Optimizing CO Coverage on Rough Copper Electrodes: Effect of the Partial Pressure of CO and Electrolyte Anions (pH) on Selectivity toward Ethylene

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Abstract: The conversion of the initial intermediate CO in the electrochemical reduction reaction of CO₂ on the surface of oxide-derived Cu electrodes has been investigated as a function of partial pressure and pH, manipulated by the composition of the electrolyte. We show that in inert gas, an increase in partial pressure of CO results in a continuous increase in Faradaic efficiency (FE) for ethylene, at various potentials ranging from −0.7 to −1.1 V versus RHE, with the highest FE of ~28% obtained using 1 bar CO at −0.8 V. When the partial pressure of CO is increased in a mixture of CO and CO₂, an optimum in the ethylene FE was found for the partial pressure of CO in the range from 0.5 bar (at −1.1 V, FE is ~45%) to 0.8 bar (at −0.9 V, FE is ~35%). At lower negative potentials (−0.8 to −0.7 V), the presence of CO₂ has negligible influence, and similar data to reduction of CO in inert gas were obtained. Variation of the anion in solution (0.1 M concentration) shows that the optimized FE toward ethylene increases from 5.2% in KH₂PO₄ to 43.2% in KOH. The observed dissolution of CO₂ acting as buffer, and the associated local pH near the surface of the electrode. Using in situ attenuated total reflection surface-enhanced infrared absorption spectroscopy (ATR-SEIRAS), it was determined that the CO coverage increases as a function of increasing pH, confirming that CO coverage and pH correlate. Collectively, the data herein outline the critical role of reactant partial pressures and the significant effect of anion composition (pH) on the surface coverage of CO and concomitant selectivity in electrochemical reduction of CO₂ to ethylene.

1. INTRODUCTION

The electrochemical reduction of CO₂ (CO₂RR) to hydrocarbons and alcohols has been subject to numerous studies since its discovery by Hori and co-workers.¹ Since the recognition of CO as the key intermediate in CO₂RR, many studies have also focused on reduction of CO (CORR). Studying CORR has the advantage that less reaction intermediates and steps are involved. In addition, with the elimination of dissolved CO₂ acting as buffer, CORR allows for a wider range of pH conditions to be examined.

CO gas streams are industrially available in the form of syngas, and CO is also a co-product of steel manufacturing, ranging in CO concentration from 10 to 60% in off-gas, often also consisting of CO₂.²⁻⁴ Direct conversion of waste gas mixtures to hydrocarbons avoids costly purification steps. This underlines the importance of investigating electrocatalytic activity of gas mixtures containing CO in inert gas or CO in the presence of CO₂. A number of reports have investigated the effect of CO partial pressure (P_CO) in inert gas on product selectivity of copper electrodes, with different outcomes. Schreier et al.⁵ or Li et al.⁶ demonstrated that with decreasing P_CO ethylene partial current density either was unvaried (in an ethanol-based electrolyte)⁵ or decreased,⁶ whereas both studies reported significantly⁵ or moderately⁶ improved methane production rates at relatively low P_CO. Wang et al.⁷ found correspondingly low CO reduction rates at low P_CO without extensively addressing relative changes in FEs. A recent study by Li et al.⁸ examined the effect of local CO concentrations on ethylene selectivity and oxygenates, both theoretically and experimentally. They showed that constraining CO partial pressure favors ethylene production, optimizing within ~10% (in inert gas) under a specific set of experimental conditions (gas diffusion electrode, −0.44 V vs RHE, 1 M KOH).

In CORR, a wide range of pH values can be investigated. Different values of pH can be achieved by changes in the composition of anions in solution. The CORR on copper is also known to depend on pH, while the pH dependency varies for different products.⁹ Increasing the electrolyte alkalinity is known to enhance the selectivity toward ethylene while...
suppressing the competitive hydrogen evolution reaction.\textsuperscript{9–11} The dramatic pH impact on selectivity toward C\(_2\) or C\(_1\) pathways has been explained by differences in rate-determining proton–electron transfer steps.\textsuperscript{12} Electron transfer during CO dimerization or a second proton-assisted electron transfer is a rate-determining step in the formation of C\(_1\) products or methane, respectively.\textsuperscript{13,14}

In a previous study, we studied the effect of CO\(_2\) partial pressure (\(P_{CO_2}\)) on CO\(_2\)RR using oxide-derived copper electrodes\textsuperscript{15} and reported improved ethylene formation rates by decreasing the \(P_{CO_2}\). So far, however, there is less published data on the performance of such electrodes in the reduction of CO/CO\(_2\) gas mixtures.\textsuperscript{16,17} The importance and originality of this study are the exploration of the effect of CO/CO\(_2\) partial pressures on selectivity toward hydrocarbons. We also show that the electrolyte anion greatly influences the activity and selectivity toward C\(_1\) and C\(_2\) pathways. Besides, we employ ATR-SEIRAS to understand dynamic adsorption of CO including atop-adsorbed and bridge-adsorbed CO as a function of potential and applied anions in the electrolyte. We demonstrate that the CO surface coverage can be moderated by the ratio of CO and CO\(_2\) in the feed gas and the establishment of the local pH by variation of the anion.

2. EXPERIMENTAL SECTION

2.1. Materials and Film Deposition. Cuprous oxide films were prepared by electropolishing (in 85% phosphoric acid, potentiostatically at 2.1 V versus a graphite foil counter electrode) of copper foils (Alfa Aesar, 99.99%), followed by electodeposition. A Cu\(_2\)\textsuperscript{+}-containing electodeposition solution was prepared using 0.4 M CuSO\(_4\) (Sigma-Aldrich, 99%) and 3 M lactic acid (Sigma-Aldrich) at 60 °C, according to a published procedure.\textsuperscript{18} A one-compartment, three-electrode cell with Cu foil as the working electrode, Pt mesh as the counter electrode, and Ag/AgCl (3 M NaCl) as the reference electrode were used. The pH of the solution was adjusted to 12 using NaOH (Sigma-Aldrich, 98%). Galvanostatic deposition was performed at 0.8 mA cm\(^{-2}\) using a potentiostat (PAR, VersaStat 3) until a plateau potential was reached at 2.1 V. A two-compartment electrochemical cell (total volume 170 mL) made of glass, using a three-electrode potentiostat. A two-compartment electrochemical cell (total volume 170 mL) made of glass, using a three-electrode potentiostat (PAR, VersaStat 3) until a plateau potential was reached at 2.1 V. A two-compartment electrochemical cell (total volume 170 mL) made of glass, using a three-electrode potentiostat (PAR, VersaStat 3) until a plateau potential was reached at 2.1 V.

2.2. Electrochemical Measurements. All electrochemical measurements were carried out using a Bio-Logic VSP potentiostat. A two-compartment electrochemical cell (total volume 170 mL) made of glass, using a three-electrode assembly, was used to carry out the CO\(_2\)/CO electrochemical reduction. The as-prepared cuprous oxide films with the thickness of 3 C were used as the working electrode. Glassy carbon (SIGRADUR G) was used as the counter electrode and was separated from the working electrode using an anion exchange membrane (Selemon AMV, AGC, Inc.). Ag/AgCl in 3 M NaCl was used as a reference electrode. The distance between the working and reference electrodes was kept small (3 mm) to reduce cell resistances. Using the potentiostat, an iR compensation was applied using the “Ohmic drop determination-current interrupt” technique. Using this technique, the resistance values for each electrolyte were measured and 85% compensation was applied. All potentials were converted to the reversible hydrogen electrode (RHE) scale by

\[
V_{\text{RHE}} = V_{\text{measured vs Ag/AgCl}} + 0.198 + 0.059 \times (\text{pH of solution})
\]

The gas mixture (CO\(_2\), CO, and He) was continuously purged through a glass frit at a rate of 20 mL min\(^{-1}\) for 30 min before each experiment using two mass flow controllers, to attain a steady CO\(_2\)/CO concentration in the electrolyte. The flow rate was then decreased to 5 mL min\(^{-1}\) during the electrochemical reduction experiment. The reactor effluent was vented directly into the gas sampling loop of a micro-gas chromatograph (micro-GC) equipped with a pulsed discharge detector every 4 min. The micro-GC was equipped with two different columns (Molsieve plot and Rt-Q Bond) for separation of H\(_2\), CO, CO\(_2\), and hydrocarbons. The mass balance was typically closed within +90%, and therefore, the electrolyte was not analyzed for liquid-phase products, which, based on other studies, most likely contains some formate/formic acid. Average faradaic efficiencies were obtained by averaging results from the last three injections. Each experiment was repeated three times to establish statistical significance of the data. Error between measurements was calculated by means of standard deviation of the mean for Figures 1 and 2. Due to an error margin less than 10%, the error bars are not included in the other figures for clarity.

2.3. In Situ ATR-SEIRAS. All electrochemical experiments were performed in a custom-made three-electrode cell, with a sputtered Cu film as the working electrode. A graphite rod was used as the counter electrode, while a Ag/AgCl electrode (3 M NaCl, BASi) was used as the reference electrode. A VersaSTAT 3 potentiostat was used to perform the electrochemical measurements. The experiments were conducted in a Bruker Vertex 70 spectrometer equipped with a liquid nitrogen-cooled MCT detector and a Veemax III ATR accessory. Spectra were taken with 4 cm\(^{-1}\) resolution during CV with a scan rate of 2 mV/s, under continuous purge of 1 bar CO.

3. RESULTS AND DISCUSSION

3.1. Effect of \(P_{CO}\) on CORR. To investigate the effect of CO coverage on product distribution, the CO partial pressure was varied at several fixed potentials. Figure 1 shows the faradaic efficiency (FE) of ethylene, ethane, and methane as a function of \(P_{CO}\) between −1.1 and −0.7 V (see Figure S1 for the FE of hydrogen and Figure S2 for the FE vs potential of the same products). Based on Figure 1a, an increase in partial pressure of CO results in a continuous increase in FE for ethylene. This is in line with theoretical and experimental studies that propose that a high CO coverage favors CO dimerization.\textsuperscript{5,20–22} Consequently, the highest FE was obtained at 1 bar CO (at −0.8 V, the FE is −28%, while the dominant product is hydrogen). This will be discussed in more
Formation of ethane, albeit formed in very small quantities, also increases as a function of increasing $P_{CO}$ (Figure 1b, the optimized FE is $\sim$1.5%) up to 0.8 bar, after which the FE decreases at $-0.7$ and $-0.8$ V.

Similar to ethane, the other minor product, methane (Figure 1c), also displays optimum selectivity at a $P_{CO}$ of 0.8 bar, but now, the highest FE is obtained at $-1.1$ V. Such trends in methane and ethane formation support previous observations, implying that a Langmuir–Hinshelwood mechanism can be in play. Based on this mechanism, both CO and H compete for surface sites, and increasing the $P_{CO}$ improves coverage and activity toward formation of carbon-containing products. The
optimum in $P_{\text{CO}}$ for ethane and methane formation is in agreement with the hypothesis that the formation of these products also requires a significant quantity of activated H on the surface. This is also in agreement with Figure S1, which shows a continuous increase in hydrogen production as a result of a decrease in the $P_{\text{CO}}$.

### 3.2. Reduction of Mixtures of CO and CO$_2$.

To assess the influence of CO$_2$ on the electrochemical reduction of CO, the partial pressure of CO was varied and the total pressure was balanced to 1 bar with CO$_2$, rather than with He. When comparing Figures 1a and 2a, at the potentials of $-0.7$ and $-0.8$ V, a quite similar increasing trend in the formation of ethylene is observed when the $P_{\text{CO}}$ is increased, and a comparable FE toward ethylene is obtained (at $-0.8$ V and 1 bar, the FE is again $\sim 28\%$). In agreement with the literature, CO$_2$ is not electrocatalytically activated at potentials less negative than $-0.8$ V, and hence, CO$_2$ does not contribute to product formation. As shown in Figure 2a, at potentials more negative than $-0.8$ V, an optimum in the production of ethylene as a function of $P_{\text{CO}}$ becomes apparent, shifting toward lower $P_{\text{CO}}$ in the potential series of $-0.9$, $-1.0$, and $-1.1$ V, with the highest ethylene FE of $\sim 45\%$ at $P_{\text{CO}} = 0.5$ bar and at $V = -1.1$ V versus RHE.

These data suggest that at potentials more negative than $-0.8$ V, the reduction of CO$_2$ is dominating product formation, with little contribution of the presence of CO. Turning to Figure 2b, methane formation was observed to be the highest at $P_{\text{CO}} = 0.8$ bar (and $P_{\text{CO}} = 0.2$ bar) at the two most negative potentials, again showing similar trends and values as compared to Figure 1c.

The observations for the formation of ethylene at potentials more negative than $-0.8$ V are very similar to those observed by varying the partial pressure of CO$_2$ in inert balance gas, also showing an optimum in FE of ethylene at $P_{\text{CO}} \sim 0.5$ bar; see Figure 3a. Figure 3a shows the results from this work and previously published data on $P_{\text{CO}}$ measured at $\sim 1.1$ V vs RHE (see also Figures S3 and S4 for other potentials). The relatively low FE toward ethylene induced by reduction of CO could be related to the large difference in aqueous solubility of CO (1 mM) and CO$_2$ (33 mM).

The trend in ethylene production rate in Figure 3a is partly consistent with that in a recent study on CO$_2$/CO co-feeds, which assigned the highest rate of ethylene formation to reduction of CO$_2$ in a mixture with CO, followed by pure CO$_2$ and finally pure CO.

The positive effect of CO at relatively high pressures may be explained by the higher coverage of adsorbed CO on the Cu surface. As previously stated, a high CO surface coverage enhances the CO dimerization rate, and due to the low solubility of CO, the $P_{\text{CO}}$ needs to be relatively high for the CO feed to contribute to the optimized balance between surface CO and H. Apparently at relatively low $P_{\text{CO}}$ (and thus high $P_{\text{CO}_2}$), the coverage of the surface with CO$_2$-derived CO is already sufficient, and having additional CO leads to sub-optimal deviation of the optimized CO/H surface ratio.

A negative effect of CO on the conversion of CO$_2$ to methane is apparent over the entire range of partial pressures but most prominently apparent at a $P_{\text{CO}}$ of $\sim 0.8$ bar. This is contrary to observations in ref 25, where CO reduction was determined to lead to the highest rate in formation of methane, rather than reduction of CO$_2$. We hypothesize that this discrepancy can be attributed to a difference in local pH near the electrode. The effect of the pH of the electrolyte on methane formation is well established. The formation of methane is highly dependent on availability of protons or hydrogen. The mentioned study was conducted in 0.1 M K$_2$HPO$_4$/KH$_2$PO$_4$ electrolyte (pH = 6.9), while we used the more basic 0.1 M KHCO$_3$ (pH = 8.4). Consequently, in our study, the alkalinity of the electrolyte likely suppressed methane formation in the reduction of CO. This effect will be discussed in more detail in Section 3.3.

### 3.3. Effect of Electrolyte Anions on CORR.

Since not only the $P_{\text{CO}}$ but also the local pH is likely to affect the FE toward ethylene, we studied the effect of the anion composition of the electrolyte on the performance of the oxide-derived copper surface. To assess the effect of the anionic species associated with potassium on the CO reduction activity, the FE and partial current densities (see Figures S5 and S6) of the reduction products were measured at the potential range from $-0.4$ to $-1.4$ V in various electrolytes. Anionic species such as ClO$_4^-$, HCO$_3^-$, and H$_2$PO$_4^-$ greatly affect the selectivity of the CORR products due to their different buffering strengths. Phosphate buffers and 0.1 M KOH were employed to minimize the changes in local pH due to the generated OH$^-$ at the electrode surface during the CORR from hydrogen and hydrocarbon formation. In the presence of a buffering anion, the released OH$^-$ is instantly neutralized by the following reactions:

$$\text{OH}^- + \text{HCO}_3^- \rightarrow \text{H}_2\text{O} + \text{CO}_3^{2-}$$  
$$\text{OH}^- + \text{H}_2\text{PO}_4^- \rightarrow \text{H}_2\text{O} + \text{HPO}_4^{2-}$$

On the other hand, the low buffer capacity of 0.1 M KHCO$_3$ and absent buffering capacity of KClO$_4$ solutions would result in significant enhancement of the pH near the electrode surface during the CORR.

Table 1 shows the bulk pH and resistance of the 0.1 M electrolyte solutions prior to electrochemical reactions.

**Table 1. pH and Resistance of Various 0.1 M Electrolytes**

| electrolyte | KH$_2$PO$_4$ | KH$_2$PO$_4$/K$_2$HPO$_4$ | KClO$_4$ | KHCO$_3$ | KOH |
|-------------|--------------|----------------------------|---------|----------|-----|
| pH          | 4.6          | 5.9                        | 5.9     | 8.4      | 13  |
| resistance (Ω) | 86           | 78                         | 64      | 78       | 34  |

Despite minimizing the pH changes at the electrode, phosphate which is a strongly adsorbing anion could act as a hydrogen donor. As a result, it can negatively affect CORR and promote the hydrogen evolution reaction, based on the following reaction:

$$2\text{H}_2\text{PO}_4^- + 2e^- \rightarrow \text{H}_2 + 2\text{HPO}_4^{2-}$$

Turning now to the experimental evidence, Figure 4 compares the product distribution of CORR in various electrolytes (see Figure S7 for the FE of Hydrogen). We begin by examining and explaining ethylene formation.

#### 3.3.1. Ethylene.

In Figure 4a, we can see a significant difference in the position (potential) at which the ethylene optimizes. This is related to the way the data have been plotted, that is, versus potential in the RHE scale. Figure 4d represents ethylene FE in the standard hydrogen electrode (SHE) scale. Comparing Figure 4a,d, it can be seen that ethylene formation is pH-dependent in the SHE scale but (roughly) pH-independent in the SHE scale. These results...
reflect previous analyses of similar data by the groups of Hori, Jaramillo,7 and Koper.27−29 Figure 4d shows that the ethylene FE is strongly anion-dependent. The highest FE was observed for KOH (43.2%), followed by for KClO4 (36.7%) and KHCO3 (28.7%), while the phosphate-containing solutions hardly result in the formation of ethylene. In Figure 5, the values for the FE are plotted against the pH of the solution, showing an increasing trendline as a function of increasing pH.

Clearly, the data for KClO4 do not follow the trendline, suggesting that for this anion, the local pH near the surface of the electrode is significantly higher than that measured in solution, as indicated by the extrapolation (blue dotted arrows) in Figure 5.

The trendline in Figure 5 shows once more how strongly dependent the ethylene formation in Cu-catalyzed reduction is on alkalinity. In addition to electrolyte pH and buffering capacity, it is necessary to address conductivity as another aspect of the electrolyte.30 Please note that also, the resistance of the solution appears solution pH-dependent, ranging from 85 to 30 Ω, as shown in Figure 5. What stands out in this graph is that KClO4 did not conform to the overall trend in conductivity, again suggesting that the actual pH on the electrode surface is higher than the bulk value. Based on the relationship between pH, resistance, and ethylene efficiency, the actual pH value can be estimated to be ~9.5−11.

Hori et al. have suggested that ethylene can be formed by two mechanisms.29 The first involves the dimerization of two adsorbed CH2 intermediate species, and in the second one, a combination of adsorbed CH2 and CO plays a role. Recent theoretical and experimental studies have provided strong evidence that ethylene is formed through hydrogenation of surface-adsorbed CO to form the CHO intermediate, also a common intermediate in the route toward methane.31,32 In addition, previous research has established that a CO dimer is the first intermediate toward ethylene formation.33,34 Formation of the *C2O2 dimer consists of CO coupling, mediated by electron transfer. The overall reaction to form ethylene is

\[ 2\text{CO} + 8(\text{H}^+ + \text{e}^-) \rightarrow \text{C}_2\text{H}_4 + 2\text{H}_2\text{O} \]  

(4)

In conclusion, the effect of the anion can be correlated to the (local) pH; when this is at the highest, the activity of C2

Figure 4. Faradaic efficiencies of ethylene, ethane, and methane as a function of applied potential in (a–c) RHE and (d–f) SHE scales in various electrolytes. Potentials were converted to the SHE scale by \( E_{\text{SHE}} = E_{\text{RHE}} + 0.197 \).
products is most abundant, consistent with other reports that demonstrate that OH$^-$ promotes C−C coupling.$^{28}$

3.3.2. Ethane. To date, few studies have investigated ethane formation, which is only observed on very rough copper surfaces. Surface defects associated with roughness most likely favor the reaction of the adsorbed hydrogen species crucial for ethane formation.$^{29}$ Ethane can be formed through two proposed mechanisms. One pathway involves dimerization of CO followed by hydrogenation of the ethylene intermediate,$^{35,36}$ while the second pathway suggests dimerization of the CH$_3$ species,$^{37}$ which is also a proposed intermediate for methane formation.$^{34}$

Figure 4b compares ethane formation in various electrolytes. From this figure, we can see that the production of ethane is suppressed in highly alkaline and very acidic electrolytes. The highest FE is observed in 0.1 M KHCO$_3$ (pH = 8.4) followed by that in 0.1 M KClO$_4$ (solution pH = 5.9). It should be noted that the local pH of the latter is likely higher and is possibly moderately basic, supported by experimental evidence of this study. Besides, comparing Figure 4a,b also revealed a smaller overpotential for the ethane production as opposed to maximum ethylene selectivity, similar to that in a previous study.$^{37}$

Formation of ethane is highly dependent on the adsorbed hydrogen species. High concentrations of adsorbed hydrogen are expected at lower pH. On the other hand, ethane formation also requires dimerization of CO (or CH$_3$), which is enhanced at high pH. As a result, ethane was not significantly formed in the lower pH range and was inhibited at very high pH.

Turning to Figure 4e, it is apparent that formation of ethane is pH-dependent in the RHE scale but pH-independent in the SHE scale, similar to ethylene. It is therefore likely that a shared mechanism exists between ethane and ethylene. However, further studies need to be undertaken to further analyze the formation of ethane, including the hydrogenation of ethylene.

3.3.3. Methane. During CORR at low pH, the copper surface is enriched with the adsorbed hydrogen species. The availability of protons or hydrogen species favors the formation of methane. As a result, methane formation and hydrogen evolution are major reactions in acidic electrolytes. The hydrogen evolution reaction has been well studied, and the formation of adsorbed hydrogen proceeds as follows, either through reactions 5 and 6 or through reactions 5 and 7.$^{36,39}$

$$\text{H}^+ + e^{-} \rightarrow \text{H}_{\text{ads}}$$  \hspace{1cm} (5)

$$2\text{H}_{\text{ads}} \rightarrow \text{H}_2$$  \hspace{1cm} (6)

$$\text{H}_{\text{ads}} + \text{H}^+ + e^{-} \rightarrow \text{H}_2$$  \hspace{1cm} (7)

The methane formation route proceeds through protonation of adsorbed CO to form CHO or COH intermediates.$^{29,40,41}$ Previous research has established that breaking of the C−O bond occurs after protonation of CO to produce CHO or COH.$^{29,34}$

Formation of methane was fully suppressed in basic electrolytes with the exception of 0.1 M KHCO$_3$, where a minor amount of methane was formed (see Figure 4c). The large amount of methane and small amount of ethylene produced at low pH values demonstrate that the protonation of CO is favored over the CO dimerization.

Interestingly, buffer solutions of 0.1 M KClO$_4$ and 0.1 M KH$_2$PO$_4$/K$_2$HPO$_4$ have a similar pH of 5.9, yet the local pH close to the electrode surface of these two differ significantly. As a result, formation of methane was not observed in KClO$_4$, providing further evidence for a rise in local pH at the electrode surface.

A comparison of Figure 4c,f reveals that the onset potential for formation of methane takes place at the same potential in the RHE and SHE scale. However, since we did not carry out further experiments at more negative potentials, a peak in methane formation was not observed, and hence, we cannot derive any mechanistic conclusions.

3.4. In Situ ATR-SEIRAS to Study CO Adsorption. To further understand the effect of electrolyte anions on the CORR mechanism, ATR-SEIRAS was used to investigate CO adsorption on the Cu electrode. Figure 6 represents in-situ ATR-SEIRA spectra during CVs from −0.7 to −1.5 V versus Ag/AgCl in 0.1 M solutions of KH$_2$PO$_4$, KClO$_4$, KHCO$_3$, and KOH. Due to the pH dependence of the RHE, the potentials in this section are reported versus the Ag/AgCl reference electrode. The reference spectra were taken at −0.8 V. Figure 7

![Figure 6. In situ ATR-SEIRA spectra of CO$_{ad}$ and CO$_2$ as a function of applied potential in CO-saturated 0.1 M KH$_2$PO$_4$, KClO$_4$, KHCO$_3$, and KOH in H$_2$O. The reference spectrum was recorded at −0.8 V.](https://doi.org/10.1021/acs.jpcc.0c10792)
shows the corresponding integrated areas of CO\textsubscript{atop} bands taken from Figure 6.

![Figure 7](image-url)

Figure 7. Integrated band area of CO\textsubscript{atop} as a function of applied potential in CO-saturated 0.1 M KH\textsubscript{2}PO\textsubscript{4}, KClO\textsubscript{4}, KHCO\textsubscript{3}, and KOH in H\textsubscript{2}O.

As shown in Figure 6, the band corresponding to linearly bound CO at an atop site (CO\textsubscript{atop}) appears at ∼−1 V and then gradually increases until the highest value at −1.4 V. The CO\textsubscript{atop} band consists of two bands at 2040 and 2075 cm\textsuperscript{−1} attributed to the low frequency band (LFB) and high frequency band (HFB), respectively.\textsuperscript{42} The sharp HFB is assigned to CO adsorbed on coordinatively unsaturated metal sites, while the more narrow LFB is attributed to CO adsorption on coordinatively more saturated sites. Apart from linearly bound CO which is the focus of this study, in KClO\textsubscript{4} and KHCO\textsubscript{3}, bridge-bound CO (CO\textsubscript{b}) can also be observed at 1900 and 1940 cm\textsuperscript{−1}. Based on previous studies, CO\textsubscript{b} is unreactive and predominantly appears under alkaline conditions.\textsuperscript{43,44} However, appearance of this band seems to be a complex function of pH, time, and cation identity,\textsuperscript{46} and more specific details require further investigation. Analysis of Figure 6 further reveals that the onset potential of CO adsorption is not dependent on anion identity, again consistent with the literature.\textsuperscript{46} In addition, a significant difference between the adsorption intensity of the CO bands is observed as a function of the anion.

In the previous section, we illustrated the effect of the electrolyte anion on catalytic performance and showed that an increasing ethylene FE was achieved in the order of KH\textsubscript{2}PO\textsubscript{4} < KHCO\textsubscript{3} < KClO\textsubscript{4} < KOH. Turning to the spectroscopic evidence in Figure 7, it can be seen that the integrated band areas are also strongly dependent on anion identity and increase in the order of KH\textsubscript{2}PO\textsubscript{4} < KClO\textsubscript{4} < KHCO\textsubscript{3} < KOH. Although other factors such as differences in surface orientation and dipole–dipole interactions might affect infrared band intensities of adsorbed CO, it is now well established from a variety of studies that the integrated band area of CO is proportional to CO coverage.\textsuperscript{42,45,47−51} Based on this, observing the lowest CO\textsubscript{atop} band area (and consequently the CO coverage) for KH\textsubscript{2}PO\textsubscript{4} is consistent with the low formation of C\textsubscript{2} products and relatively high methane production. At low CO coverage and high coverage of adsorbed hydrogen (associated with the low pH), protonation of CO is favored over CO dimerization. On the other hand, the highest CO coverage in KOH can explain the high ethylene FE of ∼43% since a high CO coverage on the surface kinetically favors C–C coupling and ethylene formation.\textsuperscript{52} Interestingly, KClO\textsubscript{4} showed a relatively low CO coverage compared to KHCO\textsubscript{3} despite having higher ethylene FE. This discrepancy has been proposed to be related to competitive adsorption of the perchlorate,\textsuperscript{46} although given the high FE toward ethylene, this appears to be not very likely. Alternatively, the combination of a low surface coverage with CO and a superior production of ethylene could be explained by an enhanced stimulated rate of CO dimerization in a perchlorate environment, although the origin of this phenomenon is not yet fully understood.\textsuperscript{53}

4. CONCLUSIONS

In summary, we have shown that a high FE toward ethylene in the electrochemical reduction of CO is dependent on a delicate balance of the ratio of CO and H coverage of the surface of the copper electrodes. This ratio can be manipulated by the applied potential, the partial pressure of CO in inert gas or CO\textsubscript{2} and the anion in solution. An optimized FE toward ethylene was obtained using an applied potential of −0.8 V versus RHE, a partial pressure of 1.0 bar CO, and KOH as the electrolyte. When CO\textsubscript{2} is present, a ratio of 0.4 bar CO to 0.6 bar CO\textsubscript{2} appears optimal, at an applied potential of −1.1 V versus RHE.

Further experiments on electrolyte anions confirmed that the concentration of the adsorbed hydrogen is associated with the formation of the dominant hydrocarbon. At lower pH, where adsorbed hydrogen is abundant, methane formation is prevalent. At higher pH, where less adsorbed hydrogen is available and C–C coupling is enhanced, ethylene formation is predominant over ethane formation. Moreover, in-situ ATR-SEIRAS studies revealed that anions play an important role in determining the CO surface coverage. It was revealed that with an increase in pH, CO coverage was significantly increased, favoring the CO dimerization pathway toward ethylene. Taken together, these results highlight the significant role of CO partial pressure and electrolyte anions in the selective production of hydrocarbons.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.0c10792.

Faradaic efficiency versus \(P_{\text{CO}}\) of hydrogen, faradaic efficiency versus \(E\), comparison of faradaic efficiency of ethylene and methane versus \(P_{\text{CO}}\) or \(P_{\text{H}}\), partial current densities of ethylene, ethane, and methane, sum of hydrocarbons partial current densities, and total current densities (PDF)

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https://doi.org/10.1021/acs.jpcc.0c10792

J. Phys. Chem. C 2021, 125, 6546−6554
A. Selecting CO2 Sources for CO2 Utilization by Environmental-Selectivity toward Multicarbon and Oxygenated Products. 
Polycrystalline Copper: Effects of Potential, Pressure, and pH on C.; Jaramillo, T. F. Electrochemical Carbon Monoxide Reduction on 
Guio, C. G.; Liu, X.; Higgins, D. C.; Chan, K.; Nørskov, J. K.; Hahn, Sinton, D.; Sargent, E. H. CO2 electroreduction to ethylene via 
copper single crystal electrodes. 

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.jpcc.0c10792

Funding

MM was financially supported by the NWO financed Solar to Products project 733.000.008 — “electrochemical reduction of CO2 to ethylene”

Notes

The authors declare no competing financial interest.

REFERENCES

(1) Hori, Y.; Kikuchi, K.; Suzuki, S. Production of CO and CH4 in electrochemical reduction of CO2 at metal electrodes in aqueous hydrogen carbonate solution. Chem. Lett. 1985, 14, 1695–1698.

(2) Spurgeon, J. M.; Kumar, B. A comparative technoeconomic analysis of pathways for commercial electrochemical CO2 reduction to liquid products. Energy Environ. Sci. 2018, 11, 1536–1551.

(3) von der Assen, N.; Müller, L. J.; Steingrube, A.; Voll, P.; Bardow, A. Selecting CO2 Sources for CO2 Utilization by Environmental-Merit-Order Curves. Environ. Sci. Technol. 2016, 50, 1093–1102.

(4) Li, J.; Wang, Z.; McCallum, C.; Xu, Y.; Li, F.; Wang, Y.; Gabardo, C. M.; Dinh, C.-T.; Zhang, T.-T.; Wang, L.; Howe, J. Y.; Ren, Y.; Sargent, E. H.; Sinton, D. Constraining CO coverage on copper promotes high-efficiency ethylene electroproduction. Nat. Catal. 2019, 2, 1124–1131.

(5) Schreier, M.; Yoon, Y.; Jackson, M. N.; Surendranath, Y. Competition between H and CO for active sites governs Cu mediated electrosynthesis of hydrocarbon fuels. Angew. Chem., Int. Ed. 2018, 57, 10221–10225.

(6) Li, J.; Chang, K.; Zhang, H.; He, M.; Goddard, W. A.; Chen, J. G.; Cheng, M.-J.; Lu, Q. Effectively Increased Efficiency for Electrocatalysis of Carbon Monoxide Using Supported Polycrystalline Copper Powder Electrocats. ACS Catal. 2019, 9, 4709–4718.

(7) Wang, L.; Nitopi, S. A.; Bertheussen, E.; Orazov, M.; Morales-Guo, C. G.; Liu, X.; Higgins, D. C.; Chan, K.; Nørskov, J. K.; Hahn, C.; Jaramillo, T. F. Electrochemical Carbon Monoxide Reduction on Polycrystalline Copper: Effects of Potential, Pressure, and pH on Selectivity towards multi-carbon and Oxygenated Products. ACS Catal. 2018, 8, 7445–7454.

(8) Hori, Y.; Takahashi, I.; Koga, O.; Hoshi, N. Selective formation of C2 compounds from electrochemical reduction of CO2 at a series of copper single crystal electrodes. J. Phys. Chem. B 2002, 106, 15–17.

(9) Dinh, C.-T.; Budryn, T.; Kibria, M. G.; Seifitokaladani, A.; Gabardo, C. M.; García de Arquer, F. P.; Kiani, A.; Edwards, J. P.; De Luna, P.; Bushuyev, O. S.; Zou, C.; Quintero-Bermudez, R.; Pang, Y.; Sinton, D.; Sargent, E. H. CO2 electroreduction to ethylene via hydroxide-mediated copper catalyst at an abrupt interface. Science 2018, 360, 783–787.

(10) Joung, M.; Luc, W.; Jiao, F. High-rate electroreduction of carbon monoxide to multi-carbon products. Nat. Catal. 2018, 1, 748–755.

(11) Xiao, H.; Cheng, T.; Goddard, W. A.; Sundaramaran, R. Mechanistic Explanation of the pH Dependence and Onset Potentials for Hydrocarbon Products from Electrochemical Reduction of CO on Cu (111). J. Am. Chem. Soc. 2016, 138, 483–486.

(12) Liu, X.; Schlexer, P.; Xiao, J.; Ji, Y.; Wang, L.; Sandberg, R. B.; Tang, M.; Brown, K. S.; Peng, H.; Ringe, S.; Hahn, C.; Jaramillo, T. F.; Nørskov, J. K.; Chan, K. pH effects on the electrochemical reduction of CO2 towards C2 products on stepped copper. Nat. Commun. 2019, 10, 32.

(13) Calle-Vallejo, F.; Koper, M. T. Theoretical considerations on the electroreduction of CO to C2 species on Cu (100) electrodes. Angew. Chem., Int. Ed. 2013, 52, 7282–7285.

(14) Garza, A. J.; Bell, A. T.; Head-Gordon, M. Mechanism of CO2 Reduction at Copper Surfaces: Pathways to C2 Products. ACS Catal. 2018, 8, 1490–1499.

(15) Moradzaman, M.; Martínez, C. S.; Mul, G. Effect of partial pressure on product selectivity in Cu-catalyzed electrochemical reduction of CO2. Sustainable Energy Fuels 2020, 4, 5195–5202.

(16) Wang, X.; de Araujo, J. F.; Ju, W.; Bagger, A.; Schmies, H.; Kühl, S.; Rossmeisl, J.; Strasser, P. Mechanistic reaction pathways of enhanced ethylene yields during electroreduction of CO2 on Cu feeds on Cu and Cu-tandem electrocatalysts. Nat. Nanotechnol. 2019, 14, 1063–1070.

(17) Lym, T. J.; Ager, J. W. Evidence for product-specific active sites on oxide-derived Cu catalysts for electrochemical CO2 reduction. Nat. Catal. 2019, 2, 86–93.

(18) Golden, T. D.; Shumsky, M. G.; Zhou, Y.; VanderWerf, R. A.; Van Leeuwen, R. A.; Switzer, J. A. Electrochemical deposition of copper (I) oxide films. Chem. Mater. 1996, 8, 2499–2504.

(19) Moradzaman, M.; Mul, G. Infrared Analysis of Interfacial Phenomena during Electrochemical Reduction of CO2 over Polycrystalline Copper Electrodes. ACS Catal. 2020, 10, 8049–8057.

(20) Sandberg, R. B.; Montoya, J. H.; Chan, K.; Nørskov, J. K. CO2 coupling on Cu f acets: Coverage, strain and field effects. Surf. Sci. 2016, 654, 56–62.

(21) Montoya, J. H.; Shi, C.; Chan, K.; Nørskov, J. K. Theoretical Insights into a CO Dimerization Mechanism in CO2 Electro-reduction. J. Phys. Chem. Lett. 2015, 6, 2032–2037.

(22) Huang, Y.; Handoko, A. D.; Hirunsit, P.; Yeo, B. S. Electrochemical Reduction of CO2 Using Copper Single-Crystal Surfaces: Effects of CO Coverage on the Selective Formation of Ethylene. ACS Catal. 2017, 7, 1749–1756.

(23) Cheng, T.; Xiao, H.; Goddard, W. A. Full atomistic reaction mechanism with kinetics for CO reduction on Cu(100) from ab initio molecular dynamics free-energy calculations at 298 K. Proc. Natl. Acad. Sci. U.S.A. 2017, 114, 1785–1800.

(24) Sanchez-Sanchez, C. M.; Esposito, E.; Batanero, B.; Montiel, V.; Barba, F.; Aldaz, A. Electrochemical Carbonylation. Carbon Dioxide Could be a Useful Compound for Synthesis. In Trends in Electrochemistry and Corrosion at the Beginning of the 21st Century; Brillas, E., Cabot, P.-L., Eds.; Universitat de Barcelona: Barcelona, 2004; pp 431–442.

(25) Katayama, Y.; Nattino, F.; Giordano, L.; Hwang, J.; Rao, R. R.; Andreussi, O.; Marzari, N.; Shao-Horn, Y. An In Situ Surface-Enhanced Infrared Absorption Spectroscopy Study of Electrochemical CO2 Reduction: Selectivity Dependence on Surface C-Bound and O-Bound Reaction Intermediates. J. Phys. Chem. C 2019, 123, 5951–5963.

(26) Hori, Y.; Murata, A.; Takahashi, R. Formation of hydrocarbons in the electrochemical reduction of carbon dioxide at a copper electrode in aqueous solution. J. Chem. Soc., Faraday Trans. 1 1989, 85, 2309.

(27) Koper, M. T. M. Theory of multiple proton–electron transfer reactions and its implications for electrocatalysis. Chem. Sci. 2013, 4, 2710–2723.

(28) Schouten, K. J. P.; Pérez Gallent, E.; Koper, M. T. M. The influence of pH on the reduction of CO and CO2 to hydrocarbons on copper electrodes. J. Electroanal. Chem. 2014, 716, 53–57.

(29) Hori, Y.; Takahashi, I.; Yoshinami, Y.; Murata, A. Electrochemical Reduction of CO at a Copper Electrode. J. Phys. Chem. B 1997, 101, 7075–7081.

(30) Lv, J.-J.; Joung, M.; Luc, W.; Zhu, W.; Zhu, J.-J.; Jiao, F. A Highly Porous Copper Electro catalyst for Carbon Dioxide Reduction. Adv. Mater. 2018, 30, 1803111.

(31) Schouten, K. J. P.; Qin, Z.; Pérez Gallent, E.; Koper, M. T. M. Two Pathways for the Formation of Ethylene in CO Reduction on Single-Crystal Copper Electrodes. J. Am. Chem. Soc. 2012, 134, 9864–9867.

(32) Peterson, A. A.; Ablid-Pedersen, F.; Stufert, F.; Rossmeisl, J.; Nørskov, J. K. How copper catalysts the electroreduction of carbon
dioxide into hydrocarbon fuels. Energy Environ. Sci. 2010, 3, 1311–1315.

(33) Gattrell, M.; Gupta, N.; Co, A. A review of the aqueous electrochemical reduction of CO$_2$ to hydrocarbons at copper. J. Electroanal. Chem. 2006, 594, 1–19.

(34) Schouten, K. J. P.; Kwon, Y.; van der Ham, C. J. M.; Qin, Z.; Koper, M. T. M. A new mechanism for the selectivity to C$_1$ and C$_2$ species in the electrochemical reduction of carbon dioxide on copper electrodes. Chem. Sci. 2011, 2, 1902–1909.

(35) Chen, C. S.; Wan, J. H.; Yeo, B. S. Electrochemical Reduction of Carbon Dioxide to Ethane Using Nanostructured Cu$_2$O-Derived Copper Catalyst and Palladium(II) Chloride. J. Phys. Chem. C 2015, 119, 26875–26882.

(36) Kas, R.; Kortlever, R.; Milbrat, A.; Koper, M. T. M.; Mul, G.; Baltrusaitis, J. Electrochemical CO$_2$ reduction on Cu$_2$O-derived copper nanoparticles: controlling the catalytic selectivity of hydrocarbons. Phys. Chem. Chem. Phys. 2014, 16, 12194–12201.

(37) Handoko, A. D.; Chan, K. W.; Yeo, B. S. –CH$_3$ Mediated Pathway for the Electroreduction of CO$_2$ to Ethane and Ethanol on Thick Oxide-Derived Copper Catalysts at Low Overpotentials. ACS Energy Lett. 2017, 2, 2103–2109.

(38) Gerischer, H.; Mehl, W. Zum Mechanismus der kathodischen Wasserstoffabscheidung an Quecksilber, Silber und Kupfer. Z. Elektrochem. 1955, 59, 1049–1059.

(39) Horiuti, J.; Keii, T.; Hirota, K. mechanism of hydrogen electrode of Mercury: “electrochemical mechanism”. J. Res. Inst. Catal., Hokkaido Univ. 1951, 2, 1–72.

(40) Kortlever, R.; Shen, J.; Schouten, K. J. P.; Calle-Vallejo, F.; Koper, M. T. M. Catalysts and Reaction Pathways for the Electrochemical Reduction of Carbon Dioxide. J. Phys. Chem. Lett. 2015, 6, 4073–4082.

(41) Cheng, T.; Xiao, H.; Goddard, W. A. Full atomistic reaction mechanism with kinetics for CO reduction on Cu (100) from ab initio molecular dynamics free-energy calculations at 298 K. Proc. Natl. Acad. Sci. U.S.A. 2017, 114, 1795–1800.

(42) Gunathunge, C. M.; Li, X.; Li, J.; Hicks, R. P.; Ovalle, V. J.; Waagele, M. M. Spectroscopic Observation of Reversible Surface Reconstruction of Copper Electrodes under CO$_2$ Reduction. J. Phys. Chem. C 2017, 121, 12337–12344.

(43) Gunathunge, C. M.; Ovalle, V. J.; Li, Y.; Janik, M. J.; Waagele, M. M. Existence of an Electrochemically Inert CO Population on Cu Electrodes in Alkaline pH. ACS Catal. 2018, 8, 7507–7516.

(44) Couto, A.; Rincón, A.; Pérez, M. C.; Gutiérrez, C. Adsorption and electrooxidation of carbon monoxide on polycrystalline platinum at pH 0.3–13. Electrochim. Acta 2001, 46, 1285–1296.

(45) Gunathunge, C. M.; Ovalle, V. J.; Waagele, M. M. Probing promoting effects of alkali cations on the reduction of CO at the aqueous electrolyte/copper interface. Phys. Chem. Chem. Phys. 2017, 19, 30166–30172.

(46) Ovalle, V. J.; Waagele, M. M. Impact of Electrolyte Anions on the Adsorption of CO on Cu Electrodes. J. Phys. Chem. C 2020, 124, 14713–14721.

(47) Wuttig, A.; Liu, C.; Peng, Q.; Yaguchi, M.; Hendon, C. H.; Motobayashi, K.; Ye, S.; Osawa, M.; Surendranath, Y. Tracking a Common Surface-Bound Intermediate during CO$_2$-to-Fuels Catalysis. ACS Cent. Sci. 2016, 2, 522–528.

(48) Koga, O.; Teruya, S.; Matsuda, K.; Minami, M.; Hoshi, N.; Hori, Y. Infrared spectroscopic and voltammetric study of adsorbed CO on stepped surfaces of copper monocrystalline electrodes. Electrochim. Acta 2005, 50, 2475–2485.

(49) Lee, S.; Lee, J. Ethylene Selectivity in CO Electroreduction when using Cu Oxides: An In Situ ATR-SEIRAS Study. ChemElectroChem 2018, 5, 558–564.

(50) Samjeské, G.; Komatsu, K.-i.; Osawa, M. Dynamics of CO oxidation on a polycrystalline platinum electrode: A time-resolved infrared study. J. Phys. Chem. C 2009, 113, 10222–10228.

(51) Hori, Y.; Koga, O.; Yamazaki, H.; Matsu, T. Infrared spectroscopy of adsorbed CO and intermediate species in electrochemical reduction of CO$_2$ to hydrocarbons on a Cu electrode. Electrochim. Acta 1995, 40, 2617–2622.

(52) Elert, A.; Cavalca, F.; Roberts, F. S.; Osterwalder, J.; Liu, C.; Favaro, M.; Crumlin, E. J.; Ogasawara, H.; Friebel, D.; Pettersson, L. G. M.; Nilsson, A. Subsurface Oxygen in Oxide-Derived Copper Electro catalysts for Carbon Dioxide Reduction. J. Phys. Chem. Lett. 2017, 8, 285–290.

(53) Sartin, M. M.; Yu, Z.; Chen, W.; He, F.; Sun, Z.; Chen, Y.-X.; Huang, W. Effect of Particle Shape and Electrolyte Cation on CO Adsorption to Copper Oxide Nanoparticle Electro catalysts. J. Phys. Chem. C 2018, 122, 26489–26498.

https://doi.org/10.1021/acs.jpcc.0c10792