

Advanced Catalytic Polyolefin and Polyamide Recycling: Toward a Circular Plastics Economy

Carter Edenfield, Qingheng Lai, Kristen B. Beckett, Liwei Ye, Yosi Kratish, Tobin J. Marks

Tobin J. Marks, Department of Chemistry and the Trienens Institute for Energy and Sustainability, Northwestern University, t-marks@northwestern.edu. 1-847-502-3687.

Primary Topic: Building a Sustainable Circular Economy for Materials & Products

Secondary Topic: Design for Remanufacturing & Recycling for the Circular Economy

Abstract

Plastics are integral to modern society, with global production rising exponentially from 200 million tons (MT) annually in 2002 to 395 MT in 2018, and projected to triple by 2050. This increase has significant environmental and resource implications, including the accumulation of non-degradable plastic waste and the depletion of fossil feedstocks. Polyolefins, which constitute a major portion of single-use plastics, present a recycling challenge due to their chemically inert saturated hydrocarbon structures. Similarly, polyamide engineering plastics such as Nylon-6 resist deconstruction due to their robust mechanical and environmental resilience. Addressing these issues is critical for advancing a circular plastics economy, and is the focus of this presentation.

To deal with polyolefin waste streams, a series of highly electrophilic groups IV and V metal hydrides ($M = \text{Ti, Zr, Hf, Ta}$) was created by adsorbing the corresponding MNP_4 molecules ($M = \text{Ti, Zr, Hf}$) or $\text{Np}_3\text{Ta}=\text{CH}^t\text{Bu}$ on highly Brønsted acidic sulfated alumina (AIS), yielding loosely coordinated electrophilic single-site catalytic centers bound to AIS (AIS/MNP_2 , $\text{Np} = \text{neopentyl}$). These surface species were in-depth characterized by a battery of modern chemical, spectroscopic, and theoretical techniques—we know exactly what they look like. These molecule-derived adsorbates readily react with H_2 to yield AIS/M(alkyl)H catalysts, which are highly active for the solventless H_2 C-C cleavage of diverse commercial additive-containing polyethylenes, α -olefin-ethylene copolymers, isotactic polypropylene, and post-consumer polyolefins including high-density polyethylenes, yielding medium and small linear and branched hydrocarbons at turnover frequencies approaching $36,300 \text{ h}^{-1}$ at $200 \text{ }^\circ\text{C}/17 \text{ atm H}_2$! For identical polyolefin reaction conditions, turnover frequencies scale as $M = \text{Zr} > \text{Hf} \approx \text{Ta} > \text{Ti}$, while catalyst thermal stability scales as $M = \text{Ta} > \text{Hf} \approx \text{Zr} > \text{Ti}$. These trends parallel the theoretical analyses and gaseous propane deconstruction in a flow system where turnover numbers approach 100,000.

For polyamide waste streams, we designed non-toxic, earth-abundant catalysts that solventlessly depolymerize Nylon-6 to ϵ -caprolactam with unparalleled efficiency. These catalysts achieve turnover frequencies approaching $810 \text{ mol}(\epsilon\text{-caprolactam}) \cdot \text{mol}(\text{Cat.})^{-1} \cdot \text{h}^{-1}$ at $240 \text{ }^\circ\text{C}$, yielding $>99\%$ product purity. Catalyst loadings approach $0.04 \text{ mol}\%$ at $220 \text{ }^\circ\text{C}$ —the mildest conditions reported to date. This method is adaptable to continuous processes to produce high-quality recycled Nylon-6 through catalytic repolymerization. Mechanistic insights provided by combined experimental and DFT analyses reveal pathways involving intra-chain "unzipping," and inter-chain "hopping." Robust organolanthanide catalysts enable the highly selective depolymerization of diverse Nylon-6 articles, including fishing nets, carpets, medical gloves, and diverse plastics mixtures.