First-principles microkinetics simulations of electrochemical reduction of CO$_2$ over Cu catalysts

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ABSTRACT

Electrochemical reduction of CO$_2$ can contribute to the storage of excess renewable electricity in chemical bonds. Here we incorporate reaction energetics for CO$_2$ reduction on Cu(111) and Cu(211) determined by DFT calculations in microkinetics simulations to predict the influence of surface topology, the presence of water and possible diffusion limitations on current density-potential curves and Faradaic efficiencies. A reaction-diffusion model was used that takes into account the effect of electrochemical potential on the stability of intermediates and associated activation barriers in proton-coupled electron transfer steps as well as diffusion of protons and CO$_2$ from the bulk electrolyte to the electrode surface. The basic model can well reproduce hydrogen evolution including the effect of proton diffusion limitations and a shift of proton reduction (low potential) to water reduction (high potential). Considering CO$_2$ electro-reduction, the stepped Cu(211) surface is more active than the Cu(111) terrace towards HCOO(H), CO and CH$_4$. The presence of a catalytic H$_2$O molecule increases the overall rate and selectivity to products (CO and CH$_4$) derived from dissociated CO$_2$. A catalytic H$_2$O molecule facilitates the difficult electrochemical CO$_2$ activation step to COOH and suppresses the competing activation step towards HCOO, which mainly yields HCOO(H). In general, the current densities increase at higher negative potential and the products follow the sequence CO$_2$ / CO / CH$_4$. That is to say, CO$_2$ is converted to CO via COOH dissociation, followed by CO hydrogenation. Trendwise, the simulated product distribution follows the potential-dependent distribution observed in experiment. The low selectivity to CH$_3$OH can be understood from the fast electrochemical steps that lead to CH$_x$-OH dissociation. At high overpotentials the hydrogenation step from CO$_2$ to COOH controls both activity and selectivity towards CH$_4$. At high potential CO$_2$ reduction becomes increasingly diffusion-limited, thus limiting the selectivity of CO$_2$ reduction vs. hydrogen evolution. This aspect supports the need for better design of mass transfer in electrochemical reactors, which operate at high current density.

1. Introduction

Our modern highly industrialized economy is largely dependent on the availability of cheap non-renewable fossil resources. Oil, gas and coal remain the major source of energy and chemicals, resulting not only in air pollution but also in the release of large amounts of carbon dioxide (CO$_2$), one of the primary causes of global warming. It is therefore pivotal to replace these unsustainable sources of energy and chemical by renewable ones. The most likely scenario for such a transition is that a mix of renewable energy sources will increasingly contribute to the global energy demand. A major contribution will come from green electricity generated by solar panels and wind turbines. The intermittency of
such electricity requires the development of scalable and affordable energy storage. Converting excess electricity to chemicals is expected to become important in the future because of the high energy density, thereby also contributing to challenges such as mobility and sustainable chemicals production. An attractive option is to convert CO₂ into fuels and chemicals that are compatible with our current energy infrastructure. This can be done indirectly by splitting water into hydrogen and oxygen followed by reducing CO₂ with hydrogen using catalytic chemistry such as the Sabatier reaction, the Fischer-Tropsch reaction or methanol synthesis into methane, liquid hydrocarbons, and methanol, respectively. Another approach would be to directly convert CO₂ electrochemically into reduced compounds, which can serve as fuels for later conversion to energy, and starting compounds for the chemical industry [1–4].

Electrochemical reduction can be used to reduce CO₂ into carbon monoxide (CO), methane (CH₄), olefins and alcohols. A large number of metals have been investigated for the electrochemical reduction of CO₂ before [5–17]. For instance, the group of Hori has extensively studied the performance in terms of current density and product distribution achievable with common metal electrodes [12–16]. As an example, formic acid (HCOOH) and CO are the predominant products at high CO₂ pressure on Ag, Fe, Co, Rh, Ni, Pd and Pt [18], while CH₄ is the main product on Cu [12]. The CH₄ formation has also been attempts to clarify the structure sensitivity of CO₂ electro-reduction for different transition metal electrodes [11]. Currently, there is a large research effort focused on increasing the efficiency, selectivity and stability of the catalytic materials for CO₂ electro-reduction [10,19].

Cu stands out as it is the only metal that can convert CO₂ with a reasonable selectivity to valuable CH₄ and ethylene (C₂H₄) hydrocarbon products in aqueous electrolyte at ambient temperature [14,20–25]. Several works already showed that CO₂ reduction is sensitive to the surface topology of Cu [26–34]. For instance, Cu nanoparticles supported on glassy carbon display a current density to CH₄ that is up to four times higher than a Cu foil [29]. In a computational study of CO₂ hydrogenation on Cu clusters and nanoparticles, we showed that a Cu19 cluster displays optimum activity for methanol (CH₃OH) formation [34]. The facet-dependence of CO₂ hydrogenation activity and selectivity has also been emphasized in experimental studies [9,35–38]. For instance, the electrochemical reduction of CO₂ on Cu foams with a high surface roughness and porosity yields predominantly HCOOH with lower concentrations of CO, methane, and ethylene as compared with a smooth copper foil electrode [9].

Identification of the mechanism of electrochemical CO₂ reduction is of great significance for guiding the design of better catalysts [24,32,39–42]. A general trend is that CH₄ is the main product at high overpotential, while CO and HCOOH are dominant along with a large amount of hydrogen (H₂) at lower overpotential for most transition metal electrodes [12,13,17,33,43–46]. CH₃OH is a commonly reported side-product at higher overpotential [19,47]. For example, a small amount of CH₃OH was observed by nuclear magnetic resonance (NMR) spectroscopy during electrochemical CO₂ reduction on Cu [48]. Kinetic measurements revealed that reduction of formaldehyde (CH₂O) directly yields CH₃OH with CH₄ as a side-product. These results suggest that CH₃OH is not a likely reaction intermediate of the electrochemical reduction of CO₂ on Cu [47]. Similar to heterogeneous CO₂ hydrogenation, the formation of HCO or COH is thought to be the rate-determining step for electrochemical CO₂ reduction on Cu [24,25,49,50]. It has for example been proposed that CH₃OH is formed through a HO intermediate, while CH₄ formation involves a COH intermediate on Cu electrodes [43]. The slow steps for CH₃OH formation in the formate (HCOO)-like mechanism demonstrated by Gao and Au are the hydrogenation of HCO and H₂CO [51]. It has also been shown that the COH intermediate cannot be the key intermediate for CH₄ formation due to the higherbarrier compared to dissociation of the HCOH intermediate [4]. Besides, CO₂ reduction to CH₃OH via a H₂COOH intermediate following hydrogenation of HCOO has been proposed for a TiO₂–Ag catalyst [52]. Despite intensive research efforts, many aspects regarding the electrochemical reduction of CO₂ on Cu surfaces remain unresolved.

At the electrode-electrolyte interface, the charge separation between the electrode metal surface and counter ions in the electrolyte creates an electrostatic potential drop, influencing the local structure and adsorption strength of reaction intermediates. Accurately incorporating these aspects into density functional theory (DFT) calculations remains a challenge and requires an understanding of the exact molecular structure of the electrode-electrolyte interface. A few theoretical models have been developed to deal with these issues such as the reaction-center model [53], the vacuum interface model based on the linear free energy method [54,55], the external electric field model [56,57], and the double reference model [57,58]. The linear free energy thermochemical model developed by Nørskov and coworkers can be used to capture activity trends among different metals in a qualitative manner without taking into account explicitly the electrostatic effects. Peterson and coworkers used this method to show that the key step in the formation of CH₄ and H₂ on Cu is the hydrogenation of CO to HCO. These authors also found that the CH₃OH selectivity during electrochemical CO₂ reduction is determined by the rate of the hydrogenation of the methoxy (CH₃O) intermediate [59].

In the present work, we used DFT calculations together with the linear free energy model to investigate electrochemical CO₂ reduction on two periodic Cu surfaces. We limited ourselves to the formation of C₁ species, given the complexity of the formation of C₂C bonds [34]. We took into account the dependence of the activation barriers of elementary reaction steps involving H atoms on electrochemical potential. Microkinetics simulations were performed to compute CO₂ conversion and product formation rates as a function of the applied electrochemical potential. The rate-limiting steps for electrochemical CO₂ reduction were determined as well. The surface of Cu(111) and stepped Cu(211) surfaces were considered in our work in order to shed light on the structure sensitivity of Cu nanoparticle-catalyzed electrochemical CO₂ reduction. Although the electrolyte was not taken into account explicitly, we evaluated the impact of water molecules on the activation barriers of the elementary reaction steps of the more active stepped Cu(211) surface. While we only included a single H₂O molecule in our calculations, we observed changes in the transition state stabilities relating to hydrogen-bonding interactions. More accurate results could be achieved in further studies by taking into account more water molecules and explicitly taking the electrolyte buffer into account. We focused on the formation of HCOO, CO, CH₃OH and CH₄ and also considered the recently increasingly recognized problem of mass transfer limitations resulting in depletion of reactants like protons and CO₂ near the electrode surface. Recent work emphasizes that this aspect may render interpretation of kinetic data difficult at commercially-relevant current densities, as CO₂ electro-reduction and especially hydrogen evolution may be partially limited by slow diffusion of reactants from the bulk electrolyte [60]. The results in our work show that the current density and product distribution depend strongly on the Cu surface topology, the applied potential and the stabilization of transition states by water. Diffusion limitations significantly affect the rate and product distribution. We discuss the influence of removing such limitations on the product distribution by simulating a rotating disc electrode. While previous DFT studies have already pointed out the overall pathways for CO₂ reduction,
our integrated microkinetic model provides direct insight into the rate-controlling elementary steps under realistic diffusion limited conditions. These insights cannot be derived directly from DFT alone.

2. Methodology

2.1. Computational details

All DFT calculations were performed by using the Vienna ab initio simulation program (VASP), along with projected augmented wave (PAW) [61] pseudopotentials and the Perdew-Burke-Ernzerhof (PBE) functional [62]. p(3 × 4) and (1 × 4) periodic slab models were used to compute the energies of stable adsorption geometries and transition states that separate these stable states for the Cu(111) and Cu(211) surface models. Both periodic surfaces were simulated using four equivalent (111) atomic layers. Neighboring slabs were separated by a vacuum of 20 Å to avoid spurious self-interactions. Monkhorst-Pack k-point meshes of 5 × 3 × 1 were used for these periodic models. An energy cutoff of 400 eV was employed for the plane-wave basis set. The convergence threshold for electronic steps was 1 × 10⁻⁴ eV. Geometries were deemed converged when the forces on each atom were below 0.02 eV/Å. A frequency analysis was carried out on the stable states in order to confirm that these represent genuine minima. All of the electronic energies were corrected for zero-point energy (ZPE) contributions. The improved force-reversed method [63] was used to determine transition states with a force tolerance of 0.02 eV/Å. Some transition states were confirmed by using the climbing image nudged elastic band method (CI-NEB) [64]. We verified that the transition states were accompanied by a single vibrational frequency along the reaction coordinate.

2.2. Potential-dependent reaction barriers

The mechanism of electrochemical CO₂ reduction involves adsorption of CO₂ on the Cu surface followed by two types of reactions: (i) potential-dependent elementary reactions involving a series of proton-coupled electron transfer (PCET) steps in the associative pathway (electrochemical reactions) and (ii) potential-independent elementary reactions (non-electrochemical reactions) [65–67].

For potential-dependent electrochemical reactions of the type

\[ A + H^+ + e^- \rightarrow \text{AH} \] (1)

the reaction free energies were calculated based on the computational hydrogen electrode (CHE) model [55]. In this model the reference potential is set to the standard hydrogen electrode (0 V vs. SHE). At this potential, the reaction \( H^+ + e^- \rightarrow \frac{1}{2} H_2 \) is equilibrated at pH = 0 and 1 bar of H₂ in the gas phase at 298 K. This potential can be shifted by \(-0.059 \times \text{pH}\) to reach 0 V vs. the reversible hydrogen electrode (RHE) at any pH. For example, at pH = 6.8 the potential of 0 V vs. RHE is equal to \(-0.40 \text{ V vs. SHE}\). Although the reaction free energy is independent of pH on the RHE scale, barrier heights still vary as a function of pH, but constant potential vs. RHE. Therefore, all barrier heights were defined with respect to the SHE potential. The chemical potential of the proton-electron pair can be calculated at 0 V vs. SHE using DFT and statistical mechanics relationships to determine the free energy of gaseous H₂. The dependence of the proton-electron pair free energy on the electrode potential can be simply determined using the linear free energy dependence of the electron energy on this potential, shifting the electron energy by \(-eU\),

\[ \mu(H^+) + \mu(e^-) = \frac{1}{2} \mu(H_2) - eU \] (2)

where e is the elementary positive charge and U the electrode potential of interest on the SHE scale. The free energy change of a specific electrochemical reaction, \( \Delta G \), can be written as

\[ \Delta G = \Delta G^0 + eU \] (3)

where \( \Delta G^0 \) is the reaction free energy at 0 V vs. SHE and U is the potential measured vs. SHE.

In order to account for the influence of the electrode potential on the activation barrier of electrochemical reaction steps, we first determined the activation barrier for an equivalent hydrogenation reaction of the type

\[ A + H^* \rightarrow \text{AH}^* \] (4)

The activation barrier \( (E_a) \) for this reaction can be obtained by standard DFT approaches. At equilibrium \( H^+ + e^- \rightarrow H^* \) conditions, the activation barrier \( E_a^DFT \) for \( A + H^+ + e^- \rightarrow \text{AH}^* \) equals to \( E_a^{DFT} \). Here, \( E_a^{DFT} \) is the potential relative to SHE that equals \( -E_{ad}(H^*) \) for a particular surface.

The activation barriers at 0 V vs. SHE for \( A + H^+ + e^- \rightarrow \text{AH}^* \) can then be computed following the Butler–Volmer formalism [66].

\[ E_a^{0, \text{forw}} = E_a^{DFT} + \alpha \left( -eU^0 \right) \] (5)

The reaction barriers for the backward reactions were calculated in a similar way, leading to

\[ E_a^{0, \text{back}} = E_a^{DFT} - \beta \left( -eU^0 \right) \] (6)

Here, \( \alpha \) and \( \beta (\beta = 1 - \alpha) \) are effective symmetry factors, which are approximated as Bronsted–Evans–Polanyi coefficients [68] describing the relationship between activation barriers and reaction energies. In the current work, \( \alpha \) and \( \beta \) were set to 0.5 for all elementary steps as an approximation. In reality these symmetry factors can deviate from 0.5 and be different for each reaction. These differences could result in slightly different onset potentials than found in the modeling results here. The barrier can then be extrapolated from 0 V vs. SHE to other potentials by involving the electrode potential \((U)\)

\[ E_a^{\text{forw}}(U) = E_a^{0, \text{forw}} + \alpha(eU) \] (7)

For the backward reactions, the potential dependent activation barriers were calculated in a similar manner

\[ E_a^{\text{back}}(U) = E_a^{0, \text{back}} - \beta(eU) \] (8)

We also took into account potential-dependent electrochemical steps of the type

\[ A + H_2O + e^- \rightarrow \text{AH} + \text{OH}^- \] (9)

Following the work of Liu and co-workers [69], we took the activation barriers for these reactions the same as for the corresponding reactions of eq. (1), with the exception of the Volmer and Heyrovsky barriers, which we increased to satisfy the experimentally observed lower rate of hydrogen evolution via water reduction compared to proton reduction. The effect of applied potential vs. SHE is the same for both types of reactions, i.e. we assume similar effective symmetry factors. The effect of pH changes will be different, as \( H^+ \) is a reactant in eq. (1), while \( \text{OH}^- \) is a product in eq. (2). Therefore, increasing pH will slow down proton reduction,
while the forward rate for the water reduction step is unaffected. Combined, this has the consequence that increased pH, at constant potential vs. RHE, will lead to a decrease in proton reduction and an increase in water reduction [70].

2.3. Microkinetics simulations

Microkinetics simulations of electrochemical CO2 reduction were carried out using the MKMXX software package [71]. The basic methodology for these simulations is described elsewhere [72]. The rate constants for each electrochemical reaction step, i, is assumed to take the functional form

\[ k_i = A_i \exp \left( - \frac{E_i(U)}{k_B T} \right) \]  

(10)

where \( A_i \) is an effective pre-factor. As an approximation, the pre-factor was set to equal \( \frac{2 \pi}{\beta} \) s\(^{-1}\) for all the surface elementary reactions. This approximation is decent for reactions involving intermediates that are strongly bounded to the catalyst surface, and may not fully describe the reactions involving free protons. The pre-factors might also change with the applied potential for real systems. Therefore, the rate constants in this study should be interpreted as qualitative, rather than quantitative. The non-electrochemical reaction steps are described in the same way without the potential dependency

\[ k_i = A_i \exp \left( - \frac{E_{\text{act}}}{k_B T} \right) \]  

(11)

We took as the active site area \( 5.68 \times 10^{-20} \text{ m}^2 \), corresponding to two-adjacent 3-fold sites on the Cu(111) surface. We took into account literature data to simulate the hydrogen evolution reaction on Cu surfaces. The exchange current density for hydrogen evolution on Cu (at 0 V vs. SHE, standard hydrogen electrode) is approximately \( 1 \times 10^{-3} \text{ mA/cm}^2 \) [73]. This was taken into account as activated hydrogen evolution with an energy barrier of 87 kJ/mol. It is known that, at high current densities obtained at high overpotentials, the availability of H\(^+\) close to the electrochemical surface will be decreased due to diffusion limitations [60,74]. To simulate this, we included a diffusion layer from the bulk solution to the catalyst surface. The diffusion coefficient \( D \) of H\(^+\) in water was taken as \( 9.31 \times 10^{-9} \text{ m}^2/\text{s} \) [73]. The diffusion layer thickness for H\(^+\) was calculated from the Levich equation [75].

\[ \delta = 1.6126D \nu^{1/2} \]  

(12)

where \( \delta \) is the diffusion layer thickness in m, \( \nu \) the kinematic viscosity of the solution in m\(^2\)/s\(^{-1}\) and \( \omega \) the rotation rate of the rotating disc electrode in rad s\(^{-1}\). The concentrations are then solved simultaneously with the surface kinetics using Fick's second law of diffusion perpendicular to the surface

\[ \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \]  

(13)

in which \( C \) is the location- and time-dependent concentration of the diffusing compound, \( t \) the time, \( D \) the diffusion coefficient and \( x \) the distance from the surface. Discretization of the diffusion layer was done using 50 grid points employing a 3-point 2nd order central difference scheme. We also took diffusion of CO\(_2\) (\( D = 2 \times 10^{-5} \text{ m}^2/\text{s} \)) and OH\(^-\) (\( D = 5.27 \times 10^{-9} \text{ m}^2/\text{s} \)) into account, for which we used as a first approximation the same diffusion layer thickness as for H\(^+\). As the effective surface pH will be increased at high overpotential, we may expect that the water reduction reaction will start to dominate (\( A + \text{H}_2\text{O} + e^- \rightarrow \text{AH} + \text{OH}^- \)) over the proton reduction mechanism. We assumed a water activity coefficient of unity and a water reduction barrier of 135 kJ/mol at 0 V vs. SHE (standard hydrogen electrode) based on the onset potential determined by Ooka et al. [74]. All elementary reaction steps involving hydrogen following the proton reduction mechanism as well as the water reduction mechanism were taken into account. We assumed that H\(_2\) dissociation on Cu(111) and Cu(211) is activated with a barrier of 50 kJ/mol [76,77]. For the non-electrochemical formation of H\(_2\) from two adsorbed H species, we included entropy corrections. We assumed a zero free energy difference between CO\(_2\) adsorbed on the electrode surface and CO\(_2\) in solution. A solvated CO\(_2\) concentration of 0.033 mol/l was used corresponding to experimental conditions of 1 bar CO\(_2\) and water at 298 K [78]. Barriers for adsorption and desorption of CO\(_2\) were set at 35 kJ/mol, the same as the entropy contribution of solvated CO\(_2\) to the free energy [73]. We assume that this barrier provides a reasonable approximation for the speed at which solvated CO\(_2\) at the interface equilibrates with adsorbed CO\(_2\). We found that small deviations of this barrier do not significantly influence the simulation results. The CO desorption barriers were corrected with a value of 30 kJ/mol, taking into account regained entropy upon desorption and were further reduced by 23 kJ/mol to correct for overlapping considering the used DFT functional in this work [79]. For the other desorbing species, we assumed the barriers to be equal to the enthalpic differences as determined by DFT.

The Faradaic efficiencies were calculated by dividing the partial current to each product by the total current:

\[ \text{FE}_i = \frac{z_i f_i}{\tau_e} \]  

(14)

Here, \( z_i \) is the number of electron transfers needed for production of \( i \), \( f_i \) is the rate of production of \( i \) and \( \tau_e \) is the total rate at which electrons are consumed. We also performed a sensitivity analysis for every elementary reaction step in order to determine the degree of rate control (DRC) [80] and the degree of selectivity control (DSC) [81]:

\[ \text{DRC}_i^{\text{CO}} = \left( \frac{\partial n_i}{\partial n_{\text{CO}}} \right) k_{\text{CO}}, k_i \]  

(15)

\[ \text{DSC}_i^{\text{CH}_4} = S_i \cdot \left( \text{DRC}_i^{\text{CH}_4} - \text{DRC}_i^{\text{CO}} \right) \]  

(16)

3. Results and discussion

DFT calculations were performed to determine the adsorption energies of reaction intermediates and activation barriers of candidate elementary reaction steps involved in electrochemical CO\(_2\) reduction on terrace (111) and stepped (211) Cu surfaces. The explored reaction mechanisms for electrochemical reduction of CO\(_2\) to HCO\(_2\)(H), CO, CH\(_3\)O, CH\(_4\) and CH\(_3\)OH are presented in Scheme 1. In the modeling of the CO\(_2\) reduction pathway we include three sets of elementary reaction steps. The first set consists of potential-independent steps. This includes C-O dissociation steps of (partially hydrogenated) CO\(_2\) and CO intermediates as well as H\(_2\) evolution via the Volmer-Tafel mechanism [82,83]. These reactions (eq. (4)) do not depend on the applied potential, because they do not involve either solvated protons (eq. (1)) or electrochemically active water molecules (eq. (9)). All electrochemical steps in Scheme 1 were also included in the potential-independent set, as these steps can proceed as well with surface-adsorbed atomic hydrogen. The second and third reaction sets in the microkinetic model are all
electrochemical steps involving respectively solvated protons or water molecules. Table 1 shows the adsorption and desorption barriers used in the microkinetic model. These values are based on the computed enthalpies of adsorption and on entropic considerations. CO$_2$ adsorbs very weakly on Cu surfaces with adsorption energies of only a few kJ/mol on Cu(111) and Cu(211). The adsorption energy is slightly increased (~5 kJ/mol) on the latter surface in the presence of H$_2$O as a co-adsorbate. As the actual adsorption and desorption rate constants are difficult to predict, we assumed in the microkinetic model a similar forward and backward barrier of 35 kJ/mol for CO$_2$ adsorption on all surfaces. Hydrogen adsorption on Cu(211) is 22 kJ/mol more favorable as compared to the Cu(111) surface, while the presence of H$_2$O destabilizes hydrogen on Cu(211) by 7 kJ/mol. The computed activation barriers for the non-electrochemical surface reaction steps are presented in Table 2. Potential-dependent elementary reaction steps refer to electrochemical reactions in which a hydrogenation step is involved from either a proton in the solution or an electrochemically active water molecule. Examples are the formation of (partially hydrogenated) CO$_2$ and CO intermediates. As the stability of the H atom depends on the applied potential, it will not only affect the initial and final state of an elementary reaction step but also the activation barrier. The activation barriers were determined by DFT calculations and Eqs. (7) and (8). Equivalent reactions involving water as a proton source were also included in the microkinetic model. The activation barriers for all of the considered reactions are collected in Table 3. Direct CO$_2$ dissociation is easier on the corrugated surface (102 kJ/mol) than on the planar terrace (140 kJ/mol). Water as a co-adsorbate lowers the barrier on the Cu(211) surface to a value of 83 kJ/mol. Alternative pathways for CO$_2$ activation involving hydrogenation prior to C-O bond cleavage were also considered. These hydrogenation steps involve electrochemical reduction of CO$_2$ with protons (Table 3). Then, the overall barrier for these pathways will...

Table 1

<table>
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<tr>
<th>Elementary reaction</th>
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<th>Cu(211)</th>
<th>Cu(211) + H$_2$O</th>
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<td>$E_{act,b}$</td>
<td>$E_{act,f}$</td>
</tr>
<tr>
<td>CO$_2$ adsorption</td>
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Table 2

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<td>CO$_2$ $\approx$ CO + O</td>
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</table>
depend on the applied electrochemical potential. This will be considered below. Here, we will focus on the gas-phase reaction energetics. Dissociation of HCOO (formate) to HCO and O is more difficult than direct CO2 dissociation. This is in accord with an earlier report [84]. Pathways via the carboxyl intermediate are very facile on Cu(111) and Cu(211). However, formation of the COOH intermediate from CO2 is difficult (Table S1), exhibiting barriers of 145 kJ/mol for Cu(111), 140 kJ/mol for Cu(211) and 130 kJ/mol for Cu(211) in the presence of H2O. Thus, from an energetics point of view, direct CO2 dissociation is favored under non-electrochemical conditions. However, under electrochemical conditions the barrier of the COOH formation step will be reduced. Furthermore, COOH is more stable by 34 kJ/mol on Cu(211) compared to Cu(111). Then, Cu(211) is the preferential surface for CO2 dissociation via the carboxyl pathway. The corresponding transition state for the formation of the carboxyl intermediate on the Cu(211) surface is shown in Fig. 1. The transition states for formation of HCOO, HCO, and HCOH can be found in Figs. S16-S17.

Dissociation of the C-O bond in adsorbed CO was also considered. CO dissociation has the highest activation barrier among the non-electrochemical elementary reactions (Cu(111): 373 kJ/mol; Cu(211): 291 kJ/mol; Cu(211) with H2O: 307 kJ/mol). The activation barriers for C-O bond scission of CHnO (n = 1–3) intermediates were also considered and are in the 119–172 kJ/mol range for Cu(111), the 110–166 kJ/mol range for Cu(211) and the 108–188 kJ/mol range for Cu(211) in the presence of H2O. The lowest barrier for C-O dissociation without added water is for the CH2O surface intermediate with only small variation between the two surfaces. In the presence of H2O, the COH dissociation has the lowest barrier on Cu(211). Considering the different stability of CHnO intermediates compared to CO, we determined overall barriers for C-O bond cleavage in HCO of 247 kJ/mol for Cu(111), 230 kJ/mol for Cu(211) shown in Fig. 1. Transition state geometries (top and side views) for the formation of COOH on (a) Cu(211) and (b) Cu(211) in the presence of a catalytic H2O molecule.

### Table 3

Energetics for electrochemical reactions in CO2 reduction on Cu surfaces at a potential of 0 V vs. SHE (Eact,f forward activation energy, Eact,b backward activation energy, all energies in kJ/mol). In the microkinetic model all elementary reaction steps are possible both with H as proton source and with H2O as proton source. For the latter, the same barriers were used.

<table>
<thead>
<tr>
<th>Elementary reaction</th>
<th>Cu(111)</th>
<th>Cu(211)</th>
<th>Cu(211) + H2O</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Eact,f</td>
<td>Eact,b</td>
<td>Eact,f</td>
</tr>
<tr>
<td>O + H ⇌ OH</td>
<td>96</td>
<td>151</td>
<td>100</td>
</tr>
<tr>
<td>OH + H ⇌ H2O</td>
<td>143</td>
<td>209</td>
<td>145</td>
</tr>
<tr>
<td>C + H ⇌ CH</td>
<td>68</td>
<td>166</td>
<td>74</td>
</tr>
<tr>
<td>CH + H ⇌ CH2</td>
<td>48</td>
<td>88</td>
<td>64</td>
</tr>
<tr>
<td>CH2 + H ⇌ CH3</td>
<td>52</td>
<td>117</td>
<td>54</td>
</tr>
<tr>
<td>CH3 + H ⇌ CH4</td>
<td>74</td>
<td>146</td>
<td>90</td>
</tr>
<tr>
<td>CO + H ⇌ COH</td>
<td>123</td>
<td>23</td>
<td>121</td>
</tr>
<tr>
<td>CO + H ⇌ HCO</td>
<td>105</td>
<td>8</td>
<td>101</td>
</tr>
<tr>
<td>HCO + H ⇌ HCOH</td>
<td>67</td>
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<td>59</td>
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<tr>
<td>HCO + H ⇌ CH2O</td>
<td>65</td>
<td>72</td>
<td>48</td>
</tr>
<tr>
<td>CO + H ⇌ HCOH</td>
<td>111</td>
<td>69</td>
<td>131</td>
</tr>
<tr>
<td>HCOH + H ⇌ CH2OH</td>
<td>67</td>
<td>109</td>
<td>51</td>
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<tr>
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<tr>
<td>HCO + H ⇌ CH + H2O</td>
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<td>CH3O + H ⇌ CH3 + H2O</td>
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<td>214</td>
<td>94</td>
</tr>
<tr>
<td>CO2 + H ⇌ COOH</td>
<td>147</td>
<td>79</td>
<td>137</td>
</tr>
<tr>
<td>CO2 + H ⇌ HCOO</td>
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<td>141</td>
<td>127</td>
</tr>
<tr>
<td>COOH + H ⇌ HCOOH</td>
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<td>175</td>
<td>212</td>
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<tr>
<td>HCOOH + H ⇌ HCOOH</td>
<td>151</td>
<td>115</td>
<td>142</td>
</tr>
<tr>
<td>COOH + H ⇌ CO + H2O</td>
<td>95</td>
<td>203</td>
<td>66</td>
</tr>
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</table>
and 266 kJ/mol for Cu(211) in the presence of H2O. Over barriers for COH scission are 243 kJ/mol for Cu(111), 256 kJ/mol for Cu(211) and 211 kJ/mol for Cu(211) in the presence of H2O. Over barriers for C-O bond dissociation in CH2O are 170 kJ/mol for Cu(111), 173 kJ/mol for Cu(211) and 175 kJ/mol for Cu(211) in the presence of H2O. C-O bond dissociation in CH2O is more facile with overall barriers of 199 kJ/mol for Cu(111), 185 kJ/mol for Cu(211) and 192 kJ/mol for Cu(211) in the presence of H2O. Although C-O bond cleavage in CH2O is substantially more difficult than in CH3O, CH3O is much more stable on the Cu surfaces. Thus, the overall barriers for C-O bond dissociation in CH3O are 243 kJ/mol for Cu(111), 256 kJ/mol for Cu(211) and 211 kJ/mol for Cu(211) in the presence of H2O. Obviously, these values reflect the overall barriers with reference to the non-electrochemical experiment.

A general observation is that the non-electrochemical elementary reaction steps are easier on the stepped Cu(211) surface than on Cu(111). The higher reactivity of the stepped surface relates to the presence of low-coordinated Cu surface atoms as well as a favorable topology for C-O dissociation reactions [85,86]. In the presence of H2O, the absolute change in the difference in the free energy between reactant and product states is only 12 kJ/mol, similar to the results presented by Goodpaster et al. [87]. Furthermore, H2O appears to lower the barriers related to X-OH intermediates.

We next took into account the effect of applying an electrochemical potential on the reaction energy diagrams. For this, we take the RHE as reference at pH = 6.8. Thus 0 V vs. RHE and −1 V vs. RHE correspond to, respectively, −0.4 V vs. SHE and −1.4 V vs. SHE. Relevant diagrams for the formation of COOH and HCOO and the dissociation of one of the C-O bonds in these intermediates as well as in adsorbed CO2 are shown in Fig. 2. This figure immediately shows that the PCET steps become easier when a negative potential is applied. At an applied potential of −1.0 V vs. RHE, the formation of COOH and HCOO is preferred over direct CO2 dissociation for most of the considered models. While the barriers for the formation of COOH and HCOO at both potentials considered are quite similar for the different surfaces, COOH dissociation to CO + OH is always significantly easier than HCOO dissociation to HCO + O. The reaction energy diagrams suggest that at −1.0 V vs. RHE mechanisms involving HCOO and COOH exhibit similar overall activation barriers, because the rate is typically determined by the first hydrogenation step.

Fig. 3 shows the barriers for direct and H-assisted CO dissociation pathways. Direct non-electrochemical CO scission has such a high barrier that these pathways do not play a role in electrochemical CO activation. We also took into account two pathways
involving direct formation of H$_2$O from adsorbed HCOH and adsorbed COH. Independent of the applied potential, the H-assisted pathways are always preferred. In general, we find that, while formation of partially hydrogenation CO intermediates is possible, further direct dissociation to generate CH$_x$ species requires overcoming a high activation barrier. Only at a potential of 1.0 V vs. RHE, the barrier for direct COH dissociation on the Cu(211) in the presence of H$_2$O presents a relatively low barrier of 108 kJ/mol. Taking into account an additional PCET step in the mechanism of CO dissociation for HCOH and COH intermediates, much more reasonable activation barriers are obtained. Even at 0 V vs. RHE (0.40 V vs. SHE at pH 6.8), such a H$_2$O removal step from the HCOH state is fast. The barrier for HCO formation is slightly lower than for COH formation, suggesting that the CO/HCO/HCOH pathway is favored (Fig. S18).

As we are primarily concerned to understand the selectivity towards CH$_4$ vs. CH$_3$OH during electrochemical CO$_2$ reduction, we provide in Fig. 4 reaction energy diagrams at 0 V and −1.0 V vs. RHE for the formation of these two products. We start from the HCOH state as this is a likely intermediate based on the results from Fig. 3. Both pathways from HCOH to CH$_4$ and CH$_3$OH are thermodynamically and kinetically favorable, suggesting that both products can be formed. However, at high negative potential the proton-assisted electrochemical splitting of CH$_3$OH into CH$_3$ and OH can become very fast, providing a tentative explanation for typically observed higher selectivity of CH$_4$ over CH$_3$OH [14,33].

Using microkinetic modeling we first investigated the H$_2$ evolution reaction over Cu(111) in the absence of CO$_2$. Under acidic conditions (pH 2.5), we varied the diffusion layer thickness, which we linked to the rotation speed in a rotating disk electrode (RDE) configuration. Fig. 5a shows an onset potential around 0.5 V for which H$_2$ evolution reaches current densities above 1 mA cm$^{-2}$. This is in keeping with the experimental literature [74]. Around 0.7 V vs. RHE, a plateau is reached as a result of diffusion limitations of protons through the diffusion layer to the electrochemical surface. This is because proton diffusion cannot keep up with the H$_2$ evolution rate at the electrode surface. A quadratic increase of the rotation speed roughly doubles the current density at this plateau, which is in accordance with the halved diffusion layer thickness as follows from the Levich equation. Fig. 5b shows that the local pH at the electrode surface strongly increases when the negative potential is increased. These observations are in line with the results from the reaction energy diagrams in Fig. 3.
At potentials below $-1.0 \text{ V vs. RHE}$, the hydrogen evolution reaction occurs under alkaline conditions at the electrode surface. In the simulations, we see a shift from the proton reduction to the water reduction mechanism around a potential of $-1.2 \text{ V vs. RHE}$ (Fig. S1 in the supporting information).
reduction in a solution, which is usually carried out at neutral pH and a high negative potential, is mostly governed by a surface from which hydrogen evolves via the water reduction mechanism.

Next, we performed microkinetic simulations of electrochemical CO$_2$ reduction on the different models at 298 K and pH 6.8. The rotation speed of the RDE configuration was set at 100 rpm. Fig. 6a shows the total electrochemical current densities. The onset and magnitude of the currents are similar to those observed by Kuhl et al. [48]. Our simulations show that Cu(211) is more active than Cu(111), which is in line with the work of Hori et al. [33]. Adding a catalytic H$_2$O molecule to the stepped surface further increases the current density. From the computed reaction energies, we infer that the activity increase with respect to CO$_2$ in the presence of a catalytic H$_2$O molecule is due to the lower barrier for COOH formation. Fig. 6b–f shows the Faradaic efficiencies for the different surfaces. Notably, the Cu(111) surface mainly produces H$_2$. On the stepped Cu(211) model, CO$_2$ reduction to formate competes with H$_2$ evolution. The lower barrier for HCOO formation on Cu(211) compared to Cu(111) results in higher Faradaic efficiency to HCOO (formate), competing with H$_2$ formation. The efficiency differences between the two surfaces are larger than what would be expected from the single crystal studies of Hori et al. We expect that real terrace surfaces contain a small amount of step sites that contribute to the CO$_2$ reduction activity. Also, we did not observe significant amounts of CO, CH$_3$OH, or CH$_4$ for the simulations shown in Fig. 6b–c. We therefore considered the effect of water molecules on the Faradaic efficiency for the more active stepped surface. Fig. 6d shows that addition of a catalytic H$_2$O molecule...

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**Fig. 6.** Microkinetics simulations of electrochemical CO$_2$ reduction on Cu(111), Cu(211) and Cu(211)÷H$_2$O surfaces on a rotating disc electrode at 100 rpm and a bulk pH of 6.8: (a) total electrochemical current; (b–f) Faradaic efficiency of various products.
shifts the product distribution to CO at low negative potential and CH₄ at high negative potential in competition with H₂ formation. Only a small amount of CH₃OH is formed at intermediate negative potential for this latter model. Although these results are in rough correspondence with the literature, the onset potential of −0.5 V vs. RHE for CH₄ production is lower than expected [49, 90]. While we include the effect of a catalytic H₂O molecule, the influence of a real electrolyte is much more complex [91–94]. Our DFT modeling suggests that the COOH formation barrier is an important parameter in the CO₂ reduction pathway. To verify its role, we carried out additional microkinetics simulations for the Cu(111) and Cu(211) models in which both forward and backward energy barriers for the hydrogenation of CO₂ to COOH were lowered by 10 kJ/mol. While this has no significant effect on Cu(111), it results in a strongly increased activity for competitive adsorption. Instead of predominantly HCOO, also CH₄ and CO are formed in this case. These results as shown in Fig. 6f more closely correspond to the experimental literature discussed above. This crude sensitivity analysis shows the important role of HCOO and COOH pathways with respect to the product distribution.

Fig. 7 shows the composition of the surface-adsorbed layer. Compared to the Cu(111) surface, the stepped Cu(211) surface already has an appreciable H coverage at low potential, which increases with more negative potential. CO₂ coverages are expectedly low, but highest for the least reactive surface. Two aspects influence the CO₂ coverage. Firstly, the presence of H at the surface limits the CO₂ coverage because of competitive adsorption. Secondly, when CO₂ reduction proceeds, the CO₂ coverage will also decrease. This decrease is mostly due to the transport limitations of CO₂ at high current densities. Fig. 8 shows that at −1.05 V vs. RHE the CO₂ concentration near the surface can decrease by as much as 50%. We confirmed that this transport limitation of CO₂ is reduced for higher RDE rotation rates (Figs. S2–S5). Proton transport limitations are much stronger due to the already low bulk concentration at pH 6.8. This does not limit the H coverage however, as hydrogen atoms can still be deposited via the water reduction mechanism. Notably, for the standard DFT parameters we observe that the main surface intermediates are H and CO₂. Only when COOH formation barriers are decreased, we observed some OH as a surface intermediate. This effect is most pronounced for the Cu(111) surface, where easier formation of COOH results in a higher concentration of OH upon COOH dissociation.

To better understand the high selectivity to CO and CH₄ for the Cu(211)+H₂O surface, we compared the carbon-based rates at −0.5 V and −1.0 V vs. RHE. These results can be seen in Fig. 9 in which the rates are expressed as relative rates. At −0.5 V about two thirds of the carbon-based conversion rate towards CO results from direct CO₂ dissociation, while the rest goes through the COOH intermediate. The other surfaces did not present a high rate for direct CO₂ dissociation (Figs. S6–S9). Clearly, the barriers for this non-electrochemical step are too high without the presence of a catalytic H₂O molecule, emphasizing the role of the solvent. At −1.0 V the electrochemical steps again dominate as major pathways, and CH₄ is the main product. No contribution of HCOO dissociation was observed, also not for the HCOO-producing surfaces. All pathways leading to CH₄ go through a CHₓOH(x = 1–3) intermediate. Clearly, the fast removal of OH from these intermediates prevents the formation of CH₃OH as a final product and CH₄ formation involves hydrogenation of CO to at least HCO or HCOH (depending on the potential) before C-O bond scission takes place. This is expected as

Fig. 7. Microkinetics simulations of electrochemical CO₂ reduction on Cu(111), Cu(211) and Cu(211)+H₂O surfaces on a rotating disc electrode at 100 rpm and a bulk pH of 6.8: (a) H coverage; (b) CO₂ coverage; (c) OH coverage; (d) empty site coverage.
Cu is usually considered a low reactive metal among the first-row transition metals, which is not able to directly dissociate the triple C-O bond in CO.

OH removal can originate from non-electrochemical dissociation and electrochemical removal to H₂O via either free protons or water reduction. To discriminate between these steps and to understand the steps that limit the formation of particular products, we performed a degree of rate control (DRC) analysis [80]. We carried out this analysis for the different Cu(211) surfaces. Here we discuss the rate control for the Cu(211) + H₂O surface, while data for the other surfaces can be found in the supporting information.

Fig. 10 shows the 6 elementary reactions steps with the strongest control on the rate of CH₄, CH₃OH, HCOO and CO formation. As expected, COOH formation is strongly controlling the rate for all products in which one of the C-O bonds is cleaved (CH₄, CH₃OH and CO). Conversely, HCOO formation is rate-limiting for the formation of formate. We observe that all these reactions involve H₂O instead of protons, consistent with the depletion of protons across the

Fig. 9. Reaction network analysis of electrochemical CO₂ reduction on the Cu(211) + H₂O surface at 100 rpm and a bulk pH of 6.8: (a) -0.50 V vs. RHE; (b) -1.00 V vs. RHE.

Fig. 8. Microkinetic simulations of electrochemical CO₂ reduction on Cu(111), Cu(211) and Cu(211) + H₂O surfaces on a rotating disc electrode at 100 rpm and a bulk pH of 6.8: (a) Percentage of near-surface concentrations of CO₂ compared to bulk CO₂ concentrations; (b) local pH near the electrochemical surface.
diffusion layer in the potential range where CO2 is reduced. Reactions that control the formation of CH4 are HCOH formation at low potential and HCO formation at higher potential. The latter step also controls the rate of CH3OH formation. Notably, an important step that inhibits CH3OH formation is its dissociation into CH3. Faster desorption of CH3OH can counteract this inhibiting effect. CH3OH is then produced with formaldehyde (CH2O) as an intermediate. Possibly, we overestimate the rate of CH3OH scission, as kinetic measurements suggest that reduction of formaldehyde should yield more CH3OH than CH4 [47]. Therefore, the more likely pathway to produce CH4 is to hydrogenate HCO to HCOH, rather than CH2O. The selectivity towards CO strongly depends on the adsorption strength of CO. Decreased binding of CO will lead to higher Faradaic efficiencies of CO. Removal of H adsorbates from the surface facilitates all of these reactions, as this process generates empty sites for CO2 adsorption.

We also discuss the degree of selectivity control (DSC) [81]. Although faster removal of H adsorbates can increase the total current density towards CO2 reduction, the same applies for the current towards H2 (Fig. S12). A DSC analysis of the Cu(211) + H2O surface is presented in Fig. 11. Here, positive DSC values indicate that promoting a step results in enhanced Faradaic efficiency for the corresponding product, while negative DSC values indicate a lowered Faradaic efficiency by promoting a specific step. Again, the CO2 hydrogenation steps towards COOH and HCOO are significantly controlling the selectivity to either CH4, CH3OH, and CO, or to HCOO. Furthermore, we find that formation of adsorbed H is more inhibiting selectivity than H2 formation from adsorbed H. This shows that adsorbed H is not used to reduce CO2, and that this process requires electrochemically active species.

Finally, we briefly discuss the possible formation of C2H4, which is often observed during CO2 electro-reduction on Cu surfaces [95,96]. Especially, open surface like Cu(100) can yield C2H4, which can be formed due to the coupling of two CO molecules and subsequent reduction via multiple pathways. Typically, the onset potential of C2H4 formation is lower than that of CH4 formation. We can speculate that CO-CO coupling might occur below the onset of CH4 formation, when CO is a dominant product. Once the potential
is negative enough to facilitate CH₄ formation, the lower amount of CO will probably limit the amount of C₂H₄. This can provide a tentative explanation for the observation of C₂H₄ as an intermediate in CO₂ electroreduction with respect to CH₄ formation.

4. Conclusions

The first-principles microkinetics simulations as described herein were conducted to explain the electrochemical reduction of CO₂ into CO, HCOO(H), CH₃OH and CH₄ over a copper electrode. We took into account the Cu(111) and Cu(211) surfaces to model both terrace- and step-site topologies. The influence of the electrochemical potential on the activation barriers was taken into account in the simulations. Using this approach, we reproduced the effect of proton transport limitations to the electrode surface in a typical hydrogen evolution experiment. The resulting current density plateaus indicate that current densities at high overpotentials are the result of water reduction instead of the reduction of free protons due to the high pH occurring at the electrode surface. By including CO₂ reduction, current densities as a function of potential (i-V curves), Faradaic efficiency, and surface coverage were computed. The data show that hydrogen evolution and CO₂ reduction compete on these surfaces. The stepped Cu(211) surface is more active than the Cu(111) terrace for electrochemical CO₂ reduction. While Cu(211) still forms HCOO as the main CO₂ reduction product, the presence of a catalytic H₂O molecule (a crude approximation of the electrolyte solvent) increases the overall rate and selectivity to the more reduced products CO and CH₄. The simulations show that this is due to a lowering of the barriers of X-OH formation. An analysis of the degrees of rate and selectivity control show that the hydrogenation step from CO₂/COOH is critical in the formation of CO and CH₄. The simulated product distribution as a function of potential is in reasonable agreement with experiment. A small change in the barrier for COOH formation within the accuracy of DFT results in a much better correspondence. A reaction network analysis shows that CH₄ is formed mainly via the CO → HCO → HCOH → CH + OH pathway and CH₃OH species, which are potential precursors to CH₃OH.
rapidly dissociated to CH₄ and H₂O in a PCET step, explaining why at high potential typically CH₄ is observed instead of CH₃OH. At high potential, CO₂ diffusion can limit the current density, which negatively affects CO₂ reduction vs. proton reduction.

**CRediT authorship contribution statement**


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**Appendix A. Supplementary data**

Supplementary data to this article can be found online at https://doi.org/10.1016/j.electacta.2020.135665.

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