Catalytic Methods for Production of Chemical Feedstock from Biomass-Derived Molecules

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Impact on California Agriculture: This project aims to develop catalytic methods for converting lignocellulosic biomass into value-added biobased chemicals. The development of such methods would allow for the utilization of agricultural waste/residue as raw material or feedstock in biobased industries. California being the nation's top agricultural state has contributed significantly to the growth of biobased industry in the US. The US biobased industry contributed ~$489 billion to the economy in 2021 with California (ranked #1) registering a 17% increase in its contribution between 2013-2017. In the biobased chemicals segment, California ranked #2 in the country and contributed $294 million to the economy while supporting ~1000 jobs in 2021.

Rationale/Introduction: Lignocellulosic biomass is highly oxygenated, and its valorization requires the development of processes that will decrease oxygen content. The cellulosic part of biomass has vicinal diol moieties in it which can be transformed to olefins using the deoxydehydration reaction. The lignin component of lignocellulose on the other hand is rich in aromatic residues like those obtained from the processing of aromatic petrochemicals. β-O-4 linkages account for ~30-50% of the linkages in lignin structure and various strategies are being explored for cleaving these bonds with the objective of producing value-added chemicals. This project aims to evaluate the potential of practical and readily accessible metal catalysts for studying the deoxydehydration of cellulosic biomass as well as the oxidative cleavage of lignin model compounds that feature the abundant β-O-4 linkage to develop structure-activity relationships (SARs). The development of such SARs will guide future catalyst development and help understand the mechanism of these oxidative cleavage reactions.

Experimental Approach: A variety of metal complexes featuring steric and electronic modulations of the supporting ligand were synthesized and chemically characterized. The ligands were used for synthesizing vanadium and molybdenum complexes which were subsequently used as catalysts. Catalytic studies were performed using 1-10 mol% of the metal catalyst and the model compound to study the deoxygenation and oxidative cleavage reactions. The catalytic reactions were characterized by ^{1}H NMR spectroscopy with reference to authentic samples. The yields of both products were quantified using 1,3,5-trimethoxybenzene and/or 1,3,5-tri(*tert*-butyl)benzene as an internal standard. Catalytic reactions were optimized by varying the reaction time and temperature and structure-activity relationships were established to inform development of superior catalysts.

Major Conclusion: The catalysts tested were found to be effective in catalyzing the oxidative cleavage and deoxydehydration reaction. Under the optimized conditions, high conversions (>80%) as well as high yields (>60%) of products were obtained. Both temperature and reaction time were observed to have a significant effect on the reaction outcome. Additionally, significant influence of the ligand backbone on catalytic activity of these metal complexes were uncovered; this helped establish structure-activity relationships.

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