

# **Mechanistic Insights into Multi-functional Catalysts for Biomass Conversion to Bio-diesel and Bio-surfactant**

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With increasing concerns about CO<sub>2</sub> emissions and energy supply, research on renewable production of fuels and chemicals from biomass has surged. Although significant progress has been made, realizing a commercial bio-refinery is still challenging due to technological difficulties associated with the over functionalization of biomass-derived oxygenates. Developing effective catalytic processes to selectively tailor desired products requires deep mechanistic understandings of catalysis and process conditions. This thesis sheds lights on the catalytic roles of acid and base sites of multi-functional catalysts and their synergy in the production of the potential bio-diesel and bio-surfactants.

We undertake a comprehensive mechanistic and kinetic investigation of the multi-step conversion of biomass-derived glucose to 2,5-bis(alkoxymethyl)furan (di-ether), a potential bio-diesel product. To reduce the number of reaction steps and increase efficiency, we aim to develop two tandem catalytic processes with multi-functional acid-base catalysts to effectively facilitate each process. In the first process, glucose is isomerized to fructose, which undergoes dehydration to 5-hydroxymethylfurfural (HMF) in water by homogeneous metal chlorides. Using catalyst characterization, structure-activity relationships, and isotopic labeling experiments, we reveal that the metal salts, owing to their hydrolysis, induce Lewis acidity with an adjacent base site, and Brønsted acid as active species for isomerization and dehydration, respectively. In light of the findings, H-BEA zeolite is employed as the multi-functional solid acid catalyst for glucose conversion to HMF. A robust kinetic model is developed to optimize the reaction conditions and identify key limitations of zeolite catalysts.

Next, the multi-functionality of metal chlorides is explored for the second tandem process of reductive etherification of HMF to di-ether in 2-propanol. We report for the first time reactivity of metal chlorides for HMF reduction (transfer hydrogenation). Key

catalytic design features are elucidated. Specifically, a Lewis acid-base pair is necessary for HMF transfer hydrogenation, and a Brønsted/Lewis acid can enable subsequent etherification. Supported zirconia on silica is identified as a potentially desirable heterogeneous catalyst. The catalyst is synthesized, characterized, and assessed for activity and stability. The di-ether yield is improved by more than two-fold compared to the metal salts.

Besides bio-diesel, biomass-derived furanics are promising intermediates for other valuable chemicals, including oleo furan sulfonates (OFS), which recently emerged as excellent bio-surfactants. An original method is proposed to synthesize 2-dodecanoyl furan as OFS precursor from cross-ketonization of biomass-derived 2-furoic acid and vegetable oil's C<sub>12</sub> fatty acid (lauric acid). The Earth abundant iron oxides exhibit high activity and selectivity towards 2-dodecanoyl furan formation. Extensive catalyst characterization, active site elucidation and reaction mechanism investigation are conducted to provide mechanistic insights into the relatively unexplored cross-ketonization reaction, and pave ways for future research direction to optimize the catalyst and process design.