

Article

Carbonate Inhibition in Au-Cu/ γ -Al₂O₃ Catalysts for CO Oxidation

Karla López ¹, Gamaliel Che-Galicia ^{1,*}, Rodolfo Zanella ², Jesús F. Guayaquil-Sosa ³ and Alvaro Sampieri ^{1,*}
¹ Facultad de Ingeniería Química, Benemérita Universidad Autónoma de Puebla, Av. San Claudio s/n, Col. San Manuel, Ciudad Universitaria, Puebla 72570, Mexico

² Instituto de Ciencias Aplicadas y Tecnología, Universidad Nacional Autónoma de México, Circuito Exterior s/n, Ciudad Universitaria, Mexico City 04510, Mexico; rodolfo.zanella@icat.unam.mx

³ Innovations in Advanced Materials and Bioprocess Development Laboratory, Chemical and Petroleum Engineering, Schulich School of Engineering, University of Calgary, Calgary, AB T2N 1N4, Canada; jesus.guayaquilsosa@ucalgary.ca

* Correspondence: gamaliel.che@correo.buap.mx (G.C.-G.); alvaro.sampieri@correo.buap.mx (A.S.)

Abstract

Incorporating Cu into gold-based catalysts effectively reduced nanoparticle sintering and free carbonate accumulation, promoting long-term preservation of catalytic surface area over time. This study explores the catalytic activity of monometallic Au and bimetallic AuCu catalysts with varying Au:Cu atomic ratios (1:0.5, 1:1, and 1:1.5) that were synthesized on γ -Al₂O₃ via sequential deposition–precipitation with urea. The catalysts were pretreated in either air or H₂ and evaluated for CO oxidation activity and stability. A comprehensive characterization (EDS, BET, TEM, H₂-TPR, O₂-TPO, XPS, DRIFTS, and UV–Vis) was used to investigate particle size, metal oxidation states, and redox properties. Among all materials, the AuCu 1:1 catalyst exhibited the highest low-temperature CO conversion (>90% at 0 °C) and improved stability during 24 h tests, reflecting minimal nanoparticle sintering as confirmed by TEM analysis. In situ DRIFTS revealed that the presence of Cu⁺ and Cu²⁺ minimizes the accumulation of free carbonates (one of the main deactivation pathways in Au/ γ -Al₂O₃) while promoting the formation of reactive intermediates that facilitate CO₂ production. Notably, air pretreatment at moderate temperature proved as effective as H₂ pretreatment in activating both monometallic and bimetallic catalysts. These findings highlight the role of Cu as a structural and electronic promoter of gold, offering practical guidelines for designing durable, cost-effective catalysts for low-temperature CO oxidation on non-reducible supports.

Keywords: in situ DRIFTS; CO oxidation; catalyst deactivation; carbonates adsorption; sintering



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1. Introduction

Carbon monoxide (CO) is a harmful air pollutant principally released from the incomplete combustion of fossil fuels, such as coal and oil, as well as many organic materials. Despite several advances, controlling CO emissions remains a key area of research due to their significant impact on air quality and public health [1]. For instance, it has a 250 to 300 times greater affinity for blood than O₂ in humans due to the formation of carboxyhemoglobin, which impairs the ability of red blood cells to carry and deliver oxygen from the lungs to the tissues. Exposure to CO can result in severe tissue hypoxia and potentially fatal outcomes [2,3]. Currently, extensive research has been conducted on gold

catalysts in CO oxidation, revealing their activity at low temperatures ($-70\text{ }^{\circ}\text{C}$) when gold is present as metallic nanoparticles ($<2\text{ nm}$) and homogeneously dispersed on supports [4]. Numerous supports have been evaluated, including reducible oxides (e.g., TiO_2 , Fe_2O_3 , and CeO_2) [5–7] and non-reducible supports (e.g., Al_2O_3 and SiO_2) [7,8]. Among the wide variety of studied supports, $\gamma\text{-Al}_2\text{O}_3$ has attracted recent interest owing to its surface OH groups, which contribute directly to CO oxidation via metal–support interactions [9,10]. Additionally, $\gamma\text{-Al}_2\text{O}_3$ is widely used across catalytic processes within the automotive, chemical, and petroleum industries [11,12] due to its low cost, high surface area, pore volume, and acid-base surface properties [13].

Nevertheless, research on bimetallic Au-Cu catalysts supported on $\gamma\text{-Al}_2\text{O}_3$ remains limited, despite the individual significance of both metals and the widespread use of this support. In particular, the combined effect of Au and Cu on non-reducible supports has not been extensively explored for CO oxidation under low-temperature conditions. While the Au/ $\gamma\text{-Al}_2\text{O}_3$ catalyst suffers from stability loss due to nanoparticle sintering [14], the introduction of a second transition metal component, such as Ag, Ni, Pt, or Cu, has shown promise in reducing this issue and enhancing catalytic activity. Several studies have highlighted the strong influence of copper on CO oxidation. For instance, Sandoval et al. [15] proposed that, in AuCu/ TiO_2 catalysts, the oxygen from CuO_x species interacts with CO molecules to generate CO_2 . They observed that Au nanoparticles deposit on copper oxides, reducing nanoparticle sintering. Additionally, Najafshirtari et al. [16] have observed that forming CuO clusters close to Au benefits oxygen adsorption and activation, thereby enhancing catalytic activity. Nevertheless, adding an excess of copper reduces CO conversion, as Cu species block the active sites of Au nanoparticles [17]. However, most studies focus on reducible supports, and the impact of Cu loading on non-reducible supports like Al_2O_3 remains poorly understood in CO oxidation.

CO oxidation is widely used as a model reaction to evaluate heterogeneous catalysts due to its sensitivity to the nature and accessibility of active sites, as well as to redox behavior and surface oxygen mobility under mild conditions. This context underscores the importance of exploring new catalytic combinations that preserve activity and stability while utilizing economically viable materials [18]. It is well known that the activity and stability of gold-supported catalysts can vary depending on the preparation method due to alterations in the structure of the active sites. Moreover, the interactions through which the supports and promoters influence the active phases may provide new opportunities to design novel materials, elucidate reaction mechanisms, and identify the causes of catalyst deactivation. Therefore, understanding how Cu modifies activity and stability on non-reducible supports such as $\gamma\text{-Al}_2\text{O}_3$ remains crucial for explaining long-term deactivation resistance.

In this work, we developed a series of active and stable Au-Cu/ $\gamma\text{-Al}_2\text{O}_3$ catalysts using the deposition–precipitation with urea (DPU) method, aiming to gain a better understanding of how copper species influence gold-based catalysts and their interaction with $\gamma\text{-Al}_2\text{O}_3$ support during the CO oxidation. A broad suite of characterization techniques was employed: XPS, DRIFTS, TEM, EDS, H_2 -TPR, TPO, UV-Vis, and N_2 physisorption, which enabled us to connect structural features, active sites and carbonate species with catalytic performances. We further evaluated the effect of calcination and reduction treatments on the behavior of the catalysts.

2. Results

2.1. Effect of Atomic Au:Cu Ratio, Atmosphere, and Temperature Pretreatment on CO Catalytic Activity

Figure 1a shows the CO conversion as a function of reaction temperature for the AuCu bimetallic catalyst with different nominal ratios (1:0.5, 1:1, and 1:1.5) activated under air

at 300 °C. The results for Au and Cu monometallic catalysts are also presented for comparison, as well as the reaction with no catalyst or support. Although the Au monometallic catalyst was the most active between −5 °C and 100 °C, showing a CO conversion of 98% at 36 °C, the conversion decreased to 92% at 164 °C and increased again to 99% at 300 °C. Although this behavior has been reported multiple times in previous studies [17,19–21], its underlying mechanisms remain unexplained. In contrast, the Cu monometallic catalyst was inactive below 90 °C and achieved complete CO conversion at 280 °C. Concerning the bimetallic AuCu catalysts, Figure 1a shows that the CO conversion is reached 100% under 250 °C except for the AuCu 1:0.5 sample, which showed the lowest CO conversion of the bimetallic catalysts. The samples containing more copper (1:1 and 1:1.5) exhibited similar conversion rates, but the AuCu 1:1 sample was the most active. In these catalysts, the presence of Cu prevents the decrease in CO conversion as the reaction temperature increases. CO oxidation occurred even without a catalyst or support (Figure 1a), but at much higher temperatures, starting at around 210 °C (2% conversion) and reaching a complete conversion by 350 °C.

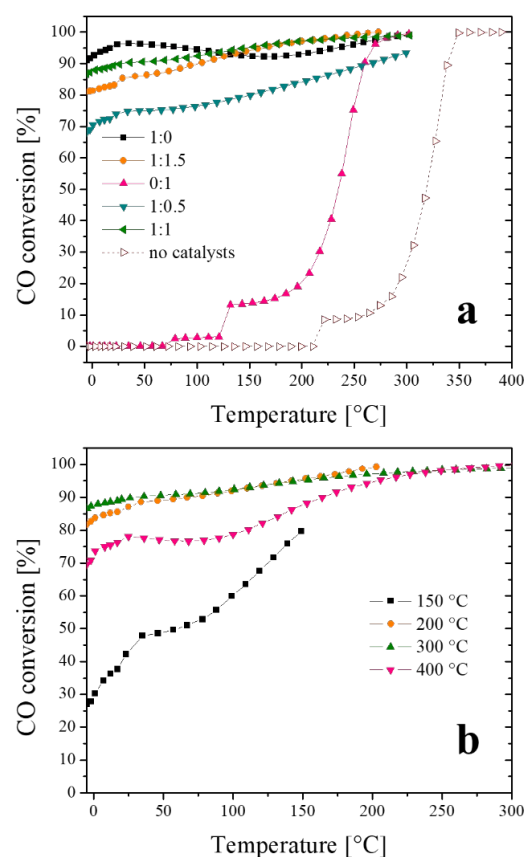


Figure 1. CO conversion as a function of temperature (a) for mono- and bimetallic Au and Cu catalysts pretreated at 300 °C in airflow, and (b) AuCu 1:1 catalyst as a function of the pretreatment temperatures.

The influence of the pretreatment temperature in an air atmosphere was studied only for the AuCu 1:1 catalyst, ranging from 150 to 400 °C (Figure 1b). At 200 °C and 300 °C, a similar CO conversion rate is observed. However, at a pretreatment temperature of 400 °C, the conversion fell below 80% at low temperatures (Figure 1b). Additionally, like the Au monometallic catalyst, a decrease in conversion was observed, followed by a gradual increase at higher reaction temperatures. The pretreatment at 150 °C triggered a catalyst with low activity, achieving only 80% CO conversion at this temperature.

Activation of AuCu catalysts with H_2 at 200 °C (Figure 2a) resulted in lower CO conversion at reaction temperatures below 50 °C compared to activation with air at 300 °C (Figure 1a). However, CO conversion increased rapidly, reaching 100% at temperatures below 200 °C. Following H_2 activation at 200 °C, the monometallic Au catalyst exhibited higher activity, displaying a similar trend in response to the behavior observed under air activation at 300 °C. Notably, the AuCu 1:1 became more active than the monometallic Au catalyst above 90 °C. Additionally, Figure 2b shows the effect of pretreatment temperature under H_2 flow on the performance of the AuCu 1:1 catalyst, which achieved its highest activity after pretreatment at 200 °C. According to the literature, Suo et al. [22] synthesized the AuPd/ Al_2O_3 catalyst via impregnation pretreated with airflow within a temperature range of 120–400 °C. The sample pretreated at 200 °C exhibited the highest CO conversion, reaching 10% at 100 °C. Similarly, Lu et al. [23] prepared an Au/ $NiAl_2O_3$ catalyst using the deposition–precipitation (DP) method with $(NH_4)_2CO_3$, followed by either calcination in air or reduction with H_2 at 250 °C. The reduced material achieved a CO conversion of 90%. Meanwhile, Hellmer et al. [24] synthesized the $AuCo_3O_4/Al_2O_3$ catalyst via DPU and calcined it at 400 °C. Although the catalyst reached 90% CO conversion at 50 °C, complete conversion was not reached.

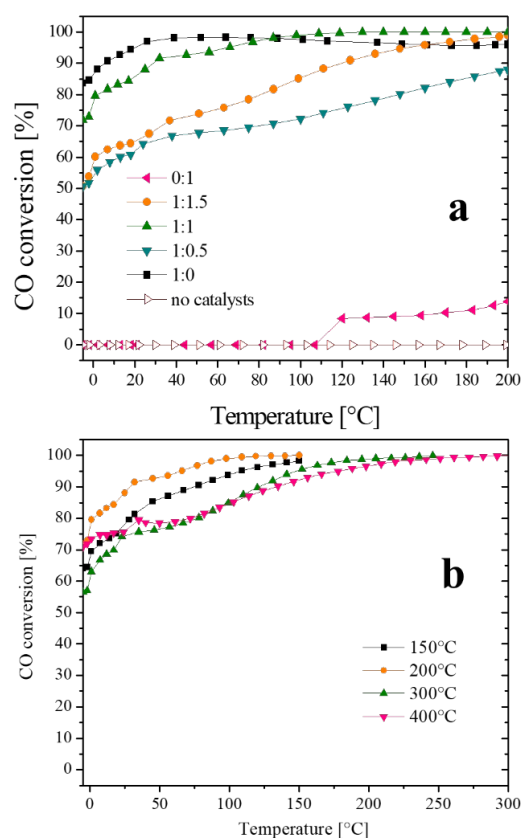


Figure 2. CO conversion as a function of temperature: (a) for mono- and bimetallic Au and Cu catalysts pretreated at 200 °C in H_2 flow, (b) AuCu 1:1 catalyst as a function of the pretreatment temperatures.

Time-on-stream experiments were performed at 20, 50, and 100 °C for 24 h to determine the stability of the AuCu 1:1 and monometallic Au catalysts activated in air at 300 °C (Figure 3a). The monometallic Au catalyst exhibited progressive deactivation at all reaction temperatures, as evidenced by an 18% drop in CO conversion at 20 °C (from 93% to 74%). Although the bimetallic AuCu 1:1 catalyst was more stable, showing only a 1.5% decrease in initial activity (Figure 3b), the catalytic stability of the Au bimetallic catalyst

decreased with the increase of the reaction temperature. The CO conversion was declining by 5% at 50 °C and 8% at 100 °C. These results indicated that adding Cu to Au catalysts enhanced their stability. The deactivation observed in the Au catalysts could be attributed to several factors, including nanoparticle sintering, surface poisoning by carbonate species, and the loss of OH groups from the catalyst surface. These aspects will be examined in more detail afterward.

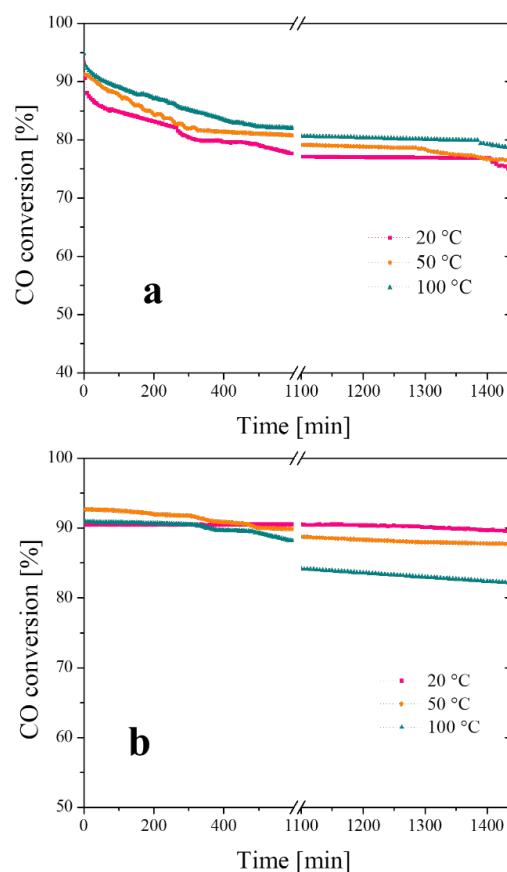


Figure 3. Evaluation of CO conversion as a function of reaction time at 20, 50 and 100 °C on: (a) Au and (b) AuCu 1:1 catalysts pretreated in air at 300 °C. Reaction conditions: 100 mL/min of 1% CO, 1% O₂ and 98% N₂.

2.2. Superficial Elemental Analysis and Textural Properties

Table 1 compares the nominal and the actual surface metal loadings in wt.% and the Au:Cu atomic ratios for the bimetallic samples AuCu. The theoretical metal loadings for the monometallic catalysts were 3 wt.% for Au and 0.98 wt.% for Cu. According to the EDS analysis, the percentage amount of the total Au concentration ranged from 2.42% to 2.64% and from 0.34% to 0.97% for Cu. The AuCu 1:1 sample exhibits the highest deposition percentages, with 2.64 wt.% for Au and 0.97 wt.% for Cu.

The BET methodology was employed to measure the specific surface area, using γ -Al₂O₃ as the reference (115 m²/g). After loading metals on γ -Al₂O₃, the specific surface areas are reduced to 91.77, 68.64, and 82.16 m²/g for the Au, Cu, and AuCu samples, respectively (Table 1). For the bimetallic samples AuCu, the specific surface area and pore size decreased with the increase in the Cu amount, accompanied by an increase in the nanoparticle size.

The N₂ adsorption/desorption isotherm curves and pore size distribution are shown in Figure S1 (Supplementary Information). The samples exhibited a typical IV-type isotherm, as defined by the IUPAC [25], with H3-type hysteresis observed at a relative pressure

(P/P_0), ranging from 0.85 to 1 [26]. The isotherm shapes can be attributed to the capillary condensation of N_2 molecules or the mesoporous structure of Al_2O_3 . From Figure S1b (Supplementary Information), the pore size distribution of the samples was composed of a narrow unimodal distribution, and it was centered at 32.1, 34.3, and 28.3 nm for Au, Cu, and AuCu, respectively. The Cu particles gradually fill up the pores of Al_2O_3 , resulting in a reduction in the specific surface area and pore volume. However, the mesoporous structure remained unchanged.

Table 1. Metal loading and textural properties of the mono- and bimetallic catalysts.

Material	Nominal Au Loading	EDS Au Surface Loading ⁺	Nominal Cu Loading	EDS Cu Surface Loading ⁺	Actual Atomic Ratio	Nanoparticle Size [nm]		Specific Surface Area	Pore Size
	wt. %	wt. %	wt. %	wt. %	Au:Cu	Air [*]	H ₂ ^{**}	[m ² /g]	[nm]
Au	3	2.56 (0.25)	-	-	1	2.83	2.36	91.77	32.19
Cu	-	-	0.98	0.74 (0.14)	1	-	-	68.64	34.32
AuCu 1:0.5	3	2.42 (0.22)	0.49	0.34 (0.08)	1:0.34	2.81	2.72	89.58	23.75
AuCu 1:1	3	2.64 (0.44)	0.98	0.97 (0.17)	1:0.98	2.89	2.78	82.16	28.37
AuCu 1:1.5	3	2.46 (0.24)	1.47	0.95 (0.11)	1:0.84	4.13	4.04	80.40	21.44

^{*} Pretreatment at 300 °C. ^{**} Pretreatment at 200 °C. ⁺ The standard deviation is shown in parentheses.

2.3. Size of the Au Nanoparticles After Activation and Reaction

Figure 4 shows a high-resolution TEM image of monometallic Au and Cu, as well as bimetallic AuCu samples, which were pretreated at 300 °C in air. Figure 4a shows micrographs corresponding to the Au sample, where the size distribution comprises particles ranging from 1.5 to 6.0 nm. The calculated value of the crystalline interplanar distance (d) was 0.234 nm, which corresponded to the spacing value of Au⁰ (111) lattice planes (0.235 nm, JCPDF 01-1172). For the Cu sample, it was impossible to observe Cu nanoparticles due to the lack of contrast between Cu and Al on Al_2O_3 . The calculated value of d (Figure 5b) was 0.248 nm, corresponding to the CuO (111) lattice planes (0.25 nm, JCPDS 48-1548). In the case of bimetallic samples AuCu, the average particle size was slightly bigger (2.89 nm) than that of the monometallic Au (2.83 nm). These crystallographic planes were not observed in the XRD patterns (Supplementary Information, Figure S2) due to the low metal content; only the Al_2O_3 diffraction peaks were detected.

The calculated d -spacing for the bimetallic AuCu 1:1 sample (0.234 nm) corresponds to the Au⁰ (111) plane, while the interplanar distances of 0.443 and 0.24 nm are related to the (113) and (118) planes of Al_2O_3 , respectively (0.456 and 0.259 nm, JCPDF 56-1186). However, the value of d = 0.24 nm is also identified for CuO, so the assignment could be uncertain. Table 1 summarizes the nanoparticle size in the AuCu catalysts with different Au:Cu ratios after thermal treatment at 300 °C in air and 200 °C in H₂. For air-treated samples, the average particle size increased with the Cu content, ranging from 2.81 to 4.13 nm. A similar trend was observed in bimetallic samples activated under H₂, where particle sizes increased from 2.72 to 4.04 nm with rising Cu content. However, samples treated in H₂ exhibited slightly smaller particle sizes than those treated in air, attributed to the lower reduction temperature under H₂. Additionally, the stronger interaction between Cu and γ - Al_2O_3 helped prevent particle sintering [27].

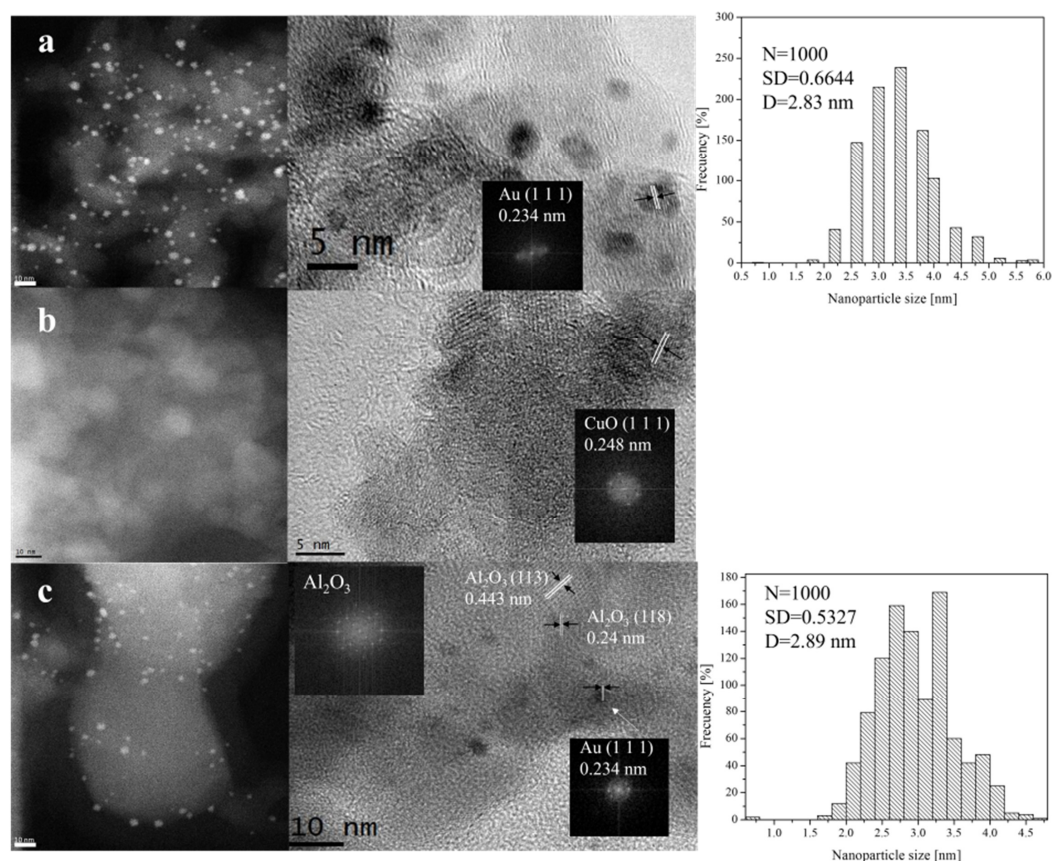


Figure 4. HRTEM images and nanoparticle size frequency histogram of pretreated catalyst at 300 °C with air: (a) Au, (b) Cu, and (c) AuCu 1:1.

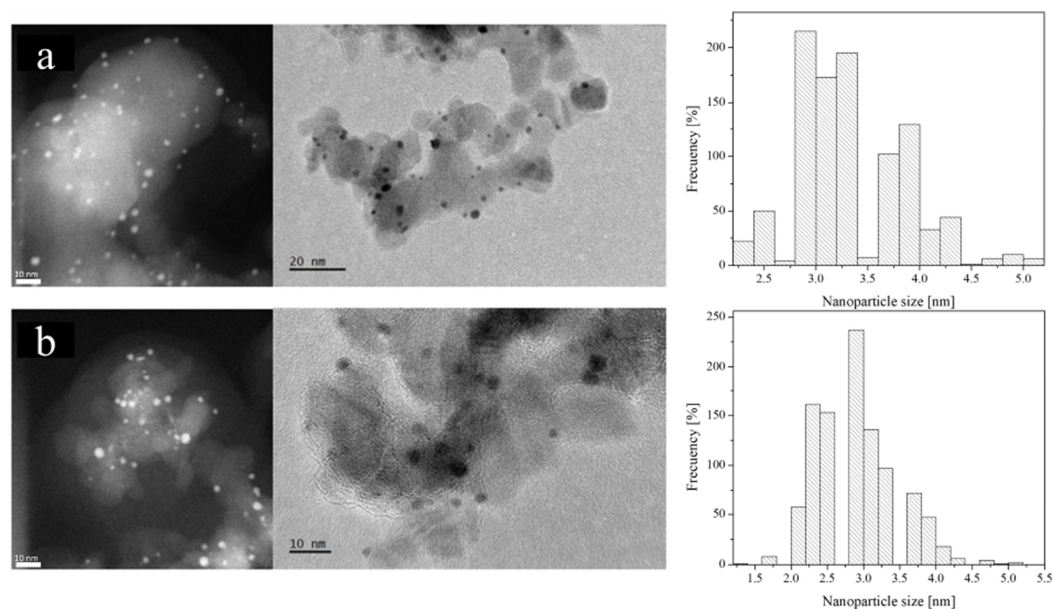


Figure 5. HRTEM images and nanoparticle size frequency histogram of pretreated catalyst at 300 °C with air: (a) Au and (b) AuCu 1:1 after the reaction test. Reaction conditions: 100 mL/min of 1% CO, 1% O₂ balanced N₂ at 20 °C for 24 h.

TEM characterization of the Au and AuCu catalysts after stability tests at 20 °C (Figure 5) revealed a noticeable increase in nanoparticle size of both materials compared to the earlier micrographs. The average size of the Au sample increased significantly, around 0.52 nm, while the AuCu particle size increased by 0.05 nm. The addition of Cu to

Au/Al₂O₃ catalysts inhibited the agglomeration of Au nanoparticles. This phenomenon may occur during prolonged reaction times and at temperatures above 100 °C. Moreover, the incorporation of Cu suppressed the sintering of Au nanoparticles by modifying the surface energy and local redox environment that limit the surface mobility of Au [28]. Furthermore, to enhance the interaction between the metals and the support, Cu species could promote stronger anchoring and thereby prevent their migration, and the catalytic activity remained stable [29,30].

2.4. Temperature-Programmed Reduction and Oxidation (TPR/TPO) Analysis

H₂-TPR technique was applied to study the reducibility of the Au, Cu, AuCu, and γ -Al₂O₃ samples, Figure 6a. In the case of the monometallic Au sample, the reduction profile appears as a peak between 130 and 210 °C with a maximum at 178 °C, which has been attributed to the reduction of Au³⁺ to Au⁰ [5,23]. For the monometallic Cu sample, the first peak emerged at 94 °C and the second at 160 °C. The low reduction temperature peak, 94 °C, was observed for all CuO_x nanopowders [31] and a highly dispersed CuO_x species [32]. The second peak was attributed to CuO bulk and highly dispersed Cu²⁺ species in strong interaction with the support [33]. The presence of Cu²⁺ and Cu⁺ species was attributed to the direct reduction of Cu²⁺ to Cu⁺, which is then further reduced to Cu⁰, a process that requires low energy [34].

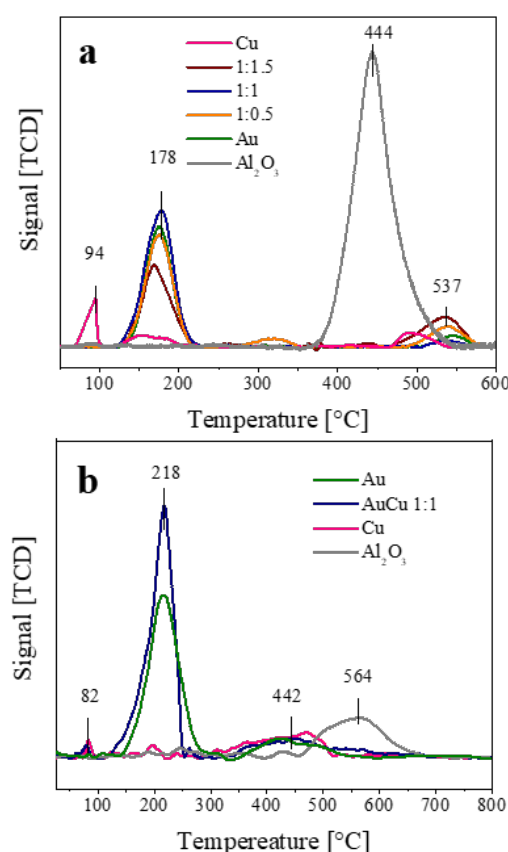


Figure 6. (a) H₂-TPR and (b) O₂-TPO for mono- and bimetallic dry samples.

For the bimetallic samples, the reduction profile was also characterized by a peak for Au reduction that shifted from 178 to 168 °C as the nominal Cu content in the sample increased, indicating that Cu species affect the reducibility of Au species. Notice that the peak at 168 °C corresponds to the sample with high nominal Cu content (AuCu 1:1.5). Nevertheless, these shifts were unobserved for the other bimetallic samples due to overlap with the reduction peak of Au³⁺ (178 °C). The temperature reduction of Au species

differed between mono- and bimetallic catalysts, indicating an interaction between Au and Cu particles.

To observe the influence of the support, 100 mg of γ -Al₂O₃ was also analyzed, presenting a single reduction peak at 444 °C. However, due to the metal interaction with the support M^+-Al^{3+} [35], the reduction peak shifted to a higher temperature, from 470 °C for Cu monometallic samples to around 537 °C for Au-containing samples.

O₂-TPO profiles were obtained to determine the oxidation temperature in Au, Cu, AuCu 1:1, and γ -Al₂O₃ dry samples (Figure 6b). A prominent peak at 218 °C was observed for the Au and AuCu 1:1 samples, indicating oxygen desorption from Au₂O₃ species as it was reduced to metallic gold (Au⁰). This occurred because Au oxides decompose at temperatures above 121 °C due to their instability (activation energy of dissociation: 57 kJ/mol) [36]. In the Cu sample, the thermogram shows a minor peak at 82 °C, corresponding to the decomposition of Cu(OH)₂ and Cu⁺ oxide species, characterized by low thermal stability and its decomposition starting from RT up to 200 °C [37]. Remarkably, the γ -Al₂O₃ profile presents a peak at 564 °C associated with the desorption of surface lattice oxygen species. However, the incorporation of Au and Cu causes this peak to shift toward lower temperatures, which was attributed to enhanced oxygen mobility within the γ -Al₂O₃ support.

2.4.1. XPS

The XPS analysis of the mono- and bimetallic samples pretreated with airflow at 300 °C is shown in Figure 7. For the Au and AuCu catalysts (Figure 7b,f), the high-resolution Au 4f spectra exhibit two deconvoluted peaks at 81.52 (Au 4f_{7/2}), and 85.18 (Au 4f_{5/2}) eV for the monometallic sample, and two peaks at 81.45 and 85.16 eV for the bimetallic one. These peaks are characteristic of the metallic gold, Au⁰. This close binding energy value of the Au 4f_{7/2} peaks (~81.5 eV) suggests a strong metal–support interaction (or alloying with Cu), which may result in electron-rich Au species [38,39]. For the Cu component in the monometallic Cu and bimetallic AuCu samples (Figure 7d,g), the high-resolution Cu 2p spectra display two peaks at 930.65 eV and 950.79 eV for the Cu sample, and at 930.31 eV and 950.03 eV for the bimetallic material. These binding energies, which closely match values reported in the literature, are due to the presence of Cu⁰ and Cu⁺ species.

The XPS spectra deconvolution reveals that the signals at 932.94 eV (Cu2p_{3/2}) and 954.51 eV (Cu2p_{1/2}) are assigned to Cu²⁺ species, as shown in Table 2. These signals indicate the oxidation of Cu⁺ to Cu²⁺, attributed to the shake-up satellite located at 942.2 eV [40,41]. The presence of a shake-up satellite in the Cu 2p_{3/2} region of both spectra demonstrates the coexistence of Cu²⁺ and Cu⁺ species, likely resulting from partial oxidation of the samples upon exposure to ambient air [42]. The O1s spectra (Figure 7a,c,e) show two peaks upon deconvolution, centered at 528.21 and 530.20 eV, which correspond to the lattice oxygen of metal oxide (I) and hydroxides (II), respectively [43,44].

Table 2. Atomic percentages (at.) from XPS deconvolution of O 1s, Au 4f, and Cu 2p peaks in mono- and bimetallic catalysts treated in air at 300 °C.

Material	Au	Cu		O	
	Au ⁰	Cu ⁺	Cu ²⁺	O(I)	O(II)
Au	100	-	-	31.02	68.98
Cu	-	78.54	21.46	54.27	45.73
Au:Cu	100	86.49	13.51	95.10	4.90

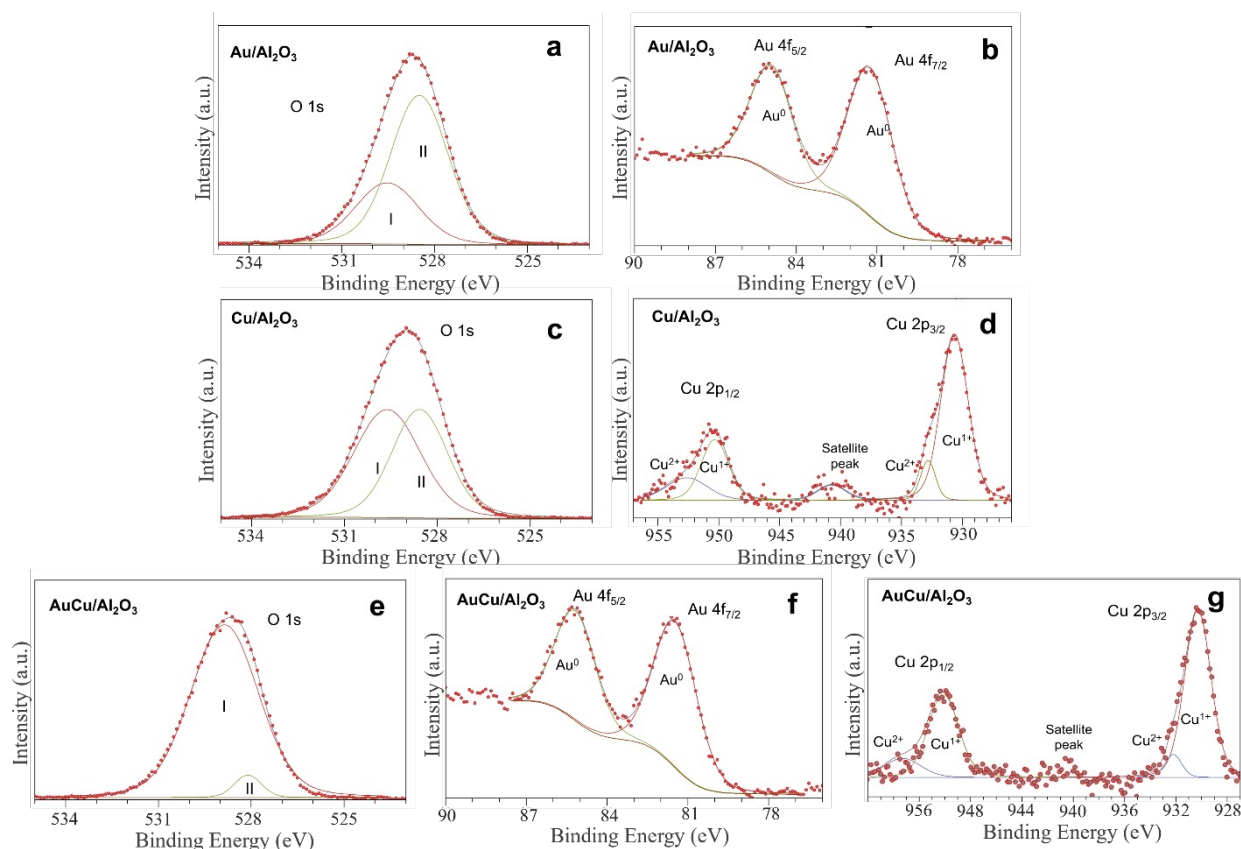


Figure 7. XPS spectra for O1s (a–c), Cu 2p (d,e), and Au 4f (f,g) pretreated at 300 °C in air flow.

2.4.2. Surface Composition by CO Adsorption by DRIFTS Analysis

DRIFTS was employed to analyze the in situ activation on monometallic Au, Cu, and bimetallic AuCu (1:1) catalysts through the CO adsorption in either air at 300 °C or H₂ at 200 °C. Figures 8 and 9 present the DRIFT spectra for each activation temperature and atmosphere conditions, while Figure 10 shows the spectra under reaction conditions. For the monometallic Au sample (Figure 8a), activated in situ with air from RT to 300 °C, an intense band appears at 2100 cm^{−1}, which gradually decreases in intensity with increasing temperature and becomes undetectable at 250 °C. This band is attributed to CO adsorbed on low-coordinated surface Au⁰ atoms (Au⁰-CO) [41–43]. Concomitantly, a new band emerges at 2038 cm^{−1}, associated with CO adsorbed linearly on small clusters of negatively charged gold carbonyls (Au^{δ−}-CO). This phenomenon arises from the electron transfer from the support to the gold cluster and the back-donation from gold to the antibonding orbitals of carbon monoxide [6,45]. As this band decreases, the band at 1973 cm^{−1}, corresponding to bridging CO on Au^{δ−} species, starts to emerge and increases until it vanishes at 200 °C. The band observed between 2400–2150 cm^{−1} corresponds to the gaseous CO in the sample chamber. In the OH stretching region (4000–3700 cm^{−1}), hydration behavior is observed from RT to 300 °C due to the release of hydroxyl groups from γ-Al₂O₃ [46]. At 50 °C, bands at 3732 and 3683 cm^{−1} appear, corresponding to a doubly bridging hydroxyl and triply bridging acid hydroxide, respectively. Upon the temperature increases to 250 °C, a 3759 cm^{−1} band emerges, which is associated with more basic surface hydroxyls [47]. Therefore, an increase in surface hydroxide concentration corresponds with enhanced absorption in the carbonate region (1500 to 1200 cm^{−1}) at 150 °C, indicative of formates, monodentate and bridged carbonates species [48,49].

When the CO adsorption on the monometallic Cu catalyst is examined, Figure 8b, two bands appear at 2100 and 2043 cm^{−1}, corresponding to CO adsorption on unlike Cu⁺

centers with different σ - π^* feedback bonds (Cu^+-CO) [29,50]. In the hydroxyl region, the band at 3732 cm^{-1} starts to increase at $100\text{ }^\circ\text{C}$, while the shoulders of the bands at 3759 and 3683 cm^{-1} emerge at $200\text{ }^\circ\text{C}$. As observed for the Au catalyst, the doubly bridging hydroxyl group is the predominant species. Starting at $200\text{ }^\circ\text{C}$, a reaction likely occurs between the adsorbed CO and the O_2 in the CuO_x species, as evidenced by a band at 1453 cm^{-1} , assigned to the formation of monodentate carbonates [51]. Although Cu adsorbs more CO molecules at RT (as observed in all samples), the amount of adsorbed CO decreases significantly with increasing temperature (Figure 8b). Consequently, monometallic Cu catalyst exhibits negligible CO_2 formation below $100\text{ }^\circ\text{C}$ (Figure 1a). Incorporating Cu species into the Au catalyst significantly improves its catalytic stability and markedly reduces deactivation.

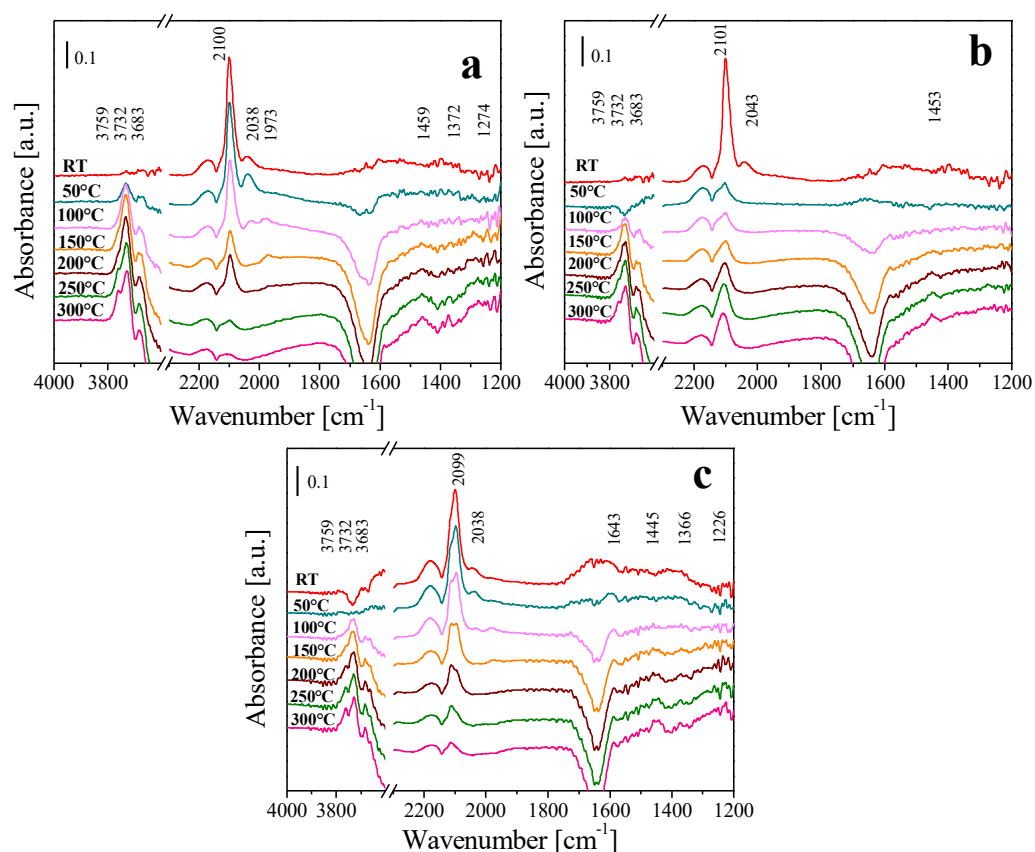


Figure 8. DRIFT spectra of CO adsorbed at different temperatures on (a) Au, (b) Cu, and (c) AuCu 1:1 thermally treated at $300\text{ }^\circ\text{C}$ in air.

In the bimetallic AuCu 1:1 sample, the bands appear with lower intensity than in the monometallic Au sample (Figure 8c). As the CO adsorption temperature increases from $25\text{ }^\circ\text{C}$ to $300\text{ }^\circ\text{C}$, the band at 2103 cm^{-1} gradually shifts to lower frequencies. After reaching $100\text{ }^\circ\text{C}$, the signal evolves into a two-band feature centered at 2103 and 2099 cm^{-1} , respectively. The band at 2103 cm^{-1} could be ascribed to the adsorption of CO first occurring in the Au nanoparticles [5], while the band at 2099 cm^{-1} is related to the adsorption in the particles with a strong geometric effect between Au and Cu or by the charge transfer from both metals ($\text{Au}^0/\text{Cu}^+-\text{CO}$) [30]. It is also worth mentioning that the band attributed to $\text{Au}^{\delta-}-\text{CO}$ and Cu^0-CO (2038 cm^{-1}) decreases with the temperature. In the hydroxyl region, the bands at 3683 and 3732 cm^{-1} increase in intensity at $100\text{ }^\circ\text{C}$, while the band at 3759 cm^{-1} begins to rise at $200\text{ }^\circ\text{C}$. As the hydroxyl concentration increases, the band at 1643 cm^{-1} decreases, suggesting an inverse correlation with the presence of bi- and monodentate carbonates observed in the 1200 – 1500 cm^{-1} region.

A similar CO adsorption study by DRIFT was performed on Au, Cu, and AuCu 1:1 after in situ reduction at 200 °C, Figure 9. For the monometallic Au sample (Figure 9a), the introduction of CO leads to the appearance of a carbonyl band at 2097 cm^{-1} due to the linear adsorption of CO on Au^0 ($\text{Au}^0\text{-CO}$) [23,52]. This band decreases with increasing temperature but does not entirely disappear at 200 °C. The band observed at 2034 cm^{-1} , assigned to CO linearly adsorbed on negatively charged clusters ($\text{Au}^{\delta-}\text{-CO}$) [45], is thermally unstable and disappears at 150 °C. In the hydroxyl region, the band at 3732 cm^{-1} , attributed to doubly bridging hydroxyls, increases in intensity with rising temperature, whereas the band at 3683 cm^{-1} , corresponding to triply bridging hydroxyls, emerges at 200 °C. The broad peaks around the carbonate region, with maxima bands at 1652, 1590, and 1373 cm^{-1} , suggest either a vibration of the asymmetric carbon in bicarbonate species on the surface or asymmetric stretching modes of carbonates [53].

For the monometallic Cu catalyst, the $\text{Cu}^0\text{-CO}$ band at 2102 cm^{-1} overlaps with the bands of gaseous CO due to its low intensity (Figure 9b). Indeed, when the temperature is increased to 200 °C, a slight increase in the CO adsorption intensity on the Cu^0 species is observed. It is also noteworthy that no band between 2050 and 2000 cm^{-1} region is detected, as no reduction of Cu occurs through the interaction with CO because it is already fully reduced. Simultaneously, the band attributed to double bridging hydroxyls (3732 cm^{-1}) increases with temperature, whereas in the carbonate region, bicarbonates and carbonates only appear below 100 °C.

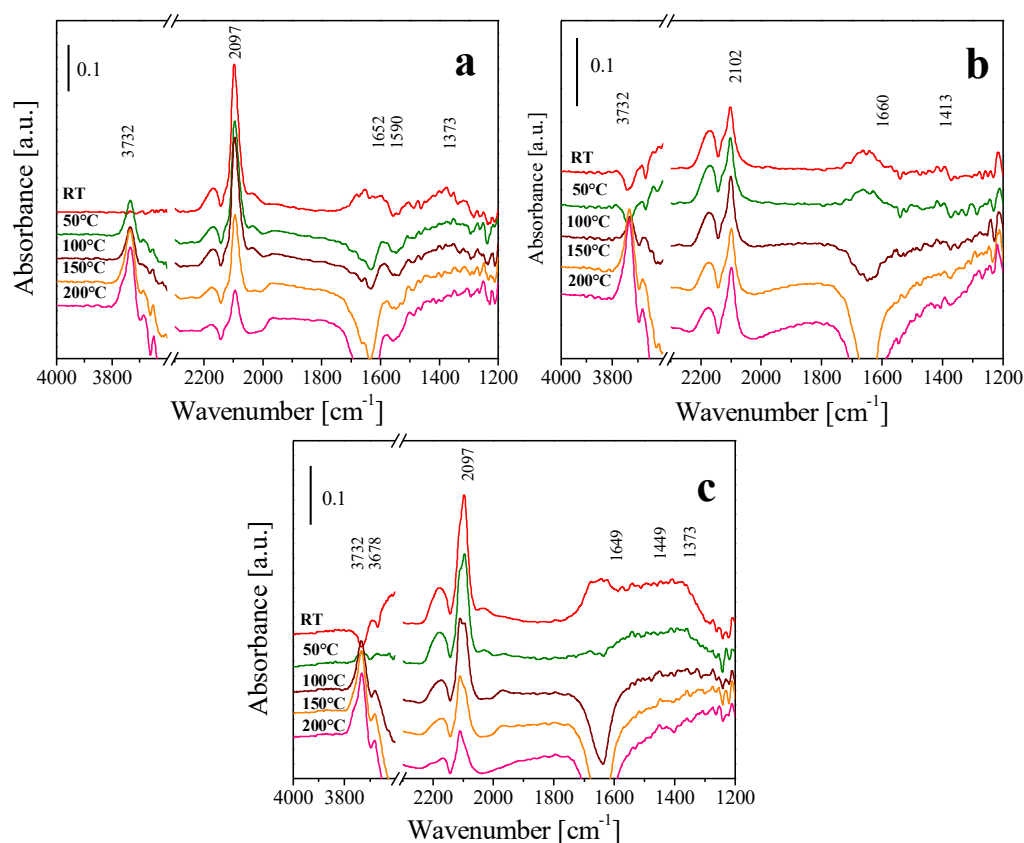


Figure 9. DRIFT spectra of CO adsorbed at different temperatures on (a) Au, (b) Cu, and (c) AuCu 1:1 thermally treated at 200 °C in H_2 .

The DRIFT spectrum of the bimetallic AuCu 1:1 catalyst activated with H_2 , shows a lower CO adsorption than the monometallic Au catalyst. Figure 9c, indicating an interaction among Cu^0 and Au^0 species on its surface structure. The band associated with these species is shifted from 2097 to 2115 cm^{-1} , suggesting that CO adsorption occurs primarily on

Au^0 species. Additionally, the band related to $\text{Au}^{\delta-}\text{-CO}$ emerges with lower intensity than in the Au catalyst. Moreover, a broad band in the carbonate region suggests the presence of carbonates and bicarbonates on the $\gamma\text{-Al}_2\text{O}_3$ surface. However, while most bands gradually decrease in intensity with increasing temperature, the hydroxyl bands at 3732 and 3678 cm^{-1} increase from $100\text{ }^\circ\text{C}$ to $200\text{ }^\circ\text{C}$.

An additional in situ DRIFT analysis was performed under reaction conditions ($\text{CO}:\text{O}_2:\text{N}_2 = 1:1:98$) for the Au and AuCu 1:1 catalysts (activated with air at $300\text{ }^\circ\text{C}$), as shown in Figure 10. According to DRIFT spectrum of the monometallic Au catalyst, represented in Figure 10a, the adsorption of CO on Au^0 species is observed at 2107 cm^{-1} from RT to $200\text{ }^\circ\text{C}$. Moreover, hydration due to the generation of hydroxyl groups from alumina is displayed, where the bands at 3759 , 3732 , and 3683 cm^{-1} , associated with different types of hydroxyls (e.g., doubly bridging hydroxyls, triply bridging acid hydroxide, and basic surface hydroxyls), increase in intensity as the temperature increases. In the spectral region between 1700 and 1200 cm^{-1} , a prominent band at 1438 cm^{-1} is observed, attributed to the formation of monodentate or free carbonate [54]. This band appears at $50\text{ }^\circ\text{C}$ and increases in intensity as the reaction temperature rises. The negative signal at 1640 cm^{-1} precisely corresponds to the positive signals of the hydroxyl groups, and it is associated with bidentate bicarbonates [46,54], which are absent in this monometallic catalyst. Notably, the catalyst lacks the generation of $\text{Au}^{\delta-}$ sites under oxygen.

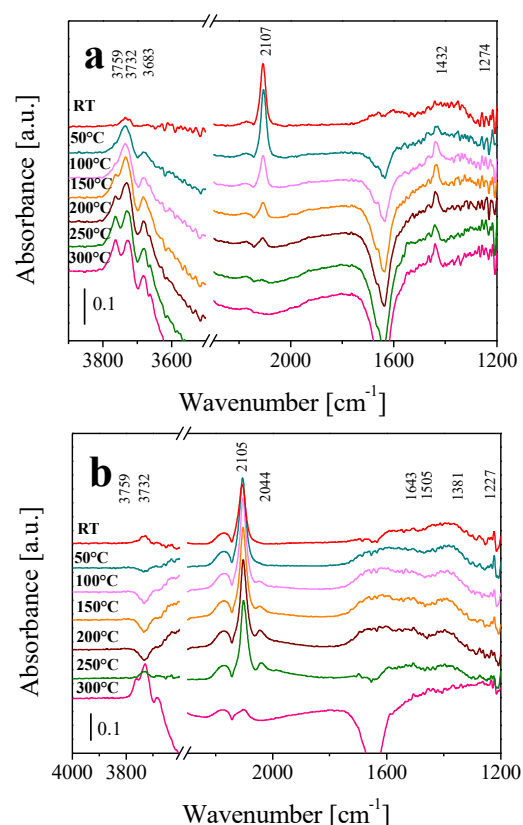


Figure 10. DRIFT spectra of CO adsorbed under $\text{CO} + \text{O}_2 + \text{N}_2$ flow at different reaction temperatures on (a) Au and (b) AuCu 1:1 activated with air at $300\text{ }^\circ\text{C}$.

For the bimetallic AuCu 1:1 catalyst, CO adsorption is observed at 2105 cm^{-1} , which is assumed to be a site composed of Au^0 and Cu^+ species. This band slightly decreases in intensity with increasing temperature, disappearing entirely at $300\text{ }^\circ\text{C}$. The formation of the $\text{Au}^{\delta-}\text{-CO}$ site (2044 cm^{-1}) occurs at $50\text{ }^\circ\text{C}$ and increases in intensity with rising temperature. Since this band does not appear in the monometallic Au catalyst, these negatively charged sites may result from the interaction of Au nanoparticles with copper oxides, as CO

adsorption modifies the electronic density of the adsorption sites [30]. Chakarova et al. [55] and Del Rio et al. [49] suggest that negatively charged gold sites are highly reactive, weakening the CO bond and promoting the formation of bicarbonates and formates. The bands 1643, 1505, 1381 and 1227 cm^{-1} are associated with the adsorption of bidentate bicarbonate, an asymmetric stretch of formates, and the adsorbed hydrogen carbonate species [49,54,56]. The band at 1643 cm^{-1} appears as the formation of $\text{Au}^{\delta-}$ sites increases, corresponding to the adsorption of bicarbonates, which act as intermediates in the CO oxidation on the AuCu catalyst. DRIFT analysis indicates that as the intensity of hydroxyl group bands decreases, bicarbonate species increase, suggesting a surface transformation during the CO reaction. At 300 °C, the hydroxyl groups reappear, coinciding with the absence of adsorbed carbonaceous species, which implies desorption or decomposition of carbon intermediates at this temperature.

2.4.3. UV-Vis Characterization

The UV-Vis spectra of the catalysts were recorded during an in situ pretreatment under airflow from RT to 300 °C (Figure 11). For the Au and AuCu samples, two bands between 300 and 700 nm increase in intensity as the temperature rises. The band centered at 512 nm corresponds to the Surface Plasmon Resonance (SPR) of Au^0 [14,57], and it becomes visible at 230 °C and fully develops up to 270 °C. The Au^0 peak of the monometallic Au sample induced by the SPR is higher than that of the bimetallic sample, indicating that the surface electron density on the monometallic Au sample is also higher [57]. According to the literature, the band that develops from 300 to 450 nm corresponds to the contribution of $\gamma\text{-Al}_2\text{O}_3$ [58,59]. In the case of the monometallic Cu sample, the SPR is undeveloped because Cu remains in the form of copper oxide.

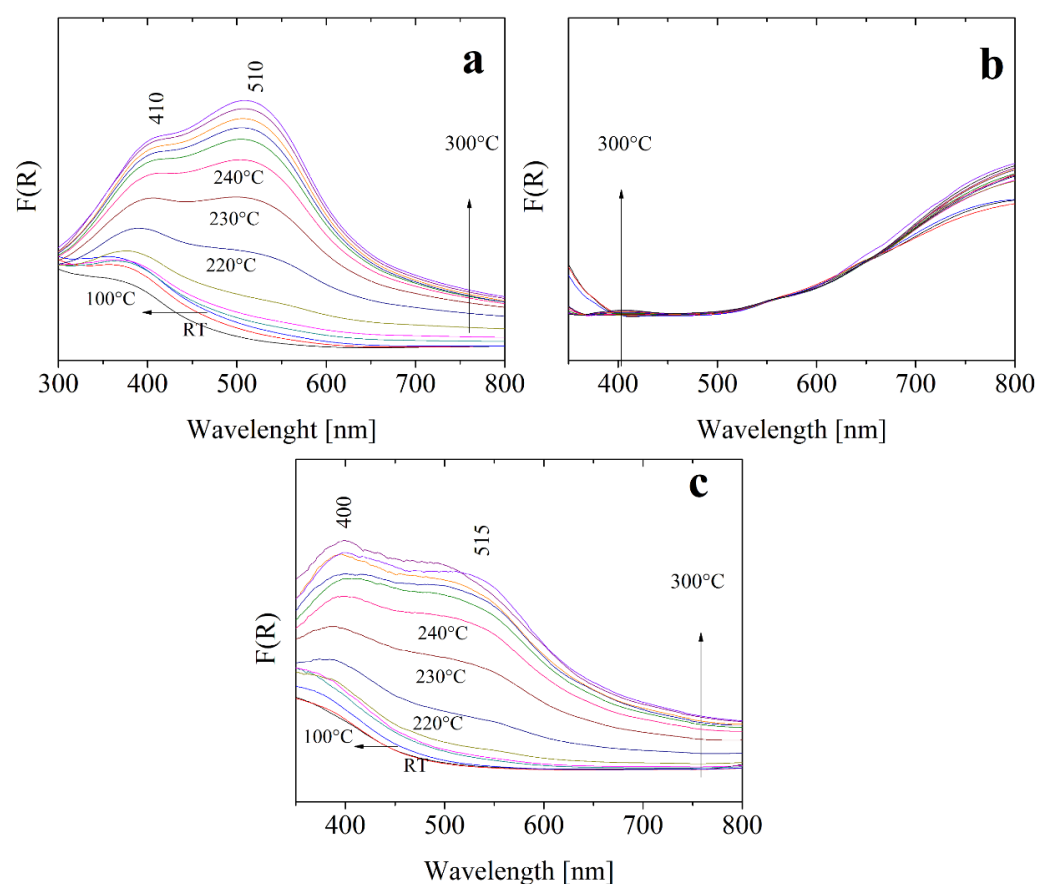


Figure 11. UV-Vis spectra of (a) Au, (b) Cu, and (c) AuCu 1:1, calcined in situ with air from RT to 300 °C.

The mono- and bimetallic samples pretreated in situ between RT and 200 °C under H_2 (Figure 12) exhibit a band that increases in intensity as the reaction temperature rises. For the Au^0 in mono- and bimetallic samples, the maxima bands are at 501 and 450 nm, respectively, while the SPR band appears at 180 °C and is already completely developed at 200 °C. The band centered at 566 nm for the monometallic Cu sample is due to the SPR of Cu^0 , whereas in the bimetallic sample, it is not observed. Interestingly, the Cu content in the bimetallic sample causes a blueshift of the Au spectrum toward low wavelengths. These observations align with the H_2 -TPR results (Figure 6) and confirm that some gold species are partially oxidized in the dried samples. The temperature differences and position of the SPR result from the interaction between the Au and Cu species and the support. Furthermore, the difference in the SPR band appearance is attributed to the type of sample treatment (Table 1), as hydrogen activation results in smaller Au nanoparticles.

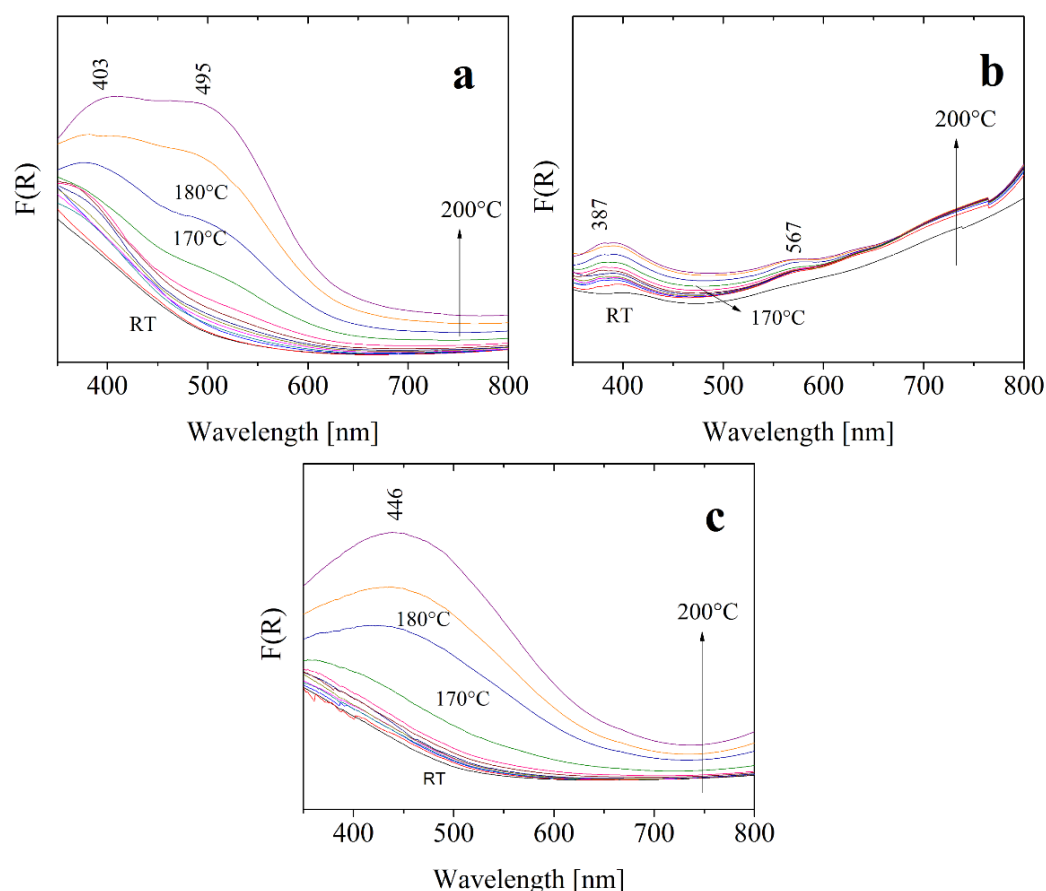


Figure 12. UV-Vis spectra of (a) Au, (b) Cu, and (c) AuCu 1:1 catalysts after in situ reduction with H_2 from RT to 200 °C.

3. Discussion

3.1. Catalytic Performance over Au and AuCu/ Al_2O_3 Catalysts

The heat treatment under an air atmosphere triggers more active catalysts at low reaction temperatures (<100 °C) than those pretreated under H_2 . The formation of CuO_x and AuO_x may occur due to the presence of oxygen in the inlet flow. Consequently, these species may increase catalytic activity. According to the TPO results (Figure 6b), the Au species are only partly reduced at 200 °C, and DRIFT also detects no CO signals, as CO adsorption occurs predominantly in Au^0 nanoparticles.

Park et al. [60] studied the pretreatments of the Au/ Al_2O_3 catalyst. They observed, through XAFS, that air treatment produces more active catalysts due to the formation of

an interface between the metal and the support, which is crucial for high activity in the CO oxidation. Furthermore, to generate Au⁰ nanoparticles, a pretreatment is required at temperatures above 240 °C, whether with air or H₂. Therefore, in this work, the Au catalysts exhibit greater activity than the bimetallic ones at temperatures below 100 °C due to the generation of this type of active site, Au⁰. Meanwhile, in the bimetallic AuCu catalysts, Cu species may have inhibited the interaction between Au and Al₂O₃, resulting in reduced CO adsorption, as evidenced by the DRIFTS spectra (Figures 8c and 9c). Additionally, in the in situ DRIFT spectra (Figure 10b), hydroxyl groups and carbon species progressively diminish from 200 °C onwards in the Cu-containing catalysts, likely due to the presence of CuO_x species. As a result, in the light-off curves, the bimetallic and Cu catalysts exhibit a marked increase in CO conversion starting at 200 °C, particularly for catalysts with higher Cu loadings, which also show improved resistance to deactivation. Adding Cu to the Au/Al₂O₃ catalyst also produces more stable materials against the sintering of Au nanoparticles due to increased reaction time and temperature. During the stability test, the Au catalyst showed an 18% decrease in CO conversion over 24 h, attributed to carbonate adsorption and nanoparticle sintering, as evidenced by the increase in particle size from 2.83 to 3.32 nm after the reaction test (Figure 5). In contrast, no increase in the size of Au nanoparticles is observed in the bimetallic catalyst. Moreover, during the CO reaction on the monometallic Au catalyst, a decline in catalytic activity is observed between 50 and 200 °C for the air-pretreated catalyst (Figure 1a), and between 100 and 200 °C for the sample pretreated with H₂ (Figure 2a). This reduction in activity is attributed to catalyst deactivation caused by the adsorption of carbonate species on the surface, as evidenced by the in situ DRIFTS spectra (Figure 10a). Carbonate formation begins at 50 °C, as indicated by the band at 1438 cm⁻¹. Conversely, the rise in CO conversion above 200 °C results from the combined effects of the catalytic activity and the contribution of the gas-phase reaction, leading to an apparent increase in overall catalytic activity. Notably, this decrease in catalytic activity is unobserved in the bimetallic catalyst, as Cu species promote the formation of intermediates, such as bicarbonates and formates, that facilitate CO₂ production.

3.2. Formation of Intermediaries over AuCu/Al₂O₃ Catalyst

The DRIFT spectra were obtained under a CO flow in the absence of O₂ as well as in a reaction mixture with CO and O₂ for both monometallic and bimetallic catalysts. Numerous studies [61,62] have suggested that the active site consists of the metal and a hydroxyl group from the support, e.g., Au⁰-OH and Cu⁺-OH.

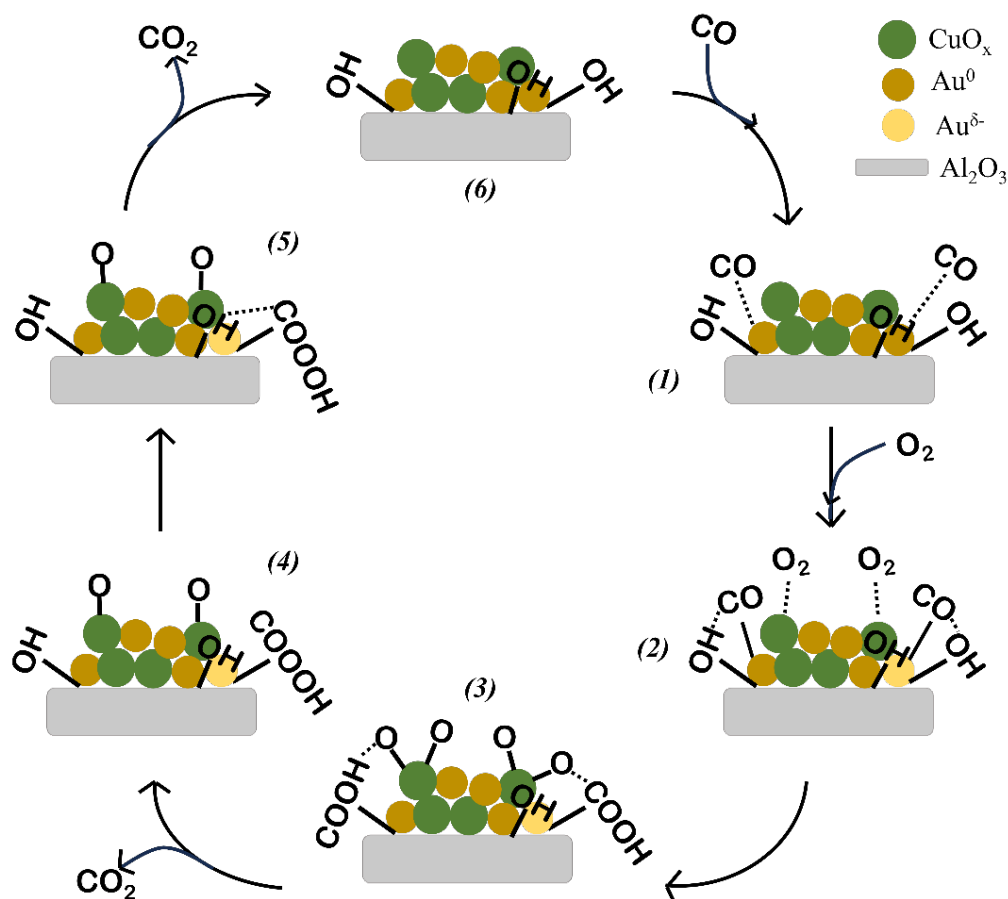
Our results show that the pretreatment condition significantly affects the nature and concentration of the hydroxyl groups, which are associated with catalytic activity as they promote a partial dehydroxylation through the removal of surface water, potentially altering the availability and reactivity of active sites. For instance, in air-pretreated catalysts, three types of hydroxyl groups were present, as observed in the bands at 3759, 3732, and 3683 cm⁻¹, identified as doubly bridging hydroxyls, a triply bridging acid hydroxide, and basic surface hydroxyls, respectively. Although H₂ pretreatment results in more intense hydroxyl bands, identified at 3732 and 3678 cm⁻¹, when high pretreatment temperatures are applied, a decrease in these bands is observed, indicating the removal of hydroxyl groups from active sites. This observation suggests that a dihydroxylation of Au⁺-OH may destabilize isolated metal sites, leading to particle sintering and a consequent loss in catalytic performance [61,62].

In the region associated with carbonyl compounds, CO adsorption is more pronounced on Au⁰ sites in the catalysts pretreated with air. This adsorption favors the formation of Au^{δ-} sites, which are recognized as promoters of intermediate species for CO₂ production. Both Au and AuCu 1:1 catalysts exhibit carbonates (CO₃²⁻), bicarbonates (HCO₃⁻), and

formates (HCOO^-). In the Au monometallic catalyst, CO_2 (2358 cm^{-1}) is formed without the presence of gaseous O_2 [62,63].

When the Au monometallic sample was exposed under reaction conditions ($\text{CO} + \text{O}_2$), the catalytic surface was fully covered by CO, leading to the formation of a $\text{Au}^0\text{-OH}$ bond and generating a hydroxycarbonyl species (2107 cm^{-1}). This species subsequently reacts with oxygen to form bicarbonates or formates, which contribute to the production of CO_2 (2358 cm^{-1}) and the saturation of the surface by forming carbonates (1438 cm^{-1}) [64,65]. It should be noted that these carbonates may act as spectator species since they do not “disappear” as the temperature increases. Oxygen activation is currently unclear; however, it is suggested that it adsorbs on the support or the metal and immediately dissociates to produce an “active” oxygen species [65,66], which then reacts with an adsorbed CO to produce CO_2 or a bicarbonate species.

In the bimetallic catalyst, a variety of carbon species are anchored on the surface. Throughout the CO oxidation reaction (Scheme 1), the adsorption of the CO molecule occurs on a complex, probably formed by the interaction with Au^0 and Cu^+ (2105 cm^{-1}), as indicated by the shift in the band compared to the monometallic catalyst and particularly by the generation of the negatively charged Au adsorption site ($\text{Au}^{\delta-}$, 2044 cm^{-1} ; steps 1 and 2 in Scheme 1).



Scheme 1. Proposed reaction pathway for the CO oxidation over the AuCu/ Al_2O_3 catalyst.

The $\text{Au}^{\delta-}$ site leads the formation of intermediates, as evidenced by the simultaneous increase in the intensity of the 2044 cm^{-1} band and the region between 1650 and 1200 cm^{-1} . In this region, bicarbonates (HCO_3^- , 1643 cm^{-1}) are formed on surface hydroxyl groups (3759 and 3732 cm^{-1} ; steps 3 and 4 in Scheme 1). The band at 1227 cm^{-1} is identified as the stretching vibration of bicarbonate, whereas the bands at 1505 and 1381 cm^{-1} corre-

spond to monodentate carbonate (CO_3^{2-}) or the symmetric stretch vibrations of formate species (HCOO^-) [6]. In this catalyst, no formation of carbonate species (1432 cm^{-1}) was observed, unlike in the monometallic Au system; consequently, no decrease in CO conversion occurred above $50\text{ }^\circ\text{C}$. These results indicate that the presence of Cu suppresses carbonate formation and markedly reduces the catalytic deactivation typically observed above this temperature in its absence. Moreover, Cu promotes CO_2 formation (2358 cm^{-1}) and facilitates surface rehydration through hydroxyl groups at 3759 and 3732 cm^{-1} (steps 5 and 6 in Scheme 1).

Table 3 summarizes the proposed mechanism from Scheme 1, including all the reaction steps and the Horiuti number (σ), which represents the number of times an elementary step must occur to obtain the overall chemical reaction for CO oxidation. The Horiuti number was obtained based on a balance of the species produced and consumed in each elementary step of the overall reaction.

Table 3. Reaction steps and catalytic cycle of the CO oxidation on AuCu/ Al_2O_3 .

Step	Elementary Reaction Step	σ
1	$\text{CO} + \text{Au}^0\text{Cu}^+-\text{OH} \rightleftharpoons \text{CO}(\text{Au}^0\text{Cu}^+-\text{OH})$	2
2	$\text{O}_2 + 2\text{Au}^0\text{Cu}^+-\text{OH} \rightleftharpoons 2\text{O}(\text{Au}^0\text{Cu}^+-\text{OH})$	1
3	$\text{CO}(\text{Au}^0\text{Cu}^+-\text{OH}) \rightarrow \text{CO}(\text{Au}^0\text{Cu}^+-\text{OH})^{\delta-}$	1
4	$\text{CO}(\text{Au}^0\text{Cu}^+-\text{OH}) + \text{O}(\text{Au}^0\text{Cu}^+-\text{OH}) \rightarrow \text{CO}_2 + 2\text{Au}^0\text{Cu}^+-\text{OH}$	1
5	$\text{CO}(\text{Au}^0\text{Cu}^+-\text{OH})^{\delta-} + \text{O}(\text{Au}^0\text{Cu}^+-\text{OH}) \rightarrow \text{COO}(\text{Au}^0\text{Cu}^+-\text{OH})^{\delta-} + \text{Au}^0\text{Cu}^+-\text{OH}$	1
6	$\text{COO}(\text{Au}^0\text{Cu}^+-\text{OH})^{\delta-} + \text{Au}^0\text{Cu}^+-\text{OH} \rightarrow \text{O}_2 + 2\text{Au}^0\text{Cu}^+-\text{OH}$	1

4. Experimental

4.1. Catalysts Preparation

4.1.1. Monometallic Samples

The Au/ Al_2O_3 and Cu/ Al_2O_3 materials were prepared using the DPU method established by Sandoval et al. [15]. Aerioxide Alu C (99.8%) was used as the support ($\gamma\text{-Al}_2\text{O}_3$) and dried at $80\text{ }^\circ\text{C}$ for at least 24 h before preparation. A solution of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (Aldrich 99.999%) and $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ (Aldrich 99.9%) was used as gold and copper precursors for the monometallic catalyst, with nominal metal loadings of 3 wt.% for Au and 0.98 wt.% for Cu.

The 3 wt.% Au/ $\gamma\text{Al}_2\text{O}_3$ catalyst was prepared using a solution of HAuCl_4 ($4.2 \times 10^{-3}\text{ M}$) and urea (0.42 M) dissolved in 74 mL of distilled water. Then, 2 g of $\gamma\text{-Al}_2\text{O}_3$ was added to the solution, and the temperature was increased to $80\text{ }^\circ\text{C}$. After reaching this temperature, it was maintained at this temperature under stirring for 16 h. 0.98 wt.% Cu/ Al_2O_3 was prepared using the same method, where a solution of 74 mL containing $\text{Cu}(\text{NO}_3)_2$ ($4.2 \times 10^{-3}\text{ M}$) and urea (0.42 M) was dissolved with 2 g of Al_2O_3 . The resulting suspension was stirred at $80\text{ }^\circ\text{C}$ for 4 h. Afterward, each sample was washed with 200 mL of distilled water at $60\text{ }^\circ\text{C}$, centrifuged four times, and dried under vacuum for 3 h at $80\text{ }^\circ\text{C}$. They were then stored in a vacuum capsule at room temperature (RT) in the absence of light.

4.1.2. Bimetallic Samples

The bimetallic samples were synthesized using the sequential deposition–precipitation method with urea as the precipitating agent. The nominal gold loading was 3 wt.%, while copper was added at different nominal Au:Cu atomic ratios: 1:0.5, 1:1, and 1:1.5, i.e., 0.49, 0.98, and 1.47 wt.% Cu, respectively. Before DPU incorporated gold, copper was first deposited on Al_2O_3 , as described above. As mentioned above, these samples were also washed, dried, and stored. The samples were identified as AuCu, followed by the atomic ratios AuCu 1:1, AuCu 1:0.5, and AuCu 1:1.5.

4.2. Catalytic Activity

The CO oxidation was evaluated in a 0.01 m internal diameter fixed-bed quartz reactor at atmospheric pressure and in a temperature range from $-5\text{ }^{\circ}\text{C}$ to pretreatment temperature (150, 200, 300, and $400\text{ }^{\circ}\text{C}$). Before the catalytic tests, 0.04 g of catalyst with a particle size less than $100\text{ }\mu\text{m}$ was treated in situ for 2 h in a 40 mL/min flow of air or hydrogen with a heating rate of $2\text{ }^{\circ}\text{C}/\text{min}$ to reach the final temperature between 150 and $400\text{ }^{\circ}\text{C}$. Afterward, the reactor was cooled to $-5\text{ }^{\circ}\text{C}$, and a reactant gas mixture of 1 vol.% CO and 1 vol.% O_2 balanced with N_2 was injected into the reactor at 100 mL/min. The output gases were analyzed with an Agilent Technologies 6890N (Agilent Technologies, Inc., Santa Clara, CA, USA) chromatograph equipped with a FID detector, a methanizer, and an HP Plot Q column. A blank experiment (without the catalyst or support) was realized under the same conditions described before. For testing catalyst deactivation, an additional set of experiments was conducted at 20, 50, and $100\text{ }^{\circ}\text{C}$ for 24 h after airflow (40 mL/min) activation in situ at $300\text{ }^{\circ}\text{C}$ ($2\text{ }^{\circ}\text{C}/\text{min}$) under the same reaction conditions previously employed. To ensure that all experimental data were collected under intrinsic kinetic conditions, external and internal mass and heat transport limitations were evaluated using the criteria established in the literature [67]. Table S1 (Supplementary Information) summarizes the evaluated kinetic criteria for an experiment conducted under extreme conditions to maximize the CO reaction rate.

4.3. Characterization Techniques

In the dried samples, surface chemical analyses of Au and Cu were performed using energy dispersive X-ray spectroscopy (EDS) in a JEOL Model 5900-LV (JEOL Ltd., Tokyo, Japan) with an Oxford Model ISIS microanalysis system. The Au and Cu were expressed in wt.%.

The specific surface area of the samples was determined using the Brunauer-Emmett-Teller (BET) method, while the pore diameter distribution was estimated using the Barrett-Joyner-Halenda (BJH) method applied to the N_2 desorption isotherm measured at $-196\text{ }^{\circ}\text{C}$ in a Micromeritics ASAP 2020 apparatus. Before the analysis, the sample was degassed under vacuum conditions at RT for 18 h.

Transmission electron microscopy (TEM) studies were conducted using a JEOL 2200FS microscope (JEOL Ltd., Tokyo, Japan) equipped with GIF and Z-contrast annular detectors. Micrographs were acquired for samples pretreated with air at $300\text{ }^{\circ}\text{C}$ for 2 h and for samples used after the CO oxidation stability reaction. The average size of the gold particles was determined by measuring 1000 particles for each catalyst.

The hydrogen temperature-programmed reduction (H_2 -TPR) analysis of the dried catalysts (40 mg) was performed using a Micromeritics AutoChem II system with a flow of 10% H_2/Ar gas mixture (25 mL/min) and a heating rate of $10\text{ }^{\circ}\text{C}/\text{min}$ from RT to $600\text{ }^{\circ}\text{C}$. The catalysts (50 mg) were examined in the same system by oxygen temperature-programmed oxidation (TPO) with a 25 mL/min flow of 10% O_2/He . The samples were heated from RT to $800\text{ }^{\circ}\text{C}$ at a rate of $10\text{ }^{\circ}\text{C}/\text{min}$.

CO adsorption was monitored using diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), and the samples were analyzed with a Nicolet 670 FT-IR spectrophotometer equipped with a Praying Mantis accessory and a low/high-temperature reaction chamber by Harrick. For each experiment, 50 mg of dried sample were packed in the sample holder and pretreated in situ under airflow (50 mL/min) at $300\text{ }^{\circ}\text{C}$, with a heating rate of $2\text{ }^{\circ}\text{C}/\text{min}$ for 1 h. Afterward, the sample was cooled to RT using the same gas flow and purged with N_2 . Subsequently, a flow of 5% CO and 95% N_2 (50 mL/min) was introduced into the sample cell, and several spectra were recorded as the temperature increased. Additionally, the Au and Au-Cu 1:1 samples, pretreated with air at $300\text{ }^{\circ}\text{C}$,

were analyzed in the spectrometer under reaction conditions with the introduction of a gas mixture composed of 1% CO, 1% O₂, and 98% N₂ as the temperature was increased from RT to 300 °C.

Diffuse reflectance UV-Vis spectra of the samples were obtained using a CARY 5000 (UV-VIS-NIR) spectrophotometer (Agilent Technologies, Inc., Santa Clara, CA, USA) equipped with a Praying Mantis and a high-temperature reaction chamber by Harrick. In each experiment, 50 mg of the dried sample was packed and pretreated in situ at 300 °C under airflow (50 mL/min), with the spectra recorded during the treatment process. A spectrum of Teflon (from Aldrich (MilliporeSigma, Louis, MO, USA)) was used as a reference.

The X-ray photoelectron spectroscopy (XPS) experiments were performed using a Kratos AXIS Ultra spectrometer (Kratos Analytical Ltd., Manchester, UK) equipped with a hemispherical electron analyzer and AlK α radiation source (1486.6 eV) energized at 15 kV and 30 mA. The spectrometer operated with a step energy of 23.5 eV and a pressure of 3×10^{-8} bar in the analysis chamber to avoid surface contamination by reaction with the ambient atmosphere. Spectra peak deconvolution, positions, and areas were obtained by fitting a weighted least-squares model (50% Gaussian, 50% Lorentzian) to the experimental data.

X-ray diffraction (XRD) measurements were performed using a Bruker D8 Discover diffractometer (Bruker AXS GmbH, Karlsruhe, Germany) equipped with a copper radiation source ($\lambda = 1.5418 \text{ \AA}$). Data were collected over a $2\theta^\circ$ range from 10° to 80° , with a step size of 0.04° and a counting time of 0.6 s per step.

5. Conclusions

The incorporation of copper significantly enhances the catalytic performance of Au/ γ -Al₂O₃ by improving its structural stability and mitigating deactivation. This promotional effect is attributed to the inhibition of gold nanoparticle sintering and the reduction of carbonate accumulation on active sites. We show that low-temperature air pretreatment serves as an effective activation strategy for both monometallic Au and bimetallic AuCu catalysts, resulting in higher CO conversion than H₂-pretreated counterparts. Regardless of the pretreatment atmosphere, the presence of Au⁰ and CuO_x species contributes to catalytic activity, although these species remain only partially reduced even at 200 °C. Furthermore, calcination at 300 °C facilitates the formation of Cu⁺/Cu²⁺ and reduced Au species. The increase in surface hydroxyl groups observed between 100 °C and 200 °C likely promotes active-site regeneration and enhances catalyst stability, particularly in Cu-containing systems. In contrast to the rapid deactivation of monometallic Au catalysts, primarily caused by carbonate accumulation, the incorporation of copper in bimetallic systems suppresses carbonate coverage at elevated temperatures, resulting in markedly improved thermal stability. Overall, these findings underscore the dual role of copper as both a structural and functional promoter, thereby enabling the rational design of durable, thermally robust, and cost-effective catalytic systems for low-temperature CO oxidation on non-reducible supports.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal15111080/s1>, Figure S1: (a) N₂ adsorption/desorption isotherms and (b) pore size distributions of mono- and bimetallic samples; Figure S2: XRD patterns of samples Au and AuCu 1:1 supported on Al₂O₃ calcined at 300 °C; Table S1: Assessment of the intrinsic kinetic and ideal plug flow regime criteria in the CO oxidation tests.

Author Contributions: K.L.: Investigation; Writing—original draft, G.C.-G.: Conceptualization, Funding acquisition, Methodology, Project administration, Resources, Supervision, Writing—review & editing. R.Z.: Conceptualization, Funding acquisition, Methodology, Writing—review & editing. J.F.G.-S.:

Resources, Writing—review & editing. A.S.: Conceptualization, Funding acquisition, Methodology, Project administration, Resources, Supervision, Writing—review & editing. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflicts of interest.

Abbreviations

The following abbreviations are used in this manuscript:

CO	Carbon monoxide
DPU	Deposition–precipitation with urea
DRIFTS	Diffuse Reflectance Infrared Fourier Transform Spectroscopy
EDS	Energy Dispersive X-ray Spectroscopy
H ₂ -TPR	Hydrogen Temperature-Programmed Reduction
TPO	Oxygen Temperature-Programmed Oxidation
RT	Room temperature
SPR	Surface Plasmon Resonance
TEM	Transmission Electron Microscopy
XPS	X-ray Photoelectron Spectroscopy

References

1. Kasmi, A.E.; Arshad, M.F.; Waqas, M.; Monguen, C.K.F.; Azar, F.Z.; Wu, L.N.; Tian, Z.Y. Insights into Catalytic Oxidation Mechanism of CO Over Cu Catalyst: Experimental and Modeling Study. *Mater. Res. Bull.* **2023**, *166*, 112343. [\[CrossRef\]](#)
2. Guo, S.; Zhang, Q.; He, M.W.J.; Liu, J.; Ming, C.; Qi, J.; Wang, C. Study on CO migration characteristics and hazard potential function under ventilation after roof cutting blasting. *J. Wind Eng. Ind. Aerodyn.* **2023**, *239*, 105464. [\[CrossRef\]](#)
3. Ruas, F.; Mendonca, C.; Corte-Real, F.; Nunp-Vieira, D.; Teixeira, H. Carbon monoxide poisoning as a cause of death and differential diagnosis in the forensic practice: A retrospective study 2000–2010. *J. Forensic Leg. Med.* **2014**, *24*, 1–6. [\[CrossRef\]](#)
4. Haruta, M. When gold is not noble: Catalysis by nanoparticles. *Chem. Rec.* **2003**, *3*, 75–87. [\[CrossRef\]](#)
5. Sandoval, A.; Gómez-Cortés, A.; Zanella, R.; Díaz, G.; Saniger, J. Gold nanoparticles: Support effects for the WGS reaction. *J. Mol. Catal. A Chem.* **2007**, *278*, 200–208. [\[CrossRef\]](#)
6. Bocuzzi, F.; Chiorino, A.; Manzoli, M.; Andreeva, D.; Tabakova, T. FTIR study of the low-temperature water-gas shift reaction on Au/Fe₂O₃ and Au/TiO₂ Catalysts. *J. Catal.* **1999**, *188*, 176–185. [\[CrossRef\]](#)
7. Che-Galicia, G.; Ruíz-Santoyo, V.; Zanella, R.; Mendoza-González, N.Y.; Ruiz-López, I.I.; Sampieri, A. Kinetic mechanism of CO oxidation on gold catalyst supported on TiSBA-15 previously treated in a hydrogen atmosphere. *Chem. Eng. J.* **2021**, *405*, 126644. [\[CrossRef\]](#)
8. Zou, X.; Qi, S.; Suo, Z.; An, L.; Li, F. Activity and deactivation of Au/Al₂O₃ catalyst for low-temperature CO oxidation. *Catal. Commun.* **2007**, *8*, 784–788. [\[CrossRef\]](#)
9. Sui, Q.; Cao, M.; Zhang, Y.; Li, Q.; Ding, J. Monolithic CoMgAl mixed metal oxide nanosheets on Al₂O₃ granules for the efficient advanced oxidation process. *Mater. Lett.* **2023**, *353*, 135302. [\[CrossRef\]](#)
10. Ivanova, A. Aluminum oxide and systems based on it: Properties and applications. *Kinet. Catal.* **2012**, *53*, 425–439. [\[CrossRef\]](#)
11. Wu, X.; Xu, L.; Weng, D. The thermal stability and catalytic performance of Ce-Zr promoted Rh-Pd/ γ -Al₂O₃ automotive catalysts. *Appl. Surf. Sci.* **2004**, *221*, 375–383. [\[CrossRef\]](#)
12. Chen, C.; Li, Y.; Ma, W.; Guo, S.; Wang, Q.; Li, Q. Mn-Fe-Mg-Ce loaded Al₂O₃ catalyzed ozonation for mineralization of refractory organic chemicals in petroleum refinery wastewater. *Sep. Purif. Technol.* **2017**, *183*, 1–10. [\[CrossRef\]](#)
13. Liu, Q.; Wang, A.; Wang, X.; Gao, P.; Wang, X.; Zhang, T. Synthesis, characterization and catalytic applications of mesoporous γ -alumina from boehmite sol. *Microporous Mesoporous Mater.* **2008**, *111*, 323–333. [\[CrossRef\]](#)

14. Gluhoi, A.; Bogdanchikova, N.; Nieuwenhuys, B. The effect of different types of additives on the catalytic activity of Au/Al₂O₃ in propene total oxidation: Transition metal oxide and ceria. *J. Catal.* **2005**, *229*, 154–162. [\[CrossRef\]](#)
15. Sandoval, A.; Louis, C.; Zanella, R. Improved activity and stability in CO oxidation of bimetallic Au-Cu/TiO₂ catalysts prepared by deposition-precipitation with urea. *Appl. Catal. B Environ.* **2012**, *140*, 363–377. [\[CrossRef\]](#)
16. Najafshirtari, S.; Brescia, R.; Guardia, P.; Marras, S.; Manna, L.; Colombo, M. Nanoscale transformations of alumina-supported AuCu ordered phase nanocrystals and their activity in CO oxidation. *ACS Catal.* **2015**, *5*, 2154–2163. [\[CrossRef\]](#)
17. Mozer, T.; Dziuba, D.; Vieira, C.; Passos, F. The effect of copper on the selective carbon monoxide over alumina supported gold catalysis. *J. Power Sources* **2009**, *187*, 209–215. [\[CrossRef\]](#)
18. Stadnichenko, A.I.; Slavinskaya, E.M.; Stonkus, O.A.; Boronin, A.I. Low-Temperature CO Oxidation by the Pt/CeO₂ Based Catalysts. *ChemCatChem* **2024**, *16*, e202301727. [\[CrossRef\]](#)
19. Moroz, B.; Pyryaev, P.; Zaikovskii, V.; Bukhtiyarov, V. Nanodispersed Au/Al₂O₃ catalysts for low-temperature CO oxidation: Results of research activity at the Boreskov Institute of Catalysis. *Catal. Today* **2009**, *144*, 292–305. [\[CrossRef\]](#)
20. Miao, Y.; Wang, J.; Li, W. Enhanced catalytic activities and selectivities in preferential oxidation of CO over ceria-promoted Au/Al₂O₃ catalysts. *Chin. J. Catal.* **2016**, *37*, 1721–1728. [\[CrossRef\]](#)
21. Ribeiro, N.; Mendes, F.; Perez, C.; Souza, M.; Schmal, M. Selective CO oxidation with nano gold particles-based catalysts over Al₂O₃ and ZrO₂. *Appl. Catal. A Gen.* **2008**, *347*, 62–71. [\[CrossRef\]](#)
22. Suo, Z.; Ma, C.; Jin, M.; He, T.; An, Li. The active phase of Au-Pd/Al₂O₃ for CO oxidation. *Catal. Comm.* **2008**, *9*, 2187–2190. [\[CrossRef\]](#)
23. Lu, R.; He, L.; Wang, Y.; Gao, X.; Li, W. Promotion effects of nickel-doped Al₂O₃-nanosheet-supported Au catalysts for CO oxidation. *Chin. J. Catal.* **2020**, *41*, 350356. [\[CrossRef\]](#)
24. Hellmer, A.; Mendoza-Cruz, R.; Zanella, R. Enhancement of the CO oxidation reaction: Impact of the precursor addition sequence on the synthesis of Au-Co₃O₄/Al₂O₃ catalysts. *MRS Commun.* **2024**, *14*, 1184–1190. [\[CrossRef\]](#)
25. Thommes, M.K.K.; Neimark, A.; Oliver, J.; Rodríguez-Reynoso, F.; Rouquerol, J.; Sing, K. Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report). *Pure Appl. Chem.* **2015**, *87*, 1051–1069. [\[CrossRef\]](#)
26. Xu, Y.; Du, X.; Li, J.; Wang, P.; Zhu, J.; Ge, F.; Zhou, J.; Song, M.; Zhu, W. A comparison of Al₂O₃ and SiO₂ supported Ni-based catalysts in their performance for the dry reforming of methane. *J. Fuel Chem. Technol.* **2019**, *47*, 199–208. [\[CrossRef\]](#)
27. Zanella, R.; Louis, C. Influence of the conditions of thermal treatments and storage on the size of the gold particles in Au/TiO₂ samples. *Catal. Today* **2005**, *107*, 768–777. [\[CrossRef\]](#)
28. Dandekar, A.; Vannice, A. Determination of the dispersion and surface oxidation states of supported Cu catalysts. *J. Catal.* **1998**, *178*, 621–639. [\[CrossRef\]](#)
29. Yue, L.; Zhao, W.; Li, J.; Wu, R.; Wang, Y.; Zhang, H.; Zhao, Y. Low-temperature CO preferential oxidation in H₂-rich stream over Indium modified Pd-Cu/Al₂O₃ catalyst. *J. Colloid Interface Sci.* **2024**, *662*, 109–118. [\[CrossRef\]](#)
30. Miao, Y.; Shi, L.; Sun, Q.; Li, W. A highly efficient potassium-treated Au-Cu/Al₂O₃ catalyst for the preferential oxidation of carbon monoxide. *RSC Adv.* **2016**, *6*, 24603. [\[CrossRef\]](#)
31. Svintsitskiy, D.; Kardash, T.; Stonkus, O.; Slavinskaya, E.; Stadnichenko, A.; Koscheev, S.; Chupakhin, A.; Boronin, A. In Situ XRD, XPS, TEM, and TPR study of highly active in CO oxidation CuO nanopowders. *J. Phys. Chem. C* **2013**, *117*, 14588–14599. [\[CrossRef\]](#)
32. Poreddy, R.; Engelbrekt, C.; Riisager, A. Copper oxide as efficient catalyst for oxidative dehydrogenation of alcohols with air. *Catal. Sci. Technol.* **2015**, *5*, 2467–2477. [\[CrossRef\]](#)
33. Camposeco, R.; Regmi, C.; Lee, S.; Rodríguez-González, V. Tailoring surface nanotube properties with copper nanoparticles for hydrogen production performance. *Mater. Lett.* **2021**, *290*, 129500. [\[CrossRef\]](#)
34. Hoang, D.; Dang, T.; Engeldinger, J.; Schneider, M.; Radnik, J.; Richter, M.; Martin, A. TPR investigations on the reducibility of Cu supported on Al₂O₃, zeolite Y and SAPO-5. *J. Solid State Chem.* **2011**, *184*, 1915–1923. [\[CrossRef\]](#)
35. Jansson, J. Low-temperature CO oxidation over Co₃O₄/Al₂O₃. *J. Catal.* **2000**, *194*, 55–60. [\[CrossRef\]](#)
36. Tsai, H.; Hu, E.; Perng, K.; Chen, M.; Wu, J.; Chang, Y. Instability of gold oxide Au₂O₃. *Surf. Sci.* **2003**, *537*, 447–450. [\[CrossRef\]](#)
37. Cudennec, Y.; Lecerf, A. The transformation of Cu(OH)₂ into CuO, revisited. *Solid State Sci.* **2003**, *5*, 1471–1474. [\[CrossRef\]](#)
38. Chang, S.; Jampang, A. Enhanced adsorption selectivity of Au(III) over Cu(II) from acidic chloride solution by chitosan/palm kernel fatty acid distillate/magnetite nanocomposites. *Int. J. Biol. Macromol.* **2023**, *252*, 126491. [\[CrossRef\]](#)
39. García-Serrano, J.; Galindo, A.; Pal, U. Au-Al₂O₃ nanocomposites: XPS and FTIR spectroscopic studies. *Sol. Energy Mater. Sol. Cells* **2004**, *82*, 291–298. [\[CrossRef\]](#)
40. Megginson, R.; Grillo, F.; Francis, S.; Paes, V.; Trombini, H.; Grande, P.; Rossall, A.; Van Den Berg, J.; Baddeley, C. Thermal behavior of Cu and Au nanoparticles grown on CeO₂ thin films. *Appl. Surf. Sci.* **2022**, *575*, 151656. [\[CrossRef\]](#)
41. Guan, Y.; Fu, S.; Song, W.; Zhang, X.; Liu, B.; Zhang, F.; Chai, F. Controllable synthesis of sea urchin-like Cu-Au bimetallic nanospheres and their utility as efficient catalyst for hydrogenation of 4-nitrophenol. *J. Solid State Chem.* **2023**, *322*, 123968. [\[CrossRef\]](#)

42. Camposeco, R.; Hinojosa-Reyes, M.; Zanella, R. Highly efficient photocatalytic hydrogen evolution by using Rh as co-catalyst in the Cu/TiO₂ system. *Int. J. Hydrogen Energy* **2021**, *46*, 26074–26086. [\[CrossRef\]](#)
43. Zhou, X.; Li, L.; Li, Z.; Fan, L.; Kang, W.; Cheng, B. The preparation of continuous CeO₂/CuO/Al₂O₃ ultrafine fibers by electro-blowing spinning (EBS) and its photocatalytic activity. *J. Mater. Sci. Mater. Electron.* **2017**, *28*, 12580–12590. [\[CrossRef\]](#)
44. Rotole, J.; Sherwood, P. Gamma-alumina by XPS. *Surf. Sci. Spectra* **1998**, *5*, 112910. [\[CrossRef\]](#)
45. Islas, S.; Zanella, R.; Saniger, J. Thermal activation process of Au/TiO₂ system: A molecular spectroscopy study. *RSC Adv.* **2016**, *6*, 42554. [\[CrossRef\]](#)
46. Leba, A.; Davran-Candan, T.; Önsan, Z.; Yildirim, R. DRIFTS study of selective CO oxidation over Au/ γ -Al₂O₃ catalyst. *Catal. Commun.* **2012**, *29*, 6–10. [\[CrossRef\]](#)
47. Zeinalipour-Yazdi, C.; Cooksy, A.; Efstathiou, A. A diffuse reflectance infrared Fourier-Transform spectra and Density Functional Theory study of CO adsorption on Rh/ γ -Al₂O₃. *J. Phys. Chem. C* **2007**, *111*, 13872–13878. [\[CrossRef\]](#)
48. Reina, T.; Ivanova, S.; Idakiev, V.; Delgado, J.; Ivanov, I.; Tabakova, T.; Centeno, M.; Odriozola, J. Impact of Ce-Fe synergism on the catalytic behavior of Au/CeO₂-FeO_x/Al₂O₃ for pure H₂ production. *Catal. Sci. Technol.* **2013**, *3*, 779. [\[CrossRef\]](#)
49. Del Río, E.; Collins, S.; Aguirre, A.; Chen, X.; Delgado, J.; Calvino, J.; Bernal, S. Reversible deactivation of Au/Ce_{0.62}Zr_{0.38}O₂ catalyst in CO oxidation: A systematic study of CO₂-triggered carbonate inhibition. *J. Catal.* **2014**, *316*, 210–218. [\[CrossRef\]](#)
50. Vila, F.; López, M.; Ojeda, M.; Fierro, J.; Mariscal, R. Glycerol hydrogenolysis to 1,2-propanediol with Cu/ γ -Al₂O₃: Effect of the activation process. *Catal. Today* **2012**, *187*, 122–128. [\[CrossRef\]](#)
51. Haneda, M.; Watanabe, T.; Kamiuchi, N.; Ozawa, M. Effect of platinum dispersion on the catalytic activity of Pt/Al₂O₃ for the oxidation of carbon monoxide and propene. *Appl. Catal. B* **2013**, *142*, 8–14. [\[CrossRef\]](#)
52. Liao, X.; Liu, Y.; Chu, W.; Sall, S.; Petit, C.; Pitchon, V.; Caps, V. Promoting effect of Au-Cu/CeO₂-catalyzed CO oxidation: A combined kinetic and in situ DRIFT study. *J. Catal.* **2020**, *382*, 329–338. [\[CrossRef\]](#)
53. Wijnja, H.; Schulthess, C. ATR-FTIR and DRIFT spectroscopy of carbonate species at the aged γ -Al₂O₃/water interface. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **1999**, *55*, 861–872. [\[CrossRef\]](#)
54. Gaur, S.; Wu, H.; Stanley, G.; More, K.; Kumar, C.; Spinvey, J. CO oxidation studies over cluster-derived Au/TiO₂ and AUOLite Au/TiO₂ catalysts using DRIFTS. *Catal. Today* **2013**, *208*, 72–81. [\[CrossRef\]](#)
55. Chakarova, K.; Mihaylov, M.; Ivanova, S.; Centeno, M.; Hadjiivanov, K. Well-defined negatively charged gold carbonyls on Au/SiO₂. *J. Phys. Chem. C* **2011**, *115*, 21273–21282. [\[CrossRef\]](#)
56. El-Moemen, A.; Abdel-Mageed, A.; Bansmann, J.; Parlinska-Wojtan, M.; Behm, R.; Kucerová, G. Deactivation of Au/CeO₂ catalysts during CO oxidation: Influence of pretreatment and reaction conditions. *J. Catal.* **2016**, *341*, 160–179. [\[CrossRef\]](#)
57. Yang, K.; Liu, J.; Si, R.; Chen, X.; Dai, W.; Fu, X. Comparative study of Au/TiO₂ and Au/Al₂O₃ for oxidizing CO in the presence of H₂ under visible light irradiation. *J. Catal.* **2014**, *317*, 229–239. [\[CrossRef\]](#)
58. Chen, B.; Zhu, X.; Crocker, M.; Wang, Y.; Shi, C. Complete oxidation of formaldehyde at ambient temperature over γ -Al₂O₃ supported Au catalyst. *Catal. Commun.* **2013**, *42*, 93–97. [\[CrossRef\]](#)
59. Eskandari, M.; Shafyei, V.; Karimzadeh, F. One-step fabrication of Au@Al₂O₃ core-shell nanoparticles by continuous-wave fiber laser ablation of thin gold layer on aluminum surface: Structural and optical properties. *Opt. Laser Technol.* **2020**, *126*, 106066. [\[CrossRef\]](#)
60. Park, E.; Lee, J. Effects of pretreatment conditions on CO oxidation over supported Au catalysts. *J. Catal.* **1999**, *186*, 1–11. [\[CrossRef\]](#)
61. Costello, C.; Yang, J.; Law, H.; Wang, Y.; Lin, J.; Marks, L.; Kung, M.; Kung, H. On the potential role of hydroxyl groups in CO oxidation over Au/Al₂O₃. *Appl. Catal. A* **2003**, *243*, 15–24. [\[CrossRef\]](#)
62. Kung, M.; Davis, R.; Kung, H. Understanding Au-catalyzed low-temperature CO oxidation. *J. Phys. Chem. A* **2007**, *111*, 11768. [\[CrossRef\]](#)
63. Miao, Y.; Shi, L.; Cai, L.; Li, W. Alumina hollow microsphere supported gold catalysts for low temperature CO oxidation: Effect of the pretreatment atmospheres on the catalytic activity and stability. *Gold Bull.* **2014**, *47*, 275–282. [\[CrossRef\]](#)
64. Wang, D.; Hao, Z.; Cheng, D.; Shi, X.; Hu, C. Influence of pretreatment conditions on low-temperature CO oxidation over Au/MO_x/Al₂O₃ catalysts. *J. Mol. Catal. A Chem.* **2003**, *200*, 229–238. [\[CrossRef\]](#)
65. Min, B.; Friend, C. Heterogeneous gold-based catalysis for green chemistry: Low temperature CO oxidation and propene oxidation. *Chem. Rev.* **2007**, *107*, 2709–2724. [\[CrossRef\]](#) [\[PubMed\]](#)
66. Daté, M.; Imai, H.; Tsubota, S.; Haruta, M. In situ measurements under flow condition of the CO oxidation over supported gold nanoparticles. *Catal. Today* **2007**, *1222*, 222–225. [\[CrossRef\]](#)
67. Perego, C.; Peratello, S. Experimental methods in catalytic kinetics. *Catal. Today* **1999**, *52*, 133–145. [\[CrossRef\]](#)

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