Texas Tech University
Department of Chemical Engineering
Seminar Series

Reaction Mechanisms and Structure Sensitivity for Heterogeneous Catalyst Discovery from First-Principles

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Abstract

First-principles calculations have emerged as a key contributor towards the fundamental understanding of heterogeneous catalysis and the educated discovery of improved catalytic materials. By choosing the example of formic acid (HCOOH) decomposition on transition metals and alloys, we demonstrate how a deep mechanistic understanding of selective versus unselective routes can help with designing more selective catalysts. HCOOH is a simple molecule that is an abundant product of biomass processing and can serve as an internal source of hydrogen for oxygen removal and upgrading of biomass to chemicals and fuels. In addition, HCOOH can be used as a fuel for low temperature direct fuel cells. We start by presenting a systematic study of the HCOOH decomposition reaction mechanism starting from first-principles and including reactivity experiments and microkinetic modeling. In particular, periodic self-consistent Density Functional Theory (DFT) calculations are performed to determine the stability of reactive intermediates and activation energy barriers of elementary steps. Mean-field microkinetic models are developed and calculated reaction rates, orders, etc are then compared with experimentally measured ones. These comparisons provide useful insights on the nature of the active site, most-abundant surface intermediates as a function of reaction conditions and feed composition. Trends across metals on the fundamental atomic-scale level up to selectivity trends will be discussed. Finally, we identify from first-principles alloy surfaces, which may possess better catalytic properties for selective dehydrogenation of HCOOH than monometallic surfaces, thereby guiding synthesis towards promising novel catalytic materials.

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