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# Atomistic Mechanisms Underlying Selectivities in C<sub>1</sub> and C<sub>2</sub> Products from Electrochemical Reduction of CO on Cu(111)

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**ABSTRACT:** Practical environmental and energy applications of the electrochemical reduction of CO<sub>2</sub> to chemicals and fuels require far more efficient and selective electrocatalysts beyond the only working material Cu, but the wealth of experimental data on Cu can serve to validate any proposed mechanisms. To provide design guidelines, we use quantum mechanics to predict the detailed atomistic mechanisms responsible for C<sub>1</sub> and C<sub>2</sub> products on Cu. Thus, we report the pH dependent routes to the major products, methane and ethylene, and identify the key intermediates where branches to methanol, ketene, ethanol, acetylene and ethane are kinetically blocked. We discovered that surface water on Cu plays a key role in the selectivity for hydrocarbon products over the oxygen-containing alcohol products by serving as a strong proton donor for electrochemical dehydration reductions. We suggest new experiments to validate our predicted mechanisms.

## INTRODUCTION

Electrochemical reduction of CO<sub>2</sub> (CO<sub>2</sub>RR) to chemicals and fuels provides both a promising industrial-scale means to reduce the carbon footprint under mild conditions and a candidate for energy storage of electrical power from intermittent renewable sources into stable chemical forms.<sup>1</sup> The only known electrode material that produces significant amounts of valuable products (primarily methane and ethylene, with minor alcohol products)<sup>2-7</sup> is copper, which suffers from high overpotentials and a lack of selectivity, precluding practical applications. In order to provide the basis for developing more efficient and selective electrocatalysts, we report here the complete mechanistic understanding of the pH dependent processes on Cu based on grand canonical quantum mechanics (GC-QM) including solvation.

In the course of CO<sub>2</sub>RR on Cu, CO is produced with the lowest overpotential and the electrochemical reduction of CO (CORR) on Cu delivers the same product spectrum as that of CO<sub>2</sub>.<sup>8,9</sup> Thus CORR determines the overpotentials and selectivities for additionally reduced products from CO<sub>2</sub>RR, so we focus here on CORR. Cu(111) serves as a model electrocatalyst that delivers the essential chemistry of CORR,<sup>10</sup> and it has been confirmed to be stable under electrochemical working conditions,<sup>11</sup> so we focus here on CORR on Cu(111).

Several computational investigations with density functional theory (DFT) methods have proposed mechanisms for CORR on Cu surfaces.<sup>12-19</sup> However, early studies ignored reaction barriers and made only very approximate corrections for the effect of solvation.

In 2013, Nie *et al.*<sup>14,15</sup> reported the first study that includes transition states (TS) for CORR on Cu(111) but with a very limited description of solvation. They concluded that COH<sub>ad</sub> is the kinetically dominant key inter-

mediate, leading to CH<sub>x</sub> (x = 0 to 4) species sequentially, and proposed that C<sub>2</sub>H<sub>4</sub> formation occurs from the CH<sub>2,ad</sub> step, which is contradicted by the experimental conclusion that pathways to CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub> branch at an early stage of CORR.<sup>20,21</sup> Indeed, in 2015, Montoya *et al.*<sup>16</sup> predicted the barriers of CO dimerization on Cu(111) and (100) to be sufficiently low that C-C coupling should take place at the very beginning of CORR. This study used an oversimplified charged water layer to mimic the electrochemical environment for highly negative applied potentials.

However, all previous calculations were compromised by oversimplified treatments of solvation and the assumption that the number of electrons ( $N_e$ ) remains constant along each elementary step, whereas the electrochemical half-cells are open systems operating at applied constant electrochemical potentials ( $\mu_e$ ). Such calculations with constant  $N_e$  admit large variations in  $\mu_e$ ,<sup>14</sup> which introduces significant deviations through the  $\mu_e N_e$  contribution to free energies. Such inconsistency precludes quantitative predictions.

We recently reported the first quantum mechanics (QM) study with explicitly constant  $\mu_e$  for CORR<sup>18</sup> which has now been validated by Goodpaster *et al.*<sup>19</sup>. Our GC-QM calculations were realized within the framework of joint DFT (JDFT),<sup>22</sup> that introduces solvation effects using the CANDLE implicit model<sup>23</sup> and retains a fixed external potential by variationally optimizing  $N_e$  along the reaction path (the resulting net charge is handled by ionic screening).<sup>24</sup> These GC-QM studies allowed us to predict the initial steps for pH-dependent mechanisms underlying the competition between C<sub>1</sub> and C<sub>2</sub> pathways on Cu(111). We found that the C<sub>1</sub> pathway dominates kinetically through COH<sub>ad</sub> formation at low pH, whereas the C<sub>2</sub> pathway opens up by direct CO<sub>ad</sub> dimerization at high pH while at neutral pH we find a novel CO-COH coupling that shares the common intermediate COH<sub>ad</sub>

with the C<sub>1</sub> pathway.<sup>18</sup> Based on the GC-QM, we predicted the onset potentials (U) for C<sub>1</sub> and C<sub>2</sub> products, in excellent agreement with experiment (within 0.05 V) for pH = 1, 7 and 12.<sup>18,25,26</sup> We should note that possible complications in real experiments might compromise the comparison, including the difference between local and bulk pH and imperfections present in the electrode surface. Nevertheless, these recent studies<sup>18,19</sup> examined only the first few steps of CORR providing overpotentials and selectivity for single-carbon *vs* multi-carbon products. A complete picture of the final product spectrum, particularly the selectivity for hydrocarbon *vs* alcohol products, has not previously been established.

Here we use these GC-QM methods to determine the complete C<sub>1</sub> and C<sub>2</sub> pathways for CORR on Cu(111). A very important element of our new mechanisms is the **critical role of surface bound H<sub>2</sub>O in electrochemical dehydration reduction**. Starting from our previous work establishing that C<sub>1</sub> pathways up to CHO-H<sub>ad</sub> are enabled for pH ≤ 7 while C<sub>2</sub> pathways up to CO-COH<sub>ad</sub> are accessible for pH ≥ 7,<sup>18</sup> we now investigate the constant  $\mu_e$  free energy barriers for all possible competing pathways to provide the roadmap of pH dependent routes to the major products and to identify the key intermediates at which branches to other products are blocked. Then we use our new mechanism to suggest experiments using probe molecules to experimentally validate details of our mechanisms. A critical point here is our discovery that **surface water on Cu provides the key to selectivity of hydrocarbon *vs* alcohol products**. The supporting information (SI) provides reaction barriers and energies for all competing pathways studied, of which only the dominant ones are discussed here.

## COMPUTATIONAL DETAILS

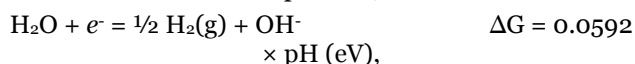
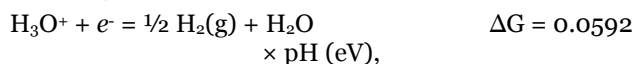
The calculations were first performed with VASP package<sup>27-29</sup>, using the PBE flavor<sup>30</sup> of DFT and the projector augmented wave (PAW) method<sup>31</sup> to account for core-valence interactions. The kinetic energy cutoff for plane wave expansions was set to 400 eV, and reciprocal space was sampled by  $\Gamma$ -centered Monkhorst-Pack scheme with a grid of 3×3×1. The Cu(111) surface slabs were constructed with 3 layers (bottom layer fixed) using the PBE-optimized lattice parameter of 3.635 Å, with vacuum layers of at least 15 Å, and the slab sizes are 4 × 4, 4 × 5 or 5 × 5, depending on the adsorbates for low coverage limit. Please refer to the SI Appendix for coordinates of all structures studied.

The convergence criteria are 1 × 10<sup>-5</sup> and 1 × 10<sup>-7</sup> eV energy differences for solving for the electronic wavefunction for local minima (initial states (IS) and final states (FS)) and TS, respectively. The Methfessel-Paxton smearing of second order with a width of 0.1 eV was applied. All IS, TS, and FS geometries (atomic coordinates) are converged to within 3 × 10<sup>-2</sup> eV/Å for maximal components of forces. The TS search was conducted with using climbing image nudged elastic band (CI-NEB) method<sup>32</sup> to generate initial guess geometries, followed by the dimer method<sup>33</sup> to converge to the saddle points.

Zero-point energies (ZPE), enthalpy and entropy contributions to free energies at room temperature (298.15

K) were calculated from vibrational modes of surface species, which were computed with density functional perturbation theory (DFPT). Note that very low frequency modes were obtained in some cases, because the explicit water molecules are not properly constrained by the hydrogen bonding network present in water bulk. Such low frequency modes can cause unphysically large entropy contributions, so they were reset to a threshold value of 60 cm<sup>-1</sup>, corresponding to the acoustic translational mode of the six-member rings in water bulk.<sup>34,35</sup>

For steps where the surface H model was used to locate TS's, IS's were referenced back to with the H<sup>+</sup>(H<sub>3</sub>O<sup>+</sup>/H<sub>2</sub>O) + *e*<sup>-</sup> pair through free energy differences between the surface H and H<sub>2</sub>(g), based on the half-cell reactions,



Thus the pH effect is introduced into the free energy profiles with the reference. In addition to vibrational contributions, the translational and rotational contributions to the free energy of H<sub>2</sub>(g) were included, assuming the ideal gas model. For the models where H<sub>3</sub>O<sup>+</sup> is explicitly present or H<sub>2</sub>O acts as the proton source with releasing OH<sup>-</sup> (see below), the pH enters the free energy profiles naturally as the reactant or product, similar to other work<sup>36</sup>.

The explicit constant electrochemical potential ( $\mu_e$ ) calculations with implicit CANDLER solvation model<sup>23</sup> were performed upon all IS, TS, and FS geometries using JDFTx<sup>37</sup>. The GBRV<sup>38</sup> ultrasoft pseudopotentials (USPP) were used, with a plane wave cutoff of 544 eV (20 a.u.). All other settings are similar to those in VASP calculations. The ionic screening of net charges resulting from the constant  $\mu_e$  condition was achieved with cation (0.1 M K<sup>+</sup>) and anion (0.1 M F<sup>-</sup>) components in the fluid model<sup>24</sup> under the JDFT framework<sup>22</sup>. The algorithm employed by JDFTx variationally minimizes the grand free energy at fixed electron chemical potential with respect to Kohn-Sham orbitals,<sup>39</sup> fluid bound charge and an auxiliary Hamiltonian for the occupations.<sup>40</sup> Previously we have found that the relative free energies (barriers  $\Delta G^\ddagger$  and reaction energies  $\Delta G$ ) are linearly dependent on the applied potential U for |U| < ~2 V (vs standard hydrogen electrode (SHE)),<sup>18</sup> so the U-dependence of all  $\Delta G^\ddagger$  and  $\Delta G$  was calculated assuming linear relationship between U = 0.0 and -1.2 V. Note that here all U's are referenced to SHE.

The minimal onset potentials U<sub>min</sub> were then determined by solving the equation  $e|U_{\text{min}}| = \max(\Delta G^\ddagger, \Delta G)$ ,<sup>18</sup> which assumes that the energy of eU brought by the incoming electron is fully utilized to overcome the highest point on the free energy surface and thus drive the reaction. The comparison between  $\Delta G^\ddagger$  and  $\Delta G$  is necessary, because for some ranges of U, the TS can be lower in energy than the final state, making the step a simple uphill process.

## RESULTS AND DISCUSSION

In examining each electrochemical reduction step, we assume that the proton source ( $\text{H}_3\text{O}^+$  or  $\text{H}_2\text{O}$ ) and electron source are refilled in advance, in the form of surface H that is taken as the starting point to locate the TS.  $\Delta G^\ddagger$  and  $\Delta G$  are later corrected by referencing back to the  $\text{H}^+(\text{H}_3\text{O}^+/\text{H}_2\text{O}) + e^-$  pair through  $\text{H}_2$ . This surface H model is reasonable for finding the lowest energy barrier pathway, particularly for hydrogenation of C atoms (which are partially positive charged, and thus prefer the surface H which acquires a partially negative charge from the metal).

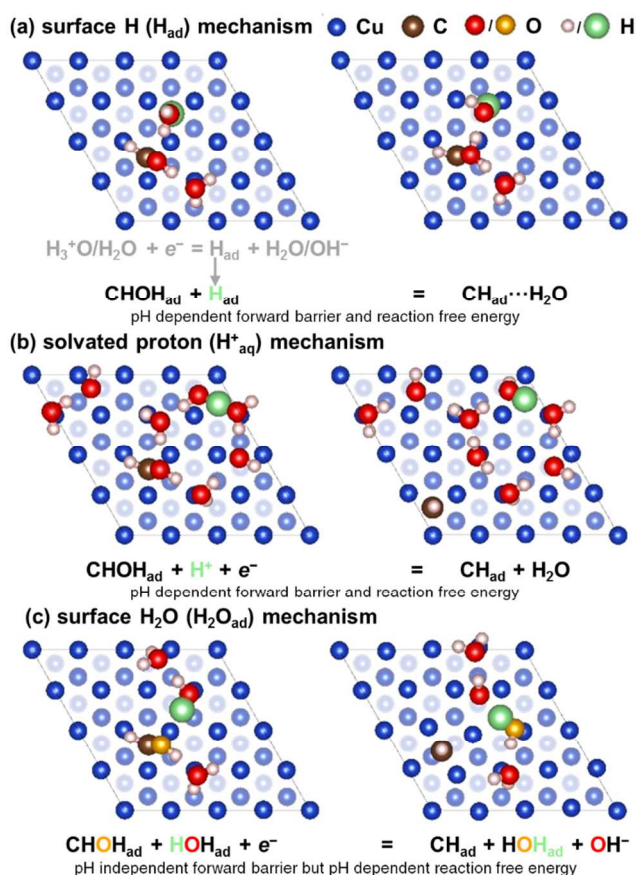
Our studies using QM based molecular dynamics (QMD) including five layers of explicit solvent and a proton,<sup>17</sup> showed that at low pH, the dehydration step through hydrogenation of the hydroxyl group of the  $\text{CHOH}_{\text{ad}}$  intermediate favors direct protonation mediated by aqueous water, instead of the surface H. There we speculated that at neutral and high pH, “hot” surface  $\text{H}_2\text{O}$  plays the essential role as the direct proton source, because the negatively charged O atom in the hydroxyl group is attractive to the positively charged proton in either  $\text{H}_3\text{O}^+$  or “hot” surface  $\text{H}_2\text{O}$ .

Herein we use GC-QM to examine:

(a) the standard surface H ( $\text{H}_{\text{ad}}$ ) Langmuir-Hinshelwood (LH) mechanism illustrated in Fig. 1a, in which  $\text{H}_{\text{ad}}$  activates an on-top aqueous water to provide the proton to the hydroxyl group;

(b) the solvated proton ( $\text{H}^+_{\text{aq}}$ ) Eley-Rideal (ER) mechanism illustrated in Fig. 1b, where the excess proton in solution arrives at the hydroxyl group via a Grotthuss mechanism, as observed in our previous QMD calculations on  $\text{Cu}(100)$ <sup>17</sup>;

(c) a new surface  $\text{H}_2\text{O}$  ( $\text{H}_2\text{O}_{\text{ad}}$ ) LH mechanism not previously considered. This “hot  $\text{H}_2\text{O}$ ” mechanism is illustrated in Fig. 1c, where  $\text{H}_2\text{O}_{\text{ad}}$  donates a proton directly to the hydroxyl group (or in some cases mediated by an aqueous water via a Grotthuss mechanism), leaving behind OH bonded to the metal. The reason that it is favorable for a  $\text{H}_2\text{O}_{\text{ad}}$  to donate a proton is that the final  $\text{OH}_{\text{ad}}$  is bound by 2.3 eV to the Cu surface, whereas  $\text{H}_2\text{O}_{\text{ad}}$  is bound by less than 0.1 eV. Under constant  $\mu_e$  calculations with JDFT the product  $\text{OH}_{\text{ad}}$  turns into  $\text{OH}^-$ .



**Figure 1.** The three mechanisms for electrochemical dehydration reduction illustrated with the  $\text{CHOH}_{\text{ad}}$  case: (a) surface H ( $\text{H}_{\text{ad}}$ ), (b) solvated proton ( $\text{H}^+_{\text{aq}}$ ) and (c) surface  $\text{H}_2\text{O}$  ( $\text{H}_2\text{O}_{\text{ad}}$ ). In each case the H initiating the reaction is shown in light green. Note that in (b) the final position of  $\text{CH}_{\text{ad}}$  has moved substantially from the initial position of  $\text{CHOH}_{\text{ad}}$ . This is where  $\text{CH}_{\text{ad}}$  ends up in our minimization procedure. We assume that it is due to the repulsion between  $\text{CH}_{\text{ad}}$  and the lone pair on  $\text{H}_2\text{O}$  being formed.

Figure 1 illustrates these three mechanisms for the  $\text{CHOH}_{\text{ad}}$  dehydration step. A notable characteristic of these mechanisms is the pH dependence:

(a) for the  $\text{H}_{\text{ad}}$  mechanism, the formation of the  $\text{H}_{\text{ad}}$  next to the reactant involves implicitly either  $\text{H}_3\text{O}^+$  or  $\text{OH}^-$ , so both  $\Delta G^\ddagger$  and  $\Delta G$  are pH dependent;

(b) the same applies to  $\text{H}^+_{\text{aq}}$  mechanism, since the proton enters directly the reactant side;

(c) however for our new  $\text{H}_2\text{O}_{\text{ad}}$  mechanism,  $\Delta G^\ddagger$  is generally pH independent, while the  $\text{OH}^-$  present at the product side makes  $\Delta G$  pH dependent. This makes the  $\text{H}_2\text{O}_{\text{ad}}$  mechanism advantageous for kinetics at higher pH.

At pH = 1 and 7 (Figure 2), we showed previously that the first step (1a) is hydrogenation of  $\text{CO}_{\text{ad}}$  by  $\text{H}_{\text{ad}}$  to form  $\text{COH}_{\text{ad}}$  with a predicted rate limiting  $U = -0.80$  and  $-1.17$  V (vs  $U_{\text{exp}} = -0.76$  and  $-1.21$  V), respectively, and the next step (1b) is the formation of  $\text{CHOH}_{\text{ad}}$  by the  $\text{H}_{\text{ad}}$  mechanism.<sup>18</sup>

At pH = 1, the hydrogenation of  $\text{CHOH}_{\text{ad}}$  to  $\text{CH}_2\text{OH}_{\text{ad}}$  (1c) follows dominantly, while the dehydration of  $\text{CHOH}_{\text{ad}}$  driven by the  $\text{H}^+_{\text{aq}}$  mechanism (see Table S1 in SI), is

kinetically blocked, with a barrier higher by 0.16 eV (rate lower by factor of 500). This is due to the conjugation of the C-O and C-Cu bonds in  $\text{CHOH}_{\text{ad}}$ , making the C-O bond relatively strong (1.37 Å).

At pH = 7, the hydrogenation step (1c) remains kinetically accessible, but the dehydration path (1e) to  $\text{CH}_{2\text{ad}}$  by the  $\text{H}_2\text{O}_{\text{ad}}$  mechanism forks to a competing branch, with a barrier slightly lower by 0.03 eV.

For  $\text{CH}_2\text{OH}_{\text{ad}}$ , the C-O bond (1.45 Å) is weaker (a normal C-O single bond), and the subsequent dehydration to  $\text{CH}_{2\text{ad}}$  (1d) by either the  $\text{H}^+_{\text{aq}}$  mechanism at pH = 1 or the  $\text{H}_2\text{O}_{\text{ad}}$  mechanism at pH = 7 kinetically dominates over further hydrogenation toward methanol production, with barriers lower by 0.05 eV and 0.29 eV, respectively (rates down by factors of 7 and 80,000). The resulting  $\text{CH}_{2\text{ad}}$  proceeds to the final methane product using  $\text{H}_{\text{ad}}$  for both pH. Hence, at pH 1 and 7,  $\text{CH}_2\text{OH}_{\text{ad}}$  is the key intermediate that decides the selectivity of CORR on Cu(111) for methane over methanol, and the “hot” surface water plays the critical role in the dehydration step at neutral pH, the most common scenario.

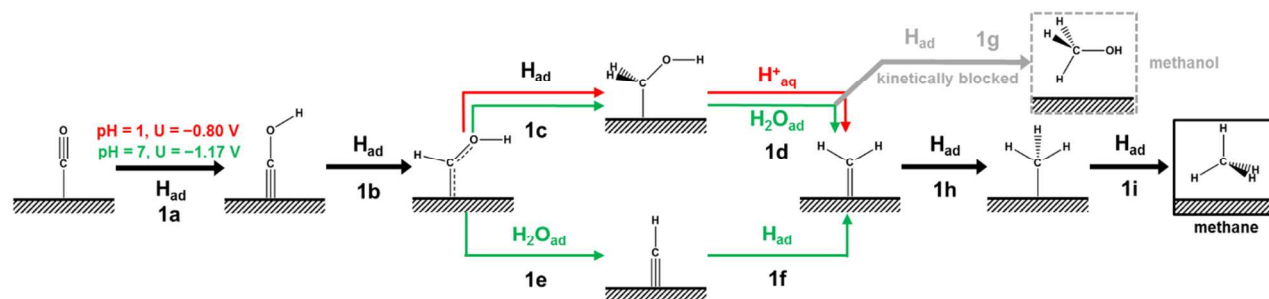
At pH = 13 (Figure 3), we showed previously that the first step (2a) is dimerization of  $\text{CO}_{\text{ad}}$  to form  $\text{OC-CO}_{\text{ad}}$  with a predicted rate limiting  $U = -1.21$  V (vs  $U_{\text{exp}} = -1.26$  V), followed by the hydrogenation (2b) with  $\text{H}_{\text{ad}}$  to form  $\text{OC-COH}_{\text{ad}}$ .<sup>18</sup> We show here that the next step has two competing branches with comparable kinetics: formation of  $\text{HOC=COH}_{\text{ad}}$  (2d) by acquiring a proton from a “hot” surface  $\text{H}_2\text{O}$  with a pH independent  $\Delta G^\ddagger$  of 0.01 eV but an uphill pH dependent  $\Delta G$  of 0.83 eV, and formation of  $\text{O=C=C}_{\text{ad}}$  (2e) by the  $\text{H}_2\text{O}_{\text{ad}}$  mechanism with  $\Delta G^\ddagger$  of 0.83 eV. Thus the “hot” surface water plays an essential role in both the dehydration and the pronation of the C=O group. Here the coupling to a third  $\text{CO}_{\text{ad}}$  (3a) to initiate  $\text{C}_3$  products with a  $\Delta G^\ddagger$  of 1.00 eV is blocked kinetically by both branches.

Following formation of  $\text{HOC=COH}_{\text{ad}}$ , the next step (2f) is dehydration to  $\text{HOC=C}_{\text{ad}}$  via  $\text{H}_2\text{O}_{\text{ad}}$  mechanism with  $\Delta G^\ddagger = 0.99$  eV (pH independent). This mutes the hydro-

genation to  $\text{HO(CH)-COH}_{\text{ad}}$  channel (not shown) which has a pH dependent  $\Delta G^\ddagger = 1.62$  eV. Then,  $\text{HOC=C}_{\text{ad}}$  undergoes dehydration (2h) to a surface dicarbide state ( $\text{C=C}_{\text{ad}}$ ) with  $\Delta G^\ddagger = 1.10$  eV, instead of hydrogenation (2k) to  $\text{HO(CH)=C}_{\text{ad}}$  ( $\Delta G^\ddagger = 1.43$  eV due to the pH increase). Then  $\text{C=C}_{\text{ad}}$  is further hydrogenated (2m) by  $\text{H}_{\text{ad}}$  to form  $\text{C=CH}_{\text{ad}}$ .

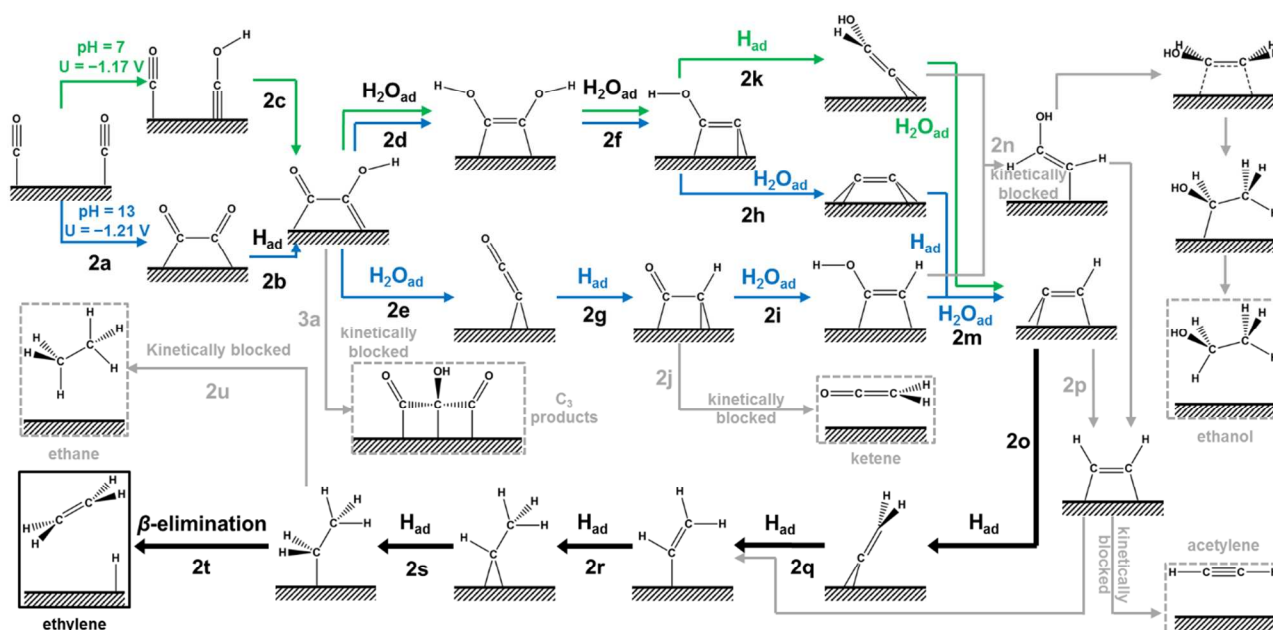
The formation of  $\text{O=C=C}_{\text{ad}}$  via  $\text{H}_2\text{O}_{\text{ad}}$  (2e), then proceeds to  $\text{OC-CH}_{\text{ad}}$  via  $\text{H}_{\text{ad}}$  (2g), followed by protonation of the C=O group by  $\text{H}_2\text{O}_{\text{ad}}$  (2i) to form  $\text{HOC=CH}_{\text{ad}}$ , with an uphill  $\Delta G = 0.86$  eV. The production of ketene (2j) is kinetically forbidden with  $\Delta G^\ddagger = 1.47$  eV. Dehydration of  $\text{HOC=CH}_{\text{ad}}$  with  $\text{H}_2\text{O}_{\text{ad}}$  (2m) forms  $\text{CCH}_{\text{ad}}$  (2m) with  $\Delta G^\ddagger = 1.16$  eV. This constitutes convergence with the 2d-2f-2h-2m pathways. Further hydrogenation (2n) to form  $\text{HO(CH)=CH}_{\text{ad}}$  which would lead to ethanol production, has  $\Delta G^\ddagger = 1.46$  eV, making it kinetically forbidden. Thus, “hot” surface water eliminates both ketene and ethanol products.

At pH = 7, we showed previously that the  $\text{C}_2$  pathways are accessed via a novel  $\text{OC-COH}$  coupling (2c) that shares the common intermediate  $\text{COH}_{\text{ad}}$  with the  $\text{C}_1$  pathways.<sup>18</sup> We show here that the  $\text{C}_2$  pathway leads to formation of  $\text{HOC=COH}_{\text{ad}}$  via  $\text{H}_2\text{O}_{\text{ad}}$  (2d) just as for pH = 13, but with a lower uphill pH dependent  $\Delta G$  of 0.47 eV, which then blocks kinetically the branch to  $\text{O=C=C}_{\text{ad}}$  formation (2e). Just as for pH = 13, the  $\text{C}_2$  pathway is followed by production of  $\text{HOC=C}_{\text{ad}}$  via  $\text{H}_2\text{O}_{\text{ad}}$  (2f). The next step at pH = 7 is hydrogenation with  $\text{H}_{\text{ad}}$  (2k) to form  $\text{HO(CH)=C}_{\text{ad}}$  with  $\Delta G^\ddagger = 1.08$  eV, instead of the dehydration by  $\text{H}_2\text{O}_{\text{ad}}$  (2h) to form  $\text{C=C}_{\text{ad}}$  that occurs at pH = 13. Next,  $\text{H}_2\text{O}_{\text{ad}}$  drives further dehydration (2m) of  $\text{HO(CH)=C}_{\text{ad}}$  to  $\text{C=CH}_{\text{ad}}$  ( $\Delta G^\ddagger = 0.86$  eV). This kinetically blocks the hydrogenation pathway (2n) to  $\text{HO(CH)=CH}_{\text{ad}}$  ( $\Delta G^\ddagger = 1.13$  eV) that would produce ethanol. Thus, at neutral pH, the “hot” surface water plays the key role in ruling out both  $\text{C}_3$  and ethanol products. This provides a hint that to promote alcohol production, we should destabilize the  $\text{H}_2\text{O}_{\text{ad}}$  pathways.



**Figure 2.** Predicted complete pH dependent pathways for  $\text{C}_1$  products.





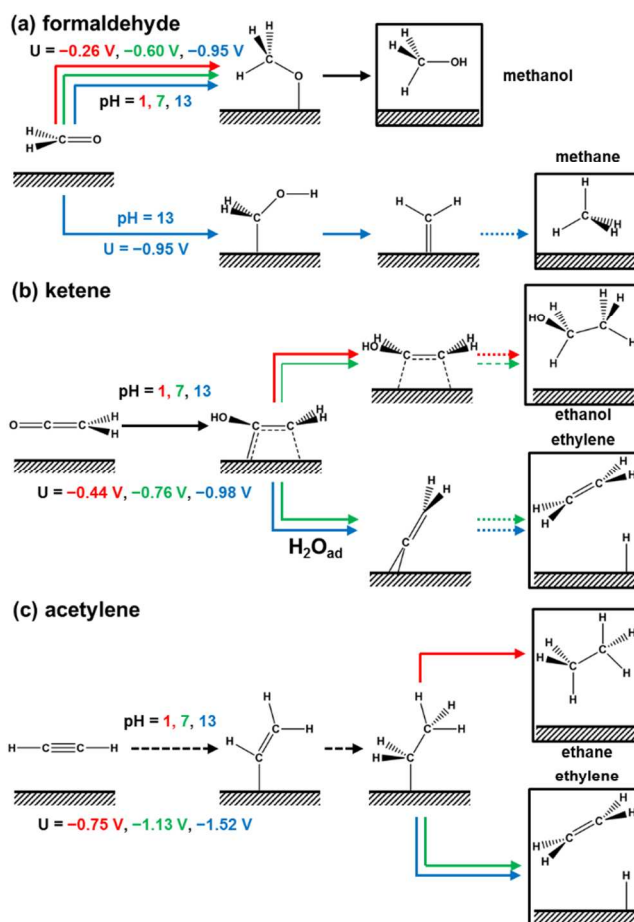
**Figure 3.** Predicted complete pH dependent pathways for C<sub>2</sub> products.

Following  $\text{HC}=\text{C}_{\text{ad}}$ , further electrochemical reduction kinetically favors formation of  $\text{H}_2\text{C}=\text{C}_{\text{ad}}$  via  $\text{H}_{\text{ad}}$  (2o) with  $\Delta G^\ddagger$  lower by 0.20 eV than for formation of  $\text{HC}=\text{CH}_{\text{ad}}$ . Even if  $\text{HC}=\text{CH}_{\text{ad}}$  were formed, the non-electrochemical desorption of acetylene has  $\Delta G = 1.0$  eV, making it slow, and  $\text{HC}=\text{CH}_{\text{ad}}$  favors the electrochemical hydrogenation to form  $\text{H}_2\text{C}=\text{CH}_{\text{ad}}$ . Thus, we predict that acetylene is *not* formed under these conditions, which is consistent with experiment.<sup>6</sup> Sequential hydrogenation of  $\text{H}_2\text{C}=\text{C}_{\text{ad}}$  with  $\text{H}_{\text{ad}}$  (2q–2r–2s) leads to  $\text{CH}_3\text{CH}_{2,\text{ad}}$ . Surprisingly, the last step is non-electrochemical  $\beta$ -elimination (2t with  $\Delta G^\ddagger = 0.59$  eV) that delivers the final ethylene product, leading to very fast kinetics, with a turn over frequency (TOF) of  $7 \times 10^2 \text{ s}^{-1}$ , based on the Eyring–Polanyi equation. No ethane should be produced since further hydrogenation (2u) has a barrier of 0.88 eV at pH = 7 and 1.23 eV at pH = 13. In fact, ethane has been reported occasionally as a minor product from CORR on specifically designed nanostructured Cu electrodes.<sup>41–43</sup> This suggests that morphology of the Cu surface might be tuned to suppress the fast  $\beta$ -elimination process to enable ethane production.

In our previous work,<sup>18</sup> we showed that our GC-QM methodology leads to onset potentials within 0.05 eV of experiment for pH = 1, 7, and 12, validating the accuracy of the level of DFT theory, the CANDLE solvation model, and the GC-QM method. In order to provide additional experimental tests of our very detailed mechanisms for subsequent product formation during CORR on Cu(111), we propose here several specific probe molecules that could be introduced to access new pathways at each pH while avoiding the constraint in CORR whereby pH selects C<sub>1</sub> or C<sub>2</sub> pathways. Figure 4 shows three candidates:

- (a) formaldehyde to probe the key intermediate  $\text{CH}_2\text{OH}_{\text{ad}}$  that selects methane production over methanol in C<sub>1</sub> pathways,

- (b) ketene to probe the predicted intermediate  $\text{HO}(\text{CH})=\text{CH}_{2,\text{ad}}$  that leads exclusively to ethanol production once formed, and
- (c) acetylene for verifying the predicted mechanisms for selectivity of C<sub>2</sub>H<sub>4</sub> vs C<sub>2</sub>H<sub>6</sub>.



**Figure 4.** Proposed experimental validations of our proposed mechanisms by introducing probe molecules (a) formaldehyde, (b) ketene and (c) acetylene (with their predicted pH dependent product spectra). These studies would probe and validate (hopefully) our predicted CORR mechanisms. Note that the predicted onset potentials  $U$  are referenced to SHE.

With formaldehyde, we expect to form a surface methoxy intermediate  $\text{CH}_3\text{O}_{\text{ad}}$  by the  $\text{H}_{\text{ad}}$  mechanism, which leads to methanol production exclusively, as suggested previously.<sup>14,15</sup> In contrast the target  $\text{CH}_2\text{OH}_{\text{ad}}$  pathways are not switched on until  $\text{pH} \geq 10.1$ , due to the potential limiting step of dehydration to  $\text{CH}_{2,\text{ad}}$ , at which point the methane production has comparable kinetics (see Table S1 and S3 in SI). This might resolve an apparent contradiction in the experimental literature: Schouten *et al* reported methanol as the only major product from electrochemical reduction of HCHO on Cu at  $\text{pH} = 7$  using a  $\text{K}_2\text{HPO}_4/\text{KH}_2\text{PO}_4$  buffer,<sup>20</sup> but a more recent experiment reported both methane and alcohol as major products.<sup>44</sup> Here a main difference in the setup is the use of  $\text{KHCO}_3$  solution, which gives a  $\text{pH} = 8.2$  and does not form a buffer without input of  $\text{CO}_2$ . Thus the electrochemical reduction of HCHO takes place at basic pH and even higher local pH due to consumption of protons. So our predicted mechanisms fit both experiments. Note also that our predicted  $U = -0.60$  V for formation of methanol at  $\text{pH} = 7$  matches well the reported experimental value of  $-0.6$  to  $-0.7$  V.<sup>20</sup>

When ketene is fed at acidic pH, the pathways to target  $\text{HOCHCH}_{2,\text{ad}}$  are kinetically favored, and thus our prediction is that ethanol is the only final product. But as pH increases to 7, a new pathway of dehydrating  $\text{HOCCH}_{2,\text{ad}}$  to  $\text{H}_2\text{C}=\text{C}_{\text{ad}}$  becomes slightly more favored kinetically, again through the  $\text{H}_2\text{O}_{\text{ad}}$  mechanism, and at basic pH, this route to ethylene production is totally dominant (see Table S3 in SI). This demonstrates again that the “hot” surface water promotes hydrocarbon products over alcohol products.

Feeding acetylene produces no pH dependent branches, until it reaches our target intermediate  $\text{CH}_2\text{CH}_{3,\text{ad}}$ , at which we predict production ethane at acidic pH, with  $\Delta G^\ddagger = 0.52$  eV for the final hydrogenation step, which is slightly lower than the  $\Delta G^\ddagger = 0.57$  eV for the  $\beta$ -elimination process. At neutral and basic pH, the final hydrogenation to ethane is kinetically blocked, just as in CORR. Experimental confirmation would validate our prediction that the absence of ethane in product spectrum is due to the combination of the fast  $\beta$ -elimination to form ethylene and the constraint in CORR that  $\text{C}_2$  pathways are only enabled at neutral and basic pH.

## SUMMARY

Summarizing, we present a complete roadmap to the mechanisms for CORR on Cu(111) that we expect to be valuable for developing new selective catalysts. Using the GC-QM for computational electrochemistry, we predict the full mechanistic description of  $\text{C}_1$  and  $\text{C}_2$  pathways in CORR on Cu(111) that explains the selectivity of methane *vs* methanol and the selectivity of ethylene *vs* ketene, ethanol, acetylene and ethane. In addition, we propose new experiments to provide direct experimental tests of

our detailed mechanisms. The introduction of probe molecules can insert into the mechanisms at specific spots to modify product distributions. This will allow detailed experimental checks on key intermediates in our predicted mechanisms.

An important discovery here is the critical role of surface  $\text{H}_2\text{O}$  on Cu in promoting dehydration and thus controlling the selectivity for hydrocarbon products, over oxygen-containing alcohol products. We expect this concept to provide an important principle in designing new electrocatalyst to promote selectivity for liquid fuel oxygenates by modifying the “hotness” of surface water (for example nanoscale sculpting of the surface).

## ASSOCIATED CONTENT

**Supporting Information.** Reaction barriers and energies for all pathways considered, coordinates for all structures studied. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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## TOC artwork

