Mechanistic Explanation of the pH Dependence and Onset Potentials for Hydrocarbon Products from Electrochemical Reduction of CO on Cu (111)

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Supporting Information

ABSTRACT: Energy and environmental concerns demand development of more efficient and selective electrodes for electrochemical reduction of CO₂ to form fuels and chemicals. Since Cu is the only pure metal exhibiting reduction to form hydrocarbon chemicals, we focus here on the Cu (111) electrode. We present a methodology for density functional theory calculations to obtain accurate onset electrochemical potentials with explicit constant electrochemical potential and pH effects using implicit solvation. We predict the atomistic mechanisms underlying electrochemical reduction of CO, finding that (1) at acidic pH, the C₁ pathway proceeds through COH to CHOH to form CH₄ while C₂ (C₃) pathways are kinetically blocked; (2) at neutral pH, the C₁ and C₂ (C₃) pathways share the COH common intermediate, where the branch to C–C coupling is realized by a novel CO–COH pathway; and (3) at high pH, early C–C coupling through adsorbed CO dimerization dominates, suppressing the C₁ pathways by kinetics, thereby boosting selectivity for multi-carbon products.

Electrochemical reduction of CO₂ (CO₂RR) to fuel and chemical products using renewable electricity is a promising technique to achieve carbon neutrality under mild conditions. Copper is the only known electrode material that delivers appreciable amounts of hydrocarbons, primarily methane and ethylene, with minor alcohol products. Since Cu is the only pure metal exhibiting reduction to form hydrocarbon chemicals, we focus here on the Cu (111) electrode. We present a methodology for density functional theory calculations to obtain accurate onset electrochemical potentials with explicit constant electrochemical potential and pH effects using implicit solvation. We predict the atomistic mechanisms underlying electrochemical reduction of CO, finding that (1) at acidic pH, the C₁ pathway proceeds through COH to CHOH to form CH₄ while C₂ (C₃) pathways are kinetically blocked; (2) at neutral pH, the C₁ and C₂ (C₃) pathways share the COH common intermediate, where the branch to C–C coupling is realized by a novel CO–COH pathway; and (3) at high pH, early C–C coupling through adsorbed CO dimerization dominates, suppressing the C₁ pathways by kinetics, thereby boosting selectivity for multi-carbon products.

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Electrocatalysis in advance of experiment. This paper is meant to provide the first step toward this goal. In addition, it provides a detailed reaction mechanism explaining the very complex ways that the products of CO2RR on Cu (111) depend on applied potential and pH, which we expect to be useful in designing modified catalysts or conditions.

In CO2 reduction on Cu, CO is produced at the lowest overpotential and the electrochemical reduction of CO gives the same product spectrum as that of CO2.7,8 Thus, it is believed that CO is the essential intermediate linking CO2 to more reduced products, and we focus here electrochemical reduction of CO.

Several QM computational investigations have suggested rationalizations of experimental results3–5,8–10 in terms of postulated mechanisms for CO electrochemical reduction (COER) on Cu surfaces. In 2010, Peterson et al.11 examined this reaction for the Cu (211) surface and suggested a pathway along which the potential-limiting step is formation of CHOad this reaction for the Cu (211) surface and suggested a pathway between whereas the major selectivity issue in COER is the competition overpotentials and selectivity. Thus, we can approximate the half-cell with a closed system in which the reaction energy profile is obtained using standard DFT techniques [see Supporting Information (SI) for details]. For a protonation step, our model uses a hydrogen atom bonded to the surface to locate the TS and then references this back to the $H^+(H_2O/H_2O) + e^−$ pair through $H_2$ (details in SI). Thus, our model restores the reference energy of the correct initial state for the reaction energy profile, allowing the pH dependence to be introduced naturally.

Furthermore, we perform explicit constant $\mu_e$ calculations for all states along the reaction coordinate. This is done through variationally optimizing $N_e$ to minimize the grand free energy at fixed $\mu_e$ and the resulted net electronic charge is balanced by ionic screening in the electrolyte,17 which is treated here using the CANDLE implicit solvation model.18 Consequently this provides a realistic description of the electrochemical interface,19 which includes both the external potential and solvation effects (details in SI). The final free energy profiles include zero-point energy, enthalpy, and entropy contributions from vibrations of surface species. For example, the free energy barrier $\Delta G^\ddagger$ for CO formation is given by

$$\Delta G^\ddagger(COH) = 0.63 + 0.0592 \times pH - 0.0959 \times U(eV)$$

while $\Delta G^\ddagger$ for CO dimerization is given by

$$\Delta G^\ddagger(CO\rightarrow CO) = 1.15 + 0.0510 \times U(eV)$$

where $U$ is referenced to the SHE. Note that $\Delta G^\ddagger(CO\rightarrow CO)$ is independent of pH, since no proton is involved in the reaction. The minimal onset potential for each step is simply

$$|U|_{\text{min}} = \max(\Delta G^\ddagger, \Delta G)/e$$

where $H^+(H_2O/H_2O) + e^−$ for each step provides the energy input of $U$. Here we must compare both $\Delta G^\ddagger$ and $\Delta G$ because for some ranges of $U$, the TS can be lower in energy than the final state for some reactions, making the step a simple uphill process.

We use the PBE flavor of DFT theory, as implemented in VASP using cutoffs and core effective potentials (pseudopotentials) as described in the SI.

The Cu (111) surface serves as a simple but useful model for validating our particular combination of methods since accurate experimental data are available showing a broad range of chemistries20 with strong pH- and potential-dependent selectivity. The pathways considered are shown in Figure 1:

- starting from adsorbed CO, the (R1) COH and (R2) CHO pathways for protonation and the (R3) CO→CO path for dimerization constitute all competing options;
- the COH path (R1) further branches into three channels: advancing along the C1 path through either (R1a) the C path by removing the OH group or (R1b) the CHOH path, and more interestingly, opening up a
new C₂ path by C−C coupling through (R1c) the CO−COH path;

- the CHO path (R2) converges with the COH path (R1b) at the point of forming CHOH while the CO−CO path (R3) converges with the CO−COH path (R1c) at the point of forming the COCOH adsorbate.

All free energy profiles including the pH and U dependence are listed in the SI. This is the first proposal of C−C coupling through the CO−COH path. It leads to a much lower barrier of 0.87 eV at U = 0 V than the 1.15 eV barrier for the CO−CO path, (previously proposed as the path to C₂ products).¹²,¹⁵ This low barrier arises from the ability of COH adsorbate to acquire radical character (see discussion in the SI), which remains in the COCOH adsorbate until it forks to a new C₃ path by further coupling with another CO (discussed in the SI). This might explain why up to 4% C₃ products are observed experimentally, but not beyond C₃.⁵

For C₁ pathways, all reactions are modeled at the low coverage limit (θ_CO = 1/9 or 1/16, see Table S1) assuming universal availability of surface hydrogen. Since C−C coupling must start with a local coverage of 4/9, we provide a penalty of 0.12 eV²¹ for this C₂ pathway to put it on an equal footing with the C₁ pathway. This accounts for the energy cost of switching H with CO to achieve the high local θ_CO.

To determine the onset potentials, we consider three typical experimental situations, pH = 1, 7, or 12.

**Case A:** At pH = 1 (Figure 2), the earliest onset potential of −0.80 V starts the C₁ path through COH formation, while the CHO and CO−CO pathways lead to barriers higher by 0.08 and 0.43 eV, corresponding to kinetic rate ratios at 300 K of 4 × 10⁻²:1 and 5 × 10⁻³:1 to the COH path, respectively. Although their barriers show a positive dependence on U, it requires potentials as negative as −1.75 for CHO and −3.95 V for CO−CO paths, to have kinetics comparable with the COH path.

Following COH formation, the lowest barrier C₁ path proceeds through CHOH_{ad} (instead of the previously proposed C_{ad}, which has a barrier 0.56 eV higher), while the new C₂ branch which proceeds by the CO−COH path, is suppressed by kinetics (a rate lower by 1 × 10⁻⁷:1 at 300 K compared to the CHOH path). Thus, both C−C coupling mechanisms are blocked kinetically. Consequently there are essentially no C₂ products at pH = 1. This is consistent with the experimental observation that no C₂H₄ is produced on Cu (111) at pH = 1.¹⁶ Our predicted onset potential of −0.80 V for C₁ products is in excellent agreement with the experimental value of −0.76 V (vs SHE) for CH₄.¹⁶

**Case B:** At pH = 7 (Figure 3), the COH path is again first with a predicted onset potential of −1.17 V. The CHO and CO−CO pathways are now accessible by kinetic rate ratios at 300 K of 0.1:1 and 0.2:1 to the COH path, respectively. More interestingly, along the dominant COH path, the branch into C₂ products through CO−COH coupling is also viable kinetically, with rate ratio at 300 K of 0.2:1 to the C₁ channel through the CHOH path. Consequently the C₁ and C₂ pathways share the COH_{ad} common intermediate. This confirms the experimental conclusion on Cu (111) at pH = 7 that the pathway to C₂H₄ has a common intermediate with that to CH₄ (based on the same potential dependence, although the common intermediate was incorrectly speculated to be the CHO_{ad}). Our predicted onset potential of −1.17 V for the COH path agrees with the experimental value of −1.21 V for both CH₄ and C₂H₄,¹⁰ and our predicted rate ratio of 0.2:1 for C₂:C₁ along the major COH path agrees with the experimental C₂H₄:CH₄ product ratio of 0.2:1.²⁰

**Figure 1.** Pathways for the first two steps of COER.

**Figure 2.** COER free energy profiles at pH = 1. The blue line shows the only pathway with significant rates. The predicted onset potential of −0.80 is in excellent agreement with the experimental value of −0.76 V (vs SHE) for CH₄.¹⁶

**Figure 3.** COER free energy profiles at pH = 7. The blue line indicates the dominant path, but we predict that the rate for the green line is 20% of that for the blue line, in agreement with the experimental C₂H₄:CH₄ product ratio of 0.2:1.²⁰ Our predicted onset potential of −1.17 V for the COH path agrees with the experimental value of −1.21 V for both CH₄ and C₂H₄.¹⁰
Case C: At pH = 12 (Figure 4), the CO–CO path is now initiated at the onset potential of −1.21 V, which agrees with the experimental value of −1.26 V for C2H4 production at pH = 12 on Cu (111).16 Here, both C1 pathways through COHld and CHOld are kinetically inhibited, by rate ratios at 300 K of \(\sim 10^{-2}\) compared to the CO–CO path. Indeed the experiments report very small amounts of CH4 with an onset potential of −1.46 V.16 This might originate from isolated surface regions where sufficiently high local \(\theta_{\text{CO}}\) for C–C coupling cannot be reached, due for example, to defects or inhomogeneities in the CO distribution, in which case C1 pathways might be the only option (if so, our results predict onset potentials for COH and CHO paths of −1.48 and −1.51 V, respectively, in agreement with the experimental values). Nevertheless, the experiments suggested that local high pH might contribute to suppressing formation of CH4.14 High pH was used in the case where only C2 and C3 products are produced.22 These results are consistent with our suggestion that high pH boosts selectivity for C2 and C3 products by kinetically blocking C1 pathways. But a major possible complication is the promotion of the hydrogen evolution reaction (HER) by high pH, which reduces the Faraday efficiency of COER.

![Figure 4](https://example.com/figure4.png)

**Figure 4.** COER free energy profiles at pH = 12. The light green line shows the dominant pathway (by a factor of 10^9 at 300 K). The predicted onset potential of −1.12 V agrees with the experimental value of −1.26 V for C2H4 production at pH = 12.16

Summarizing, we demonstrate a new methodology for accurate prediction of onset potentials from QM calculations while including the pH-dependent mechanisms underlying selectivity for C1 vs C2 (C3) products of COER on Cu (111). At low pH = 1, we find that multi-carbon production is suppressed kinetically, so that the C1 pathway proceeds through COHld to CHOld formation. At neutral pH, we identify a common intermediate COHld for the major mechanism that branches into C1 and C2 (C3) production. At high pH = 12, we find that selectivity for multi-carbon products arises by kinetically blocking C1 pathways. Of course to selectively produce these C containing products, we must protect the HER, e.g., structurally engineering Cu to behave like the oxide-derived surface.24 We consider that these excellent results with experiment validate the particular combination of methods used here, justifying this as the starting point for examining other electrochemical reactions.

**REFERENCES**


**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b11390.