Descriptors for $C_1$ product selectivity in Electrochemical CO$_2$R
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The conversion of CO$_2$ back into chemical fuels via electricity involves very complex reaction mechanisms. In this study, we combine evidence from the experimental literature with a theoretical analysis of energetics to rationalize that not all reaction steps in the reduction of CO$_2$ are concerted proton-electron transfer steps. This insight enables us to create a selectivity map for two-electron products (carbon monoxide (CO) and formate) on pure metal surfaces using only the CO and OH binding energies as descriptors. We find Cu to be uniquely capable of reducing CO$_2$ to products beyond 2-electrons via the proposed COH pathway and we identify atomic carbon as the key component leading to the production of methane.

Abstract:

Introduction
- Hydrogen evolution reaction (HER) competes with CO$_2$R under reducing potentials (< 0V vs. RHE).
- CO (and further products) compete with formate on Cu surfaces across varying applied potentials
- Hydrocarbon formed at potentials where CO onset has occurred.
- There is very little to no methanol produced at early potentials
- Previous studies rely on the assumption that all intermediate steps in CO$_2$R are proton-electron transfer steps, directly from water.

Results, Highlights, and Accomplishments

- Assuming similar field effects and solvation effects on OCHO* and COOH*, there should be a strong preference to form formate across all potentials.
- Because OCHO* binds much stronger vs. COOH* on Cu(100), we postulate that it is unlikely OCHO* forms electrochemically
- CO* vs. OH* as descriptors to relate $\Delta G_{\text{CO}}$ vs $\Delta G_{\text{COOH}}$ selectivity
- Overpotential drives the HER Volmer step where formate is produced via CO$_2$ attacking H*; in contrast, overpotential drives the COOH* formation step directly.
- At high overpotentials, selectivity moves from formate production to CO production: $\Delta G_{\text{COOH}} < \Delta G_{\text{OCHO}}$ (relative to H*)

Outlook
- Validate the formation of surface carbon or the formation of formyl (CHO) intermediate
- Examine the kinetics of the methanol pathway on Cu(100)

Broad Impact
- We have developed a theoretical model to understand how different materials selectively convert CO$_2$ into valued products used in industry.

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Reference