Plastics have become ubiquitous in modern life, leading to global plastic production of 460 Mt in 2019, which is expected to triple by 2019. However, 99% of all plastic waste has been disposed of via dead-end methods (i.e., incineration, landfills, and the environment). Alternative strategies must be developed for managing plastics waste. Mechanical recycling is an established, cost-effective method for reutilizing thermoplastics. Polyolefins, such as polyethylene (PE) and polypropylene (PP), comprise 57% of plastics production and are unsuitable for mechanical recycling techniques. Chemical recycling is an attractive alternative to reutilizing polyolefins by converting them into valuable chemicals and fuels. Hydroconversion processes, including hydrocracking and hydrogenolysis, are promising for chemical recycling polyolefins to C\textsubscript{1}-C\textsubscript{30} alkanes that can be utilized in petroleum refineries. This thesis aims to develop high-performance catalysts for polyolefin hydroconversion, elucidate the reaction networks and mechanism, and identify catalyst descriptors to control the deconstruction catalysis.

The first focus of this dissertation is the development and fundamental understanding of polyolefin hydrocracking. We detail the discovery and optimization of mechanical catalyst blends containing platinum tungstated zirconia (PtWZr) with solid acid catalysts for LDPE hydrocracking to generate fuel range hydrocarbons. We reveal hydrocracking is initiated over PtWZr while the solid acid refines the product distribution. Deeper fundamental investigations over PtWZr alone expose several similarities and differences between polyolefin and model alkane hydrocracking.
Importantly, we unveil polymer chains strongly adsorb to the catalyst surface resulting in extensive polymer isomerization while restricting secondary cracking reactions. We identify the catalyst metal-acid balance as a descriptor for controlling the cracked product distribution and polymer isomerization. Lastly, we showcase nickel supported on BEA zeolite (Ni/BEA) catalysts as an earth-abundant metal-based alternative for polyolefin hydrocracking. We demonstrate Ni/BEA is ideal for naphtha generation, with productivities that surpass Pt- and other earth-abundant metal-based catalysts. We deduce Ni/BEA operates in a nonideal (metal-deficient) hydrocracking regime and reveal that LDPE chains can directly diffuse into the zeolite pores.

In the second part of this dissertation, we shift to the development and fundamental investigation of polyolefin hydrogenolysis. We demonstrate nickel supported on silica (Ni/SiO2) as the first earth-abundant metal-based hydrogenolysis catalyst active for producing diesel-range alkanes and waxes. We unveil strong polymer adsorption onto the catalyst surface is also prevalent in hydrogenolysis, leading to excessive methane formation. We elucidate the divergent hydrogenolysis mechanism and expose that LDPE hydrogenolysis is dominated by slow internal C-C bond scission followed by terminal cascades that generate methane. Next, we developed nickel aluminate (NiAl) catalysts to reduce methane formation. We demonstrate that decreasing the reduction temperature from 550 to 350 °C reduces methane selectivity to <5%. We establish the presence of metallic Ni nanoparticles and metal-Lewis acid pairs (MLAPs) and elucidate the active site formation mechanism. Reactivity correlations expose metallic Ni sites that primarily facilitate internal C-C bond scission, whereas MLAPs enhance the rate of terminal cascades that produce methane. Lastly, we extend polyolefin hydrogenolysis with Ni/SiO2 to polystyrene (PS) feedstocks to produce lubricant base oils with Group IV properties. Unlike polyolefin feedstocks, we demonstrate that methane production is absent in PS hydrogenolysis. Our process optimization establishes that PS hydrogenation and deconstruction have a strong H2 and temperature dependence. We reveal PS deconstruction occurs sequentially with significant aromatic ring hydrogenation preceding molecular weight reduction, as ring hydrogenation is 1000x faster than C-C bond cleavage.