ADVANCED CATALYTIC POLYOLEFIN AND POLYAMIDE RECYCLING: TOWARD A CIRCULAR PLASTICS ECONOMY

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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. In this article we address two of these issues critical for advancing a circular plastics economy: **1)** Polyolefins and **2**) Nylons. **1)** For polyolefin waste streams, a series of highly electrophilic groups IV and V metal hydrides (M = Ti, Zr, Hf, Ta) was created by adsorbing the corresponding MNp_4 molecules (M = Ti, Zr, Hf) or $Np_3Ta{=}CH^tBu$ on highly Brønsted acidic sulfated alumina (AlS), yielding loosely coordinated electrophilic single-site catalytic centers bound to AlS (AlS/MNp_2, Np = neopentyl). The structures of these surface species are in-depth characterized by a battery of chemical, spectroscopic, and theoretical techniques. They react with H_2 to yield AlS/M(alkyl)H catalysts, which are highly active for solventless C-C cleavage of diverse commercial additive-containing polyolefins, yielding medium and small linear and branched hydrocarbons at turnover frequencies approaching 36,300 $mol(CH_2\ units)\cdot mol(Zr)^{-1}\cdot h^{-1}$ at 200 °C/17 atm H_2. These trends parallel DFT analysis and propane catalytic results in a flow system where turnover numbers approach 100,000. **2)** For polyamide waste streams, we created non-toxic, earth-abundant catalysts that solventlessly depolymerize Nylon-6 to ε-caprolactam with unparalleled efficiency. These catalysts achieve turnover frequencies approaching 810 $mol(\varepsilon\text{-caprolactam})\cdot mol(Cat.)^{-1}\cdot h^{-1}$ at 240 °C, yielding >99% product purity. Catalyst loadings approach 0.04 mol% at 220 °C—the mildest conditions reported to date. This method is adaptable to continuous processes to produce high-quality Nylon-6 through repolymerization. Mechanistic insights provided by experimental and DFT analyses reveal pathways involving intra-chain "unzipping," and inter-chain "hopping." Robust organolanthanide catalysts enable the depolymerization of diverse Nylon-6 articles, including fishing nets, carpets, and diverse plastics mixtures.

Introduction and Motivation

Our modern society is heavily dependent on plastics-based materials, as evident by the steady growth in their production. In 2002, 200 MT of plastic was produced annually worldwide; in 2018, this output doubled (395 MT), and by 2050 it is expected to triple (~1.2 BT).[1] This is occurring despite the negative worldwide environmental and health consequences associated with unimaginable amounts of non-degradable waste plastic accumulation and the significant depletion of virgin fossil feedstocks.

Commodity polyolefins (POs), derived from simple or substituted alkenes, constitute the majority (> 2/3) of modern plastics. Their large-scale production and low cost have driven widespread short-term usage, significantly increasing waste generation. Globally, ~19% of PO waste is incinerated, a process that recovers only a small fraction of the energy expended during production, primarily as heat, but also generating toxic combustion byproducts and greenhouse gases such as CO_2, rendering it unsuitable as a "green" solution.[2] Additionally, the extreme durability of POs—owing to their content of robust, chemically inert C–C and C–H bonds—makes landfilling the predominant disposal method, an unsustainable option. For the same reasons, POs cannot be efficiently depolymerized back to their monomeric forms, unlike heteroatom-containing polymers such as polyethylene terephthalate (PET), which are more amenable to chemical recycling. As an alternative, upcycling—defined as the conversion of waste into products with greater value than the original material—offers a promising approach for managing polyolefin waste.

Engineering plastics such as polyamides are one class of commonly used plastics for applications in which the material/product must withstand harsh mechanical and environmental conditions. Nylon-6 is a thermoplastic polyamide produced industrially by water-assisted ring-opening polymerization (ROP) of ε-caprolactam on a 10^6 ton annual scale, with the market size expected to reach $21.5 billion in 2026. It is the material of choice in many

applications, such as the automotive, packaging, infrastructure, textile, and fishing gear industries, due to its physical and chemical properties, including elasticity, high tensile strength, and high chemical and abrasion resistance. However, these same properties also impede biodegradation,[3] leading to persistence and accumulation in landfills and the environment. Nylon abandoned fishing nets comprise ca.10% of ocean plastic and require ~600 years to degrade.[4] Furthermore, Nylon production has a high carbon footprint[5] associated with significant greenhouse gas emissions[6].

Review of Related Work

Many approaches to dealing with plastic waste have been explored, but all have significant limitations. Mechanical recycling is possible for most plastics but is not effective long-term and seldom cost-effective since the post-recycled product has generally inferior mechanical and optical properties, and mixed plastic waste separation is costly.[2] Energy recovery by combustion is also commonly employed to deal with plastics pollution, but is marginally economical, produces greenhouse gases, and is considered a last resort in waste management. For Nylon, combustion is particularly problematic, as it releases toxic byproducts such as HCN, CO, CO_2, and NH_3.[7] The lack of economical and/or environmentally compatible methods has motivated great interest in alternative plastics recycling approaches. Chemical upcycling of waste polymers is a promising approach that has received growing attention. One homogeneous approach uses an Ir catalyst and metathesis with an alkane to lower the polyolefin molecular mass.[8] The conversion of polyethylene to long-chain alkyl aromatics was also demonstrated using a Pt catalyst supported on γ-alumina.[9] Recently, catalytic polyolefin hydrogenolysis has attracted greater attention since it employs H_2 as a cost-effective deconstruction agent, and the overall process is thermodynamically favorable. Currently, the most common approaches involve using heterogeneous precious-metal catalysts such as Ru and Pt to transform POs into wax-range and lighter hydrocarbons.[10-16] Such processes typically employ high temperatures/pressures and extended reaction times. Earth-abundant metal polyolefin hydrogenolysis catalysts have received relatively less attention compared to precious metal catalysts, with very limited examples employing Zr and Ni metals supported on silica,[17-20] which mediate relatively slow hydrogenolysis, and require high temperatures (250-300 °C) and far higher catalyst loadings. Alternative catalytic systems with earth-abundant metals and having better defined structural characteristics are crucial to address the growing demand for practical PO upcycling.

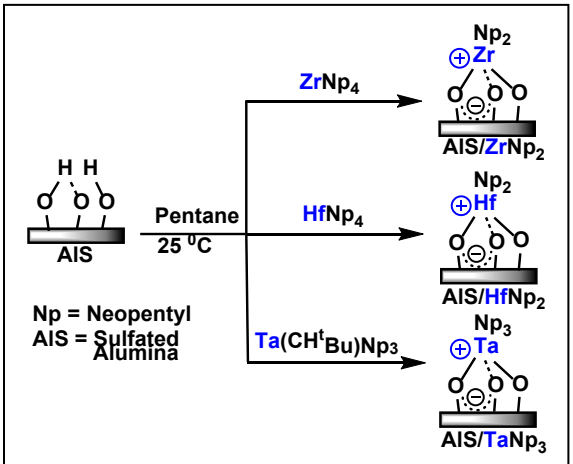
Chemical recycling[21, 22] is an alternative approach, mainly used for polyesters to recover the starting monomers, and would likewise be attractive for Nylon-6. If efficient, chemical recycling of Nylon-6 would provide an attractive route to regenerate caprolactam monomer, which is currently produced from fossil feedstocks and contributes significantly to greenhouse gas emissions. Conventional catalytic depolymerization processes require elevated temperatures and high steam pressures. Kamimura and Yamamoto reported Nylon-6 depolymerization in ionic liquids to produce e-caprolactam in 55-85% yields with 5 wt% 4-dimethylaminopyridine (DMAP) as catalyst. [23-25] Note that this process requires temperatures above 300 °C, ionic liquids that decompose at these temperatures, and DMAP, which is toxic. In 2020, Milstein et al. reported a novel homogenous Ru-catalyzed deconstruction of Nylons to linear amino alcohols via hydrogenation at 70 bar H_2 pressures and 48 h reaction times.[26] For Nylon-6, 24-48 % yields of 6-amino-1-hexanol are obtained.[26] Thus, inventing new, more selective, atom-efficient, cleaner, more sustainable catalytic processes to address polyamide pollution is critical yet underexplored.

Technology Approach

Polyolefin hydrogenolysis.

The d^0 transition metal species chemisorbed on solid supports such as silica or alumina are known to cleave C-C bonds in alkanes and POs.[27, 28] This

class of catalysts generally offers greater thermal stability than typical homogeneous catalysts and more uniform active sites than conventional heterogeneous catalysts, which enhances structural and mechanistic understanding. However, formally neutrally charged surface d^0 transition metal centers exhibit lower C-C cleavage activity than precious metal-based catalysts. Given that POs consist exclusively of non-polar C–H and C–C bonds, the Marks group conceived more active



Scheme 1. *Synthesis of early transition metal cationic single-site hydrogenolysis catalysts.*

hydrogenolysis catalysts by increasing the electrophilicity of early transition metals using "super acidic" sulfated alumina supports (Scheme 1). This report highlights our recent advances in Group IV and V catalyst-mediated C-C cleavage. Specifically, the initial focus was on well-defined electrophilic/cationic organozirconium systems, which exhibit hydrogenolysis activity 100x higher than that of formally neutral Zr catalysts.[29] Subsequent systematic investigations of Group IV catalysts were conducted to delineate intrinsic activity and stability trends within the group.[30] By introducing more efficient stirring to address mass transfer limitations, the hydrogenolysis activity was further enhanced by an additional order 10x. Meanwhile, an organo-tantalum catalyst with higher thermal stability was developed to explore different C-C cleavage pathways.[31] The active sites of these highly active hydrogenolysis catalysts were rigorously characterized EXAFS, XANES, ICP, DRIFTS, elemental analysis, SSNMR, and DFT computation. To better understand the intrinsic properties of these highly active hydrogenolysis catalysts, a detailed kinetic/mechanistic study of propane hydrogenolysis catalyzed by the Zr and Hf catalysts was achieved using an Altamira BenchCAT™ 4000R HP plug-flow reactor, revealing turnover numbers approaching 10^5. [32]

Nylon 6 depolymerization

Lanthanide catalysts were shown in the past to efficiently activate amide bonds in deoxygenative reductions of amides with pinacolborane[33]. Therefore, these complexes were chosen as a starting point to investigate the catalytic chemical recycling of polyamides such as Nylon6. In contrast to noble metals, lanthanides are attractive due to their earth-abundance (comparable to Ni, Co, Cu), low toxicity, low cost (La is >2000x cheaper/mole than Rh), relatively stable supply, and less explored catalytic properties. Regarding abundance, recent reports forecast near-term stabilization of price and supply. Governmental initiatives, WTO rulings against monopolistic practices and trade violations, and reopening closed and/or opening new mines caused a worldwide fall in lanthanide prices to pre-2011-crisis levels, guaranteeing a continuous supply.

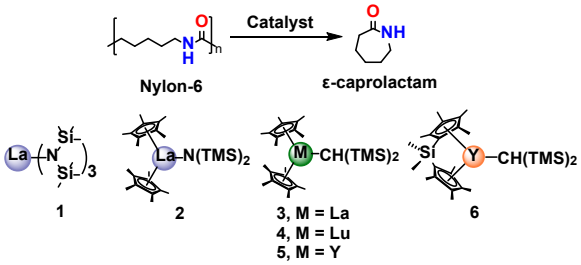


Figure 1. *The Nylon-6 depolymerization process with catalyst structures explored in these studies.*

Here we summarize our recent advances in the very effective lanthanide-catalyzed, solvent-free depolymerization of Nylon-6 (Figure 1). We first introduce our initial discovery of commercially available tris[bis(trimethylsilyl)amido] lanthanide complexes (**Ln^{NTMS}**), which efficiently catalyze the conversion of Nylon-6 to ε-caprolactam. We then discuss the development of second-generation lanthanide catalysts, which incorporate carefully designed achiral ligands to enhance stability and activity, focusing on post-consumer Nylon-6-containing products and catalyst recyclability. Both efforts rely on kinetic and mechanistic studies using experimental and computational techniques.

Discussion

Cationic Organo-Zr Catalyzed PO Hydrogenolysis. Sulfated alumina (AlS), a well-known highly Brønsted acidic sulfated metal oxide, yields molecular adsorbates with exceptional catalytic activities in various hydrocarbon transformations.[34] $ZrNp_4$ chemisorption on sulfated alumina was reported by Mason et al. to mediate rapid and efficient hydrogenolysis of polyethylene and other polyolefins under mild conditions using a glass vessel (Figure 2. 150 °C, 2 atm H_2). With activity reaching over 4000 mol(CH_2 units)·mol(Zr)$^{-1}$·h^{-1} at 200 °C/2 atm H_2 pressure. The mechanistic analysis reveals a β-alkyl transfer as the turnover-limiting step rather than conventional σ-bond metathesis, offering new theoretical insights and practical applications in PO degradation.

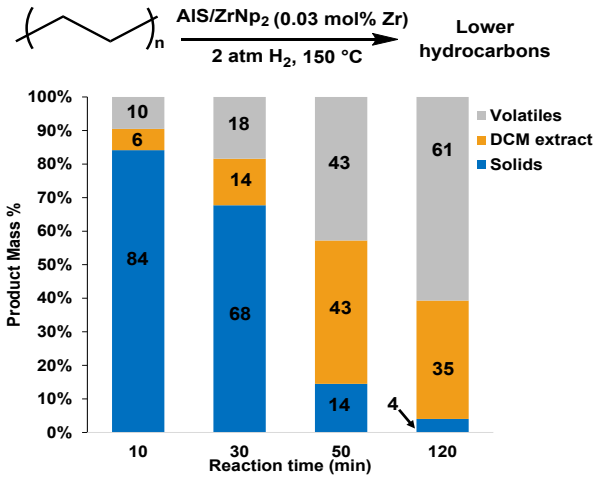


Figure 2. *Temporal product distributions for AlS/$ZrNp_2$-catalyzed PE hydrogenolysis (150 °C, 2.0 atm H_2, 0.03 mol% Zr).*

PO Hydrogenolysis Catalyzed by Organo Group IV Catalysts: Edenfield et al. expanded research into a series of Group IV metal hydrides, including Ti, Zr, and Hf, systematically probing their hydrogenolysis activity and stability. Notably, turnover frequencies scale approximately as Zr > Hf > Ti, while the thermal stability scales approximately as Hf ≈ Zr > Ti. These trends qualitatively align with DFT analysis, providing a deeper understanding of electronic factors influencing catalyst performance. Additionally, the study investigates the correlations between catalytic activity and stirring efficiency. Utilizing a Parr reactor equipped with magnetically coupled stirring, achieving record-breaking turnover frequencies as high as 36,300 mol(CH_2 units)·mol(Zr)$^{-1}$·h^{-1} at 200 °C/17 atm H_2. This advance underscores the importance of reactor design in optimizing catalyst performance and provides insights into overcoming operational challenges in hydrogenolysis processes.

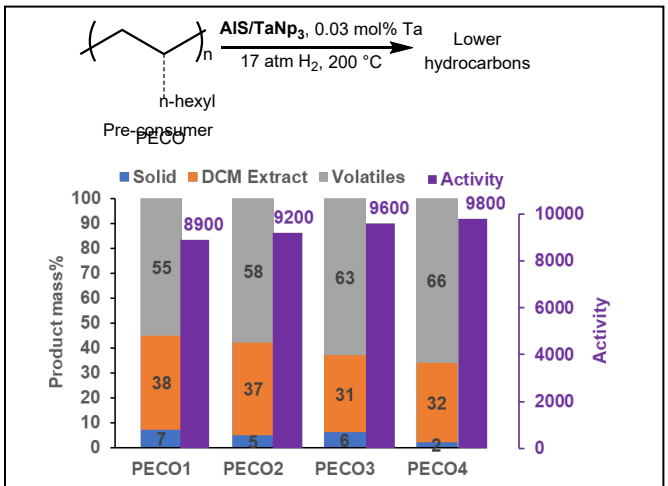


Figure 3. *Product distribution and activity of commercial PECOs hydrogenolysis catalyzed by AlS/TaNp$_3$ in a Parr reactor (data are the average of two hydrogenolysis reactions).*

Cationic organo-Ta catalyzed PO Hydrogenolysis: Unlike group IV adsorbates, supported organo-Ta species are known to cleave C-C bonds under various pathways, such as α-alkyl transfer (carbene extrusion),[35] alkane metathesis, and β-hydride elimination followed by olefin metathesis.[36] Tantalum alkylidenes also exhibit qualitative advantages in thermal robustness compared to $ZrNp_4$ adsorbates. Lai et al. explore the effectiveness of Ta adsorbates for polyolefin hydrogenolysis, where the catalyst demonstrates exceptional activity, achieving rates as high as 9800 mol(CH_2 units)·mol(Ta)$^{-1}$·h^{-1} (Figure 3) and displays greater thermal stability compared to its Group IV counterparts. The potential for alternative C-C cleavage pathways, such as α-alkyl transfer, is further supported by ethane hydrogenolysis experiments. *i.e.,* unlike the group (IV) catalysts, the Ta catalyst is active in ethane hydrogenolysis, highlighting the catalyst's versatile reactivity. Furthermore, the groups (IV) and (V) AlS-supported catalysts demonstrate applicability to real-world post-consumer POs, such as milk jugs, bottle caps, and sandwich bags. Despite significant mass transfer challenges, these catalysts maintain comparably high activities, highlighting the promising potential of this catalytic concept for practical polyolefin upcycling.

Motivated by the remarkable catalytic outcomes described above, a more detailed mechanistic picture would significantly enhance polyolefin hydrogenolysis catalyst discovery and optimization. However, the mass transfer effects with viscous polymer melt having conversion-dependent and homogeneity-dependent Mw and rheology, competing hydrogenolysis reaction pathways, minor materials impurities, possible catalyst thermal decomposition, and volatile product condensation in the cooler reactor headspace introduce significant complexities in reaction pathway characterization and kinetic quantification. To circumvent the complexities, Mason et al. undertook a vapor phase kinetic/mechanistic study of alkane hydrogenolysis catalyzed by the above AlS/MNp_2 catalysts (M = Zr, Hf) using propane as a model alkane to refine the understanding of the catalytic processes at a fundamental level. Combining with DFT calculations, the kinetic data reveals that both β-alkyl scission and M–C bond hydrogenolysis contribute to the overall reaction rate having almost equivalent energetic barriers in group IV catalysts mediated C-C hydrogenolysis (Figure 4).

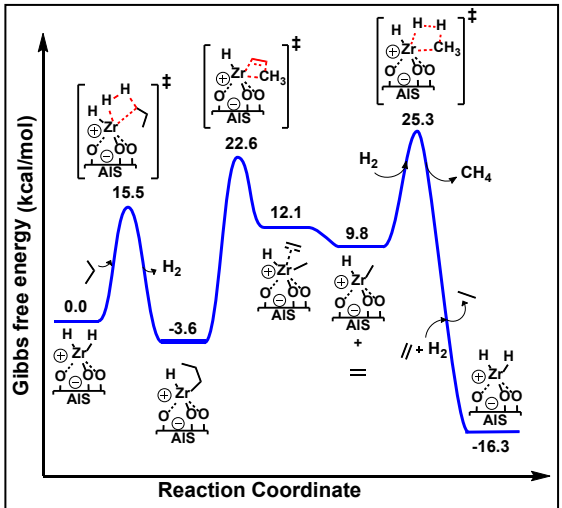


Figure 4. *DFT computed reaction coordinates for AlS/ZrH_2- catalyzed propane hydrogenolysis based on C–C scission via intramolecular ß-alkyl transfer.*

Nylon-6 Depolymerization.

Generation 1 Catalysts: Initial studies demonstrated the efficient depolymerization of Nylon-6 into ε-caprolactam, its industrial monomer, using commercially available lanthanide trisamido $\mathbf{Ln^{NTMS}}$ catalysts under mild, solvent-free conditions.[37] Heating Nylon-6 with 5 mol% $\mathbf{La^{NTMS}}$ at 240°C under a static vacuum (10^{-3} Torr) achieves 90% yield of ε-caprolactam in 4 hours (Table 1, entry 1), [37] with the product subliming and crystallizing on the reactor walls.. To optimize reaction conditions and explore the reaction mechanism, a screening of ligand and metal effects was performed. Replacing the -N(TMS)$_2$ ligands with weaker bases such as -N(Tf)$_2$ or -OTf significantly reduced ε-caprolactam yields to 7% and 5%, respectively, highlighting the critical role of highly basic ligands in facilitating initial amide N-H deprotonation during catalyst-polymer coordination. Catalytic activity correlates with the Ln center ionic radius, with $\mathbf{La^{NTMS}}$ achieving the highest yield (83% in 2 hours). Smaller lanthanide homologs like Lu^{NTMS} (45%) and Sc^{NTMS} (39%) show lower activity due to steric constraints in the transition state, as verified by DFT calculations.

A kinetic study with $\mathbf{La^{NTMS}}$ revealed a linear relationship between ε-caprolactam yield and time, indicating zero-order kinetics in Nylon-6. This suggests that the catalyst resting state involves the polyamide bound to the La center via Nylon amide/bis(trimethylsilyl)amine exchange. The catalyst likely binds at the Nylon-6 terminal amide, stabilized by the free amine at the chain end. Gel permeation chromatography (GPC) reveals a gradual molecular mass decrease with constant dispersity, consistent with a backbiting mechanism where ε-caprolactam is sequentially excised from the polymer-activated chain end in each catalytic cycle. The relationship of depolymerization yield to catalyst concentration provides informative mechanistic insights. Below 1.5 mol% $\mathbf{La^{NTMS}}$, no activity is observed due to catalyst deactivation by the reactive nylon carboxylic acid chain ends. Treating Nylon-6 with KOH to neutralize acidic ends restores catalytic efficiency, achieving rapid and nearly complete depolymerization with just 1 mol% $\mathbf{La^{NTMS}}$ loading (Table 1, entry 2). The reaction rate increases linearly from 1.5 to 3 mol%, indicating first-order dependence on catalyst concentration. Above 3 mol%, the reaction shows saturation, with minimal rate improvement, suggesting a turnover-limiting step. Using thermogravimetric analysis (TGA), the estimated activation energy was determined to be 31.4 ± 3.1 kcal/mol.

Next, the effectiveness of $\mathbf{La^{NTMS}}$ in depolymerizing Nylon-6 in the presence of other polymers was tested, as post-consumer waste often contains mixed plastics and additives. In 1:1 mixtures of Nylon-6 with

Table 1. Catalytic depolymerization of powder and post-consumer Nylon-6

Entry	Nylon-6 Plastic	Catalyst	Catalyst Loading (mol%)	Time (h)	Temperature (°C)	Yield of ε-caprolactam (%)
1	Powder†	**1**	5.0	4.0	240	90
2	Powder	**1**	1.0	1.0	240	94
3	Powder	**2**	1.0	6.0	240	17
4	Powder	**3**	1.0	1.0	240	99
5	Powder	**3**	0.2	1.0	240	93
6	Powder	**3**	0.2	4.0	220	95
7	Powder	**4**	1.0	1.0	240	24
8	Powder	**5**	1.0	1.0	240	2.2
9	Powder	**6**	1.0	1.0	240	94
10	Medical gloves†	**6**	1.0	12	240	89
11	Fishing net† + bottle cap†	**6**	1.0	12	240	95
12	Fishing net†	**6**	1.0	6.0	240	94

† Not KOH-treated

common polymers PE, PP, and PET, PE, and PP had no negative effect on catalytic activity, yielding 93% and 91% ε-caprolactam, respectively. PET admixture slightly reduces activity, likely due to the carboxylic acid and hydroxyl end groups. The catalyst also successfully depolymerizes post-consumer Nylon-6 yarn, yielding 78% ε-caprolactam. However, slower reaction times were observed due to heat and mass transfer limitations, such as slow melting and minimal stirring.

The $\mathbf{Ln^{NTMS}}$ system offers distinct advantages for Nylon-6 chemical recycling, including high yields of ε-caprolactam using an earth-abundant metal catalyst under mild, solventless conditions. However, challenges exist in achieving consistent yields from consumer-grade Nylon-6 products, as the partial volatility of the catalyst requires thorough mixing during polymer melting, often achieved only with cryogenic milling, yielding moderate results for

Nylon-6 yarn. The simple tris-amido ligation also limits mechanistic tuning and increases the risk of catalyst immobilization via cross-linking. These issues led to exploring more tunable, less volatile metallocene catalysts for a mechanism-focused design approach.

Generation 2 Lanthanide & Yttrium Metallocene Catalysts: In a second study, to enhance depolymerization efficiency, Ln^{3+} catalysts were modified with stable π-ligands like bis(pentamethylcyclopentadienyl) (Cp^*_2) to shield the metal center while maintaining substrate access (Figure 1B).[38] Thus, $Cp^*_2LaN(TMS)_2$ (**2**) was tested for Nylon-6 depolymerization but showed reduced activity (Table 1, entry 3), likely due to low La-NTMS basicity and was not pursued further.[38] However metallocene catalyst $Cp^*_2LaCH(TMS)_2$ (**3**) demonstrates exceptional efficiency in Nylon-6 depolymerization, achieving a 99% yield in 1 hour at 240°C with 1 mol% loading (Table 1, entry 4). Even at a reduced 0.2 mol% loading, it delivers a 93% yield (Table 1, entry 5), vastly outperforming La^{NTMS} (**1**) (5.6% yield under identical conditions). This highlights the significant impact of σ-bonded ligands, as verified by DFT analysis. Another consideration was the depolymerization temperature, as typical Nylon-6 recycling processes require high temperatures (>300°C), leading to thermal decomposition. Catalyst **3** operates effectively at 220°C, the lowest temperature to date for Nylon-6 depolymerization and just above the melting point, achieving up to 95% yield with 0.2 mol% loading (Table 1, entry 6). In addition, size effects of Ln^{3+} ions showed that La-based catalyst **3** outperformed smaller Lu^{3+} (**4**) and Y^{3+} (**5**) analogs.[39] Catalyst **3** is 240x more active than the previous $Ln(NTMS_2)_3$ catalyst **1**, demonstrating the superior performance of metallocene ligation (Figure 5).

Yttrium metallocenes, with their smaller ionic radius, show high thermal stability due to reduced thermolytic reactivity.[40-42] To enhance catalytic activity, further ligand modifications were explored beyond the less active Y^{NTMS} and the promising $Cp^*_2YCH(TMS)_2$ catalysts. Ansa-lanthanocenes (Figure 1B) with chelating ligands and larger bite angles significantly increase catalytic activity, achieving 10–100x higher turnover frequencies than Cp^*_2LaR analogs. Chelation also enhances thermal stability. The $Me_2SiCp''_2YCH(TMS)_2$ (**6**) catalyst increases Nylon-6 depolymerization yields from 2% to 94%, with over 99% conversion in extended reaction times, illustrating the impact of ligand engineering. Furthermore, catalyst **6** efficiently depolymerizes diverse waste plastics, including medical gloves (Table 1, entry 10) and mixed plastics with Nylon-6 and polyolefins such as PE. Thus, a 1:1 mixture of Nylon-6 fishing nets and PE bottle caps affords 95% ε-caprolactam yield while leaving PE unchanged, showing compatibility with mixed waste processing (Table 1, entry 11). Unlike homoleptic catalyst **1**, which requires pretreat-ment, catalyst **6** depolymer-izes various consumer Nylon-6 products directly, performing well even in the presence of dyes and additives. To demonstrate full Nylon circularity, ε-caprolactam recovered from depolymerized end-of-life fishing nets (Table 1, entry 12) was successfully re-polymerized using anionic initiation with N-acetylcaprolactam at 140°C. NMR, MALDI-TOF MS, and GPC analyses confirmed the purity and identity of the recycled Nylon-6, which was obtained in 99.3% yield with a higher M_n = 43.6 kg/mol, than the original waste (M_n = 21.7 kg/mol). This process highlights the effectiveness of chemical recycling/upcycling, enabling high-quality monomer recovery and promoting sustainable Nylon reuse.

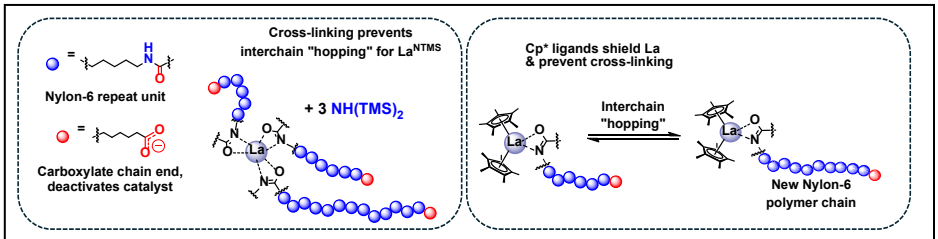


***Figure 5**. Depolymerization pathways for homoleptic catalyst **1** (left) and metallocene catalyst **3** (right).*

Catalyst **3** was scrutinized to understand the metallocene-mediated depolymerization mechanism by comparing it with homoleptic catalyst 1, both containing La^{3+} centers. For virgin Nylon-6 with a degree of polymerization (DP) of ~130 (M_n = 14,800 g/mol), a 1 mol% catalyst loading provides a polymer chain-to-La^{3+} ratio of 1:1.3, enabling stepwise caprolactam excision without requiring interchain hopping. At this loading, catalysts **1** and **3** yield 69% and 91% ε-caprolactam, respectively. However, interchain hopping is necessary at 0.2 mol% loading (5:1 polymer chain-to-La^{3+} ratio). Catalyst **1** shows only a 5.6% yield, while catalyst **3** maintains high efficiency, demonstrating its superior performance at lower concentrations. Furthermore, in our initial study, it was noted that catalyst **1** releases 2.5 equivalents of TMS_2NH ligands at the onset of the reaction, suggesting each ligand is replaced by coordinated Nylon-6 chains. This cross-linking may explain the inability of catalyst **1** to interchain "hop" after consuming a single Nylon chain. This likely leads to catalyst deactivation by the Nylon chain-end carboxylates. In contrast, catalyst **3**, with its non-dissociable Cp^*_2 ligands, sterically shields the La center, preventing cross-linking and enabling effective interchain hopping, especially at low catalyst loadings. This behavior is supported by DFT analysis.

In situ ^{1}H NMR revealed gradual protonolysis of the La-CH(TMS)$_2$ bond, producing 95% of the expected CH$_2$(TMS)$_2$ product, with minimal Cp*H detected, confirming the stability of the Ln-Cp* ligation. The proposed Nylon-6 depolymerization mechanism involves interchain "unzipping" by catalyst **3**. Unlike catalyst **1**, catalyst **3** reduces deactivation at the chain ends via efficient interchain hopping, enabling high-yield depolymerization at low catalyst loadings. Catalyst deactivation at polymer chain ends was studied, hypothesizing that interaction with carboxylate groups forms an inert carboxylate complex, reducing activity. Adding a second 100 mg of Nylon after initial depolymerization resulted in a reduced yield (30%). However, adding 200 mg of Nylon at once achieved a 94% yield, indicating that higher polymer availability minimizes catalyst deactivation by reducing interactions with chain-end carboxylates.

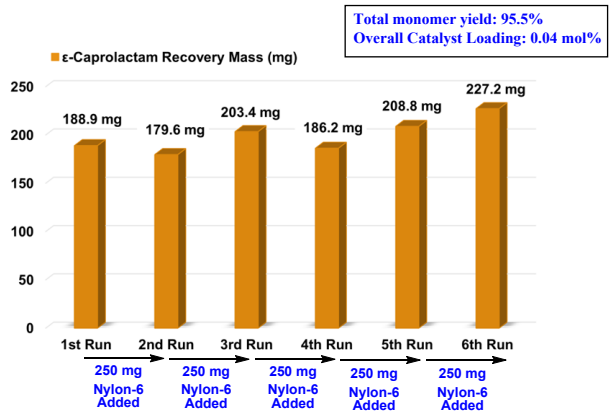


***Figure 6**. Nylon-6 continuous process simulation using the Cp*$_2$LaCH(TMS)$_2$ catalyst. Conditions: 240°C; 1.5 h for run 1, 2 h for runs 2-5, overnight for run 6.*

The kinetic profile of **3**-mediated depolymerization reveals a linear increase in ε-caprolactam yield over the first 30 minutes, reaching 81% before plateauing. This plateau suggests the catalyst has reached carboxylate chain ends and has become deactivated. When the reaction was paused at 30 minutes, and fresh Nylon-6 was added, the yield grew linearly, supporting our hypothesis that the catalyst can "hop" from shorter to longer chains, enabling sustained depolymerization even at lower catalyst loadings. The study demonstrates efficient Nylon-6 depolymerization using ultra-low catalyst loadings in a simulated continuous process (Figure 6). Fresh Nylon-6 was added between cycles while reusing catalyst **3**, achieving consistent ε-caprolactam yields and retaining catalyst activity. Without adding fresh Nylon-6, the final run completed depolymerization with an overall 95.5% yield at just 0.04 mol% catalyst loading. This scalable, sustainable method offers a cost-effective approach to Nylon-6 recycling.

This study demonstrates efficient, solventless Nylon-6 recycling using advanced lanthanide and yttrium metallocene catalysts. Catalyst **3** achieves >99% ε-caprolactam yield under mild conditions (220°C, 0.2 mol%) and is reusable at ultra-low loadings (0.04 mol%). Mechanistic studies highlight efficient unzipping and interchain hopping pathways. For complex waste Nylon-6 products, ansa-yttrocene complex **6** excels in handling mixed and contaminated plastics. A closed-loop model is shown by re-polymerizing waste-derived ε-caprolactam into high-quality Nylon-6.

Conclusions & Recommendations

The single-site, highly electrophilic catalysts obtained by chemisorption of early transition metals on super acidic sulfated alumina collectively advance polyolefin recycling technology, as these catalysts demonstrate exceptional efficacy and stability, achieving high turnover frequencies under mild conditions and effectively converting a wide variety of polyolefin wastes into value-added products. In addition to polyolefins upcycling, breakthroughs in Nylon-6 recycling were achieved using lanthanide-organic catalysts with an innovative ligand design, exhibiting remarkable depolymerization rates and selectivity under mild conditions, providing a sustainable approach to recycling Nylon-6. The well-characterized active catalytic sites and detailed kinetic and mechanistic investigations establish a robust foundation for future research. This groundwork is pivotal for advancing the application of these catalytic systems and developing innovative catalytic designs aimed at the effective and sustainable recycling of plastic materials.

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