Ph.D. DISSERTATION DEFENSE

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Date:	Friday, May 2, 2025.
Time/Location:	12:00 PM EST at Gateway South 121.
Title:	The Design of Bimetallic Catalysts for the Upgrading of Carboxylic Acids.
Chairperson:	Dr. Alyssa Hensley, Department of Chemical Engineering and Material Science, Charles V. Schaefer, Jr. School of Engineering & Science.
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ABSTRACT

The next couple of decades are gearing up to be pivotal in reducing our energy reliance on fossil fuels. The environmental consequences of fossil fuel combustion grow increasingly dire, and their reserves are diminishing. To get in front of this, sustainable alternative sources of energy are intensely sought out. Among these, biomass-derived fuels (known as biofuels) show the most potential due to their compatibility with our existing internal combustion engine designs, offering a transitional bridge between current systems and a greener future. However, biomass is initially broken down into raw form called biooils which is unusable due in part to its high oxygen content. Thus, necessitating a second step upgrading of the oxygenated functional groups that populate the biooils into usable biofuels. Catalytic upgrading strategies, most notably hydrodeoxygenation (HDO) and aqueous phase reforming (APR), have emerged as green and efficient approaches for converting these complex mixtures into higher-quality fuels. Transition metal catalysts are widely employed in these processes, and bimetallic catalysts have been shown to provide promising activity, selectivity, and stability. Yet, critical challenges/knowledge gaps linger: (1) Experimental testing of various bimetallic catalysts to find optimal combinations is time consuming and expensive; (2) Existing computational studies oversimplify what is happening on the catalyst surface, focusing on low coverage conditions inconsistent with experimental realities; (3) Unknown mechanisms connecting nanoscale interactions at the catalyst surface with observed macroscale

catalyst performance. These gaps hinder the rational design of more efficient catalysts and limits progress toward efficient biofuel production.

In this work, I employed multi-scale approaches integrating *ab initio* modeling with experimental validation to investigate Pt, Ni, and Ru monometallic and bimetallic catalysts for biooil upgrading. Seven carboxylic acids were studied as representative undesirable biooil compounds. To demonstrate model accuracy, I first validated the modeled coverages of key surface intermediates on the monometallic surfaces under a wide range of reaction conditions against experimental adsorption results. Nanoscale insights were then derived by parameterizing adsorption energies into two key components: adsorbate-surface and adsorbate-adsorbate (intermolecular) interactions. Elucidation of such previously unexplored interactions allowed the prediction of these nanoscale interactions on catalyst surfaces and how they influence reaction energies, activation barriers, favored pathways, and the resulting potential energy surfaces for carboxylic acid catalytic upgrading. A key insight that emerged was the identification of two dominant adsorption modes that dictate catalytic behavior: (1) Transition metal catalysts that favor carboxylic acids adsorbing as dimers favor C–C scissions while (2) Transition metal catalysts that promote dissociative adsorption through deprotonation to form bidentate surface carboxylates favor C–O scissions and follow pathways more selective toward alkane formation. By balancing these two descriptors, I developed a unified framework that captures both catalyst activity and product selectivity trends across a broad range of metals, allowing the improvement of monometallic surfaces through doping for bimetallic and even trimetallic catalyst combinations.

Taken together, this work offers an accelerated, insight-driven route for catalyst discovery for sustainable fuel production, one that bridges nanoscale interactions with macroscale performance. These findings not only deepen our fundamental understanding of catalytic upgrading mechanisms but also advance the transformation process of biomass into commercially viable and sustainable biofuels towards more efficient levels.