Development and Evaluation of Catalytic Systems for Polyolefin Deconstruction

by

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Abstract

Plastics have been widely used due to their extreme versatility and durability, but these attributes are responsible for limited degradation capability, leading to accumulation in the environment and landfills. Mechanical recycling alone is insufficient, as only 9% of plastic in the United States is recycled, and when implemented, the plastic is of lower quality and value. Consequently, alternative strategies for chemical deconstruction are required to address the growing plastic crisis. Recently, hydrogenolysis and hydrocracking have emerged as promising approaches for polyolefin deconstruction under relatively mild conditions, producing fuels and chemical feedstocks. In this work, we developed methods to accurately quantify polyolefin deconstruction products and designed new catalytic systems to enhance both activity and selectivity.

First, we identified the major sources of product loss and developed capture methods to improve quantification accuracy. Seven supplemental techniques were evaluated, targeting either increased vapor recovery or enhanced retention in the liquid phase. Among these approaches, a flow collection method using a continuous helium sweep and downstream gas sampling bag capture achieved the highest recovery (96 ± 9.2%). However, the efficacy of any method was strongly dependent on the product distribution, highlighting the need for method-specific workup strategies and demonstrating that no single protocol is universally optimal. This work provides general guidelines for selecting and implementing robust product capture techniques, enabling accurate yield and selectivity determinations in polyolefin hydrocracking systems.

Next, guided by process modeling results, we investigated the role of metal oxides in tuning hydrocracking selectivity toward light hydrocarbons. We demonstrated that extra-framework gallium oxide selectively enhances propane formation, increasing selectivity from 35 wt.%, achieved over ZSM-5, to nearly 60 wt.%, reaching a combined propane and butane selectivity of 85 wt.%, while maintaining solids conversion. Propane selectivity was highly sensitive to the spatial proximity of GaO_x to Brønsted acid sites, with surface oxidic species exhibiting the greatest enhancement. Vapor phase flow studies using a model compound revealed increased direct cracking to terminal products, indicating that GaO_x facilitates reactivation of intermediate species prior to desorption, favoring terminal product formation. The optimized catalyst was validated across diverse

polyolefin substrates and consistently yielded greater than >80 wt.% combined C_3-C_4 selectivity.

Finally, we examined how tailoring MFI zeolite morphology influences hydrocracking activity and selectivity toward valuable light olefins. Seven distinct MFI morphologies, including bulk commercial samples, nanoparticles, fins, nanoplates, nanosheets, nanosponges, and self-pillared architectures, were systematically evaluated to establish structure-property relationships and identify optimal catalyst designs. Among the materials evaluated, nanoscale morphologies such as nanoplates, nanosponges, and self-pillared nanosheets exhibited superior performance. Nanosponges increased hydrocracking activity 8x compared to bulk MFI, while nanoplates enhanced gaseous olefin selectivity from 5 wt.% over bulk samples to >30 wt.%. These findings highlight the critical role of morphology engineering in enabling more efficient and selective pathways for polyolefin upcycling.

Overall, this work demonstrates how polyolefin hydrocracking selectivity can be systematically tuned to target different classes of products. Continued feedback from process modeling and optimization of these systems can allow for the development of effective solutions for the catalytic deconstruction of polyolefin waste.

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