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Doctoral Dissertation

Doctoral Program in Physics (37th cycle)

Computational Screening of Cu-based Catalysts for CO₂ electrochemical valorization

By

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Summary

The electrochemical reduction of carbon dioxide (CO₂RR) is a promising route for the sustainable production of valuable chemicals and fuels. However, one of the main challenges associated with this process is its low selectivity toward specific products, particularly ethylene and ethanol. CO₂RR can lead to a wide distribution of reaction products, including carbon monoxide (CO), formic acid (HCOOH), methane (CH₄), and other hydrocarbons, making it difficult to efficiently direct the reaction toward the desired C₂/C₂₊ products (i.e. those containing 2 or more C atoms). Among the various metal catalysts studied for CO₂RR, copper (Cu) is unique in its ability to promote the formation of C₂ species. Despite this advantage, Cu itself is not inherently selective, as it also facilitates competing reaction pathways that lead to other products, such as CH₄. This lack of selectivity is a major limitation in the practical application of Cu-based catalysts for CO₂ electroreduction. A key aspect of CO₂RR is the role of CO as a crucial intermediate in the formation of C₂ products. The adsorption energy of CO on the catalyst surface significantly influences reaction pathways: if the CO binding is too weak, the molecule desorbs before undergoing further reduction; if too strong, it inhibits subsequent reaction steps, potentially leading to catalyst poisoning. Beside the adsorption energy, also the CO coverage of the catalyst surface and its geometry (e.g. the ratio between bridge and top site occupancy) play a key role. Indeed, it is well established that adsorption arrangements strongly influence C-C coupling, enhancing or suppressing CO dimerization and thus the formation C₂ products. A well-controlled CO adsorption behavior is therefore essential to optimize selectivity toward C₂ products.

In this thesis, we explore how alloying Cu with different secondary metals (one at a time) affects CO adsorption behavior, and investigate the preferred adsorption sites and patterns at varying CO coverages on pristine Cu. To achieve these goals,

we employ data-driven modeling approaches based on Density Functional Theory (DFT), Machine Learning (ML), and Cluster Expansion (CE). We first built two datasets and trained multiple ML models to predict CO adsorption behavior on Cu-based bimetallic alloys using both classification and regression techniques, focusing in particular on how alloying affects the strength of CO binding. With the first dataset, we demonstrated that even when trained on structures with a surface impurity concentration (denoted as x) of about 2.8%, the considered ML models, in particular the Gradient Boosting Classifier (GBC) and the Gradient Boosting Regressor (GBR), could accurately predict CO adsorption behavior on structures with impurity concentrations up to $x=16.7\%$. However, we also identified some critical limitations, such as the lack of a description for molecular adsorption on bridge sites of the (111) surface and on sites close to impurity clusters. The second dataset was then specifically designed to overcome these weaknesses. Among the tested models, the GBC and GBR once again achieved the highest accuracy, with an F1 score of 0.95, and an R^2 score of 0.95 and an RMSE of 0.085 eV on the test sets, respectively. Given their strong predictive performance, we used these models for a high throughput screening of Cu-based alloys as potential catalysts, identifying CuAg, CuAl, CuAu, CuZn, CuGa, and CuIn as promising candidates for CO₂RR to C₂ products. Next, we focused on CO adsorption patterns, using the CE method to analyze CO coverages on pristine Cu(111) and Cu(100), and to identify the preferred adsorption sites and binding arrangements across coverages ranging from 0 to 1 monolayer (corresponding to one adsorbate per surface atom). On Cu(111), preferred adsorption sites shift from hollow to top positions as coverage increases, whereas on Cu(100), bridge and top sites dominate across the entire concentration range, with their relative ratio varying with coverage. The most stable configurations identified could serve as a basis for future studies on CO dimerization.

The discussion is organized as follows. Chapter 1 outlines the fundamental aspects of the CO₂RR process, exploring its underlying mechanisms, the devices used to drive it, and the strategies to improve its selectivity and potential applications. It also provides an overview of the role of theoretical modeling in CO₂RR catalyst design. Chapter 2 focuses on the computational methodology used in this thesis work to generate the datasets and analyze CO behavior. In particular, it provides a detailed description of the theory behind DFT, including practical aspects of its implementation, describes the basic concepts of ML along with the main ML models employed in this work,

and illustrates the CE method from both a theoretical and practical perspective. In Chapter 3, we investigate how different Cu-based bimetallic alloys influence CO adsorption behavior by employing ML models trained on DFT-calculated CO binding energies. The study focuses on two Cu surfaces, specifically (111) and (100), which are known to exhibit different catalytic behaviors and are widely studied for CO₂RR applications. In our simulations, CO is adsorbed on Cu(111) and Cu(100) containing surface substitutional impurities at very low concentration ($x \approx 2.8\%$), testing different impurity elements one at a time. Our ML analysis is structured into two main steps: first, we employ classification models to determine whether a given adsorption site is stable (i.e., whether CO remains at the initially chosen site or migrates to another); second, we use regression models to predict the adsorption energy of CO on sites classified as stable. A key limitation of the ML model developed in Chapter 3 is that it only considers isolated impurities, which makes it less effective in cases when impurities tend to cluster. At higher impurity concentrations, certain adsorption sites that are unstable at lower stoichiometries can become stable due to local electronic and geometric effects. To address this issue, Chapter 4 extends the analysis by incorporating a more diverse training dataset that includes structures with different impurity arrangements and higher impurity concentrations. This refinement significantly improves the predictive performance of our ML models, especially in the "critical" structures where the first model exhibited lower accuracy, allowing for high throughput screening of a vast number of potential catalysts. We then focused on a specific bimetallic compound, the CuGa, and validated the ML predictions by explicitly calculating the reaction energy and the kinetic energy barrier of the rate determining step leading to C₂ products, namely the dimerization of two adsorbed CO molecules. In Chapter 5, we shift our focus to adsorbed CO behavior as a function of its surface coverage. To carry out this analysis, conducted on pristine Cu(111) and Cu(100), we fit two separate CE (one for each surface) with several DFT-computed energies corresponding to different CO coverage configurations. This approach allows us to gain valuable physical insights into the interactions between adsorbed molecules and, additionally, to construct phase diagrams that describe CO coverage behavior on each surface. These phase diagrams are particularly important, as they can be used to identify the ground state coverages, which represent solid starting points for future studies aimed at determining which configurations effectively promote CO dimerization. In the last

Chapter, we summarize the key findings presented throughout the thesis and outline their possible implications for future works.