Catalyst and Process Design for the Hydroconversion of Multilayer and Crosslinked Plastics

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Global plastics production exceeds 400 million tons annually, yet recycling rates remain around 10%. Mechanical recycling is effective for single-stream thermoplastics but cannot handle complex waste streams such as polyethylene (PE) and poly(ethylene-*co*-vinyl alcohol) (EVOH) multilayer packaging and crosslinked polyethylene (XLPE) due to layer immiscibility and permanent crosslinks, respectively. Catalytic hydroconversion, including hydrogenolysis and hydrocracking, offers a promising route to convert these challenging waste plastics into fuels, lubricants, or chemical feedstocks. However, the effects of EVOH and crosslinked networks on hydroconversion activity, selectivity, and catalyst stability remain poorly understood. This dissertation combines catalyst synthesis and characterization, polymer characterization, and reactivity tests of model and realistic polymer feedstocks to elucidate the fundamental limitations of EVOH multilayer film and XLPE hydroconversion, and to develop improved catalysts and processes to overcome such limitations.

First, an investigation into EVOH and PE/EVOH hydrogenolysis over a Ru/ZrO_2 catalyst revealed that polyaromatic intermediates generated during EVOH thermal degradation severely inhibited catalyst activity. Elevated hydrogen pressures were shown to hydrogenate these aromatic intermediates, mitigating deactivation and improving hydrocarbon product yields.

Next, the hydrocracking of EVOH, PE/EVOH blends, and commercial multilayer films was investigated over a bifunctional Pt/BEA catalyst targeting liquefied petroleum gas (LPG) and naphtha-range hydrocarbons. Pt/BEA exhibited high tolerance toward EVOH-containing feeds.

Mechanistic studies revealed competing effects of EVOH-derived products: aromatic species promoted catalyst deactivation through condensation reactions, while water generated during EVOH dehydration enhanced hydrocracking activity through favorable interactions with zeolite Brønsted acid sites. Balancing these effects through catalyst and process design enabled efficient hydrocracking of realistic multilayer plastic packaging.

Then, building on these mechanistic insights, a tandem catalyst system was developed to further mitigate EVOH-induced limitations during PE/EVOH multilayer film hydroconversion. Lower loadings of Pt on BEA maximized metal-specific hydrocracking activity by positioning small, confined metal nanoparticles in proximity to Brønsted acid sites; however, catalyst stability remained limited by polyaromatic accumulation. To reduce deactivation, a complementary hydrogenation catalyst was incorporated to saturate aromatic intermediates. Systematic evaluation of support pore sizes identified Pt/MCM-41 as an effective hydrogenation catalyst due to its highly dispersed Pt nanoparticles. The resulting tandem system (Pt/BEA + Pt/MCM-41) achieved improved catalyst stability and LPG/naphtha selectivity compared to hydrocracking alone, highlighting its promise for hydroconversion of multilayer plastic packaging.

Finally, the hydroconversion of peroxide- and silane-crosslinked polyethylene thermosets was investigated. Crosslinked networks were found to impose mass transfer limitations, resulting in hydroconversion rates up to 20 times slower than those of the analogous thermoplastic PE. However, thermal blank reactions demonstrated rapid thermal decrosslinking at elevated temperatures. Leveraging this behavior, a two-step thermal-catalytic process was developed in which rapid non-catalytic decrosslinking precedes lower-temperature catalytic hydroconversion. Application of this strategy to commercial cable insulation demonstrated a promising pathway for the catalytic recycling of realistic XLPE waste streams.

Collectively, these findings establish fundamental relationships between polymer structure, polymer degradation pathways, and catalyst performance during hydroconversion of PE/EVOH multilayer films and XLPE, while providing practical strategies for converting these waste streams into valuable hydrocarbon products.