CATALYST INNOVATION FOR PROCESSING MOLECULAR CHEMICALS AND POLYOLEFIN PLASTICS

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The escalating global crisis of plastic waste, primarily driven by non-degradable polyolefins such as low-density polyethylene (LDPE), demands the urgent implementation of efficient upcycling technologies. The conventional mechanical and chemical recycling techniques are often limited by material degradation, low selectivity, and substantial energy requirements. This dissertation addresses these obstacles by implementing advanced catalytic hydroconversion techniques, including hydrogenolysis, for converting LDPE waste into valuable liquid fuel-range hydrocarbons with a C_5-C_{35} range. This work addresses macromolecular diffusion issues and low catalytic rate by using defect-engineered metal oxides and two-dimensional (2D) MXene-based materials to enhance yield and selectivity under moderate reaction conditions.

Chapter 2 presents an innovative oxy-hydrogen flame treatment process operated under vacuum to develop defect-engineered ceria (CeO_2) catalysts. The method successfully produced a high concentration of stable oxygen vacancies, leading to improved platinum (Pt) nanoparticle dispersion and enhanced metal-support interactions. The defective ceria improved the reaction efficiency and chemoselectivity of the hydrogenation of 3-nitrostyrene. This work has shown that oxygen vacancies serve as essential anchoring sites, modifying reaction pathways and enhancing catalyst performance by altering the electronic properties of the supported metal.

In Chapter 3, we extend defect-engineering principles to various metal oxide systems, comprising ZrO_2, Cr_2O_3, and Fe_2O_3, to assess the impact of support reducibility on catalytic performance. It was demonstrated that the formation of oxygen vacancies directly determines the catalytic performance of supports. When ruthenium (Ru) nanoparticles were deposited onto defective ceria treated by the flame process, the resulting material outperformed untreated ceria in converting LDPE into valuable liquid hydrocarbons. The creation of oxygen vacancies in reducible supports has proven to be a practical approach for directing reaction pathways in polymer deconstruction processes by minimizing the production of light gases.

Chapter 4 introduces 2D MXene ($Ti_3C_2T_x$) materials as catalyst supports to address the primary challenge of macromolecular diffusion. This work establishes the application of MXene-supported Ru catalysts for the hydrogenolysis of polymers. We synthesized silica-pillared MXene (P-MXene), resulting in a mesoporous structure with an expanded interlayer distance of 3.5 nm. This structural modification enabled superior mass transport, allowing large LDPE chains and their intermediates to reach catalytic sites more effectively. The Ru@P-MXene catalyst system proved to be highly active in converting LDPE into C_5-C_{35} liquid hydrocarbons at a fast rate and with minimal methane production compared to conventional catalysts. The 2D MXene layers confined Ru nanoparticles in a way that restricted their geometric shape, resulting in reduced methane production.

Chapter 5 introduces a vapor-phase pillarization (VPP) strategy for engineering hierarchical interlayer porosity in MXenes. Using silica as a model pillar precursor, the VPP method overcomes the excessive solvent use and multistep processing of conventional liquid-phase pillarization, introducing pillars with high precursor-usage efficiency through a simplified workflow. The resulting silica-pillared MXene exhibits significantly increased surface area and mesoporosity that can be readily tuned by the VPP synthesis conditions. When applied as a ruthenium (Ru) catalyst support for the hydrogenolysis of low-density polyethylene (LDPE), the mesoporous silica-pillared MXene enabled high Ru dispersion and catalytic activity, demonstrating the effectiveness of mesoporous two-dimensional MXene supports in overcoming mass-transport and active-site accessibility challenges in plastics upcycling.

Finally, Chapter 6 outlines promising research directions that build on the findings of this dissertation, including the further architectural tuning of pillared MXenes to generate tailored porosity for enhanced LDPE hydrogenolysis and the development of sustainable, hierarchically porous catalysts through continued porosity optimization.