Effect of the **electrode** surface on the activity of a heterogeneous catalyst: combining old approaches with new methods

Sudarshan Vijay

Department of Materials Science, University of California Berkeley

In this two-part seminar, I will present theoretical and computational approaches to model the electrochemical reduction of carbon dioxide (CO_2R) to carbon monoxide (CO). CO is the simplest product of CO_2R, but accurately determining its rate-limiting step and reaction kinetics across materials remains challenging. I will present a unified view[1] of CO_2R to CO by describing different and sometimes competing effects at the electrochemical interface.

In the first seminar, we will examine the influence of the ***electrode*** surface on the activity of a catalyst. We will begin by developing an approach to determine accurate adsorption energies, a central quantity in surface catalysis, from temperature-programmed desorption (TPD) experiments.[2] Our method fits the long tail of the TPD curve to an expression for the configurational entropy.[3] This approach allows us to determine reliable adsorption energies and adsorbate-adsorbate interaction parameters to benchmark our first-principles computations.

We will explore trends in adsorption energies across different surfaces and reaction intermediates. To provide an appropriate description of the metal-adsorbate bond and describe the process of adsorption from the first principles, we will develop a model combining a modified form of the Newns–Anderson hybridization energy with an effective orthogonalization term.[4] Through this model, we will describe the conditions for the adsorption energies of different reacting species to scale with one another, allowing for a general and quick estimation of reaction rates based on a simplified description of the adsorbate-metal bond. Using this model, we will describe chemical bonding features unique to single-atom alloys and show the atomic-scale modifications required to improve the activity of transition metals catalysts.[5]

[1] Vijay, Ju, Brückner, Tsang, Strasser, Chan. ***Nature Catal.*** (2021)
[2] Vijay, Gauthier, Heenen, Bukas, Kristoffersen, Chan. ***ACS Catal.*** (2020)
[3] Vijay, Kristoffersen, Katayama, Shao-Horn, Chorkendorff, Seger, Chan. ***Phys. Chem. Chem. Phys.*** (2021)
[4] Vijay, Kastlunger, Chan, Nørskov. ***Journal of Chemical Physics*** (2022)
[5] Rosen, Vijay, Persson. ***ChemRxiv*** (2022)