

Homogeneous and Heterogeneous Catalysis for Biomass Upgrading to Platform Chemicals and End Products

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Today, a variety of products, including automotive fuels and lubricants, plastics, and fabrics, are derived from petroleum, a nonrenewable feedstock that contributes to greenhouse gas emissions. Bioderived, renewable feedstocks can mitigate environmental challenges, while providing comparable or even superior properties to their petroleum-derived counterparts. Among the renewable energy sources, nonedible lignocellulosic biomass is one of the most promising petroleum alternatives; however, the high oxygen content in biomass is one of the most significant barriers for its conversion into low-oxygen containing fuels and chemicals traditionally derived from petroleum. As a result, multiple processes have been studied for oxygen removal. A common strategy is to form oxygenated furans, known as platform chemicals, from biomass-derived sugars. From there, oxygenated furans undergo additional upgrading to form high-value products, such as lubricants. This then requires an appropriate homogeneous or heterogeneous catalyst to enable the formation of platform chemicals. While heterogeneous catalysts are often favored over their homogeneous counterpart, carbonaceous by-products can deposit in the catalyst pores, requiring frequent catalyst regeneration. The objective of this thesis is therefore to provide insights into select catalytic systems and processes to obtain products from biomass.

In this work, we began by studying the active species of the homogeneous metal salt, AlCl_3 , which enables the conversion of sugar (glucose, C-6) in biomass to the platform chemical, 5-hydroxymethylfurfural (HMF). While homogeneous metal salts have been shown to catalyze sugar chemistries, direct experimental evidence in support of the catalytically active species remains elusive. Here, direct speciation measurements are coupled with kinetics to provide strong evidence for the active species of AlCl_3 in glucose conversion in water. A speciation

model is used to predict aluminum species, while simultaneously an experimental protocol is developed to quantify the various aluminum species. Linear scaling between the glucose conversion rate and the speciation measurements at sufficiently high temperatures indicates that a hydrolyzed Al(III) complex is the active species in glucose conversion. Knowledge of the active species will aid in future catalyst development to produce platform chemicals.

Next, the focus shifts from producing platform chemicals to using them as reagents to produce bio-lubricant base oils. Our strategy involves coupling 12-tricosanone, obtained from bioderived fatty acids, with furfural, a platform chemical obtained from hemicellulose, to form a highly branched bio-lubricant base oil. The viscous properties of the final product are comparable to commercial petroleum-derived Group III and Group IV base oils.

Another major challenge in biomass conversion is catalyst deactivation. Despite its importance, in situ characterization of materials is not always easy. In the last section of this thesis, the effects of mild hydrothermal treatment on siliceous nanomaterials are monitored in situ by infrared reflection absorption spectroscopy (IRRAS). Well-ordered, siliceous materials called zeosils are commonly employed as supports for metal catalysts in biomass upgrading, but require frequent regeneration to remove carbonaceous by-products from their pores. In the past, monitoring the effects of mild hydrothermal conditions, in situ, on siliceous materials has been challenging to observe by IRRAS, which often requires electrically conductive substrates. The emergence of 2-D siliceous nanomaterials deposited on metal single crystals overcomes this limitation. In this work, elevated temperatures and pressures of water increase the formation of silanol (SiOH) groups in the MFI nanosheets, but do not change the polymorphous bilayer silicate. The effects are fully reversible in the MFI nanosheets. Implications shown here may be useful when considering the effects of mild hydrothermal treatment experienced during regeneration on zeosils used in biomass upgrading.