Pathways across the barrier: CO_2 adsorption and dissociation on vicinal Cu surfaces

Cu-based catalysts show promising activity towards *CO_2 reduction*, in heterogeneous as well as electrocatalytic reaction pathways, despite the thermodynamic stability and chemical inertness of the CO_2 molecule. Understanding the chemical composition of the catalyst surface in situ is essential to improving catalyst design and making reaction conditions more efficient. Crystalline Cu-surfaces are frequently used as model catalysts for fundamental studies on this reaction. At pressures > 0.01 mbar, they have been found to catalyze the dissociation of the CO_2 molecule - the first and most important step towards its catalytic conversion into, e.g. methanol. Atomic sites with lower coordination, such as steps (7-fold) and kinks (6-fold), may increase catalytic activity but the role of these active sites has not been studied comprehensively. In the work presented here, we employ a *curved model catalyst with variable surface structure* to study CO_2 adsorption and dissociation at near-ambient pressure. Using XPS to probe reactant and product species, we follow the reaction on the highly symmetric (111) surface, as well as increasingly corrugated surfaces. We observe how the coverage of competing surface species evolves over time, as CO_2 adsorbs into *physisorbed and chemisorbed* states and eventually dissociates into CO gas and atomically adsorbed O, forming distinct surface oxides. Finally, we discuss how the observed differences can be linked to specific surface sites (terraces, steps, kinks) and how the prevailing experimental conditions (pressure, temperature, molecular excitation) impact particular reaction pathways.