INVITED ORAL PRESENTATION

New first-principles methods and insights into surface catalysis: reconstructions, pathways, and mechanochemistry

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Theoretical understanding of chemical processes occurring at surfaces can enable new technological advances toward a future powered with renewable energy. In this talk, we will first present works which showcase the role of surface reconstruction in driving electrocatalytic CO_2 reduction reaction (CO_2RR) toward value added chemicals and green H_2 production. Next, bioinspired active site design to attain facile CO_2 activation on a metallic surface will be presented. At the end, we will show how one can perform dynamic catalysis by exploiting mechanochemical molecular motion and a new method to predict lowest-energy reconstructed surfaces in an automated way.

Nickel phosphides (Ni_xP_y) can be deployed as cost-effective electrocatalysts, as they are made from earth abundant elements. Via density functional theory calculations, we first investigate the stoichiometric and non-stoichiometric surface reconstructions of six different Ni_xP_y under electrochemical conditions and illustrate the implications of such reconstructions for the catalytic activity toward electrocatalytic hydrogen evolution reaction (HER). We identify that surface P sites with P-P bonds offer the best HER catalytic performances, and therefore we predict that active site engineering to maximize the abundance of such surface motifs can further improve the HER activity. We then demonstrate how pH and electrode potential dependent surface reconstruction of Ni_2P can offer an exclusive pH and electrode potential window for performing selective CO_2RR. We find that the hydrogen affinity of the Ni_2P surface and the dynamic surface reconstruction via H adsorption facilitate selective CO_2 reduction and C–C coupling on Ni_2P, ultimately leading to selective formation of C_3 and C_4 multi-carbon products. Our results show that one can leverage the role of surface reconstructions under electrocatalytic conditions to perform selective HER and CO_2RR. Furthermore, we predict that dual atom alloys (DAAs), homo- and heterodimer islands in a Cu matrix, can offer stronger covalent CO_2 binding than pristine Cu. We discover that molecules non-covalently interacting with graphene selectively diffuse away from the mountain (negative curvature) regions to the valley (positive curvature) regions, demonstrating that geometry-driven directional molecular motion can be attained. We further demonstrate that such directional motion of non-covalently bonded molecules can be exploited to create binding sites with tunable chemisorption energy on curved graphene. Finally, we describe our recently developed "*ab initio* grand canonical Monte Carlo" method which can produce the lowest-energy surface structures in an automated way. Overall, we will demonstrate a multi-pronged approach to understand surface chemistry and the many new opportunities it opens for realizing novel chemical transformations.