ABSTRACT
ENGINEERING THE MICROENVIRONMENT OF SINGLE-ATOM CATALYSTS THROUGH SURFACE MODIFICATION FOR CROSS-COUPLING REACTIONS

Aray Yesmakhan

Marquette University, 2026

Single-atom catalysts (SACs) have emerged as a promising class of heterogeneous catalysts capable of bridging the gap between homogeneous and heterogeneous catalysis. By distributing isolated metal atoms across a solid support, SACs offer uniform active sites, near-total metal utilization, straightforward separation and recyclability. These features make SACs compelling candidates for reactions traditionally catalyzed by homogeneous transition-metal complexes, such as carbon–carbon cross-coupling reactions. However, unlike homogeneous catalysts, SACs lack molecular ligands that can be rationally tuned to control the environment around the active metal center. This dissertation demonstrates that organic ligands bound to the support surface can be used to modify the microenvironment around the active sites and enhance SAC performance in cross-coupling catalysis.

Chapter 1 provides a brief review of the SAC field, covering its historical development, synthesis and characterization techniques, and catalytic applications. Chapter 2 introduces the surface-modification strategy by coating Pd/CeO_2 SAC with benzoic acid-based ligands and systematically investigating their electronic properties. The study then evaluates the substituent effects on the aryl bromide and organoboron coupling partners for both uncoated and coated Pd/CeO_2. We find that coating the support with benzoic acid-based molecules increases the yield of Suzuki reaction several-fold, an effect that holds across a broad range of reactants and substituted benzoic acids.

Chapter 3 extends this surface-modification strategy to Sonogashira coupling, demonstrating that carboxylate-based ligands similarly enhance the activity of Pd/CeO_2 for this distinct reaction class. The chapter first establishes how the effect of the organic layer varies with solvent environment, then examines several possible origins of the activity enhancement by comparing aromatic carboxylate ligands with varying tether lengths and nonaromatic carboxylate ligands. Notably, both aromatic and nonaromatic ligands improve Sonogashira coupling activity regardless of tail group identity, suggesting that the carboxylate anchoring group contributes to the observed enhancement.

This is the first demonstration in the literature that support-bound carboxylate ligands can enhance the activity of SACs in carbon–carbon cross-coupling reactions. This work opens a path toward rationally designed SACs in which support–ligand interactions are deliberately engineered to create tunable microenvironments around isolated metal active sites.