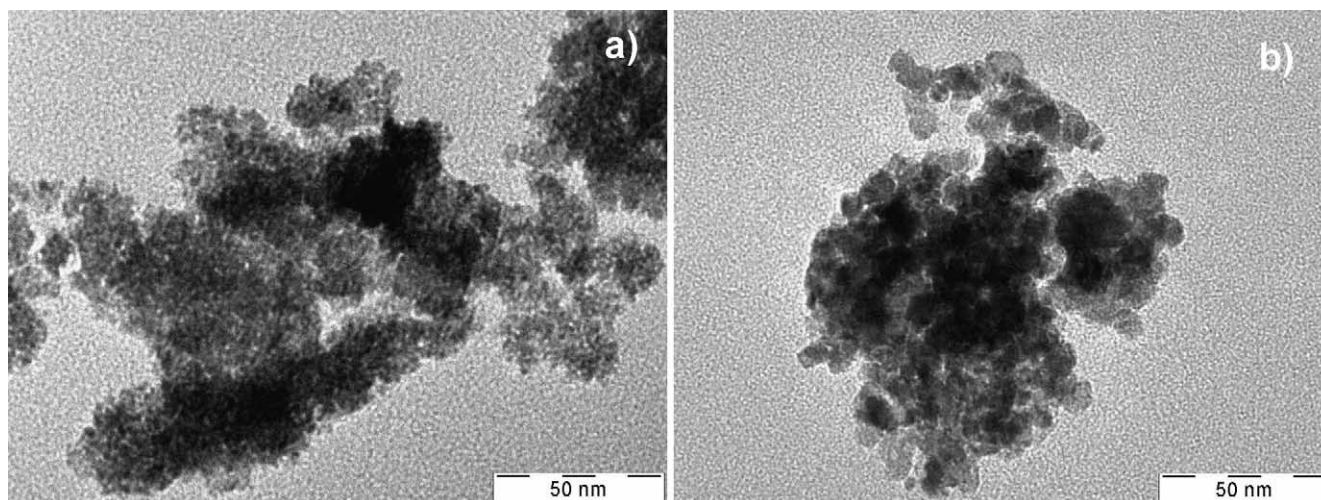


Fig. 2. Low magnification TEM images of fresh uncalcined (a) and calcined (b) Au/CeO<sub>2</sub> catalysts.

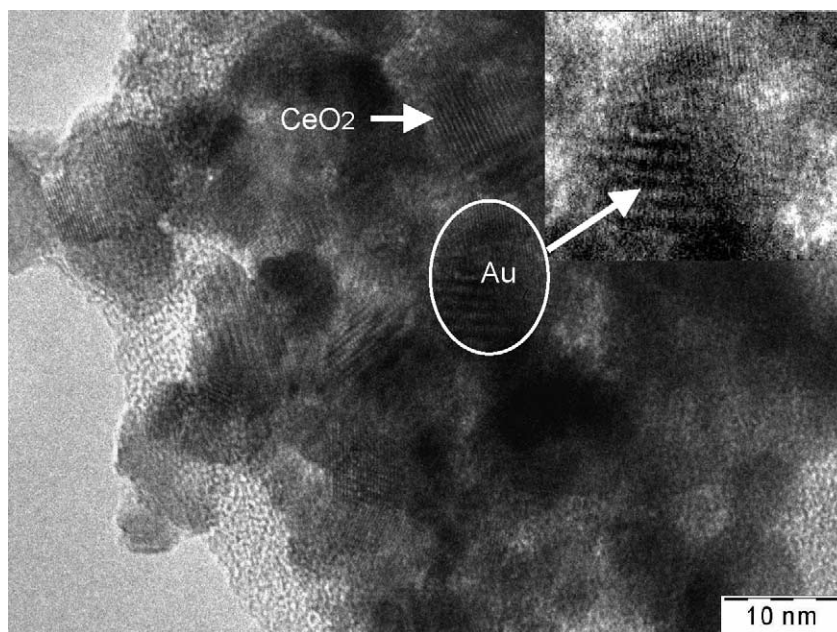


Fig. 3. High magnification TEM image of calcined Au/CeO<sub>2</sub> catalyst.

CO<sub>2</sub> decreases as the CO<sub>2</sub> concentration in the feed increases. Considering that both the contributions of the forward water gas shift reaction ( $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$ ) on CO conversion and reverse water gas shift reaction ( $\text{CO}_2 + \text{H}_2 = \text{CO} + \text{H}_2\text{O}$ ) on the observed decrease in selectivity to CO<sub>2</sub> are negligible under the present experimental conditions [4], these effects could be ascribed to the formation of carbonate ( $\text{CO}_3^-$ ) or carboxylate ( $\text{CO}_2^-$ ) species [12,24]. Deactivation of Fe<sub>2</sub>O<sub>3</sub>-supported gold catalysts, due to CO<sub>2</sub> in simulated reformat gas, was recently demonstrated [25]. In general, however, the nature of the support is thought to affect the catalyst activity and stability in the presence of CO<sub>2</sub> in the feed; acidic supports were found to be more resistant to deactivation than basic ones [12].

Results obtained in the absence of CO<sub>2</sub>, in the temperature range 80–120 °C, are shown in Fig. 5. The calcined

catalyst approaches 100% CO conversion at 120 °C; the uncalcined sample is slightly less active. However, CO conversion is slightly affected by temperature: a limited increase in CO conversion (from 83 to 98%) was observed as the reaction temperature was raised from 80 to 120 °C. On the other hand, both catalysts appear poorly selective to CO<sub>2</sub> in the entire temperature range investigated. The uncalcined catalyst exhibits a slightly higher selectivity than the calcined one but, in any case, selectivity values of about 40% were obtained; these are slightly lower than those recently reported for ceria-supported gold [7].

The response of the catalysts to very high space velocity values was also investigated since, especially for automotive application, compactness of the whole catalytic system is an obvious constraint. As shown in Table 1, at 80 °C, for both uncalcined and calcined samples,

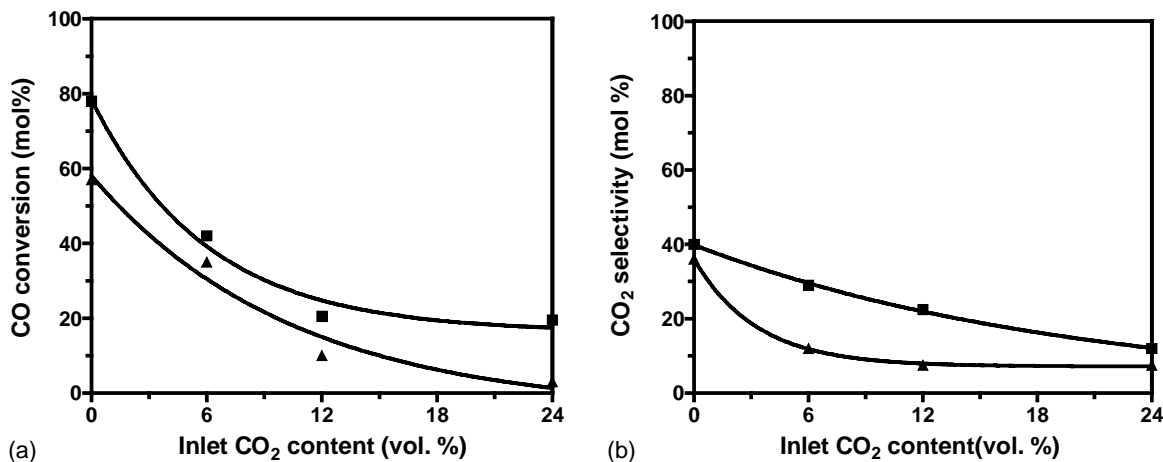


Fig. 4. Influence of CO<sub>2</sub> content in the fed gas on CO conversion (a) and CO<sub>2</sub> selectivity (b): (▲) uncalcined catalyst; (■) calcined catalyst.

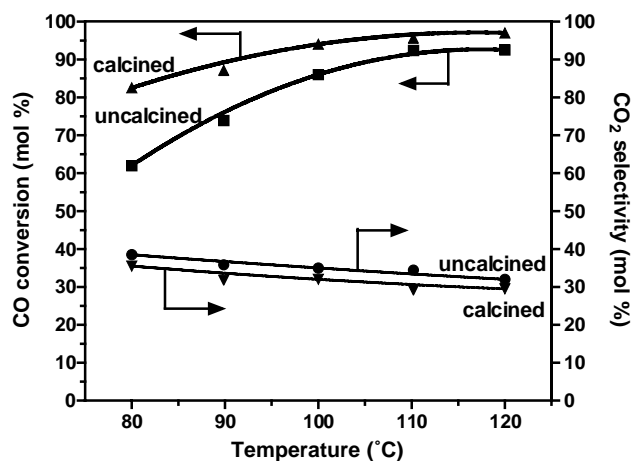


Fig. 5. Influence of reaction temperature on CO conversion and CO<sub>2</sub> selectivity.

a significant decrease in CO conversion was observed as GHSV was increased, whereas CO<sub>2</sub> selectivity only slightly increases, passing from 39% at 120,000 to 45% at 450,000 h<sup>-1</sup>.

For what concerns the influence of heat treatment on the catalyst performance, it is well known that the catalytic behaviour of oxide-supported gold catalysts towards CO oxidation is strongly affected by this parameter. Although some investigators reported high activities for uncalcined Au/Fe<sub>2</sub>O<sub>3</sub> catalysts [26,27], calcination treatments were found by several authors to be necessary to obtain highly active gold supported catalysts. Haruta et al. [10,28,29] reported that a number of coprecipitated gold catalysts exhibited the highest activities when they were calcined at 300–400 °C, whereas impregnated and reduced-deposited catalysts showed lower activities with the increase in reduction temperature. These results were explained invoking the formation, in the coprecipitated samples, of metallic gold crystallites which move out from the inner part of the coprecipitated particles towards the surface; moreover, calcination would also contribute to a stronger gold–support interaction that would prevent coagulation of the metal particles. This view was further supported by TEM observations of Au/TiO<sub>2</sub> calcined at 600 °C, showing a well defined shape change of gold from round to irregular facing, attached to the TiO<sub>2</sub> surface with a flat plane, that suggests the establishment of a strong metal–support interaction [30]. It is also

Table 1  
CO conversion and CO<sub>2</sub> selectivity as a function of GHSV

GHSV (h <sup>-1</sup> )	CO conversion (mol%)		CO <sub>2</sub> selectivity (%)	
	Calcined	Uncalcined	Calcined	Uncalcined
110,000	82	63	39	36
220,000	63	45	43	42
450,000	45	12	45	42

worth noting that the observed increase in activity occurs despite the growth of Au particles, subsequent to calcination [30,31], that would in general lead to lower performance. Thus, the effect of calcination appears to be probably connected to the high concentration of step sites over the Au surface and at the borderline with the support [32]. The size dependency of supported gold towards CO oxidation is however connected to the nature of the support material used to disperse the active metal. Accordingly, only gold supported on inert oxides, such as SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and MgO, would exhibit a strict activity–dispersion correlation; high activity can be achieved, with this kind of supports, only from highly dispersed catalysts. Examples of size dependency have been reported in several papers [5,10,16,23,28,33]. On the other hand, the ability of reducible metal oxides, such as Fe<sub>2</sub>O<sub>3</sub> or CeO<sub>2</sub>, to provide reactive oxygen reduces the dependence of catalytic activity on metal particle size and makes the interface characteristics crucial to obtain high performances. Thus, the mechanism according to which ceria would act in the catalysis of CO oxidation likely involves its redox activity and its ability in storing and releasing oxygen, thus favouring the course of the reaction. In other words ceria, similarly to other reducible oxides (such as TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, NiO) would enhance the adsorption of oxygen acting as an oxygen supplier for the reaction. The most recognized hypothesis to explain the high catalytic activity of these systems suggests, in fact, the occurrence of a synergistic mechanism at the gold–oxide interface. Accordingly, the effective reaction site would be located at the junction between the metal (responsible for CO adsorption) and the support (where O<sub>2</sub> adsorption preferably occurs) [6,13,20,22,23].

Runs of 120 h at  $T = 80\text{ }^{\circ}\text{C}$  and  $\text{GHSV} = 120,000\text{ h}^{-1}$  of both uncalcined and calcined catalysts were performed to assess the catalyst behaviour as a function of time. As it can be seen in Fig. 6, no decay of activity was observed for the entire duration of the test; this denotes a substantial stability of the catalysts, in terms of both CO conversion

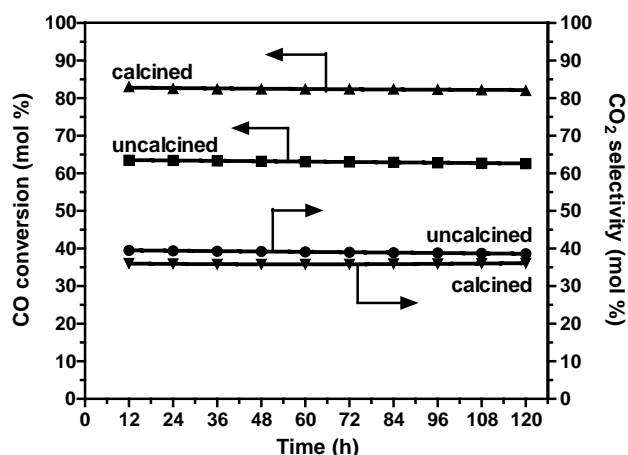


Fig. 6. Endurance tests of uncalcined and calcined Au/CeO<sub>2</sub> catalysts.

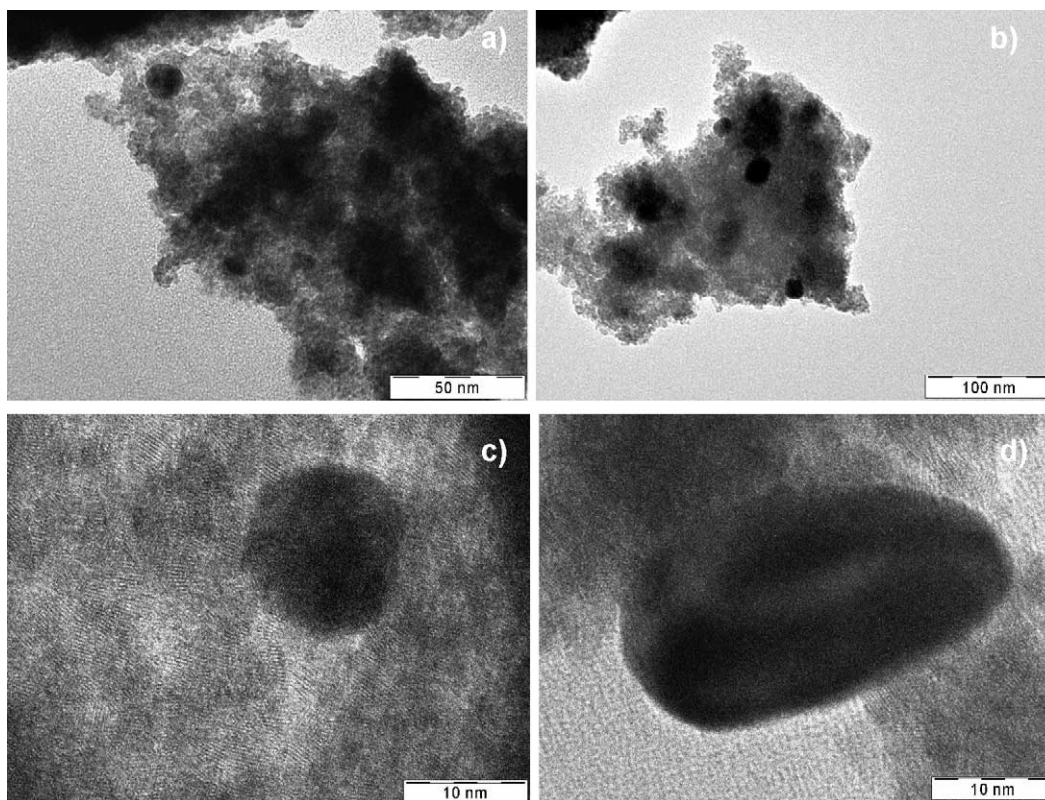


Fig. 7. Low and high magnification TEM images of used calcined Au/CeO<sub>2</sub> catalyst.

and CO<sub>2</sub> selectivity. TEM images of the used sample (see Fig. 7a and b.) revealed that the Au particles morphology changed during reaction. In fact the irregular shape of the Au crystallites observed before reaction (see Figs. 2b and 3) turned into a well defined spherical or elliptical shape as a consequence of an apparent agglomeration phenomenon (Fig. 7c and d). However, the metal surface reconstruction occurring during the reaction does not seem to affect the catalyst performance since catalyst activity remains constant all over the test (see Fig. 6). This result could indicate that, for gold supported on reducible oxides like CeO<sub>2</sub>, the catalytic activity does not strictly depend on metal dispersion, but rather on the gold–oxide interface properties.

#### 4. Conclusions

Coprecipitated gold-ceria catalysts are active in the selective oxidation of CO in H<sub>2</sub>-rich streams. Calcination significantly enhances CO conversion whereas selectivity to CO<sub>2</sub> does not exceed 40% in any investigated reaction condition. The addition of CO<sub>2</sub> to the reaction stream negatively affects both CO conversion and selectivity to CO<sub>2</sub>. Stable catalytic performance was demonstrated during a 120 h endurance test. TEM investigation of the used catalyst revealed that some surface reconstruction of Au particles occurred during reaction.

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