CO-CO Coupling on Cu Facets: Coverage, Strain and Field Effects

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ABSTRACT

We present a DFT study on the effect of coverage, strain, and electric field on CO-CO coupling energetics on Cu (100), (111), and (211). Our calculations indicate that CO-CO coupling is facile on all three facets in the presence of a cation-induced electric field in the Helmholtz plane, with the lowest barrier on Cu(100). The CO dimerization pathway is therefore expected to play a role in C₂ formation at potentials negative of the Cu potential of zero charge, corresponding to CO₂/CO reduction conditions at high pH. Both increased *CO coverage and tensile strain further improve C-C coupling energetics on Cu (111) and (211). Since CO dimerization is facile on all 3 Cu facets, subsequent surface hydrogenation steps may also play an important role in determining the overall activity towards C₂ products. Adsorption of *CO, *H, and *OH on the 3 facets were investigated with a Pourbaix analysis. The (211) facet has the largest propensity to co-adsorb *CO and *H, which would favor surface hydrogenation following CO dimerization.

Graphical Abstract

Keywords

Electrocatalysis, CO₂ reduction, C-C coupling, CO dimerization

INTRODUCTION

The electrochemical CO₂ reduction reaction (CO₂RR) has the potential to produce industrial chemicals and to mitigate the increasing CO₂ concentrations in the atmosphere. Renewable energy sources such as wind and solar have seen great increases in efficiency in recent years. However, they are intermittent and require significant energy storage. CO₂RR has the potential to store renewable electricity in the form of energy-dense fuels.

The demand for hydrocarbons and alcohols is immense, with an annual production rate on the order of 10^{13} kg/yr, or 1000 kg of production, on average, per person.[1] The two major challenges in CO₂RR are the low efficiency and selectivity of known catalysts. Polycrystalline copper, the only transition metal catalyst to produce hydrocarbons at reasonable Faradaic efficiency, produces a reasonable 1mA/cm² current density at ~1V overpotential.[2]

Reduction towards C₂ hydrocarbons and alcohols such as ethylene, an industrial building block, and ethanol, a valuable fuel, is particularly desirable due to their higher energy densities than single carbon products. Polycrystalline Cu has shown similar onset potentials for C₁ and C₂ hydrocarbons at -0.75V vs. RHE.[3] These results are consistent with calculations which showed C-C coupling to be feasible after CO is hydrogenated,[4] which suggests both C₁ and C₂ pathways to be limited by the initial hydrogenation of *CO for form *CHO. However, C₂ products have been observed at low overpotential in alkaline conditions on the Cu (100) facet[5] and with oxide-derived copper (OD-Cu).[6,7] These results suggest an alternative C-C coupling pathway that proceeds prior to *CO hydrogenation. The CO dimerization mechanism had been proposed by Gattrell and Gupta et al.[8] and was then incorporated into a CO₂ reduction mechanism.[9] The mechanism was then refined to include a solvent-stabilized *OCCO intermediate.[10] Recent calculations have found CO-CO coupling to be feasible in the presence of a solvent and cation, which induces a field in the Helmholtz plane.[11] This pathways would depend on cation concentration at the interface, which depends on the absolute, not RHE potential, and is therefore expected to depend on pH. The pH of the electrolyte, and more importantly the local pH at the electrode | electrolyte interface, has been shown to influence the distribution of C₁ and C₂ products.[7,12,13] In this paper, we extend previous theoretical studies to the stepped (211) surface and examine the effects of coverage, strain, and field on *CO dimerization energetics.

RESULTS

CO-CO coupling barriers

Figure 1 shows the calculated electronic energy barriers for CO dimerization on Cu (100), (111), and (211) in the presence of a proton in the Helmholtz plane. Although this pathway is expected to play a role in alkaline media, it is quite difficult to fully solvate hydroxide in a water layer with DFT. Therefore, a proton was used to estimate the alkaline barrier; Montoya et al. found the stabilization of a proton to be equivalent to other cations.[11] A barrier of 0.45 eV was found for Cu (100) and a barrier of 0.72 eV was found for both Cu (111) and (211). All three of these barriers are lower than 0.75 eV, corresponding to a TOF of 1 s⁻¹ at room temperature from transition state theory, which is considered to be a threshold for fast kinetics. The CO dimerization pathway is therefore expected to play a role in C₂ formation at absolute potentials negative of the Cu potential of zero charge (-0.7V vs. SHE),[14] corresponding to CO₂/CO reduction at low overpotential in alkaline media.

The corresponding work function shifts along the reaction coordinate are shown in the bottom panels. Work function changes along the coupling pathway arise due to the shift in adsorbate dipole and slight changes in water structure. Assuming an SHE work

function of 4.4 eV,[15] and from $U_{SHE} = \frac{\Phi - \Phi_{SHE}}{e}$, these calculations have been performed at $\Phi \approx -1$ to 0 eV vs SHE. Constant potential barriers can in principle be extrapolated using a computationally intensive cell-extrapolation scheme.[16] However, the key effect captured here is the cation-induced field stabilization of *OCCO, which depends on the ion distribution at the interface, and not directly on the chemical potential of electrons.[17]

Figure 1. Structures and barriers for CO dimerization.

Field effects in catalysis have been studied for decades, such as in the case of alkali promoters in ammonia synthesis.[18] The change in energy of an adsorbate in an electric field is given by:

$$\Delta E = \mu \varepsilon - \frac{1}{2} \alpha \varepsilon^2 + \dots$$

where ΔE represents the change in potential energy, ε the field strength, μ the dipole moment, and α the polarizability. Figures 2 and 3 show the effect of an applied field on CO-CO coupling as calculated via an applied sawtooth potential. Figure 2 shows the effect of field on the binding energies of the initial (2 *CO), transition (*OC-CO), and final (*OCCO) states on Cu (100), and the fitted dipole moments and polarizabilities. Across all three adsorbed species, the polarizabilities are very similar; however, the dipole moment changes significantly along the reaction coordinate. This shift in dipole moment of the *CO dimer relative to uncoupled *CO gives rise to the field stabilization of the transition and final states. Figure 3 shows the reaction energy as a function of the applied field. All three facets show a linear dependence on field, which arises from the differences in dipole moment between 2 *CO and *OCCO.

Figure 2. Adsorption energy as a function of field for CO-CO coupling adsorbates on Cu(100).

Figure 3. Reaction energy as a function of field for CO-CO coupling.

Previous work has suggested that *CO dimerization proceeds exclusively on the (100) facet.[4,5] While indeed the vacuum *OCCO binding energy is lowest on (100),

*CO-*CO coupling barriers are surmountable on all 3 facets in the vicinity of an ion. Furthermore, the stability of the (100) facet under reducing conditions remains an open question. Surface energies of bare Cu facets suggest the predominance of (111) facets to (100).[19] In different electrochemical environments, Cu has been reported to reconstruct from (100) to (011) stripes[20] and from polycrystalline Cu to (100).[21]

Coverage effects

Adsorbate-adsorbate interactions have been shown to have significant impact on reaction energetics.[22] For transition metals, *CO binding energies significantly decrease with *CO coverage, which shifts the strong *CO binding metals along the theoretical activity volcano for CO₂ reduction.[23] As discussed in the following section, Cu facets considered have calculated *CO coverage of up to 0.4 under equilibrium conditions at reducing conditions below 0V vs. RHE.

Reaction energies and barriers were calculated at various *CO coverages for all three facets. In general, the CO dimerization barrier becomes even more facile as the *CO coverage increases. Figure 4 illustrates this coverage effect on all three facets of Cu. Increasing the coverage from 1/6 ML to 2/3 ML on (100) lowers the barrier from 0.45 eV to 0.40 eV, a barrier reduction of 0.05 eV. Increasing the coverage from 1/6 ML to 1/2 ML on (111) lowers the barrier from 0.72 eV to 0.40 eV, a barrier reduction of 0.32 eV. Increasing the coverage from 2/9 ML to 5/9 ML on (211) lowers the barrier from 0.72 eV to 0.50 eV, a barrier reduction of 0.22 eV. The lowering of the barrier is attributed to adsorbate-adsorbate repulsion, which weakens the carbon bond to the surface and allows for more facile C-C bond formation.

Figure 4. CO dimerization barrier as a function of coverage on all three facets. Dashed lines are included only to guide the eye.

Strain effects

Strain can allow for a further tuning of reaction energetics.[24] Experimentally this can be induced via overlayers, where the lattice mismatch between the overlayer and host causes the overlayer to become strained.[25] Strain has also been hypothesized to play an important role in CO₂RR such as in the increase in activity on OD-Cu compared to polycrystalline Cu.[6]

Figure 5 shows the energy of initial, transition, and final states at strains ranging from -5% to 5% for the (100), (111), and (211) facets, and Figure 5 shows the corresponding free energy diagrams for Cu(100), (111), and (211) at strains of -5, 0 and 5%. Negative strain values indicate a decrease in the x and y distances in the bottom 2 fixed layers and vice versa for positive values. Overall, tensile strain decreases adsorption energies of all intermediates, and hence is expected to increase overall *CO coverage. For the case of (100), all states have very similar correlations with strain, as indicated by their similar slopes. However, for (111), the initial and final states have the same correlation but the transition state energies have a different slope. This results in a lowering of the barrier for tensile strains, with a 0.2 eV decrease in the barrier for a 5% strain. For (211), the initial and transition states have the same correlation but the final state energies have a different slope. This results in a decrease in the reaction energy for tensile strains. The trends in the energies are similar for (100) and (111), but are quite different for (211), which could arise from the additional degrees of freedom that the undercoordinated stepped sites on the (211) surface have to relax in response to strain.

The free energy diagrams in Figure 6 exhibit these changes in barrier on (111) and reaction energy on (211).

Figure 5. Energy vs strain for Cu(100), (111), and (211).

Figure 6. Free energy diagrams as a function of strain for Cu(100), (111), and (211).

The effect of strain can be attributed to both changes in electronic structure and coordination. Previous DFT calculations have shown $^*\text{CO}$ to bind stronger upon an increase in lattice constant on Ru(0001),[24] and this was also observed for $^*\text{CO}$ binding energies on all three Cu facets. For the (100) and (211) facets, there was no change in total coordination of the 2 $^*\text{CO}$ to the surface between the initial and transition states (4 in initial, 4 in transition). However, for the (111) facet, there is a large change in total coordination between the initial and transition states (6 in initial, 3 in transition).

Overall, strain increases $^*\text{CO}$ coverage on all facets, and reduces the barrier on (111) and the reaction energy on (211). These results suggest that further improvement of CO dimerization rates on Cu facets is possible via a tensile strain.

Pourbaix analysis

In the presence of cations in the Helmholtz plane, CO-CO coupling is facile on all facets, and increased $^*\text{CO}$ coverage decreases the barrier further. Therefore, at absolute potentials negative of the Cu potential of zero charge (-0.7V vs. SHE),[14] CO dimerization may not be the limiting factor in the activity towards C_2 products. Previous work on barriers for CO_2R to C_1 products have found proton-electron transfers to C to be generally difficult at low overpotential, while surface hydrogenations are generally facile, with the exception of $\text{CO} \rightarrow \text{CHO}$, which has a $\sim 0.9\text{eV}$ barrier on both Cu (111) and

(211).[26] In the presence of a cation in the Helmholtz plane, it was found that $\text{OCCO}^* + \text{H}^* \rightarrow \text{OCCHO}^*$ is also facile on (100) and (111),[11] with barriers that are only $\sim 0.05\text{eV}$ above the CO dimerization barriers. This suggests that C_2 production at low overpotential may proceed primarily through CO dimerization and subsequent surface hydrogenation steps. Surface coverages of both CO^* (which determines CO dimerization rate) and H^* (which determines surface hydrogenation rate) would therefore be crucial in determining C_2 activity.

We have explored surface coverages of H^* , CO^* , and OH^* under equilibrium conditions through Pourbaix diagrams.[27] Figures 7-9 show the Pourbaix diagrams for Cu (100), (111), and (211). Generally, as potential decreases, OH^* is replaced by CO^* , then CO^* by H^* . At the onset potential for CO reduction to C_2 products (-0.3V vs. RHE, 1 atm CO)[6], $\theta_{\text{CO}} = 0.4$ on (100), H^* dominates the (111) facet, and on (211) $\theta_{\text{CO}} = 0.1$, $\theta_{\text{H}} = 0.3$. Therefore, while (100) has the lowest barrier and highest CO coverage, its activity towards C_2 products may be limited by a low H^* coverage, which determines in part the surface hydrogenation rates. The (211) facet has a higher CO dimerization barrier, but it co-adsorbs significant coverages of both CO^* and H^* , which would favor surface hydrogenation.

Striped regions in the diagrams indicate regions of CO^* and H^* co-adsorption, and point to the propensity of the (211) facet to co-adsorb CO^* and H^* . Cu (100) and (111) contain narrow co-adsorption regions, around -0.4V and -0.2V , respectively, while Cu (211) contains a large co-adsorption region that spans the potential range of -0.6V to -0.1V . We note that under CO_2/CO reduction conditions, kinetics ultimately determine adsorbate coverage, but a thermodynamic analysis provides a first approximation of the propensity of the various facets to co-adsorb CO^* and H^* .

Figure 7. Cu(100) Pourbaix diagram.

Figure 8. Cu(111) Pourbaix diagram.

Figure 9. Cu(211) Pourbaix diagram.

CONCLUSIONS

We show CO dimerization to be feasible on basic facets of Cu, namely (100), (111), and (211), in the presence of the field induced by cations at the electrochemical interface. All three facets have free energy barriers of ~ 0.75 eV or lower, indicating fast kinetics at room temperature. CO dimerization is therefore expected to play a role in C_2 formation at potentials negative of the potential of zero charge of Cu, corresponding to CO_2/CO reduction in alkaline conditions. Cu (100) has the lowest CO dimerization barrier, but the stability of this surface remains controversial in the experimental literature.

When the coverage of *CO is increased on all three facets, the CO-CO coupling energetics become even more facile, with barrier reductions ranging from 0.05 eV to 0.32 eV. Application of a tensile strain increases the *CO coverage, and reduces the barrier on (111) and reaction energy on (211). This suggests that tensile strain, realized through overlayers, can play a role in further improving *CO - *CO coupling energetics on Cu.

Facile CO dimerization on all Cu facets suggest subsequent surface hydrogenation rates to play an important role in determining overall C_2 activity. Surface hydrogenation requires the co-adsorption of H^* . A Pourbaix analysis shows Cu (211) to have the largest propensity to co-adsorb *CO and *H , which favors surface hydrogenation.

Future work will focus on the development of a microkinetic model of CO reduction, which will incorporate the reaction energetics, strain, coverage (via adsorbate-adsorbate interaction models) and field effects discussed in this work. This kinetic model is expected to elucidate how the interplay of all such effects leads to overall activity and selectivity on the various Cu facets.

METHODS

Density Functional Theory (DFT) was used to calculate all electronic energies. Quantum Espresso was used with the BEEF-vdW exchange-correlation functional and Ultrasoft pseudopotentials. A 500eV plane-wave cutoff, 5000eV density cutoff, and a (4,4,1) k-point sampling were used for all calculations. A $4 \times 3 \times 3$ supercell of fcc Cu (100) and (111) with a single layer of eight (Cu(100)) or seven (Cu(111)) water molecules at the surface was used to model the electrochemical interface. For the (211) surface, a $3 \times 3 \times 3$ supercell with five water molecules was used. Water densities were chosen to be as close as possible to that of the Pt(111) bilayer structure as found in UHV experiments within the unit cell sizes considered.[28] Water layer structures were determined using a minima-hopping algorithm that alternates between Molecular Dynamics and geometry optimization steps to construct a series of local minima.[29] All strain calculations were done by straining the initial and final states in both the x and y directions and then performing geometry optimizations to allow for relaxation in the z direction. To simulate a charged double layer at the electrochemical interface, a single hydrogen atom was placed in the water layer. The ground-state electronic structure redistributes the charge from this atom's one electron to the metal, creating a charge-separated double layer.[16] A dipole correction in the z -direction was applied in all calculations to compensate for the field resulting from the asymmetric slab in the vacuum region.[30] The correction to the *OCCO electronic energy and *OC -CO transition state energy was also taken from previous work.[11]

The following elementary steps were considered to construct Pourbaix diagrams of *H, *OH, and *CO:

The CHE model was used to equate the chemical potential of proton-electron pairs and hydrogen gas at standard conditions (pH = 0, p(H₂) = 1 bar) and U = 0 V vs SHE:

Binding energies were calculated based on these elementary steps. Free energy corrections were applied for the references (CO_(g), H₂O_(l), H_{2(g)}) and adsorbates (*CO, *OH, *H) to determine binding free energies. Because these calculations were done in vacuum, a solvation stabilization of 0.1 eV was used for *CO and 0.5 eV for *OH to simulate an electrochemical aqueous environment.[31] These solvation corrections were determined by adsorption calculations with and without a water layer on (111) facets of Pt (for *OH) and Cu (for *CO). This 0.5 eV stabilization of *OH was applied to a maximum of 3 OH*, which represents the maximum coverage that can be hydrogen-bonded in a hexagonal ice-like water structure. Cu (100), (111), and (211) were investigated by performing a series of calculations at mixed coverages of the three adsorbates. Using a 3 × 3 unit cell (9 sites) with three different adsorbates and a vacancy (4 possibilities), hundreds of mean-field mixed coverages are possible. A machine-learning approach was used to identify energetically favorable coverages using only ~50 DFT calculations. A training set of about 10-15 mixed coverages was chosen. The free energies of these coverages were calculated and the results used as inputs to a machine-learning package. The approach, based on Gaussian process regression, aims to predict the free energy of all possible mean-field adsorbate coverages for a finite surface.[32] It efficiently identifies the most stable configurations that form the lower hull of a 1-D Pourbaix diagram as a function of applied potential. With the DFT calculated energies, a 2-D Pourbaix diagram was determined for each Cu facet as a function of both applied potential and CO_(g) pressure (figures 7-9).

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