Abstract

Exploring the Reaction Mechanism and Electronic, Thermodynamic, and Kinetic Parameters of Electrochemical CO₂ Reduction to CO on a Copper Electrocatalyst Using First-Principle Calculations †

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Introduction: The electrochemical reduction of carbon dioxide (CO₂) to carbon monoxide (CO) is a promising approach to mitigate greenhouse gas emissions and produce valuable chemicals. In this work, we investigate the reaction mechanism and kinetics of electrochemical CO₂ reduction on Cu(100) using density functional theory (DFT) calculations.

Methods: We constructed a four-layer slab of Cu(100) and placed CO₂, H₂O, CO, H, OH, and H₂ as adsorbates on the surface. We calculated the Gibbs free energies, adsorption energies, activation barriers, and reaction rates of all the elementary reactions using DFT and transition state theory. We also modeled the solvation effect by placing a monolayer of H₂O molecules on the catalyst surface.

Results: We found that the most favorable pathway for the electrochemical reduction of CO₂ to CO on Cu(100) involves the transformation of trans-COOH* and its isomerization to cis-COOH*, followed by CO* + OH → CO and CO* + H → CO + H₂O. The calculated rate constants show that CO₂* + H → trans-COOH* is the predominant form of CO₂ activation. We also investigated the effects of a water layer on the CO₂RR-to-CO kinetics. Our results showed that the majority of elementary reactions exhibited altered reaction barriers, emphasizing the profound influence of the water environment on the reaction mechanism. Furthermore, our study on the effects of introducing a layer of water molecules on the CO₂RR-to-CO kinetics showed significant changes in the rates of most elementary reactions, indicating a nuanced interaction between the water molecules and the catalyst surface.

Conclusions: Our DFT calculations provide insights into the reaction mechanism and kinetics of electrochemical CO₂ reduction on Cu(100). The results indicate that copper is a promising electrocatalyst for transforming CO₂RR to CO and highlight the importance of considering solvation effects when modeling electrochemical reactions.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/proceedings2024105020/s1.

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