

# Innovative catalytic systems driving sustainable olefin polymerization: Recent advances and green chemistry approaches

Farabi Hossain<sup>1,\*</sup>, Md Enamul Hoque<sup>2,\*</sup>

<sup>1</sup>Department of Mechanical Engineering, Military Institute of Science and Technology, Dhaka 1216, Bangladesh

<sup>2</sup>Department of Biomedical Engineering, Military Institute of Science and Technology, Dhaka 1216, Bangladesh

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## ABSTRACT

This mini-review addresses the burgeoning requirements for environmentally friendly processes in the polymer industry, focusing on recent progress in developing catalytic systems for sustainable olefin polymerization. Improvements in homogeneous and heterogeneous catalyst design have resulted in greater control over polymer properties (molecular weight, tacticity, comonomer incorporation). Particularly, Group 4 metallocene and post-metallocene catalysts have enjoyed high activity and a degree of control over polymer microstructure. Late transition metal catalysts (nickel and palladium complexes in particular) afford unique advantages in producing branched polyethylene and conducting polymerizations in polar solvents. Computational studies and novel support strategies have yielded improvements for heterogeneous Ziegler-Natta catalysts. Potential for reducing environmental impact through green catalysis approaches include enzyme-based systems, ionic liquids, and photoactivated catalysts. These catalytic advances have permitted previously unavailable control over polymer properties, including molecular weight distribution and functional group incorporation. Challenges remain regarding the stability of the catalysts, incorporation of comonomer, and economic feasibility. Future work focuses on new ligand design, extending the monomer scope to include renewable feedstocks and improving the activation procedures. There is a critical need to integrate computational modeling, machine learning, and advanced characterization techniques to facilitate catalyst discovery and understanding of complex structure-property relationships. In general, this review demonstrates the ongoing development of olefin polymerization toward more sustainable practices and describes the important role of advanced catalytic systems in determining the future of the polymer industry). **Polyolefins J (2025) 12: 1-16**

**Keywords:** Sustainable olefin polymerization; catalytic systems; metallocene catalysts; green catalysis; polymer microstructure.

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\*Corresponding Authors - E-mail: enamul1973@gmail.com;

farabihossain.mist@gmail.com

## INTRODUCTION

With the increasing demand for sustainable and environmentally friendly processes in the polymer industry, the olefin polymerization field has made great progress. Catalytic systems enable this evolution by providing novel means to improve olefin polymerization efficiency and sustainability [1-3]. Novel catalyst development and improvement of existing systems are focal points of research toward overcoming the challenges of conventional polymerization. Commonly used matrix materials include polyolefins such as polyethylene and polypropylene, which have some compatibility issues with hydrophilic natural fibers [4].

The polymerization of olefins (particularly polyethylene and polypropylene) accounts for a significant portion of the global polymer market. Applications of these materials are extensively applied in the packaging, automotive, and construction industries [1]. Nevertheless, conventional production processes typically rely on energy-intensive processes and nonrenewable resources, as well as their sustainability and environmental concerns in the long term.

While responding to these challenges, researchers have started looking at alternative catalytic systems that improve performance while meeting some sustainability goals. Another avenue of research has been the development of single-site catalysts that afford more significant control over polymer properties and can produce tailored biomolecules with desired properties [2,3]. These catalysts provide a route to more efficient use of raw materials and energy, and more generally, contribute to the sustainability of the overall polymerization process.

An important area of focus is the incorporation of renewables into the production of olefin-based polymers. In this context, alternatives to traditional petroleum-based feedstocks are being investigated using bio-based monomers and catalysts derived from sustainable sources [1-3]. In addition to playing a role in cutting our reliance on fossil fuels, it also allows us to develop new pathways to create biodegradable and compostable polymers that could eliminate end-of-life worries with conventional plastics

The effort for more sustainable olefin polymerization processes has also resulted in the development of new reaction conditions and methodologies. Researchers are looking at catalytic systems to improve efficiency and environmental performance through the use

of continuous flow reactors, alternative solvents, and innovative activation methods [2,3]. These advancements aim to minimize waste generation, reduce energy consumption, and enhance the sustainable profile of olefin polymerization processes. Advancements in the development of catalyst systems for sustainable olefin polymerization have been, and continue to be, critical research areas not only in polymer science and engineering but also chemical technology as the existing polymer industry evolves. In this mini-review, we aim to give an overview of recent progress within this field and discuss the most recent innovative ideas, challenges, and future prospects. A study of the latest progress in catalyst design, process optimization, and renewable resource integration in olefin polymerization reveals lessons for ongoing movement towards more sustainable olefin polymerization.

## RECENT DEVELOPMENTS IN CATALYST SYSTEMS

Recent advancements in catalytic systems for olefin polymerization have focused on improving catalyst efficiency, selectivity, and sustainability. These advances include both homogeneous and heterogeneous catalysts, with significant progress in metallocene, post-metallocene, and late transition metal complexes. In Table 1, the key performances, advantages, limitations and notable advancements of various catalyst systems has been shown.

### Homogeneous catalysts

Both metallocene and post-metallocene catalysts have developed into powerful instrumentalities for the tailored production of polymers with controlled microstructures. Group 4 metallocenes, especially the zirconocene complex, have shown high activity and reasonable control over polymer properties [5,19]. For example, *ansa*-zirconocenes have demonstrated a promising impact as ethylene-based copolymers of homogeneous composition and have the capability of incorporating higher olefins [5]. Olefin polymerization catalysts of vanadium coordination complexes in different oxidation states (III, IV, and V) are a new development area. The ligands present in these catalysts are varied, including N-donors, O-donors, and P-donors, all of which are used to optimize catalytic properties. Vanadium (III) complexes with

**Table 1.** An overview of catalyst systems for olefin polymerization.

| Catalyst Type                                   | Key performance metrics   | Advantages   | Limitations   | Notable advancements  | Ref(s)  |
|---|---|--|---|---|---------|
| <b>Metallocene (zirconocene)</b>                | <ul style="list-style-type: none"> <li>- High activity (up to <math>10^6</math> g PE · (mol · h)<sup>-1</sup>)</li> <li>- Molecular weight control</li> <li>- Comonomer incorporation</li> </ul>                              | <ul style="list-style-type: none"> <li>- Precise control over polymer microstructure</li> <li>- Ability to incorporate higher olefins</li> </ul>                       | <ul style="list-style-type: none"> <li>- Sensitivity to impurities</li> <li>- Complex synthesis</li> </ul>      | <ul style="list-style-type: none"> <li>- Development of <i>ansa</i>-zirconocenes for ethylene-based copolymers</li> <li>- Permethylindenyl-phenoxy (PHENI*) titanium catalyst for high to ultra-high molecular weight ethylene-<math>\alpha</math>-olefin copolymers</li> </ul> | [5-7]   |
| <b><math>\alpha</math>-Diimine nickel</b>       | <ul style="list-style-type: none"> <li>- High activity</li> <li>- Branching control (48-152 branches/1000 C)</li> <li>- Molecular weight range: <math>M_n = 12-393</math> kg/mol</li> </ul>                                   | <ul style="list-style-type: none"> <li>- Tolerance to polar monomers</li> <li>- Chain walking ability</li> </ul>   | <ul style="list-style-type: none"> <li>- Lower thermal stability compared to early transition metals</li> </ul> | <ul style="list-style-type: none"> <li>- Optimization of N-aryl substituents</li> <li>- Tuning metal center electrophilicity</li> <li>- Development of air-stable alkyl- or aryl-functionalized Ni (II) precatalysts</li> </ul>   | [8,9]   |
| <b>Salicylaldiminato nickel</b>                 | <ul style="list-style-type: none"> <li>- High molecular weight (<math>M_n &gt; 10^5</math> g/mol)</li> <li>- Stability in polar media</li> </ul>  | <ul style="list-style-type: none"> <li>- Aqueous polymerization capability</li> <li>- Control over branching</li> </ul>  | <ul style="list-style-type: none"> <li>- Limited comonomer scope</li> </ul>                                     | <ul style="list-style-type: none"> <li>- Development of water-soluble catalyst precursors</li> <li>- Perfluoroalkyl-substituted catalysts for UHMWPE synthesis</li> </ul>   | [10]    |
| <b>Palladium diimine</b>                        | <ul style="list-style-type: none"> <li>- High efficiency (&gt;95% end-capping)</li> <li>- Tunable molecular weights</li> </ul>  | <ul style="list-style-type: none"> <li>- Functional group tolerance</li> <li>- Ability to introduce reactive end groups</li> </ul>                                     | <ul style="list-style-type: none"> <li>- Lower activity compared to early transition metals</li> </ul>          | <ul style="list-style-type: none"> <li>- Use of unsaturated alcohols as chain transfer agents for aldehyde end-capped polyolefins</li> </ul>  | [11,12] |
| <b>Iron-nickel dual catalyst</b>                | <ul style="list-style-type: none"> <li>- High Markovnikov selectivity</li> <li>- Diverse substrate scope</li> </ul>   | <ul style="list-style-type: none"> <li>- Use of abundant metals</li> <li>- Functional group tolerance</li> </ul>   | <ul style="list-style-type: none"> <li>- Lower activity for challenging substrates</li> </ul>                   | <ul style="list-style-type: none"> <li>- Combination of iron-catalyzed hydrogen atom transfer with nickel-catalyzed cross-coupling</li> </ul>   | [13,14] |
| <b>Vanadium-based</b>                           | <ul style="list-style-type: none"> <li>- High activity (up to <math>4.13 \times 10^7</math> g mol<sup>-1</sup>h<sup>-1</sup>)</li> <li>- Production of UHMWPE</li> </ul>  | <ul style="list-style-type: none"> <li>- Better copolymerization with <math>\alpha</math>-olefins</li> <li>- Syndiotactic polypropylene production</li> </ul>          | <ul style="list-style-type: none"> <li>- Lower thermal stability compared to group IV metals</li> </ul>         | <ul style="list-style-type: none"> <li>- Development of N-donor and O-donor ligand complexes</li> <li>- Immobilization on supports like graphene oxide</li> </ul>   | [15]    |
| <b>Cobalt-based</b>                             | <ul style="list-style-type: none"> <li>- High activity (up to <math>1.00 \times 10^7</math> g PE mol<sup>-1</sup> (Co) h<sup>-1</sup>)</li> <li>- Excellent thermal stability</li> </ul>                                      | <ul style="list-style-type: none"> <li>- Maintains activity at high temperatures (up to 90°C)</li> <li>- Production of high molecular weight polyethylene</li> </ul>   | <ul style="list-style-type: none"> <li>- Limited control over branching</li> </ul>                              | <ul style="list-style-type: none"> <li>- Synthesis of unsymmetrical 2,6-bis(imino)pyridylcobalt(II) chloride precatalysts with bulky substituents</li> </ul>  | [16]    |
| <b>Nickel with triadamantylphosphine ligand</b> | <ul style="list-style-type: none"> <li>- Very high activity (up to 3.7 million turnovers per hour)</li> <li>- Ultrahigh molecular weight polyethylene (<math>M_n</math> up to <math>1.68 \times 10^6</math> g/mol)</li> </ul> | <ul style="list-style-type: none"> <li>- Excellent copolymerization with <math>\alpha</math>-olefins</li> <li>- Nearly linear UHMWPE with narrow dispersity</li> </ul> | <ul style="list-style-type: none"> <li>- Potential sensitivity to polar groups</li> </ul>                       | <ul style="list-style-type: none"> <li>- Development of highly active catalyst for UHMWPE production</li> </ul>   | [17]    |
| <b>Titanium [ONOO] complex</b>                  | <ul style="list-style-type: none"> <li>- Active for aqueous polymerization of acrylates at room temperature</li> </ul>  | <ul style="list-style-type: none"> <li>- Environmentally friendly aqueous polymerization</li> <li>- Syndiotactic-rich poly (methyl methacrylate) production</li> </ul> | <ul style="list-style-type: none"> <li>- Limited to specific monomer types</li> </ul>                           | <ul style="list-style-type: none"> <li>- Synthesis of asymmetric tetradentate [ONOO] titanium complex for aqueous polymerization</li> </ul>   | [18]    |

N-donor ligands have shown high activities up to  $2.22 \times 10^7$  g mol<sup>-1</sup>h<sup>-1</sup>, while those with O-donor ligands have reached even higher activities of  $4.13 \times 10^7$  g mol<sup>-1</sup>h<sup>-1</sup>. Production of high molecular weight polyethylene has also been demonstrated by vanadium (IV) and (V) complexes [15]. Chromium (III) complexes have been developed with high catalytic activity for beta-olefin derivatives, achieving significant improvements over traditional metallocene systems [20].

Significant progress has been made in developing late transition metal catalysts, especially nickel and palladium complexes, due to their unique advantages:

1. Ability to generate branched polyethylene using only ethylene as feedstock
2. Capability to conduct polymerizations in polar media
3. Direct copolymerization of ethylene with polar comonomers

These catalysts can produce polyethylene with controllable branching density and topology by altering ligand structures and polymerization conditions [21,22].

Notable developments in nickel-based catalysts include:

$\alpha$ -Diimine nickel catalysts have been optimized through strategies like modulating N-aryl substituents and tuning metal center electrophilicity [22]. Salicylaldimine nickel catalysts are capable of polymerizing ethylene to high molecular weights ( $M_n > 10^5$  g mol<sup>-1</sup>) and are stable in the presence of polar compounds, including water [10]. Phosphinophenolate nickel catalysts exhibit activities above  $10^8$  g mol<sup>-1</sup>h<sup>-1</sup> and produce polyethylene with molecular weights greater than  $4 \times 10^6$  g mol<sup>-1</sup> [23].

Other iron-based catalysts are also promising, especially those with bis(imino)pyridyl (BIP) ligands. When activated with methylaluminoxane (MAO), these catalysts display very high efficiency and selectivity for ethylene polymerization [24].

Advancements in cobalt-based catalysts have focused on enhancing thermal stability and control over polymer molecular weight. [16] The synthesized unsymmetrical 2,6-bis(imino)pyridylcobalt (II) chloride precatalysts bearing bulky dibenzocycloheptyl substituents have high activities {up to  $1.00 \times 10^7$  g PE mol<sup>-1</sup> (Co) h<sup>-1</sup>} and excellent thermal stability, maintaining significant activity even at 90°C.

### Heterogeneous catalysts

Significant progress has been made in heterogeneous Ziegler-Natta (Z-N) catalysts supported on MgCl<sub>2</sub>.

Key components and advancements include:

1. MgCl<sub>2</sub> support: Provides high surface area for catalyst adsorption. Different crystal structures ( $\alpha$ ,  $\beta$ ,  $\gamma$ ) affect catalyst performance.
2. TiCl<sub>4</sub> active catalyst
3. AlR<sub>3</sub> cocatalyst: Activates Ti catalyst and can interact with donors.
4. Internal/external donors: Control catalyst stereoselectivity. Recent work has explored phthalate-free donors like multidentate polyethyleneimines [25].

Computational studies, especially density functional theory (DFT), have provided insights into catalyst structure and mechanisms not accessible experimentally [26].

Developing an ionic anchoring strategy (IAS) to the heterogenization of homogeneous catalysts on solid supports is a significant advancement in heterogeneous catalysis. This approach enables strong catalyst-support interactions while tolerating polar functional groups. Supported nickel and titanium catalysts prepared via IAS showed significantly enhanced polymerization properties compared to their homogeneous counterparts, including higher activities, polymer molecular weights, and comonomer incorporation [23].

### Novel catalyst systems

Several promising results arose from using bimetallic catalysts featuring two polymerization active metal centers in proximity. Synergistic effects from the use of early transition metals (Ti, Zr, Hf, V) bimetallic catalysts with phenoxyimine and cyclopentadienyl-silyl-amido ligands result in higher molecular weight polymers than monometallic analogs. Specifically, late transition metal (Fe, Co, Ni) bimetallic catalysts identical to those with phenoxyimine and  $\alpha$ -diimine ligands show improved stability, activity, and comonomer incorporation [27]. Other dual catalytic systems explored include the iron-nickel system, which is used for olefin functionalization and quaternary center formation. With iron-catalyzed hydrogen atom transfer and nickel-catalyzed cross-coupling, challenging transformations are possible with this approach [13]. ‘Catalyst + X’ strategies—incorporating supports, comonomers, agents, or even light—enhance transition metal-catalyzed olefin-polar monomer copolymerization without the need for new catalyst designs. These approaches allow improved catalytic performance by adjusting catalyst interactions with external components, opening

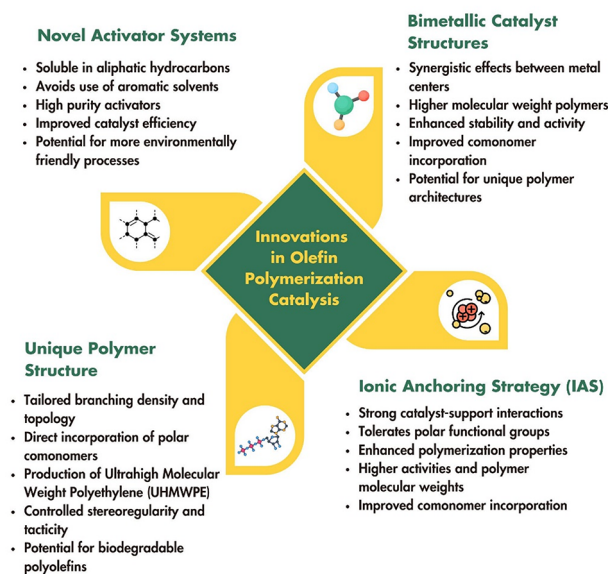
avenues for custom polyolefin functionalities [28]. Innovative catalyst modifications, such as altering ligand structures to mitigate deactivation by polar monomers, have significantly advanced the synthesis of functionalized polyolefins. Strategies now focus on overcoming steric and electronic challenges, which previously hindered polar group incorporation, thus broadening application potential in industrial polymer materials [29]. Emerging palladium and nickel catalysts show high efficiency for incorporating a variety of polar monomers in olefin copolymerization, including challenging types such as acrylates and vinyl ketones. These developments support the direct synthesis of functional polyolefins, marking a departure from reliance on post-functionalization methods [30].

### Activator technology

Advancements in activator technology have played a crucial role in improving catalyst performance. Methylaluminoxane (MAO) remains a widely used cocatalyst, but recent work has provided new insights into its multifaceted role in activating metallocene catalysts. Weak Lewis acid sites in silica-supported MAO, consisting of terminal Al atoms bonded to two methyl groups, are the origin of mobile  $\text{AlMe}^{2+}$  cations important for metallocene activation. A high concentration of MAO (around 12 wt.% Al) on silica supports is necessary to prevent metallocene leaching and reactor fouling [31,32]. Novel activators have also been developed, such as high-purity ammonium tetrakis(pentafluorophenyl)borate compounds. These activators are soluble in aliphatic hydrocarbons, allowing for more environmentally friendly polymerization processes that avoid the use of aromatic solvents [33]. In Figure 1, the innovations in catalyst systems for olefin polymerization have been presented. In Figures 2,3,4 and 5, the chemical structure of  $\alpha$ -Diimine nickel (II) catalyst, metallocene catalyst, salicylaldimine-based nickel catalyst and Ziegler-Natta catalyst are given respectively.

## GREEN CATALYSIS APPROACHES

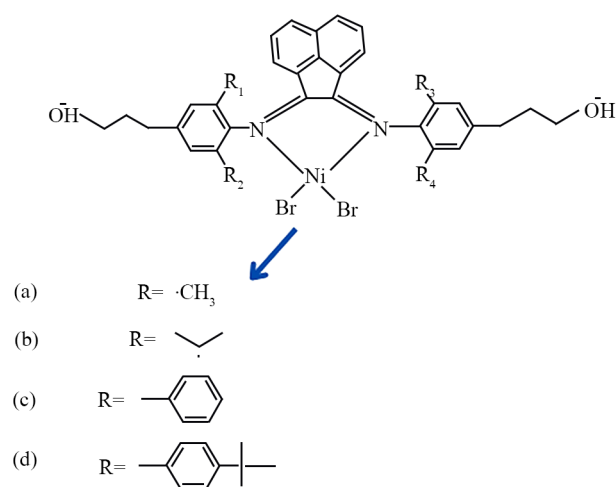
Green catalysis approaches have been made in the field of olefin polymerization with reduction of environmental impact and sustainability. These strategies include the use of biological catalysts and the design of new, more efficient, and environment-friendly chemical catalysts.



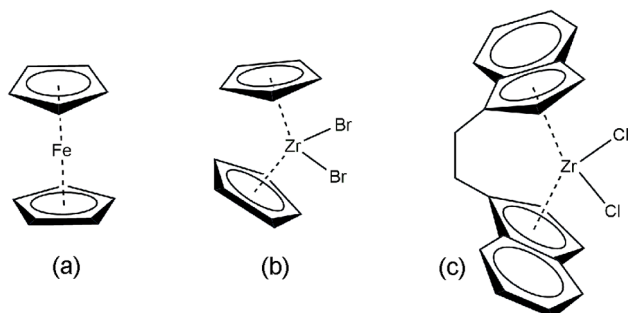
**Figure 1.** Recent innovations in catalyst systems for olefin polymerization.

Olefin polymerization is one of the most promising areas in green catalysis, where enzymes and biocatalysts are explored. They provide an attractive alternative to synthetic catalysts in terms of their ability to operate under mild conditions and their potential for using less energy and less polluting forms. Researchers are also producing nontoxic catalysts from renewable resources that reduce toxic waste and green synthesis processes with sustainable feedstock [34,35].

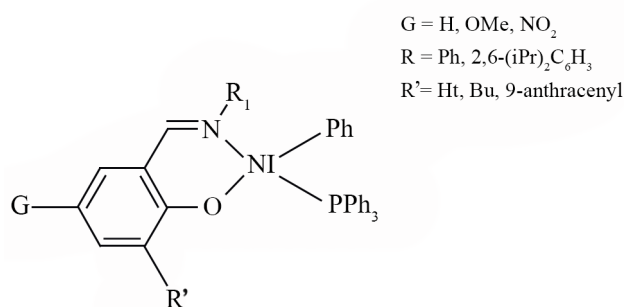
Another big step towards greener catalysis is using ionic liquids (ILs) and polyionic liquids (PILs) as alternatives to the traditional corrosive catalyst,  $\text{AlCl}_3$ . These IL-based systems reduce hazardous waste and increase the viscosity index of polyalphaolefins



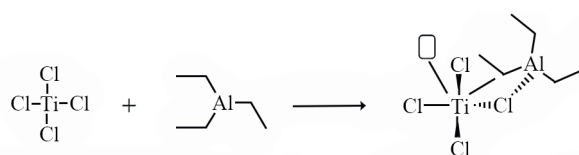
**Figure 2.**  $\alpha$ -Diimine nickel (II) catalyst; R in (a) Methyl, (b) iso-Propyl (c) Phenyl and (d) 4-tert-Butylphenyl.



**Figure 3.** Chemical structures of metallocene: (a) ferrocene, (b) zirconocene dibromide, and (c) bridged zirconocene dichloride.



**Figure 4.** Chemical structure of Salicylaldimine-based nickel catalyst.



**Figure 5.** Chemical structure of Ziegler-Natta catalyst.

(PAOs), making them environmentally friendly [36]. The  $\text{AlCl}_3/\text{H}_2\text{O}$  system has been explored as a less hazardous alternative to catalysts such as  $\text{BF}_3$ ; current research is directed toward improving reaction conditions and catalyst modifications to increase efficiency and decrease waste [37].

An environmentally friendly method emerging as photoactivated catalysts uses light as a clean energy source driving polymerization. Spatial and temporal reaction control can be achieved by using sulfur-chelated and phosphite ruthenium complexes that are activated by UV or visible light and used in stereolithographic 3D printing from metathesis-derived polymers. Some of these catalysts have been designed with 'kill switch' functionality so that this wavelength can deactivate the catalyst and put a stop to the polymerization process, which gives much more control over the polymerization process and potentially reduces some reaction waste from the

unwanted continued reaction [38].

Researchers reported a sustainable, solvent less one-pot synthesis of cyclic carbonate monomers from renewable resources such as glycerol, dimethyl carbonate, and allyl alcohol or fatty acid methyl esters. This approach reduces the environmental impact by using renewable starting materials and minimizing solvent use [39].

More efficient catalyst systems have also helped make polymerization processes greener. For example, using secondary metal cations that can increase catalyst efficiency and thermal stability simultaneously decreases energy consumption and catalyst waste in polymerization processes [40]. Better operating efficiency is achieved using carborane-based activators with neutral fluoroarylborane cocatalysts that are more stable and do not require water for temperature-dependent operating conditions [41,42].

By working on catalyst design, more efficacious systems with drastically reduced cocatalyst loadings have been realized, such as the  $\text{Al-H-Al}^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$  system that operates at lower Al/M ratios than classical systems. The resulting reduced usage of aluminum could also be more environmentally friendly processes [43].

Another critical aspect of green catalysis is using more abundant and less toxic metals in catalyst design. For instance, iron-based catalysts are sought as possible substitutes for more toxic systems at operating activity, and their selectivity is comparable to that of different monomers [24]. As for palladium, more sustainable alternatives to nickel catalysts are explored as alternative catalysts for copolymerization, which allow copolymerization under milder conditions and less waste [10,22].

Aqueous polymerization systems with water-soluble catalysts have been developed to make polymerization processes greener. Room temperature polymerization techniques, along with these systems, tend to reduce energy consumption and environmental impact manifold [18,21].

Another critical aspect of green catalysis is the development of catalysts that can operate with renewable monomers very efficiently. Olefin copolymerization using bio-based monomers like limonene or  $\beta$ -pinene is a way to increase the sustainability of polymer production using renewable feedstocks [44]. The use of diethylzinc as a chain transfer agent in metallocene systems represents a step towards greener processes by allowing controlled molecular weight reduction without hydrogen [45].

## IMPACT ON POLYMER PROPERTIES

Advanced catalytic systems have revolutionized the field of olefin polymerization, enabling unprecedented control over polymer microstructure and properties. This section explores the multifaceted impacts of these catalytic advancements on polymer characteristics, ranging from molecular weight and distribution to tacticity and functionality. In Table 2 the impact on polymer properties with examples for several catalyst systems has been shown and in Figure 6, the brief illustration on catalyst systems impacting the polymer properties has been given.

### Molecular weight control and distribution

One of the most significant impacts of advanced catalysts is the precise control over polymer molecular weight and distribution. Metallocene and post-metallocene catalysts have demonstrated remarkable capabilities in this regard. For instance, nickel complexes with dibenzocycloheptyl substituents produce highly linear polyethylene with controlled molecular weights and narrow molecular weight distributions [16]. Some catalytic systems can generate ultrahigh molecular weight polyethylene (UHMWPE) with weights ranging from 1-3 million g/mol [52]. The ability to fine-tune molecular weight distribution is equally important. *Ansa*-metallocene catalysts, for example, can influence polydispersity in ethylene/bicyclic olefin copolymers [6]. Some systems, like the Ni (II) triadamantylphosphine catalyst, produce nearly linear UHMWPE with remarkably narrow dispersity ( $\mathcal{D} = 1.3-1.7$ ) [17]

### Tacticity and stereoregularity

Advanced catalysts offer unprecedented control over polymer tacticity, a crucial factor in determining material properties. *Ansa*-metallocene catalysts can produce highly isotactic or syndiotactic polypropylene by controlling the ligand structure [58]. As shown by [1], the degree of regularity can be well tuned. In this reference, it was shown that by varying the amount of chain transfer agent in coordinative chain transfer polymerization (CCTP), it is possible to tune the tacticity of the oligomer, while the isotacticity increases linearly with increasing  $\text{ZnEt}_2$  content.

### Branching and comonomer incorporation

The ability to control branching and comonomer incorporation has been significantly enhanced by advanced catalytic systems. Nickel catalysts have

shown the ability to produce polyethylene with branching densities ranging from 17 to 106 branches per 1000 carbon atoms by varying catalyst structure [21]. This control over branching directly influences polymer properties such as crystallinity, melting point, and mechanical characteristics. Comonomer incorporation has also seen remarkable advancements. Some catalysts can achieve up to 60% incorporation of comonomers like 1-hexene [52]. Half-metallocene titanium catalysts have demonstrated the ability to produce copolymers with high comonomer incorporation (up to 35 mol% 1-octene) and uniform molecular weight distributions [33].

### Functional group incorporation

A groundbreaking advancement in catalytic systems is the ability to incorporate functional groups into polyolefins. This capability expands the potential applications of these materials significantly. For instance, copolymers of ethylene and polar monomers like acrylates can be produced with high molecular weights ( $M_n$  up to 834 kg/mol) and controlled comonomer incorporation (up to 7.4 mol%) [53]. This functionality introduction improves properties like adhesion and surface characteristics [22].

### Thermal properties

The impact of advanced catalysts on thermal properties is substantial. By controlling factors such as molecular weight, branching, and comonomer incorporation, catalysts can significantly influence melting temperatures and glass transition temperatures. For example, polyethylene produced by certain nickel complexes showed melting points ranging from totally amorphous to semicrystalline with melting points up to 111°C [21]. In another study, ENB-derived materials with glass transition temperatures ( $T_g$ ) ranging from -18°C to 178°C were synthesized, correlating with molecular weights from 400 g/mol to 25,000 g/mol [11]. Metallocene catalysts allow for precise control over polymer chain structure, resulting in materials with enhanced mechanical properties and thermal stability [59].

### Mechanical properties

The influence of advanced catalysts on mechanical properties is profound. Polyethylene generated by certain nickel complexes exhibited excellent elastic properties, with strain recovery values up to 83% and impressive tensile properties including stress-at-break values ranging from 7.4 to 16.3 MPa and strain-at-

**Table 2.** The impact on polymer properties for several catalyst systems.

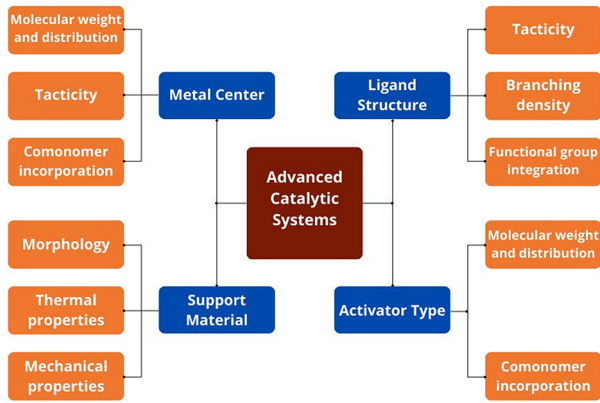
| Property                             | Impact   | Examples   | Critical Analysis  | Ref(s)           |
|--------------------------------------|--|--|--|------------------|
| <b>Molecular weight control</b>      | Precise control over a wide range of molecular weights, from oligomers to UHMWPE | - UHMWPE with $M_n$ 1-3 million g/mol<br>- Polyethylene with $M_n$ up to $2.09 \times 10^6$ g/mol<br>- Oligomers with controlled $M_n$ using metallocene catalysts | Enables tailoring of mechanical properties and processability. Critical for applications requiring high strength or specific rheological behavior.                                     | [21,46-48]       |
| <b>Molecular weight distribution</b> | Ability to produce polymers with narrow or controlled distributions              | - Dispersity ( $D$ ) as low as 1.3-1.7 for UHMWPE<br>- Controlled broadening of MWD in LLDPE   | Narrow distributions improve material consistency and performance. Broader distributions may enhance processability. Understanding multiple active sites helps explain MWD broadening. | [25,26,31,32,49] |
| <b>Tacticity control</b>             | Precise control over polymer stereochemistry                                     | - Highly isotactic or syndiotactic polypropylene<br>- Syndiotactic-rich poly (methyl methacrylate)<br>- Tunable tacticity in photo-controlled polymerizations      | Tacticity significantly influences crystallinity, mechanical properties, and thermal behavior. Critical for applications requiring specific physical properties.                       | [18,25,26,50]    |
| <b>Branching density</b>             | Tunable branching from linear to highly branched structures                      | - 17 to 106 branches per 1000 carbon atoms in polyethylene<br>- Highly branched poly(hexene) with 152 branches/1000C   | Affects polymer density, crystallinity, and mechanical properties. Crucial for producing materials ranging from rigid plastics to elastomers.  | [9,21,51]        |
| <b>Comonomer incorporation</b>       | Enhanced ability to incorporate various comonomers                               | - Up to 60% 1-hexene incorporation in polyethylene<br>- Up to 35 mol% 1-octene in ethylene copolymers  | Allows fine-tuning of polymer properties. Critical for producing LLDPE and elastomers with specific performance characteristics.   | [33,52]          |
| <b>Functional group integration</b>  | Enables incorporation of polar monomers and functional groups                    | - Copolymerization with acrylates, vinyl ethers, and silanes<br>- Incorporation of aldehyde end groups   | Expands polyolefin applications, improving adhesion, paint-ability, and compatibility in blends. Crucial for developing high-performance materials.                                    | [12,22,53]       |
| <b>Thermal properties</b>            | Influence on melting temperatures and glass transition temperatures              | - $T_g$ range from 18°C to 178°C for ENB-derived materials<br>- Melting points up to 111°C for semicrystalline polyethylene  | Determines usable temperature range and processing conditions. Critical for applications with specific thermal requirements.   | [5,11,21]        |
| <b>Mechanical properties</b>         | Affects strength, elasticity, and other physical characteristics                 | - Polyethylene with stress-at-break up to 20 MPa and strain-at-break 700%-1300%<br>- Tailored elastic properties with strain recovery up to 83%                    | Tailorable mechanical properties enable customization for specific end-use requirements. Crucial for high-performance applications.  | [21,54]          |
| <b>Morphology control</b>            | Influence on polymer particle shape and size                                     | - Fibrous vs. spherical particles in ethylene/ENB copolymers<br>- Control over polyethylene nanoparticle size in aqueous emulsions                                 | Particle morphology affects bulk properties and processability. Important for controlling material behavior during processing and in final applications.                               | [5,18,55]        |
| <b>Living polymerization</b>         | Enables synthesis of block copolymers and end-group functionalization            | - Production of polyolefin-containing block copolymers<br>- Synthesis of end-functionalized polyolefins  | Allows creation of complex architectures and functionalized polymers. Critical for developing advanced materials with unique property combinations.                                    | [56,57]          |
| <b>Copolymer composition</b>         | Allows for a continuum of copolymer compositions                                 | - Fine-tuning of material properties through statistical modeling<br>- Production of ethylene/CO non-alternating copolymers  | Enables precise control over material properties by adjusting monomer ratios. Crucial for optimizing performance in specific applications.   | [7,8,53]         |

break values ranging from 450% to 700% [54]. Some polyethylene samples showed high stress at break (ca. 20 MPa), high strain at break (700%-1300%), and elastic properties [21].

### Morphology control

Advanced catalytic systems have also demonstrated the ability to influence polymer morphology. MOF-based catalysts, for instance, have shown the ability



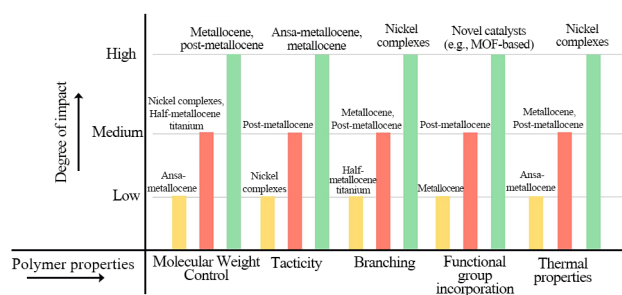


**Figure 6.** Overview of impacts on polymer properties by catalyst systems.

to produce polyethylene with distinctly different morphologies (fibers vs beads) due to subtle differences in pore structure [55]. This level of morphological control can be crucial for specific applications and processing methods. In Figure 7, the degree/level of impact on polymer properties by several catalyst systems has been presented.

## MATERIAL PROPERTIES OF RESULTING POLYOLEFINS

Polyolefins synthesized through advanced catalytic processes demonstrate a versatile range of mechanical, thermal, and chemical properties, enabling their use across diverse applications. The incorporation of polar functional groups into polyethylene introduces hydrophilicity, adhesion, and dyeability, the latter allowing for specialty properties such as elasticity, flame retardancy, and self-healing potential, mediated by transition metal catalyzed copolymerization [60]. In a research work [61], the effect of polar functional groups on the properties of polypropylene synthesized using Ziegler-Natta catalyst was also investigated, and the mechanical and thermal properties were analyzed



**Figure 7.** Degree of impact on polymer properties by catalyst systems.

using stress-strain and DSC curves. Together with the application of nickel catalyst based outer shell self-supporting methods, higher tensile strength and impact resistance are achieved, particularly for durable consumer and industrial applications [62]. The combination of low- and high-molecular weight fractions in polar bimodal polyethylene enhances mechanical strength, processability and barrier properties, with a co-anchoring catalyst approach that addresses the reduced catalytic activity due to polar groups enables minimal phase separation and excellent extrusion properties. These polar-functionalized polyolefins are particularly useful in applications demanding enhanced surface properties, such as dyeing, gas barrier functionality, and 3D printing adaptability, expanding their utility in packaging and advanced manufacturing [63]. Polar-functionalized polyolefins enhance dyeability, adhesiveness, and filler compatibility. Heterogeneous catalysts, though underexplored in this application until now, can significantly increase thermal stability and activity, while cost-effective options are provided by nickel-based catalysts. Heterogenization techniques and in situ polymerization enable tailored polyolefins with superior properties over traditional blending methods.

## RECYCLABILITY OF POLYOLEFINS

Polyolefins, such as polyethylene (PE) and polypropylene (PP) are plastics of wide use that need to be recycled to achieve environmental sustainability. Polyolefins are produced through polymerization of fossil fuel derived olefins, and share an important environmental impact highlighting the necessity for efficient recycling process. Mechanical, chemical, and feedstock recycling approaches are possible recycling approaches for polyolefins. While mechanical recycling might be common, it can reduce material quality over time; chemical recycling — such as pyrolysis — that breaks polymers down into monomers can help restore polymer quality, but is complex and expensive. Feedstock recycling can use polyolefins as raw materials for new plastic production. Yet, recycling polyolefins and mixed plastics is particularly complicated, owing to contamination, sorting issues, and economic factors like volatile oil prices. The possibility of using Multi-Block Copolymers (MBCPs) as compatibilizer additives to improve the blending of polyolefins and other plastic materials,

resulting enhancement of recycling of mixed plastic waste by enabling better material compatibility and enhanced 3D printing capabilities [64]. In a follow-up study, came up with a 'staple' strategy, using tailored molecules to enhance compatibility between difficult-to-recycle plastics such as polyethylene and polylactic acid. The recycled blends produced by this strategy have shown improved mechanical properties, and therefore recycled materials become more suitable for broader applications. Effective mixed plastic recycling strategies are essential to mitigate waste and promote sustainable resource use, the study points out [65]. Although the main focus in some research areas remains on developing degradable polymers such as thermosets, thermoplastics, and elastomers through metathesis polymerization of materials like dicyclopentadiene, this does not specifically address polyolefin recycling but contributes to the broader discussion of polymer degradation and recycling [66]. Innovations in compatibilizer technologies, such as MBCPs and stapler strategies, as well as advancements in sorting, chemical recycling, and circular economy initiatives, hold promise for more effective polyolefin and mixed plastic recyclability, supporting sustainable production and consumption.

## THERMAL STABILITY OF CATALYSTS IN PRACTICAL APPLICATIONS

Catalysts of practical application for industrial polymerization crucially require high thermal stability. High-temperature stability, excellent performance, limited process interruptions and economic viability are enabled by catalysts that remain stable under elevated conditions. Recently developed cobalt and vanadium-based catalysts have demonstrated good thermal resilience which enables their application in high-temperature polymerizations. As an example, bulky substituents, such as dibenzocycloheptyl groups, thermally stabilize cobalt catalysts up to 90°C, an advantage for high-molecular-weight polyethylene synthesis. Similarly, the incorporation of sterically hindered ligands in vanadium complexes has enhanced thermal stability, allowing for effective ethylene polymerization even under demanding thermal conditions. This stability is particularly valuable for sustaining catalyst longevity and efficiency in polymerization processes where heat buildup can otherwise lead to catalyst deactivation. Thus, there is

no doubt that the development and understanding of thermally stable catalysts is of great importance, and in addition to enhancing catalyst efficiency, it will enable the achievement of more durable and scalable polymerization technologies. These developments align with the broader goal of creating catalysts that meet both the operational demands of industrial processes and the sustainability objectives of green chemistry.

## RELATED CHALLENGES

The development of sustainable catalytic systems for olefin polymerization faces several significant challenges. In Table 3, relevant challenges and advantages for various catalyst methods have been presented. The specific limitation current researches are facing given below.

**Catalyst Efficiency and Selectivity:** Despite the improvements that metallocene catalysts have offered, it remains necessary to improve their performance. In particular, there is a necessity to enhance comonomer incorporation and control over the polymer microstructure [46]. It remains challenging for one building to balance multiple performance parameters, including catalyst activity, polymer molecular weight, and comonomer incorporation [22].

**Activation Mechanisms:** Further explanation of the activation mechanisms of supported metallocene catalysts is still needed [31,32]. Key to optimizing catalyst performance is the understanding of the complex interactions between Ti species, MAO co-catalysts, and metallocene active sites [19].

**Catalyst Stability:** However, the thermal stability of catalysts, especially those that utilize late transition metal and vanadium-based systems, remains a persistent challenge [15,21]. Many activated complexes undergo further transformations, eventually reaching catalytically less active or differently polymerized states [33].

**Comonomer Incorporation:** Remaining is improving the efficiency of incorporating polar comonomers (especially the polar monomers) beyond the current range of comonomers [53]. It is challenging to incorporate bulky or sterically hindered comonomers into polyethylene [44]. One challenge in sustainable olefin polymerization is the limited number of natural molecules containing suitable double bonds for radical polymerizations [39].

**Heterogeneous Catalysis:** It is essential to develop

**Table 3.** Relevant challenges and advantages for various catalyst methods.

| Catalyst methods                        | Limitations/Challenges  | Advantages  |
|---|---|---|
| <b>Metallocene catalysts</b>            | <ul style="list-style-type: none"> <li>- Limited thermal stability</li> <li>- Sensitivity to impurities</li> <li>- High cost of some ligands</li> </ul>                           | <ul style="list-style-type: none"> <li>- High activity</li> <li>- Precise control over polymer microstructure</li> <li>- Versatility in producing various polyolefins</li> </ul>                              |
| <b>Ziegler-Natta catalysts</b>          | <ul style="list-style-type: none"> <li>- Limited control over polymer microstructure</li> <li>- Heterogeneous nature complicates mechanistic studies</li> </ul>                   | <ul style="list-style-type: none"> <li>- High productivity</li> <li>- Cost-effective</li> <li>- Well-established industrial process</li> </ul>  |
| <b>Late transition metal catalysts</b>  | <ul style="list-style-type: none"> <li>- Lower thermal stability compared to early transition metals</li> <li>- Challenges in producing high molecular weight polymers</li> </ul> | <ul style="list-style-type: none"> <li>- Tolerance to polar functional groups</li> <li>- Ability to produce highly branched polymers</li> <li>- Potential for copolymerization with polar monomers</li> </ul> |
| <b>Supported catalysts</b>              | <ul style="list-style-type: none"> <li>- Potential for leaching</li> <li>- Complexity in understanding support effects</li> </ul>   | <ul style="list-style-type: none"> <li>- Improved heterogenization</li> <li>- Enhanced thermal stability</li> <li>- Potential for controlling polymer morphology</li> </ul>                                   |
| <b>Bimetallic catalysts</b>             | <ul style="list-style-type: none"> <li>- Complexity in synthesis and characterization</li> <li>- Challenges in optimizing synergistic effects</li> </ul>                          | <ul style="list-style-type: none"> <li>- Enhanced comonomer incorporation</li> <li>- Improved control over polymer properties</li> <li>- Potential for novel polymer architectures</li> </ul>                 |
| <b>Photocatalysts</b>                   | <ul style="list-style-type: none"> <li>- Limited wavelength range for activation</li> <li>- Potential for catalyst degradation under prolonged light exposure</li> </ul>          | <ul style="list-style-type: none"> <li>- Temporal and spatial control over polymerization</li> <li>- Potential for photo-switchable polymerizations</li> <li>- Mild reaction conditions</li> </ul>            |
| <b>Aqueous polymerization catalysts</b> | <ul style="list-style-type: none"> <li>- Lower activity compared to non-aqueous systems</li> <li>- Limited monomer scope</li> </ul>   | <ul style="list-style-type: none"> <li>- Environmentally friendly</li> <li>- Potential for producing water-soluble polymers</li> <li>- Mild reaction conditions</li> </ul>                                    |
| <b>Single-atom catalysts</b>            | <ul style="list-style-type: none"> <li>- Challenges in synthesis and characterization</li> <li>- Potential for aggregation</li> </ul>   | <ul style="list-style-type: none"> <li>- Maximum atom efficiency</li> <li>- Unique catalytic properties</li> <li>- Potential for high selectivity</li> </ul>  |

heterogeneous catalysts with high activity while preventing leaching and fouling. It is vital to understand which factors of support fragmentation and monomer diffusion play the leading role in controlling catalyst activity, especially in the case of modified supported catalysts [19].

**Economic Feasibility:** New catalyst technologies have not been economically viable compared to established processes and are still challenging [35]. The reduction of catalyst synthesis costs is a continual problem.

**Precise Control over Polymer Properties:** A critical challenge is to achieve precise control over the polymer microstructure while maintaining high efficiency and minimizing environmental impact [67]. The challenge of balancing donor coordination strength and catalytic activity is particularly apparent, as strong donor coordination stabilizes active sites but can impede monomer access [25].

**Catalyst Deactivation and Recycling:** Factors of catalyst deactivation and the development of efficient recycling methods are required for sustainable development [35].

**Aqueous Polymerization:** High catalyst activity and stability in aqueous environments are still

challenging [47].

**Chain Walking Control:** The key problem in  $\alpha$ -diimine nickel catalysis is efficiently suppressing the chain walking process to achieve regio-controlled  $\alpha$ -olefin polymerization [54].

**Functional Group Tolerance:** The significant issues that need to be investigated are the improvement of the olefin copolymerization with polar monomers and enhancing the functionality tolerance of catalysts [27].

**Quantification of Active Sites:** To better understand and optimize catalytic systems, developing more efficient methods to quantify the fraction of active catalyst sites formed during polymerization is crucial [58].

## FUTURE DIRECTIONS

There are many promising research avenues into the future of sustainable olefin polymerization catalysts. Catalyst design and optimization are still necessary with novel ligand designs, better thermal stability, and different activation methods [27,33,58]. Opportunities to expand monomer scope with functional comonomers and waste plastics or renewable feedstocks are exciting

[46,55,67]. Advanced characterization and modeling techniques such as computational modeling, machine learning, and high throughput experimentation will accelerate catalyst discovery and optimization [2,68,69]. Potentials include sustainable processes and novel catalytic systems, such as heterobimetallic catalysts and hybrids of internal and external donors [25–27,70]. Polymer microstructure can also be controlled with controlled polymerization techniques such as photo-controlled and dual catalysis systems [50]. Post-functionalization and the controlled incorporation of functional groups across the backbone generate a promise for developable materials through degradable polyolefins, especially at a molecular level [10,11,22]. Next-generation polyolefins are possible with advanced polymerization techniques such as Living Coordinative Chain Transfer Polymerization (LCCTP) and gas phase polymerization [21,56,71]. Support materials can be optimized, and the use of photo-responsive supports can be explored to improve control over polymer properties and specialist applications [23,72]. The potential for incorporating polar functional groups enhances polymer properties to a significant degree and makes it applicable for advanced manufacturing, packaging, and 3D printing. Furthermore, improved efficiency and reliability in such industrial conditions may be obtained with higher thermal stability of catalysts based on cobalt and vanadium. Finally, sustainable catalysts, including bio-derived and nontoxic donor systems and more efficient syntheses of the catalyst precursors, will be critical for truly sustainable olefin polymerization processes [10,26]. Collectively, these diverse research directions attempt to push the field of olefin polymerization catalysts toward more sustainable, efficient, and versatile systems.

## CONCLUSIONS

While providing promising future directions, the field of catalytic systems for sustainable olefin polymerization presents several challenges. The main issues include the necessity to improve catalyst efficiency and selectivity, improve stability, expand comonomer incorporation (especially of polar monomers), improve heterogeneous catalysis, economic feasibility, control of precise polymer properties, address catalyst deactivation and catalyst recycling, and enhance aqueous polymerization processes. Future research

should focus on innovative catalyst design and optimization, expanding monomer scope to include renewable feedstocks, advancing characterization and computational modeling techniques (including artificial intelligence and machine learning), developing more sustainable processes, exploring novel catalytic systems (such as heterobimetallic catalysts), refining controlled polymerization techniques, creating sustainable materials with tailored properties, and improving advanced polymerization methods like living coordinative chain transfer polymerization. Moreover, the addition of polar functional groups has become an important innovation that substantially improves polyolefins properties, including hydrophilicity, mechanical strength, and self-healing capabilities, thereby expanding their utilization in advanced manufacturing as well as packaging. In addition, improvements in thermally stable cobalt and vanadium-based catalysts show the potential to enhance the scalability and durability of polymerization technologies under industrial conditions. In addition, it will be crucial to optimize support materials for heterogeneous catalysis and to develop bio-derived, non-toxic catalyst systems. Those improvements seek to improve polymer properties and process efficiency and contribute to the circular economy of plastics, mitigating environmental issues.

## CONFLICTS OF INTEREST

The authors declared that there is no conflict of interest.

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