Modeling Surface Reconstruction of Cu-based catalysts under Electrochemical CO$_2$ Reduction Conditions

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Copper-based materials are unique in catalyzing electrochemical CO$_2$ reduction (eCO$_2$R) toward C$_{2+}$ products, such as ethylene, ethanol, and *n*-propanol.[1] However, C$_{2+}$ product distribution depends heavily on the catalyst's precursors and varies significantly over time as a result of surface reconstruction under operating conditions.[2] Among the different types of catalysts, Cu foil produces mainly ethylene with oxygenates as side-products, while oxide-derived copper (OD-Cu) has the exclusive capacity of converting CO$_2$ and CO to ethanol at high Faradaic efficiencies and low overpotentials.[3] Similarly, Cu/Zn-based materials maximize ethanol selectivity to the detriment of CO and ethylene formation.[4,5] Polarized copper sites due to residual oxygen, defects, grain boundaries, CO spillover from weak CO binding domains, and high electrochemical surface area have been deemed responsible for the high CO$_2$ reduction activity and ethanol selectivity for OD-Cu and Cu/Zn catalysts.[6] Thus, a rational design of improved catalysts requires a proper assessment of each contribution. Computational modeling allows to simulate reconstruction phenomena and to track surface composition depending on the bulk properties, enabling the characterization of the surface patterns which rule catalytic activity and selectivity. In this regard, we here report an *ab initio* molecular dynamics (AIMD) study on two classes of epitaxies, Cu$_2$O/Cu and Cu$_2$O/ZnO/Cu, to model OD-Cu and Cu/Zn-based catalysts.

In the first work,[7] by simulating seven oxygen-depleted models derived from Cu$_2$O(111) and Cu(111) pristine structures, we identified the main ensembles which control the catalytic performance of oxide-derived copper. Upon surface reconstruction and independently from the starting depletion geometry, copper can be classified into three main classes depending on its local coordination and charge: metallic Cu^0, polarized Cu$^{\delta+}$, and oxidic Cu$^+$, respectively coordinated to 0, 1, and 2 oxygens. These three species form 14 ensembles, such as 4- and 6-coordinated Cu adatoms, Cu$_3^{\delta+}$O$_3$, reconstructed (111), (110) and (100) crystalline domains, and near-surface oxygens. Together with the high atomic roughness, low coordinated Cu adatoms and polarized sites are responsible for stabilizing CO$_2$ and therefore for improving CO$_2$ reduction activity. Metastable oxygens and metallic fcc-(111) or (100)-like Cu facets promote the CO–CO dimerization step *via* a deprotonated glyoxylate configuration, whose formation is thermodynamically favored and presents a negligible kinetic barrier. Characterized by vibrational fingerprints attributable to CO$_2$ reduction species on oxide-derived copper, this new intermediate could be the elusive molecule that reduces selectively to ethanol at low onset potentials.[3] As a follow-up on the previous work, we recently modeled six Cu$_2$O(111)/Zn(0001)/Cu(111) epitaxies with different bulk Zn compositions and carried out AIMD simulations at an applied electric field of –1.0 V vs RHE. We assessed the structural properties of the reconstructed surfaces, tracking surface composition, roughness, and local environment and comparing these results with experimental observations reported in a previous work by one of our groups.[5]

Overall, this new theoretical set of modeling tools enables the assessment of complex structural rearrangements driven by surface polarization during CO$_2$ reduction conditions and provides guidelines for new synthetic protocols toward catalysts selective to ethanol.

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