



Unraveling the nature of active sites onto copper/ceria-zirconia catalysts for low temperature CO oxidation

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ABSTRACT

The aim of this research is an attempt to shed some light on the understanding of the nature of the active sites and the generated synergies in the copper/ceria-zirconia formulations for low temperature CO oxidation by means of the creation of copper entities with different physico-chemical nature. For this reason, several CuO_x/ceria-zirconia catalysts, with different Cu contents and different methods to incorporate copper species, were synthesized. Focus was specially put in this case trying to link the results of CO oxidation catalytic tests with the CO-temperature programmed reduction profiles/approximate estimations and selected characterization parameters in order to find out correlations among catalysts' properties/reducibility and catalytic behaviors, especially those corresponding to the nature and roles of the different CuO_x species in contact with ceria-based support on catalytic activity.

Results reveal a significant improvement in CO conversion compared to the ceria-zirconia support by adding a small amount of copper loading (as low as 0.5 %), emphasizing the paramount role of copper incorporated by the method of IWI. From 0.5 up to 2% of copper loading, an interesting increase gradual trend in activity and reducibility can be noted. It should be mentioned that all the catalysts obtained by this procedure are more catalytically active towards CO oxidation than 1%Pt/Al₂O₃ at low temperatures (T < 130 °C). CO-TPR results show that the reducibility of these catalysts is in line with their CO oxidation activity. The method of preparation has been revealed as a critical variable in the catalytic performance, and quite similar catalytic activities can be reached from different synthesis methods and different copper contents, due to the similar nature and type of CuO_x species generated over the catalysts' surface, identified by the CO-TPR profiles and the rest of characterization data. Finally, IWI method seems to be the best one among those tested, thus combining superior areas of both α and β contributions assigned on CO-TPR profiles, which seem to be critical in the interpretation of the catalytic behaviors.

1. Introduction

Diesel oxidation catalysts (DOCs) are used in the automotive industry to oxidize hydrocarbons and CO and convert NO to NO₂, which is critical to oxidize soot collected on DPFS and improve SCR efficiency. Nowadays, the emphasis on lowering real world driving emissions requires active catalysts for CO and hydrocarbon oxidation at temperatures significantly lower than the current state of the art to meet future pollutant emission regulations, specially associated with city driving [1]. In this regard, the U.S. Department of Energy roadmap has set the

goal to achieve greater than 90 % conversion of criteria pollutants at 150 °C or lower for the full useful life of the vehicle [2]. To tackle this challenge, new catalyst formulations are being developed in order to achieve advances in low-temperature DOCs.

In search of low-temperature CO oxidation formulations, single atom catalysts (SACs) have reported high reactivity, which also provide efficient utilization of platinum group metals (PGM) [3–5]. For instance, Datye et al. have reported high performance of Pt single atom catalysts over ceria support for low-temperature CO oxidation, reaching 90 % of CO conversion at 64 °C [6]. Nevertheless, noble metal-based catalysts

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can still be considered expensive and scarce, continuously leading to the scientific community to the search for low cost and with good performance alternatives such as inexpensive transition metals based-catalysts (i.e. Fe, Mn, Cu, Co or Ni) [7–9]. Actually, Kim et al. reported in a recent review [10], that when active metals are loaded on the CeO₂ surface, many active sites could be acquired by increasing the dispersion, and the catalytic activity can be dramatically improved by newly introducing the interfacial sites between the metals and the CeO₂ support. Among these active metals, one of the most promising candidates for the CO oxidation reaction is the CuO-CeO₂ system [11]. The reason lies in the fact that exists an important synergistic effect between copper and ceria to generate its exceptional catalytic activity [12].

Nowadays, many progress has been made in order to understand the origin of these synergies that can be generated in copper-ceria systems [10,13–21]. More specifically, the key features of the CuO-CeO₂ system which contributes to the denominated synergetic effect are: i) the facilitation of oxygen vacancies formation; ii) the redox interplay between copper and cerium pairs ($\text{Cu}^{2+} + \text{Ce}^{3+} \leftrightarrow \text{Cu}^+ + \text{Ce}^{4+}$); iii) the superior interfacial sites with enhanced reactivity; iv) the higher reducibility; and v) the enhanced oxygen mobility. Moreover, although the use of the undoped ceria as a support is well documented for copper-ceria binary systems, ceria-zirconia mixed oxide can be considered as a better alternative due to its enhanced thermal resistance and superior ability to promote the creation of oxygen vacancies and, thereby, enhancing oxygen mobility [22,23].

In light of the above aspects, the peculiar reactivity of copper/ceria-based materials is due to many different physical-chemical contributions, which results in a much rather complex system in practice. In fact, the modulation of metal-support interactions has been deeply investigated by employing different: i) ceria-based support morphologies [24–26]; ii) synthesis routes [27–29]; iii) metal oxides precursors (for copper and cerium) [15,25,26]; and even iv) inverse configurations [30,31]. In that way, significant changes have been achieved in the composition, the shape, the size, and the electronic state of these copper/ceria-based systems, resulting in different catalytic performances. Given the current requirements for highly active, efficient and selective catalysts at very low temperatures, it is imperative to keep on investigating the nature of these synergistic effects on copper/ceria-based catalysts.

This research aims to conduct a systematic study of CO oxidation reaction catalyzed by several copper/ceria-zirconia samples, evaluating factors affecting catalytic activity under different preparation routes to incorporate copper (co-precipitation, incipient wetness impregnation and physical mixing methods) and different copper contents (from 0.5–6 wt.%) for the synthesized catalysts. Focus will be put in this case linking CO oxidation catalytic results in parallel with CO-temperature programmed reduction profiles and selected characterization parameters in order to find out the correlation among catalyst' properties/reducibility and catalytic behaviors, especially those corresponding to the nature and roles of the different CuO_x species over ceria-based support on catalytic activity.

The whole study will allow us not only to provide some insight into the nature and type/s of active site/s determining the CO oxidation, mainly at low temperatures, but also if the magnitude and extent of these active sites could be modulated or controlled by choosing a preparation route and a certain copper content. This approach is of paramount importance for the effective and rational design of last-generation catalysts.

2. Materials and methods

2.1. Catalyst preparation

The Ce_{0.8}Zr_{0.2}O₂ mixed oxide (denoted as CZ) has been synthesised by the co-precipitation method in alkaline medium, by using the cerium and zirconium precursors (NH₄)₂Ce(NO₃)₆ (supplied by Panreac with

99.0 % purity) and ZrO(NO₃)₂·xH₂O (supplied by Sigma–Aldrich, with x ≈ 6, technical grade), respectively. The appropriate amounts of these precursors were dissolved in distilled water. The corresponding hydroxides of cerium and zirconium were co-precipitated by drop wise addition of a 10 % ammonia solution in water until pH = 9, under constant stirring. The solid obtained was then filtered under vacuum and the yellowish precipitate was washed with distilled water until neutral pH. Finally, it was dried overnight at 110 °C and calcined in air in a muffle at 500 °C for 1 h, with a heating rate of 10 °C/min. The composition of this mixed oxide (Ce_{0.8}Zr_{0.2}O₂) was chosen in terms of optimal thermal resistance towards sinterisation and good response towards other catalytic reactions studied by some of these authors [32,33] if compared with bare ceria and other Ce/Zr compositions analyzed.

Ce_{0.8}Zr_{0.2}O₂-supported copper catalysts with Cu wt.% of 0.5, 1, 2, 4 and 6 (denoted as Cu0.5CZ-IWI, Cu1CZ-IWI, Cu2CZ-IWI, Cu4CZ-IWI and Cu6CZ-IWI, respectively) were prepared by incipient wetness impregnation with Cu(NO₃)₂·3H₂O (supplied by Panreac with 99.0 % purity) solutions of different concentration. After impregnation, the samples were dried overnight in an oven at 110 °C and thereafter calcined under air at 500 °C for 1 h, with a heating rate of 10 °C/min. Due to the limitations of the Cu(NO₃)₂·3H₂O solubility in water, the Cu 0.5 %, Cu 1% and Cu 2% catalysts were impregnated in a single step, while Cu 4% and Cu 6% were prepared by successive impregnations with the solution used to prepare Cu 2% (two and three consecutive impregnations, respectively).

In order to study the influence of copper entities in contact with ceria-zirconia, which eventually yield synergistic catalytic effects, several samples with different preparation routes have been prepared with a same copper loading (2%).

The Ce_{0.76}Zr_{0.19}Cu_{0.05}O₂ sample (named as Cu2CZ-CP) was synthesized by the co-precipitation method in alkaline medium, by using the following cerium, zirconium and copper precursors: (NH₄)₂Ce(NO₃)₆ (supplied by Panreac with 99.0 % purity), ZrO(NO₃)₂·xH₂O (supplied by Sigma-Aldrich, with x ≈ 6, technical grade) and Cu(NO₃)₂·3H₂O (supplied by Panreac with 99.0 % purity), respectively. The same amounts of precursors than those used for the Cu2CZ-IWI synthesis were dissolved in distilled water, and after jointly co-precipitation, a 2 wt.% of copper was achieved. This co-precipitation procedure continues exactly as described above for the CZ catalyst.

Bulk CuO was obtained by calcination of Cu(NO₃)₂·3H₂O in air, at 500 °C during 1 h with a heating rate of 10 °C/min. It was used to prepare the physically-mixed samples, and also as a catalyst itself.

A physically-mixed sample of bulk CuO with ceria-zirconia was also prepared. Physical mixing between CuO and CZ have been conducted by *tight contact* mode in an agate mortar with pestle, and consisted of an intimate mixture of the proper amount of CuO and CZ, during 5–6 min, to yield a 2 wt.% of copper. Afterwards, it was calcined in air at 500 °C for 1 h, with a heating rate of 10 °C/min. The sample obtained after this treatment is denoted as Cu2CZ-PM.

The commercial 1%Pt/Al₂O₃ catalyst was supplied by Sigma-Aldrich (with BET surface area of 160 m²/g).

2.2. Catalytic activity

Catalytic tests for CO oxidation were carried out in a U-shaped quartz reactor (16 mm inner diameter), loaded with 50 mg of catalyst and 100 mg of silicon carbide. The total flow rate of the feed gas (1000 ppm CO and 10 % O₂ in He) was 100 mL/min, corresponding to GHSV of 90000 h⁻¹. The catalytic tests consisted of Temperature-Programmed Reactions, where the temperature was increased from room temperature up to 300 °C at 5 °C/min under the reactive atmosphere. Previously, the samples were pretreated in situ at 500 °C under a flow of 5% O₂/He (100 mL/min) for 30 min. The outlet gases were analyzed using a gas chromatograph (HP model 6890 Plus Series) equipped with two columns: Porapak Q 80/100 for CO₂ separation and Molecular Sieve 13X for O₂ and CO separation, coupled to a thermal conductivity detector

(TCD). The CO conversion (X_{CO} , %) was calculated as follows (1):

$$X_{\text{CO}}(\%) = \frac{[\text{CO}]_{\text{in}} - [\text{CO}]_{\text{out}}}{[\text{CO}]_{\text{in}}} \times 100 \quad (1)$$

where $[\text{CO}]_{\text{in}}$ and $[\text{CO}]_{\text{out}}$ are the CO concentration (ppm) in the inlet and outlet gas streams, respectively.

Reaction rates were estimated as $\mu\text{mol CO}_2$ produced/ $\text{g}_{\text{Cu}}\cdot\text{s}$, at certain temperatures, and apparent activation energies (E_a) were calculated assuming differential conditions (CO conversions $\leq 20\%$). Repeatability of the catalytic measurements considering different batches was quite good.

2.3. CO-TPR measurements

Temperature-programmed reduction (TPR) measurements employing CO as a reductant were carried out using the same experimental setup than that employed for the catalytic tests for CO oxidation. The total flow rate of the feed gas (5% CO in He) was 35 mL/min. The temperature was increased from room temperature up to 650 °C at 5 °C/min under the reactive atmosphere. Prior to every run, the catalysts were pretreated in situ at 500 °C under flow of 5% O₂/He for 30 min, and then, the catalysts were cooled down to room temperature in the gas flow and purged under inert gas. The whole details of the procedure are described elsewhere [34].

2.4. Characterization techniques

A very complete description of the classical characterization techniques, used for the investigation of the physico-chemical features (surface, textural and structural properties), of the fresh catalysts used in this work is described in depth elsewhere [35,36]. The protocol for determining the copper dispersion data in selected catalysts, by means of H₂ volumetric studies.

3. Results and discussion

3.1. Catalytic testing

Catalytic testing was performed to understand the effect of the amount and nature of copper species present on the catalysts on activity. CO oxidation was performed first on IWI-samples with various copper loadings, including the undoped Ce_{0.8}Zr_{0.2}O₂ sample and a reference CuO sample calcined at the same temperature (Fig. 1). Complete

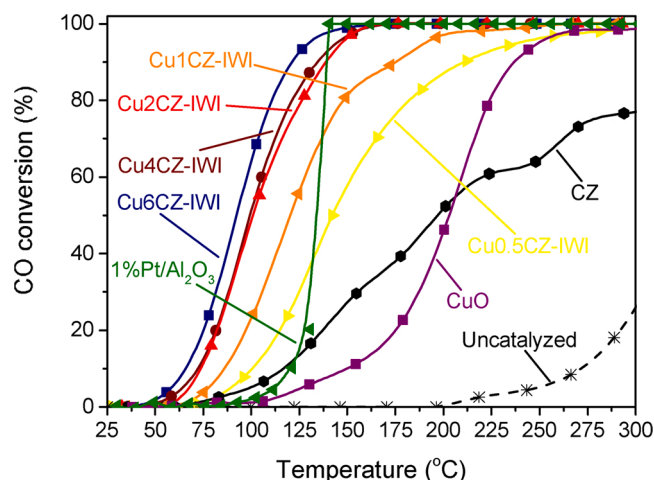


Fig. 1. CO oxidation light-off curves for catalysts obtained by incipient wetness impregnation. CuO, ceria-zirconia (CZ), 1%Pt/Al₂O₃ and uncatalyzed reaction are included for comparison purposes.

conversion of CO is achieved for all the catalysts, at temperatures lower than 300 °C, with the exception of the undoped ceria-zirconia (CZ). The amount of copper significantly affects the ignition, that occurs at temperatures as low as 50 °C for the best catalysts, and the oxidation rate, that gradually increases with temperature. The slope of the light-off curve seems to be influenced by the copper contents onto the catalysts, the higher the copper loading, the more pronounced the slope. The shape of the curves, in general, differs from that of the 1%Pt/Al₂O₃ commercial catalyst (chosen as an effective benchmark, due to its high activity towards other oxidation reactions and high BET surface area), which is characterized by an abrupt ignition between 110 °C and 140 °C. This characteristic rapid increase from low to high conversion can be explained due to the first-step coverage of the active sites with CO at low temperatures, inhibiting initially the CO oxidation reaction [37,38]. Conversely, all the synthesised ceria-based catalysts are active at temperatures as lower as 75 °C, including the support. Interestingly, the bulk CuO seems to be quite active, if compared with the uncatalyzed reaction, and around 200 °C even outperforms the support's activity. The fact that CuO entities (like CuO bulk) can be active towards CO oxidation under these experimental conditions, could partially account for the non-gradual increasing trend in activity with the highest copper contents of the catalysts.

Fig. 2 depicts the effect of copper content on the CO oxidation activity expressed at the temperatures at which several CO conversions are reached: 10 % (T_{10}), 50 % (T_{50}) and 90 % (T_{90}), respectively. As the copper loading increases, (in the range among 0.5 and 2%), those parameters are lowered indicating that the catalyst activity becomes better. However, the profile of these curves exhibits minor decrements of T_{10} , T_{50} and T_{90} temperatures with the highest copper contents (4 and 6%). Zhu et al. have studied the CO oxidation behavior of related formulations, where copper was incorporated by incipient wetness impregnation over a Ce_{0.5}Zr_{0.5}O₂ support, and have reported an optimal copper oxide loading around 5.25 % [39].

Following with the ideas of presenting reliable comparisons with an effective benchmark, (the commercial platinum's catalyst), Table 1 compiles the list of the intersection temperatures of the copper-containing catalysts' curves with regard to the Pt's curve. The fact that copper/ceria-zirconia catalysts prepared from IWI method outperforms Pt's activity in a wide range of low temperatures, can point to high degrees of CuOx entities' dispersion, and consequently, quite small average crystallite sizes, since will be discussed later. The more copper content on the catalysts, the higher the temperature should be reached by the platinum's catalyst to achieve the same value of conversion than those of the corresponding copper catalysts.

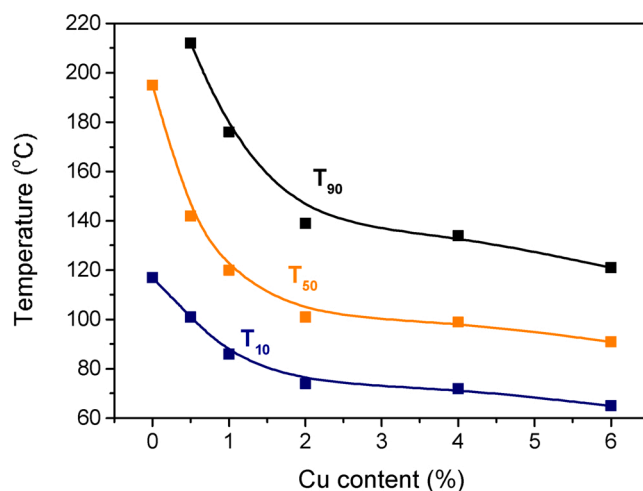


Fig. 2. T_{90} , T_{50} and T_{10} temperatures of CO oxidation for catalysts obtained by incipient wetness impregnation.

Table 1

Intersection temperature of 1%Pt/Al₂O₃ conversion profile with those catalysts obtained by incipient wetness impregnation. Ceria-zirconia (CZ) is included for comparison purposes.

Catalyst	Intersection temperature of 1%Pt/Al ₂ O ₃ conversion profile (°C)
CZ	123
Cu0.5CZ-IWI	132
Cu1CZ-IWI	137
Cu2CZ-IWI	139
Cu4CZ-IWI	140
Cu6CZ-IWI	140

In our work, the copper-containing catalysts exhibit decrease of BET surface area with increase in metal loading due to partial blocking of porosity as a consequence of the IW method, but, on the other hand, the incorporation of copper seems to be critical to define the activity. To ascertain and split the influence of both effects, Fig. 3 shows specific rates for this set of catalysts normalized to catalyst surface area. Surface-area normalized values were derived from the rate of CO₂ production per second and per square meter of solids' surface areas. By comparing Fig. 1 with Fig. 3, it can be said that the differences are becoming larger for the normalised parameters with the copper content. By comparing the lowest copper contents catalysts (0.5, 1 and 2% with regard to CZ), the values seem to increase proportionally with the copper content. This trend is quite interesting suggesting that the concentration of active sites per m² increases in a gradual way with the copper loading, thus pointing out the goodness of the preparation method under low copper contents (providing this interesting trend). This tendency is also consistent with the extremely low (and similar) copper crystallite sizes (1.7 nm for Cu0.5CZ-IWI, 1.7 nm for Cu1CZ-IWI and 1.8 nm for Cu2CZ-IWI, respectively, see Table S2 on SI) which provides certain evidences of very well-spread CuOx entities able to create a relatively high population of active interfaces. When increasing the contents up to 4 and 6%, the increase is not gradual anymore. This is reflected in Fig. 4 for three representative temperatures of reaction (80, 100 and 120 °C, respectively). These trends could suggest the co-existence of several active sites of different nature/relevance for this catalytic process. It should be reminded that: i) both support and CuO bulk are active for the process and ii) the IW process brings differences in the steps conducted, because for samples Cu4CZ-IWI and Cu6CZ-IWI successive impregnation steps were needed to incorporate the desired copper contents (two and three consecutive impregnations, respectively). Despite this consideration involved in the preparation method, Cu crystallite size is still very low for Cu4CZ-IWI (2.3 nm) and Cu6CZ-IWI (2.7 nm), which justifies that the CO oxidation activity remains high.

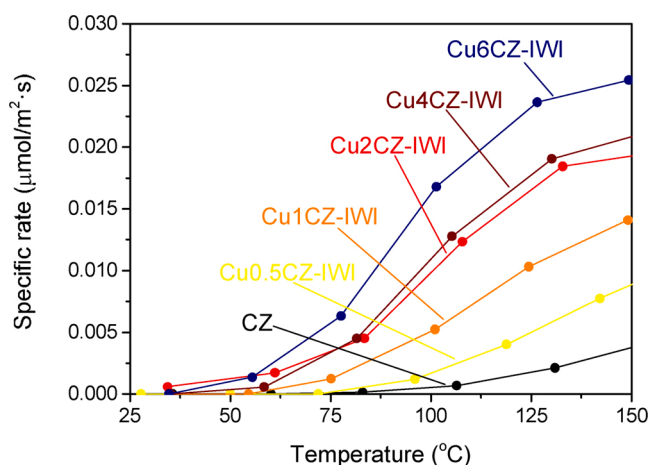


Fig. 3. Specific rates of CO₂ emission as a function of temperature (low temperature range) for catalysts obtained by incipient wetness impregnation. Ceria-zirconia (CZ) is included for comparison purposes.

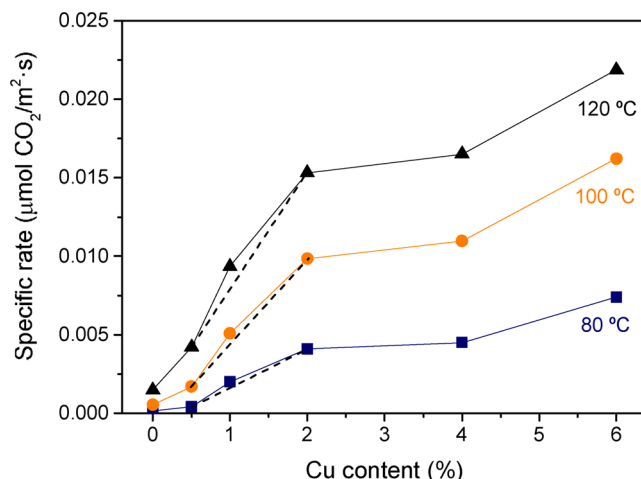


Fig. 4. Specific rates of CO₂ emission for the incipient wetness impregnation catalysts at different temperatures (80, 100 and 120 °C) according to copper content.

It should be noted that crystallite size determined by H₂ chemisorption method is a measure of metallic copper particle size. However, CuOx entities are the supposed active species towards CO oxidation. CuO particle size can be calculated from metallic Cu particle size by assuming that CuO will adopt a spherical or near-spherical shape when they are dispersed over ceria-zirconia. Therefore, the size of CuO crystallite is only slightly larger than that of metallic copper particle (Table S2).

It is relevant in this context, as well, to compare the reactivity per total metal content on the catalysts. Therefore, the representation of reaction rate (μmol CO₂/g_{Cu}·s) versus the inverse of reaction temperature is illustrated on Fig. 5. Consistently with the information shown on Fig. 4, by increasing the copper contents in the range of 0.5, 1 up to 2%, the representation of the reaction rate expressed per gram of copper versus the inverse of temperature is almost identical for these three catalysts indicating that the number of active sites participating in the process seem to grow in a gradual way when adding more copper contents in this range. However, the representation of 4 and 6% Cu contents falls below the trend traced by the mentioned three catalysts, thus suggesting a lowest effectivity for copper metal atom into these two catalysts. All these evidences are in general agreement with the trend in copper dispersion data.

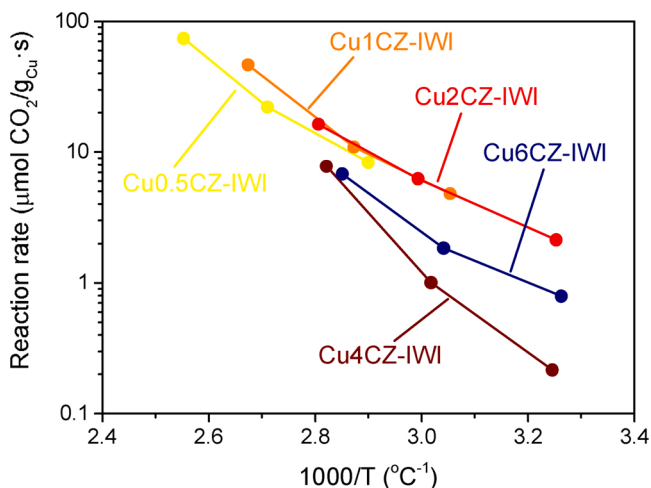


Fig. 5. CO oxidation reaction rate as function of the inverse of temperature for catalysts obtained by incipient wetness impregnation (with values which correspond to CO conversion percentages ≤ 20 %).

The composition of 2% of copper loading was selected to analyse the relevance of the preparation method thus unraveling if CuO_x entities of different nature can exist and which is the relationship among their type and amount with their own catalytic activity. Indeed, given the complexity of the copper/ceria-zirconia system, it is challenging to shed light on the preliminary identification of the active sites and their correlation with catalytic activity. For this purpose, three different preparation routes (very different among them, regarding their physico-chemical fundamentals) were approached. It is supposed that different procedures of copper incorporation onto the catalyst will yield different degrees of contact/distribution/nature of copper species onto the ceria-zirconia catalyst.

In line with these ideas, three catalysts with the same 2% copper content were synthesized. The corresponding nomenclature is: Cu2CZ-IWI, Cu2CZ-CP and Cu2CZ-PM. The second solid was prepared by a combined co-precipitation procedure of the metallic precursors and the third solid was obtained by an intimate physical mixture of the support and the copper precursor and, subsequent calcination a 500 °C (see Section 2 for additional details). Besides, the BET surface areas obtained for the three catalysts are highly similar (71, 72 and 70 m^2/g , respectively), thus allowing us a reliable comparison of the influence of the different nature of the copper species, since both parameters (copper content and exposed surface areas) are practically identical in the three samples considered. The corresponding CO conversion curves are depicted on Fig. 6. These three copper/ceria-zirconia catalysts were found to be more active than unsupported ceria-zirconia and bulk CuO . It is relevant to point out that the route of procedure significantly affects the catalytic activity, both the onset reaction temperature and the slope of the curve. The order of activity is as follows:

$\text{Cu2CZ-PM} < \text{Cu2CZ-CP} < \text{Cu2CZ-IWI}$

In accordance with the exposed ideas, reaction rates against the reciprocal of temperature for these three catalysts show the highest values for the catalyst prepared by the IW method on Fig. 7. To better understand the differences in reactivity provided with the different variables studied (copper content and type of preparation procedure), CO-TPR experiments are presented below, with the aim to determine the distinctions among all the catalysts in the reaction between CO and oxygen from the surface/lattice of the catalysts. The combined analysis of all the experimental data (catalytic tests, CO-TPR results and characterization of the catalysts) will allow us to ascertain if the nature and type of copper species can play a role during the promotion/activation of oxygen from the catalysts, taking part in the catalytic reaction.

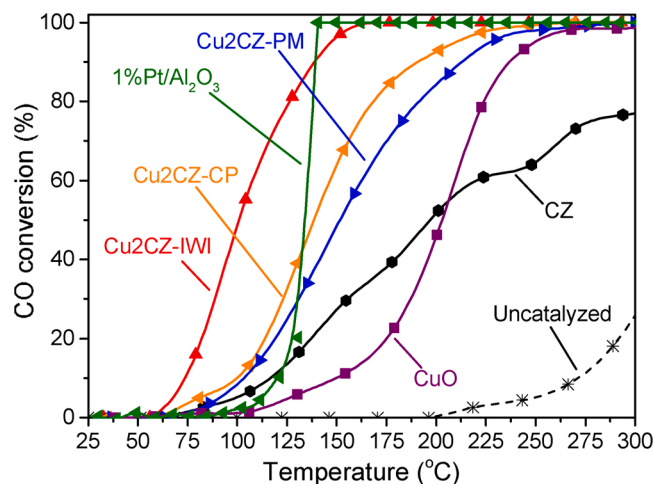


Fig. 6. CO oxidation light-off curves for catalysts obtained by different synthesis techniques. CuO , ceria-zirconia (CZ), 1%Pt/ Al_2O_3 and uncatalyzed reaction are included for comparison purposes.

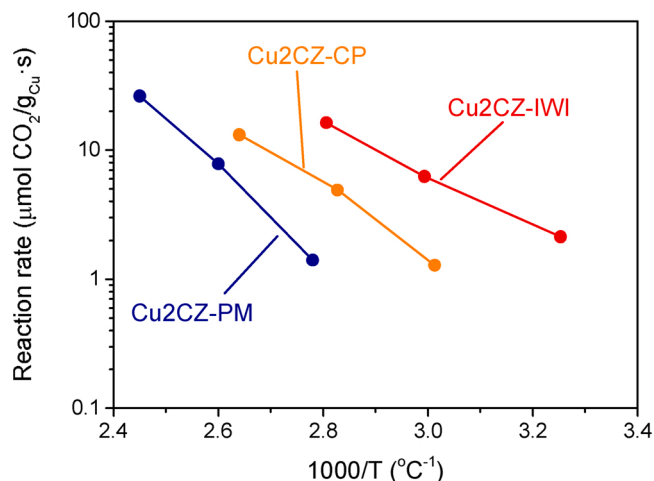


Fig. 7. CO oxidation reaction rate as function of the inverse of temperature for catalysts obtained by different synthesis techniques (with values which correspond to CO conversion percentages $\leq 20\%$).

3.2. CO temperature-programmed reduction

CO-TPR has been widely used to characterize reducibility of the CuO-CeO_2 systems [40]. Additionally, with the general purpose to infer some arguments which can assist the understanding of the trends in the catalytic activity towards CO oxidation of the different sets of catalysts, the use of CO is preferred as a probe molecule instead of H_2 [41]. Nevertheless, the discussion of the influence of copper contents and preparation procedure on the H_2 -TPR profiles for the catalysts studied was presented elsewhere [35,36] and the corresponding data and additional interpretation for selected catalysts is reported on the next section.

CO-TPR experiments have been performed in order to investigate the influence of copper entities of different possible nature and interaction degree with the support on the catalysts' reducibility [42]. In fact, if several CuO_x species co-exist onto these samples, they could play different roles during the activation of surface/sub-surface oxygen from the ceria-based support, which could produce, eventually, characteristic CO_2 emission profiles for this type of copper/ceria-zirconia systems [13, 40,42,43]. Besides, by comparing the corresponding profiles of the different catalysts prepared with those of bulk CuO and the bare support, possible synergetic effects among CuO_x species well spread onto the catalysts' surface and the cerium centers in close vicinity with them (thus facilitating ceria's reduction due to close interfacial interactions, well commented on literature [18,20]) could be evidenced.

Fig. 8A and B shows CO_2 emission profiles during CO-TPR experiments for the two sets of copper/ceria-zirconia catalysts analyzed in this work. The reduction profile of pure CuO , is characterized by a single and broad peak in a temperature range from 120 to 260 °C, indicating the temperature window where the unsupported CuO tenorite-like species reduction is expected to take place. In this case, CuO sample's profile is presented on the Fig. 8 like a calculated curve corresponding to 2% of bulk CuO profile, for comparative purpose. Considering the conditions employed, this broad peak can be ascribed to direct reduction to metallic copper, in agreement with previous studies [13,44,45]. The undoped ceria-zirconia profile exhibits an asymmetric first broad peak starting at 80 °C, which can be also considered a shoulder of a second one centered at around 430 °C. Unfortunately, the interpretation of its CO-TPR profiles becomes extraordinarily complex due to the simultaneous occurrence of the water-gas shift (WGS) reaction and Boudouard reaction, according to these Eqs. (2) and (3), respectively):



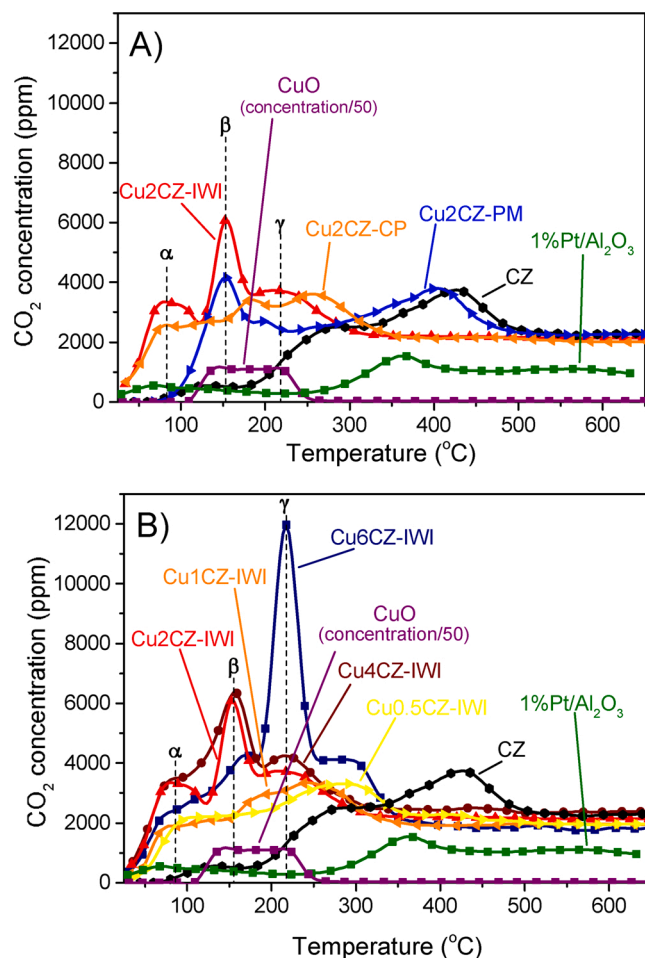


Fig. 8. CO-TPR profiles of copper/ceria-zirconia catalysts obtained by: A) different synthesis techniques, and B) different copper content. CuO, ceria-zirconia (CZ), 1%Pt/Al₂O₃ and uncatalyzed reaction are included for comparison purposes.

thus providing a constant CO₂ emission level at high temperatures during the experiments, which makes that the profile does not return back completely to the baseline. Many authors have revealed the contribution of these side reactions catalyzed by ceria-based catalysts, under CO-TPR experiments [13,46–48], mainly at medium temperature range (> 275 °C) for WGS reaction and high temperature range (> 400 °C) for Boudouard reaction. For the sake of a reliable comparison and taking into account that the most interesting/representative peaks or contributions appear on the corresponding patterns of copper/ceria-zirconia catalysts at low/medium temperatures, the subtraction of the whole profile of the bare support to those corresponding to the catalysts prepared, was conducted in an attempt to remove the side effects of the WGS and Boudouard reactions (whatever the extension at which both reactions take place). Additionally, this subtraction highlights in an adequate manner: i) the CuO_x entities' reduction patterns and ii) possible synergetic effects arisen from the copper entities in close contact with ceria-zirconia's surface, consisting of "extra" cerium centers' reduction as a consequence of promoted interfacial interactions.

In line with these exposed ideas, Fig. 9A and B depicts the "treated" profiles after conducting these subtractions. Assuming that the Boudouard reaction occurs in similar extent for all the catalysts, Fig. 9A shows two different low-temperature peaks or contributions, that can be ascribed to the CuO_x species reduction or to the mentioned interfacial interactions which could yield to additional cerium centers reduction. Cu₂CZ-IWI and Cu₂CZ-CP presents a very low temperature broad contribution, centered at around 80 °C and completely absent both in

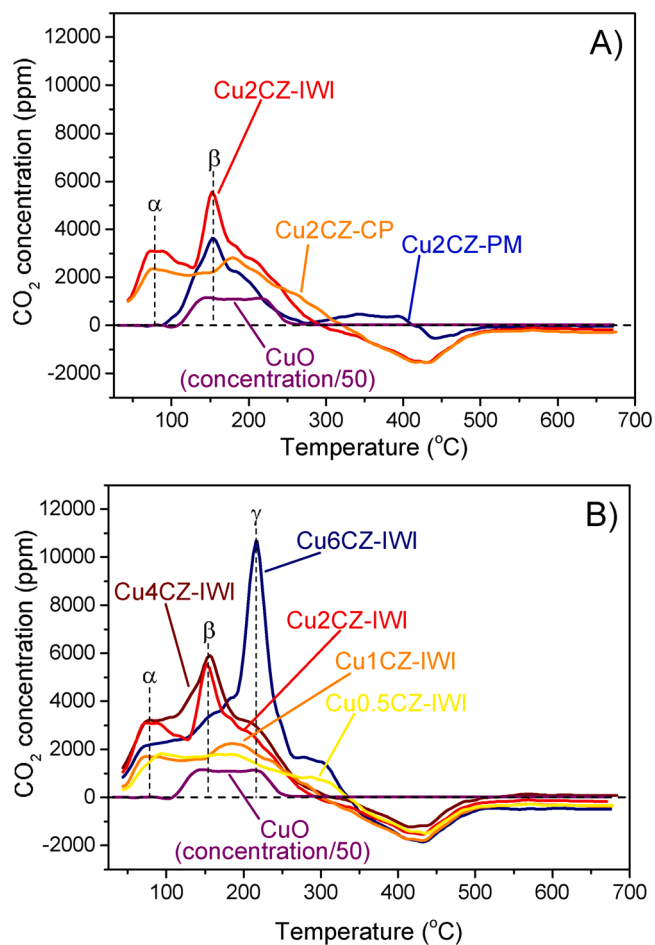


Fig. 9. Subtracted CO-TPR profiles with respect to ceria-zirconia for copper/ceria-zirconia catalysts obtained by: A) different synthesis techniques, and B) different copper content. CO-TPR profile of CuO is included for comparison purposes.

the catalyst prepared by physical mixing method and in the CuO bulk sample. Some authors reported in the literature that this first contribution could be ascribed to very finely CuO dispersed onto ceria-based materials or to the reduction of copper species strongly interacting with ceria [40]. The experimental fact that this α contribution arises at lower temperature than those reported in other papers is consistent with the very high activity of these catalysts towards CO oxidation (even outperforming that of Pt's catalyst) [40]. This comparison also suggests that the physical mixture method yields a poorer copper/support contact or a lack of these very finely dispersed CuO_x species and for this reason this catalyst presents much lower activity in the range of low temperatures compared with their counterparts having the same copper loading. This behavior is consistent with the high copper crystallite size for Cu₂CZ-PM (32.7 nm) and low dispersion data (3%), estimated from H₂ adsorption volumetric studies.

Conversely, the second contribution (β) appears as a clear peak (specially for Cu₂CZ-IWI and for Cu₂CZ-PM) in the temperature window of the unsupported CuO. Interestingly, by comparing the relative areas of the CuO bulk (2% of the whole profile) against these catalysts, the inferior area of the reference CuO can be clearly seen whatever the catalyst considered, but specially for Cu₂CZ-IWI. Moreover, the profiles are negative at medium temperatures. A reasonable explanation for this observation is that a concomitant reduction of cerium centers is taking place in this temperature range (occurring at higher temperatures in the bare support). In order to tentatively distinguish if it is motivated by an "anticipated" reduction of the support or if, additionally, "extra"

reduction of cerium centers, in close vicinity with the several active CuO_x species, takes place, additional quantifications were estimated and compiled on Table 2, as commented on below.

Regarding the effect of the copper content for IWI-catalysts (Fig. 9B), three contributions (α , β and γ) are presented in different extensions and relative importance, being γ specially relevant for the catalyst prepared with 6% of copper loading (this peak appears like a very low and broad contribution or is absent for the rest of catalysts). All the IWI catalysts show the contribution at low temperatures (α), which seems to reach maximum values for Cu2CZ-IWI and Cu4CZ-IWI. For these two catalysts, the second contribution (β), emerging in the temperature window of the unsupported CuO tenorite-like species, presents the highest values of the series as well. Conversely, the Cu6CZ-IWI catalyst exhibits less intensity for these two first contributions (α and β) in favor of a very prominent and sharp peak at higher temperature (γ). It is worth reminding that this catalyst was prepared by three successive impregnations of the copper precursor solution.

As advanced, Table 2 compiles additional quantifications estimated from Fig. 9A and B. The data on the second column correspond to the integrated amounts of CO_2 emitted by each catalyst after subtraction of the CO_2 emission corresponding to the ceria-zirconia support. The third column collects these values after subtraction of the theoretical CO_2 emissions corresponding to the stoichiometric reduction of the CuO molar contents of the different catalysts, according to this global stoichiometry (4), (by assuming a general formula of CuO for all the CuO_x entities):



Assuming the validity of these subtractions, the “extra” amounts obtained as $\mu\text{mol CO}_2/\text{g}$ of every catalyst (Table 2) suggest that whatever the method of preparation of the catalyst or the amount of copper introduced by the IWI method, “additional” or “extra” cerium centers reduction can be measured, thus suggesting a good degree of interaction copper/ceria-zirconia and an excellent reducibility under CO in the systems prepared. Following with this discussion and in an attempt to

Table 2
Quantitative analysis of CO-TPR data from copper/ceria-zirconia catalysts.

Catalyst	CO-TPR			
	CO_2 emitted after subtraction of the support ($\mu\text{mol}/\text{g}$) ^a	Theoretical CO_2 emission ($\mu\text{mol}/\text{g}$) ^b	CO_2 “extra” emission ($\mu\text{mol}/\text{g}$) ^c	Potential cerium centers affected/CuO ratio ^d
Cu0.5CZ-IWI	516	79	437	11.2
Cu1CZ-IWI	442	156	286	3.6
Cu2CZ-IWI	1087	308	779	5.0
Cu4CZ-IWI	1541	617	925	3.0
Cu6CZ-IWI	1584	925	659	1.4
Cu2CZ-CP	841	308	533	3.4
Cu2CZ-PM	618	308	309	2.0

^a This parameter corresponds to the CO_2 emitted subtracting the contribution of its corresponding ceria-zirconia support.

^b Theoretical CO_2 emission was calculated from the required CO amount to reduce the nominal amount of CuO to Cu.

^c CO_2 “extra” emission corresponds to the CO_2 emitted subtracting the contribution of its corresponding ceria-zirconia support and the “theoretical CO_2 emission”.

^d This parameter was calculated from “ CO_2 “extra” emission” normalized by the “theoretical CO_2 emission” and multiplied per 2 (due to stoichiometry of the Eq. (5)).

rationalize these “extra” amounts along the sets of catalysts, the CO_2 $\mu\text{mol}/\text{g}$ estimated values were referred to the CuO molar content of the different catalysts. Assuming the general stoichiometry of cerium cations’ reduction on ceria’s surface (5):



the last column on Table 2 compiles the potential number of cerium centers surrounding the CuO_x entities which are supposed to suffer reduction according to these quantifications. It is clearly demonstrated that more cerium centres are affected due to improved synergetic interactions according to this order in terms of the method of preparation:



This was the order observed for the catalytic activity, and as well, the order also agrees with the contribution of the α peak (at the lowest temperature), which is more prominent for the IWI-catalyst.

Regarding the effect of copper content, generally speaking, the approximate calculations report a trend consisting of more cerium centers affected by CO reduction in the vicinity of CuO_x entities as the copper loading decreases. However, this seems not to be a linear effect with the copper loading. This observation can be tentatively explained by the variety of CuO_x entities which seem to coexist on this set of catalysts.

3.3. Characterization and identification of CuO_x species in relation to the preparation method used

In recent years, copper/ceria-based catalysts have attracted considerable attention due to their low cost and excellent catalytic performance in many oxidation reactions [49]. Nevertheless, due to their inherent reactivity, the use of classical methods to determine copper entities’ dispersion by means of traditional chemisorption procedures is very problematic due to the existence of large spillover phenomena, (in the case of H_2 chemisorption methods), or the possibility of concomitant oxidation of cerium centers if other probe molecules (CO and N_2O , as examples) are used for chemisorption studies after a previous reduction step. In this context, H_2 adsorption isotherms at sub-ambient temperatures or sophisticated imaging analysis techniques such as HAADF-STEM might be applied to determine reliable copper dispersion data in recent years (but with certain amount of difficulties) [50].

Since it is widely recognized that the dispersion states, redox properties and catalytic performances of CuO/ceria-based catalysts are critically dependent on the preparation methods [49], this section will be devoted to a comparative analysis considering the characterization’s features of some representative catalysts of this study. On this basis, implications will be intended to be extracted concerning the nature and roles of the different CuO_x species on catalytic activity. By a combined discussion considering the whole characterization data obtained from catalysts prepared by different methods, CO-TPR results and CO oxidation activity data, an interesting interpretation of the correlation among catalyst’ properties and catalytic behaviors can be obtained.

By having a look at the rate of CO_2 production during the catalytic tests of CO oxidation at a representative temperature (e.g. 80°C), it can be noted that the catalyst prepared by physical mixture presents a rate of CO_2 production of $0.020 \mu\text{mol}/\text{g}\cdot\text{s}$ (being an intermediate value among that of the bare support -0.011- and that of the lowest copper content catalyst prepared by IWI method (0.037), but quite far from that of the catalyst with a same copper content, (2%), prepared by IWI method as well (0.290). On the other hand, the coprecipitation method yields a catalyst whose rate of CO_2 production (0.094) is much more similar to that of the 0.5 % Cu (0.037) and far from that of its counterpart 2% copper content (0.290). These data provide some signs about the relevance of the preparation method on the type, amount and nature of active sites on these complex systems.

In order to have in mind the complete picture, Fig. 10A and B

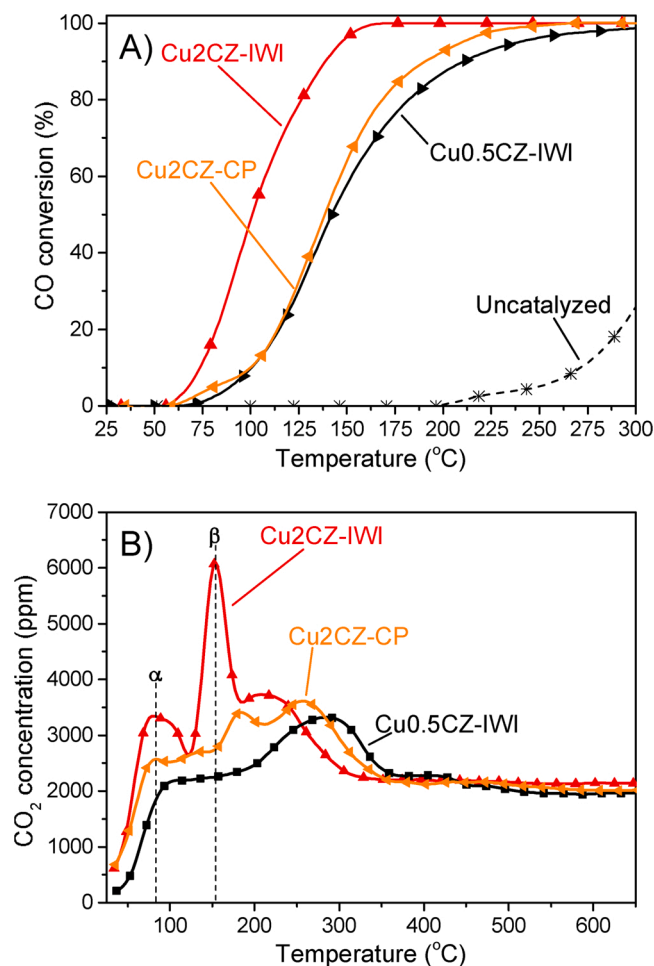


Fig. 10. A) CO oxidation light-off curves and B) CO-TPR profiles for Cu2CZ-CP, Cu2CZ-IWI and Cu0.5CZ-IWI catalysts.

illustrates the representations of the CO oxidation activities and the CO₂ production profiles (obtained from the CO-TPR profiles) for selected catalysts. It is interesting to note that the nature and type of CuO_x species generated onto the catalysts, modulated by the different methods, seem to exhibit more influence on catalytic activity values and catalysts' reducibility than the whole content of CuO onto them. According to these results, Cu0.5CZ-IWI (prepared by incipient impregnation method) presents the same activity and similar redox properties than Cu2CZ-CP, prepared by a coprecipitated method of the three metal precursors, in spite of having 4 times less copper content.

In order to shed light on these experimental observations, comparative characterizations results will be presented now. As commented earlier, the whole characterization results, dealing separately the effect of copper content and the influence of preparation method on the activity towards diesel soot combustion, were presented elsewhere [35, 36]. For the discussion presented in this section, only representative characterization results of selected catalyst will be shown.

First of all, XPS analyses will be presented. Cu-2p_{3/2} photoelectron spectra of selected catalysts (Cu0.5CZ-IWI, Cu2CZ-CP and Cu2CZ-IWI) were depicted on Fig. 11. As illustrated, Cu0.5CZ-IWI with Cu2CZ-CP present much more similarities on their XPS spectra than Cu2CZ-CP with Cu2CZ-IWI (its counterpart with the same copper content). To deepen into the mode in which copper distribution takes place among the surface with regard to the bulk of the catalysts in terms of the synthesis route and the amount of copper for representative catalysts, Table 3 collects the corresponding Cu/(Cu + Ce + Zr) surface atomic ratios (designated as Cu/(Cu + Ce + Zr)_{sur}) and the estimated bulk

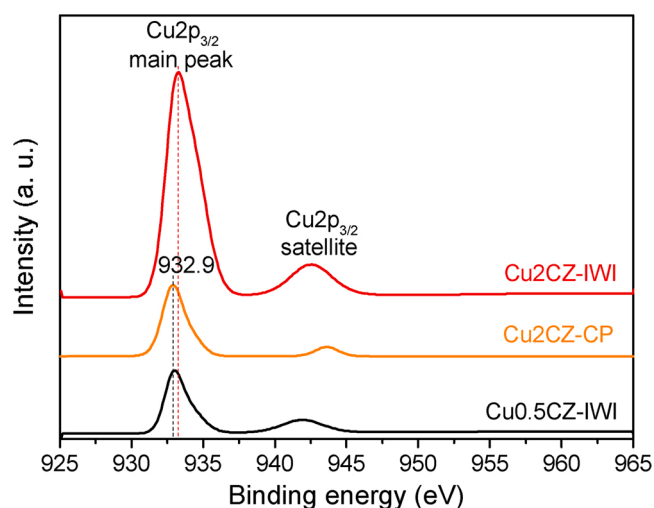


Fig. 11. Cu-2p_{3/2} XPS profiles of Cu2CZ-CP, Cu2CZ-IWI and Cu0.5CZ-IWI catalysts.

Table 3

Surface and nominal Cu atomic ratios.

Catalyst	Cu/(Cu + Ce + Zr) _{sur} ^a	Cu/(Cu + Ce + Zr) _{nom}
Cu0.5CZ-IWI	0.015	0.013
Cu2CZ-IWI	0.028	0.051
Cu2CZ-CP	0.095	0.051

^a Experimental values estimated by XPS.

atomic ratios (designated as Cu/(Cu + Ce + Zr)_{nom}). The catalysts prepared by incipient wetness impregnation present higher Cu surface atomic ratios than the theoretical bulk values, which means that copper is finely dispersed onto the support's surface, partially blocking porosity, as inferred from previous publications [35,36]. Cu2CZ-CP has a lower surface atomic ratio than the theoretical bulk value, thus indicating that copper has been (at least in part) incorporated into the ceria-zirconia lattice or subsurface due to the combined coprecipitated method of preparation used. This makes that the fraction of Cu atoms exposed for Cu2CZ-CP remains much lower than that obtained by incipient wetness impregnation method, and yields values close to those shown by Cu0.5CZ-IWI.

To approach the discussion about reducibility of the catalysts and trying to complement the data obtained by means of CO-TPR, results obtained by H₂-TPR for selected catalysts are presented on Fig. 12, whose detailed discussion was presented elsewhere [35,36]. Again, a relevant similarity can be found by comparing the profiles of Cu0.5CZ-IWI and Cu2CZ-CP (in terms of intensity and shape of the patterns), however, the catalyst prepared by incipient wetness impregnation presents the profile a little bit moved forward to lower temperatures, indicating a promoted reducibility at lower temperatures. Anyway, both profiles are considerably lower than that of the Cu2CZ-IWI, in agreement with the rest of catalytic and characterization data presented so far.

With the aim of supporting the discussion regarding the extension of the reduction process occurring onto the copper-containing catalysts (if only "anticipated" cerium centers reduction, compared with the reduction of bare support, takes place, or if, additionally, "extra" or "new" cerium centers, not susceptible to be reduced in the case of the bare support, can be affected by the reduction process due to an excellent quality of the interphase copper species/ceria-zirconia, the same estimations, based on subtractions conducted for CO-TPR profiles, were carried out, now, with the data obtained from H₂-TPR profiles, considering the following stoichiometries ((6) and (7)):

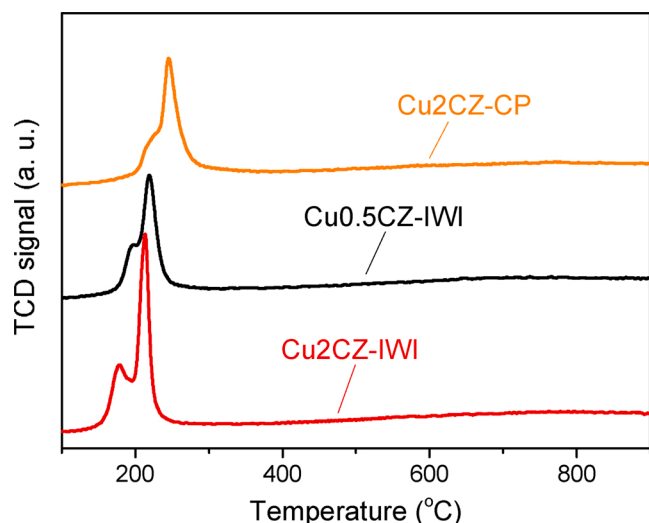


Fig. 12. Reducibility profiles of Cu2CZ-CP, Cu2CZ-IWI and Cu0.5CZ-IWI obtained from H₂-TPR.



In this case, the results (not shown for the sake of brevity), yield that, approximately, the same amount of cerium centers that suffer reduction onto the bare support are reduced “in advance”, but not “extra” cerium centers reductions are evidenced after the corresponding subtractions. These discrepancies can be motivated by two reasons: i) the estimations are subjected to several source of errors and, as a consequence, they need to be viewed as “approximate results” and ii) CO can be considered a compound with a more pronounced reducing character than H₂ towards these catalysts (actually, having been conducted under the same experimental conditions, CO-TPR profiles are moved toward lower temperatures with regard to H₂-TPR ones).

3.4. Contributions of different CuO_x species to catalytic activity

This study has revealed that very high but different ranges of catalytic performances can be reached by means of different CuO/ceria-zirconia catalysts and that CO-TPR curves seem to be very sensitive to the presence of several types of CuO_x entities onto this support, thus displaying several CO₂ contributions/peaks due to the optimal interaction of CO molecules with the oxygen from the own reservoir of every catalyst. Both CuO_x entities and ceria-zirconia were more readily reduced than, at least, the corresponding independent components. In addition, it is suggested that “extra” cerium cations could be reduced in variable amounts due to the excellent qualities of the interfaces created. Even though the whole estimations should be considered taking into account that some assumptions or oversimplifications were taken, attempts were tried to estimate the “extra” cerium centers affected by the reduction under CO, which is a primary trial of “titrating” the quality and extension of the interphase CuO_x/ceria-zirconia, responsible of improvements of redox properties and catalytic responses in these systems with regard to CuO_x well-dispersed onto different nature supports. These values are suggested to be influenced by copper content, (linked to dispersion of CuO_x species) but more importantly to the method of preparation.

To clarify the connection or coupling between the profiles obtained by CO oxidation (CO₂ formed by reacting 1000 ppm of CO with 10 % of O₂) and by CO-TPR patterns (CO₂ originated by reacting 5% of CO with the oxygen coming from the own catalysts), a combined representation of both profiles expressed as μmol CO₂/g_{cat}·s is presented versus temperature for selected samples on Fig. 13. Dotted lines correspond to the rate profiles from CO-TPR and solid lines to those of CO oxidation in

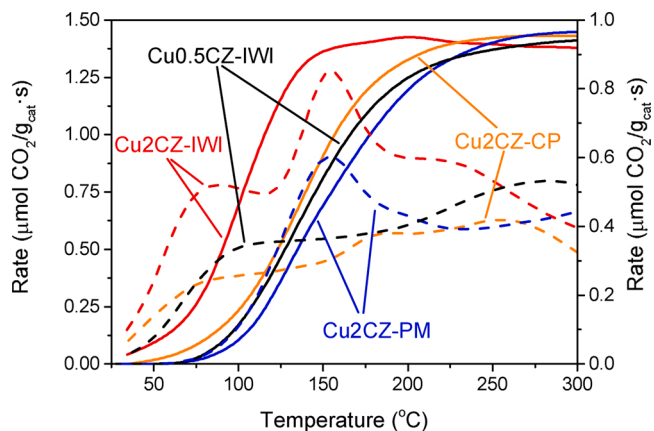


Fig. 13. CO₂ emission rate during CO oxidation catalytic tests (continuous lines and Y axes to the left) and CO-TPR tests (dotted lines and Y axes to the right) for copper/ceria-zirconia catalysts.

presence of O₂. The catalysts prepared by “chemical” routes (co-precipitation or incipient wetness impregnation) exhibit a remarked ability to activate and oxidize CO molecules with their own oxygen (coming from CuO_x entities or surrounding ceria-zirconia’s surface). Conversely, the sample prepared by physical mixing between copper precursor and ceria-zirconia (and subsequent calcination) does not possess the “active sites” responsible of oxidizing CO at very low temperatures (α contribution is absent for this catalyst) and, accordingly, the CO₂ production curve is delayed with regard to the rest of the catalysts. From the combined analysis illustrated on Fig. 13, the best catalytic response shown by Cu2CZ-IWI can be attributed to a joint presence of a relevant α contribution (probably CuO_x entities very well-dispersed onto ceria-zirconia, proved by extremely low size of copper crystallite) and accessible CuO-like tenorite entities, (β contribution) similar to those presented by bulk CuO and Cu2CZ-PM (with high average crystallite size). These entities are probably at a surface level and very accessible and are able to promote reduction of cerium centers in close vicinity, as inferred for the respective comparison with bulk CuO area presented above. Conversely, the sample prepared by co-precipitation, shows much lower β and a slightly lower α contribution than its counterpart prepared by IWI. Part of its CuO species seem to be more “buried” onto the catalyst’s sub-surface, and as a consequence of this different copper distribution/accessibility, the resultant catalytic behavior reaches the same level than that of a catalyst prepared with much lower copper content, but more accessible on surface (Cu0.5CZ-IWI), as previously pointed out.

It is assumed that oxidation of CO onto these catalysts proceeds though a Mars-van Krevelen mechanism, which has been previously invoked by ceria-based materials with very positive effect of facile oxygen transfer from the catalysts due to a favorable formation of oxygen vacancies. This is clearly promoted by the presence of CuO_x species, because the relevant step during CO oxidation is the reaction between adsorbed CO and oxygen from the own reservoir of the catalyst. In this sense, CO-TPR studies were approached in order to analyze possible differences in the catalysts with the different amount and nature of CuO_x species. Nevertheless, whatever the copper-containing catalyst studied, CO conversion is coupled with CO₂ production during CO-TPR, evidencing a fast and facile transfer of oxygen from the catalyst (CuO_x species/ceria-zirconia’s surface) towards CO molecules in the absence of O₂-gas phase, which could, eventually replenish the own reservoir of oxygen under oxidant atmosphere.

These experimental evidences are congruent with the values of apparent activation energies (E_a) estimated from CO oxidation catalytic tests. The corresponding values are presented on Table 4 for all the catalysts studied. For most of the cases, CZ presents a higher apparent activation energy (68 kJ/mol) than that of copper-containing catalyst. It

Table 4
Apparent activation energies (E_a) estimated from CO oxidation catalytic tests.

Catalyst	E_a^* (kJ/mol)
CZ	68
Cu0.5CZ-IWI	52
Cu1CZ-IWI	50
Cu2CZ-IWI	38/42
Cu2CZ-CP	52
Cu2CZ-PM	73
Cu4CZ-IWI	70
Cu6CZ-IWI	46/43
1%Pt/Al ₂ O ₃	61

* Estimation of apparent E_a was carried out assuming differential conditions (with CO conversion values $\leq 20\%$). Reproducibility measurements were reasonably good considering two selected catalysts (Cu2CZ-IWI and Cu6CZ-IWI).

is worth noting that the couple of catalysts previously discussed because of similarities among physico-chemical features and CO-TPR profiles, (Cu0.5CZ-IWI and Cu2CZ-CP) are characterized by presenting a same value of this parameter (52 kJ/mol, lower than that of the bare support), supporting the idea that a similar number and type of active sites are present on these catalysts. On the contrary, Cu2CZ-IWI, showing a highlighted ability to transfer oxygen to CO molecules (prominent α and β peaks) presents the lowest E_a values (38/42 kJ/mol) in agreement with the idea of a higher number of active sites on this catalyst. This E_a value is even lower than that estimated for 1%Pt/Al₂O₃ catalyst, in agreement with a poorer reducibility of this catalyst. In this sense, the CO oxidation mechanism of alumina-supported platinum catalyst is known to take place via a single-site competitive Langmuir–Hinshelwood mechanism (suprafacial mechanism) [37]. The non-participation of oxygen lattice from the support in this mechanism provokes the low reducibility of 1% Pt/Al₂O₃ under CO-TPR conditions [51]. This contrasts with copper-containing catalysts, in which the high participation of the lattice oxygen atoms from these catalysts seen under CO-TPR conditions is indicative for the dominating Mars-van Krevelen mechanism (intrafacial mechanism). However, Cu2CZ-PM presents even a higher value of E_a (73 kJ/mol) than 1%Pt/Al₂O₃ and, accordingly, this catalyst is characterized by a reduced capacity to transfer oxygen to CO molecules, since the α contribution is completely absent for this catalyst.

4. Conclusions

This research has been dedicated to the preparation and study of the catalytic activity of different copper/ceria-zirconia catalysts in order to understand the nature of the active sites and the generated synergies for CO oxidation reaction at low temperature. The general conclusions that have been drawn are the following:

- All the catalysts obtained by incipient wetness impregnation method are more catalytically active towards CO oxidation than 1%Pt/Al₂O₃ at low temperatures ($T < 130\text{ }^\circ\text{C}$), due to the high synergies created among CuO_x species and the ceria-zirconia support, even at copper loading as low as 0.5%. This seems to be connected with a very high copper's dispersion degree reached with this procedure, yielding significantly low copper crystallite sizes.
- Regarding the IW-catalysts, the CO oxidation activity increases linearly with Cu loading up to 2 wt.%. When increasing the contents up to 4 and 6 wt.%, respectively the increase is not gradual anymore.
- The synthesis method significantly affects the CO oxidation activity. The catalytic activity increases along the series: Cu2CZ-PM < Cu2CZ-CP << Cu2CZ-IWI.
- Different CO-TPR peaks/contributions were observed in different extensions and relative importance for copper/ceria-zirconia

catalysts. Remarkably, Cu2CZ-IWI and Cu4CZ-IWI exhibit the most intense low-temperature contribution (α peak), as well as β contribution.

- Quite similar CO oxidation activities can be reached from different synthesis methods and different copper contents (Cu0.5CZ-IWI and Cu2CZ-CP), evidencing the importance of the nature and the type of CuO_x species generated over the catalysts' surface, which can be modulated by the synthesis procedure. These features seem to be more relevant than the own CuO content on catalysts.
- From the combined study of CO-TPR and H₂-TPR profiles, it can be seen that CuO_x entities are reduced at low temperatures (very dependent on the preparation method) onto ceria-zirconia, but, importantly all the cerium centers susceptible to be reduced under CO and/or H₂ in the support, are reduced in an anticipated way, with regard to the interval of temperatures where this reduction process takes place in the bare support. The detailed investigation of the several contributions and peaks that appear on the CO-TPR profiles, compared with the bare support and with the CuO bulk profile has been revealed as very useful for a first approach into the understanding of the synergies created on this system. Finally, the evidences provided by the reducibility and catalytic profiles of the catalysts prepared by the different procedures can contribute, interestingly, to the clues about the features which should be determinant for these catalyst to present very high catalytic activity towards CO oxidation, mainly at low temperatures.

CRedit authorship contribution statement

J.C. Martínez-Munuera: Conceptualization, Methodology, Investigation, Validation, Visualization, Writing - original draft. **V.M. Serrano-Martínez:** Investigation. **J. Giménez-Mañogil:** Investigation. **M.P. Yeste:** Investigation, Validation, Visualization. **A. García-García:** Conceptualization, Methodology, Writing - original draft, Supervision, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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