

Elucidating the Facet-dependent Selectivity for CO₂ Electroreduction to Ethanol of Cu-Ag Tandem Catalysts

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Abstract

Despite being desirable high-value products of the electrochemical CO₂ reduction reaction (CO₂RR), alcohols are still obtained with lower selectivity compared to hydrocarbons and the reaction pathways leading to their formation are still under debate. In this joint experimental-computational work, we exploit structural sensitivity effects to elucidate the ethanol-producing active sites on Cu-Ag CO₂RR tandem catalysts. Specifically, methane-selective Cu nano-octahedra (Cu_{oh}), enclosed by (111) facets, and ethylene-selective Cu nano-cubes (Cu_{cub}), enclosed by (100) facets, are mixed with CO-selective Ag nanospheres (Ag_{sph}) to form Cu_{oh}-Ag and Cu_{cub}-Ag bimetallic catalysts. Ethanol is selectively enhanced via the *CH_x-*CO coupling pathway at the terraces of Cu_{oh}-Ag in the CO-enriched environment generated by the Ag_{sph}. Conversely, on Cu_{cub}-Ag ethanol is selectively produced via the same pathway at the edges and corners of Cu_{cub} while ethylene continues to be produced at the terraces. Such facet dependence explains the higher ethanol-to-ethylene ratio on the Cu_{oh}-Ag. These findings illustrate how tandem catalysis and structure-sensitive effects can be combined to obtain notable changes in the selectivity of electrochemical reactions.

Introduction

The electrochemical CO₂ reduction reaction (CO₂RR) is a promising approach to mitigate the rising atmospheric CO₂ levels by converting it into fuels and chemical feedstocks, which becomes a means to store renewable energy.^{1,2} Among single-metal surfaces, copper is the only catalyst capable of generating significant amounts of higher-value hydrocarbons and oxygenates.^{1,3,4} Until now, most studies have focused on hydrocarbons and these efforts have resulted in Faradaic efficiencies (FE) up to 83% for ethylene production.^{5,6} Instead, while being extremely valuable products, alcohols are still obtained with considerably lower efficiencies.
1,2

Recently, tandem schemes have emerged as a promising strategy to promote C₂₊ and alcohols.^{7–13} In these schemes, a CO-producing domain (i.e. Au, Ag, Zn, Fe porphyrins) is coupled to a Cu catalyst. In all studies, the local enrichment of the CO intermediate is shown to suppress the competing hydrogen evolution reaction (HER) while enhancing the selectivity towards C₂₊ products. In particular, ethanol (C₂H₅OH) and ethylene (C₂H₄) were both promoted in most cases.^{7–9,11–13} The current state-of-the-art FE for C₂H₅OH is 41% and was achieved by functionalizing the Cu surface with CO-producing Fe porphyrin complexes, thus demonstrating the huge potential of tandem electrocatalysts.¹¹

In general, the knowledge of the reaction pathways, strategies, structural and compositional sensitivities favouring the formation of C₂H₅OH over C₂H₄ still remains limited.^{11–19} A few experimental and computational studies have suggested that the pathways toward C₂H₅OH and C₂H₄ on Cu share several intermediates.^{15,20} Li et al. calculated that, under high *CO coverage, the C₂H₅OH pathway is favored to a larger extent on Cu(111) with respect to Cu(100) via a mechanism that bifurcates from the C₂H₄ pathway several steps after *CO dimerization.¹¹ On the contrary, Ting et al. predicted that Cu(111) under high *CO coverage could stabilize the C₂H₅OH-yielding intermediate through a *CH_x-*CO coupling step, bypassing *CO dimerization.¹² Investigating the effect of elevated *CO coverages in the presence of Cu surfaces that favor either *CH_x or dimerized *CO could aid in addressing this confusion, possibly leading to strategies to promote C₂H₅OH over C₂H₄. No experimental work has specifically investigated facet-dependent selectivity of tandem catalysis in CO₂RR so far.

Shape-controlled nanocrystals (NCs) have been demonstrated to be ideal platform to translate into more realistic conditions the structure-dependent selectivity identified on metal single crystals.^{6,21–28} In CO₂RR, Cu nano-octahedra (Cu_{oh}), enclosed by (111) facets, and Cu nanocubes (Cu_{cub}), enclosed by (100) facets, were found to be selective towards methane (CH₄) and ethylene (C₂H₄), respectively, in agreement with studies on Cu surfaces.^{18,24,25,29–32} The facet-dependent selectivity of Cu NCs involves stabilization and high coverage of *CH_x species for CH₄ on Cu(111) and *CO-*CO coupling for C₂H₄ on Cu (100).^{15,19,33,34}

Herein, we couple shape-controlled Cu NCs and Ag NCs to exploit structural effects in CO₂RR tandem catalysis and to elucidate the C₂H₅OH vs C₂H₄ branching point in the reaction pathway. Specifically, Cu_{oh} and Cu_{cub} are mixed with Ag nanospheres (Ag_{sph}) to form Cu_{oh}-Ag and Cu_{cub}-Ag bimetallic catalysts, respectively. In agreement with previous studies, our tandem catalysts display increasing C₂₊ and alcohol selectivity. At the same time, we show that the C₂H₅OH/C₂H₄ selectivity ratios attained on the Cu_{oh}-Ag are higher than those on the Cu_{cub}-Ag (2.4 vs 1.5) and are, to the best of our knowledge, among the highest reported on electronically unaltered Cu. Mechanistically speaking, we find that the alternative pathway via CH_x-CO coupling to produce ethanol can also be opened on (100) facets and, by virtue of its structural sensitivity, the production of C₂ species is boosted. However, on the Cu (111) facet, only the ethanol pathway is specifically enhanced without competition with the ethylene formation.

Results and Discussion

In order to explore structural effects in tandem catalysts for the CO₂RR, we prepared Cu-Ag catalysts by homogeneously mixing Ag_{sph} with Cu_{oh} and Cu_{cub}, with average sizes of 9, 80 and 40 nm, respectively (**Figure S1**). These sizes were chosen as they were found in previous studies to be optimal for the production of CO, CH₄ and C₂H₄, respectively.^{24,25,35}

Transmission electron microscopy (TEM) was used to characterize the morphology and structure of the two catalysts before and after the CO₂RR. The as-prepared catalysts consist of homogeneously mixed and well dispersed Cu and Ag NCs with a Cu:Ag mass ratio of 2:3 (**Figure 1a,b**). After only 15 minutes of electrolysis, the Cu_{cub} and Cu_{oh} preserve their morphologies, while the Ag_{sph} form a network structure intimately surrounding the Cu NCs (**Figure 1c,d**), in agreement with previous studies.^{24,25,35} These structures remain unchanged

after one hour of operation. The corresponding X-Ray Diffraction (XRD) patterns (**Figure 1e**) evidence the characteristic features of the Cu_{oh} and Cu_{cub} , with preferential orientation along the (111) and (100) directions, respectively. The peak corresponding to the Ag NCs is less intense and broader due to the much smaller size of the crystallites. X-ray photoelectron spectra (XPS) (**Figure 1f** and **Figure S2**) of the Cu-Ag catalysts revealed that the Cu component is largely in its metallic state. The $\text{Cu}2\text{p}_{3/2}$ peaks appeared at similar values of 932.68 and 932.64 eV for the Cu_{cub} and Cu_{oh} , respectively. Both Cu-Ag catalysts also presented similar $\text{Ag}3\text{d}_{5/2}$ spectra, with the $\text{Ag}3\text{d}_{5/2}$ peaks appearing at 368.36 and 368.18 eV for the $\text{Cu}_{\text{cub}}\text{-Ag}$ and $\text{Cu}_{\text{oh}}\text{-Ag}$, respectively. Additional loss features in the $\text{Ag}3\text{d}_{5/2}$ spectra indicate that Ag is in a metallic state, and the Ag MNN Auger spectra are also reminiscent of metallic Ag. Following the CO_2RR , both $\text{Cu}_{\text{oh}}\text{-Ag}$ and $\text{Cu}_{\text{cub}}\text{-Ag}$ presented near-identical XPS spectra; the $\text{Cu}2\text{p}_{3/2}$ and $\text{Ag}3\text{d}_{5/2}$ peaks were unchanged, as were the Cu LMM and Ag MNN Auger spectra. These results allow us to rule out major changes in electronic structure which would manifest via a more pronounced peak shifting.³⁶ While surface alloying limited to a few atomic layers cannot be completely excluded^{37,38}, we expect any effect deriving from those to be the same in both $\text{Cu}_{\text{oh}}\text{-Ag}$ and $\text{Cu}_{\text{cub}}\text{-Ag}$. Hence, any difference between the two systems can be interpreted within the framework of tandem catalysis, wherein an increasing local supply of CO is provided to the faceted Cu NCs.

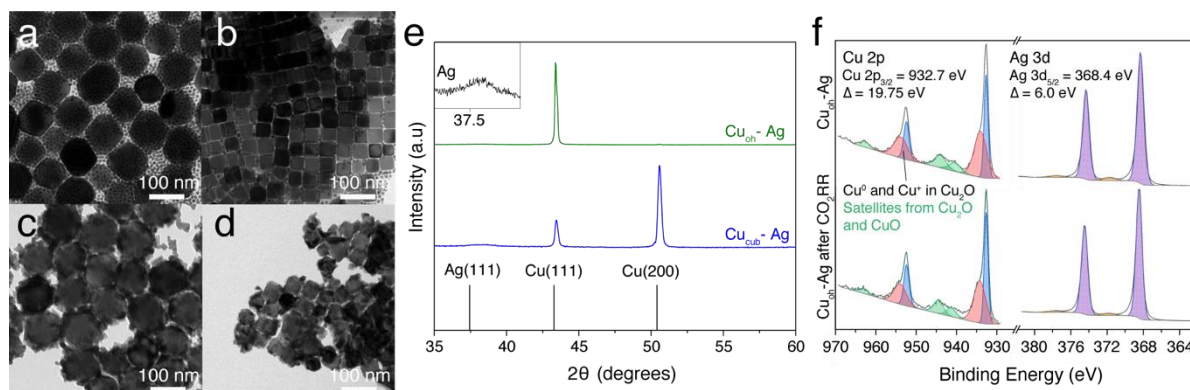


Figure 1. TEM images of (a) $\text{Cu}_{\text{oh}}\text{-Ag}$ and (b) $\text{Cu}_{\text{cub}}\text{-Ag}$ as prepared. TEM images of (c) $\text{Cu}_{\text{oh}}\text{-Ag}$ and (d) $\text{Cu}_{\text{cub}}\text{-Ag}$ after 15 minutes of electrolysis in 0.1 M KHCO_3 at $-1.3 \text{ V}_{\text{RHE}}$. (e) XRD of the catalysts drop-cast onto a Si wafer (inset shows a magnified Ag peak). (f) XPS analysis of the $\text{Cu}_{\text{oh}}\text{-Ag}$ showing the $\text{Cu}2\text{p}$ and $\text{Ag}3\text{d}$ regions before and after 15 minutes of electrolysis in 0.1 M KHCO_3 at $-1.3 \text{ V}_{\text{RHE}}$.

The performance of the Cu_{oh}-Ag and Cu_{cub}-Ag catalysts for CO₂RR were evaluated in a typical H-type liquid cell with the catalysts drop-cast on flat glassy-carbon electrodes. Potentials were applied between -1.1 and -1.4 V_{RHE} (RHE: reversible hydrogen electrode); outside of this range, the Cu NCs alone yielded hydrogen as the major product, which is consistent with previous studies.^{24,25,39,40}

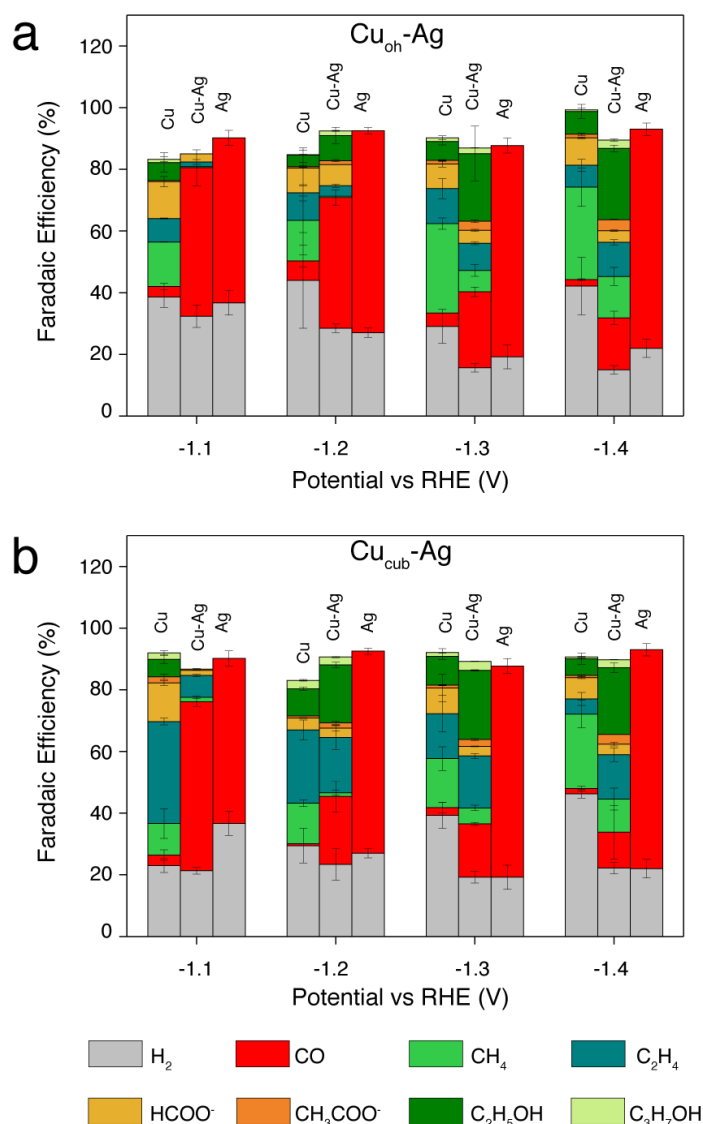


Figure 2. FEs for (a) Cu_{oh}-Ag and (b) Cu_{cub}-Ag at variable potentials, where the Cu mass loading is 15 $\mu\text{g}/\text{cm}^2$. For comparison, FEs are shown for the bare Cu and Ag NCs at the same loading. CO₂RR measurements were carried out using glassy-carbon electrodes as the substrate and CO₂-saturated 0.1 M KHCO₃ electrolyte. The reported values are averages of three independent experiments.

Figure 2 reports the FEs toward gas and liquid products for Cu_{oh}-Ag (**Figure 2a**) and Cu_{cub}-Ag (**Figure 2b**), which are compared with the respective bare Cu NCs and Ag_{sph} at different potentials. All values at each potential are reported in **Table S2**. The following major trends are observed. With the exception of $-1.1 V_{RHE}$, the addition of Ag NCs suppresses the HER and enhances the CO₂RR on both the Cu_{oh} and Cu_{cub}. This result is in agreement with previous literature on tandem catalysts and can be attributed to the local generation of CO.^{9,41} At potentials more cathodic than $-1.1 V_{RHE}$, the CO FEs are dramatically lower on the Cu-Ag catalysts when compared to the bare Ag NCs, which is consistent with the CO formed on the Ag_{sph} being consumed by Cu via tandem catalysis. Values of the partial current densities and of the fractional CO₂ consumption support such statement (**Figure S3** and relative discussion in the Supporting Information). The CO FE decreases from 48.2% to 16.8% on Cu_{oh}-Ag and from 54.8% to 11.7% on Cu_{cub}-Ag as the potential shifts from -1.1 to $-1.4 V_{RHE}$, implying that the effectiveness of the tandem catalysis mechanism improves concomitantly with Cu becoming more efficient in converting CO.⁸

Turning towards a more detailed analysis of the CO₂RR products, the FE of CH₄ is suppressed on the Cu-Ag catalysts across the entire potential range. For example, it drops from 29% on the Cu_{oh} to 6.9% on the Cu_{oh}-Ag catalyst at $-1.3 V_{RHE}$. Similarly, it goes from 15.9% on the Cu_{cub} to 5.2% on the Cu_{cub}-Ag catalyst at $-1.3 V_{RHE}$. More cathodic potential promotes CO hydrogenation over C-C coupling thereby promoting C₁ pathways enhancing CH₄ FE.^{17,33}

Concerning the C₂ products, the FEs of C₂H₄ on the Cu_{oh} are in the 7% – 11.4% range from $-1.1 V_{RHE}$ to $-1.4 V_{RHE}$ and do not change appreciably in the Cu_{oh}-Ag catalyst. For Cu_{cub}, the C₂H₄ FE decreases steadily from 33.1% at $-1.1 V_{RHE}$ to 4.9% at $-1.4 V_{RHE}$. Compared to these values, the FE of C₂H₄ for Cu_{cub}-Ag remains within the standard deviation of the measurements at $-1.2 V_{RHE}$ (from 23.7% to 18%) and at $-1.3 V_{RHE}$ (14.6% to 16.8%), instead it increases at $-1.4 V_{RHE}$ (4.9% to 14.4%). This shows that C₂H₄ active sites, namely, the dominant CO₂RR active sites on Cu_{cub}, possibly benefit from the local CO supply in the Cu_{cub}-Ag at a high overpotential.

The C₂H₅OH selectivity increases on both Cu-Ag catalysts compared to the bare Cu NCs. In particular, the C₂H₅OH FE increases from 3.7% to 8.1% at $-1.2 V_{RHE}$, 6.1% to 21.9% at $-1.3 V_{RHE}$ and 7.4% to 23.1% at $-1.4 V_{RHE}$, respectively, when comparing the Cu_{oh} with the Cu_{oh}-

Ag. Similarly, on Cu_{cub}-Ag, the C₂H₅OH FE goes from 8.8% to 18.8%, 9.3% to 22.5% and 5.4% to 21.6% at the same potentials when compared to the Cu_{cub}. Apart from the suppression of formate on the Cu-Ag catalysts with respect to the Cu NCs, no other major changes were observed in the liquid products. This finding is in agreement with the fact that no Cu-Ag alloying occurs in our catalysts, as the concurring electronic effect could have resulted in the generation of carbonyl-containing compounds.^{37,42} We note that the Cu:Ag 2:3 mass ratio was found to be optimal with regard to consumption of the local amount of supplied CO (**Figure S4**).

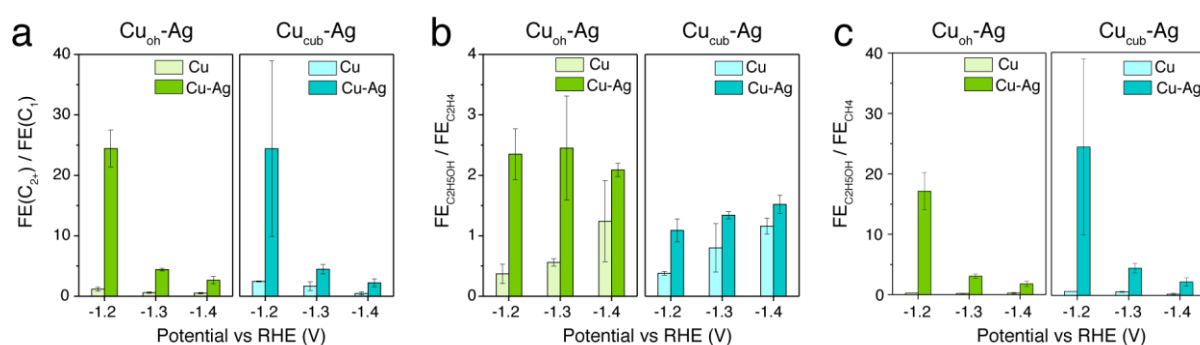


Figure 3. (a) $FE_{C_2^+}/FE_{C_1}$, (b) $FE_{C_2H_5OH}/FE_{C_2H_4}$ (c) $FE_{C_2H_5OH}/FE_{CH_4}$ for Cu_{oh}-Ag and Cu_{cub}-Ag at variable potentials, where the Cu mass loading is 15 $\mu\text{g}/\text{cm}^2$. The CO₂RR measurements were carried out using glassy-carbon electrodes as the substrate and CO₂-saturated 0.1 M KHCO₃ electrolyte. The reported values are averages of three independent experiments.

To facilitate the comparison among samples and the identification of specific trends, **Figure 3** shows the FE ratios of C₂⁺/C₁, C₂H₅OH /C₂H₄ and C₂H₅OH/CH₄ for Cu_{oh}-Ag and Cu_{cub}-Ag compared with the bare Cu NCs in the potential window where tandem catalysis was the most effective (−1.2 to −1.4 V_{RHE}). As observed in previous studies on tandem schemes,^{7–13} the C₂⁺/C₁ ratios are higher on the Cu-Ag catalysts and they decrease on both the Cu and the Cu-Ag catalysts as the potential becomes more cathodic (**Figure 3a**), which is in agreement with more negative potentials favoring C₁ pathways over C-C coupling.^{17,33} In terms of selectivity towards alcohols, **Figure 3b** illustrates an increased C₂H₅OH/C₂H₄ ratio on the Cu-Ag catalysts, which is more pronounced on the Cu_{oh}-Ag and at lower overpotentials.

A maximum ratio of 2.4 is observed on the Cu_{oh}-Ag at −1.3 V_{RHE}. Instead, the C₂H₅OH/C₂H₄ ratio on Cu_{cub}-Ag reaches a maximum of 1.5 at −1.4 V_{RHE}. Notably, the C₂H₅OH/CH₄ ratio

increases two orders of magnitude on both bimetallic catalysts as compared to the respective bare Cu NCs at the lowest potential (**Figure 3c**). Indeed, it goes from below 1.0 on the Cu_{oh} and Cu_{cub} to 17.1 and 24.4 on Cu_{oh}-Ag and Cu_{cub}-Ag, respectively.

To assess whether these trends are related to an increased rate of ethanol production or to a suppression of the methane pathway, the partial current densities for methane, ethylene and ethanol are plotted in **Figure 4** for the two Cu-Ag catalysts.

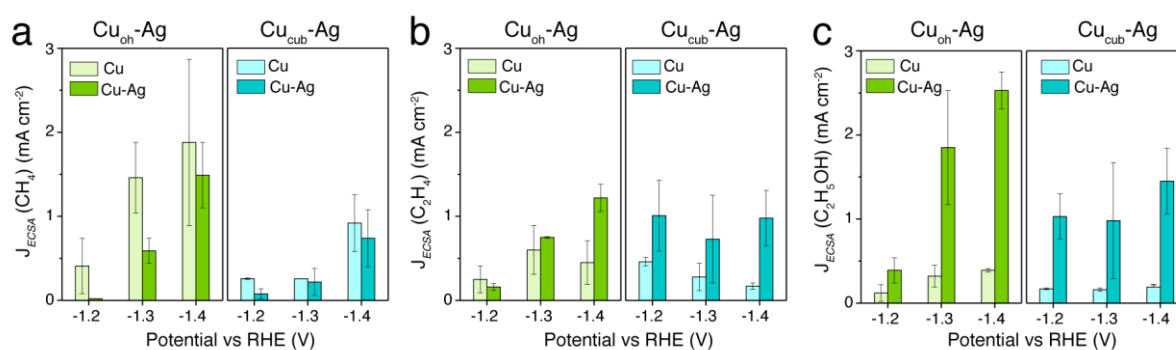


Figure 4. ECSA-normalized partial current densities (J_{ECSA}) for (a) CH_4 , (b) C_2H_4 and (c) $\text{C}_2\text{H}_5\text{OH}$ of the Cu_{oh}-Ag and Cu_{cub}-Ag catalysts, where the Cu mass loading is $15 \mu\text{g}/\text{cm}^2$. CO_2RR measurements were carried out using glassy-carbon electrodes as the substrate and CO_2 -saturated 0.1 M KHCO_3 electrolyte. The reported values are averages of three independent experiments. The total current densities are shown in **Figure S5**.

Figure 4 reports the partial current densities normalized by the electrochemically active surface area (ECSA) for the catalysts studied. Notably, $J_{\text{ECSA}}(\text{CH}_4)$ decreases on both Cu_{oh}-Ag and Cu_{cub}-Ag compared to the bare Cu NCs at all potentials (**Figure 4a**), indicating that the production rate of methane is actually suppressed. Instead, $J_{\text{ECSA}}(\text{C}_2\text{H}_4)$ and $J_{\text{ECSA}}(\text{C}_2\text{H}_5\text{OH})$ clearly increase on both catalysts (**Figures 4b** and **4c**). However, while the absolute values of $J_{\text{ECSA}}(\text{C}_2\text{H}_4)$ on both bimetallic catalysts are quite similar to each other, $J_{\text{ECSA}}(\text{C}_2\text{H}_5\text{OH})$ is considerably higher on the Cu_{oh}-Ag catalysts than on Cu_{cub}-Ag. For example, $J_{\text{ECSA}}(\text{C}_2\text{H}_5\text{OH})$ reaches $2.5 \text{ mA}/\text{cm}^2$ on Cu_{oh}-Ag and $1.4 \text{ mA}/\text{cm}^2$ on Cu_{cub}-Ag at $-1.4 \text{ V}_{\text{RHE}}$. Concomitantly, the enhancement factors for CH_4 , C_2H_4 and $\text{C}_2\text{H}_5\text{OH}$ clearly show that on the Cu_{cub}-Ag the production of both ethylene and ethanol is enhanced; instead, on the Cu_{oh}-Ag the ethanol pathway is selectively promoted (**Figure S6**).

As mentioned in the introduction, a consensus on the ethanol formation pathway is yet to be reached. Most of the reports support the hypothesis that the C_2H_5OH vs C_2H_4 bifurcation occurs after CO dimerization.^{11,15,19,33} Only a few studies have proposed the bifurcation to happen prior to CO dimerization (via $*CH_x$ - $*CO$ coupling).^{12,13} As a reminder, the Cu_{oh} are enclosed by (111) facets, which are intrinsically more selective towards methane.²⁴ CH_4 active sites probably have an appreciable coverage of $*CH$, $*CH_2$ and/or $*CH_3$ intermediates. When supplied with a high local concentration of CO, these intermediates may couple with it before undergoing further reduction.¹ Indeed, Ting et al. suggested $*CH$ or $*CH_2$ coupling with $*CO$ and further reducing to C_2H_5OH in an ethanol-selective pathway that is favorable on Cu(111) only under elevated $*CO$ coverage.¹² Such a prediction is consistent with our results. At this point, we decided to look further into the structural sensitivity of ethanol evolution via $*CH_x$ - $*CO$ coupling by computationally studying it on stepped Cu(100) surfaces, bearing in mind that previous studies did so for Cu(111) terraces and that step sites at Cu(111) likely remain methane-selective at high CO coverage.¹²

First of all, the highly favourable production of CO from CO_2 on Ag nanoparticles and extended surfaces is well known.^{12,43,44} Therefore, in the following we will focus on the coupling between $*CH_x$ and $*CO$ and the subsequent reduction of $*CHCO$ to C_2H_5OH . We calculated the kinetic barriers for $*CH$ and $*CH_2$ coupling with CO, since these will strongly determine if the alternative pathway that circumvents $*CO$ dimerization is open or not. The calculations were performed for both the terrace and the step of a Cu (711) surface. The (711) terraces correspond to the (100) facets of the cubes, instead the (711) steps correspond to the edges of the cubes (**Figure S7**). The barriers shown in **Table 1** for $*CO$ coupling with $*CH$ differ drastically for the step and terrace sites of Cu(711), with little to no coupling barrier (0.09 eV) for the step edge and a large one on the terrace (1.32 eV). We also calculated the kinetic barrier for the association of $*CO$ and $*CH_2$ and found a substantial yet surmountable coupling barrier (0.49 eV) for the step edge and a larger one at the terrace (0.85 eV). In both cases the barriers are lower at the steps compared to the terraces. In brief, we conclude that the edges should be highly active for $*CH + *CO$ coupling, and modestly active for $*CH_2 + *CO$ coupling. Conversely, the analogous coupling reactions at terraces are unlikely.

Table 1. Calculated barriers (in eV) for *CO association with *CH and *CH₂ on the Cu(711) step-edge and terrace sites. For comparison, data for the flat Cu(111) surface are provided, taken from the work by Ting et al¹².

| Coupling step | Barrier on the (100) terrace of Cu(711) | Barrier on the step edge of Cu(711) | Barrier on Cu(111) |
|------------------------|---|-------------------------------------|--------------------|
| *CO + *CH | 1.32 | 0.09 | 0.70 |
| *CO + *CH ₂ | 0.85 | 0.49 | 0.71 |

Moving forward along the reaction pathway toward ethanol, we calculated the minimum-energy pathway for the reaction intermediates starting from *CHCO. The results obtained from these calculations are shown in **Figure 5**, while a more detailed view on other possible intermediates, including the *CH₂CO intermediate, for both the step and terrace sites is shown in **Figure S8**. Our results indicate that the most-stable intermediates along the reaction pathway are identical to those found on Cu(111).¹² However, the energetics are quantitatively different, as Cu(111) terraces bind the CO₂RR intermediates more weakly than Cu(100) terraces and steps, in line with previous observations for C₁ intermediates.^{45,46}

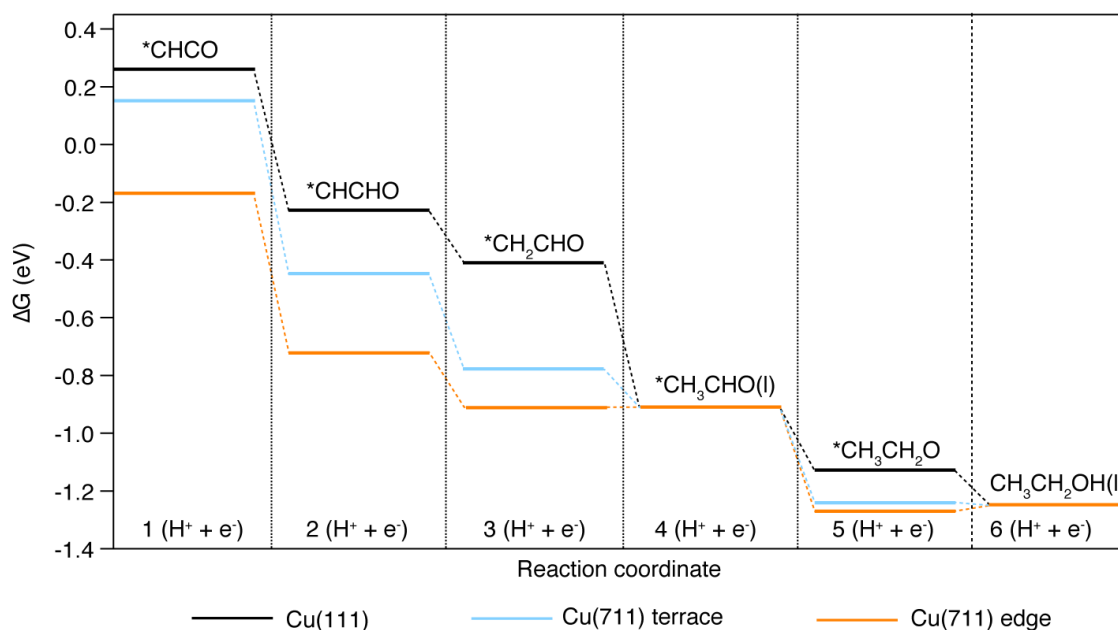


Figure 5. Reaction energies for the most stable intermediates along the *CHCO reduction pathway to ethanol at 0 V vs RHE. Data for Cu(111) were adapted from previous work.¹²

We note that C₂ species are readily formed on Cu(100) sites via *CO-*CO coupling, and that Cu(100) usually favours ethylene production over ethanol.¹⁻³ Thus, increasing the *CO coverage on the Cu(711) terraces should not enhance the production of ethanol with respect to

ethylene. Along these lines, for Cu_{cub}-Ag, the enhancement in ethanol production probably stems only from edge and corner sites. In the following, we will analyse the implications of this conclusion (see full details in section 2.4 in the SI). The partial current densities (J_i) (for i = ethylene and ethanol) can be expressed as the sum of the current densities of the active sites, which comprise (100) terraces and defects such as edges and corners ($J_i = J_i^{terraces} + J_i^{defects}$). Since ethylene and ethanol both require 12 electrons to be obtained from CO₂RR, the ratio of their partial current densities is equivalent to the ratio of Faradaic efficiencies. Given that ethylene is mostly produced on the (100) terraces, we have the following approximation for Cu_{cub}:

$$\left(\frac{FE_{C_2H_5OH}}{FE_{C_2H_4}} \right)_{Cu_{cub}} \approx \frac{J_{C_2H_5OH}^{terraces} + J_{C_2H_5OH}^{defects}}{J_{C_2H_4}^{terraces}} \quad (1)$$

The ratio of Faradaic efficiencies for the Cu_{cub}-Ag tandem catalyst is the same as for Cu_{cub}, except for an additional term that accounts for the activity of step sites owed to the *CH-*CO pathway. This leads to Equation 2, which connects the ratio of the Faradaic efficiencies in the bare Cu cubes and in the Cu-Ag catalyst:

$$\left(\frac{FE_{C_2H_5OH}}{FE_{C_2H_4}} \right)_{Cu_{cub}-Ag} \approx \left(\frac{FE_{C_2H_5OH}}{FE_{C_2H_4}} \right)_{Cu_{cub}} + \frac{A_{C_2H_5OH}^{defects}}{A_{C_2H_4}^{terraces}} e^{\frac{-0.5(\Delta G_{C_2H_5OH}^{\#} - \Delta G_{C_2H_4}^{\#})}{k_B T}} \quad (2)$$

where 0.5 is a typical value for the symmetry factor⁴⁷, $\Delta G_i^{\#}$ is the activation free energy of the rate-limiting step and A_i are surface areas. From the experiments in Figure 3b, the average $\left(FE_{C_2H_5OH} / FE_{C_2H_4} \right)_{Cu_{cub}-Ag} \approx 1$, whereas $\left(FE_{C_2H_5OH} / FE_{C_2H_4} \right)_{Cu_{cub}} \approx 0.5$. Since the area occupied by edge and kink sites on a 40 nm Cu cube is approximately 2.6% of the area occupied by the terrace sites (where *CO-*CO dimerization is still favourable and leads to ethylene), we conclude that the exponential term in Equation 2 is 19.2. Thus, on Cu_{cub}-Ag the ethanol-producing edges and corners are roughly 19 times more active than ethylene-producing terrace sites, but they are not abundant. Conversely, considering the predominance of (111) terraces on the Cu_{oh} and the relative unfavorability of competing *CO-*CO dimerization pathways, it is possible to rationalize why Cu_{oh}-Ag catalysts selectively promote ethanol.

Conclusions

The facet-dependent CO₂RR selectivity of Cu catalysts in a tandem configuration was studied using Cu_{oh}, terminated by (111) facets, and Cu_{cub}, terminated by (100) facets, with CO-producing Ag_{sph}. Both Cu-Ag catalysts showed enhanced selectivity and activity for C₂H₅OH and C₂H₄ and suppressed selectivity and activity for CH₄ and H₂. At the same time, we found a considerably higher selectivity towards C₂H₅OH on the Cu_{oh}-Ag catalysts with the C₂H₅OH/C₂H₄ ratio reaching 2.4 versus 1.5 on the Cu_{cub}-Ag catalyst under the same conditions. To the best of our knowledge, this value represents the state of the art in the C₂H₅OH/C₂H₄ ratio from electronically unaltered Cu electrodes.

DFT calculations and a simple model evidenced that, under high *CO coverage, the active sites on Cu_{cub}-Ag catalyst responsible for the enhancement of ethanol production are located at edge and corner sites and favour *CH_x and *CO coupling and its subsequent reduction, while the more extended (100) facets still promote ethylene. In addition, the (111) facets on Cu_{oh}-Ag catalyst also catalyze the *CH_x-*CO coupling and following reduction to C₂H₅OH. Since the ethanol-producing active sites are in greater number on Cu_{oh}-Ag compared to Cu_{cub}-Ag catalyst, it follows that the ethanol selectivity of Cu_{oh}-Ag catalysts is larger.

Overall, our results suggest that a catalyst exhibiting a high selectivity for CH₄ (thereby harboring a dense population of *CH_x intermediates under reaction conditions) should yield high C₂H₅OH FEs under a local excess of CO. Additionally, the theoretical findings suggest that a boost to the ethanol selectivity of Cu_{cub}-Ag could be achieved by using particles with high defect-to-terrace ratios, which will be the aim of future studies.

Supporting Information.

Chemicals used, synthesis protocols, structural characterization, electrode preparation and CO₂RR analysis method, electrochemical data, solvent contributions to free energies, adsorption energies, kinetic barriers. and optimized geometries used in DFT calculations.

Acknowledgments

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