



The Impact of Ceria Loading on the $\text{CuO}_x\text{--CeO}_2$ Interaction and Performance of $\text{AuCu/CeO}_2\text{--SiO}_2$ Catalysts in CO-PROX Reaction

Tanna Elyn Rodrigues Fiuza,^[a, b] Danielle Santos Gonçalves,^[a] and Daniela Zanchet^{*,[a]}

The use of CeO_2 as a promoter for non-reducible supports, such as SiO_2 , enhances the catalytic activity by facilitating the activation of species such as O_2 and H_2O . However, in the case of the bimetallic nanoparticles (NPs), the presence of promoters may also influence the migration of the metallic species, dramatically impacting the stabilization of catalytic sites and as consequence, the overall catalytic performance. In the case of AuCu alloy supported catalysts, the reduced form, i.e., AuCu alloy, or the oxidized form, i.e., Au--CuO_x species, present different activities/selectivities. Moreover, several parameters, such as reactional conditions, AuCu particle size, support

nature, and pretreatments dictate which species are stabilized on the catalyst surface. The preferential oxidation of CO (CO-PROX) reaction, that takes place under the H_2 -rich stream, favors the stabilization of the reduced form of the AuCu catalysts. However, the Cu distribution in the crystal lattice and the final composition of the AuCu NPs are dependent on the mobility of the Cu species on the support. In this work, we show that the loading of the CeO_2 as a promotor in AuCu/SiO_2 catalysts impacts the CeO_x species and the Cu reincorporation into the Au lattice and consequently, the activity and stability of the catalysts under CO-PROX reaction.

Introduction

It is well-known that the nature of the support impacts the catalytic performance, due to the stabilization of different species on the catalysts' surface. The reducible oxides, such as CeO_2 , TiO_2 , and V_2O_5 ,^[1,2] are a special class of supports that have attracted attention due to their high oxygen storage capacity (OSC) and the presence of oxygen vacancies, that can participate in bifunctional mechanisms.^[3–8] Additionally, the nature of the support, particularly in the case of the reducible ones, impacts the metallic dispersion, avoiding sintering,^[9] and may lead to the creation of unique catalytic sites at the metal-oxide interface.^[10] A pioneer work by Tauster in the 80s showed that the metal-support interaction plays a role in the stabilization of the metallic phase on the support.^[11] Under harsh reductive treatments under H_2 flow at 800°C , the Pt supported on SiO_2 sintered, while those supported on TiO_2 remained stable.^[11] This was associated with the strong metal-support interaction (SMSI) and the covering of the metallic particles by a layer of the support oxide. This effect has been widely studied

until nowadays, not only due to the importance of the metal-support interaction in the sintering-resistance of the metallic phase but also due to the advances in the characterization tools that now allow probing in detail the atomic structure at metal-support interfaces.^[12–15]

In the case of supported bimetallic nanoparticles (NPs), the scenario becomes more complex, since the metal-support interaction also impacts in the composition of the alloy (segregation, reincorporation, etc.). However, depending on the preparation method of the catalysts, the addressing of each distinct effect (i.e., metal-support interaction, alloy composition, stability of the alloy under reaction stream) becomes a challenge. In this context, the use of pre-made alloy NPs as a metallic precursor may provide interesting information that can be hardly identified in a more complex system, shedding light on the impact of the support on the stabilization of the alloy phase and its correlation with the catalytic performance. Destro et al.^[16,17] extensively showed that the nature of the support (SiO_2 and Al_2O_3) dramatically affects the sintering-resistance H_2 -rich stream of the AuCu NPs, the dealloy-re-alloy process under oxidizing and reducing atmosphere (pre-treatments and/or reactional atmosphere), and the formation of catalytic sites at the metal-support interface. The oxidizing atmosphere of the CO oxidation (CO-OX) induces the segregation of the AuCu alloy, favoring the formation of the Au--CuO_x species but the stabilization of an interface by their intimate contact was affected by the nature of the support.^[16,17]

CeO_2 is another support vastly explored in catalysis, applied in several reactions due to its strong interaction with the metallic phase, including charge transfer effects.^[18–22] The CeO_2 -promoted catalysts also hinder the coke formation by oxygen transfer. In the case of supported-AuCu alloy catalysts, besides the well-known improvement of the catalytic activity when

[a] Dr. T. E. Rodrigues Fiuza, D. Santos Gonçalves, Prof. Dr. D. Zanchet
Institute of Chemistry
University of Campinas
13083-970, Campinas, São Paulo, Brazil
E-mail: zanchet@unicamp.br
<https://www.iqm.unicamp.br/institucional-departamentos/daniela-zanchet>

[b] Dr. T. E. Rodrigues Fiuza
Present address: Brazilian Nanotechnology National Laboratory (LNNano)
Brazilian Center for Research in Energy and Materials (CNPEM)
13083-100, Campinas, São Paulo, Brazil

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supported on CeO₂ (despite the preparation method), we had demonstrated that the activation step affected the nature of the active sites. Also, we found that the Cu–CeO₂ interaction induced the partial segregation of the AuCu alloy at room temperature, whereas the higher mobility of CuO_x species on this support favored the Cu reincorporation under reducing atmosphere, increasing its stability in the preferential oxidation of CO (CO-PROX) reaction when compared to AuCu supported on SiO₂.^[23] However, depending on the reactional conditions, mainly when submitted to harsher thermal treatments, CeO₂ may sinter,^[24] decreasing its surface area and favoring the sintering of the metallic phase. One successful strategy to avoid it, it is to employ CeO₂ as a promotor, supported on other high surface area oxide, such as SiO₂ and Al₂O₃.^[25–27] The morphology and size of the CeO₂ crystalline domains impact the Ce⁺³/Ce⁺⁴ redox pair and the oxygen vacancy formation. Meira et al.^[28] reported that CeO₂ as the promoter for Pt/Al₂O₃ catalyst increased the reaction rate in water-gas shift (WGS) reaction and different CeO_x species were stabilized on the catalyst surface depending on the CeO₂ loading. Caldas et al.^[29] reported that CeO₂-promoted Cu/Al₂O₃ catalyst presented a linear correlation between the CeO₂ loading and the Cu–O bond length, which directly impacted the WGS catalytic activity. Qian et al.^[30] found a significant enhancement of the CO conversion in presence of the 6%wt. of CeO₂ in Au/SiO₂ catalysts, associating it to the Au–CeO₂ interface. Hossain et al.^[31] reported the improvement of the catalytic activity of CuO supported on CeO₂ nanorods when using a mixture of 40–50% of nanorods with SiO₂ spheres since it avoided the CeO₂ aggregation, which would decrease the exposed surface for the reactants. Taufiq-Yap et al.^[32] evaluated CeO₂-promoted Ni/SiO₂ catalysts for dry reforming of CH₄ with loadings from 3 to 30% wt., but there was no significant increase in the catalytic performance with CeO₂ content above 9%wt. In general, several works indicate that there is an optimal CeO₂ loading to optimize the catalytic performance.

It is clear that the CeO₂ presents a positive impact on the catalytic activity in different reactions, and it is possible to expect that, for nanostructured CeO₂, the intimate AuCu–CeO₂ interaction can lead to a significant enhancement of catalytic performance. In this work, we supported AuCu NPs on SiO₂ promoted with different CeO₂ loadings to show its impact on

the formation of the nanostructured CeO₂ phase as well as on the catalytic activity and the stability of the AuCu alloy under the CO-PROX atmosphere. CO-PROX is an important reaction in the H₂ production chain, due to the decreasing of CO amount to a level acceptable to be employed in fuel cells.^[33] Besides CO and O₂ in the presence of H₂-rich stream (> 70%), the CO-PROX atmosphere takes place in the presence of water and CO₂, that can significantly impact the catalytic activity, mainly at lower temperature.^[34,35] Here, we employed the CO-PROX in ideal condition (CO, O₂ and H₂), as a probe reaction to address the impact of different parameters on the catalysts.^[23,36–38] In addition, characterization techniques, including HAADF-STEM and in situ XRD and XAFS data, were explored to understand how the CeO₂ loading affected the AuCu alloy NPs and the formation and stability of the active sites.

Results and Discussion

The AuCu NPs (~6 nm) (Figure S3a,b) were successfully synthesized, with Au:Cu molar ratio of 1:1, similar to the results reported in our previous work.^[23] The XCe supports with nominal loadings of 4, 13, and 19%wt. CeO₂ on SiO₂ were prepared by impregnation, leading to the formation of CeO₂ nanocrystalline domains with fluorite structure (Figure S3c). Table 1 presents the final CeO₂ and metal loading (%wt.) of the AuCuXCe catalysts. The STEM images of the supports (Figure 1a–c) show a population of CeO₂ particles larger than 5 nm, and the increase of the CeO₂ loading led to a higher number of these particles.

Additionally, smaller CeO₂ particles dispersed on the supports, including highly dispersed CeO_x clusters and single atoms were formed (Figure 1d). The analysis of the XANES spectra at Ce–L₃ absorption edge of the 4Ce and 19Ce bare supports (Table 1) showed a larger fraction of Ce³⁺ in the former. It has been demonstrated that the Ce³⁺ fraction increases in smaller particles and the XANES results agreed with the STEM analysis. After the impregnation of the colloidal AuCu NPs, no shift in the XRD peaks positions was found for the AuCu alloy or CeO₂ (Figure S3d). Also, the AuCu NPs were randomly dispersed on the supports (Figure 1e–g). Figure 1h

Table 1. CeO₂ and metal loadings of the AuCuXCe catalysts. Maximum CO conversion (MC), and temperature of maximum CO conversion (TMC) of the reduced AuCuXCe catalysts during the heating and cooling steps, and normalized CO₂ production rate at 100 °C. % of Ce³⁺ obtained by XANES and OSC of the bare XCe supports and AuCuXCe catalysts.^[a]

Sample	CeO ₂ [wt%]	Total metal loading [wt%]	MC [%]		TMC [°C]		mmols CO ₂ min ^{−1} / (mol CeO ₂ *mol metal)		[%] Ce ³⁺		OSC mol O ₂ / mol CeO ₂
			Red. H/C	Oxid. H/C	Red. H/C	Oxid. H/C	Red. H/C	Oxid. H/C	Calcined	Red.	
AuCu4Ce	3.9	2.9	20/15	16/17	225/265	286/260	67.6/4.9	2.9/3.9	18.0	51.5	0.9
AuCu13Ce	12.9	3.8	30/28	26/29	186/210	230/222	25.8/12.1	11.1/12.4	10.1	38.4	0.3
AuCu19Ce	19.3	3.0	40/44	30/35	168/171	170/168	40.6/25.2	27.2/24.7	11.0	31.9	0.2
AuCu_CeO ₂ ^[b]	97.2	2.8	73/74	76/74	220/200	210/196	1.1/2.4	2.6/2.8	[c]	[c]	[c]
4Ce	3.9	–	–	–	–	–	–	–	9.5	[c]	0.3
19Ce	12.9	–	–	–	–	–	–	–	4.3	[c]	0.1

[a] Red.= reduced; Oxid.= oxidized; H= heating step; C= cooling step. [b] Similar AuCu NPs supported on commercial CeO₂, reported in our previous work.^[23] [c] Not measured.

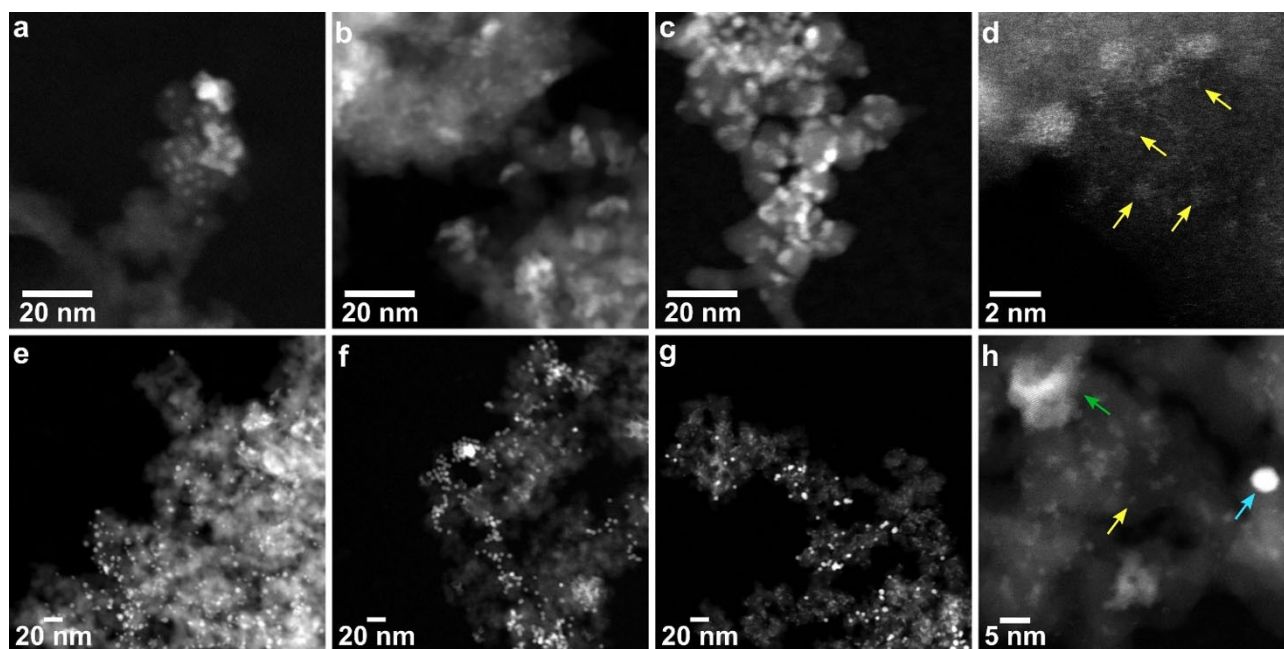


Figure 1. (a–c) High-angle annular dark-field (HAADF) STEM images of (a) 4Ce, (b) 13Ce, and (c) 19Ce supports. Scale bar: 20 nm. (d) High-resolution HAADF-STEM image of 4Ce support. Yellow arrows indicate the highly dispersed Ce atoms and clusters. Scale bar: 2 nm. (e–g) HAADF-STEM images of (e) AuCu4Ce, (f) AuCu13Ce, and (g) AuCu19Ce supports. Scale bar: 20 nm. (h) High-resolution HAADF-STEM image of AuCu4Ce support. Cyan arrow indicates the AuCu NP, green arrow indicates a larger CeO₂ particle and yellow arrow indicates the highly dispersed CeO_x species. Scale bar: 5 nm.

shows in detail the AuCu4Ce catalyst, indicating the presence of dispersed CeO_x species, larger CeO₂ particles, and an AuCu NP.

The fresh AuCuXCe catalysts were calcined to remove the capping ligands, exposing the metallic surface. This step causes gradual segregation of AuCu alloy forming Au NPs and CuO_x species, as followed by in situ XRD (Figure S4a–c). The experimental protocols of the in situ measurements are shown in Figure S1. After the calcination, the complete dealloy was confirmed by XAFS analysis, in which the XANES spectra at Au–L₃ (Figure S4d) and Cu–K (Figure S4e) edges of the catalysts matched the Au foil and CuO standards. The XANES analysis at the Ce–L₃ edge of the calcined catalysts (Table 1, Figure 2a) showed that the Ce³⁺ fraction was larger than the corresponding bare supports and decreased with the CeO₂ loading. It is known that the metal–CeO₂ interaction enhances the support reducibility.^[37,39,40]

Before the catalytic tests, a reductive pretreatment (activation) was required to partially recover the AuCu alloy (Au_{1–x}Cu_x).^[16,17,23,41] In this work, the term “reduced” was used to describe the AuCuXCe catalysts after this activation step. We had previously demonstrated that the removal of organic ligands from AuCu NPs can be done directly under H₂ flow, avoiding the dealloy; however, an AuCu–CeO₂ catalyst, prepared by depositing AuCu NPs in commercial CeO₂, became less active for CO–OX reaction than when the sequential activation, i.e., calcination followed by reduction, was performed.^[23]

To shed light on the species that were formed after activation on each catalyst studied in this work, we performed a detailed characterization by in situ XAFS and XRD. As men-

tioned before, after calcination, the AuCu NPs segregated due to Cu oxidation, forming Au NPs and CuO_x species (Figure S4). In situ XRD showed that Cu was reduced and partially reincorporated into the Au lattice during the pretreatment under H₂, decreasing the lattice parameter and shifting the XRD peaks to higher values (Figure 2c–e). There was a significant decrease of the temperature threshold for Cu reincorporation as a function of the CeO₂ loading; the XRD peak shift could be detected at ~180 °C, ~160 °C, and ~125 °C for AuCu4Ce, AuCu13Ce, and AuCu19Ce, respectively (Figure 2f). At 400 °C, based on the peak positions and the Vegard’s law, about 60% of the initial Cu was realloyed to the Au, a little smaller fraction for the AuCu4Ce (~50%). The slight asymmetric peak profiles indicated, however, that the Cu reincorporation was not homogeneous. Figure S5 shows the HAADF STEM images and the respective elemental maps of the reduced AuCu4Ce catalyst; the signals corresponding to the Au and Cu phases were superposed and quite similar in many regions, confirming the presence of AuCu alloy. It is also possible to identify Cu signal outside the NPs, corroborating the co-existence of CuO_x species dispersed on the support. The analysis of the XANES spectra at Au–L₃ and Cu–K edges (Figure 2g,h) collected at room temperature after the reductive pretreatment confirmed the XRD results. The Au–L₃ edge spectra showed a higher absorption intensity at 11930 eV (Au–L₃ edge) in comparison with the metallic standard, which is characteristic of the AuCu alloy formation.^[42–44] The Cu–K edge spectra were also in agreement with the alloy formation and the increase in the intensity of the absorption at 8993 eV as a function of the CeO₂ loading reflected a higher probability to create a Cu–CeO₂

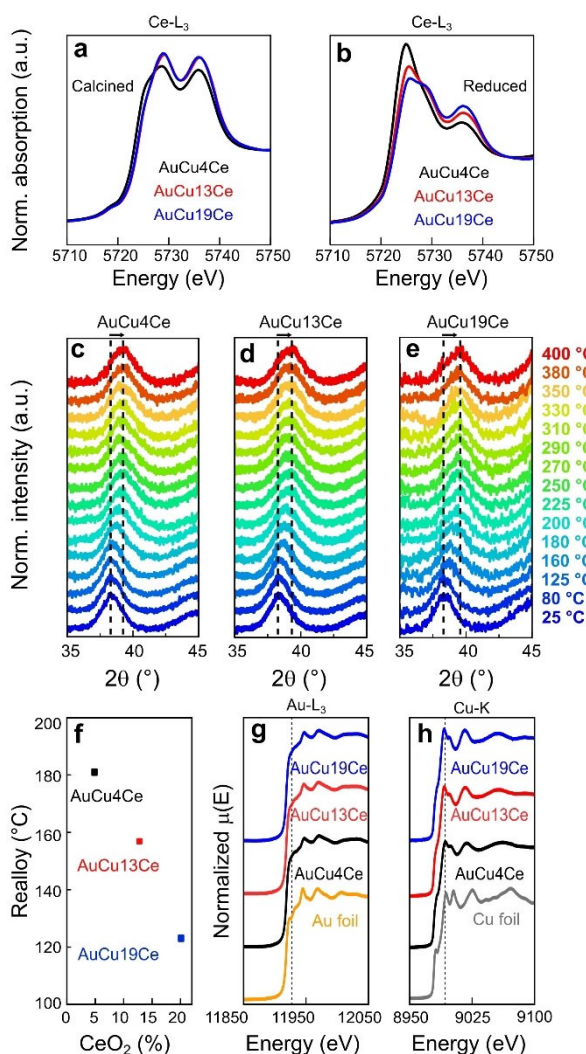


Figure 2. XANES spectra at Ce L₃ edge of (a) calcined and (b) reduced catalysts. (c–e) in situ XRD patterns of calcined AuCu₄Ce, AuCu₁₃Ce, and AuCu₁₉Ce catalysts, respectively, during the reductive pretreatment (H₂/He 5% 50 mL min^{−1}; 5 °C min^{−1}). The temperature increases from the bottom (room temperature, blue) to the top (400 °C, red), as indicated by the arrow. The dashed lines indicate the initial and final position of (111) metallic fcc peak; the black arrows above the dashed lines indicate the direction of the shift in the peak position. (f) plot of the temperature in which the Cu starts to be reincorporated into the Au lattice as a function of the CeO₂ content, obtained from the in situ XRD. The black, red, and blue squares indicate, respectively, the AuCu₄Ce, AuCu₁₃Ce, and AuCu₁₉Ce catalysts. (g, h) XANES spectra of the reduced AuCu₄Ce (black line), AuCu₁₃Ce (red line), and AuCu₁₉Ce (blue line) catalysts at Au–L₃ and Cu–K edges, respectively, compared with Au foil (yellow line) and Cu foil (gray line) in each respective edge. The dashed line in (h) corresponds to the energy of 8993 eV.

interface. This was corroborated by the increase of Ce³⁺ fraction of the reduced catalysts (Table 1, Figure 2b), that were larger than the corresponding values for the bare supports and decreased with the CeO₂ loading.

It is worth noting that in the case of Cu–CeO₂ systems, there is the formation of the Cu²⁺/Cu⁺ and Ce³⁺/Ce⁴⁺ redox pairs.^[45–48] The OSC normalized per mol of CeO₂ confirmed differences in the nature of the CeO_x species among the catalysts, presenting a similar trend found for the Ce³⁺ fraction

(Table 1). It has been shown that the increase of the CeO₂ particle size decreases the OSC,^[49,50] thus, the higher OSC of the AuCu₄Ce can be related to the higher ratio of dispersed : larger CeO₂ NPs. Therefore, the differences in the CeO₂ loading modifies not only the amount of the CeO₂ particles on the surface but also the nature of the stabilized species and its interaction with the CuO_x/Cu⁰ species.

By the EXAFS analysis (Figure S6, Table S1), it was possible to identify the species formed in each catalyst. At the Au–L₃ edge, the analysis was less sensitive to the changes in the composition of the alloy (Figure S6c–e, Table S1) but confirmed that a partial realloy process took place after reduction. For all catalysts, the increase in the experimental average Au–Au bond length (2.81 Å) in comparison to the Au–Cu distance (2.68 Å) and the value expected for a random AuCu alloy (2.69 Å) was in agreement with a heterogeneous Cu reincorporation, forming an Au-enriched core.^[16,23] Although we cannot rule out that the chemical heterogeneity could come from the presence of NPs with variable Cu content, the use of pre-made AuCu NPs, with narrow size distribution, should minimize these differences among the NPs. Looking at the Cu–K edge results (Figure S6f–h and Table S1), there was a significant decrease in the Cu–Cu bond length in the reduced AuCu₄Ce catalyst (2.56 Å), in comparison with the expected value (2.69 Å).^[16,23] The shortening of the Cu–Cu bond together with the high coordination number (CN) related to the Cu–Cu scattering in this catalyst suggests a significant contribution of metallic Cu outside the NPs. In other words, after the reductive pretreatment, the AuCu₄Ce catalyst was composed of a mixture of Au_{1–x}Cu_x alloy and Cu⁰. With the increase of CeO₂ content, the Cu–Au coordination number and the Cu–Cu bond length increased for AuCu₁₃Ce and AuCu₁₉Ce, indicating a higher Cu reincorporation in the Au lattice, and consequently, reducing the amount of Cu⁰ outside the NPs. These results indicate that the CuO_x species formed during calcination had its mobility reduced in the AuCu₄Ce, making more difficult the AuCu realloy process.

The reduced AuCuXCe catalysts were evaluated in the CO-PROX reaction (Figure 3a–d, Table 1); the performances during heating and cooling steps are shown. The increase of the CeO₂ loading increased the maximum CO conversion (MC, %), reduced the temperature of maximum conversion (TMC, °C), and slightly decreased the selectivity towards CO₂ at low temperatures. The differences between MC e TMC during heating and cooling steps also decreased for higher CeO₂ loading. Interestingly, when the CO₂ production normalized by the metal and CeO₂ loadings at 100 °C were considered, a less clear trend was found. As comparison, the AuCu–CeO₂^[23] catalyst achieved CO conversion of ~70% at 220 °C (Table 1) but the CO₂ production rate, taking into account the CeO₂ %wt., was much lower than the values found for all AuCuXCe catalysts.

Looking to the catalytic data in more detail (Table 1), the AuCu₄Ce catalyst initially showed at least two times higher CO₂ production rate than the other catalysts (heating step). However, while AuCu₁₃Ce and AuCu₁₉Ce catalysts presented small changes in their performance during the heating/cooling cycle, a significant loss of activity was found for the AuCu₄Ce

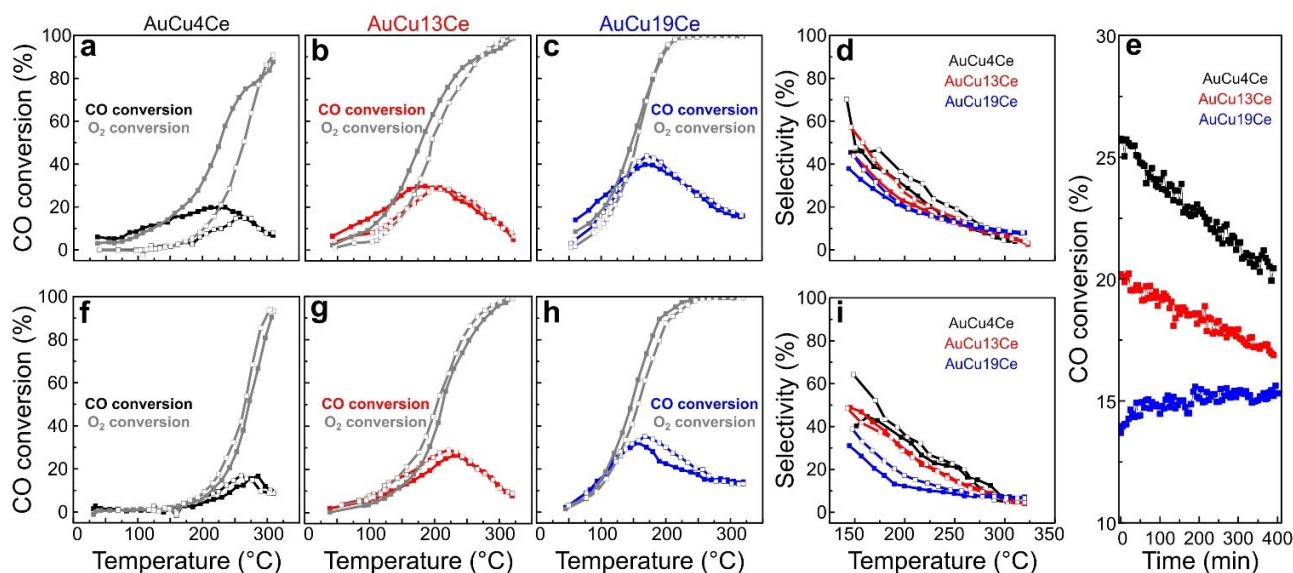


Figure 3. CO and O₂ conversion as a function of temperature of the reduced (a–c) and oxidized (f–h) catalysts: (a,f) AuCu4Ce, (b,g) AuCu13Ce, and (c,h) AuCu19Ce catalysts in CO-PROX reaction. Black, red, and blue lines indicate, respectively, the CO conversion of AuCu4Ce, AuCu13Ce, and AuCu19Ce catalysts. The gray line indicates the O₂ conversion for all catalysts. Filled and empty squares indicate the heating and cooling steps, respectively. Selectivity to CO₂ as a function of the temperature of the reduced (d) and oxidized (i) catalysts. (e) Stability tests of reduced catalysts in CO-PROX reaction at 170 °C.

catalyst during the cooling step. To confirm the differences in the stability of the catalysts under reaction conditions, a stability test under the CO-PROX stream was performed (Figure 3e). While the AuCu19Ce remained stable during the test, the AuCu4Ce catalyst deactivated at a faster rate than the AuCu13Ce catalyst. The CO₂ selectivity did not significantly change during the stability test, with values between 32–36% for all catalysts.

Therefore, there was a clear correlation between catalytic performance (activity and stability) and the CeO₂ loading, which we associate to the ratio of the different CeO₂ species that co-exist, i.e., CeO₂ NPs and highly disperse species.

The higher initial CO₂ production rate of the AuCu4Ce catalyst agrees with the literature, in which the higher OSC has been associated with the increase of the catalytic performance for different reactions.^[27,51,52] In comparison with bulk CeO₂, the CeO₂ NPs present more oxygen vacancies on their surface, which are currently associated with the stabilization of different species against sintering and increasing significantly the catalytic performance.^[53] It is important to remark, however, that OSC values depend on the conditions. In our case, the CeO₂ was reduced at high temperature (400 °C) before the OSC experiments, similar to the procedure used before the catalytic tests and the OSC values may not reflect the kinetic availability of lattice oxygen during CO oxidation. Nevertheless, the trends are consistent, also following the XANES results, that showed that the Ce³⁺ fraction was different for each sample, decreasing from AuCu4Ce to AuCu19Ce (Table 1). More important, the decrease in the Cu reincorporation in the reduced AuCu4Ce catalyst pointed out by the EXAFS analysis is consistent with the anchoring effect of the CuO_x species by the oxygen vacancies from the dispersed CeO₂, due to a stronger Cu/

CuO_x–CeO₂ interaction. In addition, despite the higher initial CO₂ production rate, the AuCu4Ce deactivated faster than AuCu13Ce under CO-PROX condition whereas the AuCu19Ce was stable (Figure 3e). In our previous work, we compared the performance of AuCu NPs supported either on commercial SiO₂ or commercial CeO₂ and we found that the AuCu/SiO₂ presented deactivation at 200 °C under CO-PROX stream.^[23] We associated the deactivation with the gradual oxidation of Cu from AuCu alloy since the AuCu alloy was more active than the Au–CuO_x species at this temperature and the reaction stream was not able to keep the alloy stable. Increasing the temperature, the H₂-rich atmosphere became enough to reduce and stabilize the alloy, and the CO conversion was recovered. On the other hand, since the AuCu alloy was formed at a lower temperature in contact with the CeO₂ support, the AuCu/CeO₂ catalyst remained stable under similar conditions.^[23]

To evaluate the impact of oxidation in the performance of the AuCuXCe catalysts, they were oxidized under mild conditions (~250 °C under synthetic air). The oxidized AuCuXCe catalysts presented initially lower conversions during the heating step (MC and CO₂ production rate at 100 °C) compared to the reduced forms, with TMC higher for AuCu4Ce and AuCu13Ce (Figure 3f–h, Table 1). However, during the cooling step under reaction conditions, the performance of all oxidized catalysts resembled the results found during the cooling ramp of the reduced catalysts. Consequently, despite the initial pretreatment (reduction or oxidation), the CO-PROX conditions determined the final catalytic species and although the AuCu4Ce was initially more active, the species were not the most stable. We proposed that by increasing the CeO₂ loading, a higher number of active sites available to the CO oxidation were formed; however, these active sites may not be the most

active ones but were more stable. Since the fraction of large CeO₂ NPs increases with the CeO₂ loading, we speculated that the highly dispersed CeO_x species interacted more strongly with the CuO_x/Cu⁰ species and hindered the Cu reincorporation to the Au lattice. Under reaction conditions, these species probably agglomerated leading to the more extensive deactivation of the AuCu₄Ce catalyst. Increasing the CeO₂ loading favored the AuCu realloy and led to an active and more stable catalyst.

Conclusion

The employment of the different amounts of CeO₂ on SiO₂ provided meaningful information about the role of the mobility of the CuO_x in the realloy process and its impact in the catalytic performance. The presence of highly dispersed species of CeO₂ in the AuCu₄Ce catalyst improved the CuO_x–CeO₂ interaction, decreasing the Cu reincorporation, leading to the formation of Cu⁰ outside the particles. Despite of it, the CO₂ production rate was initially higher for this catalyst, suggesting the presence of fewer but more active sites than for the higher CeO₂ loadings. However, these active sites were less stable, and the AuCu₄Ce catalyst presented a significant loss of catalytic activity during the cooling step or under stream. The higher CeO₂ loading of the AuCu₁₉Ce catalyst led to a more stable catalyst.

Experimental Section

Chemicals: All reactants were used without further purification: HAuCl₄·3H₂O (99%; Sigma Aldrich), Cu(CH₃COO)₂·H₂O (99%; Fluka), Oleylamine (OIAM, 70%; Sigma Aldrich); Oleic acid (OIAc, 90%; Sigma Aldrich), 1,2,3,4-Tetrahydronaphthalene – “TET” (99%; Sigma Aldrich), (CH₃)₃CNH₂·BH₃ – “TBAB” (97%; Sigma Aldrich).

Synthesis of AuCu NPs: The synthesis of the 6 nm AuCu NPs (Au:Cu 1:1) was performed following our previous work.^[23] The Au-seeds were prepared at 2°C using HAuCl₄·3H₂O dissolved in OIAM and TET (capping ligands/solvent). The reducing agent (TBAB) was dissolved in the same solvents and quickly injected. After 1 h, the Au-seeds were purified and dispersed in hexane. To produce the AuCu NPs, the Cu precursor (Cu(CH₃COO)₂·H₂O) was added to OIAM and after the injection of OIAc, the dispersion was heated. The solution was kept for 30 min at 80°C to completely dissolve the Cu precursor. At the end of the soak time at 80°C, the Au-seeds dispersed in hexane were injected. The solution was heated until 120°C and kept at this temperature for 30 min to evaporate the hexane. The dispersion was heated to 280°C and kept at this temperature for 1 h to form the AuCu alloy NPs. The solution was cooled to around 60°C and the purification was carried out. Both colloidal Au and AuCu NPs were analyzed by X-ray diffraction (XRD) in a Shimadzu XRD-7000 diffractometer (Cu–K α radiation, 2 θ range: 30–90°, step: 0.1° and 10 s/step) operating at 40 kV and 30 mA. The colloidal samples were concentrated and slowly deposited on a silicon wafer. The Au:Cu ratio in colloidal NPs was obtained by inductively coupled plasma optic emission spectrometry (ICP-OES) (Perkin Elmer, Optima 8000) in triplicate, after the digestion using aqua regia (HCl:HNO₃ 3:1) and filtration to remove the suspended particles. The metal and CeO₂ loading were obtained by X-ray fluorescence (XRF, Shimadzu XRF1800). The morphology of the colloidal NPs was analyzed by transmission electron microscopy in

conventional mode (CTEM), at LNNano (Brazilian Nanotechnology National Laboratory) using a JEOL JEM-2100 microscope. The colloidal NPs were dripped on Cu grids (400 Mesh) covered by ultra-thin carbon film, measuring around 300 particles randomly selected to obtain the average particle size.

Synthesis of XCe supports: One g of SiO₂ aerosil (Evonik, 380 m²g^{−1}) was dispersed in 25 mL of ethyl alcohol using an ultrasonic bath and kept under stirring at 600 rpm. Appropriate amounts of Ce(NO₃)₃·6H₂O (Acros, 99.999%) were dissolved in 10 mL of ethyl alcohol and slowly dripped on the SiO₂ to produce supports with 4, 13, and 19%wt of CeO₂. The mixture was kept under stirring for 1 h. The solvent was removed under vacuum and the solid was dried at 70°C overnight. The dried solids were calcined under synthetic air flow (100 mLmin^{−1}) at 500°C/4 h (10°Cmin^{−1}). The samples with nominal loading of 4, 13, and 19% wt of CeO₂ were labeled as 4Ce, 13Ce, and 19Ce, respectively. Through the text, the label XCe generally refers to all samples. The XCe supports were analyzed by XRD as described for the colloidal AuCu NPs. High-angle annular dark-field (HAADF) images were obtained in a Titan Themis Cubed (FEI Company) microscope operating in scanning mode (STEM). The samples were prepared by dispersing of powders in isopropyl alcohol using an ultrasonic bath and depositing a few droplets on Cu grids (400 Mesh) covered by amorphous carbon film. Additionally, X-ray fluorescence (XRF) was carried out (Shimadzu, XRF1800) to determine the CeO₂ loadings.

Preparation and characterization of the AuCuXCe catalysts: The AuCuXCe catalysts were prepared by wet impregnation. Briefly, the XCe supports were dispersed in hexane using an ultrasonic bath and kept under stirring. The same batch of colloidal AuCu NPs dispersion was slowly dripped onto the supports and the mixture was kept under stirring for 30 min. The solvent was removed under vacuum, the solid was dried at 70°C overnight. The fresh catalysts were labeled AuCu₄Ce, AuCu₁₃Ce, and AuCu₁₉Ce; the label AuCuXCe is used in the text to generally describe the samples. The AuCuXCe catalysts were characterized similarly as described for the XCe supports. Additionally, in situ XRD was performed at the XPD beamline at LNLs (Brazilian National Synchrotron Laboratory), using 8 keV X-ray beam. The calcination was carried out using synthetic air (50 mLmin^{−1}) from room temperature up to 350°C (Figure S1a). The activation (reductive pretreatment) was performed from room temperature up to 400°C under 5% H₂/He flow (total flow: 50 mLmin^{−1}) (Figure S1b), using a homemade furnace working in θ – 2θ mode. XAFS (X-ray absorption fine structure spectroscopy) measurements at Au–L₃ (11919 eV), Cu–K (8979 eV), and Ce–L₃ edges (5723 eV) were carried out at XAFS2 beamline at LNLs,^[54] in transmission mode. The samples were analyzed before (just calcined) and after the activation (Figure S1c). The detailed information about the XAFS data process is described in section S1.2 from Supporting Information and Figure S2. The oxygen storage capacity (OSC) measurements were collected using cyclic thermogravimetric analysis (TGA) in commercial TGA equipment (TA SDT Q600). The sample was reduced under 2% H₂/N₂ (100 mLmin^{−1}) at 400°C/1 h, similar to the activation step before the catalytic tests. The sample was cooled down to 200°C and the OSC measurements were collected at this temperature. Briefly, oxygen (2% O₂/N₂) and hydrogen (2% H₂/N₂) were alternately introduced into the equipment using a flow of 100 mLmin^{−1} for 10 min for each gas, add up to 5 cycles of oxidation/reduction. The OSC was calculated as the mass gained during oxidation (oxygen incorporation) and the mass loss during reduction (oxygen release). The OSC results were expressed per mol of CeO₂.

Preferential oxidation of CO (CO-PROX): 50 mg were diluted in 150 mg of quartz 100 Mesh and the mixture was placed in a

tubular reactor with quartz wool fixed bed, fixing the same metal amount for each catalyst. The CO-PROX reaction was carried out using the catalysts after the calcination followed by the activation (reductive pretreatment) at 400 °C/1 h under 35 mL min⁻¹ of H₂. The reaction atmosphere was composed of a total flow of 100 mL min⁻¹ (1:1:70 CO:O₂:H₂; He balance). The experimental protocol of the CO-PROX reaction is shown in Figure S1d. The effluent gases from the reaction were measured by gas chromatography using a thermal conductivity detector (TCD). The CO (X_{CO}) and O₂ conversion (X_{O₂}), and selectivity to CO₂ (S_{CO₂}) were calculated by the Eq 1, 2, and 3:

$$X_{CO} (\%) : ((CO_{in} - CO_{out}) / CO_{in}) \times 100 \quad (1)$$

$$X_{O_2} (\%) : ((O_{2in} - O_{2out}) / O_{2in}) \times 100 \quad (2)$$

$$S_{CO_2} = (1/\lambda) \times (X_{CO}/X_{O_2}) \times 100; \lambda = 2 \quad (3)$$

The stability test was carried out for the reduced AuCuXCe catalysts, with appropriated amounts to achieve CO conversion ~15–25% at 175 °C, based on the results of the catalytic cycles.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Atom Mobility · Ceria · Copper · CO-PROX · Gold

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