



# WGS and CO-PrOx reactions using gold promoted copper-ceria catalysts: “Bulk CuO–CeO<sub>2</sub> vs. CuO–CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> with low mixed oxide content”



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## ABSTRACT

A copper-ceria bulk catalyst has been compared to a series of catalysts designed according to the as called “supported approach”, corresponding to the dispersion of low content mixed copper-ceria oxide on alumina matrix. The principal characteristics of both types of catalysts are contemplated and the differences in their electronic and redox properties discussed in details. As a plus, the gold metal promotion of the catalysts is also envisaged. The advantages of the systems in the CO clean up reactions, WGS and CO-PrOx are commented. While the WGS activity appears to be ruled especially by the Cu/Ce surface to volume ratio, the CO-PrOx reaction is governed by the CuO loading. Gold addition provides benefits only at the low temperature WGS regime. Very importantly, the supported systems are always superior to the bulk configuration in terms of specific activity, a key factor from the catalyst's design perspective.

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## 1. Introduction

Following the spirit of this special issue a good example of ceria success and reliability is the CuO–CeO<sub>2</sub> mixed oxide catalyst and its application for CO-clean up goals in the context of hydrogen fuel cells. The overall selectivity in generating a low CO content hydrogen stream required by the PEM fuel cell catalyst is dependent on the efficiency of the catalysts in each segment of the fuel processor [1]. In this sense highly effective catalysts are required for both the water gas shift (WGS) reaction and the preferential CO oxidation (CO-PrOx), which are considered as purification processes for the production of clean hydrogen. This is carried out in fuel processors where WGS and CO-PrOx reactions are coupled as integrated stages. Even several units for every process may be included depending on the design of the fuel processor, in order to maximize the production and the energetic efficiency [2–7]. Herein, CuO–CeO<sub>2</sub> systems have demonstrated outstanding activity for the mentioned reactions and therefore they are intimately linked to the development of the last generation of hydrogen alimented fuel cells [8–13].

To a certain extension the WGS and the CO-PrOx process can be considered as “sister reactions” especially when they are applied to purify hydrogen streams. Even historically, CuO/CeO<sub>2</sub>-like catalysts started to be applied in both reactions almost at the same time. More precisely, the group of Flytzani-Stephanopoulos presented the first report on Cu–CeO<sub>2</sub> for WGS in 2000 [14] while one of the first reports of CuO/CeO<sub>2</sub> for the CO-PrOx appears in 2001 from Ioannides' group [15].

One of the main advantages of the Cu–CeO<sub>2</sub> for the WGS reaction is its ability to be used as prepared without any previous activation, which is one of the major drawbacks of the traditional Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts used in industrial applications [16–18]. The success of CuO/CeO<sub>2</sub> mixtures for the WGS reaction is also reflected by the high activity exhibited by the inverse CeO<sub>2</sub>/CuO catalysts [19]. The excellent catalytic performance of both types of configurations underlines the importance of the metal/oxide interface as a very reactive site where most of the relevant reaction steps take place [20]. Moreover Cu itself is an active metal for the shift reaction and combined with the high oxygen mobility provided by ceria results in an optimum catalyst for the WGS.

Concerning the CO-PrOx reaction, the performance of CuO/CeO<sub>2</sub> has been compared to that of platinum and gold based catalysts [21]. It was found that nanostructured CuO/CeO<sub>2</sub> catalyst is superior to noble metal based systems in the low-temperature range, because it has the best compromise between activity, selectivity and price. Furthermore CuO/CeO<sub>2</sub> based catalysts have demonstrated to be particularly convenient for deposition on diverse

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geometries of structured systems as for example, honeycomb monoliths or microchannel reactors [22,23]. This scalability from powder solids to structured catalysts provides a series of benefits including improved mass and heat transfer and reduced reactor volumes, a critical factor for mobile applications [23].

On the other hand the activity of the ceria based catalysts in both WGS and CO-PrOx can be greatly promoted by the inclusion of small amounts of gold in the catalysts' composition [24–26]. The combination of the high CO oxidation activity of gold nanoparticles and the presence of oxygen vacancies in ceria results in a perfect synergy. For instance, CO can easily interact with Au while H<sub>2</sub>O (in the case of WGS) or O<sub>2</sub> (in the case of CO-PrOx) can be activated in the oxygen vacancies of ceria which play a vital role in both reactions. Furthermore, these structural defects are view as preferential sites for gold nucleation facilitating the noble metal dispersion and enhancing the overall activity [24,25]. Apart from the well-studied Au/CeO<sub>2</sub> systems, a multicomponent Au, CuO and CeO<sub>2</sub> catalyst represents an interesting approach [25]. In fact, as recently reported Au–Cu alloys supported on ceria are rather efficient catalysts for the PrOx process [26].

Despite the cited benefits of the inclusion of gold in the formulation of CuOCeO<sub>2</sub> catalysts, the addition of a noble metal (even in low quantities) would increase the cost of the final catalyst. However as a way to partially compensate this expense, the amount of copper and ceria can be largely reduced by dispersing the mixed oxide on a high surface carrier. In this sense, recent reports of our group demonstrated that this approach of using alumina as a massive component of the ceria-based catalysts allows optimizing the expense of ceria resulting in highly active catalysts for WGS and PrOx with considerable lower quantities of ceria [27,28]. Greater surface to volume ratio is attained when small ceria particles are dispersed on alumina leading to enhanced oxygen mobility and excellent catalytic skills [28].

For all stated above, in this work we have developed a series of CuOCeO<sub>2</sub> catalysts dispersed on alumina with a reduced content of active phase (copper and cerium). These systems have been comparatively studied with a reference CuOCeO<sub>2</sub> bulk material for both WGS and CO-PrOx reactions. Moreover, the use of gold nanoparticles as promoter for both processes is also considered. Finally the main reasons guiding the catalytic trends have been discussed and interrelated with the physicochemical properties of the designed materials.

## 2. Experimental

### 2.1. Catalyst preparation

#### 2.1.1. CuOCeO<sub>2</sub> bulk catalyst

The synthesis of the CuO/CeO<sub>2</sub> bulk catalyst (15 CuO wt.% and 85 CeO<sub>2</sub> wt.%) has been previously published [25] and the coprecipitation method was employed. The required amounts of Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (Fluka®) and Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (Alfa Aesar®) were dissolved in the adequate amount of distilled water to obtained a 0.5 M solution of the cationic precursors. Later, NaOH solution (2 M) was added dropwise until a stable pH of 9. The obtained precipitate was filtered and washed with distilled water. Then, it was dried overnight at 60 °C and finally calcined at 300 °C (10 °C/min) for 2 h. The sample prepared following this procedure will be labelled as *CuCe bulk*.

#### 2.1.2. CuOCeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> samples

The CuOCeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> samples were synthesized by the coprecipitation method. The necessary amounts of metal nitrate precursors (cerium and copper nitrates, Sigma-Aldrich) were coprecipitated on  $\gamma$ -alumina powder (Sasol). The impregnation was

carried out in 50 mL of ethanol, evaporated at reduced pressure in rotary evaporator (Heidolph) at 50 °C till obtaining a dry solid which was subsequently treated with ammonia solution for 10 min. The support dried overnight at 80 °C and calcined at 500 °C during 4 h.

A series of catalysts with remarkable lower CuOCeO<sub>2</sub> loading compared to that of the bulk system was prepared using the above described procedure. The catalysts were synthesized using growing CuO/CeO<sub>2</sub> ratios (0.4, 0.6 and 0.8) and a total CuO + CeO<sub>2</sub> loading lower than 25 wt.% in all the cases. For sake of simplicity, oxygen is omitted in the selected nomenclature and the samples will be labelled according to their Cu/Ce weight ratio. For example the catalyst labelled as CuCe-0.8 is composed by a mixed CuOCeO<sub>2</sub> oxide with a CuO/CeO<sub>2</sub> weight ratio of 0.8 dispersed on alumina.

#### 2.1.3. Gold deposition

Gold was deposited by the direct anionic exchange method (DAE), assisted by NH<sub>3</sub> as described in literature [29]. A 10<sup>-4</sup> mol L<sup>-1</sup> aqueous solution of the gold precursor HAuCl<sub>4</sub> (Alfa Aesar) was used in order to obtain a final Au loading of 2 wt.%. The support used to prepare the gold based catalysts was sieved and the 100–200  $\mu$ m fractions retained were employed in the synthesis. After Au deposition, the solid was dried at 100 °C overnight and calcined in air at 350 °C for 4 h.

### 2.2. Catalyst characterization

X-ray microfluorescence spectrometry (XRMF) was used to determine the chemical compositions and the analysis were performed in EDAX Eagle III spectrophotometer with Rh source of radiation.

X-ray diffraction (XRD) analysis was carried out on X'Pert Pro PANalytical instrument. Diffraction patterns were recorded using Cu K $\alpha$  radiation (40 mA, 45 kV) over a 2 $\theta$ -range of 10–80° and using a step size of 0.05° and a step time of 240 s.

The Raman spectra were recorded in a dispersive Horiba Jobin Yvon LabRam HR800 spectrometer, with a 20 mW He–Ne green laser (532.14 nm) operating at 5 mW. The microscope used a 50x objective and a confocal pinhole of 1000  $\mu$ m.

The UV–vis spectra were recorded on an Avantes spectrometer model AvaLight-DH-S-BAL using BaSO<sub>4</sub> as reference. All the spectra were collected in a diffuse reflectance mode and transformed to a magnitude proportional to the extinction coefficient through the Kubelka–Munk function  $F(\alpha)$ . From UV–vis spectra, ceria direct and indirect band gap were estimated by plotting  $[(F(R)h\nu)^{1/2}]$  against energy and the linear part of the curve further extrapolated to  $[(F(R)h\nu)^{1/2}] = 0$  for the indirect gap and the same procedure but using  $[(F(R)h\nu)^2]$  function was used for the direct band gap.

H<sub>2</sub>-TPR was carried out on 50 mg of sample charged in a conventional U-shaped reactor as a function of temperature with constant heating rate of 10 °C min<sup>-1</sup> till 900 °C. 50 mL min<sup>-1</sup> certified 5% H<sub>2</sub> in Ar gas mixture was used and the H<sub>2</sub> consumption was followed by TCD detector and quantified by using CuO standard (99,999%).

### 2.3. Catalytic activity

#### 2.3.1. Water-gas shift

Water-gas shift reaction was performed in a stainless steel tubular flow reactor (0.75 cm ID) at atmospheric pressure in the 180–350 °C temperature range. The catalysts were pelletized and sieved with the 600–800  $\mu$ m fraction employed for the test. The following conditions were applied: catalyst bed volume 1.5 cm<sup>3</sup>, space velocity 4000 h<sup>-1</sup> and gas composition: 30% vol. H<sub>2</sub>O + 4.5% vol. CO balance in N<sub>2</sub>. Water was injected into flowing gas stream by HPLC pump, vaporized and homogenized with the gas feed before entering the reactor. This is a model reaction mixture which is usually employed to test catalysts for the clean H<sub>2</sub> production via WGS.

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