

Engineering Active Sites of Multifunctional Catalysts for Biomass Transformation

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CLB 366 | Zoom: <https://udel.zoom.us/j/93082044212> | (Password: InverseCatalyst)

The transformation of biomass-derived oxygenates into value-added products provides a sustainable solution to rising energy demands and environmental crises. Central to this process is the rational design of catalysts for selective biomass deoxygenation. Supported metal-metal oxide (M_1 - M_2O_x) catalysts in inverse configurations, where reducible metal oxide shells on metal cores, offer metal, acid, and redox sites, exhibiting superior performance. However, their structural complexity and dynamic response to the working environment, where active sites may transform, cooperate, or function independently, complicate the understanding of structure-activity relationships. The lack of a systemic approach to capturing these dynamics hinders the advancement of active site engineering, underscoring the need for advanced analytical techniques.

This thesis presents a comprehensive strategy for elucidating the nature and dynamics of active sites, both Brønsted acid and metal, in M_1 - M_2O_x inverse catalysts by integrating material synthesis, *in situ* catalyst characterization, reaction kinetics, and theoretical calculations. We systematically investigated the nature of active sites by individually examining the support, metal cores, metal oxide shells, and the coverage of oxide shells on metal cores. This exploration spans four core chapters, each providing valuable insights into the role of active sites in catalytic performance.

Carbon, as the support in M_1 - M_2O_x catalysts, exhibits superior catalytic performance in biomass valorization; however, its intricate surface microenvironment poses significant challenges for a comprehensive investigation. We first developed a methodology to identify and quantify acidic sites in oxygenated carbon support for solid acid catalyst-driven chemistry by combining

probe reactions, multimodal characterizations, data analysis, and density functional theory (DFT) calculations. Our results demonstrated that phenolic groups (-OH) are the dominant acid sites in alcohol dehydration and exhibit higher acidity than carboxylic groups (-COOH). The carbon microenvironment significantly influences the performance of these acidic oxygenated groups due to electron density delocalization caused by neighboring aromatic rings and various functionalities. The analytical approaches and findings can be extended to other carbon-based acid site-driven heterogeneous catalysis and materials containing other heteroatoms.

Next, we examined the role of metal cores (Pt, Ru, Rh, Pd, Ni) in modulating the structure, density, and strength of Brønsted acid sites (BAS) on fully oxidized and pre-reduced oxide overlayers, uncovering intricate, metal-dependent dynamics during reduction, hydrogen spillover, and water hydrolysis. By integrating *in situ* characterizations, probe chemistry, and DFT calculations, we elucidated that metals with varying work functions modulate BAS acidity by adjusting deprotonation energy (DPE) and oxidation states through reduction. The feasibility of water splitting and hydroxylation on pre-reduced WO_x is metal-specific, with precious metals such as Ru- WO_x being thermodynamically favorable and exhibiting a higher dehydration rate than base metals like Ni- WO_x , leading to enhanced activity with optimized periodic H_2 pulsing frequency. This fundamental understanding provides a potential descriptor for optimizing catalytic performance.

Next, we investigated the role of metal oxide shells ($\text{MO}_x = \text{WO}_x, \text{MoO}_x, \text{ReO}_x, \text{NbO}_x$) in the tetrahydrofurfuryl alcohol (THFA) ring-opening (RO) reaction, focusing on their loading, structure, acid strength, coverage, and stability on the inverse catalyst. Leveraging probe reactions, microscopic characterizations, and CO chemisorption, we revealed that a saturated submonolayer MO_x coverage with a 2D atomic structure on Pt is crucial for performance. To optimize the structure of inverse configuration and enhance the dispersion of oxide shells on Pt, a strategy that selectively removed the MO_x from support with high-pressure wash treatment was introduced. This work deepens the understanding of the structure-activity relationship in inverse catalysts.

Lastly, we presented a strategy for precisely engineering active sites of supported metal catalysts, leveraging the foundational insights gained, the material synthesis method built, and characterization techniques established from the inverse catalysts studied in previous chapters. We demonstrated that submonolayer WO_x with adjustable coverage decorates well-coordinated Pt terrace sites, serving as a stable oxide ligand. A combination of experimental kinetics, *in situ* spectroscopies, and first-principles modeling technique allows us to fine-tune the metal-to-acid site balance by tailoring the WO_x coverage on Pt, resulting in optimal reactivity for metal-acid bifunctional catalyzed reactions at a specific metal, NPs size, and support-dependent coverages. The WO_x coverage modifies reactant adsorption modes, shifting selectivity from terrace- to step-dominated pathways in structure-sensitive hydrogenation reactions. This fundamental study allows more effective metal-metal oxide catalysts for sustainable heterogeneous catalytic transformations.