



Effect of the preparation method and calcination temperature on the oxidation activity of CO at low temperature on CuO–CeO₂/SiO₂ catalysts



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ABSTRACT

The effect of preparation method, either coimpregnation or sequential impregnation, and of calcination temperature (between 500 °C and 700 °C) of CuO–CeO₂/SiO₂ catalysts on the CuO–CeO₂ interface and on their activity in the oxidation of CO with O₂ at low temperatures is studied. The catalysts are characterized by BET, XRD, TPR and UV–vis DRS. The results show that the preparation method has a substantial effect on the kind of CuO species formed on the surface. At calcination temperatures in the 500–600 °C range, coimpregnation leads to the formation only of Cu species that interact strongly with CeO₂, while sequential impregnation leads also to the formation of bulk CuO species that do not interact, or interact weakly, with CeO₂. In the case of sequential impregnation the concentration of the different CuO and CeO₂ species and of the sites on the interface depends on the impregnation sequence of the support with the precursors of the oxides of both metals. On the other hand, the activity of the catalysts in the oxidation of CO at low temperatures (less than 180 °C) does not differ substantially with the preparation method, provided the calcination temperature remains in the 500–600 °C range. If the catalysts are calcined at 700 °C, the CuO–CeO₂ interface, and therefore the activity of the catalysts, is strongly dependent on the preparation method and on the impregnation sequence of both oxides. Using sequential impregnation, impregnating first with the Ce precursor, produces a catalyst whose activity is substantially higher than that of the catalysts prepared by the other methods after calcining at 700 °C.

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1. Introduction

Since the publication of the work of Stephanopoulos et al. [1–3] on the high catalytic activity of the CuO–CeO₂ system in the oxidation of CO with O₂, numerous studies have been made that involve this system in the absence or presence of H₂ [4–20]. In many of these papers the precursors of CuO and CeO₂ are placed on a support, often Al₂O₃ [10–13] or ZrO₂ [14,15]. Recently, SiO₂ as support has also been the subject of some studies [16–20] which show that the CuO–CeO₂ system has an interesting catalytic activity, even higher than that shown when the other supports are used [16].

The high activity of the CuO–CeO₂ system is associated with the formation of sites at the interface between both oxides, in which the oxygen can be easily abstracted by CO to form CO₂ [2,3]. The oxygen vacancy generated is then filled with oxygen from the gas phase, allowing the continuity of the catalytic cycle. Martinez-Arias et al.

[21] published a detailed mechanism that describes the activity of the sites at the CuO–CeO₂ interface.

In previous work by our group [16], the activity of CuO and CeO₂ supported on silica, alumina and zirconia was compared, concluding that the systems with the highest activity are those with SiO₂, followed by ZrO₂ and finally Al₂O₃. The greater activity of the CuO–CeO₂/SiO₂ system was attributed to the inert character of silica, which facilitates the mobility of both oxides, allowing the formation of a high concentration of interfacial sites, specifically sites formed by highly dispersed CuO in contact with CeO₂ particles. A different activity sequence was found by Rao et al. [19] when cerium oxide is mixed with SiO₂, Al₂O₃ and ZrO₂, and then CuO is supported on these mixed oxides. They found that the highest activity is obtained with the CuO/CeO₂–Al₂O₃ catalyst. The optimum relation between Cu and Ce, as well as the total load of both metals on SiO₂ were the central topics of a second paper by our group [17]. We found that the optimum relation between Cu and Ce is achieved in a catalyst with 3% Cu and 7% Ce, which is not much different from what is reported in the literature for the CuO–CeO₂/Al₂O₃ system [10], whose maximum activity is found in a catalyst with 2% Cu and 8% Ce. On the other hand, in our previous work we determined

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that the optimum total load for both metals is 18%, on which essentially bulk CuO is formed, a species that contributes marginally to the catalyst's activity at low temperatures. Both the optimum load and the optimum Cu/Ce ratio maximize the formation of the highly dispersed CuO interface with the cerium oxide particles. Luo et al. [18] showed that not only the addition of Ce, but also the porosity of the SiO₂ can have a positive influence on the activity of Cu and Ce supported on SiO₂. Recently, Ma et al. [20] reported the generation of a high activity catalyst in the low temperature oxidation of CO by supporting Ce and Cu on a hierarchically porous silica prepared by a sol–gel method.

In the previous work of our group [16,17] the catalysts were prepared by coimpregnation of the precursors of both oxides on SiO₂. In the present paper we go more deeply into the knowledge of the CuO–CeO₂/SiO₂ system, studying the influence of two important variables on the preparation of the bimetallic catalysts of supported Cu and Ce. The first variable is the preparation method, comparing the coimpregnation method with the sequential impregnation method with the CuO and CeO₂ precursors, varying the impregnation sequence of the precursors of both oxides. The second variable is the calcination temperature of the catalyst. The catalysts are adequately characterized to find the relation between the kind of Cu and Ce species formed on the surface of the SiO₂ support and its catalytic activity in the oxidation reaction of CO with O₂ at low temperatures.

2. Experimental

The catalysts were prepared by two general methods: coimpregnation (CI) and sequential impregnation (SI), using Aerosil 200 (Degussa) as SiO₂ support. In the case of coimpregnation, the two precursors are impregnated simultaneously, using the dry impregnation method with an aqueous solution of the required concentrations of Cu(NO₃)₂·3H₂O (Merck, p.a.) and Ce(NO₃)₃·6H₂O (Sigma–Aldrich, p.a.). The concentrations of both precursors were adjusted to generate a load of 2% Cu and 8% Ce, which were close to the optimum loads found in previous work [17]. The solid was dried at 105 °C overnight, and then calcined at temperatures between 500 °C and 700 °C for 3 h in a muffle furnace. The samples were identified as CI-500, CI-600, CI-625, CI-650, CI-675 and CI-700, the number indicating the calcination temperature of the catalyst. For sequential impregnation the impregnation sequence with the precursors of both oxides was varied, using the same Cu and Ce loads as in coimpregnation. This gave rise to two series of catalysts prepared by sequential impregnation. In the first series, SI-Cu/Ce, the silica support is impregnated first with the Ce(NO₃)₃·6H₂O precursor. After drying at 105 °C, the support impregnated with the Ce precursor was calcined at 500 °C to form the cerium oxide supported on SiO₂. Then it was impregnated with the Cu(NO₃)₂·3H₂O precursor, dried overnight at 105 °C, and calcined at different temperatures for 3 h in a muffle furnace. The catalysts were identified as SI-Cu/Ce-500, SI-Cu/Ce-600 and SI-Cu/Ce-700, respectively, for the samples calcined at final temperatures of 500 °C, 600 °C, and 700 °C. In the second series (SI-Ce/Cu), the SiO₂ support was impregnated first with the Cu(NO₃)₂·3H₂O precursor, dried overnight at 105 °C, and calcined at 500 °C for 3 h in a muffle furnace. It was then impregnated with the Ce(NO₃)₃·6H₂O precursor, dried overnight at 105 °C, and calcined at 500 °C, 600 °C and 700 °C. The catalysts were identified as SI-Ce/Cu-500, SI-Ce/Cu-600 and SI-Ce/Cu-700, respectively.

For reference, single metal catalysts were prepared separately with 2% Cu supported on SiO₂ and 8% Ce supported on SiO₂. The dry impregnation method was used in both cases, and the resultant catalysts were calcined at 500 °C and 700 °C. Those calcined at 500 °C are identified as Cu-500 and Ce-500, and those calcined at 700 °C as Cu-700 and Ce-700.

Table 1
Specific surface area (BET) of some catalysts.

Catalyst	BET area (m ² /g)
CI-500	185
CI-700	178
SI-Cu/Ce-500	183
SI-Cu/Ce-700	178
SI-Ce/Cu-500	187
SI-Ce/Cu-700	175

The samples were characterized by N₂ adsorption, X-ray diffraction (XRD), temperature programmed reduction (TPR) in a hydrogen stream, and UV–vis DRS. Determination of the specific surface area of the catalysts was made by N₂ adsorption in a Micromeritics Model ASAP 2010 sorptometer. The samples were previously degassed at 200 °C. The crystal structure of the different catalysts was determined on a Siemens D-5000 diffractometer using Cu K α radiation and a scan rate of 0.02°/min. The temperature programmed reduction analyses were made on a conventional system equipped with a TCD detector, with a flow of 20 cm³/min of a gaseous mixture of 5% H₂ in Ar at a heating rate of 10 °C/min between ambient temperature and 600 °C. The UV–vis analyses were made on a Perkin Elmer Lambda 650 instrument equipped with a Praying Mantis and a Harrick powder cell.

The kinetics tests were made in a flow type quartz tubular reactor, with a stream of 2% CO and 3% O₂ in He, and a total flow of 100 cm³/min. Prior to the kinetics determination the catalyst (0.2 g) was treated at 500 °C for 1 h in a 20 cm³/min stream of pure O₂. The temperature was then reduced to ambient temperature, the reacting mixture was introduced, and the temperature was increased at a constant rate of 3 °C/min from ambient temperature to 180 °C. The effluent of the reactor was analyzed in a Perkin-Elmer Autosystem gas chromatograph instrument equipped with a CTR I (Alltech) packed column and a thermal conductivity detector (TCD), allowing the analysis of CO, O₂, and CO₂.

3. Results and discussion

3.1. Characterization of the catalysts

The BET specific surface area measurements included in Table 1 showed that the surface areas of the different catalysts are very similar and do not vary more than 12% with respect to that measured for the SiO₂ support (198 m²/g), indicating that the different methods of preparation and pretreatment do not cause substantial pore occlusion. This is not unexpected, knowing that Aerosil 200 does not have micropores that can be occluded at these metal loads and that it has high heat stability in the range of calcination temperatures used in this work.

The results of the characterization by TPR and XRD of the catalysts prepared by CI and calcined in the 500–700 °C range are shown in Fig. 1A and B, respectively.

As seen in Fig. 1A, the TPR spectrum of the CI-500 catalyst shows two H₂ consumption peaks with maxima around 185 °C and 210 °C. As discussed in our previous paper [17], these peaks have been observed by different authors. The lower temperature peak is attributed to the reduction of highly dispersed CuO species that interact strongly with CeO₂, and the higher temperature peak to the reduction of bigger CuO clusters, but also in contact with CeO₂ particles. As the calcination temperature is increased to 600 °C (catalyst CI-600), a slight displacement of the maximum of the second peak to a higher reduction temperature is seen. At the same time, the second peak gets wider toward higher temperatures and its height decreases, indicating the formation of particles with less interaction with CeO₂, and therefore harder to reduce. It should be noted that the reduction process with H₂ begins practically at the same

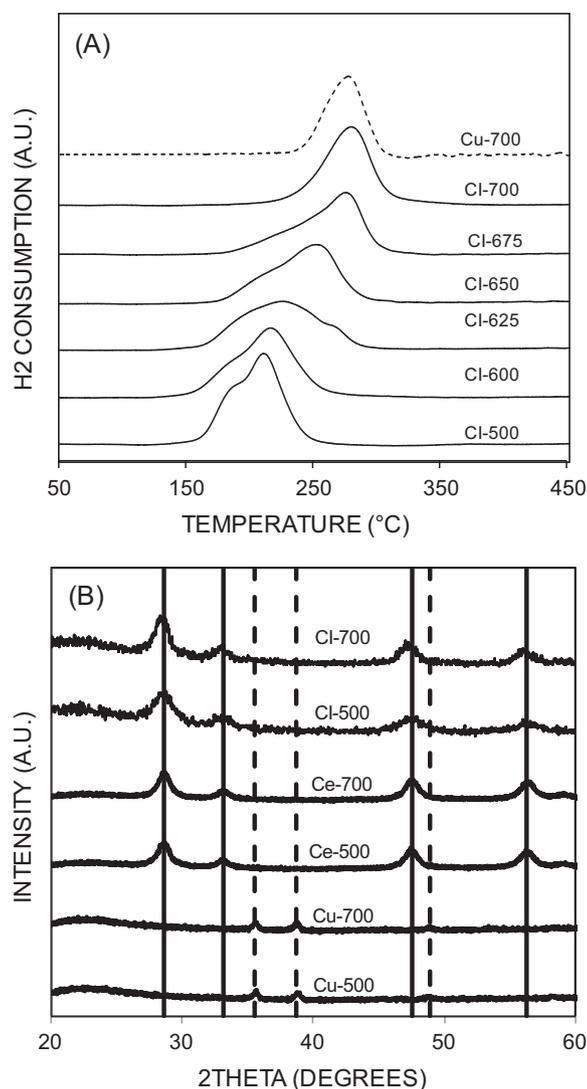


Fig. 1. Characterization of catalysts prepared by coimpregnation (A) H_2 consumption profiles during TPR experiments. (B) X-ray diffraction patterns. (–) CuO diffraction peaks; (–) CeO_2 diffraction peaks. The X-ray diffraction pattern of monometallic CuO and CeO_2 supported catalysts are also included for comparison.

temperature in both cases, around $140^\circ C$, indicating the existence of the highly dispersed CuO– CeO_2 interface in both catalysts. The TPR spectra of the catalysts calcined at intermediate temperatures, between $625^\circ C$ and $675^\circ C$, show that the concentration of the highly dispersed CuO particles and the CuO clusters interacting with CeO_2 decreases gradually, while CuO particles that interact weakly with CeO_2 are formed, as reflected by the displacement to higher temperatures of the reduction peak maxima. Dramatic changes are seen in the reduction spectrum of catalyst CI-700: the first two reduction peaks practically disappear, and only one peak is seen with a maximum at around $280^\circ C$, which has been attributed to the formation of bulk CuO not interacting with CeO_2 [16 and references therein]. In fact, the TPR spectrum of CI-700 is very similar to that of the monometallic catalyst of CuO supported on SiO_2 (Cu-700), whose TPR spectrum is also included in Fig. 1A. It is clear, therefore, that calcination of the bimetallic catalyst at $700^\circ C$ causes a phase separation of CuO and CeO_2 on the surface of the support.

Table 2 shows the total consumption of H_2 of the different catalysts prepared by coimpregnation, and Table 3 shows the consumption of H_2 of the monometallic catalysts calcined at $500^\circ C$ and $700^\circ C$. Using as a reference the average consumption of H_2 of the

Table 2

H_2 consumption and mean particle size (from XRD results) for catalysts prepared by coimpregnation.

Catalyst	H_2 consumption (a.u.)	CeO_2 particle size (nm)	CuO particle size (nm)
CI-500	0.135	5.9	–
CI-600	0.121	–	–
CI-625	0.119	–	–
CI-650	0.114	–	–
CI-675	0.112	–	–
CI-700	0.108	9.0	–

monometallic catalysts with 2% Cu/ SiO_2 (catalysts Cu-500 and Cu-700), which corresponds to 0.104 a.u., it is seen that the catalysts prepared by coimpregnation and calcined at the lower temperatures show a substantial overconsumption of H_2 with respect to the monometallic Cu catalysts that is due to the reduction of part of the cerium oxide in contact with copper oxide [2,17,22 and references therein]. As calcination temperature increases, overconsumption decreases, indicating that the increase in calcination temperature causes a decrease of the CuO– CeO_2 interface sites. In fact, when calcination is at $700^\circ C$, H_2 overconsumption is very slight, suggesting that in this catalyst the species on the surface are essentially non-interacting particles of CuO and CeO_2 .

Fig. 1B shows the diffraction patterns of the CI-500 and CI-700 catalysts prepared by coimpregnation calcined at $500^\circ C$ and $700^\circ C$, respectively. The diffraction patterns of the monometallic CuO and CeO_2 catalysts supported on SiO_2 and calcined at the same temperatures are included for reference. The XRD diffraction patterns of the catalysts prepared by coimpregnation, shown in Fig. 1B, confirm, in general, the peak assignments and the conclusions obtained in the discussion of the TPR spectra of Fig. 1A. The catalyst calcined at $500^\circ C$ (CI-500), only shows the diffraction peaks attributable to the fluorite structure of CeO_2 (straight vertical solid lines on the XRD spectra). The characteristic peaks of CuO (straight vertical dashed lines on the XRD spectra) are absent in the XRD spectrum of catalyst CI-500, indicating that copper is in the form of highly dispersed particles, of very small size or amorphous, in agreement with the peak assignments in the TPR experiments. When the catalyst is calcined at $700^\circ C$, the XRD spectrum of catalyst CI-700 shows that the peaks attributed to crystalline CeO_2 increase in size and get sharper, indicating that the size of the CeO_2 particles increases from 5.9 nm to 9.0 nm by calcining between $500^\circ C$ and $700^\circ C$, as shown in Table 2. On the other hand, the presence of crystalline CuO in the catalyst calcined at $700^\circ C$ (CI-700) is not shown by XRD. This suggests that the bulk CuO species not interacting, or interacting weakly, with CeO_2 that are identified in the TPR experiments still have a small size or has a poor degree of crystallinity to be detected by XRD.

It is interesting to compare the effect of calcination temperature on CuO and CeO_2 particles in the catalysts prepared by coimpregnation with the effect of this variable on monometallic catalysts. In the first place, catalyst Cu-500 shows clearly the diffraction peaks of the tenorite structure of CuO, which are absent in the CI-500 catalyst. Even when calcining at $700^\circ C$, the peaks of CuO are still not visible in the catalyst prepared by coimpregnation. It is clear, therefore, that the presence of CeO_2 on the surface of the silica prevents

Table 3

H_2 consumption and mean particle size (from XRD results) for monometallic Cu and Ce catalyst.

Catalyst	H_2 consumption (a.u.)	CeO_2 particle size (nm)	CuO particle size (nm)
Cu-500	0.105	–	19.8
Cu-700	0.103	–	19.8
Ce-500	n.d.	9.2	–
Ce-700	n.d.	9.2	–

the agglomeration and formation of large CuO particles. This effect of CeO₂ of dispersing CuO on the surface of the support was seen in the CuO–CeO₂/Al₂O₃ system by Cheekatamarla et al. [11]. In relation to the CeO₂ particles, the results of Tables 2 and 3 show that in the catalyst prepared by coimpregnation and calcined at 500 °C, the size of the CeO₂ particles (5.9 nm) is substantially smaller than in the monometallic Ce-500 catalyst (9.2 nm). Therefore, the existence of CuO also prevents the formation of larger CeO₂ particles. When calcining at 700 °C, the particle size of CeO₂ in catalyst CI-700 is very similar to that seen in the monometallic CeO₂ catalyst, 9.0 nm and 9.2 nm, respectively. The above is consistent with a separation of the CuO and CeO₂ particles by calcining at 700 °C, as deduced from the TPR experiments.

Thus, the TPR and XRD results suggest that calcination between 500 °C and 700 °C of the catalysts prepared by coimpregnation causes the growth of the CuO and CeO₂ particles on the surface of the SiO₂, but without forming large and highly crystalline CuO particles. This particle growth obviously leads to a decrease of the probability of contact between both oxides, and therefore of the CuO–CeO₂ interface. In particular, calcining at 700 °C shows the complete disappearance of the highly dispersed CuO–CeO₂ interface. These results agree, in general, with those for mixed CuO–CeO₂ oxides of Djinojic et al. [23], who report the growth of the CuO and CeO₂ particles with the subsequent decrease of the CuO–CeO₂ interface as the calcination temperature increases from 400 °C to 750 °C.

A completely different situation occurs with the catalysts prepared by sequential impregnation (SI), whose TPR spectra are shown in Fig. 2A. In this case the CeO₂ precursor is impregnated, it is calcined at 500 °C, and then the CuO precursor is impregnated. The bimetallic catalyst is then calcined at 500 °C (SI-Cu/Ce-500), 600 °C (SI-Cu/Ce-600) and 700 °C (SI-Cu/Ce-700). As seen in Fig. 2A, the SI-Cu/Ce-500 catalyst shows clearly the peaks corresponding to highly dispersed CuO in contact with CeO₂ (peak maximum at 165 °C), clusters of CuO in contact with CeO₂ (peak maximum at 190 °C), and particles of bulk CuO not interacting (or interacting poorly) with CeO₂ (peak maximum at 260 °C). The latter peak is the one with the largest area, and it contrasts with the nil existence of this species in the case of the catalysts prepared by coimpregnation. It is clear then, that sequential impregnation allows a fraction of the Cu precursor to be deposited on the silica, forming isolated domains that do not interact with the CeO₂ particles previously formed on the surface of the support. When they are calcined, these species give rise to isolated particles of bulk CuO. At the same time, the other fraction of the Cu precursor enters in contact with the CeO₂ particles, so when the catalyst is calcined, the two low temperature reduction peaks attributed to the reduction of CuO species interacting with CeO₂ are seen.

Upon calcining at 600 °C the SI-Cu/Ce-600 catalyst shows a slight increase of the peak corresponding to cluster CuO interacting with CeO₂, but the peak corresponding to highly dispersed CuO interacting with CeO₂ remains clearly visible. When the calcination temperature increases to 700 (catalyst SI-Cu/Ce-700), a noticeable decrease of the peak of the highly dispersed CuO species interacting with CeO₂ is seen. The second peak, corresponding to cluster CuO interacting with CeO₂ is clearly visible, and the peak of bulk CuO not interacting (or interacting weakly) with CeO₂ increases substantially. This spectrum contrasts with that of the catalyst prepared by coimpregnation and calcined at 700 °C, which showed only the peak of bulk CuO not interacting with CeO₂.

The H₂ consumption of these catalysts is presented in Table 4, which shows that it practically does not vary when the catalyst is calcined between 500 °C and 600 °C, and it is slightly reduced by calcining at 700 °C. However, in all these cases there is an overconsumption of H₂, indicating that part of the CeO₂ is reduced at low temperatures. This suggests that although the type of Cu species

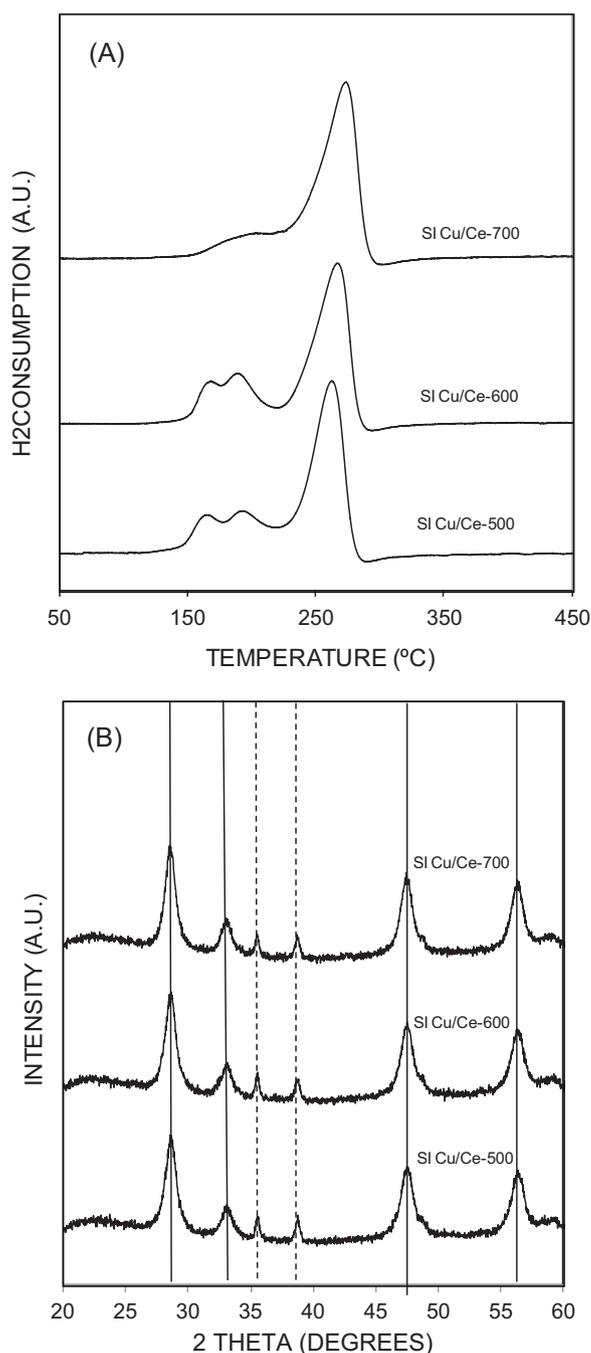


Fig. 2. Characterization of catalysts prepared by sequential impregnation, impregnating first the CeO₂ precursor. (A) H₂ consumption profiles during TPR experiments. (B) X-ray diffraction patterns. (–) CuO diffraction peaks; (---) CeO₂ diffraction peaks.

on the surface varies, the CuO–CeO₂ interface exists in all cases, which is consistent with what is seen in the TPRs of these catalysts. Fig. 2A shows that even when calcining at 700 °C the reduction

Table 4
H₂ consumption and mean particle size (from XRD results) for catalysts prepared by sequential impregnation, impregnating first the Ce precursor.

Catalyst	H ₂ consumption (a.u.)	CeO ₂ particle size (nm)	CuO particle size (nm)
SI Cu/Ce-500	0.132	9.4	31.9
SI Cu/Ce-600	0.132	10.1	31.9
SI Cu/Ce-700	0.124	11.0	31.9

peaks associated with the cluster CuO interface interacting with CeO₂ are clearly visible.

The results of the XRD analyses of the SI-Cu/Ce catalysts are shown in Fig. 2B. Here, in contrast with the catalysts prepared by coimpregnation, the presence of crystalline bulk CuO is seen clearly, regardless of the calcination temperature of the catalyst. This result agrees perfectly with the TPR spectra, which show the presence of bulk CuO in all the catalysts. Compared to what happens with the coimpregnated catalysts, in this case the size of the bulk CuO particles and their degree of crystallinity are sufficient to allow their detection by XRD. Increasing the calcination temperature of the bimetallic catalyst causes a slight increase of the CeO₂ particle size reported in Table 4. On the other hand, the average size of the CuO particles does not vary with increasing calcination temperature, as is also seen in Table 4.

Therefore, it can be concluded that the sequential impregnation method, impregnating first with the CeO₂ precursor and then with the CuO precursor, causes a substantial part of the CuO to form bulk CuO particles that do not interact (or interact weakly) with the CeO₂ particles, even when the calcination temperature is only 500 °C. In spite of the above, a copper fraction interacts with ceria, allowing the formation of the highly dispersed CuO–CeO₂ and cluster CuO–CeO₂ interfaces. This type of interface does not vary much by calcining between 500 °C and 600 °C. However, when the calcination temperature is increased to 700 °C, the highly dispersed CuO–CeO₂ interface practically disappears completely, but the cluster CuO–CeO₂ interface is retained. Compared with the results of the catalysts prepared by coimpregnation, which show the complete disappearance of the CuO–CeO₂ interface when calcining at 700 °C, it is clear that the sequential impregnation method generates a catalyst in which the CuO–CeO₂ interface is more stable to temperature increase.

When the impregnation sequence of the precursors of CuO and CeO₂ is changed, impregnating first with the Cu precursor, calcining to form the CuO over SiO₂, and then impregnating with the CeO₂ precursor, some interesting changes are generated in the type of species on the surface of the support. Fig. 3A shows the consumption curves of H₂ in the TPR experiments. Similarly to the previous case, the SI-Ce/Cu-500 catalyst shows the peaks corresponding to highly dispersed CuO–CeO₂, cluster CuO–CeO₂, and bulk CuO not interacting (or interacting weakly) with CeO₂. However, in this case the concentration of bulk CuO is substantially lower than that seen when impregnating first with the CeO₂ precursor (catalyst SI-Cu/Ce-500). This indicates that greater interaction is generated between the CuO and CeO₂ particles on the surface if the impregnation is done first with the CuO precursor. Increasing the calcination temperature to 600 °C, it is seen that in the H₂ consumption curve of the SI-Ce/Cu-600 catalyst the peak corresponding to highly dispersed CuO–CeO₂ decreases and that of cluster CuO–CeO₂ increases. At the same time, the bulk CuO peak is displaced to higher temperature, suggesting the formation of larger bulk CuO particles and/or with even less interaction with CeO₂. Calcining at 700 °C, catalyst SI-Ce/Cu-700, the peaks corresponding to highly dispersed CuO–CeO₂ and cluster CuO–CeO₂ practically disappear, and only two peaks with maxima at 245 °C and 280 °C are observable. The higher temperature peak (280 °C) is clearly the one attributed to bulk CuO, previously seen in the catalysts calcined at 500 °C and 600 °C. The lower temperature peak (245 °C) would be attributable to smaller bulk CuO particles originating from the cluster CuO–CeO₂ interface. These CuO particles would be prevented from growing due to the presence of CeO₂ on the surface. The H₂ consumption of these catalysts is shown in Table 5. As can be seen, H₂ overconsumption is similar to that found in the previous case (Table 4) calcining at 500 °C and 600 °C. However, calcining at 700 °C the H₂ consumption of the catalyst drops substantially, and catalyst SI-Ce/Cu-700 shows H₂ consumption practically the same as that of

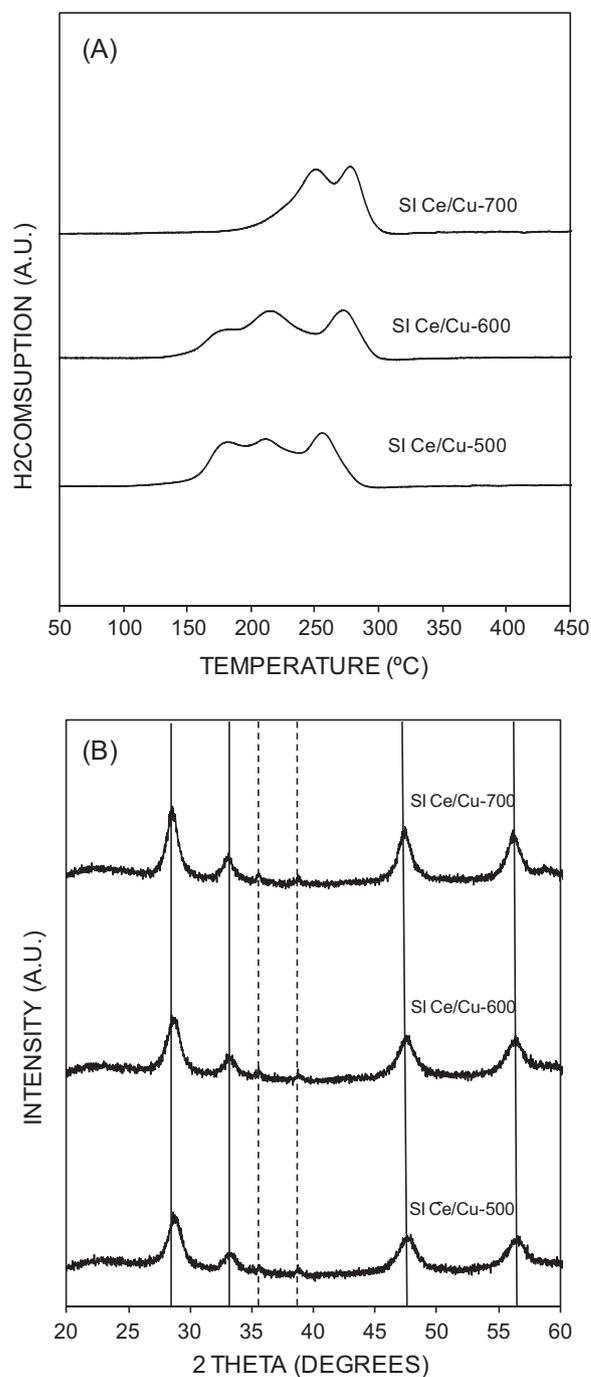


Fig. 3. Characterization of catalysts prepared by sequential impregnation, impregnating first CuO precursor. (A) H₂ consumption profiles during TPR experiments. (B) X-ray diffraction patterns. (–) CuO diffraction peaks; (—) CeO₂ diffraction peaks.

Table 5

H₂ consumption and mean particle size (from XRD results) for catalysts prepared by sequential impregnation, impregnating first the Cu precursor.

Catalyst	H ₂ consumption (a.u.)	CeO ₂ particle size (nm)	CuO particle size (nm)
SI Ce/Cu-500	0.130	7.9	–
SI Ce/Cu-600	0.133	7.9	–
SI Ce/Cu-700	0.103	9.9	–

monometallic CuO catalyst shown in Table 3. The above reflects that the concentration of sites in the CuO–CeO₂ interface is very low, and therefore there is practically no reduction of CeO₂.

The XRD results shown in Fig. 3B are consistent with what was commented previously. Regardless of calcination temperature, the XRD spectra of the catalysts show very weak diffraction peaks in the crystalline CuO zone, indicating that the CuO particles are very small, or are weakly crystalline, as was also found in the catalysts prepared by coimpregnation. This result contrasts with that when impregnation was done first with CeO₂, where the peaks of crystalline CuO are clearly seen.

So comparing both methods of sequential impregnation it is clear that impregnating first with the Cu oxide precursor yields a catalyst with smaller CuO and CeO₂ particle size, with a greater degree of mixing of both oxides on the surface of the support. In this sense, catalyst SI-Ce/Cu tends to be more similar to the catalyst obtained by coimpregnation.

UV–vis DRS analysis of some of these catalysts confirms the ideas stated earlier. Fig. 4 shows the UV–vis spectra of the catalysts prepared by coimpregnation and sequential impregnation calcined at 500 and 700 °C. Fig. 4A includes as reference the monometallic catalysts with 2% Cu supported on SiO₂, Cu-500 and Cu-700, and the catalysts with 8% Ce supported on SiO₂, Ce-500 and Ce-700. The spectrum of Cu-500 shown in Fig. 4 is very similar to that of unsupported pure CuO reported by Hu et al. [24], which is consistent with the inert character of silica. The spectrum is characterized by an absorption band around 600 nm associated with d–d transitions in an octahedral environment [25–27] and another one close to 290 nm associated with O²⁻ → Cu²⁺ charge transfer [28,29]. The edge adsorption characteristic of bulk CuO particles at wavelengths longer than 750–800 nm is also seen clearly [30]. The spectrum of the Cu-700 catalyst does not show significant changes with respect to that calcined at 500 °C, neither in the absorption bands nor in the position of the absorption edge. The fact that the position of the absorption edge does not change is consistent with the XRD results, which show that the mean size of the CuO particles does not change with calcination temperature. Therefore, the UV spectrum confirms the presence of bulk CuO particles in the monometallic copper catalysts supported on SiO₂ calcined at 500 °C and 700 °C, detected by XRD. On the other hand, the spectrum of the Ce-500 catalyst shows an absorption band around 290 nm that can be assigned to allowed O²⁻ → Ce⁴⁺ charge transfer transitions [29]. Above 400 nm no absorption bands are seen in this system. The same as in the case of the Cu catalysts, when calcining at 700 °C no important changes are seen in the UV spectrum of the Ce-700 catalyst.

Fig. 4B shows the spectra of the bimetallic catalysts prepared by the different methods. The spectrum of the coimpregnated catalysts calcined at 500 °C and 700 °C show clearly the band at 290 nm attributed to cerium oxide. Between 300 nm and 900 nm a continuous decrease of the absorbance is seen with both catalysts. However, in the case of the catalyst calcined at 700 °C the adsorption edge seen with the monometallic Cu-500 and Cu-700 catalysts is insinuated. This indicates that calcination at 700 °C leads to growth of the bulk CuO particles on the surface of the silica, in agreement with what was seen in the TPR spectra of these catalysts, even though XRD indicates that these particles are small or poorly crystalline.

On the other hand, the UV spectra of catalysts SI-Cu/Ce-500 and SI-Cu/Ce-700 showed that calcination temperature does not cause important changes in their UV spectra. In both catalysts the zone of wavelengths shorter than 380 nm is relatively similar to that of the catalysts prepared by coimpregnation. However, above 400 nm the absorbance vs. wavelength curve does not decay in a pronounced way as in the coimpregnated catalysts, and it tends to be similar to that of the monometallic Cu-500 catalyst. Both in catalysts SI-Cu/Ce-500 and SI-Cu/Ce-700 the adsorption edge above 750 nm,

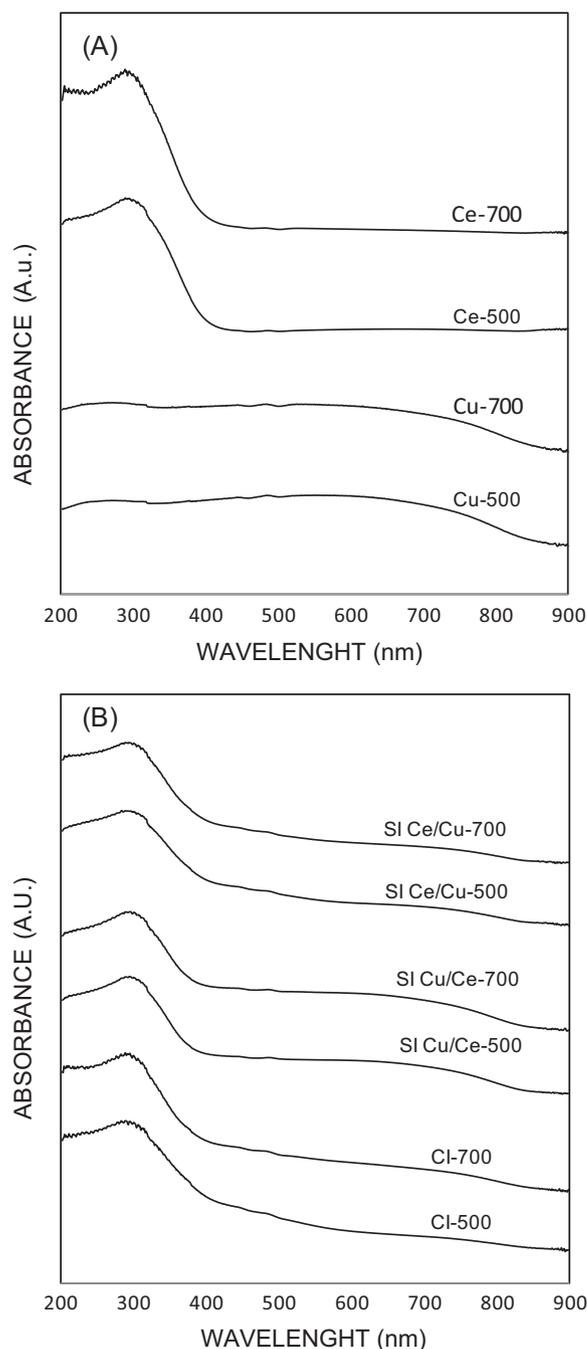


Fig. 4. (A) UV–vis DRS spectra of monometallic catalysts calcined at 500 °C and 700 °C. (B) UV–vis DRS spectra of bimetallic catalysts obtained by the different preparation methods calcined at 500 °C and 700 °C.

characteristic of bulk CuO particles can be seen clearly. The above is in complete agreement with the TPR and XRD results of the previous figures, which show the formation of bulk CuO in these catalysts regardless of calcination temperature (500 °C or 700 °C).

The UV spectra of the catalysts prepared by sequential impregnation, but impregnating first with the Cu precursor, show some important differences with the catalysts in which impregnation is made first with the CeO₂ precursor. In fact, the UV spectrum of catalysts SI-Ce/Cu-500 and SI-Ce/Cu-700 looks more like that of the catalysts prepared by coimpregnation than like that of the catalysts prepared by sequential impregnation discussed above (SI-Cu/Ce-500 and SI-Cu/Ce-700). The adsorption edge of the CuO particles, clearly visible in the catalysts in which the CeO₂

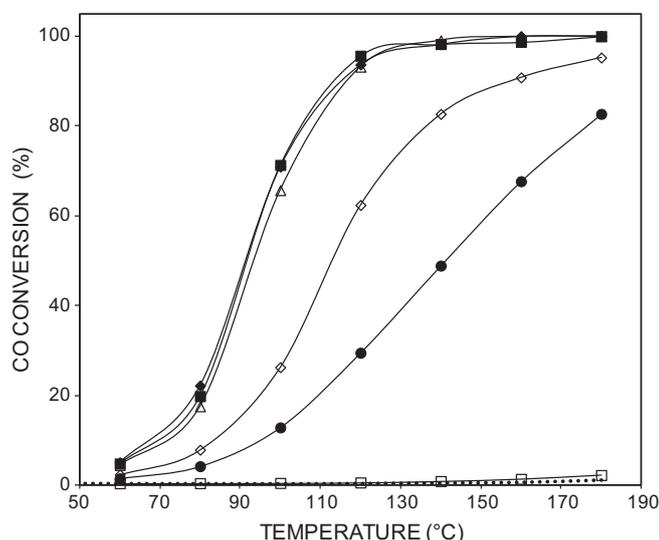


Fig. 5. CO conversion versus temperature for catalysts prepared by coimpregnation and calcining the bimetallic catalysts at different temperatures: CI-500 (◆), CI-600 (■), CI-625 (△), CI-650 (◇), CI-675 (●) and CI-700 (□).

precursor is deposited first, is now barely perceptible, confirming the XRD results, where the intensity of the diffraction peaks of crystalline CuO is very low. On the other hand, calcination between 500 °C and 700 °C does not produce important changes in the UV spectrum of the catalysts, also in agreement with the XRD results, which do not show important changes in the crystallinity and particle size of those catalysts.

3.2. Activity of the catalysts

The literature [8,13,31] proposes that the sites of greatest catalytic activity in the oxidation of CO at low temperatures correspond to the highly dispersed CuO–CeO₂ interface. The sites of the interface CuO cluster–CeO₂ are considerably less active, but obviously more active than the CuO bulk species non interacting with CeO₂, which as it will be shown above, are almost inactive in the temperature range considered in this work.

Fig. 5 shows the conversion curves of CO vs. temperature during the CO oxidation reaction for the catalysts prepared by coimpregnation. It is seen that the activity practically does not vary under calcination between 500 °C and 600 °C. In fact, the conversion vs. temperature curves are practically overlapped in the CI-500 and CI-600 catalysts. The TPR spectra in Fig. 1A of the CI-500 and CI-600 catalysts show that in both catalysts exist the highly dispersed CuO–CeO₂ interface and the CuO cluster–CeO₂ interface, and the largest changes occur on the less active cluster CuO–CeO₂ species. Therefore, the high activity sites, corresponding to the highly dispersed CuO–CeO₂ interface, are not affected importantly when calcined between 500 °C and 600 °C. As calcination temperature is increased to 625 °C (catalyst CI-625), the activity decreases more noticeably, and this is consistent with the decrease of the first peak reduction in the TPR spectrum, corresponding to the highly dispersed CuO–CeO₂ interface. As the temperature increases, the activity decreases in parallel with the decrease of the most active species observed in the TPR spectra. After calcining at 700 °C (catalyst CI-700) the activity falls to values lower than 2% of conversion below 180 °C, in agreement with the complete disappearance of the highly dispersed CuO–CeO₂ and cluster CuO–CeO₂ interfaces, as shown in the TPR spectra of Fig. 1A. In fact, the activity of catalyst CI-700 is almost the same as that of catalyst Cu-700, which is shown by the dotted line in the same figure. The above supports the idea that in this catalyst the bulk CuO species on the surface do

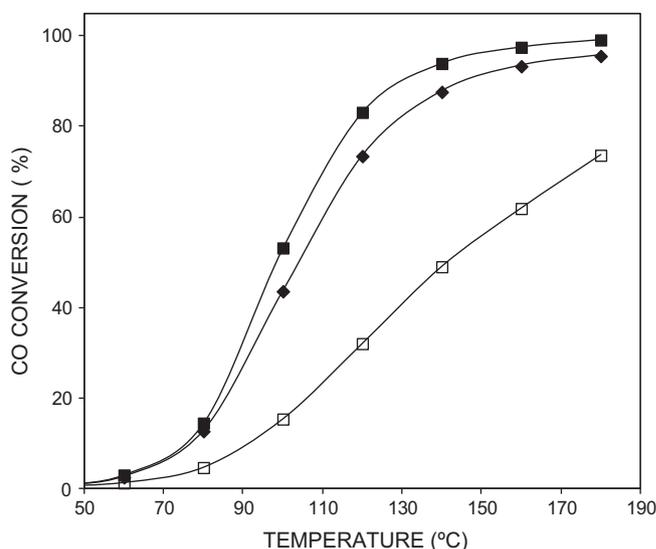


Fig. 6. CO conversion versus temperature of catalysts prepared by sequential impregnation, impregnating first the CeO₂ precursor and calcining the bimetallic catalyst at different temperatures: SI-Cu/Ce-500 (◆), SI-Cu/Ce-600 (■) and SI-Cu/Ce-700 (□).

not interact with the CeO₂ particles or do so marginally. It is interesting to note the even when the H₂ consumption decreases in the range 500–625 °C (see Table 2), the activity of the catalysts remains almost the same. These results show that H₂ overconsumption is related with all Cu–Ce species and not specifically with the most active highly dispersed Cu–Ce interface.

The catalytic activity of the systems prepared by sequential impregnation, impregnating first with the CeO₂ precursor is shown in Fig. 6. It is seen that catalyst SI-Cu/Ce-500 has high catalytic activity, but somewhat lower than that of catalyst CI-500 prepared by coimpregnation (Fig. 5). This result may seem unexpected, considering the substantial differences in the TPR spectra of these catalysts. In fact, in the catalyst prepared by coimpregnation only the highly dispersed CuO and cluster CuO species were seen, both interacting with CeO₂. On the other hand, in the catalyst prepared by sequential impregnation, besides these two species there is the presence of a large amount of bulk CuO not interacting, or poorly interacting with CeO₂. Keeping in mind the low activity of the bulk CuO species, a much lower activity would be expected with the catalyst prepared by sequential impregnation, but this is not what happens. The explanation of this is that both catalysts have highly dispersed CuO species interacting with CeO₂. As mentioned earlier, these species have the highest catalytic activity, much higher than that of other species: cluster CuO–CeO₂ and bulk CuO. Therefore, the proportion of the cluster CuO–CeO₂ and CuO species not interacting with CeO₂ does not affect greatly the activity of the catalysts, because this difference is masked by the very high activity of the highly dispersed CuO–CeO₂ species.

When the calcination temperature is increased to 600 °C, catalyst SI-Cu/Ce-600, the activity increases slightly. This activity increase may be due to the formation of larger CeO₂ particles, but without affecting the number of sites of the highly dispersed CuO–CeO₂ interface. Martinez-Arias et al. [32] have proposed that the growth of three-dimensional CeO₂ particles is beneficial for the activity of the sites on the highly dispersed CuO–CeO₂ interface. However, as the catalyst's calcination temperature continues to increase to 700 °C (catalyst SI-Cu/Ce-700), the activity decreases, but still is noticeable higher than the activity of the coimpregnated catalyst calcined at 700 °C. This decrease of the activity is consistent with the disappearance of the highly dispersed CuO–CeO₂ interface that is seen in Fig. 2A, and the remaining activity can be explained

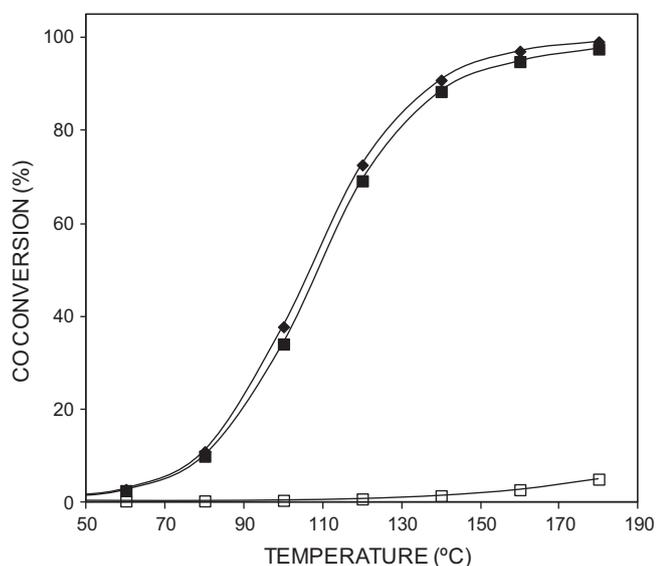


Fig. 7. CO conversion versus temperature of catalysts prepared by sequential impregnation, impregnating first the CuO precursor and calcining the bimetallic catalyst at different temperatures: SI-Ce/Cu-500 (◆), SI-Ce/Cu-600 (■) and SI-Ce/Cu-700 (□).

by the existence of the cluster CuO–CeO₂ interface, as seen in its TPR spectrum in Fig. 2A.

Finally, Fig. 7 shows the results of the activity of the catalysts prepared by sequential impregnation, but impregnating first with the CuO precursor. It is seen that the activity of SI-Ce/Cu-500 is similar to that found for SI-Cu/Ce-500, so the impregnation sequence does not seem to be very important when calcining at 500 °C. On the other hand, calcination between 500 °C and 600 °C does not cause greater changes in the activity of these catalysts, and it is seen that the conversion vs. temperature curves are very similar for the SI-Ce/Cu-500 and SI-Ce/Cu-600 catalysts. However, calcination at 700 °C causes a strong decrease of the activity, and catalyst SI-Ce/Cu-700 has an activity similar to that of the monometallic Cu catalyst, Cu-700, shown in Fig. 5. This large activity drop can be ascribed to the disappearance of sites on the CuO–CeO₂ interface, as shown by the TPR curve of the SI-Ce/Cu-700 catalyst of Fig. 3A.

Thus, the impregnation sequence with the CuO and CeO₂ precursors in the catalysts prepared by sequential impregnation, even though it does not produce important differences in the activity of the catalysts calcined at 500 °C, it can affect substantially the activity of the catalysts calcined at 700 °C, due to differences in the stability of the CuO–CeO₂ interface.

4. Conclusions

The method of catalyst preparation, co-impregnation and sequential impregnation, and the sequence in which the CuO and CeO₂ precursors are impregnated affect substantially the concentration of the CuO species formed on the surface and their interaction with the CeO₂ particles. In particular, the concentration

of bulk CuO varies considerably with the method of preparation. However, in all cases, within the 500–600 °C calcination range, the interface of highly dispersed CuO in contact with CeO₂ is formed, which explain the high catalytic activity of these samples. When calcining at 700 °C the CuO–CeO₂ interface in catalysts prepared by the CI and SI-Ce/Cu methods almost disappears showing negligible activity. On the other hand, the SI-Cu/Ce catalyst calcined at 700 °C shows an important activity, because it is the only one that allows the existence of some interaction between CuO and CeO₂ particles after calcinations at this high temperature.

Therefore, the order of the activity of the catalysts calcined in the 500–600 °C range for the conversion of CO is: CI > SI-Cu/Ce ≈ SI-Ce/Cu. However, at higher temperatures (700 °C), the order changes to SI-Cu/Ce » CI ≈ SI-Ce/Cu.

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