

Catalyst Development and Reaction Engineering for Chemical Upgrading of Emerging Feedstocks

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Catalysis is a cornerstone of the chemical manufacturing industry enabling the production of fuels, polymers, and commodity chemicals. Consequently, the development of new catalytic technologies is critical for transitioning petrochemical based industries to more sustainable feedstocks. My research has focused on the design and synthesis of catalyst architectures and reaction engineering to address major challenges in the conversion of cellulosic biomass to ethylene glycol. I have also applied the principles of reaction and reactor engineering to study radical pathways for polypropylene deconstruction.

While cellulosic biomass has been studied extensively as a feedstock to produce ethylene glycol, all reported technologies suffer from harsh reaction conditions and challenges to polyol selectivity. A major contributor to this is the lack of hydrogenation selectivity for carbohydrate mixtures over supported Ni catalysts. Encapsulation of active Ni particles inside silicious zeolites can improve hydrogenation selectivity towards ethylene glycol and expand the operating regime (temperature, catalyst loadings). A novel synthetic approach for Ni encapsulation, based on Ni dissolution, was developed. Contrary to previously reported hydrothermal methods, size-selective hydrogenation catalysts can be synthesized from existing zeolites through impregnation, and post-synthetic treatments. Ex-situ physical characterization and reactivity tests were performed on the catalysts before implementation in the biomass system.

The conversion of cellulose (or glucose) to ethylene glycol involves 2 reactions, occurring in a one-pot tandem system. The retro-aldol reaction fragments glucose into glycolaldehyde which can undergo hydrogenation to ethylene glycol. However, the retro-aldol reaction is equilibrium limited and the subsequent hydrogenation is necessary to drive the equilibrium forward by consuming the glycolaldehyde. Mo and W based oxides are known to be good catalysts for the retro-aldol reaction with Mo exhibiting superior performance at lower temperatures. However, initial investigations of Mo based systems revealed poor performance in the tandem system. This is due to the deactivation of Mo under the reducing reaction conditions which is not observed with W, and for this reason W is chosen as the retro-aldol catalyst. The interaction of Mo with Ni is an interesting motif commonly observed in hydrogenation catalysis which inspired further characterization of the deactivated materials. These studies revealed the existence of specific Mo-Ni interactions exhibiting unique consequences for hydrotreatment processes. Nonetheless, for

biomass conversion, the primary focus is on W based retro-aldol catalysts and zeolite encapsulated Ni catalysts.

Combining both retro-aldol and hydrogenation systems requires careful engineering of reaction conditions. By adjusting catalyst loadings, high yields of ethylene glycol were achieved while maintaining size selectivity and preventing sugar hydrogenation. The consequence of encapsulation is evident in the selectivity but also in the ability to reduce reaction temperatures by ~ 50 °C from > 220 °C to 170 °C. Additionally, these systems exhibit a unique regime where ethylene glycol selectivity is independent of catalyst composition (i.e. Ni:W ratio). Consequently, this is the first example of high ethylene glycol yields from batch reactions of glucose at 170 °C. This performance was also extended to polysaccharide systems of starch and cellulose, with further tuning of reaction conditions for each substrate.

Another emerging field in the catalysis community is the deconstruction (and upcycling/upgrading) of polymer waste. The enormous demand for polymers results in the accumulation of long-lasting nonbiodegradable waste, a major component of which is polyolefins. Leveraging the thermodynamic implications of radical (de)polymerization can be an interesting avenue to produce high-value products such as alkenes from polypropylene waste streams. The strong entropic driving force for polymer deconstruction suggests that at elevated temperatures, initiated polypropylene chains should undergo chain scission reactions resulting in degraded polymers of lower molecular weight. To this end, a range of benzyl dimers are investigated as potential high-temperature initiators ($150 - 250$ °C). TGA-MS analyses of PP + initiator mixtures reveal the temperature ranges where initiation can occur. A modified Parr reactor with flow-thru capabilities was constructed and tested for this process. Proof-of-concept tests with PP and different initiators are being studied to understand the impact of reaction parameters using chromatographic techniques.

Upgrading of diverse feedstocks is an emerging topic in catalysis requiring more research. Fundamental understanding of the challenges in processing new feedstocks is necessary to devise innovative solutions. Leveraging the properties of catalyst architecture, reaction conditions, and reactor designs, can provide new opportunities to solve challenges arising from chemical equilibria, and complex reaction networks. The work discussed is an example of this approach to engineering solutions for challenges in catalysis.