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## **Electroreduction of nitrate and carbon dioxide on copper electrodes: a mechanistic study**

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### **Citation**

Perez Gallent, E. (2018, February 1). *Electroreduction of nitrate and carbon dioxide on copper electrodes: a mechanistic study*. Retrieved from <https://hdl.handle.net/1887/61142>

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**Author:** Perez Gallant, E.

**Title:** Electroreduction of nitrate and carbon dioxide on copper electrodes: a mechanistic study

**Issue Date:** 2018-02-01

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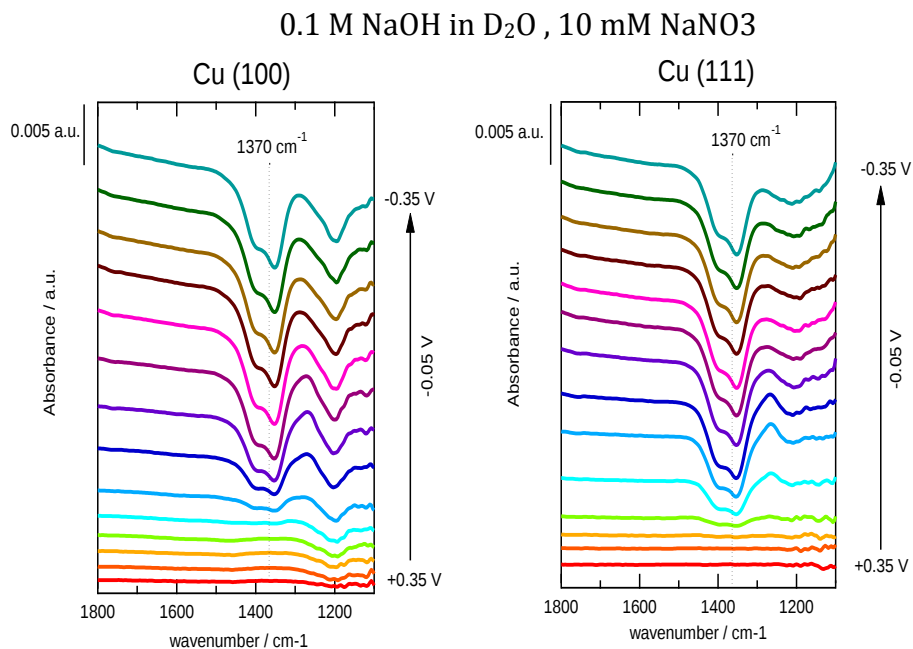


# Appendix I

## Supporting information to chapter 2

### I.1 Results

The reduction of nitrate ( $\text{NO}_3^-$ ) in a 0.1 M NaOH solution prepared in  $\text{D}_2\text{O}$  was also studied by FTIR on both copper surfaces in order to confirm the absence of the bands corresponding to NO. Figure AI.1 shows potential dependent absorbance spectra of Cu(100) (left panel) and Cu(111) (right panel) in 0.1 M NaOH solution in the presence of 10 mM  $\text{NaNO}_3$ . The reference spectrum is taken at +0.35 V and additional spectra are provided for +0.30, +0.25, +0.20, +0.15, +0.10, +0.05, +0.00, -0.05, -0.10, -0.15, -0.20, -0.25, -0.30, -0.35 V (all reported potentials are in the RHE scale). In agreement with the onset potentials for nitrate reduction observed in the CVs (fig. 2.1), IC (fig. 2.4) and FTIR (fig. 2.6), the absorbance spectra show that the onset potential for the reduction of nitrate is +0.15 V on Cu (111) and +0.1 V on Cu (100), as observed by a negative band at  $1370\text{ cm}^{-1}$  associated with the consumption of nitrate. However, the simultaneous formation of nitrite that was observed by the positive band at  $1231\text{ cm}^{-1}$  when the experiments were carried out in  $\text{H}_2\text{O}$  (fig. 2.6) is not observable in the experiment carried out in  $\text{D}_2\text{O}$  because the band corresponding with nitrite ( $\text{NO}_2^-$ ) is masked by the D-O stretching band. There is no band at  $1690\text{ cm}^{-1}$  that would correspond to NO, confirming the absence of formation of NO, in agreement with the results obtained with Online Mass Spectrometry (fig. 2.5).



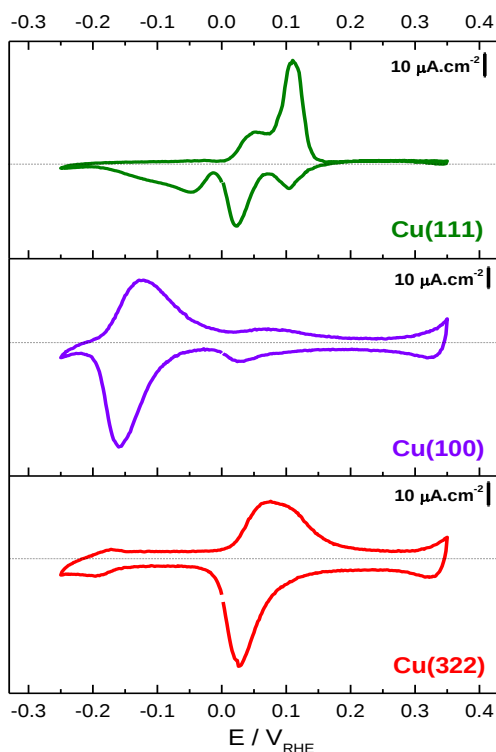
**Figure AI.1:** Potential dependent absorbance spectra for the reduction of 10 mM NaNO<sub>3</sub> on Cu (100) (left panel) and on Cu (111) (right panel) electrode in 0.1 M NaOH solution in D<sub>2</sub>O. Reference spectrum recorded at 0.35 V vs. RHE. Potential step is 0.05V.

## Appendix II

### Supporting information to chapter 3

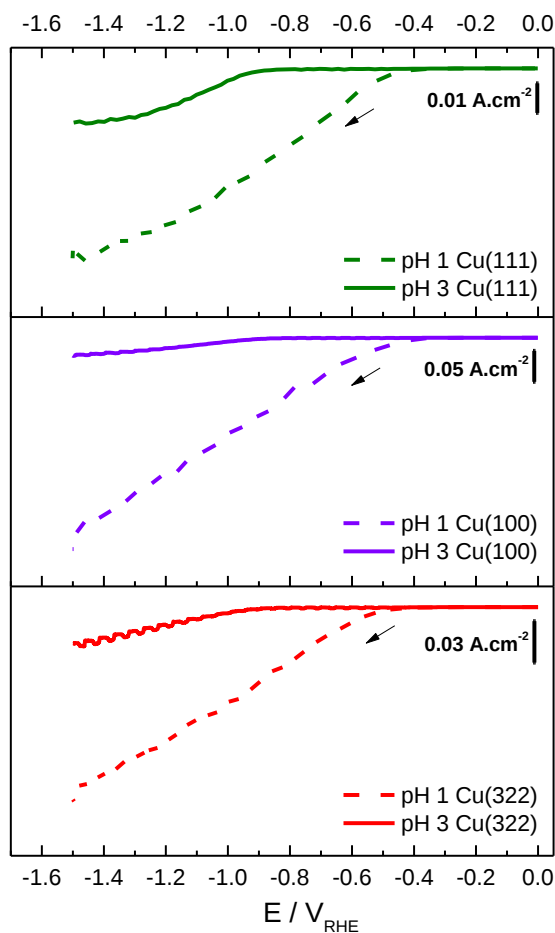
#### II.1 Voltammetric characterization of copper single-crystals electrodes

Figure AII.1 shows the characteristic features of the copper single-crystal surfaces, between -0.25 and 0.35  $V_{\text{RHE}}$ , in agreement with those previously reported by Schouten et al <sup>91</sup>.



**Figure AII.1:** Cyclic voltammetries for Cu(111), Cu(100) and Cu(322) electrodes in 0.1 M NaOH; scan rate:  $50 \text{ mV s}^{-1}$ , Ar-atmosphere.

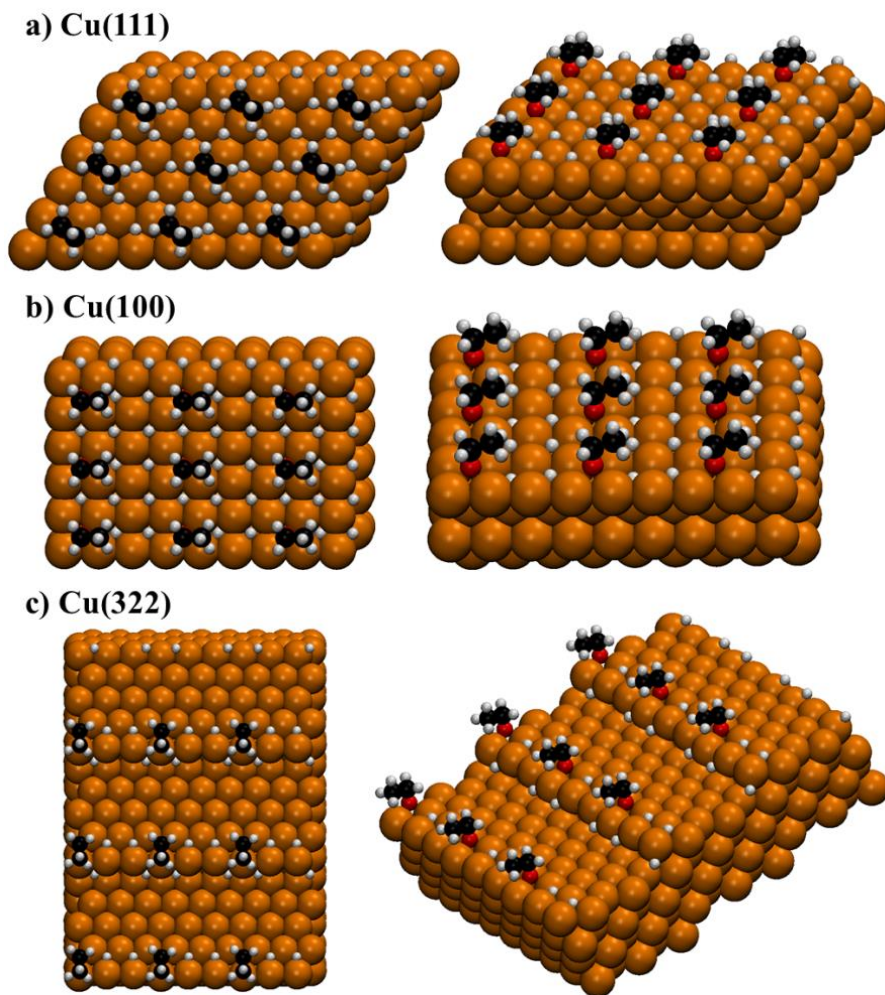
Figure AII.2 shows the linear sweep voltammetries for acetaldehyde reduction on three copper single-crystal surfaces, between 0.0 and -1.5  $V_{\text{RHE}}$ , at pH 1 and 3.



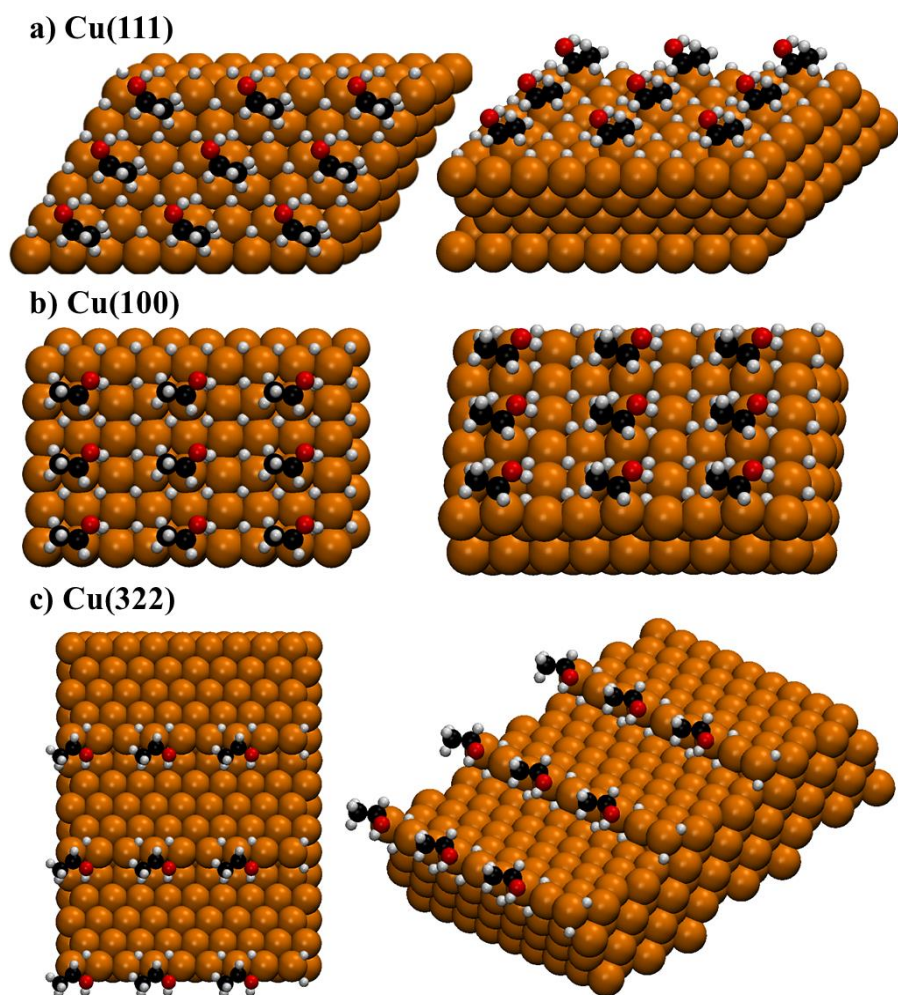
**Figure AII.2:** Linear sweep voltammetries for acetaldehyde reduction on Cu(111), Cu(100) and Cu(322) electrodes. The solutions used were: 0.1 M  $\text{HClO}_4$  + 0.1 M acetaldehyde (pH 1), and 0.001 M  $\text{HClO}_4$  + 0.099 M  $\text{KClO}_4$  + 0.1 M acetaldehyde (pH 3). Scan rate:  $1 \text{ mV s}^{-1}$ , Ar-atmosphere.

## II.2 DFT simulations in a high H-coverage regime

Figures AII.3 and AII.4 contain the most stable adsorption configurations of  $\text{CH}_3\text{CH}_2\text{O}^*$  and  $\text{CH}_3^*\text{CHOH}$  in the presence of coadsorbed hydrogen on the three crystals under study.



**Figure AII.3:** Coadsorption of  $\text{H}^*$  and  $\text{CH}_3\text{CH}_2\text{O}^*$  on a) Cu(111), b) Cu(100), c) Cu(322). Left: top views, right: side views.



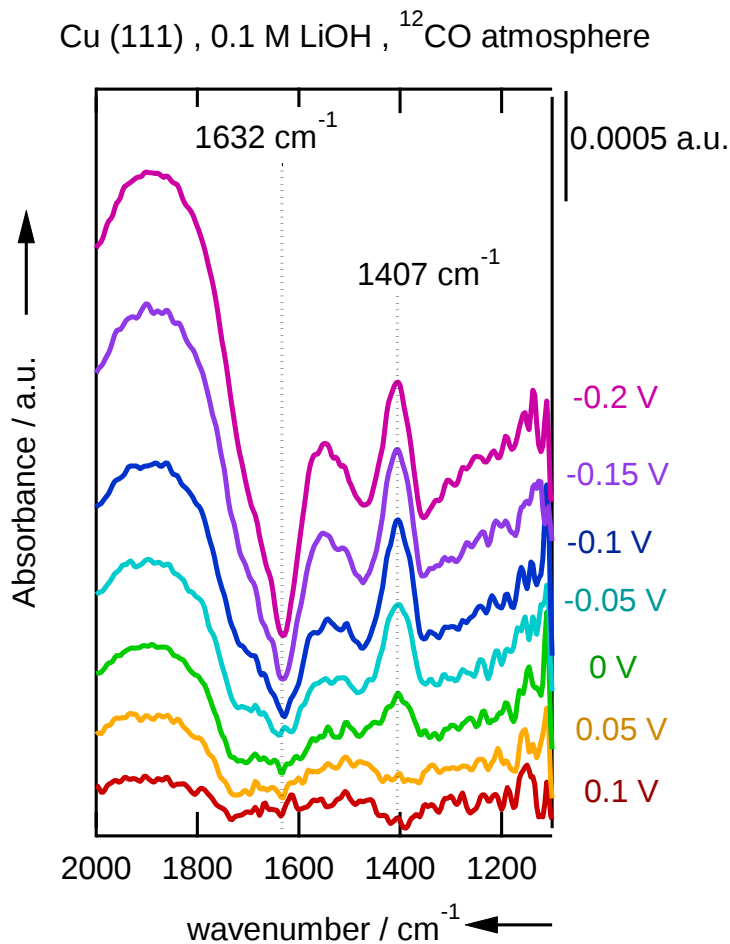
**Figure AII.4:** Coadsorption of  $\text{*H}$  and  $\text{CH}_3\text{*CHOH}$  on a) Cu(111), b) Cu(100), c) Cu(322). Left: top views, right: side views.

## Appendix III

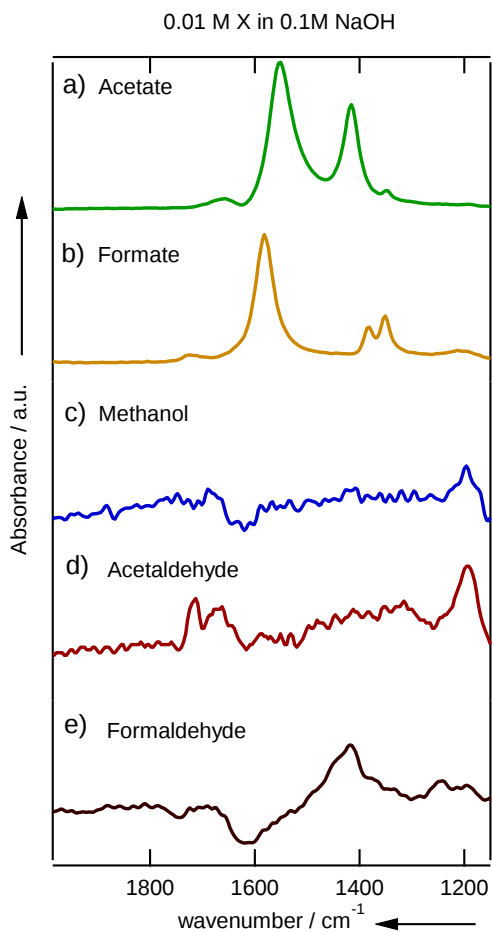
### Supporting information to chapter 4

#### III.1 Results and discussion

Figure AIII.1 shows the potential-dependent absorbance spectra of Cu(111) in 0.1 M LiOH solutions in CO atmosphere. The reference spectrum is taken at +0.1 V and additional spectra are provided for +0.05, 0.00, -0.05, -0.10, -0.15 and -0.2 V (all reported potentials are on the RHE scale). The spectra show two bands at 1632 and 1407  $\text{cm}^{-1}$ . The band at 1632  $\text{cm}^{-1}$  corresponds to the OH bending mode of  $\text{H}_2\text{O}$ . This band causes fluctuations in the baseline of the spectra. The band at 1407  $\text{cm}^{-1}$  is assigned to formaldehyde according to the transmission spectra obtained for this species in solution (See Figure AIII.2 e). Formaldehyde has been suggested to be an intermediate of the reduction of CO to  $\text{CH}_4$  on Cu(211) <sup>57</sup>. During the reduction of CO on Cu(111), there is no band around 1680  $\text{cm}^{-1}$  that would correspond to adsorbed CO <sup>131</sup>. The band at 1191  $\text{cm}^{-1}$  that is assigned to the C-OH stretching on Cu(100) for the hydrogenated dimer is absent in the spectra obtained on Cu(111), confirming the favorability of square sites for the formation of the hydrogenated dimer as an early intermediate of CO reduction. The transmission spectra of other C1 and C2 species such as acetate, formate, acetaldehyde, formaldehyde and methanol were also recorded (Figure AIII.2). The lack of a match of the bands obtained during CO reduction with the bands observed in the transmission spectra of this C1 and C2 species, rules out the possibility of having these species as intermediates in CO reduction on Cu(100) electrodes.



**Figure AIII.1:** Potential-dependent absorbance spectra for Cu(111) in the presence of CO in a 0.1 M LiOH solution. Reference spectrum recorded at +0.1 V vs. RHE. Highlighted bands and their correspondent frequency are indicated with a vertical line at 1407  $\text{cm}^{-1}$  for  $^{12}\text{C}$ -OH stretching and 1632  $\text{cm}^{-1}$  for O-H bending.



**Figure AIII.2:** Transmission spectra of 0.01 M of: a) acetate, b) formate, c) methanol, d) acetaldehyde, and e) formaldehyde in 0.1 M NaOH solution.



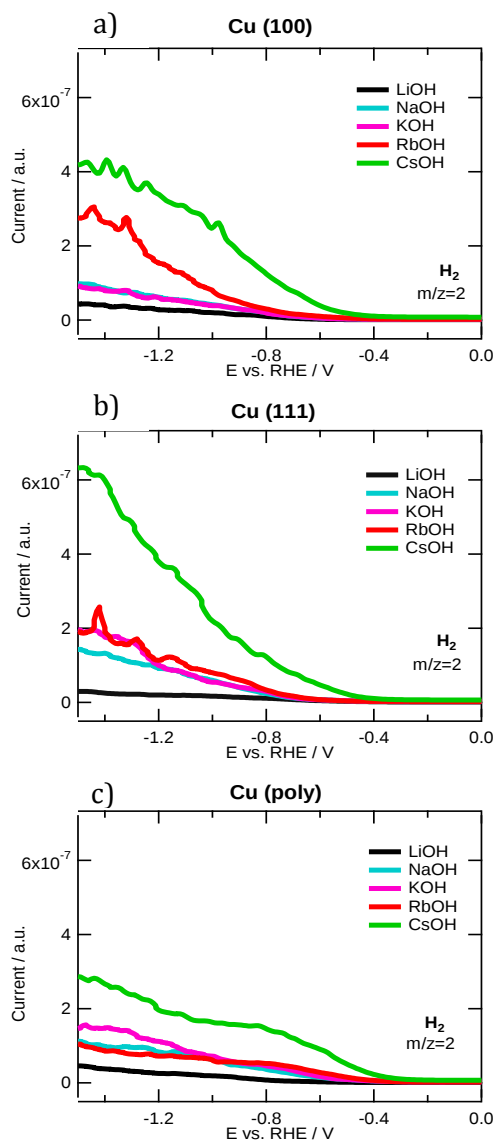
## **Appendix IV**

### **Supporting information to chapter 5**

#### **IV.1 OLEMS measurements**

##### **IV.1.1 Hydrogen evolution reaction**

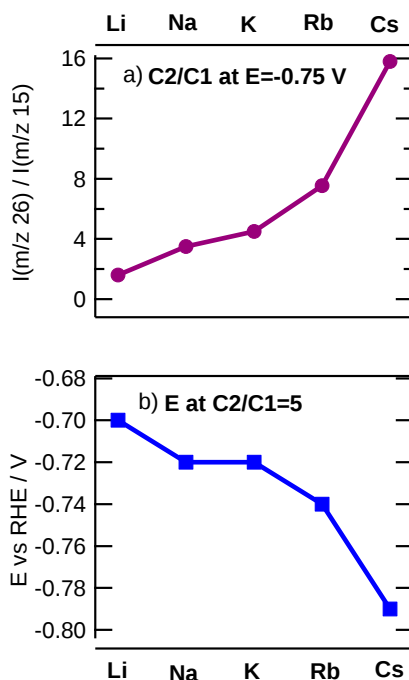
Figure AIV.1 show the mass fragment  $m/z = 2$  associated with the formation of  $H_2$  from the competitive hydrogen evolution reaction (HER) during CO reduction on Cu(100), Cu(111) and polycrystalline Cu. On all copper surfaces, hydrogen evolution starts at ca. -0.4 V for all different cations except  $Cs^+$ , for which it starts at slightly less negative potentials. The amount of hydrogen produced as well as its formation rate increases with the size of the cation in the electrolyte for every copper surface



**Figure AIV.1:** OLEMS mass fragment  $m/z=$  associated with the formation of  $H_2$  during CO reduction on a) Cu(100) , b) Cu(111) and c) polycrystalline Cu for different 0.1 M alkaline hydroxide solutions.

## IV.1.1 Cation effect for ethylene selectivity

Figure AIV.2 illustrates the cation effect on the selectivity of ethylene versus methane on Cu(100) electrodes during CO reduction. The values in Figure AIV.2 have been extracted from Figure 5.1 for a clearer representation of the cation effect for ethylene selectivity.



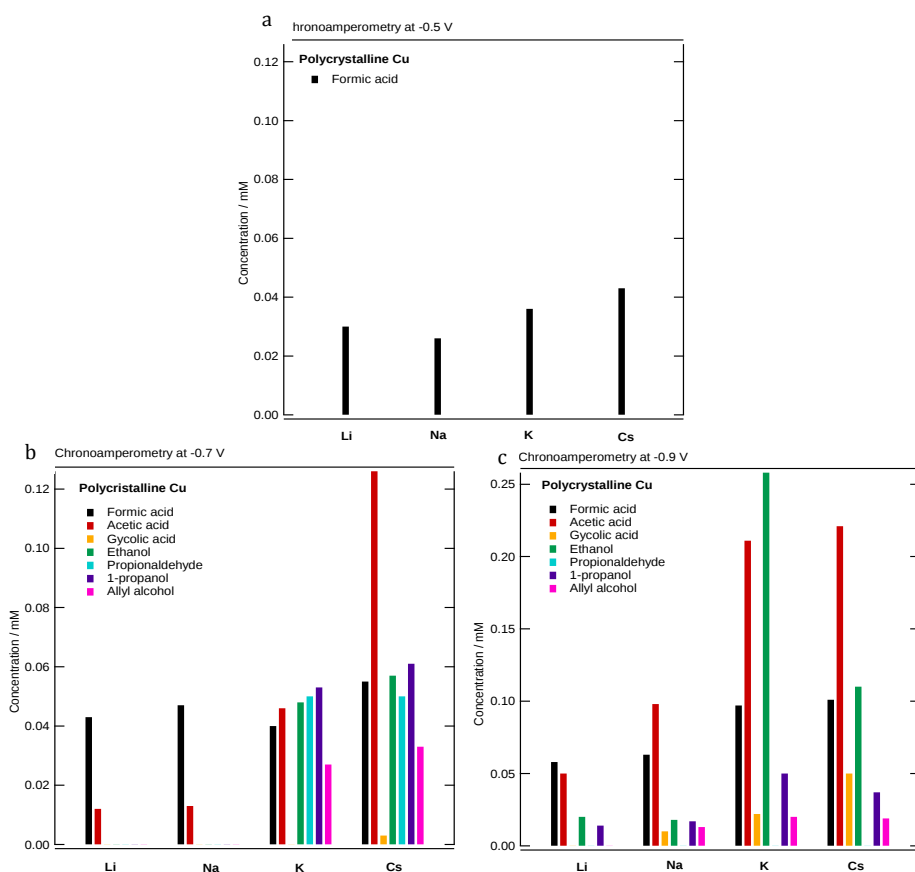
**Figure AIV.2:** a) ratio ethylene/methane at a representative potential of -0.75 V vs RHE for different alkali cations. b) potential for which a fixed value of 5 for the ratio ethylene/methane is obtained for different alkali cations.

Figure AIV.2a shows the ratio  $C_2/C_1$  at a representative potential of -0.75 V vs RHE for different alkaline cations. Figure AIV.2b shows the potential for which a fixed value of 5 for the ratio ethylene/methane is obtained for the different alkaline cations. The values of the

ethylene/methane ratio at -0.75 V show a clear effect of the cation towards ethylene formation that monotonically follows the cation sizes. In addition, the potentials for which a fixed value of 5 for the ratio ethylene/methane show that larger cations can maintain the same selectivity for ethylene at more negative potentials compared to smaller cations, suggesting that the selectivity for ethylene is enhanced in a larger potential range when larger cations are used.

## IV.2 HPLC measurements

During CO reduction on polycrystalline copper, the minor liquid products formed were collected and analyzed by High- Performance Liquid Chromatography (HPLC).



**Figure AIV.3:** Concentration analyzed with HPLC of different liquid products obtained during the reduction of CO after 2h of electrolysis at a) -0.5 V b) -0.7 V and c) -0.9 V on polycrystalline Cu with 0.1 M solutions of alkaline hydroxides.

Chronoamperometry experiments were carried out at three different potentials: -0.5, -0.7 and -0.9 V, with different alkaline hydroxides as electrolytes. The results are summarized in Figure AIV.2. Experiments with RbOH showed an anomalously low amount of product formation, which we ascribe to the combination of low purity and long experimentation time. Therefore, data obtained with Rb cations are not included in the results described below.

When chronoamperometry experiments were performed at -0.5 V vs RHE for 2 h (See Figure AIV.3a), the only product observed was formic acid. The concentration of this acid does not greatly change along with the cation in solution, being the concentration in the range 0.025 – 0.043 mM. Note that the formation of formic acid has been never reported as a CO reduction product. We attribute its formation here to the Cannizzaro reaction, a base-catalyzed aldehyde disproportionation resulting in the formation of the corresponding acid and alcohol. In this specific case, the formaldehyde formed during CO reduction disproportionates into methanol and formic acid. We recently pointed out the importance of this reaction<sup>149</sup>, as it explains the concomitant formation of acids and alcohols observed during CO<sub>2</sub> reduction as a result of a local pH increase due to OH<sup>-</sup> generation from the simultaneous hydrogen evolution reaction. Formate might as well be produced after \*CO is hydrogenated to \*CHO, and \*CHO combines with OH<sup>-</sup> according to Zheng et al.<sup>171</sup>

At more negative potentials (-0.7 V and -0.9 V), we observed more significant differences in terms of product distribution and concentration. The products obtained were: formic acid as C<sub>1</sub> product; acetic acid, glycolic acid, ethylene glycol and ethanol as C<sub>2</sub> products; propionaldehyde, 1-propanol and allyl alcohol as C<sub>3</sub> products. The C<sub>2</sub> and C<sub>3</sub> products obtained during CO reduction have been reported previously<sup>50, 61</sup>.

At -0.7 V, formic acid is formed on all electrolytes with slight differences in concentration. However, the concentration of acetic acid, increases

with the cation size. Ethanol, propionaldehyde, 1-propanol and allyl alcohol were only observed when  $K^+$  and  $Cs^+$  were present in the electrolyte, with slightly higher concentrations observed for the latter. In addition, with  $Cs^+$  a small amount of glycolic acid was produced. Ethylene glycol was also detected in KOH and CsOH, although an accurate quantification was not possible due to an overlap with the intense peak of acetic acid.

During CO reduction at more negative potentials (-0.9 V), higher concentrations of products were generally obtained. Formic acid and acetic acid were formed for all cations, with their concentrations increasing with the cation size. Ethanol and 1-propanol were also detected for every cation with the highest concentration corresponding to  $K^+$ . Small amounts of allyl alcohol were detected for  $Na^+$ ,  $K^+$  and  $Cs^+$ , without significant differences in concentration. Glycolic acid was also observed for  $Na^+$ ,  $K^+$  and  $Cs^+$ , with a clearer trend regarding the size of the cation. Ethylene glycol was detected with  $K^+$  and  $Cs^+$ , but a clear quantification was not possible. In general, larger cations ( $Cs^+$ ) promote CO reduction to  $C_2$  species compared to small cations ( $Li^+$  and  $Na^+$ ), in agreement with the results by Hori et al<sup>65</sup>.

### **IV.3 $^1H$ -NMR**

The samples collected after 2h of CO reduction by chronoamperometry at -0.9 V vs. RHE in 0.1 M NaOH, KOH and CsOH solutions were analyzed by  $^1H$ -NMR. The  $^1H$ -NMR spectra are shown in Figure AIV.4.

Solvent suppression was employed to reduce the size of the peak corresponding to water in order to magnify the peaks corresponding to CO reduction products. The product distribution obtained is similar, regardless of the cation size, although differences in the intensity of the peaks were observed.

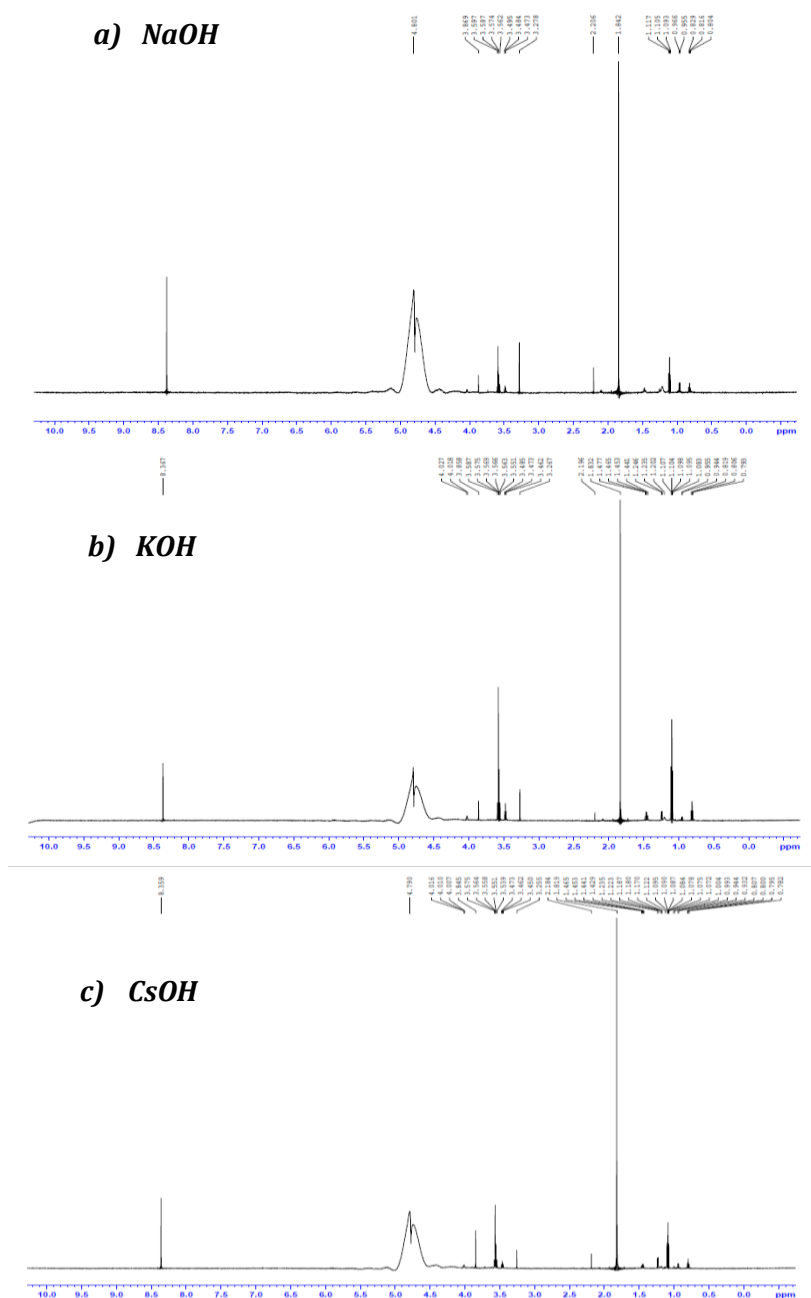
The products observed were formic acid, acetic acid, ethylene glycol, glycolic acid, ethanol and 1-propanol, in agreement with the products

observed with HPLC. In addition, methanol was also observed as a CO reduction product for all three electrolytes analyzed. The detection of methanol by HPLC analysis was not possible due to the overlap of the corresponding peak with the peaks of the eluent. The amount of these reduction products was higher for CsOH and KOH, compared to NaOH, although an accurate quantification was not made.

Table AIV.1 shows an overview of the products detected by  $^1\text{H}$ -NMR for the electrolysis experiments performed at -0.9 V vs. RHE in NaOH, KOH and CsOH 0.1 M solutions.

**Table AIV.1:**  $^1\text{H}$ -NMR chemical shift for the products detected after reduction of CO at -0.9 V vs. RHE in 0.1 M NaOH, KOH and CsOH solutions.

| Compound        | Proton             | Nb H | Mult. | Delta /<br>ppm<br>(Na <sup>+</sup> ) | Delta /<br>ppm<br>(K <sup>+</sup> ) | Delta /<br>ppm<br>(Cs <sup>+</sup> ) |
|-----------------|--------------------|------|-------|--------------------------------------|-------------------------------------|--------------------------------------|
| Formic acid     | -H                 | 1    | s     | 8.376                                | 8.367                               | 8.359                                |
| Acetic acid     | -CH <sub>3</sub>   | 3    | s     | 2.206                                | 2.196                               | 2.184                                |
| Ethylene glycol | -CH <sub>2</sub> - | 4    | t     | 3.484                                | 3.470                               | 3.462                                |
| Glycolic acid   | -CH <sub>2</sub> - | 2    | s     | 3.869                                | 3.858                               | 3.845                                |
| Methanol        | -CH <sub>3</sub>   | 3    | s     | 3.278                                | 3.267                               | 3.255                                |
| Ethanol         | -CH <sub>2</sub> - | 2    | q     | 3.587                                | 3.566                               | 3.558                                |
|                 | -CH <sub>3</sub>   | 3    | t     | 1.105                                | 1.104                               | 1.090                                |
| 1-propanol      | -CH <sub>3</sub>   | 3    | t     | 0.816                                | 0.806                               | 0.807                                |
|                 | -CH <sub>2</sub> - | 2    | qt    | 1.105                                | 1.098                               | 1.095                                |
|                 | -CH <sub>2</sub> - | 2    | t     | 3.587                                | 3.56                                | 3.473                                |



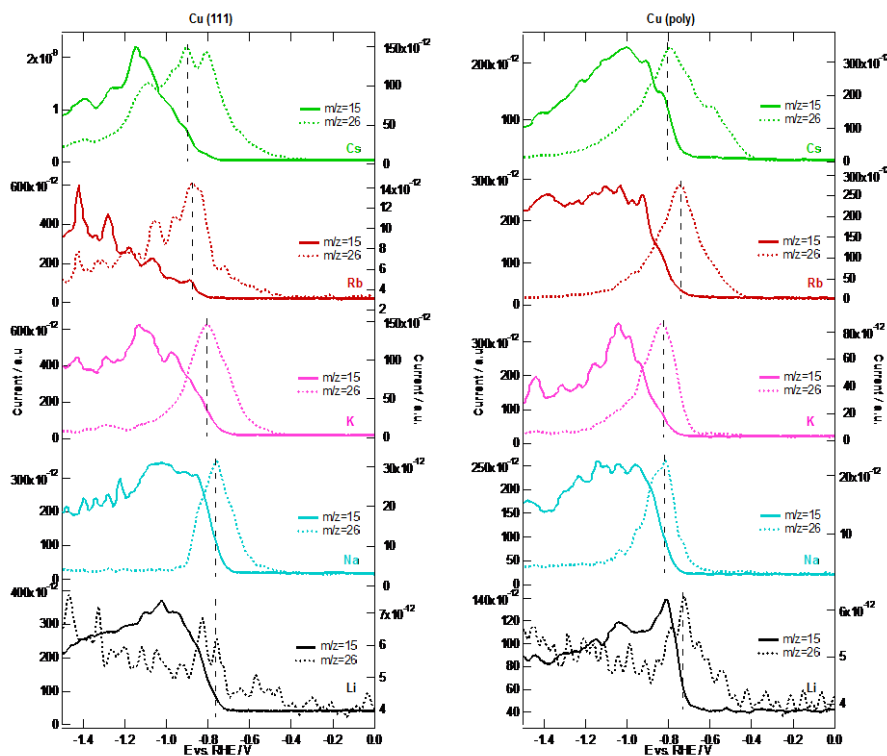
**Figure AIV.4:**  $^1\text{H}$ -NMR spectra of the samples obtained during CO reduction on polycrystalline copper after 2h of chronoamperometry at -0.9 V vs RHE in a) NaOH, b) KOH and c) CsOH 0.1 M solutions.

#### IV. 4 Mechanistic implications

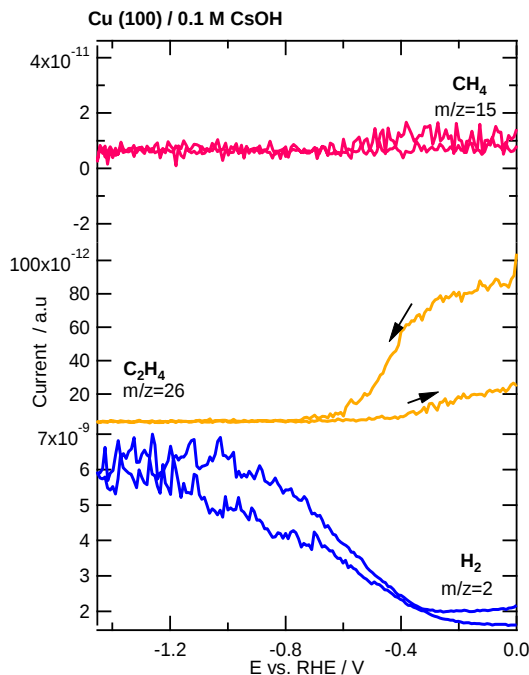
During the electroreduction of CO, a relation between the formation of ethylene and methane was noted: an increase in  $m/z = 15$  (corresponding to methane) occurs when  $m/z = 26$  (corresponding to ethylene) starts to decay. Figure AIV.5 shows the relation between these two mass fragments for Cu(111) and Cu(polycrystalline) in different alkaline hydroxide solutions, which complement Figure 5.4 in chapter 5.

The possibility that methane formation be the result of ethylene reduction has been tested. Figure AIV.6 shows the reduction of ethylene on Cu(100) in 0.1 M CsOH solution. When ethylene is reduced, only the formation of hydrogen from the competitive hydrogen evolution reaction (HER) was observed. The absence of methane formation rules out the possibility that the relation observed between methane and ethylene is due to methane production as a following step in the  $C_2$  pathway. It is important to mention that ethane was not detected during the reduction of ethylene, either.

The decay in  $m/z = 26$  during CO reduction due to the reduction of ethylene has also been considered. The experiments show that ethylene reduction starts at ca. -0.4 V achieving its maximum reduction current at ca. -0.6 V vs RHE, and the decay of  $m/z = 26$  during the reduction of CO occurs at ca. -0.7 V. Thus, the possibility of the decay of the ethylene signal due to its reduction has also been ruled out. Hence, we propose that the  $C_2$  pathway gets blocked by the enhancement of the  $C_1$  pathway and discard the hypothesis that  $C_2$  products are transformed to produce  $C_1$  species.

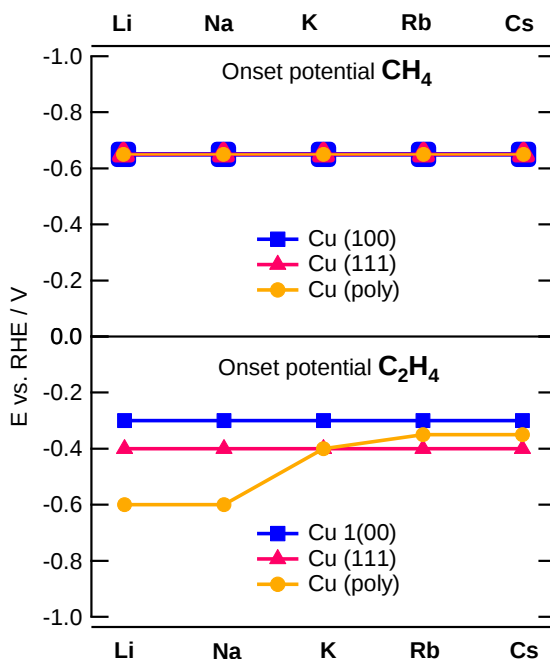


**Figure AIV.5:** OLEMS mass fragments associated with the reduction products formed during CO reduction on Cu(111) (left panel) in different 0.1 M alkaline hydroxide solutions. Dashed lines correspond to  $m/z = 26$  associated with the formation of ethylene, plotted against the right axis. Full lines correspond to  $m/z = 15$  associated with the formation of methane, plotted against the left axis.



**Figure AIV.6:** OLEMS mass fragments associated with the reduction of ethylene on Cu(100) in 0.1 M CsOH solution. The bottom panel displays  $m/z = 2$  associated with the formation of  $H_2$ , the middle panel displays  $m/z = 26$  associated with the reduction of  $C_2H_4$  and the top panel displays  $m/z = 15$  associated with  $CH_4$ .

The onset potential for the formation of methane and ethylene during the reduction of CO is displayed in figure AIV.7. The onset potential for ethylene formation depends on the facet, being lower for copper single crystals than for polycrystalline copper. In addition, the onset potential for ethylene is not affected by the cation size when CO reduction is performed on copper single crystals, whereas on polycrystalline copper the onset potential depends on the cation, being -0.6 V for  $Li^+$  and  $Na^+$ , -0.4 V for  $K^+$  and -0.35 V for  $Rb^+$  and  $Cs^+$ . On the other hand, the onset potential for methane formation is independent of both cation nature and surface structure.



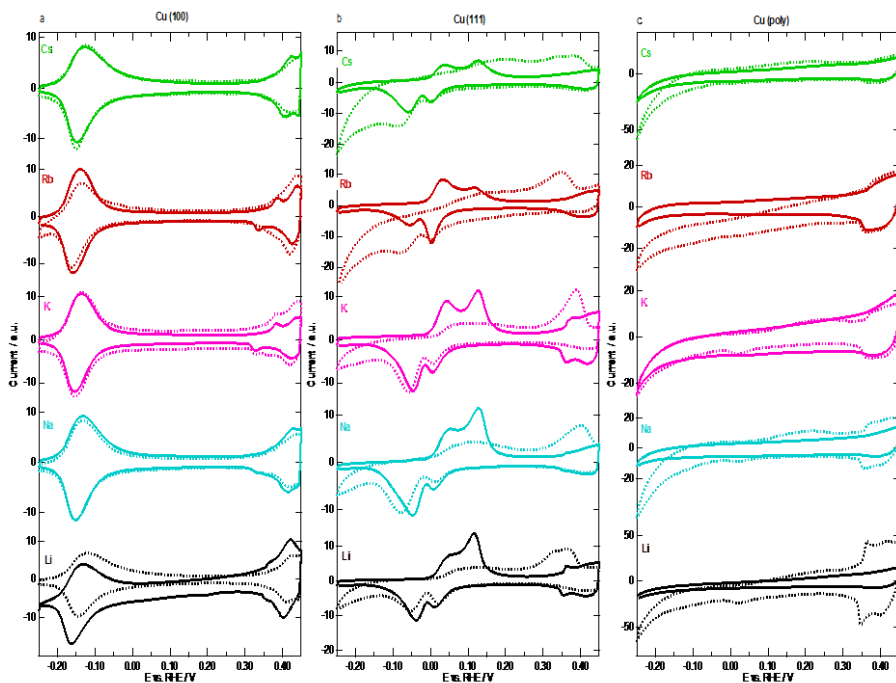
**Figure AIV.7:** Onset potential for the formation of methane (top panel) and ethylene (bottom panel) dependent on the cation nature and surface structure.

## IV.5 Electrode surface characterization

The structure of copper electrodes is a key factor in tuning the selectivity of CO electroreduction.<sup>64, 144</sup> Therefore, cyclic voltammetry before and after the reduction of CO (Figure AIV.8) has been carried out in order to determine the initial state of the electrode surface and to assess its change after CO reduction.

Prior to CO reduction, the voltammograms exhibit the characteristic peaks according to the specific copper surface, in agreement with the study of Schouten et al.<sup>91</sup> However, the state of the electrode surface

at the end of the experiments displays some differences with respect to the initial state. . While the surfaces of Cu(100) and Cu(poly) electrodes remain relatively unchanged, Cu(111) underwent major modifications. Thus, the variation in product distribution is merely due to the nature of the cation in solution and structural factors must not be considered. On Cu(100) OH<sup>-</sup> adsorption/desorption peaks at -0.15 V are present before and after the experiment. However, the OH<sup>-</sup> adsorption/desorption peaks on Cu(111) decrease in current intensity after the experiment. In addition, a new irreversible anodic peak appears at +0.35 V, suggesting that the well-defined (111) arrangement has been partially lost at the end of the OLEMS experiments. This new anodic peak might be due to specific cation adsorption or to OH<sup>-</sup> adsorption on a reconstructed surface.



**Figure AIV.8:** Cyclic voltammety characterization of a) Cu(100), b) Cu(111) and c) Cu(poly) in different 0.1 M alkaline hydroxide solutions before OLEMS experiments (full lines) and after OLEMS experiments (dashed lines).

First, according to DFT calculations in which solvation effects are considered, the specific adsorption of alkaline cations on fcc (111) transition metals occurs in the same potential range of HER<sup>172</sup>. Secondly, Jović et al. reported the slow Cu(111) surface reconstruction induced by adsorption/desorption of OH<sup>-</sup>, when the potential is scanned between -0.25 V and +0.45 V vs. RHE<sup>173</sup>. Both processes might give a possible explanation for the modification of the Cu(111) surface.

## **IV.6 Computational details**

Cu(100) was modeled with (3×2) slabs that contained four atomic layers. For such slabs, we sampled the Brillouin zones with 6×8×1 Monkhorst-Pack grids.<sup>115</sup> The geometry optimizations were carried out using a plane-wave cut-off of 450 eV, employing the conjugate-gradient scheme until the maximum force on any atom was below 0.05 eV Å<sup>-1</sup>, and allowing the two topmost layers and the adsorbates to relax in all directions, while the 2 bottommost layers were frozen at the optimized bulk distances. The separation between periodical images was more than 16 Å in the z direction and dipole corrections were also applied. The Fermi level in the calculations was smeared using the Methfessel-Paxton method<sup>116</sup> with an electronic temperature of 0.2 eV, and all energies were extrapolated to T = 0 K.

The chemical potential of protons and electrons was calculated from that of H<sub>2</sub>(g) using the computational hydrogen electrode<sup>121</sup>. The free energies of the species were calculated as:  $G = E_{DFT} + ZPE - TS + E_{solvation}$ , where  $E_{DFT}$  is the total energy calculated in the manner described before,  $ZPE$  is the zero-point energy calculated through the harmonic oscillator approximation, and  $TS$  (with T = 298.15 K) is the total entropy correction for H<sub>2</sub>(g) and H<sub>2</sub>O(l), whereas it corresponds to the vibrational entropy part for the adsorbed species. We applied the solvation corrections ( $E_{solvation}$ ) reported before for \*CO (-0.1 eV/CO)<sup>57</sup>, \*OCCO (-0.3 eV/\*OCCO) and \*OCCOH (-0.48 eV/\*OCCOH)<sup>53</sup> and included

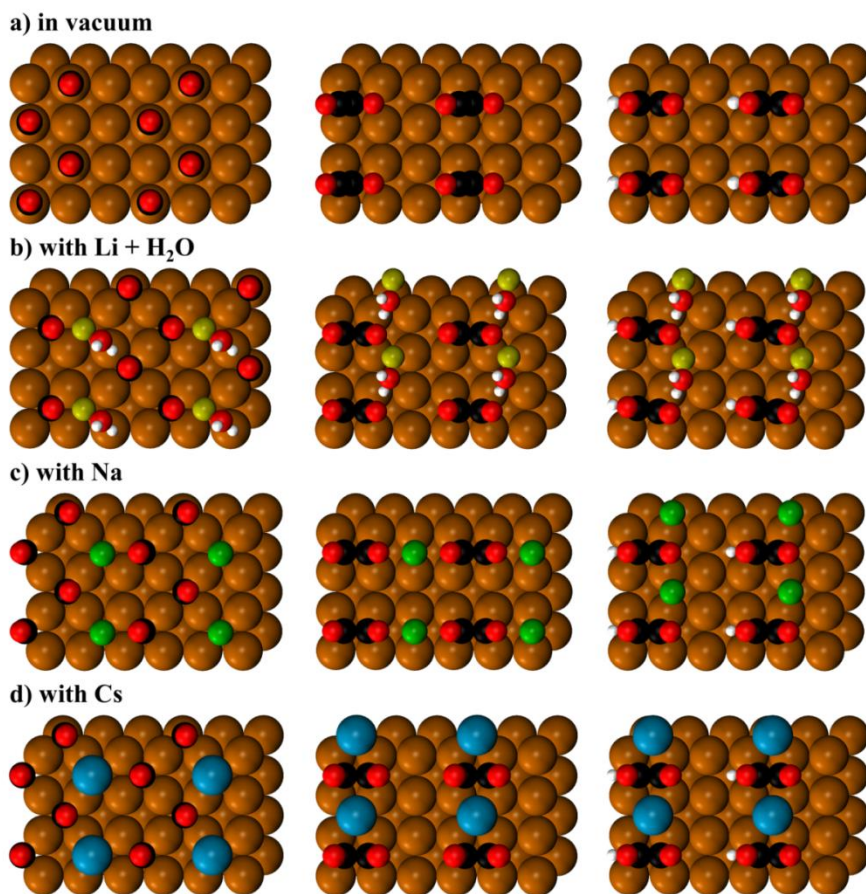
explicit water in the calculations to solvate only the alkaline cations. Given the known problems of PBE for the description of CO(g)<sup>57</sup>, we corrected its total energy by -0.24 eV as described elsewhere<sup>53</sup>.

Figure AIV.9 contains the adsorption configurations of 2\*CO, \*C<sub>2</sub>O<sub>2</sub> and \*C<sub>2</sub>O<sub>2</sub>H on Cu(100) in vacuum and in presence of the alkaline cations Li<sup>+</sup>, Na<sup>+</sup> and Cs<sup>+</sup>. Only in the case of Li<sup>+</sup>, the calculations included one explicit water molecule, as the adsorption energy of H<sub>2</sub>O over adsorbed Li, Na and Cs was -0.32, 0.04, and 0.19 eV, respectively.

This different solvation upon adsorption reflects the fact that in solution, the number of water molecules in the first solvation shell decrease as a function of the cation size, so that Li<sup>+</sup>, Na<sup>+</sup>, Cs<sup>+</sup> are surrounded by ~5, 3-4 and 2 H<sub>2</sub>O molecules, respectively<sup>174</sup>. However, the adsorption energetics in presence of the cations are rather similar in presence and absence of water, as shown in Table AIV.2.

**Table AIV.2:** Energetics of adsorption on Cu(100) of two CO molecules (2\*CO), their dimer (\*C<sub>2</sub>O<sub>2</sub>), and hydrogenated dimer (\*C<sub>2</sub>O<sub>2</sub>H). All values are in eV.

| species | vacuum | Li    | Li +<br>H <sub>2</sub> O | Na   | Na +<br>H <sub>2</sub> O | Cs    | Cs +<br>H <sub>2</sub> O |
|---------|--------|-------|--------------------------|------|--------------------------|-------|--------------------------|
| 2*CO    | -0.44  | -0.77 | -0.77                    | 0.74 | -0.81                    | -1.04 | -0.96                    |
| *C2O2   | 0.56   | -0.51 | -0.48                    | 0.64 | -0.67                    | -0.76 | -0.63                    |
| *C2O2H  | 0.44   | -0.54 | -0.68                    | 0.58 | -0.72                    | -0.77 | -0.66                    |



**Figure AIV.9:** Adsorption on Cu(100) of 2\*CO (left), \*C<sub>2</sub>O<sub>2</sub> (center) and \*C<sub>2</sub>O<sub>2</sub>H (right) in a) vacuum, and with b) Li, c) Na, and d) Cs. Color code: C: black, Cs: blue, Cu: orange, H: white, Li: yellow, Na: green, oxygen: red.

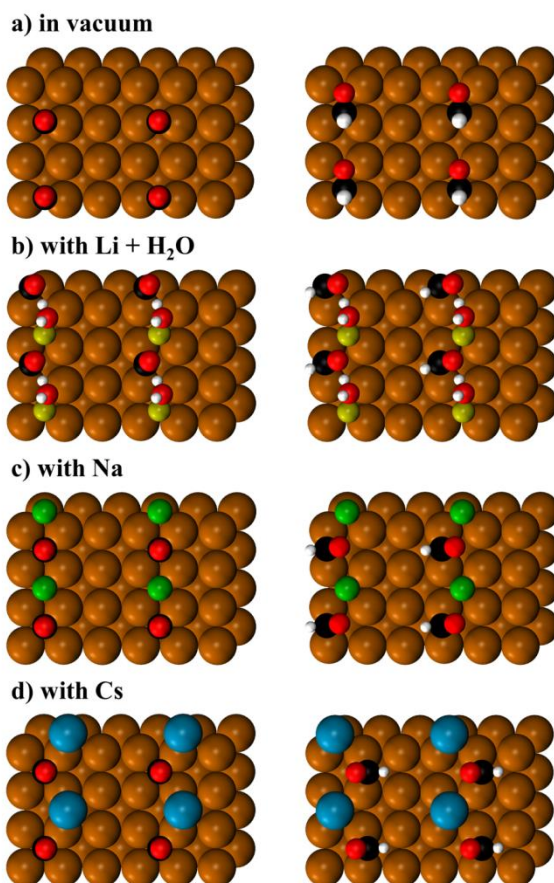
Essentially, the commonality between the three analyzed cations is that their effects are only present when they are relatively close to the adsorbates. The distances to the closest O atoms in the dimer vary considerably with cation: 1.88, 2.37, and 3.08 Å for Li<sup>+</sup>, Na<sup>+</sup> and Cs<sup>+</sup>, respectively.

Regarding the C<sub>1</sub> pathway, Figure AIV.10 contains the adsorption configurations of \*CO and \*CHO on Cu(100) in vacuum and in presence of the alkaline cations Li<sup>+</sup>, Na<sup>+</sup> and Cs<sup>+</sup>. Based on the adsorption energies

of water on the cations provided above, only in the case of  $\text{Li}^+$  the calculations included one explicit water molecule. In any case, the adsorption energetics are rather similar in presence and absence of water, as shown below in Table AIV.3 for Li.

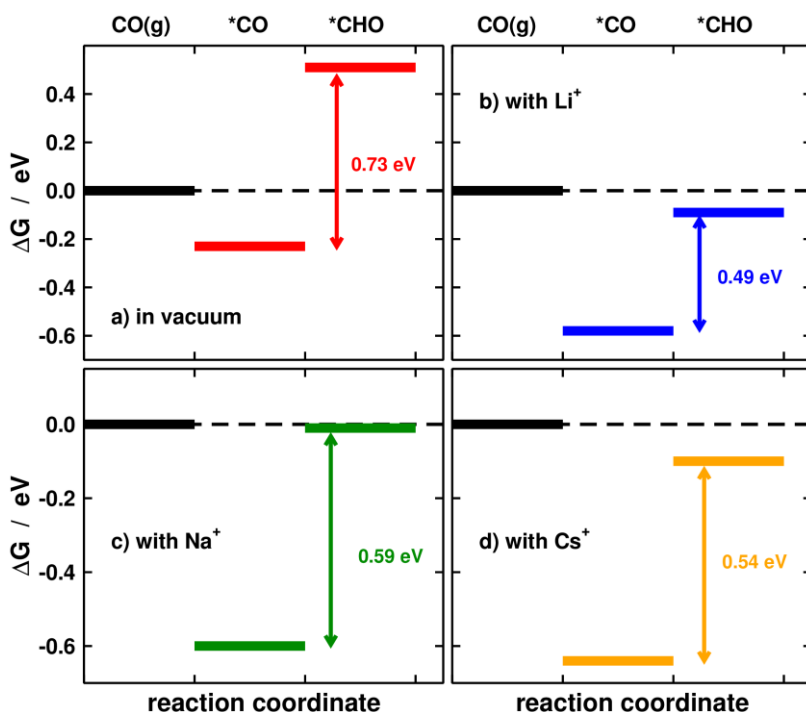
**Table AIV.3:** Energetics of adsorption on Cu(100) of  $^*\text{CO}$  and  $^*\text{CHO}$ . All values are in eV.

| species        | vacuum | Li    | Li + $\text{H}_2\text{O}$ | Na    | Cs    |
|----------------|--------|-------|---------------------------|-------|-------|
| $^*\text{CO}$  | -0.23  | -0.60 | -0.58                     | -0.60 | -0.64 |
| $^*\text{CHO}$ | 0.51   | -0.10 | -0.09                     | -0.01 | -0.10 |

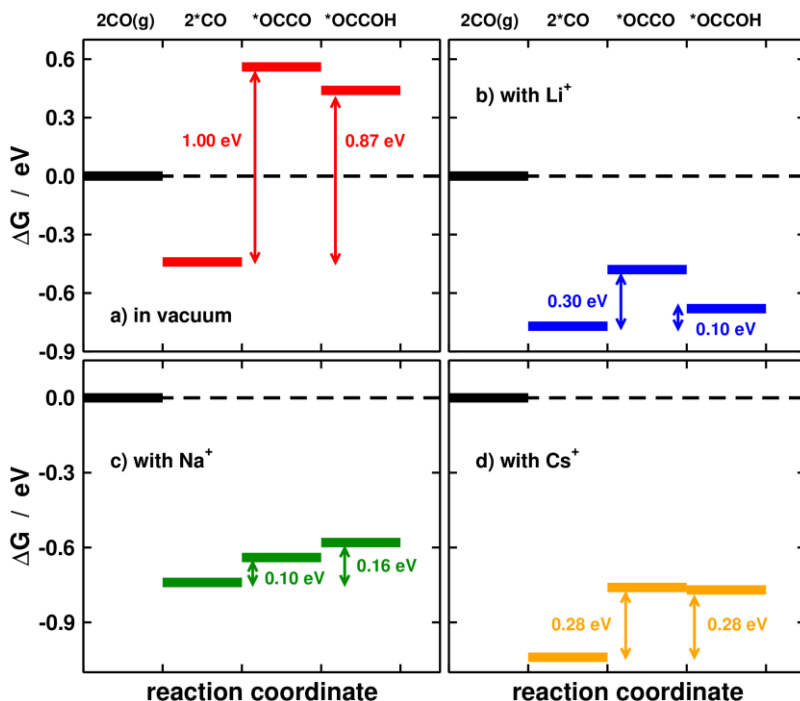


**Figure AIV.10:** Adsorption configurations on Cu(100) of  $^*\text{CO}$  (left) and  $^*\text{CHO}$  (right) in: a) vacuum, and with b) Li, c) Na, and d) Cs. Color code: C: black, Cs: blue, Cu: orange, H: white, Li: yellow, Na: green, oxygen: red

Finally, in Figures AIV.11 ( $C_1$  pathway) and AIV.12 ( $C_2$  pathway) we use the results in Tables AIV.2 and AIV.3 to calculate the energetics of CO adsorption, dimerization and protonation in vacuum and in presence of the cations. Note that the average values of Figures AIV.10 and AIV.11 were used to build Figure 5.3 in chapter 5.



**Figure AIV.11:** Energetics of the first electrochemical step of CO reduction for the  $C_1$  pathway on Cu(100) at 0 V vs RHE. a) In vacuum, and with b) Li, c) Na and d) Cs.



**Figure AIV.12:** Energetics of the first electrochemical step of CO reduction for the C<sub>2</sub> pathway on Cu(100) at 0 V vs RHE. a) In vacuum, and with b) Li, c) Na and d) Cs.

## IV.7 Exclusion of the formation of oxalates

We have collected the solubility of some alkaline oxalates in Table AIV.4. Lithium oxalate has a solubility in water at 20 °C of 80 g/l. On the other hand, the concentration of our hydroxides was 0.1 M. If all of the Li ions reacted to form Li<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, then 5.1 g/l would be formed. This means that all lithium oxalate that might be formed would be readily dissolved in water. Therefore, we do not expect any salt deposition during our experiments, which is corroborated by the identical cyclic voltammograms before and after electrolysis experiments.

Furthermore, we had a look at the spectra of hydrogen oxalate compounds<sup>175</sup> and noticed that it present a band at  $1195\text{ cm}^{-1}$ . However, these compounds also present a prominent band at  $1440\text{ cm}^{-1}$  corresponding to C-O stretching and a band at  $1737\text{ cm}^{-1}$  that corresponds to C=O stretching<sup>175</sup>. The absence of the latter two bands in the spectra recorded during CO reduction makes it possible to rule out the formation of lithium salts of hydrogen oxalate.

We would also like to annotate that (i) we did not detect any carbonate ( $\text{CO}_3^{2-}$ ) in our experiments, and (ii) oxalate ( $\text{C}_2\text{O}_4^{2-}$ ) is a negatively charged dimer of  $\text{CO}_2$ . Taking into account that all our experiments focused on CO reduction and that carbonate was not observed, any CO-associated dimer should only have 1 or maximum 2 oxygen atoms in its structure. Therefore, if oxalate were detected from CO reduction experiments, it would counterintuitively imply that CO is first oxidized and then subsequently reduced to ethylene. Note as well that if oxalate formed from dimerization of hydrolyzed  $^*\text{CO}$ , its formation rate would be slow<sup>171</sup> and would not account for the significant amounts of ethylene observed.

For all those reasons, we believe that oxalate is not responsible for the two bands that we attribute to the hydrogenated dimer.

**Table AIV.4:** Solubility in g/100 ml of several alkali oxalates

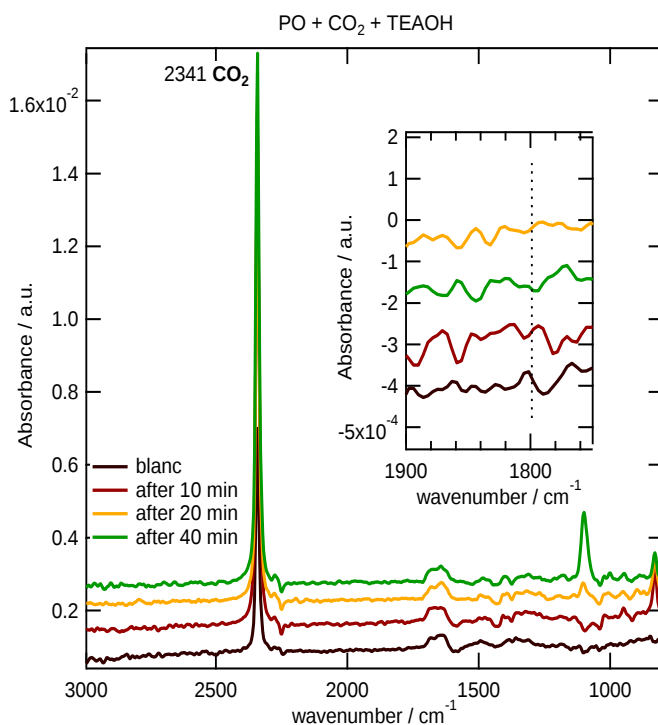
| Alkali oxalate | Solubility in g/100 ml |
|----------------|------------------------|
| Li             | 8                      |
| Na             | 3.7                    |
| K              | 36.4                   |
| Cs             | 313                    |



## Appendix V

### Supporting information to chapter 6

#### V.1 Results



**Figure AV.1:** Time dependent absorbance spectra of a solution containing 0.1 M of propylene oxide, saturated carbon dioxide atmosphere in a 0.1M TEAClO<sub>4</sub> in acetonitrile solution in the absence of TEAOH (black) and in the presence of 1M TEAOH after 10 minutes (red), 20 minutes (yellow) and 40 minutes (green). The insert displays the zoom-in of the region between 1900 - 1750 cm<sup>-1</sup>

Figure AV.1 shows the time dependent absorbance spectra of propylene oxide and CO<sub>2</sub> in the presence of a strong base (TEAOH) in a 0.1 M TEAClO<sub>4</sub> in acetonitrile solution. The spectra were recorded in order to ensure that the formation of propylene carbonate from propylene oxide and CO<sub>2</sub> is an electrochemical process and not a chemical synthesis catalyzed by the presence of OH<sup>-</sup> which can be formed during water reduction. The spectra show an intense band at 2341 cm<sup>-1</sup> corresponding to C=O stretching from CO<sub>2</sub> in solution. Less intense bands at 1670 cm<sup>-1</sup> corresponding to decomposition products from the acetonitrile are also observed. However, the absence of a band at 1800 cm<sup>-1</sup> that would correspond to propylene carbonate, supports the electrochemical nature of the synthesis of propylene carbonate instead of a chemical reaction catalyzed by OH<sup>-</sup>, in accordance with the results observed by Yang et al.<sup>78</sup>