Engineering Catalyst Active Sites For Plastics Waste Reutilization

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The accumulation of plastic waste presents severe global environmental and health challenges, driving an urgent need for sustainable waste management strategies to address the rising production of common polyolefins including Low-density polyethylene (LDPE) and *isotactic*-polypropylene (*i*-PP). Chemical upcycling *via* hydroconversion offers a promising route to transform polyolefin waste into valuable petrochemical feedstocks using existing refining infrastructure. However, developing efficient catalysts requires a deeper understanding of how catalyst structure, polymer transport, and feedstock composition dictate reaction pathways. This dissertation addresses these challenges by establishing fundamental structure-performance relationships to optimize and advance the design of polymer hydroconversion systems.

The first part of this work establishes the role of metal active-site structure in polyolefin hydrogenolysis. Using Ru/C as a model catalyst and comprehensive catalyst characterization, metal particle size was shown to control the relative rates of carbon–carbon bond cleavage and stereoisomerization during *i*-PP conversion. The balance between these concurrent pathways governs polymer deconstruction and product distributions, determining the selective formation of lower-molecular-weight waxes and lubricant-range hydrocarbons.

Next, a strategy to enhance the hydrocracking efficiency of earth-abundant metal (EAM) catalysts *via* metal site promotion is introduced. The incorporation of CeO_2 into Ni/BEA catalysts increased Ni dispersion, reducibility, hydrogenation functionality, and resistance to deactivation. These structural and electronic enhancements significantly improved LDPE conversion and enabled high productivity toward valuable naphtha-range (C_5-C_{12}) hydrocarbons, demonstrating that metal promoters can enable high-performance EAM hydrocracking catalysts as cost-effective alternatives to conventional noble metal systems.

While catalyst structure–performance relationships are well established for small-molecule hydrocarbons, the steric and diffusion limitations of polymer chains can fundamentally alter their interactions with catalytic active sites. As such, the interplay between catalyst architecture and polymer transport in governing hydrocracking performance was then investigated. By controlling the accessibility of metal and Brønsted acid sites in Ni/MFI catalysts while systematically varying polymer architecture, the relationship between active-site placement, polymer accessibility, and hydrocracking performance was established. Polyolefin molecular weight and branching density strongly influence pore diffusion and pore confinement, directly linking polymer architecture to active-site accessibility, hydrocracking activity and selectivity. These findings provide key engineering considerations for optimizing microporous catalysts for the hydroconversion of macromolecular feedstocks.

Finally, these mechanistic insights were extended to the hydrocracking of complex, multicomponent plastic mixtures containing polymer classes beyond polyolefins. Through systematically designed model mixtures, the individual effects of feedstock composition and contaminants on hydrocracking pathways, product distributions, and catalyst deactivation were isolated. The resulting understanding of feedstock–catalyst interactions enabled the development of process optimization and contaminant mitigation strategies that were successfully applied to post-consumer plastic waste, demonstrating the robustness of hydrocracking catalysts toward feedstock heterogeneity and advancing their practical implementation.

This dissertation establishes how catalyst active-site structure, catalyst architecture, and catalyst–feedstock interactions collectively control polymer hydroconversion pathways, providing a framework for developing practical and robust catalytic systems for plastic waste upcycling.