

Review

Catalytic Pyrolysis of Polyolefin Waste for Decarbonization and Circular Economy: A Mini-Review of Achievements and Industrial Prospects

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Abstract

Managing polymer waste, primarily polyolefins—low- and high-density polyethylene and polypropylene—is a critical challenge in the transition to a low-carbon, circular economy. Traditional approaches (landfilling and incineration) are inconsistent with sustainable development principles and increasingly stringent extended producer responsibility regulations, while chemical recycling, particularly catalytic pyrolysis, is considered a key technology for returning hydrocarbon feedstocks to the production cycle. This mini-review systematizes and analyzes current advances in the catalytic pyrolysis of polyethylene and polypropylene. An algorithm for selecting a recycling route for polyolefin-containing waste based on its composition, degree of degradation, and the presence of hazardous additives is proposed. Existing and planned industrial projects in the field of chemical recycling of polyolefins are assessed, and challenges and prospects for technology commercialization are outlined. It is demonstrated that catalytic pyrolysis has the potential to become a key element of a circular economy for plastics, ensuring decarbonization and resource conservation with further optimization of catalysts and process flowsheets.

Keywords: pyrolysis; thermolysis; polyolefins; plastic waste recycling; homogeneous catalysts; heterogeneous catalysts; selectivity; circular economy



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1. Introduction

The global transition to a low-carbon economy and closed-loop models necessitates a rethinking of approaches to plastic waste management, which has long been viewed solely as an environmental issue. Polyolefins, such as low- and high-density polyethylene (LDPE and HDPE, respectively) and polypropylene (PP), dominate polymer waste, accounting for more than half of global plastic consumption. Polyolefins, primarily polyethylene (PE) and PP, are the basis of the packaging, automotive, construction, and many other industries [1]. Due to its low cost, durability, and water resistance, PE has been one of the most readily available packaging materials since the mid-20th century, creating significant recycling challenges. In addition to controlled waste streams, a significant portion of polyolefin waste enters the environment uncontrolled, including through littering, inadequate waste collection systems, and unauthorized dumping.

Landfilling and incineration remain the primary methods of managing PE and PP waste in many countries [2]. As Romano and Garbassi note [3], although polyolefins constitute a significant portion of polymer waste, their disposal is the least environmentally preferable option. PE and PP, when subjected to anaerobic decomposition in landfills, can persist for hundreds of years, taking up valuable land. Furthermore, hazardous chemicals, including phthalates (used as plasticizers), migrate from buried waste into groundwater [4].

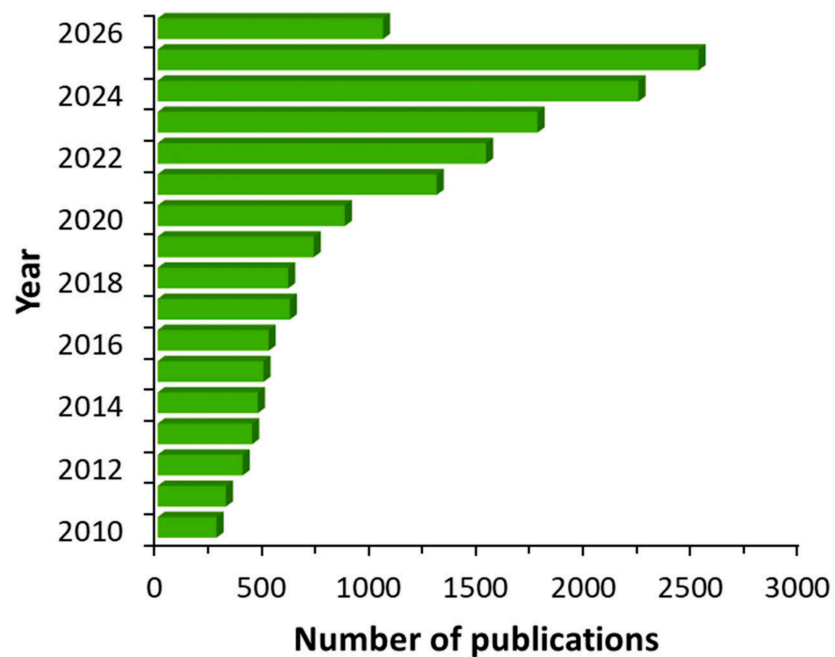
Incineration of PE and PP waste reduces waste volume and recovers energy, but it is associated with greenhouse gas emissions and potentially toxic compounds. Bora et al. [5] demonstrated in their study that incineration and landfilling of PP waste have the highest greenhouse gas emissions compared to chemical recycling methods. Chemical recycling offers the possibility of breaking down polymer chains into their original monomers, returning them to the production cycle without loss of quality [6]. Chemical recycling, including pyrolysis and gasification, is considered a promising alternative to traditional methods.

Pyrolysis stands out among other chemical recycling methods as one of the most scalable technologies, enabling the processing of complex, multi-component waste streams that do not require extensive pre-sorting into valuable chemical products and fuels [7,8]. The development and implementation of such technologies is consistent with the integrated paradigm of sustainable development, combining environmental safety, resource efficiency, and industrial decarbonization, thereby contributing to the achievement of sustainable development goal (SDG) 12 “Responsible Consumption and Production” and simultaneously addressing SDG 13 “Climate Action.” This explains the growing number of publications in the scientific literature on this topic (Figure 1a).

The keyword cloud focuses on the most frequently searched terms, “pyrolysis,” “catalytic pyrolysis,” and “plastic waste” (Figure 1b). These terms highlight the relevance of plastic waste recycling and the use of catalytic pyrolysis as a method for its disposal. Other significant keywords include “zeolite catalysts,” “recycling,” and “pyrolysis plastic,” indicating interest in the use of zeolites as catalysts and plastic recycling processes. The keyword cloud demonstrates the diversity of aspects related to catalytic pyrolysis, including catalyst types, recycling processes, and end products such as hydrocarbons and fuels.

Fundamental studies of the thermal degradation of polyolefins began in the 1960s [9] (Figure 2). In the following decades, kinetic models of the thermal decomposition of PE and PP based on the radical chain mechanism were developed. Ranzi et al. [10] proposed a detailed kinetic model, describing the radical chain reactions of pyrolysis in the liquid phase, including the stages of initiation, propagation, β -decay, chain transfer and recombination. This model showed that thermal pyrolysis of PE and PP occurs at temperatures of 400–700 °C and produces a wide range of hydrocarbons from C_1 to C_{40+} , with a predominance of waxes and heavy fractions.

In the following decades, active research into the use of catalysts for the catalytic pyrolysis of polymeric materials began. The next stage was the construction and launch of pilot and demonstration plants worldwide, followed by the transition to small- and medium-scale industrial production. Currently (2020s to present), catalytic pyrolysis technology is in the commercialization and integration phase. Legislative initiatives supporting chemical recycling are actively being adopted (the technology is included in EU circular economy and plastics strategies, as well as in EPR (extended producer responsibility) laws in several countries, and there has been a sharp increase in investment and the number of startups). Since 2022, research into the co-pyrolysis of plastics with biomass, tires, and municipal solid waste has been rapidly developing. In recent years, catalytic hydro-pyrolysis (pyrolysis in a hydrogen atmosphere) has attracted both academic and practical interest for the production of high-quality, virtually sulfur- and oxygen-free fuels, including sustainable aviation fuel (SAF).



(a)



(b)

Figure 1. Publications in the scientific literature: (a) Number of publications from 2010 to 2026, searched in Google Scholar using the keywords “catalytic pyrolysis, polyolefins” (as of 5 May 2026); (b) Visualization of network data of recent publications on the topic of catalytic pyrolysis of plastic waste.

The present review systematizes and critically analyzes current advances in the catalytic pyrolysis of polyolefins (polyethylene and polypropylene) as a key technology for decarbonization and the transition to a circular economy. Based on this analysis, existing technological solutions are assessed, allowing us to identify prospects and challenges for the rapid commercialization and industrial implementation of catalytic pyrolysis in a circular plastics economy.

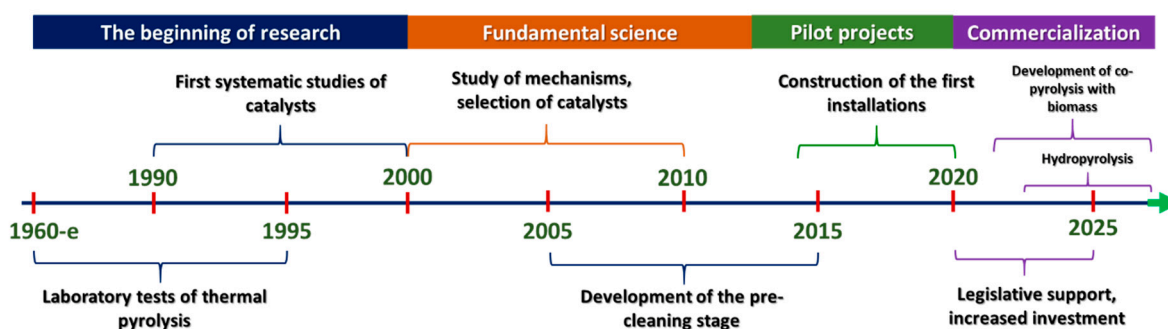


Figure 2. Progress in the development of catalytic pyrolysis technology.

2. Characterization of Polyolefins and Strategies for Their Processing

2.1. Polyolefins: Polyethylene and Polypropylene

Polyolefins—LDPE, HDPE and PP—differ in the polymerization mechanism, synthesis conditions and properties of the resulting products (Table 1).

Table 1. Characteristics of polyolefins—polyethylene and polypropylene [11–13].

Parameter	LDPE	HDPE	PP (Isotactic)
Monomer	Ethylene	Ethylene	Propylene
Type of polymerization	Radical	Coordination	Coordination stereoselective
Pressure, MPa	100–350	0.1–2.0	0.1–3.0
Temperature, °C	150–350	50–90	50–80
Catalyst	Oxygen/peroxides	TiCl ₄ /AlR ₃ (Ziegler–Natta), CrO ₃ /SiO ₂ (Phillips), metallocenes	MgCl ₂ /TiCl ₄ + AlR ₃ + donor (Ziegler–Natta), metallocenes
Chain structure	Branched (short and long branches)	Linear (minimal branching)	Linear stereoregular (iso-/syndio-)
Density, g/cm ³	0.915–0.935	0.940–0.970	0.900–0.910
Melting point, °C	105–115	125–135	160–170 (isotact.)/130–140 (syndiotact.)
Degree of crystallinity, %	45–65	70–90	50–70
Stiffness	Low-medium	High	High
Flexibility	High	Low	Low
Impact toughness	High	Medium	Low (modifiable)
Chemical resistance	Medium	High	High
Transparency	High	Low	Medium
Main areas of application	Films, bags, cable insulation	Pipes, containers, bottles, canisters	Fibers, films, car parts, household products

LDPE, obtained by radical polymerization under high pressure (100–350 MPa), is characterized by a branched structure with short and long side branches, which determines its low density (0.915–0.935 g/cm³), high flexibility, and impact strength. In contrast, HDPE is synthesized by a coordination mechanism on Ziegler–Natta catalysts, which ensures the formation of a virtually linear chain with minimal branching, a high degree of crystallinity (70–90%), and a density of 0.940–0.970 g/cm³. Polypropylene, obtained by stereoselective coordination polymerization, has the most complex microstructure: depending on the

catalytic system used, an iso- or syndiotactic chain configuration is formed, which critically affects its heat resistance (the melting point of isotactic PP reaches 160–170 °C) and rigidity. From the perspective of decarbonization and the circular economy, it is precisely these structural features that determine the routes of thermal and catalytic destruction.

2.2. Decision-Making Algorithm for Polyolefin Waste Recycling Routes

To facilitate the transition of polyolefin recycling technologies (using PE and PP as an example) from laboratory research to industrial implementation, a decision-making system is proposed that systematically compares waste characteristics with corresponding recycling options (Figure 3). This flowchart is a formalized algorithm based on binary logic that integrates key factors, including material purity and the presence of hazardous additives or fillers, as well as the degree of thermal-oxidative degradation of macromolecules. These parameters critically impact the feasibility of the process, technological efficiency, and economic viability of recycling.

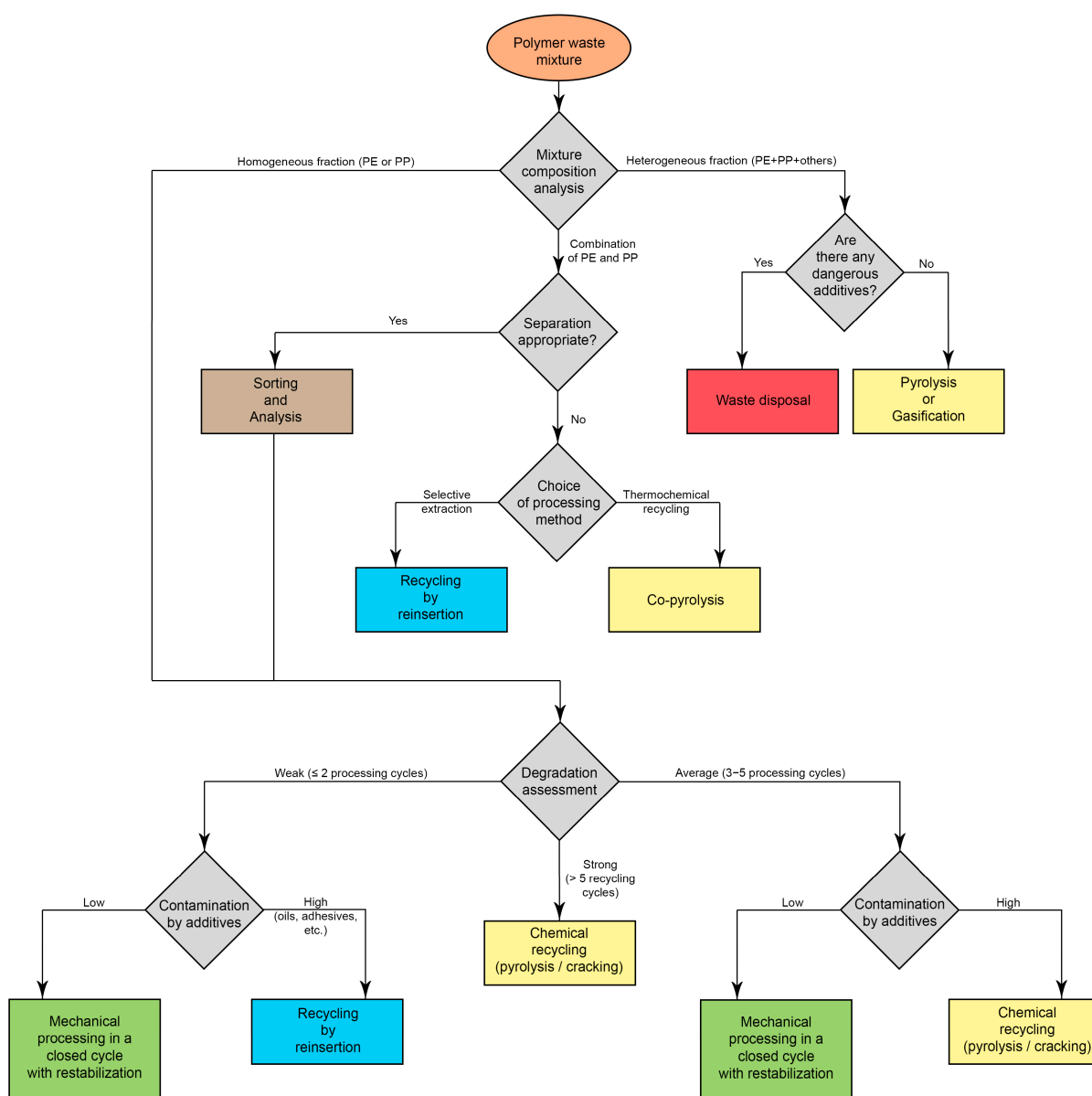


Figure 3. Decision-making scheme for choosing recycling routes for polyolefins (PE, PP) based on waste characteristics.

The algorithm begins with identifying the fraction composition. Chen A. et al. [14] developed a multi-level analytical system that allows the evaluation of incoming polymer waste using standard laboratory methods. A key step is assessing the mixture composition for the combined presence of PE and PP. For streams identified as individual polymers (PE or PP), a “layered chemical safety filter” is introduced. The first barrier is identifying the presence of hazardous additives in the mixture (e.g., persistent organic pollutants or heavy metals in pigments). If these are detected, the material stream is deemed unsuitable for reuse in consumer goods and sent for disposal at specialized landfills, preventing the recycling of toxicants into the technosphere.

If hazardous components are absent, the process proceeds to the processing method selection block, differentiated based on the number of previous processing cycles, which indirectly characterizes the molecular weight and degree of chain branching. In the absence of hazardous components, a transition is made to the block for selecting a processing method, differentiated depending on the number of cycles of previous processing, which indirectly characterizes the molecular weight and the degree of chain branching. For slightly degraded streams (less than 3–5 processing cycles), molecular purification methods are a priority: selective dissolution—dissolution of the polymer matrix followed by precipitation—allows for the removal of insoluble impurities (fillers, pigments, cross-linked gel) without disrupting the macromolecules. Recycling by reinsertion refers to the direct return of polymer waste (after sorting, washing, and granulation) to the main production cycle as a replacement for virgin polyolefin. This route is only applicable to high-purity streams with a low degree of degradation (less than 3 processing cycles) and the absence of hazardous additives. Closed-loop mechanical recycling with restabilization involves the introduction of a fresh batch of primary and secondary antioxidants into the melt after extrusion granulation. This compensates for the depletion of the stabilizing system that occurred during previous cycles of use and recycling and ensures the safe reuse of the polymer in less critical products without loss of performance properties. If the degree of degradation exceeds the permissible level or the impurity content is high, the algorithm proceeds to assess the feasibility of mechanical recycling with restabilization or thermal/catalytic pyrolysis.

In cases of severe thermomechanical degradation (over 5 processing cycles), when the melt rheology is irreversibly disrupted, and for materials that have undergone a reprecipitation unit, the algorithm proceeds to assess the level of contamination with process additives. At low impurity levels, closed-loop mechanical processing is recommended, with mandatory restabilization—the introduction of recycled primary and secondary antioxidants to compensate for the expended stabilizing package. In the proposed algorithm, pyrolysis is considered the final stage of processing, which is only resorted to after mechanical methods (including reinsertion and processing with restabilization), as well as selective dissolution methods, prove inapplicable or economically impractical. This occurs in two cases: (i) with a high degree of thermal-oxidative degradation of macromolecules (more than 5 processing cycles), when restoration of molecular weight and properties is impossible even with the introduction of fresh stabilizers; (ii) with a high level of contamination with process additives, fillers, or other polymers, making mechanical mixing ineffective. The proposed system is intended to reduce uncertainty during scale-up, but the extent of this reduction needs to be quantified in further studies. Nevertheless, it can already serve as a bridge between polymer analytical chemistry and industrial recycling plant design.

Catalytic pyrolysis thus serves as a method for closing the polymer life cycle when all milder approaches have been exhausted. It is at this stage that the correct choice of catalyst plays a key role, enabling the conversion of a complex, polluted stream into a valuable hydrocarbon feedstock.

3. Polyolefin Pyrolysis Catalysts

3.1. Zeolite Catalysts

The use of solid acid catalysts, such as zeolites, radically changes the product spectrum in favor of target compounds with high added value, while simultaneously eliminating the main disadvantages of a purely thermal process—low selectivity and product contamination [15,16]. Zeolites are microporous aluminosilicates with a crystalline structure possessing Brønsted and Lewis acid sites. Their catalytic activity in the pyrolysis of polyolefins is determined by the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio (acidity), pore size, surface area, and pore structure [15,17].

The advantages of zeolite catalysts include [15–18]: (i) a decrease in pyrolysis temperature by 75–100 °C; (ii) a decrease in activation energy by ~40%; (iii) an increase in selectivity for valuable products (olefins, aromatics); (iv) a decrease in wax yield to a virtually zero level; (v) the possibility of multiple regeneration by calcination in air. At that time, the key disadvantages of zeolite catalysts were (i) rapid deactivation due to coke deposition (the catalyst loses activity at a plastic/catalyst ratio of ~5); (ii) high aromatic content in liquid products (up to 49–58%), which requires additional hydrotreating to obtain commercial fuel; (iii) the relatively high cost of synthetic zeolites.

The most studied zeolite catalyst for the pyrolysis of PE and PP is ZSM-5 (MFI structural type). Due to the three-dimensional channel system and moderate acidity, ZSM-5 exhibits high activity in the cracking of polyolefins and selectivity for light olefins ($\text{C}_2\text{--C}_4$) and aromatic hydrocarbons [19]. Serrano et al. studied hierarchical nanocrystalline HZSM-5, obtained by silanization of seeds, in the cracking of LDPE and HDPE at 340 °C. The activity of these catalysts was 6 times higher than that of standard nanocrystalline HZSM-5, due to the large external surface area (160–240 m^2/g) and strong acidity. The main products were $\text{C}_1\text{--C}_4$ hydrocarbons (30–70%, mainly $\text{C}_3\text{--C}_4$ olefins) and $\text{C}_5\text{--C}_{12}$ (20–60%), and the amount of $\text{C}_{13}\text{--C}_{40}$ was practically zero (550 °C); secondary cracking reactions are enhanced, and the yield of gases and aromatics increases [15,17]. Increasing the catalytic cracking temperature from 460 to 500 °C on ZSM-5 (1500) led to an increase in the aromatics content from 7 to 58% [17]. PP is more susceptible to thermal degradation than PE due to the presence of tertiary carbon atoms, which facilitate the cleavage of bonds. However, in the presence of zeolites, PP cracking can be complicated due to steric hindrances created by methyl groups [20,21]. The yield of light olefins from LDPE is higher than from HDPE due to the presence of branches in LDPE [20].

Among zeolite catalysts for polyolefin pyrolysis, two-dimensional (2D) ZSM-5 zeolites, characterized by a high external surface area and mesoporosity, are attracting increasing attention. A striking example is the work of Peral et al. [22], which compared the catalytic activity of laminar (L-ZSM-5) and silica-pillared (PI-ZSM-5) ZSM-5 zeolites in the cracking of LDPE. The experiments were carried out in a batch steel reactor with a screw stirrer, providing intensive mixing of the polymer melt with catalyst particles, at atmospheric pressure in a nitrogen stream (35 mL/min), the temperature was varied from 340 to 380 °C; the reaction time after reaching the operating mode was 2 h, the mass ratio of LDPE: catalyst was 100:1. The original L-ZSM-5 was obtained in a laminar form, while PI-ZSM-5 was obtained by pillarization, which led to the formation of uniform mesopores with a size of ~3.5 nm. Nanocrystalline (n-ZSM-5) and hierarchical (h-ZSM-5) zeolites were also used for comparison. The external/mesoporous surface area of L-ZSM-5 was 242 m^2/g , while that of PI-ZSM-5 reached 498 m^2/g . Both 2D catalysts exhibited noticeable activity already at 340 °C, when the contribution of purely thermal cracking is negligible: LDPE conversion on L-ZSM-5 reached 36%, while on PI-ZSM-5 it was 27%. At 380 °C, conversion became almost complete (95–100%). Remarkably, PI-ZSM-5, despite having significantly fewer aluminum and acid sites, demonstrated comparable conversion at 360 and 380 °C to L-ZSM-5, and

even higher activity per Al atom. The authors attribute this to improved site accessibility due to the formation of uniform mesopores and the suppression of nanolayer aggregation during pillarization. The product composition was characterized by high selectivity for light C₂–C₅ olefins (60–70% of the total product), which increased with temperature, with the C₄ fraction dominating. This distribution indicates a preferential cracking pathway via end-chain scission at acid sites located at the mouths of the 10-membered rings of the MFI structure. Thus, two-dimensional ZSM-5 zeolites, especially pillared ones, provide high polyethylene conversion under mild conditions (340–380 °C) and selective formation of valuable light olefins, which makes them promising components of catalytic systems for the pyrolysis of polyolefin waste.

Yao He et al. [23] proposed to intensify the production of light aromatic hydrocarbons (BTX) in the catalytic pyrolysis of polypropylene using encapsulated ZSM-5@SBA-15 composites. Pyrolysis experiments were carried out at a temperature of 600 °C for 30 min in a fixed-bed reactor with an inner diameter of 20 mm and a heating zone of 200 mm in an air-free environment (the reactor was purged with nitrogen before the experiment). In each individual experiment, the amount of catalyst was 0.5 g (fraction 30–60 mesh), and polypropylene was 1 g (fraction < 150 µm). It was found that, compared to the conventional ZSM-5, the use of the ZSM-5@SBA-15 composite increased the BTX yield by 49.1%, reduced the content of heavy hydrocarbons by 42.2% and doubled the ratio of light hydrocarbons. The authors explain that encapsulation in SBA-15 silica pre-cleaves bulk paraffins into light aliphatic compounds, enriches these intermediates, and facilitates their diffusion into the micropores of the ZSM-5 core through an interconnected meso–microinterface, improving the accessibility of internal acid sites.

A detailed comparison of two types of zeolite catalysts, Y and H-ZSM-5, in the processing of LDPE was carried out by Jiang et al. [24]. The experiments were carried out in a two-stage system consisting of two fixed-bed reactors connected in series. In the first stage, LDPE was subjected to thermal decomposition at a temperature of 500 °C, after which the resulting vapors were sent without intermediate condensation to the second reactor filled with catalyst. The temperature of the catalytic bed was varied in the range of 400–600 °C, and the process was carried out in a nitrogen stream. Thermal pyrolysis without a catalyst resulted in a liquid product yield of 95 wt.% with minimal gas and coke formation. The introduction of zeolite expectedly changed the product distribution: for Y zeolite, the oil yield decreased, for example, to 85 wt.%, and the proportion of the gas phase increased; a further increase in the temperature of the catalytic bed enhanced this effect. Much more significant changes were observed in the chemical composition of the oil. The products of non-catalytic pyrolysis consisted almost exclusively of aliphatic hydrocarbons—alkadienes, alkenes, alkanes, and their branched isomers—with trace amounts of aromatic compounds. Treatment with zeolites, in contrast, sharply increased the aromatic fraction. Toluene, ethylbenzene, and xylenes predominated among the monocyclic aromatic hydrocarbons; naphthalene, phenanthrene, and their methylated derivatives predominated among the bicyclic and tricyclic ones. The concentration of aromatic compounds progressively increased with increasing catalytic bed temperature. The structural type of the zeolite played a decisive role. Zeolite Y, with wider pores and a high specific surface area, provided significantly deeper aromatization than H-ZSM-5. This result clearly demonstrates that transport limitations and accessibility of acid sites in the three-dimensional pore system of zeolite Y favor hydrogen transfer and cyclization reactions leading to extensive formation of aromatic hydrocarbons, while the narrower channels of ZSM-5 limit the growth of polycyclic structures.

In the context of developing approaches to the catalytic pyrolysis of polyolefins, studies that detail the relationship between the physicochemical properties of zeolites

and the mechanism of polymer degradation are of particular interest. In this regard, the results obtained by Pyra et al. [25], who conducted a fundamental study of the catalytic cracking of LDPE on β zeolites, are indicative. The authors' key objective was to establish the role of process conditions and the nature of the active sites of the catalyst on the decomposition mechanism and the composition of the final products. To separate the contributions of thermal and catalytic processes, as well as to model various pyrolysis scenarios, the researchers used two complementary experimental approaches. The first approach was aimed at modeling the dynamic heating regime and was implemented using a thermogravimetric analyzer (TGA), which served as a microreactor. A mixture of LDPE and zeolite in a 3:1 weight ratio was subjected to linear heating from 30 to 600 °C at a rate of 5 °C/min under a flow of inert carrier gas (nitrogen, 80 mL/min). This technique allowed for the reliable identification of key thermodynamic parameters, including the decomposition onset temperature, the temperature of the maximum degradation rate, and, most importantly, the temperature at which 50% conversion is reached (T_{50}). The test results convincingly demonstrated that the introduction of zeolite β leads to a significant decrease in the LDPE degradation temperature compared to the non-catalytic process (for which $T_{50} > 450$ °C). The best results were recorded for the sample modified with nitric acid (β_G/HNO_3), which allowed T_{50} to be reached at ~360 °C. This value was approximately 90 °C lower than that of the original commercial zeolite β and 60 °C lower than that of the untreated synthesized β_0 sample, clearly demonstrating the crucial role of post-synthetic modification in catalyst activation. The second approach, in contrast, aimed to study the process under strictly isothermal conditions at a low temperature of 230 °C. The choice of this temperature was crucial, as it allowed for the complete elimination of thermal cracking and the observation of the catalytic conversion process in real time. For this purpose, a unique setup was designed, combining a 1 cm³ IR reactor cell and a spectrometer, enabling simultaneous recording of changes in the catalyst surface condition and analysis of the released gaseous products. During the experiment, a tablet pressed from a mixture of LDPE and zeolite (in a 1:1 weight ratio) was maintained in a nitrogen flow (30 mL/min) at a given temperature until the polymer matrix was completely decomposed (for up to 80 min). The results of operando studies showed that the selectivity of the process critically depends on the type of dominant acid sites in the zeolite. The modified β_G/HNO_3 sample, characterized by the highest concentration of strong Brønsted acid sites and a virtually complete absence of extra framework aluminum particles, directed the reaction toward the formation of liquid products with a predominance of paraffins (~60%) and a minimal proportion of olefins. This product distribution clearly indicates the intensive occurrence of hydrogen transfer reactions and the mechanism of mid-chain carbon cleavage, realized at paired acid sites. In contrast, the initial β_G zeolite, rich in Lewis acid sites, yielded significantly higher olefin yields, owing to the dehydrogenating function of these sites. Remarkably, regardless of the catalyst used, the hydrocarbon molecular weight distribution remained similar and was characterized by a predominance of the C₅–C₁₂ fraction, which corresponds to the composition of gasoline and is of particular practical value for the conversion of polyolefin waste into motor fuel components.

Studies comparing the performance of several zeolite catalysts under identical conditions are of considerable interest for the targeted degradation of mixed polymer waste. Okonsky et al. [26] conducted a detailed study of the catalytic pyrolysis and co-pyrolysis of LDPE and polyethylene terephthalate (PET) on three industrially significant zeolites in the hydrogen form: HZSM-5, H-Beta, and HY. The experimental design combined TGA to study the decomposition kinetics and fast pyrolysis in a microreactor coupled with a gas chromatograph mass spectrometer (GC-MS) for detailed analysis of the volatile products. In TGA experiments, the polymer and catalyst were mixed in a 1:1 weight ratio and heated

in a helium flow (100 mL/min) at a rate of 10 °C/min from room temperature to 550 °C without isothermal holding. To exclude the contribution of moisture desorption from the zeolites, the signal of the pure catalyst was subtracted. It was found that the introduction of zeolites significantly reduces the temperature of the maximum decomposition rate of LDPE: the shift in $T_{\max}$ was 158 °C, 160 °C, and 128 °C for HZSM-5, H-Beta, and HY, respectively. For PET, the catalytic effect was significantly weaker (a decrease in $T_{\max}$ of 0 °C, 42 °C, and 6 °C), which is explained by the high thermal stability of polyester and a different primary degradation mechanism. Fast pyrolysis experiments were conducted at a polymer/catalyst ratio of 10:1 in a quartz tube heated at a rate of ~20 °C/ms to 500 °C with a 15 s hold under a helium atmosphere, which provided conditions as close as possible to those observed in fluidized-bed pyrolytic reactors. GC-MS analysis of LDPE fast pyrolysis products revealed that the main components are C_3 – C_{10} paraffins and olefins, as well as aromatic hydrocarbons, with the distribution strongly dependent on the pore topology and acidity of the zeolite. The highest selectivity for total aromatic compounds (31.6%) was achieved with HZSM-5, which is attributed to its narrow pores and the high strength of its acid sites, which facilitate cyclization and aromatization reactions. In contrast, the HY catalyst provided the highest yield of the C_5 – C_{10} gasoline fraction (40.9%), making it attractive for the production of motor fuels. In all cases of PET pyrolysis, benzene dominated (43.5–55.7%), while HZSM-5 demonstrated increased selectivity for polyaromatic compounds (24.7%) as a result of more intense secondary condensation reactions in a limited pore volume. Of particular practical interest are the results of the combined pyrolysis of an LDPE and PET mixture (1:1 by weight), for which clear synergistic effects were recorded. All three zeolites demonstrated a significant increase in the yield of alkylbenzenes (by 3–142%) and polyaromatics (by 105–187%), while simultaneously decreasing the yield of benzene (by 24–36%) and aliphatic hydrocarbons C_4 – C_{10} (by 27–53%). These effects are explained by the interaction of PET degradation products (oxygen-containing aromatic fragments) with the hydrocarbon chains of olefins, which opens up additional alkylation pathways. Based on a combination of indicators—high yield of gasoline fractions and maximum positive synergy in the formation of alkylbenzenes—the HY catalyst is recognized as the most promising for the conversion of mixed polyolefin/polyester waste into liquid fuels. Thus, this study clearly demonstrates that the rational choice of zeolite type and pyrolysis mode (dynamic heating in a TGA, rapid heating in a microreactor) enables targeted control of the molecular composition of the products, converting mixed plastic waste into valuable petrochemical feedstocks and fuel components within a closed-loop strategy.

In the context of the development of zeolite catalysts for the pyrolysis of polyolefins, the recent work of Rahimi et al. [27] deserves special attention. They systematically investigated composite zeolite systems based on HZSM-5, HY, and MCM-41 for the first time. Catalytic pyrolysis of PP was carried out in a two-layer fixed-bed reactor at atmospheric pressure, a temperature in the catalyst zone of 500 °C, and a reaction time of 60 min in an inert nitrogen atmosphere. The polymer was loaded into the upper zone, the catalyst—into the lower one at a polymer: catalyst weight ratio of 1:20. Both individual zeolites—high-silica HZSM-5 ($SiO_2/Al_2O_3 = 200$), low-silica HY ($SiO_2/Al_2O_3 = 3.5$) and mesoporous MCM-41—and their composites prepared by two physical mixing methods: granular (large particles) and powder (fine grinding)—were studied. All samples had high crystallinity, a specific surface area of over 360 m²/g and a developed mesoporous structure. Among the individual catalysts, HY provided the highest yield of liquid products (62.5 wt.%); however, its large pores contributed to intense coke formation. HZSM-5 showed higher selectivity for aromatic hydrocarbons, but the liquid yield was lower (54.2 wt.%). MCM-41, with its inherent weak acidity, demonstrated the lowest liquid yield (48.7 wt.%). Significantly higher efficiency was achieved with composite catalysts. The highest yield of liquid products

(up to 68.3 wt.%) was recorded for the MCM-41/HY composite, with the powder mixing method proving significantly more effective than the granular one. Analysis of the liquid fraction composition by GC-MS showed that for the MCM-41/HY composite (powder mixing), the share of gasoline-range hydrocarbons (C_5 – C_{12}) was 76.6% of the total liquid volume. The group composition of this fraction was as follows: olefins—28.3%, cyclic hydrocarbons (naphthenes)—32.4%, iso-paraffins—8.0%, aromatic hydrocarbons—5.6% and n-paraffins—1.7%. For comparison, the gasoline fraction on pure HY did not exceed ~60%, while on HZSM-5 it reached ~65%, with aromatic compounds dominating. Tests with real polypropylene waste (household packaging materials) yielded results comparable to those of the model feedstock, and stability tests confirmed the composite catalyst's high resistance to coke formation and the possibility of its regeneration. The authors explain the observed synergistic effect of the MCM-41/HY composite by the combination of MCM-41 mesopores, which ensure the efficient transport of large polymer molecules to the active sites, and moderate acidity of HY, which facilitates selective cracking to form isoparaffins and gasoline-range naphthenes. The close relative position of the two types of active sites in the powder mixture enables cascade reactions—primary cracking on the outer surface followed by isomerization and cyclization in the pores—without the deep destructive hydrogenation typical of strongly acidic catalysts. Thus, this study demonstrates that catalytic pyrolysis of polypropylene in a two-layer fixed-bed reactor at 500 °C using the MCM-41/HY composite catalyst prepared by powder blending enables the production of liquid fuel with a yield of over 68% by weight and a gasoline fraction content of up to 76.6%. The product composition (high olefin and naphthene content with a moderate aromatic content) makes it suitable for use as a component of commercial gasoline without additional upgrading, opening up new prospects for zeolite catalysts in decarbonization and closed-loop polyolefin processing technologies.

An example of the highly efficient use of zeolite catalysts for the direct degradation of polyolefins into motor fuels is the work of Kassargy et al. [28], who compared in detail the non-catalytic and catalytic pyrolysis of PE and PP in the presence of commercial ultrastable zeolite Y (USY). The experiments were carried out in a laboratory glass batch reactor at atmospheric pressure and a temperature of 450 °C in an inert nitrogen atmosphere. The USY zeolite was characterized by a molar ratio of $SiO_2/Al_2O_3 = 7.5$ and a pore size of 7.4 Å; it was introduced into the reactor at a mass ratio of catalyst:polymer = 1:10. The duration of non-catalytic pyrolysis was 60 min for PE and 40 min for PP, whereas in the presence of USY the process was accelerated, and complete decomposition was achieved in 20–30 min. Without a catalyst, the main product of PE pyrolysis was wax (80 wt.%), consisting of high-molecular linear hydrocarbons C_{20} – C_{50} , while PP destruction yielded 85.5 wt.% liquid fraction enriched in branched olefins and paraffins. The introduction of USY zeolite fundamentally changed the selectivity of the process. During catalytic pyrolysis of PE, the yield of liquid hydrocarbons increased to 71 wt.%, and wax formation decreased to trace amounts; 26.8 wt.% gas and 2.2 wt.% coke were formed simultaneously. For PP, the yield of liquid fraction decreased slightly—to 82 wt.% due to an increase in gaseous products (16.5 wt.%), while coke formation did not exceed 1.5 wt.%. The liquid products of catalytic pyrolysis were hydrocarbon mixtures of C_5 – C_{39} (from PE) and C_5 – C_{30} (from PP), indicating a deeper cracking reaction on the acid sites of the zeolite. The key practical result of the work was the demonstration of the possibility of fractionating the obtained pyrolytic oils directly into components of commercial fuels. Optimum separation was achieved by simple distillation at 170 °C. The light fraction (bp < 170 °C) accounted for 57 wt.% of the total PE oil and 60.6 wt.% for PP. In terms of its characteristics, it corresponded to gasoline fuel: the research octane number (RON) reached 97 units (PE) and 96 units (PP), the content of aromatic hydrocarbons did not exceed 35 wt. %, and olefins 25 wt.%. The fraction with a

bp. > 170 °C with a yield of 35.3 wt.% (PE) and 36.5 wt.% (PP) had the properties of diesel fuel: the calculated cetane number was 53 units and 52 units, respectively, the kinematic viscosity at a temperature of 40 °C was in the range of 2.5–3.5 mm²/s, and the pour point was not higher than minus 10 °C. Thus, the authors showed that the use of large-pore USY zeolite under mild conditions of a batch reactor (450 °C, atmospheric pressure) in combination with subsequent temperature separation at 170 °C makes it possible to obtain two commercial fractions from PE and PP that fully meet the specifications of gasoline and diesel fuel without any additional hydrofining treatment. These results clearly illustrate the potential of Y-type zeolites as catalysts for the pyrolysis of polyolefins for decarbonization and closed-loop implementation.

Among zeolite catalytic systems, the work of Fu et al. [29] deserves special attention. The authors studied microwave catalytic pyrolysis of polypropylene on zeolite HY and its modified forms containing iron, nickel, and a bimetallic FeNi composition (10 wt.% metal) for the production of aviation fuel. The process was carried out in a laboratory microwave setup (adjustable power 400–800 W, quartz reactor), loading 10 g of polymer, 1 g of catalyst, and silicon carbide (SiC) as a microwave absorber, in a nitrogen stream at atmospheric pressure. The temperature was varied in the range of 400–600 °C, and the holding time at the target temperature was 20 min. Among the tested catalysts, the bimetallic FeNi/HY demonstrated the best yield and quality of the liquid product. Under optimal conditions (500 °C, 500 W), the yield of the liquid fraction reached 67.5 wt.%. According to GC-MS, the composition of the pyrolytic oil was characterized by a high content of the target components of aviation fuel: paraffins—34.67 wt.%, naphthenes—23.02 wt.%, monocyclic aromatic hydrocarbons—31.19 wt.%, while the proportion of olefins, critically limited in aviation kerosene, did not exceed 5 wt.%. The content of hydrocarbons in the C₈–C₁₆ range (the main interval of aviation kerosene) varied from 89.28 to 97.22 wt.% depending on the mode, and the fraction, fully corresponding in composition to aviation fuel, reached 82.69 wt.%. Analysis of gaseous products recorded an increase in the yield of hydrogen and light hydrocarbons. A direct comparison with traditional electrical heating (the same catalysts, 500 °C, 20 bar H₂) revealed the fundamental advantages of microwave irradiation. By creating localized “hot spots” on the catalyst and SiC absorber surfaces, microwave irradiation stimulates the generation of free radicals and selective dehydrocyclization and isomerization reactions. This leads to a significant increase in the proportion of naphthenes in the liquid product (from 11.6 wt.% with electrical heating to 23.0 wt.% with microwave heating) and a simultaneous decrease in the olefin content. This observed effect is explained by the fact that the microwave field induces internal friction and dipole oscillations, creating an “inside-out” temperature gradient and intensifying the cleavage of chemical bonds via a radical mechanism. Thus, the combination of microwave heating and a bimetallic FeNi/HY zeolite catalyst allows for the production of a liquid product whose composition approaches the requirements of aviation fuel standards, opening up prospects for the conversion of polypropylene waste into high-quality aviation kerosene.

The main cause of loss of activity in zeolite catalysts is coke formation—the deposition of carbon compounds on the surface and in pores, blocking access to active sites. This process operates through a cascade mechanism: light olefins formed in the primary stages undergo secondary oligomerization, cyclization, and dehydrogenation reactions on the outer surface of the zeolite, first forming monoaromatic compounds and then polycyclic aromatic hydrocarbons—coke precursors. This process is particularly intense on zeolites with a high acid site density and under conditions where branched hydrocarbons formed during cracking are prone to excessive cyclization [30].

A number of strategies have been developed to combat this phenomenon. Creating a hierarchical pore structure not only improves diffusion but also reduces the residence

time of intermediates, preventing their condensation into heavy coke deposits [31]. Another effective approach is modifying zeolites with metals (Ni, Co, Pt) or phosphorus. Bifunctional metal-zeolite systems, where the metal center is responsible for hydrogenation/dehydrogenation and the acid center of the zeolite is responsible for cracking, demonstrate increased resistance to coking and extend the service life of the catalyst [32].

Restoring the activity of deactivated catalysts is critical to the economic viability of the entire refining process. The most common and well-studied method is oxidative regeneration, in which coke is burned off with oxygen or air at high temperatures. A review by Daligaux et al. [33] provides a detailed analysis of the advantages and disadvantages of various oxidative approaches, including molecular oxidation with oxygen, ozonation, and advanced oxidation processes with hydroxyl radical generation.

Thus, the activity of zeolite catalysts in polyolefin conversion processes is an integral characteristic dependent on the complex interplay of their acidic and textural properties. Achieving high selectivity for valuable products, long service life, and efficient regenerability requires fine-tuning of the catalytic system at the nanoscale. Further progress in this field is inextricably linked to the development of methods for the targeted design of catalysts that combine hierarchical porosity, controlled external acidity, and active metal sites, paving the way for sustainable and cost-effective chemical recycling of plastic waste.

3.2. Oxide Catalysts

While zeolite systems attract attention due to their ability to fine-tune their microporous structure, the shift to oxide catalysts is driven by the need to overcome their fundamental limitations when working with polymer waste. The rapid deactivation of zeolites due to coke formation in narrow pores and the diffusion barriers for bulky polyolefin macromolecules have stimulated the search for materials with more accessible active site topologies. In this context, amorphous and mesoporous metal oxides represent a special class of systems capable of ensuring efficient polymer chain degradation without excessive release of light gases, which is critical for maximizing the yield of liquid hydrocarbons—the target product for decarbonization.

Oxide catalysts are of considerable interest for tuning process selectivity, since their surface acidity or basicity directly influences the mechanism of C–C bond cleavage. Tran T. T. et al. [34] systematically investigated the effect of the nature of oxide catalysts on the pyrolysis of linear low-density polyethylene (LLDPE) in a laboratory batch reactor made of stainless steel equipped with a water condenser under an inert atmosphere (nitrogen). A comparison of thermal and catalytic processes was carried out in the range of 500–600 °C at a polymer:catalyst weight ratio of 10:1, testing acidic (Al_2O_3 , TiO_2) and basic (MgO , CaO) oxides. A key result, important for assessing the efficiency, was the critical effect of temperature and reaction time on the phase distribution of the products, established by the authors. In a purely thermal process, the liquid fraction (pyrolysis oil) with a yield of 44.31 mass % was recorded exclusively at 600 °C and a reaction time of at least 3 h, whereas at lower temperatures (500–575 °C), wax was the main product (60–78 wt.%). The use of oxide catalysts not only reduced the reaction time but also qualitatively changed the composition of liquid hydrocarbons. Al_2O_3 demonstrated the best performance: after just 2 h at 600 °C, the liquid fraction yield reached 31.68 wt.%, which contrasts with the zero liquid yield in the thermal process over the same time interval. Moreover, the catalytic liquid was characterized by significantly improved organoleptic properties—a transparent color and an odor reminiscent of gasoline, in contrast to the dark red-brown oil formed thermally. The GC-MS data confirmed that the introduction of Al_2O_3 shifts the hydrocarbon composition to the practically significant C_7 – C_{20} region, providing a balanced ratio of gasoline (C_7 – C_{12}) and diesel (C_{13} – C_{20}) fractions, while thermal pyrolysis yielded predominantly heavier

products. From the point of view of decarbonization, however, it is necessary to take into account the accompanying redistribution of carbon into undesirable products: in the presence of Al_2O_3 , the yield of the gas fraction increased to 46.98 wt.% (versus 33.69 wt. % in the thermal process for 2 h), and the yield of solid carbon residue increased more than twofold, to 21.15 wt.%. The main oxides (MgO and CaO) at a temperature of 600 °C for 2 h provided a liquid fraction yield of 29.64 and 35.08 wt.%, respectively, with a bias towards lighter hydrocarbons (mainly $\text{C}_7\text{--C}_{12}$), but provoked even more intense coke formation, especially in the case of MgO (28.64 wt.%). TiO_2 demonstrated complete inefficiency: no liquid was formed, and the yield of solid residue reached 72.17 wt.%. Thus, among the oxide systems studied, 10 wt.% Al_2O_3 at a temperature of 600 °C for 2 h represents a compromise solution that makes it possible to reduce the time for obtaining liquid fuel by a third and obtain a product with improved consumer characteristics in the $\text{C}_7\text{--C}_{20}$ range, albeit at the cost of increased gas and coke formation, which requires further optimization to improve the carbon efficiency of the process.

Among the oxide systems studied, the work of Mehdi et al. [35] stands out, in which the catalytic pyrolysis of HDPE waste was studied using mixed catalysts based on Fuller's earth and metal oxides (Fe_2O_3 , ZnO and NiO). The experiments were carried out in a cylindrical steel batch reactor (length 30.5 cm, diameter 15.2 cm) equipped with a loading lid, an expansion chamber and a condensation system for collecting liquid products. The process was carried out at a temperature of 300 °C for 30 min in a closed volume without the use of an additional gas environment, while the pressure in the system reached approximately 1.5 bar. Although the authors do not provide exact mass or molar ratios of the components, it is noted that the comparative analysis was carried out with equal contents of the clay base in the mixtures (ZnO + clay, Fe_2O_3 + clay and NiO + clay). Gas phase analysis using gas chromatography-mass spectrometry showed that the best catalytic properties were possessed by a composition based on iron (III) oxide and clay. Catalytic systems based on ZnO and NiO combined with clay demonstrated significantly lower activity.

In the context of searching for cost-effective and environmentally friendly solutions, the use of iron oxide (FeO) obtained from industrial waste is of particular interest. Hernandez-Fernandez et al. [36] demonstrated the feasibility of using FeO for the catalytic pyrolysis of hospital polypropylene waste (HPW) generated during the COVID-19 pandemic. The study was conducted using a TGA combined with a GC-MS, which served as a microreactor. Thermal decomposition of the samples was carried out in the temperature range of 40–900 °C at a heating rate of 10 °C/min in an inert nitrogen atmosphere (flow rate of 20 mL/min). To study the effect of catalyst concentration on the pathways of chemical transformations, five series of HPW mixtures (weighing 1 kg each) with different FeO loadings were prepared: 1.5 mg (sample HW-PP-0), 20 mg (HW-PP-1), 150 mg (HW-PP-2), 200 mg (HW-PP-3), and 400 mg (HW-PP-4). The mixtures were homogenized in an extruder at a temperature of 190–220 °C, after which granules were obtained for subsequent experiments. GC-MS analysis of the pyrolysis products revealed the formation of a wide range of compounds, including alkanes, alkenes, alkynes, alcohols, ketones, and carboxylic acids, with their distribution clearly correlated with the FeO content. At the minimum catalyst concentration (sample HW-PP-0), a yield typical of thermal cracking was observed: the total proportion of alkanes reached 35.65 wt.% (with the predominance of isopentane 13.5% and ethane 12.1%), and alkenes—63.7 wt.% with the dominance of propylene (58.3%). The content of oxygen-containing compounds and alkynes under these conditions was negligible (alcohols—0.12%, ketones—0.04%, carboxylic acids—0.2%, alkynes—0.3%). Increasing the FeO loading to 400 mg (sample HW-PP-4) radically changed the selectivity of the process: the yield of alkanes decreased to 8.87 wt.%, alkenes—to 42.3 wt.%, while the formation of oxidation and deep cracking products sharply intensified. The share of

alcohols increased to 28.1 wt.% (with identification of methanol 7.2% and n-propanol 4.8%), ketones—up to 9.8 wt.% (including 2-pentanone 2.8% and 2,4-pentadione 2.7%), carboxylic acids—up to 8 wt.% (mainly formic and acetic acids), and alkynes—up to 2.93 wt.%. Additional experiments on thermo-oxidative degradation in an oxygen atmosphere showed that, compared to an inert environment (nitrogen), the presence of FeO contributes to a significant increase in the yield of ketones (up to 9.8%) while suppressing the formation of alcohols. Based on the data obtained, the authors proposed a radical mechanism in which Fe^{3+} ions play a key role in the generation of various functional groups, which confirms the high catalytic activity of FeO and opens up prospects for the sustainable processing of contaminated medical polyolefins into valuable chemical products.

Among natural oxide systems, aluminosilicates and iron oxide-based minerals have attracted the attention of researchers. In the work of Eldahshory, A. I. et al. [37], a comparative study was conducted on the catalytic activity of three types of inexpensive natural materials—kaolin, hematite, and quartz sand (SiO_2 content > 97.21%)—in the process of recycled polypropylene (RPP) pyrolysis. Kaolin, which has proven itself as an effective catalyst for the destruction of polyvinyl chloride, was used as a comparison standard. The experimental results showed that an increase in the mass ratio of kaolin and RPP from 1:8 to 1:2 promotes an increase in the yield of the liquid fraction from 74.4 to 80.75 wt.%, while the yield of gaseous products decreases from 23.52 to 17.55 wt. %. A catalyst/feedstock ratio of 1:2 (liquid product yield of 80.75 wt.%) was found to be optimal for maximizing the pyrolysis oil yield. A further increase in the catalyst content to a ratio of 1:1 resulted in a decrease in the liquid product yield to 78.33 wt.%, indicating that any deviation from the optimum promotes gas formation. When using hematite, varying the ratio with waste polypropylene (WPP) from 1:8 to 1:2 increased the oil yield from 66.67 to 70 wt.%. A subsequent increase in the catalyst proportion to 1:1 resulted in a decrease in the liquid yield to 68.4 wt.%. The authors conclude that the use of hematite has little effect on increasing the oil yield under the studied conditions, which is consistent with literature data on the low efficiency of iron oxides at low heating rates and temperatures up to 600 °C. A different trend was observed for quartz sand, where an increase in its proportion in the mixture with WPP from 1:8 to 1:1 monotonically increased the yield of liquid products from 51.67 to 68 wt.%, while the gas yield decreased from 44 to 29.24 wt.%. The maximum yield of the gas phase (44 wt.%) was recorded precisely at the lowest content of quartz sand (1:8). For comparison, the basic non-catalytic pyrolysis of RPP provided a yield of liquid oil of 70 wt.%, gas of 24.3 wt.%, and solid carbon residue of 5.7 wt.%. A comparison of the maximum yields of the liquid fraction for the three studied catalysts revealed the following hierarchy of efficiency: kaolin (80.75 wt.%) > hematite (70 wt.%) > quartz sand (68 wt.%). It is noteworthy that the use of pure silicon dioxide (the main component of quartz sand) is ineffective in increasing oil yield, as this yield was lower than in the non-catalytic process (68 vs. 70 wt.%). A synergistic effect is observed with the introduction of Al_2O_3 into the silica matrix, as illustrated by the results for kaolin: the presence of an aluminosilicate structure provides a significant increase in liquid hydrocarbon yield compared to both the non-catalytic process and the use of pure SiO_2 or hematite.

An example of the effective application of mixed oxide systems in a hydrogen-free environment is the work of Xie X. et al. [38]. The researchers proposed a method for the catalytic pyrolysis of HDPE using a CuMgAlO_x catalyst. The process is carried out in a fixed-bed reactor under relatively mild temperature conditions (atmospheric pressure, 500 °C) with a controlled vapor residence time (60 s), which ensures virtually complete conversion of the polymer feedstock without the use of hydrogen or precious metals. The functional characteristics of the CuMgAlO_x catalyst distinguish it favorably from traditional zeolite-containing and individual oxide systems. The yield of liquid fuel reaches 85.7 wt.%,

and that of gaseous products is 12.6 wt.%, with coke formation minimized. This oxide catalyst dramatically alters the molecular weight distribution of the products: while non-catalytic pyrolysis converts polyethylene predominantly into solid waxes with a fraction content above C_{22} at 77.3%, the introduction of $CuMgAlO_x$ shifts selectivity toward lighter hydrocarbons. The proportion of heavy components decreases to 31.8%, resulting in the final product being a free-flowing liquid at room temperature rather than a waxy mass. The physicochemical characteristics of the resulting liquid product confirm its suitability for direct use as motor fuel. According to chromatographic analysis, the composition is dominated by alkenes (42.4%) and alkanes (39.6%), with an alkylaromatic content of 18%. The majority of hydrocarbons are concentrated in the C_6 – C_{22} range, with the yield of the C_6 – C_{22} fraction reaching 53.9% by weight. The product is characterized by a low kinematic viscosity ($1.8 \text{ mm}^2/\text{s}$), which ensures excellent flowability, a density of 823.8 kg/m^3 , and a pour point of -13°C . Particularly noteworthy is its high calorific value of 49.3 MJ/kg , which exceeds the typical range for commercial diesel fuel (42 – 46 MJ/kg) due to its high carbon and hydrogen content with minimal heteroatoms (oxygen and sulfur). A significant advantage of the $CuMgAlO_x$ catalyst is its operational stability. The catalyst demonstrates resistance to deactivation, maintaining high activity over five consecutive cycles of use without regeneration (after the fifth cycle, the liquid fuel yield remains at a high level of 79.1 wt.%).

Almeida and Marques [39] investigated the use of niobium oxide (Nb_2O_5) in the pyrolysis of polypropylene, polyethylene, and their mixtures in the study of oxide catalysts. Thermogravimetric analysis and experiments in a glass reactor revealed that Nb_2O_5 exhibited high catalytic activity, significantly accelerating the degradation of polyolefins. In the case of polypropylene, the introduction of niobium oxide reduced the onset temperature of decomposition from 386°C to 345°C , and at a temperature of 400°C , the time for complete conversion of the polymer mixture was reduced from 4 to 1 h, which represents a significant practical advantage.

However, a material balance analysis at 430°C revealed significant shortcomings in the catalytic system. In the thermal process, the yield of the liquid fraction was 25.7 wt.%, the solid residue was 10.3 wt.%, and the gas was 64.0 wt.%. With the addition of Nb_2O_5 , the liquid yield decreased to 13 wt.%, while the formation of solid residue increased to 28.3 wt.%, and the gas yield decreased to 48.7 wt.%. Thus, niobium oxide contributed to the intensification of coke formation reactions and suppressed the formation of the target liquid products. The composition of the liquid fraction, determined by gas chromatography, showed that thermal pyrolysis produces a wide range of hydrocarbons with a predominance of C_{13} (47%), C_{15} (21%), and C_{18} (17%). Catalytic pyrolysis with Nb_2O_5 did not significantly narrow the molecular weight distribution: the main components remained C_{13} (17%), C_{15} (23%), and C_{12} (9%), while the overall range still encompassed C_{10} – C_{18} . This indicates a lack of pronounced selectivity for Nb_2O_5 in the formation of light gasoline-type hydrocarbons. The authors attribute the observed catalytic effect to the presence of Lewis acid sites on the Nb_2O_5 surface, which are capable of activating carbon-carbon bonds and initiating their homolytic cleavage at lower temperatures compared to the non-catalytic process.

In the study of oxide catalytic systems for the pyrolysis of polyolefins, cobalt-containing materials based on individual and mixed oxide supports deserve special attention. Chattopadhyay et al. [40] investigated the catalytic co-pyrolysis of paper biomass and plastic mixtures including HDPE, polypropylene, and PET. The catalysts were synthesized by a co-precipitation method, depositing cobalt on aluminum oxide, cerium oxide, and a mixed oxide support CeO_2 – Al_2O_3 ; the resulting materials were characterized by low-temperature nitrogen adsorption and X-ray diffraction. A pronounced synergistic effect

was found in the co-pyrolysis of biomass and polyolefins: the proportion of liquid products increased with increasing plastic content in the feedstock mixture. The catalyst with the 40% Co/30% CeO₂/30% Al₂O₃ composition demonstrated maximum efficiency, achieving a hydrogen volume fraction in the gaseous products of up to 47%. The authors attribute this high activity to the optimal distribution of cobalt on the surface of the mixed oxide support, which ensures efficient cracking of hydrocarbon chains and subsequent steam reforming reactions of the resulting light hydrocarbons. These results clearly illustrate the potential of cobalt oxide catalysts with controlled surface morphology for hydrogen generation in the processing of mixed polyolefin-containing waste.

Thus, analysis of oxide catalytic systems demonstrates that this class of materials represents a practical alternative to microporous zeolites, overcoming diffusion limitations in the processing of bulky polymer chains. The key dilemma determining the direction of further research remains the tradeoff between achievable activity and the carbon efficiency of the process. Further progress in this area is associated with the targeted design of mesoporous and mixed oxides whose acid-base centers are optimized for the selective cleavage of C–C bonds in polyolefin macromolecules with maximum carbon conservation in target liquid products, which is fully consistent with the principles of a circular carbon economy.

3.3. Metal–Organic Frameworks

Metal–organic frameworks (MOFs) are a class of crystalline porous materials constructed from inorganic units (metal clusters) and organic linkers. Due to their unique properties—high porosity, ordered structure, the possibility of functionalization, and tunable acid-base properties—MOFs are finding increasing application in catalysis, including polymer waste recycling processes [41–43]. These technologies are in the active research and development stage, but have already shown promising results for the depolymerization of plastic waste, including for the pyrolysis they catalyze, in laboratory conditions [43–46]. MOFs, despite their enormous utility in heterogeneous catalysis, are rarely used in the depolymerization of polyolefins due to their suspected thermal instability and the inability of polyethylenes and polypropylenes to penetrate their pores.

Heng J. Z. X. et al. [47] demonstrated the possibility of using zirconium MOF (UiO-66) containing coordinatively unsaturated zirconium units as effective catalysts for the pyrolysis of PE and PP. It was found that the use of this type of catalyst significantly increases the yield of liquid and gaseous hydrocarbons, while reducing the amount of residual solids formed by almost 2 times. Although ZIF-8 (Zeolitic Imidazolate Framework-8), consisting of Zn²⁺ ions linked by imidazolate linkers, is not a classical catalyst for the pyrolysis of polyolefins, its use in the pyrolysis of polyvinyl chloride (PVC) demonstrates the potential of MOFs for the treatment of mixed plastic waste [48]. ZIF-8 was shown to effectively capture chlorine (in the form of HCl) during the pyrolysis of PVC, achieving an HCl removal rate of up to 89.5% at 300 °C. This is important because polyolefins are often contaminated with PVC, and the released HCl causes corrosion of equipment and poisons catalysts.

The article [49] presents the results of using a new hybrid nanocatalyst, GMOF (Graphene Oxide—Metal–Organic Framework), for the catalytic conversion of high-density and low-density polyethylene waste. The catalyst was synthesized by growing cerium (Ce)-based MOF rods on a flake-like graphene oxide (GO) structure. During catalytic pyrolysis in the fast pyrolysis mode (temperature 500 °C, holding time 1 min), the GMOF catalyst demonstrated high activity in polymer pyrolysis reactions. For HDPE, the selectivity for the C₂₁–C₄₀ and C₄₀₊ fractions is reduced, while the yield of C₁–C₂₀ hydrocarbons (including olefins) increases by almost 2 times, and the selectivity for CO₂ formation increases. For LDPE, an intensification of CO₂ is also observed, and the main gaseous products are propane and propylene. The authors explain the catalyst's efficiency by the synergistic

effect of its components—a high specific surface area and an ordered porous structure due to the use of MOF—while the use of Ce helps reduce coke formation.

The authors [50] developed a highly efficient Ni/Al-MOF-derived catalyst based on MOF for the pyrolysis of PP, the main component of medical masks. Catalytic pyrolysis of pure PP and whole surgical masks was carried out in a horizontal fixed-bed reactor (made of stainless steel) at temperatures of 450–550 °C under a nitrogen atmosphere with a catalyst/feedstock ratio of 1 to 10. When using surgical mask waste as a feedstock, the whole mask (without the nose clip) was placed at the bottom of a quartz tube, and the reactor was first heated to a predetermined temperature (450 °C, 500 °C, or 550 °C), then quartz containing the feedstock and catalyst was fed into the middle of the reactor. It was found that the maximum yield of liquid hydrocarbons (72.8% for PP and 58.9% for masks) was achieved using a catalyst with a 5% Ni loading and a temperature of 450 °C. The catalyst facilitated cracking and dehydrogenation reactions, ensuring the selective formation of target hydrocarbons in the gasoline (C₅–C₁₁) and diesel (C₁₂–C₂₀) ranges. Uniform distribution of nanosized Ni particles on a highly porous Al₂O₃ support was identified as a key factor maximizing catalytic efficiency.

It should be noted that, despite previous concerns regarding thermal stability and active site availability, the studies reviewed reveal the significant potential of metal–organic frameworks as highly efficient oxide catalyst systems for the pyrolysis of polyolefins. Particularly noteworthy is the hybrid nanocomposite design strategy, where the synergy of inorganic MOF units with oxide substrates (such as graphene oxide) or nanoscale metal centers enables fine-tuning of selectivity for gasoline and diesel fractions while simultaneously reducing coke formation. The transition from the pyrolysis of pure polymers to the recycling of real multicomponent waste, such as medical masks, confirms the versatility and industrial relevance of MOF-containing oxide catalysts, opening new prospects for creating a closed carbon cycle in the plastics economy.

3.4. Homogeneous Catalysts

While heterogeneous systems dominate pyrolysis research due to their operational advantages, homogeneous catalysis occupies a unique historical and methodological niche in polyolefin degradation. Interest in these catalysts within the context of decarbonization stems from inherent diffusion limitations: the extremely high viscosity of polymer melts hinders interfacial contact with solid catalyst surfaces. In contrast, homogeneous systems, molecularly dispersed in the reaction medium, can maximize heat and mass transfer rates, potentially reducing energy consumption and aligning the process with ‘clean technology’ criteria.

Homogeneous catalysts are rarely used in the pyrolysis/thermolysis of PE and PP due to their decomposition at high temperatures. Interestingly, the same catalysts used for the synthesis of PE and PP are also capable of catalyzing their degradation. Metallocenes (metallocene complexes of Group IV transition metals in combination with methylaluminoxane, MAO) are classic homogeneous catalysts for olefin polymerization [51]. It has been shown [51] that metallocene catalysts (e.g., Cp₂ZrCl₂/MAO) can, under certain conditions, promote the cleavage of carbon–carbon bonds in polyolefins, acting through the mechanisms of β-elimination and metallocene-alkyl exchange. However, their use in high-temperature pyrolysis is difficult due to their thermal degradation at temperatures above 200–250 °C.

A separate class is represented by metal octoates, salts of 2-ethylhexanoic acid that are soluble in the polymer melt. At pyrolysis temperatures (>300 °C), they decompose to form nanosized oxides or metals, which then act as heterogeneous active centers. It has been shown that tin 2-ethylhexanoate (tin octoate, Sn(Oct)₂) exhibits some efficiency

in the depolymerization reaction of plastic waste [52–54]. Yao et al. [55] studied the pyrolysis of tert-butyl peroxy-2-ethylhexanoate, a compound structurally related to octoates, and showed that the process involves several stages with different activation barriers. For metal octoates, thermal decomposition can lead to the in situ formation of active heterogeneous species, which then catalyze further polymer pyrolysis. Cobalt, manganese, and iron octoates are known as siccatives (oxidation catalysts). In the presence of oxygen, they can catalyze the oxidative pyrolysis of polyolefins. Oxidative pyrolysis leads to the formation of oxygen-containing products (aldehydes, ketones, carboxylic acids), and not only hydrocarbons. However, systematic studies of the influence of the nature of the metal cation in octoates on the mechanism of polyolefin pyrolysis are still lacking. Only a few studies have been published on the oligomerization of olefins using Co, Mn, Zn, Ca, Ba, Li, Zr, Cu, and Pb octoates [56,57].

3.5. Comparative Analysis of Catalytic Systems for the Pyrolysis of Polyolefins

To compare all the considered classes of catalysts (zeolites, oxides, metal–organic frameworks and homogeneous systems) and to facilitate the selection of the optimal strategy depending on the target products and process conditions, a summary Table 2 is presented below. The data are systematized according to the key parameters discussed in Sections 3.1–3.4.

Table 2. Comparison of the efficiency of different classes of catalysts in the pyrolysis of polyolefins (PE, PP) based on the data presented in this paper.

Parameter	Zeolite Catalysts	Oxide Catalysts	Metal–Organic Frameworks	Homogeneous Catalysts
Examples	HZSM-5, HY, H-Beta, MCM-41	Al ₂ O ₃ , MgO, CaO, kaolin, CuMgAlO _x , Nb ₂ O ₅ , FeO	UiO-66 (Zr), GMOF (Ce-MOF + GO), Ni/Al-MOF	Metallocenes (Cp ₂ ZrCl ₂ /MAO), tin octoates (Sn(Oct) ₂), Co, Mn, Fe
Activation/pyrolysis temperature	340–500 °C (a decrease of 75–100 °C compared to the thermal process)	500–600 °C (Al ₂ O ₃ , CuMgAlO _x); 300 °C (Fuller’s earth + oxides)	450–550 °C (Ni/Al-MOF); 500 °C (GMOF)	>300 °C (octoates are decomposed in situ); metallocenes degrade >200–250 °C
Products	Light olefins (C ₂ –C ₄), aromatics (up to 58 wt.%), gasoline (C ₅ –C ₁₂) Light olefins (C ₂ –C ₄), aromatics (up to 58 wt.%), gasoline (C ₅ –C ₁₂) and diesel fractions; wax is virtually absent	Mixture of C ₇ –C ₂₀ , alkanes/alkenes, diesel fuel; on basic oxides—more coke and gas, on CuMgAlO _x —a high proportion of alkenes and alkanes	Increased yield of C ₁ –C ₂₀ (olefins), CO ₂ ; hydrocracking to gasoline (C ₅ –C ₁₁) and diesel (C ₁₂ –C ₂₀) fractions; reduction in heavy waxes	A wide fraction of paraffins and olefins. In the presence of O ₂ —oxidative pyrolysis with the possible formation of ketones, acids, and alcohols in the case of PP
Resistance to coking/deactivation	Rapid decontamination	High for CuMgAlO _x (5 cycles without regeneration); low for Nb ₂ O ₅ (coke growth); moderate for Al ₂ O ₃	Better than zeolites	Not applicable (homogeneous systems are not regenerated, thermally unstable)
Regenerability	Possible (calcination in air); however, optimization is required to preserve the pore structure and surface acidity	CuMgAlO _x is stable for 5 cycles; for the others, regeneration is possible, but not detailed.	Potentially possible	Not applicable
Restrictions	High aromatization of products, cost of synthetic zeolites, sensitivity to impurities	Low selectivity for simple oxides (Al ₂ O ₃ , TiO ₂), high gas/coke yield for MgO, CaO	Thermal instability, complexity of synthesis, little study on real waste	Destruction at >250 °C, no regeneration possible, no industrial application for polyolefin pyrolysis

The presented data show that zeolites (especially modified and hierarchical ones) currently provide the best selectivity control at moderate temperatures, but are susceptible to coke formation. Oxide systems (e.g., CuMgAlOx and natural kaolin) provide high liquid yields with greater stability, although they are inferior to zeolites in selectivity for light olefins. MOFs are a promising but still immature class, requiring proof of long-term stability. Homogeneous catalysts for high-temperature pyrolysis of polyolefins are practically unusable due to thermal degradation and the lack of regeneration, and their role remains rather historical or niche (e.g., in mild solvolysis or oxidation processes). The choice of the optimal catalyst should be determined by the target product (olefins, gasoline, or diesel fuel) and the quality of the polyolefin feedstock (degree of contamination, presence of PVC, etc.).

Comparison of various catalytic systems allows identification of a key parameters set that determine the efficiency of catalytic depolymerization of polyolefins (Table 3).

Zeolites operate via a carbenium ion mechanism, which requires initial olefin formation (thermal or catalytic). Protonation of the double bond at the Brønsted acid sites results in the formation of a carbenium ion, which then undergoes β -cleavage, isomerization, hydrogen transfer, cyclization, and aromatization. This ensures high selectivity for light olefins (C₂–C₄) and aromatic hydrocarbons, but provokes rapid coking due to secondary condensation reactions in narrow pores. Diffusion limitations are particularly critical for long polyolefin chains.

Oxide catalysts, especially mesoporous and mixed oxides, predominantly follow a radical or acid-base mechanism. Heterolytic or homolytic cleavage of the C–C bond occurs at surface sites with lower activation energy than in a thermal process. Mesopores allow macromolecules to more easily penetrate to the active sites, reducing coke formation. Many oxides (e.g., CuMgAlOx) exhibit high yields of liquid hydrocarbons (up to 85 wt.%), with a predominantly diesel fraction, but their catalytic activity is generally lower than that of zeolites.

MOFs combine coordination chemistry and porosity. The mechanism involves coordination activation of the C–C bond on unsaturated metal sites, enabling depolymerization under milder conditions. However, their use is limited by thermal instability: many MOFs decompose above 400–450 °C, which is comparable to typical polyolefin pyrolysis temperatures. Homogeneous catalysts are attractive due to the absence of diffusion barriers, but at pyrolysis temperatures they decompose, effectively transforming the reaction into a heterogeneous phase. Metal octoates produce significant amounts of oxygenated compounds, which reduces the quality of fuel fractions.

Thus, it is suggested that there are several universal characteristics that determine the efficiency of depolymerization: (i) the concentration and accessibility of active sites (acidic, basic or metallic), which determine the frequency of transformation events and the reaction mechanism; (ii) the porous architecture (micro-, meso- or hierarchical), which controls the transport of bulk polyolefin chains and intermediates; (iii) thermal stability under pyrolysis conditions (usually 400–600 °C); (iv) resistance to coke formation and poisoning by heteroatoms, which determines the service life of the catalyst and the possibility of its regeneration.

Table 3. Key characteristics of catalysts that promote depolymerization of polyolefins.

Catalyst Class	Typical Depolymerization Mechanism	Active Centers	Key Feature	Effect on Depolymerization
Zeolites	Carbenium ion mechanism	Brønsted acid sites (Al in the framework), Lewis sites	SiO ₂ /Al ₂ O ₃ ratio	Balance between activity and resistance to coking
			Pore topology	Determine the molecular weight of products and the aromatic content
			Hierarchical porosity	Reduces diffusion limitations, decreases T ₅₀ by 60–90 °C
			Density of strong Brønsted centers	Promotes intra-chain scission, increases the proportion of paraffins
Oxide catalysts	Radical or concerted mechanism of C–C cleavage at acid–base sites; for metal oxides—redox mechanism	Surface OH groups (acid/base), metal cations (Lewis), oxygen vacancies	Acid–base nature of the surface	Acidic: higher liquid yield (C ₇ –C ₂₀); basic: more coke
			Specific surface area	Improves access for polymer chains, liquid yield up to 85 wt. %
			Oxidation–reduction activity (oxygen vacancies)	Initiates radical cracking; excess leads to overoxidation
MOF (UiO-66, ZIF-8, GMOF, Ni/Al-MOF)	Coordination activation of the polymer chain on unsaturated metal clusters → polarization of the C–C bond → β-alkyl transfer or radical pathways; synergy with graphene oxide	Unsaturated metal centers (Zr, Ce, Ni), structural defects	Coordinationally unsaturated metal sites	Active sites for C–C cleavage
			Synergy with a hybrid carrier	Increases selectivity for C ₁ –C ₂₀ (up to 2 times)
			Thermal stability	Allows catalytic pyrolysis without decomposition
Homogeneous catalysts (metallocenes, metal octoates)	β-Elimination from a metal-alkyl intermediate (metallocenes); thermal decomposition to nanooxides (octoates) followed by radical cracking	Molecular centers of metals dispersed in the melt	Solubility in polymer melt	Maximizes heat and mass transfer
			Thermal decomposition range	Determines applicability at pyrolysis temperatures
			In situ formation of nanoparticles	Creates active heterogeneous centers in the melt

3.6. Industrial and Pilot Projects for Chemical Processing of Polyolefins

The transition of polymer waste pyrolysis technology, including polyolefin waste, from the laboratory to the industrial scale is a key indicator of its maturity and compliance with circular economy principles. Although fundamental research into degradation mechanisms and the search for optimal catalytic systems continues to advance rapidly, a steady trend toward process scaling has been observed in recent years. The portfolio of existing, under-construction, and planned polyolefin chemical recycling plants worldwide demonstrates a shift from isolated pilot tests to the creation of industrial clusters integrated into traditional petrochemical chains (Table 4).

Table 4. Current and planned projects for the pyrolysis of polymeric materials, in particular polyolefins [15,58–62].

Company	Development Stage	Technology	Production Capacity	Raw Materials	Target Product
BASF (ChemCycling)	Industrial	Pyrolysis + steam cracking	Large-scale (up to 100 thousand tons/year of pyrolysis oil)	Mixed plastics, polyolefins	Monomers, chemicals
Plastic Energy	Industrial	Thermal anaerobic pyrolysis	2 plants in Spain (each with a capacity of ~20,000 tons/year)	Polyolefins, mixed plastics	Pyrolysis oil
SABIC (TRUCIRCLE)	Industrial	Pyrolysis + mass balance	Joint venture with Plastic Energy (Geleen, NL)	Mixed plastics, polyolefins	Circular polymers
Mura Technology (HydroPRS)	Demo-scale to industrial-scale	Hydrothermal pyrolysis (HydroPRS)	80,000 tons/year (under construction)	Polyolefins	Oils, chemicals
Dow Chemical	Industrial (in collaboration with partners)	Fluidized bed pyrolysis	Large capacities are planned	Polyolefins	Olefins, naphtha
LyondellBasell (MoReTec)	Demo-scale to industrial-scale	Molecular recycling	50,000 tons/year (under construction, Wesseling)	Polyolefins	Olefins, monomers
Braven Environmental	Industrial	Thermal pyrolysis	65,000 tons/year	Plastic waste	Diesel fraction
Quantafuel	Demo-scale	Catalytic pyrolysis	Pilot (Denmark) + industrial under construction	Polyolefins	Pyrolysis oil
Pyrum Innovations	Demo-scale	Thermal pyrolysis	Pilot installations	Mixed plastics, polyolefins	Oil, gas, carbon black
Agilyx Corporation	Demo-scale	Pyrolysis	Demonstration installations	Polystyrene, polyolefins	Monomers, oils
KIT (Karlsruhe)	Pilot stage	Bubbling fluidized bed	Pilot installation	Mixed plastics	Oils, gases, waxes
University of Hamburg	Laboratory/Pilot stage	Fluidized bed pyrolysis	Pilot	Polyolefins	Olefins C ₂ –C ₄
UPV/EHU (Spain)	Pilot stage	Rotating cone reactor integrated with a bubbling fluidized bed	Pilot	PE, PP	Oils, olefins
University of Minnesota	Laboratory/Pilot stage	Microwave pyrolysis, catalytic pyrolysis	Pilot	Polyolefins, biomass/plastic	Fuels, aromatics
Fraunhofer UMSICHT	Pilot stage	Pyrolysis, catalytic cracking	Pilot	Polyolefins	Chemical products

Leading petrochemical corporations are currently shaping the chemical recycling industry by investing in large-scale capacity. A prime example is BASF's ChemCycling project, which integrates pyrolysis oil obtained from mixed plastic waste, including polyolefins, as a secondary feedstock directly into steam cracking units. This approach utilizes existing infrastructure and enables the production of virgin polymers using mass balance, which is crucial for ensuring circularity without compromising the performance properties of the materials. A similar strategy has been implemented by SABIC (TRUCIRCLE) in cooperation with Plastic Energy.

In parallel with projects aimed at producing monomers, the field of processing polyolefins into target liquid hydrocarbons is developing, which can be used as components of motor fuels or as intermediates for further catalytic upgrading. Braven Environmental, which operates an industrial thermal pyrolysis plant with a capacity of 65,000 tons per year, is focused on producing diesel fraction from a wide range of plastic waste, confirming the economic viability of this model, provided there is a stable feedstock flow and favorable energy market conditions.

This review focuses particularly on projects that directly utilize catalytic systems in the pyrolysis stage. Quantafuel was one of the first to scale up the catalytic pyrolysis of polyolefins, implementing a pilot plant and initiating construction of an industrial plant. Quantafuel's technology involves contact of decomposition vapors with a heterogeneous catalyst, which enables deeper cracking of waxes and increases the yield of light, shelf-stable liquid products compared to conventional thermal processes. This example validates the fundamental research discussed in Sections 3.1–3.4 and demonstrates the industrial demand for scientific research in optimizing the acidic and structural properties of catalysts.

An innovative offshoot is the HydroPRS hydrothermal pyrolysis technology developed by Mura Technology. Unlike conventional processes, Mura Technology uses supercritical water as the reaction medium, ensuring efficient heat transfer and selective cleavage of polyolefin chains, producing stable hydrocarbon oil. The 80,000-ton-per-year plant under construction represents the world's first attempt to commercialize a hydrothermal route for chemical recycling of polyolefins.

Despite significant progress, commercial deployment of catalytic pyrolysis is still limited by systemic barriers. A key technological challenge remains catalyst deactivation caused by coke formation and the presence of heteroatomic impurities in real, unsorted waste streams. Maintaining the activity of catalytic systems under industrial conditions requires efficient and cost-effective regeneration protocols or a transition to two-stage schemes where primary thermal cracking precedes catalytic vapor upgrading, as implemented, for example, in the LyondellBasell (MoReTec) approach and being developed in Fraunhofer UMSICHT pilot plants. Furthermore, an essential condition for the investment attractiveness of these projects is the creation of a stable regulatory framework recognizing chemical recycling products as secondary raw materials, and the development of an EPR system that guarantees a sustainable supply of polyolefin waste. Thus, the industrial scaling of catalytic pyrolysis occurs in a close relationship between technological innovations, market mechanisms, and legislative initiatives, which together determine the pace of the transition to a closed cycle in the plastics industry.

4. Conclusions

This review systematically analyzes the current state of research and industrial implementation of catalytic pyrolysis of polyolefins (LPDE, HPDE and PP) as a key tool for decarbonization and the transition to a circular plastics economy. The data obtained convincingly demonstrate that this technology is moving beyond fundamental research and into pilot-scale and commercial implementation. A critical advantage of catalytic pyrolysis over traditional thermal pyrolysis and combustion is the ability to flexibly control process selectivity through the rational design of catalytic systems and the choice of phase contact process flow (single-stage or two-stage).

The technological maturity of the catalytic pyrolysis of polyolefins is demonstrated by a growing portfolio of industrial and demonstration projects worldwide. Despite this progress, large-scale commercialization faces several systemic barriers: (i) catalyst deactivation due to coke formation and heteroatom poisoning from real waste streams; (ii) recycling of mixed polyolefin waste containing PVC or PET; (iii) the need for energy-efficient and

cost-effective catalyst regeneration protocols; and (iv) the inadequate regulatory framework for recognizing chemical recyclates as secondary raw materials.

To bridge the gap between laboratory research and industrial design, this review proposes a multifactorial decision-making algorithm that links waste characteristics (composition, degree of degradation, presence of hazardous additives) with the optimal recycling route—mechanical recycling, selective dissolution, or chemical recycling (thermal/catalytic pyrolysis). This algorithm reduces uncertainty during scaling and facilitates the integration of catalytic pyrolysis into existing waste management systems.

Looking ahead, successful decarbonization of the plastics industry will depend on the convergence of several areas: the development of catalysts with hierarchical porosity, resistant to deactivation and capable of processing shallowly sorted streams; the validation of predictive kinetic models on real waste mixtures; life-cycle assessments confirming climate benefits compared to incineration or landfill; and the harmonization of EPR systems that ensure a stable supply of raw materials and market demand. Catalytic pyrolysis of polyolefins is no longer a future prospect, but an emerging industrial reality. Focused development of this interdisciplinary field, which lies at the intersection of solid-state chemistry, polymer degradation kinetics, and chemical engineering, has the potential to transform polyolefin waste from an environmental problem into a valuable man-made resource, close the carbon cycle, and contribute to the achievement of SDG 12 (responsible consumption and production) and SDG 13 (climate action).

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Abbreviations

The following abbreviations are used in this manuscript:

PE	Polyethylene
PP	Polypropylene
SAF	Sustainable aviation fuel
EPR	Extended producer responsibility
LDPE	Low-density polyethylene
HDPE	High-density polyethylene
TGA	Thermogravimetric analyzer
PET	Polyethylene terephthalate
MAO	Methylaluminoxane
PVC	Polyvinyl chloride
GC-MS	Gas chromatograph mass spectrometer
SDG	Sustainable development goals

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