



# Structure-sensitive electroreduction of acetaldehyde to ethanol on copper and its mechanistic implications for CO and CO<sub>2</sub> reduction



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## ABSTRACT

Ethanol is a highly desirable product of the electrochemical reduction of CO and/or CO<sub>2</sub> on copper. Although ethanol and ethylene share common intermediates at the early stages of CO/CO<sub>2</sub> reduction to C<sub>2</sub> species on copper, the pathways bifurcate and most copper surfaces favor the formation of ethylene. We present here a combined experimental-computational study of the electroreduction of acetaldehyde to ethanol on Cu(111), Cu(100) and Cu(322). The experiments show structure-sensitive onset potentials for acetaldehyde reduction such that lower overpotentials are observed for more open facets ( $\eta_{322} < \eta_{100} < \eta_{111}$ ). Our DFT calculations show that the electrochemical reduction of acetaldehyde proceeds via a CH<sub>3</sub>CH<sub>2</sub>O\* intermediate on the three electrodes at high \*H coverage, and that the stability of this weakly bound intermediate determines the onset potential. Our results suggest that during the late stages of CO/CO<sub>2</sub> reduction to C<sub>2</sub> species on copper, ethanol formation has higher energetic barriers than ethylene formation, and hence the selectivity is inclined toward the latter. Importantly, our results suggest that the barriers for ethanol formation can be lowered by making use of its structure sensitivity.

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## 1. Introduction

It is well known that CO and CO<sub>2</sub> can be reduced electrochemically to useful products. The seminal works of Hori and coworkers pointed out that copper is a unique catalyst for electrochemical CO<sub>2</sub> reduction [1,2], as it is able to produce methane, ethylene and ethanol in different proportions depending on the electrode potential and morphology. However, substantial overpotentials and low Faradaic efficiencies prevent the widespread use of electrolyzers based on copper electrocatalysts. Currently, the challenges are, first of all, to achieve a thorough understanding of the intricate multi-electron reaction mechanism, and secondly, to design efficient and selective catalysts based on such understanding.

The major C<sub>2</sub> product on copper is ethylene, while there is a marginal production of ethanol and traces of acetaldehyde [1,2]. There are several indications that these three products share the same reaction pathway up to a given key intermediate, the ease of protonation of which ultimately determines the selectivity [3,4]. Given that in the context of a solar-fuel-based economy ethanol is a highly desirable product, it is important to understand the

mechanistic features of its formation, as the C<sub>2</sub> selectivity is usually inclined toward ethylene instead of ethanol. However, Kanan and coworkers have shown recently that the selectivity of copper-based electrocatalysts for CO reduction can be steered to favor ethanol over ethylene [5], although the atomic-scale justification for such a change is still unclear.

According to previous work from our group [3,4,6], acetaldehyde reduction corresponds to the late stages of the reaction pathway of ethanol production from CO/CO<sub>2</sub>. Thus, the study of acetaldehyde reduction reaction can shed light on the features of copper electrodes that may favor ethanol production, as well as provide design principles to devise new catalysts that are selective toward ethanol.

In this article, we present a combined experimental/theoretical study of acetaldehyde reduction, taking into account pH effects and structure sensitivity. Our findings provide new insights on the reaction mechanism through which ethanol is produced on copper-based catalysts and help explain why ethylene is the major C<sub>2</sub> product of the reduction of CO/CO<sub>2</sub>.

## 2. Experimental

Prior to the experiments, all the glassware was cleaned by boiling in a sulfonitric solution, which is a mixture of concentrated sulfuric acid and nitric acid in a 3:1 ratio. After the acid bath, the

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glassware was rinsed and boiled five times with ultra-clean water (Milipore® MiliQ; resistivity >18.2 MΩ cm).

The electrochemical measurements were carried out using an METROHM μAUTOLAB III – Compact Design potentiostat connected to the three-electrode cell. The working electrodes (WE) were bead-type copper single crystals, with a polishing orientation <0.5°. These electrodes were electropolished before each experiment, using 66% H<sub>3</sub>PO<sub>4</sub> (Suprapur Merck) at 2.3 V vs a Cu counter electrode for 2 s, and in open circuit potential (OCP) for 30 s. After cleaning and rinsing with water, the electrode surfaces were characterized by performing four cycles between –0.25 and 0.35 V<sub>RHE</sub>, at 50 mV s<sup>–1</sup> in 0.1 M NaOH (Sigma–Aldrich TraceSelect), following the procedure described previously by Schouten et al. on Cu single-crystal characterization [7], see Fig. S1. The results show that the electrodes possessed their distinctive features before the electroreduction experiments. However, we do not discard H- or OH-induced surface reconstruction under reaction conditions.

The counter electrode (CE) consisted of a gold wire, while the reference electrode (RE) was a reversible hydrogen electrode (RHE). All potentials in this work are reported against the RHE, unless otherwise stated.

The experiments were carried out in a solution containing 0.1 M HClO<sub>4</sub> (Suprapur Merck) for pH1, and 0.001 M HClO<sub>4</sub> + 0.099 M KClO<sub>4</sub> (Sigma–Aldrich TraceSelect) for pH 3. These values of pH are used to guarantee the stability of acetaldehyde, which is prone to decomposition in alkaline conditions. All solutions were prepared with ultra clean water. Argon (Linde, 6.0) was used as purge gas.

The detection of ethanol from the reduction of 0.1 M acetaldehyde (puriss. p.a., anhydrous, ≥99.5% (GC) FLUKA) was monitored by means of online High Performance Liquid Chromatography (HPLC) [8] in a three-electrode cell containing solutions with pH 1 and 3, prepared as previously described. The soluble reduction products were detected by collecting from the solution in the cell using a Teflon tip (0.38 mm in diameter) by means of a fraction collector (FRC-10A, Shimadzu) during the voltammetric scan at a scan rate of 1 mV s<sup>–1</sup>. The tip was positioned in parallel configuration, approximately 10 μm from the middle of the electrode surface. The fractions collected were deposited in a 96-well microtiter plate. The flow rate of sample collection was adjusted to 60 μL min<sup>–1</sup> with a Shimadzu pump (LC-20AT). Each of the samples collected were 60 μL. The well was placed in the autosampler, and 30 μL of sample was injected in the high-performance liquid chromatography (HPLC) column. The column used was an Aminex HPX 87-H, Biorad. The temperature of the column was maintained at 85 °C in an oven (CTO-20 A).

### 3. Computational details

The DFT calculations and thermodynamic modeling in this study have been performed using the same methodologies used in our previous work [3]. Here we provide a brief description of the methods used: all adsorption energies were calculated by means of DFT calculations using the VASP code [9] with the PBE exchange–correlation functional [10] and the projector augmented wave (PAW) method [11]. The (1 1 1), (1 0 0) and (3 2 2) surfaces of copper were modeled with 4-layer-thick slabs. Cu(1 1 1) and Cu(1 0 0) used 3 × 2 supercells, while Cu(3 2 2) is 5(1 1 1) × (1 0 0) with a 3-atom wide step edge. The vertical separation between periodically repeated images was more than 16 Å and, additionally, dipole corrections were applied. The structures were optimized allowing the adsorbates and the two topmost layers to relax in all directions, while fixing the 2 bottom layers at the optimized bulk positions, where the lattice constant is 3.64 Å. The relaxations were carried out with a plane-wave cut-off of 400 eV, using the conjugate-gradient scheme until the maximum force on any atom was below

0.05 eV Å<sup>–1</sup>. The Brillouin zones of the (1 0 0) and (1 1 1) surfaces were sampled with 6 × 8 × 1 Monkhorst–Pack meshes [12], while a 4 × 3 × 1 mesh was used for the (3 2 2) surface. The Fermi level of the surfaces was smeared using the Methfessel–Paxton method [13] with an electronic temperature of 0.2 eV, and all energies were extrapolated to T = 0 K. Acetaldehyde (CH<sub>3</sub>CHO) and ethanol (CH<sub>3</sub>CH<sub>2</sub>OH) were calculated in boxes of 15 Å × 15 Å × 15 Å, with an electronic temperature of 0.001 eV, the gamma point only, and Gaussian smearing. The free energies are estimated from DFT-calculated energies in the following way:

$$G = E_{\text{DFT}} + \text{ZPE} - TS \quad (1)$$

The zero-point energies (ZPE) of the adsorbates (see Table 1) and molecules (1.468 and 2.118 eV for CH<sub>3</sub>CHO and CH<sub>3</sub>CH<sub>2</sub>OH) were calculated from vibrational frequency analysis using the harmonic oscillator approximation. Vibrational contributions to the entropy were considered only for adsorbed species and can be found in Table 1, while total entropies for molecules were taken from standard thermodynamic tables at 298.15 K and 1 bar [14], so that the gas-phase TS corrections for ethanol and acetaldehyde are 0.870 and 0.815 eV, respectively. However, ethanol and acetaldehyde are liquid at the conditions of the experiments carried out here. Although it is normally difficult to estimate the liquid-phase free energies of substances within standard DFT, there is a simple thermodynamic workaround [3,15,16]. Essentially, the substance is simulated in the gas phase and the difference between the free energies of formation of its liquid and gas phases is added to the gas-phase entropy. Such differences are 0.072 eV for ethanol and –0.056 eV for acetaldehyde, so that the final TS corrections are 0.942 and 0.759 eV, respectively. The high-coverage (HC) situations on the (1 1 1), (1 0 0) and (3 2 2) surfaces contained 5, 5, and 4 \*H coadsorbates around CH<sub>3</sub>CH<sub>2</sub>O\*/CH<sub>3</sub>\*CHOH.

We have added a solvation correction of –0.38 eV to CH<sub>3</sub>\*CHOH due to the presence of the OH group, making use of the approximations described elsewhere [3,17]. Finally, we have used the computational hydrogen (CHE) approach to simulate concerted proton–electron transfers [16]. In this approach, the energetics of H<sub>2</sub>(g) rather than that of (H<sup>+</sup> + e<sup>–</sup>) is used as electrochemical reference due to the following relationship in equilibrium:  $\mu(H^+ + e^-) = \frac{1}{2}\mu(H_2)$ .

### 4. Results and discussion

The linear sweep voltammetry (LSV) of the three copper single-crystals shows reduction currents at negative potentials which are mainly due to hydrogen evolution, see Fig. S2. To probe the reduction of acetaldehyde to ethanol, we need to use online HPLC, since LSV does not show the separate features for acetaldehyde reduction. Fig. 1 shows the HPLC results for the electrochemical reduction of acetaldehyde on three different copper electrodes and at different pH values. We observe that the onset potential for the formation of ethanol follows the trend Cu(3 2 2) > Cu(1 0 0) > Cu(1 1 1) for both values of pH (see also Fig. 4). This means that increase in surface coordination results in more negative onset potentials, as the coordination number is 7 for the step edge on the (3 2 2) electrode (note that (3 2 2) electrodes are also denoted 5(1 1 1) × (1 0 0), as they have 5-atom wide (1 1 1) terraces separated by (1 0 0) steps), and the coordination numbers are 8 and 9 on the (1 0 0) and (1 1 1) terraces, respectively. For instance, at pH 1, the onsets are located at –0.30 ± 0.03 V<sub>RHE</sub>, –0.54 ± 0.03 V<sub>RHE</sub> and –0.78 ± 0.03 V<sub>RHE</sub>, for the three facets.

Note that the equilibrium potential for this reaction is located at 0.24 V<sub>RHE</sub> at pH 0, and also that it is generally observed that adsorbates bind more strongly to undercoordinated facets [18–21]. These two observations suggest that the adsorbed intermediates

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