Review

Chemical Recycling and Upcycling of Waste Plastics: A Review

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ABSTRACT: The indiscriminate disposal of plastic waste represents a significant environmental hazard. Conventional remediation techniques, such as landfilling and incineration, also encounter limitations and are unable to adequately address the pollution issue. Chemical recycling and upcycling represent an effective method for the degradation of plastics into oligomers and subsequent transformation into other product substances. This review provides an overview of the various chemical treatment methods currently in use, from the earliest thermal degradation techniques to the emerging strategies. The conventional techniques for thermal degradation of discarded plastics frequently encounter difficulties due to the necessity for elevated temperatures, substantial energy consumption, and the generation of a heterogeneous product mixture. Significant advances have been made in the fields of catalytic solvolysis, hydrotreating, and oxidative cleavage for the recycling and upcycling of plastics under mild conditions. This review provides a comprehensive overview of the chemical treatment methods currently employed for plastics, with a particular focus on the principles and current developments, as well as the reaction mechanisms involved. Additionally, it offers a detailed introduction to various advanced catalytic technologies and the catalysts utilized. Finally, it presents prospective outlooks for different methods, based on their current development status and the gap between actual needs.

Keywords: Plastics waste; Solvolysis; Hydrotreating; Oxidative cleavage; Recycling; Upcycling

1. Introduction

Since the advent of large-scale plastic production in the 1950s, these materials have made a substantial impact on modern society, largely due to their distinctive functional properties [1]. However, the excessive utilization of plastics and the absence of effective recycling techniques over the past few decades have led to their widespread dispersion in the natural environment. It has resulted in significant environmental contamination and posed considerable health risks to humans [2].

Therefore, how to effectively achieve the recycling and treatment of plastics has become an urgent task. This has prompted a comprehensive investigation into the degradation of plastics to minimize their environmental impact [3], including physical treatment [4], chemical treatment [5], and biological treatment [6]. In the context of physical-mechanical recycling, plastic waste is collected, ground into polymer particles, and subsequently reused for the production of plastic products. While mechanical treatment is a relatively straightforward and convenient process, it has the potential to impair the quality of the plastic due to the occurrence of polymer chain breakage or cross-linking. These phenomena can be attributed to thermal, mechanical, and other forms of contamination that may arise during the mixing procedure [7]. The biodegradation of plastics is distinguished by the utilization of green and low-energy consumption processes. The utilization of microorganisms for the degradation of polyester plastics (including polyethylene terephthalate (PET), polyurethane (PU), polylactic acid (PLA), and others) represents a sustainable approach to this process [8]. Nevertheless, the biodegradation of plastics is hindered by inadequate degradation and prolonged degradation cycles. In the case of polyolefin plastics (polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), polystyrene(PS), etc.), the structure of high hydrophobicity resulting from C-C bonds leads to effective biodegradation during the actual biodegradation process [9].

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Compared with these technologies, chemical recycling represents a potential avenue for facilitating a circular economy and closed-loop treatment of plastic waste. The process of chemical degradation recycling offers many advantages, including efficiency and speed, when treating waste plastics. These are fractured and degraded into small molecule compounds through the application of heat, light, electricity, or other chemical processes [10]. The most commonly employed chemical treatments for waste plastics are pyrolysis [11], solvolysis [12], hydrotreating [13] and oxidative cleavage [14].

We searched using the keywords plastic and chemical upcycling or recycling, then collated the relevant literature over the last decade (Figure 1). It can be seen that research on this topic has increased over the years. The review examines recent developments in the chemical recycling of a range of discarded plastics, as well as the most significant innovations in chemical recycling that have emerged over the past few years. These include pyrolysis, solvolysis, hydrotreating and oxidative cleavage. We focus on the mechanistic details of a large number of chemical recycling transformations at the forefront of the field. Firstly, the review presents an overview of the development status within the mature fields of pyrolysis and solvolysis. It then proceeds to discuss the development in the emerging fields of hydrotreating, photocatalysis, and electrolysis. Finally, we examine the chemical-biological cascade treatment of plastic waste, illustrating its potential for interdisciplinary applications. In conclusion, we present a summary of the prospective evolution and challenges associated with the degradation of plastic chemicals.

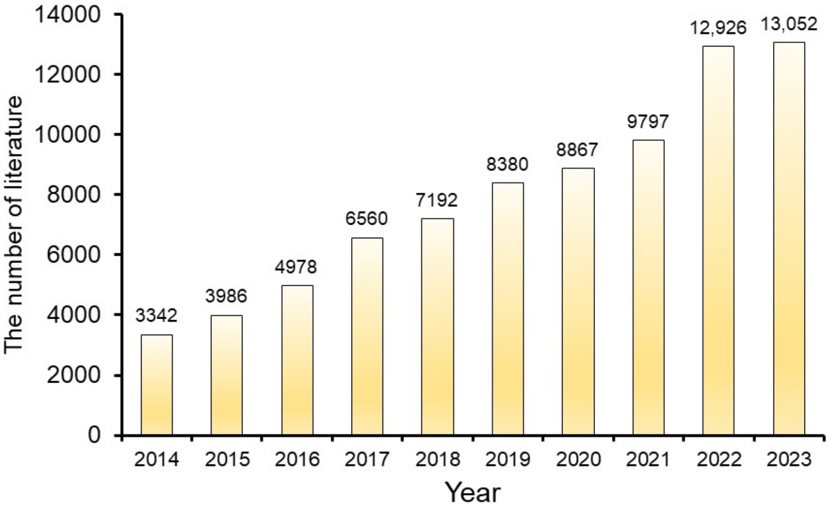

Figure 1. The number of literature published in recent years (Data sources: Web of Science, Topic: “chemical recycling” OR “chemical upcycling” AND “plastic”).

2. Pyrolysis

Pyrolysis represents a significant method of chemical recycling for plastic waste. In comparison to landfill and incineration, pyrolysis has the potential to significantly minimize the emission of harmful gases. Furthermore, the commercialization of pyrolysis products can be achieved in a relatively short timeframe [11]. Pyrolysis is conducted at a specific temperature and pressure. The liquid oil produced by pyrolysis can be employed as a direct fuel source, representing the most significant high-value end product. The residual carbon can be used as fuel or adsorbent materials [15]. This chapter examines recent advances in the pyrolysis of plastics, with a particular focus on the selective upcycling of waste plastics into high-value products such as liquid fuels or hydrocarbons.

2.1. Conventional Pyrolysis

Conventional pyrolysis may be defined as the reaction of plastics at medium to high temperatures (usually >500 °C) in an atmosphere with or without gases. Pyrolysis is well-established and used industrially for the treatment of plastic waste. It has the potential to significantly increase the recovery rate of plastic waste in comparison to landfill and incineration [16]. Furthermore, it can be employed for the remediation of mixtures of plastic waste that are unsuitable for mechanical recycling. Pyrolysis is a process that can be used to convert plastics into high-value chemicals, such as fuel oil, under a high temperature and pressure. This process can achieve high recycling rates and rapidly break down the chains of the plastic polymers, producing valuable chemicals.

The pyrolysis of PVC results in the production of approximately 50 wt% hydrogen chloride (HCl), along with a range of hydrocarbons, including toluene and benzene. These by-products are suboptimal for the manufacture of liquid products [17]. The presence of harmful HCl and its derived intermediates has given rise to significant environmental concerns. In contrast, the pyrolysis of PE has been observed to yield significant quantities of paraffins and olefins, with relatively smaller yields of naphthenes and aromatics. The pyrolysis products of PP are primarily composed of isoparaffins and iso-olefins. PS exhibits a high yield of liquid oil during pyrolysis, which is rich in aromatic compounds such as styrene. This suggests that PS has the potential to be used in the production of high-value chemicals [18].

Despite the operational simplicity of pyrolysis, the main challenge is the frequent occurrence of side reactions. This results in not only an expansion of products available but also a parallel increase in energy consumption. Furthermore, the complexity of pyrolysis is primarily attributable to the involvement of diverse reaction mechanisms, including end-chain depolymerization, random-chain depolymerization, and side-chain elimination. The interaction of these mechanisms renders a comprehensive understanding of the pyrolysis and an exhaustive summary of the mechanism an exceptionally challenging work.

2.2. Catalytic Pyrolysis

Catalytic pyrolysis employs a catalyst to regulate the reaction process and the distribution of products, achieving the breakage of polymer molecular chains. The incorporation of a catalyst serves to reduce the requisite temperature for the reaction, while simultaneously decreasing the energy consumption. Furthermore, the product sorts can be reduced and the product distribution can be optimized to achieve the enrichment of the target product [19].

In the field of catalytic pyrolysis of plastics, zeolite molecular sieve catalysts have been the subject of extensive research activity due to their highly efficient catalytic activity and selectivity. Indeed, they have constituted the dominant research direction in this field for the past decades. The most commonly used zeolite molecular sieve catalysts include ZSM-5, HZSM-5, Y-type molecular sieves, HY. Furthermore, a range of materials, including metal compounds, clays, terracotta, and activated carbon, have been extensively investigated for their potential use in the catalytic pyrolysis of waste plastics [20]. The pyrolysis products are complex and are primarily composed of light alkanes (C1–C4); light olefins (C2–C4); non-aromatic hydrocarbons (C5–C11); and aromatic compounds (C6–C11) and heavy oils (>C20) [21].

On this basis, Wang proposed a tandem catalytic pyrolysis method with dual catalysts (MCM-41 and HZSM-5) combining in-situ and non-in-situ catalysis [22]. The pre-conversion of MCM-41 has been demonstrated to inhibit the formation of polycyclic aromatic hydrocarbons (PAHs), increasing higher yields of xylenes and effectively reducing the coke yield. Furthermore, the utilization of internal acid sites was enhanced, resulting in the production of high yields of BTEX. The selectivities of total aromatics and monocyclic aromatics were found to be 100% and 85%, respectively. Subsequently, Wang investigated tandem catalytic pyrolysis of chlorine-containing mixed plastics for the production of monocyclic aromatic hydrocarbons in high yields [23]. The synergistic mechanism of hydrothermal pretreatment with a carbon-based catalyst (Fe/Ni/Mo@N/C) and zeolite (HZSM-5) in tandem catalysis has been established. The hydrothermal pretreatment reduced the pyrolysis activation energy of chlorine-containing mixed plastics, facilitated the β-cracking and alkylation reactions, and enhanced the yields of toluene and xylene, with selectivities of 84.09% and 71.29%, respectively. The combination of pretreatment and catalysis resulted in a significant enhancement in the yield of xylene, reaching 351.97 mg/g. This represents a 9.52-fold increase compared to the yield obtained through thermal cracking.

The selection of appropriate catalysts and the optimization of reaction conditions can not only reduce the generation of deleterious by-products but also enhance the economic and environmental viability of catalytic pyrolysis, which provides an efficacious pathway for the resourceful utilization of waste plastics.

2.3. External Field-Assisted Pyrolysis

In addition to conventional pyrolysis and catalytic pyrolysis, new approaches to heating methods have been introduced in recent years. In conventional heating processes, heat is typically supplied externally and transferred from the surface of the material to the interior through the mechanisms of conduction, convection, and radiation. Consequently, the efficiency of the heating process is largely contingent upon the intrinsic thermal conductivity of the material. External field-assisted pyrolysis is a technique that facilitates pyrolysis by introducing an additional energy field. The application markedly enhanced the rate, selectivity and quality of the resulting products. Compared to pyrolysis, microwave-assisted pyrolysis represents a more environmentally friendly and sustainable approach [24]. This method utilizes microwave energy to directly excite the molecules in the material, which results in rapid and uniform heating, avoiding overheating and uneven heating [25]. Furthermore, it can be combined with renewable energy sources, including solar, wind, ocean, geothermal, hydroelectric and bioenergy sources, which can be reacted at ambient pressures and temperatures.

In this study, microwave radiation and the iron-based catalyst FeAlOx were employed in a dual capacity, serving both as a catalyst and a microwave receptor material to initiate the catalytic deconstruction process. A one-step method was employed to transform mechanically pulverized commercial plastic samples into hydrogen and multi-walled carbon nanotubes within 30–90 s, with an emphasis on resolving local interfacial thermal effects and carbon nanotube formation mechanisms [26]. The final hydrogen yield was as high as 55.6 mmol/$g_{plastic}$, with the extracted hydrogen representing more than 97% of the theoretical mass.

Jiang devised a method for the synthesis of O vacancy-enriched CoO/porous carbon catalysts via microwave pyrolysis of PET waste through the incorporation of the microwave absorber cobalt nitrate and carbonized α-cellulose [27]. For industry, microwave-assisted heating offers varieties advantages in conditioning, rapid, selective and precise heating at low production costs. Given that no supplementary energy, the energy-dense by-products from microwave-assisted pyrolysis can be employed for recycling purposes, to generate microwave power through combustion and maintain temperature.

The external field-assisted pyrolysis technology markedly enhanced the efficacy of the pyrolysis and the selectivity of products, such as microwave, plasma, light, heat, magnetic, etc. The elevated temperatures typically required for conventional pyrolysis can be replaced through the external fields to facilitate adjustments to the reaction kinetics and reaction selectivity.

2.4. Co-Pyrolysis with Biomass

Biomass resources encompass a diverse range of renewable and plentiful materials, including cellulose and lignocellulose [28]. The FTIR of the lignocellulosic waste revealed the presence of functional groups, including O-H, C-OH, C-H and C=O, at the initial temperature of 473–673 K. However, as the temperature rises, the peak diminishes [29]. The product composition depends strongly on the original monomer structure of the plastic. Polyolefin plastics are known to produce hydrogen and hydrocarbons, whereas polyester plastics are observed to yield oligomers, CO_2 and coke [30].

The co-gasification of biomass and hydrogen-rich plastics represents an efficient method of aromatics selectivity enhancement and coke generation reduction. The method enhances the hydrogen-to-carbon (H/C) ratio of the gaseous product by optimizing the feedstock ratios while improving the quality of the liquid fuel [31]. The catalysts employed in the process are analogous to those used in catalytic pyrolysis and are predominantly composed of various zeolite molecular sieve catalysts, as well as other metal compounds.

A H/C ratio of less than 1 will form a quantity of coke on the zeolite catalyst, which will ultimately lead to deactivation and accelerated aging of the catalyst. The majority of biomasses exhibit H/C ratios within the range of 0–0.3. Consequently, the incorporation of hydrogen-rich feedstocks, such as HDPE, can enhance the H/C ratio and, in turn, the catalytic activity. To illustrate, a 25/75 ratio of biomass to HDPE has been demonstrated to yield higher liquid yields and selectivity, with a selectivity of over 90% for gasoline series hydrocarbons [32]. Plastics with elevated H/C ratios provide protons (H) through the processes of dehydrogenation and dibasic aldehyde reaction. Protons participate in the reduction reaction of intermediates, producing a range of liquid products, including alcohols, aromatics, alkylbenzenes, phenols and other compounds [33].

2.5. Summary

Pyrolysis is a significant contributor to the utilization of plastics and biomass, involving the degradation and recycling of polymers at elevated temperatures, which facilitates the breakdown of their molecules into small-molecule hydrocarbons (Table 1). The utilization of catalysts, such as zeolite molecular sieves, facilitates the generation of high-value chemicals, including BTX during the pyrolysis. In addition, the process of cracking and recombination produced valuable materials (hydrogen and carbon nanotubes). These technologies not only enhance the efficiency of pyrolysis but also expand the scope of pyrolysis products. The external field technologies, such as microwaves, offer novel avenues for advancing the pyrolysis process. Furthermore, co-pyrolysis with biomass and plastics has also been the subject of considerable interest and shows promising potential for industrial applications. Although these technologies are still in the research stage, they can be applied in the future to areas such as plastics recycling and biomass conversion. Furthermore, subsequent studies must consider operating conditions (reaction temperature, heating rate, pressure, reaction duration, and the selection of catalysts) to optimize the selectivity and control the distribution range of the products.

Table 1. Summary of experimental pyrolysis data.

Feed	Temperature/°C	Catalyst	Time/h	Major Products	Yield/%	Ref.
LDPE PS	500–800	Red clay	90 s	Guaiacol	3.41 ± 0.60	[21]
Mixed plastic	500–550	MCM-41 HZSM-5	20 min	BTEX	∽100%	[22]
CMP	500–550	Fe/Ni/Mo@N/ HZSM-5	20 min	MAHs	84.09	[23]
HDPE	600	None	120 s	Linear hydrocarbons	92.8	[24]
HDPE PP	620	ZSM-5	30 min	Liquid products	48.9	[25]
HDPE	300	FeAlOx	30–90 s	H_2	97	[26]
LDPE	250–500	None	110 min	oil	99.78	[34]

3. Solvolysis

Solvolysis is a chemical recycling process that employs the use of chemical reagents and thermal or thermo-catalytic treatment to decompose resins and generate small molecules, monomers, or monomer derivatives. This process is commonly utilized in the recycling of polyester plastics, with PET representing the most prevalent application. In comparison to physical recycling, the treatment of waste plastics by hydrolysis, alcoholysis, and ammonolysis is less likely to result in environmental pollution and can recover valuable chemical raw material [12]. Solvolysis reduces the reaction activation energy of the plastic waste cracking process compared to pyrolysis [35]. This section will examine four distinct dissolution treatments: alcoholysis, hydrolysis, ammonolysis, and alkene metathesis. Each process will be discussed in depth, with a particular focus on the catalytic mechanism.

3.1. Hydrolysis

Hydrolysis of ester bonds represents a well-established and straightforward depolymerization process, offering a convenient method for the depolymerization of PET into TPA and EG. The recovery of PET in the aqueous phase is achieved with high yields (>80%) of TPA and EG. In general, the hydrolysis can be carried out under neutral [36], acid [37], or alkaline [38] conditions (Figure 2). The reaction can be catalyzed by both acidic and basic catalysts, depending on the pH of the catalyst used in the aqueous phase reaction medium. Both acidic and basic reaction conditions provide hydrogen ions, which are thermodynamically more favorable for ester hydrolysis. This is achieved by providing protons to the nucleophilic center of the ester group and lowering the activation energy for water-mediated ester bond cleavage [37].

In general, neutral hydrolysis reactions must be conducted in an excess of water or steam at temperatures and pressures between 115 and 420 °C and 10 and 420 atmospheres, respectively. The harsh reaction conditions, including elevated temperatures, high pressures, and highly resistant reactors, render this technology unfeasible for commercialization for PET recycling. Alkaline hydrolysis typically employs alkaline metal oxides as catalysts. Following the completion of the hydrolysis process, the addition of acids is required to recycle TPA. It has been demonstrated that microwaves and ultrasounds can be employed as alternative heating sources. Siddiqui et al. [39] demonstrated the complete degradation of PET in 30 min using microwave-assisted heating at 180 °C and 1.25 M NaOH. Zhang et al. [40] have devised enzyme-mimicking Zn binuclear catalysts for the hydrolysis of a range of polyester-based plastics, at low temperatures and weak alkaline conditions. The biomimetic Zn-Zn sites demonstrated the capacity to activate plastics, stabilize key intermediates and achieve intramolecular hydrolysis. Subsequently, the group proceeded to enhance the foundation by modifying the Zn binuclear catalyst to improve the activity through theoretical calculations [41]. Compared to conventional alkaline hydrolysis, the catalyst demonstrated a specific activity that was increased by more than 23 times, while simultaneously reducing the alkali concentration by an order of magnitude. The acid hydrolysis has been the subject of considerable research and industrial interest due to its capacity to be conducted under milder reaction conditions [42]. Kang achieved 100% conversion of PET to TPA using microwave-assisted technology with ZSM-5 as an acidic catalyst at 30 min, 230 °C [37].

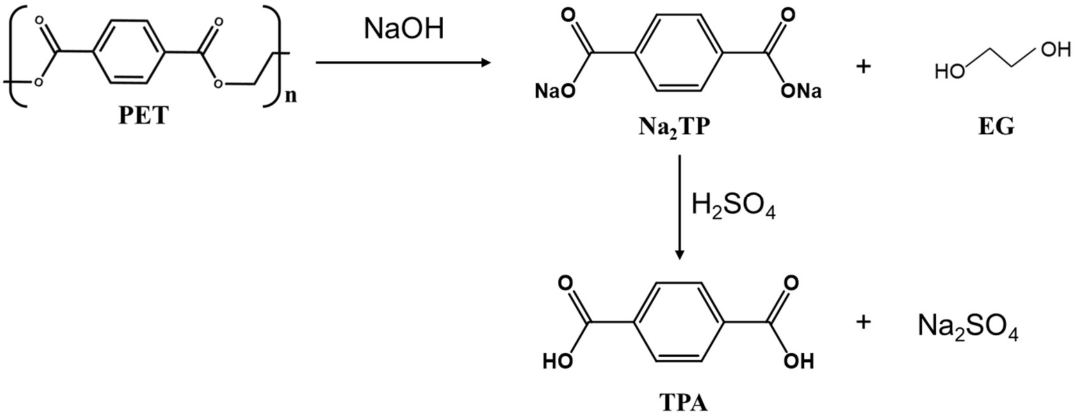

Figure 2. Alkaline hydrolysis of PET without catalysts.

3.2. Alcoholysis

Alcoholysis is the process of depolymerizing PET at temperatures (110–270 °C) and pressures (1–25 atmospheres) (Figure 3). The reaction medium can be any of the following: EG, diethylene glycol, or propylene glycol. Of these, EG is the most widely used medium [43].

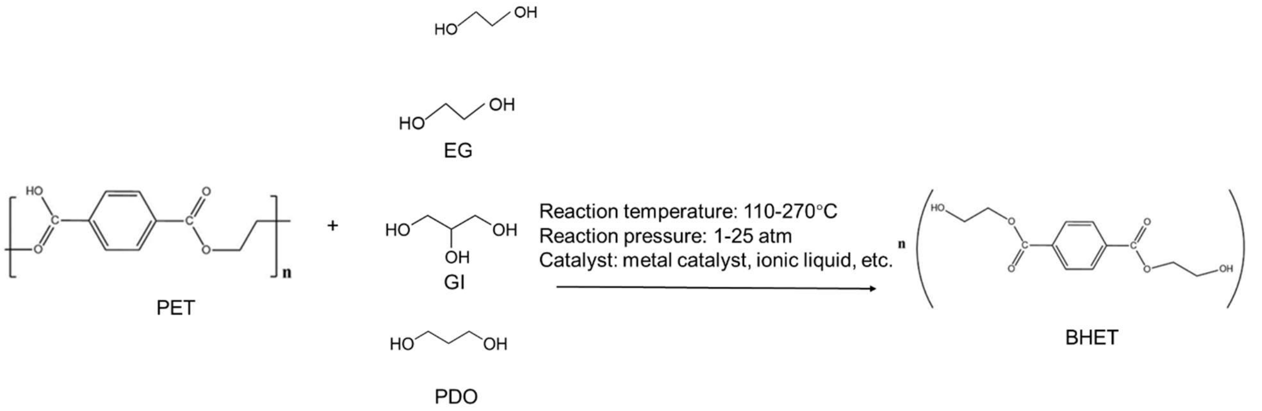

Figure 3. Schematic diagram of PET alcoholysis.

PET alcoholysis is inherently a slow process without catalysts and PET cannot be completely depolymerized into BHET. Accordingly, many widely used catalysts have been put forth as potential solutions to this issue, including metal salts, zeolites, and ionic liquids [44]. The acetates of Zn, Mn, Co, Pd as homogeneous catalysts is a common practice due to the high catalytic activity and cost-effectiveness of these compounds. Among these, zinc acetate and magnesium acetate are the most prevalent catalysts [5]. The synergistic activation of carbonyl and EG groups in the PET by metal centers and anions proved to be a highly effective strategy for the generation of BHET in high yields. BHET can be employed directly in the synthesis of new PET following purification, obviating the necessity for a repeated esterification step and thus enhancing the overall process efficiency and sustainability.

Dong et al. [45] employed a one-pot chemical-biological cascade conversion strategy, combining chemical hydrolysis with biotransformation. This approach involved biocompatible betaine as a catalyst to facilitate PET alcoholysis, generating BHET. BHET is directly subjected to enzymatic hydrolysis, producing PTA and EG without separation. These two compounds are then employed as substrates for biotransformation, whereby they are transformed into protocatechuic acid (PCA) and glycolic acid (GLA), which have potential applications in the fields of biomaterials and bioenergy. The one-pot cascade conversion process offers a simplified operational procedure, reducing production costs and enhancing raw materials. This provides a novel concept for the recycling and high-value utilization of PET.

3.3. Ammonolysis

In comparison to other chemical recycling technologies for polyester-based plastics (such as alcoholysis, hydrolysis), there has been comparatively little research conducted on ammonolysis [46]. NH_3 is typically the most commonly used reaction medium during ammonolysis, with reaction temperatures (70–180 °C). Given that ammonolysis is a considerably slower process, catalysts and elevated reaction pressures are necessary to accelerate the rate of reaction.

Currently, various amines are utilized for ammonolysis, either with or without the incorporation of catalysts (such as metal salts, metal oxides, and ionic liquids) [47]. Ammonolysis of plastic waste has been demonstrated to be an effective method for the conversion of these materials into nitrogenous chemicals, including pyrroles, pyridines, indoles, aromatic amines and acetonitrile [48]. This conversion process not only enhances the chemical recovery rate of PET but also provides a source of feedstock for the production of high-value chemicals. Furthermore, the researchers have investigated the recycling of post-consumer PET wastes through ammonolysis in the presence of various amino alcohols and organocatalysts to produce diol terephthalamides. The diol terephthalamides can be employed in the synthesis of poly(ester-amides), which are extensively utilized in a multitude of industries, including textiles, plastics, and coatings [49].

Ammonolysis, as a technology for converting waste plastics into high-value chemicals, has demonstrated potential; however, it still faces many challenges in practical application (Table 2). These challenges include high energy consumption and cost issues, which often necessitate the use of expensive catalysts or prolonged reaction times; non-broad-spectrum recyclability, which indicates that certain technologies may apply only to specific types of PET plastics; and the absence of high-value-added degradation products, which renders the conversion process intricate and costly.

Table 2. Summary of experimental solvolysis data.

Method	Feed	Temperature/°C	Pressure	Catalyst	Time/h	Yield/%	Ref.
Hydrolysis	PET	195	3 MPa	Metallic ions	2	TPA, 95	[36]
	PET	230	1 bar	ZSM-5	0.5	TPA, 100	[37]
	PET	80	1 bar	None	0.3	TPA, 95	[38]
	PET	200	1 bar	None	1	TPA, 97.9	[50]
Alcoholysis	PET	190	1 bar	[Bmim][OAc]	3	BHET, 58.2	[44]
	PET	190	1 bar	Betaine	1	TPA, 62.8	[45]
	PET	300	11 bar	None	0.4–0.8	BHET, 30	[51]
	PET	190	1 bar	Cyanamide	2.5	BHET, 95	[52]
Ammonolysis	PET	196	1 bar	Hmim.TfO	1	BHETA, 89	[47]
	PET	114	1 bar	NaOAc	4	BHET, 86	[53]

3.4. Alkene Metathesis

Alkene metathesis also represents an effective process for catalyzing the conversion of polyolefins to hydrocarbons at moderate temperatures [54]. The reaction process is primarily characterized by the involvement of one or multiple lighter alkanes, or a combination [55]. The tandem catalyst system is typically employed, which facilitates the reaction through the activation of the C-H bond in two different alkanes. The catalyst comprises two distinct components, each with a specific function: one component is responsible for the dehydrogenation reaction of the alkanes, while the other plays a role in the olefinic complex replacement process. The dehydrogenation catalyst is responsible for the dehydrogenation of PE/PP, and the formation of unsaturated intermediates in the presence of excess light alkanes introduced into the system. Subsequently, the olefin recombination catalyst facilitates the reduction in the chain length of the original polyolefin by exchanging the saturated chain, while simultaneously lengthening the light alkane chain. Finally, the unsaturated carbon chains are saturated again by hydrogenation to form new alkanes, completing the catalytic cycle [56]. The advantage of the catalytic system is that it can be conducted at relatively low temperatures and pressures, thereby reducing energy consumption and the incidence of side reactions.

In 2016, Jia et al. reported the first instance of a tandem-catalyzed cross-alkane metathesis for the efficient degradation of polyethylene under mild conditions. The system combined a homogeneous Ir-based catalyst for dehydrogenation/hydrogenation with a heterogeneous Re_2O_7/Al_2O_3 catalyst for alkene metathesis [57]. It is possible to convert common plastic wastes, such as post-consumer polyethylene bottles, bags and films, into valuable chemical feedstocks without any pre-treatment. Subsequently, Cristina [58] expanded upon this by directing particular attention toward the role of the carrier in the catalytic process, utilizing n-octane and n-dodecane as substrates (Figure 4). A tandem catalytic system was constructed using pincer-connected iridium (Ir) complexes as dehydrogenation catalysts in combination with rhenium (Re)-based complex decomposition catalysts. FT-IR was used to confirm the complex grafting and to elucidate the anchoring sites with supporting carriers. The findings of these studies contribute to our understanding of the impact of carriers on the activity, selectivity and stability of catalysts, which provide a crucial theoretical foundation for optimizing catalyst design.

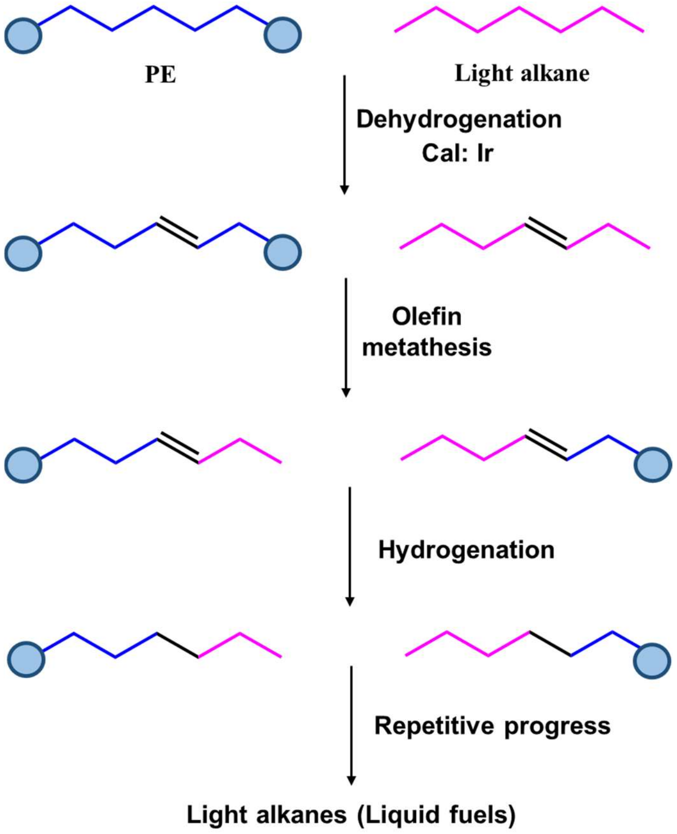

Figure 4. Tandem catalyzed crosslinked alkane metathesis degradation process of PE with light alkane. (Pink: light alkane, Blue: PE, Blue spheres: carbon chain groups).

3.5. Summary

Solvolysis of plastics, especially hydrolysis, alcoholysis ammonolysis and alkene metathesis, has emerged as an effective chemical recycling technique capable of converting waste plastics into valuable chemicals. The decomposition of plastics by chemical reagents, thermal or catalytic treatment to produce small molecules, monomers or monomer derivatives is an especially effective method for recycling polyester-based plastics, such as PET (Table 2). Hydrolysis facilitates the effective recycling of PET through the hydrolysis of ester bonds. In contrast, alcoholysis and ammonolysis employ alcohols and ammonia, respectively, as reaction media to promote the depolymerization of plastics through the action of catalysts. Despite the success of these methods on a laboratory scale, they still face challenges in commercial applications, including high temperature and pressure reaction conditions, catalyst selection and recovery, and the complexity of the product purification process. Future research will concentrate on the creation of more efficient and environmentally friendly catalysts, the investigation of milder reaction conditions, and the development of integrated processes to enhance the sustainability of the overall chemical recovery process. Furthermore, the research will concentrate on the environmental impact and economic assessment of the technologies in question to guarantee their commercial viability and environmental friendliness.

4. Hydrotreating

Hydrotreating is currently the most extensively researched and promising method for industrial applications. Consequently, it is regarded as a potential new avenue for upcycling plastics. Hydrotreating is currently the most extensively researched and promising method for industrial applications. Consequently, it is regarded as a potential new avenue for upcycling plastics. is a process whereby the C-C bond in a molecular skeleton is cleaved, followed by the addition of hydrogen atoms in the presence of a suitable catalyst. To prevent the occurrence of undesirable coking and polymerization reactions during pyrolysis, the use of high-pressure hydrogen can facilitate the promotion of heavy molecular cleavage through the process of hydrotreating is currently the most extensively researched and promising method for industrial applications. Consequently, it is regarded as a potential new avenue for upcycling plastics [13]. Compared to pyrolysis and catalytic cracking, hydrotreating results in the production of liquid products with a higher degree of saturation.

Similarly to catalytic pyrolysis, catalysts are crucial for hydrotreating, as they reduce the required temperature and operating time while increasing the selectivity of the target product [59]. Typical hydrotreating conditions are carried out at reaction temperatures of 200–450 °C. Transition metals are typically employed as catalysts for the hydrolysis depolymerization of waste plastics, like Ru、 Pt loaded on acidic carrier structures [60]. Some of the literature employs the use of inexpensive catalysts, such as Co/Ni, which are introduced into a high-pressure hydrogen environment. Furthermore, the potential of hydrogen-free depolymerization of polyolefins at low temperatures, namely tandem hydrogenolysis-aromatization, has been explored [61]. Polyethylene can be selectively decomposed into valuable long-chain alkyl aromatics and alkyl cycloalkanes [62]. This section presents an overview of the advancements in hydrotreating studies of polyesters, polyamides, and polyolefins.

4.1. Single-Atom Catalysts

Hydrotreating has become an increasingly significant area of focus in the fields of plastics recycling and chemical production in recent years. In this field, Pt- and Ba-based catalysts are the principal options, typically employed in conjunction with non-acidic carriers, including carbon materials, cerium oxide (CeO_2), titanium dioxide (TiO_2), and strontium titanate ($SrTiO_3$) [63]. The selection and design of catalysts and carriers allow for the optimization of polyolefin conversion, thereby enhancing the performance of catalysts and facilitating more efficient hydrolysis, which contributes to the development of sustainable chemical processes (Figure 5).

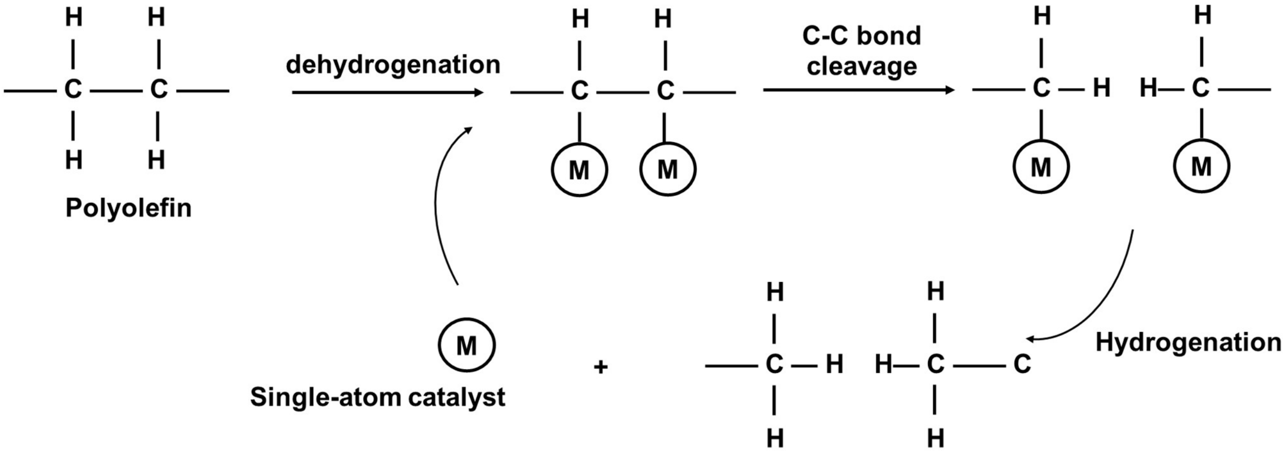

Figure 5. Schematic diagram of catalytic hydrolysis over a single-atom catalyst.

4.1.1. Pt-Based Catalysts

Gokhan et al. [64] prepared $Pt/SrTiO_3$ as a catalyst using precisely dispersed platinum nanoparticles on $SrTiO_3$ nanocubes with a chalcogenide structure by atomic layer deposition technique. The reaction was conducted for 96 at 170 psi hydrogen pressure and 300 °C to efficiently convert PE into high-quality liquid products, including lubricants and waxes. Nevertheless, atomic layer deposition is constrained by inherent limitations in terms of scalability. Peczak [65] employed an improved hydrothermal synthesis method for the large-scale production of $SrTiO_3$ nanocubes with precise shape and size specifications, which were utilized as catalyst carriers. The catalyst was prepared by depositing Pt nanoparticles on the carrier via the strong electrostatic adsorption technique. This process enabled the efficient conversion of waste polyethylene into high-quality liquid products with a conversion rate of up to 99%. Subsequently, Hackler [66] investigated the effect of PE with varying molecular weights and branching densities, and polypropylene (PP) with differing molecular weights and configurations on low-molecular-weight liquid products through hydrogenolysis. The microstructure of PE, particularly the length and density of the branched chains, is the primary factor influencing the yield. The yield of PE increases with increasing molecular weight. At a molecular weight of approximately 7600 Da, the hydrolysis yield is 55%, while at a molecular weight of approximately 50,950 Da, the hydrolysis yield is 67%. The molecular conformation of PP had a considerable impact on the molecular weight of the final product, with a relatively high yield (75–77%).

In 2020, Akalanka [67] innovatively proposed and designed the embedding of platinum (Pt) nanoparticles in ordered mesoporous silica ($mSiO_2$). The efficient and selective cleavage of chemical bonds in PE was achieved by using the pore structure to modulate the chain length of hydrogenolysis products, thereby mimicking the efficient degradation mechanism of enzymes in nature.

In a recent study, innovative reaction separation techniques were employed in the hydrocracking process of PE to product selectivity and reduce the generation of light gases [68]. A variety of platinum (Pt) catalysts with different loadings were utilized, including $mSiO_2/Pt/SiO_2$, Pt/C and Pt/SiO_2. The system demonstrated the capacity to continuously separate the liquid products, with the product distribution focusing on liquid hydrocarbons in the C10–C20 range.

Subsequently, Wu et al. [69] prepared $mSiO_2/Pt\text{-}X/SiO_2$ to study the modulation of the hydrolysis reaction by the size of Pt NPs. Among the catalysts tested, $mSiO_2/Pt\text{-}1.7/SiO_2$ (1.7 nm Pt NPs) exhibited the highest activity. After 12 h, the conversion of PE by $mSiO_2/Pt\text{-}1.7/SiO_2$ reached 62%, with the product predominantly comprising a C23-centred hydrocarbon distribution. The catalyst showed excellent cyclic stability after several cycles. Akalanka et al. [70] proceeded to optimize the catalyst by incorporating two additional mesoporous domains into the mesoporous architecture, thereby enhancing the selectivity of the catalyst $mSiO_2/Pt/MCM\text{-}48$. The polyolefins were converted into n-alkanes of approximately C20–C40, with the products being predominantly liquid n-alkanes with a Gaussian distribution centered at C28. The yields exceeded 90 wt%, and the reaction produced minimal volatile by-products. Zhao [71] employed in situ magic angle spinning (MAS), nuclear magnetic resonance (NMR), and coarse-grained molecular dynamics simulations to investigate the mechanism of the catalyst's role in the hydrocracking of polyolefins in depth. A combination of experiments and simulations was employed to investigate the impact of catalyst structure on the molecular weight distribution of hydrocracking products. The design of the catalyst was then optimized to enhance control over the molecular weight distribution of the products.

4.1.2. Ru-Based Catalysts

Sun [72] synthesized Ru/C catalysts with varying loadings using a wet impregnation method to investigate the impact of atomic structure and size on the activity and product selectivity of Ru-based catalysts in PP hydrocracking. The 0.5% Ru/C catalyst demonstrated a notable capacity for C-C bond cleavage at the outset of the reaction, attributable to its smaller particle size, which proved conducive to the generation of light products. Nevertheless, the catalyst's activity declined with the progression of the reaction, resulting in the formation of high-molecular-weight solid products. In contrast, the 2% Ru/C catalyst demonstrated superior performance in balancing C-C bond breaking and stereoisomerization, which resulted in the generation of a diverse range of products, including hydrocarbons in various forms such as solids, liquids and light hydrocarbons. By precisely adjusting the particle size and composition of the catalyst, the pathway of the catalytic reaction can be optimized, thereby enabling the precise control of the molecular weight and distribution of the products. Subsequently, Wang [73] proposed the utilization of a Ru-doped zirconium catalyst (Ru-XZr, X = Ti, Nb, Ce, W, V, Mo, Fe) under mild conditions to optimize the hydrogenolysis process of polyolefins. Among these, those doped with tungsten (W), vanadium (V), and molybdenum (Mo) exhibited the most effective inhibition of methanogenesis. The methane yield was reduced to 8.6–9.2%, while the yield of liquid products (C4–C35) was significantly increased to 63–68%. This improvement in the design effectively resolved the issue of an excessive reaction rate and methane generation during hydrogenolysis with conventional Ru-based catalysts.

Kots [74] demonstrated the successful modulation of the metal-carrier interaction through the use of ammonia (NH_3) as a moderator. It was demonstrated that the hydrogen storage capacity of Ru-based catalysts loaded on ammonia-treated TiO_2 carriers was significantly enhanced. NMR demonstrated that the ammonia-treated samples exhibited increased incorporation of hydrogen atoms at the Ru sites, resulting in the formation of additional electrons on TiO_2 carriers through the hydrogen spillover effect. This enhanced electron density facilitated the hydrogenolysis reaction, with the yield of the liquid product reaching approximately 74% within 6 h, indicative of exceptional catalytic performance.

4.1.3. Other (Co, Ni) Metal-Based Catalysts

Yan Ning et al. [75] achieved the successful conversion of PET to aromatic hydrocarbons via a one-pot reaction utilizing Co/TiO_2 as a catalyst. The research validated the efficacy of the catalyst in the hydrodeoxygenation (HDO) reaction and elucidated the fundamental reaction pathway (Table 3). The optimized conditions yielded a toluene and xylene yield of 78.9%.

Table 3. Summary of experimental hydroconversion data.

Feed	Temperature/°C	Pressure	Catalyst	Time/h	Major Products	Yield/%	Ref.
PE	280	1 bar	$Pt/\gamma\text{-}Al_2O_3$	24	liquid/wax products	80	[61]
PE	300	12 bar	$Pt/SrTiO_3$	96	liquid products	>99	[64]
HDPE	300	24 bar	$mSiO_2/Pt/SiO_2$	14	liquid products	79	[67]
PE	300	1 bar	Pt	20	olefins		[68]
PE	250	30 bar	Ru-XZr	2	non-solid	~70–80	[73]
PET	340	30 bar	Co/TiO_2	4	Arenes	79	[75]
PP	300	15 bar	Pt/C	24	Motor oil	80	[76]
PE	240	35 bar	Ru/CeO_2	8	liquid/wax products	90	[77]
PE, PP	250	40 bar	Co/ZSM-5	20	C_3H_8	84	[78]

To address the issue of COVID-19-related plastic waste, Wang Jia [79] used a combination of hydrothermal cracking (550 °C) and a downstream gas-phase hydrotreating (300 °C) tandem catalytic process to convert discarded plastics into usable fuels. The technology is substrate versatile and capable of treating a variety of plastic wastes, including polyolefins, aromatic plastics, and rubber. A diverse range of plastic wastes were successfully converted into fuel-range hydrocarbons in the presence of a non-precious metal bifunctional $Ni/NiAl_2O_4$ catalyst. Subsequently, the group proceeded to investigate the conversion of plastics to liquid fuels through hydrothermal cracking and gas-phase hydrocracking of PE in a two-step pressurized fluidized bed reactor utilizing $CoAl_2O_4$ spinel-derived catalysts. The product distribution was adjusted flexibly by modifying the operating parameters within the reactor and the Co/Al molar ratio within the $CoAl_2O_4$ spinel catalyst [80]. Following the optimization of the conditions, petrol in the C5–C12 range could be efficiently obtained from PE in an 86.0% yield using a CoAl-1 spinel catalyst with a specific Co/Al molar ratio. The researchers were able to significantly increase the yield of specific hydrocarbon products through the design of the catalyst and the optimization of the reaction conditions, thus providing an effective strategy for the chemical recycling and energy use of plastic waste.

4.2. Bifunctional Catalysts

The hydrotreating of polyolefins represents an appealing avenue for chemical recycling. This process has the dual benefit of reducing the environmental impact of plastic waste and providing a source of raw materials for the chemical industry, which allows for the conversion of polyolefins into smaller molecules of chemicals and fuels, including petrol and diesel. The design of hydrocracking catalysts typically incorporates the concept of bifunctional groups, which possess both metal and acidic sites. The metal sites are primarily responsible for the activation and hydrogenation of hydrogen, while the acid sites contribute to the cracking reaction. This bifunctional catalyst unites the hydrogenation activity of a metal catalyst with the cracking ability of a solid acid, thereby enabling the efficient fragmentation of polyolefin molecules into shorter-length hydrocarbon chains [63]. With the activation metals utilized in bifunctional catalysts, metal catalysts predominantly encompass Pt-, Pd-, Ni- [81,82], and Co- [83] based catalysts. Among these, Pt-based catalysts are the most efficacious within the hydrocracking metal. Furthermore, Pt-based catalysts have demonstrated exceptional performance in a multitude of dehydrogenation and hydrogenation reactions [65,84,85]. In addition, solid acids employed encompass zeolites [81,86,87], $WO_3\text{-}ZrO_2$ [88], and other substances. Initially, plastic waste undergoes C-H activation at metal sites, resulting in the formation of olefinic intermediates through dehydrogenation. Subsequently, the olefinic intermediates migrate to the Brønsted acid sites for backbone isomerization and β-cleavage (C-C cleavage). Finally, the cleavage and isomerization intermediates are transported to the metal site for hydrogenation, resulting in the formation of short-chain alkanes [13].

4.2.1. Pt-Based Catalysts

Wang [89] proposed a new catalyst design for efficient hydrocracking of LDPE by loading zirconium tungstate with ruthenium preparation (Ru-WZr). The hydrogen storage mechanism of $(WO_x)_n$ clusters in the catalyst was also identified, which enhanced the catalyst's activity and selectivity under conditions of insufficient hydrogen through the processes of hydrogen overflow and reverse hydrogen overflow. At 523 K and 50 bar, C20–C40 n-alkanes were the main products, with yields of over 70% for liquids and under 30% for gases. Subsequently, Vance [88] employed Pt-

WZr as a catalyst in experiments conducted in a batch reactor. The metal-acid site molar ratio (MAB) of the catalyst was adjusted by varying the loading of Pt and WZr. The products were mainly branched hydrocarbons (both n-alkanes and iso-alkanes) in the C5–C16 range. As the MAB increased, there was a shift in product distribution towards heavier hydrocarbons (C13+), accompanied by a decrease in C4–6 yield. The yields of solid residues declined, while those of extractable products remained stable, indicating that the catalyst has good cracking activity and selectivity. Zhou [90] used Y-H zeolite with Pt/Al_2O_3 to achieve a PE conversion of 96.8% and a selectivity of 90.8%, producing mainly C5–20 liquid hydrocarbons. Hydrocracking experiments on model alkanes demonstrated a linear correlation between the external surface area of Y-H zeolite and catalytic activity, indicating that the initial C-C bond breaking of macromolecular PE predominantly occurs on the nanosheets.

The incorporation of additives during the synthesis of plastics is a crucial step in enhancing the processing properties of the materials and optimizing their functional characteristics [91]. Hinton [92] investigated the impact of plastic additives, with a particular focus on phenolic antioxidants, on HDPE during hydrogenolysis over a Pt-based catalyst($Pt/WO_3/ZrO_2$). The findings of the study indicated that antioxidants resulted in a significant reduction in the yields of both gas and liquid products. Furthermore, antioxidants had a notable effect on conversion and the selectivity of individual products. The influence of antioxidants on the catalytic process was elucidated through differential reflectance infrared spectroscopy (DRIFTS). It was demonstrated that antioxidants alter the effective metal-to-acid site ratio (MAB) by reacting with the catalyst active sites, thereby influencing the catalytic cracking process.

4.2.2. Ru-Based Catalysts

Yan Ning [93] initially reported the catalytic hydrolysis of various aromatic plastic wastes, which had been upgraded to alkyne compounds, using Ru/Nb_2O_5 catalysts. The yields were found to reach 75–85%. It has been demonstrated that the small-sized Ru clusters on Nb_2O_5 are capable of effectively preventing the adsorption and excessive hydrogenation of aromatic rings. Meanwhile, the NbOx species fulfills a dual function in the catalyst: its strong oxygen affinity contributes to the activation of the C-O bond; its Bronsted acidic site favors the activation of the C-C bond. To ascertain the effect of different carriers (e.g., FAU, BEA, SiO_2, Si-BEA, SIRAL30, SIRAL40HPV, MWW, etc.) on the performance of the catalysts during the hydrogenolysis, Rorrer [94] employed Ru-based catalysts, with a particular focus on the non-terminal C-C bond breaking. The utilization of Ru/FAU and Ru/BEA catalysts permitted the effective conversion of PE to liquid alkanes in a 67% yield at 200 °C, 16 h and 30 bar hydrogen pressure. In contrast, the Ru/SiO_2 catalyst, which employs SiO_2 as the carrier, demonstrated a markedly inferior yield of 33%. The results emphasize the significance of the selection of the carrier for the performance of the catalyst. Zeolite carriers with a specific pore structure and acidic properties are capable of promoting the hydrogenolysis of polyolefins with greater efficiency.

The treatment of chlorinated plastic wastes is typically ineffective due to the generation of toxic hydrogen chloride. To address this issue, Kots [95] proposed a two-stage strategy. Firstly, a magnesium oxide-alumina mixed oxide was employed as a chlorine adsorbent to expeditiously extract chlorine from polyolefin melts by forming solid chlorides at 250 °C and 30 bar H_2. Subsequently, the dechlorinated plastics are converted to liquid hydrocarbons through catalytic hydrocracking, utilizing a Ru-based catalyst. For oxygenated aromatic plastic wastes, Wei [96] devised a catalytic system comprising $Ru\text{-}ReOx/SiO_2$ and HZSM-5 for the direct conversion of PC, PET, PBT, PPO and their blends (Figure 6). A yield of up to 99% was achieved for the conversion of oxygenated aromatic plastic wastes into cycloalkanes as LOHCs under mild reaction conditions (180 °C, 3 MPa H_2).

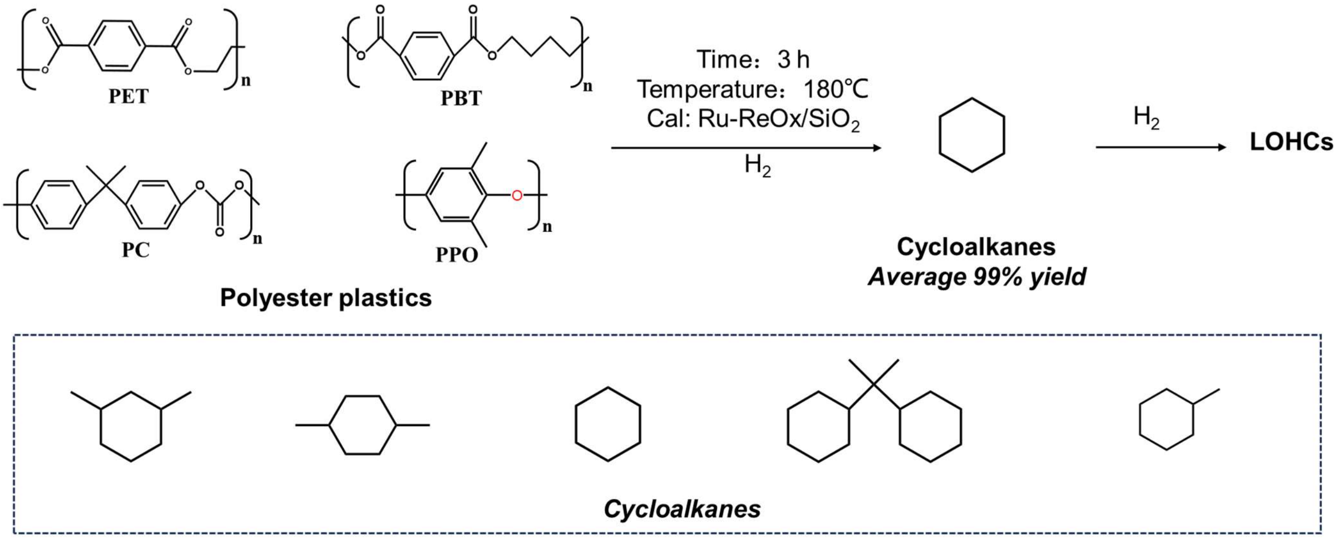

Figure 6. Hydrogenolysis based on oxygenated aromatic plastic wastes.

4.2.3. Ni-Based Catalyst

Liu [82] developed a novel Ni/HZSM-5 bifunctional catalyst capable of efficient conversion of PC plastic waste under milder conditions (190 °C, 4 MPa H_2). The PC plastic waste was directly upgraded to cycloalkanes as aviation fuels, with a high yield (99.3%) and an 81.2% yield of C15 dicycloalkanes. The selectivity of C15 dicycloalkanes was enhanced by modulating the equilibrium between the metal and acid sites and optimizing the hydrodeoxygenation activity.

These studies indicate that hydrotreating represents a promising approach to the efficient conversion of plastic waste into valuable chemicals, while simultaneously reducing dependence on fossil resources and contributing to the development of a more sustainable and environmentally friendly plastics circular economy (Tables 3 and 4). However, hydrotreating typically requires elevated hydrogen pressures and protracted reaction times. Moreover, a more profound investigation and comprehension of the precise mechanisms of selective hydrogenation of metal complexes is imperative.

Table 4. Summary of experimental bifunctional data.

Feed	Temperature/°C	Pressure	Catalyst	Time/h	Major Products	Yield/%	Ref.
PC	190	4 MPa	Ni/HZSM-5	6	cycloalkanes	99.3	[82]
LDPE	250	30 bar	$Pt/15WO_3/ZrO_2$	12	liquid products	100	[88]
PE	280	3 MPa	$FAU\text{-}Pt/Al_2O_3$	4	fuels	90.8	[90]
Aromatic plastic	200	0.3 MPa	Ru/Nb_2O_5	12	arenes	75–85	[93]
HDPE	250	30 bar	$Pt/15WO_3/ZrO_2$+HY	2	liquid products	85	[97]
LDPE	310	20 bar	Ni/BETA	0.75	liquid products	88	[98]

4.3. Summary

Hydrotreating is typically conducted within a temperature range of 200 to 450 °C, and is achieved in a high-pressure hydrogen environment using metal catalysts such as Ru, Pt, Co, Ni and acidic carriers. The current research focus on polyolefin hydrotreating is on the synergistic effect of metal and acidic sites in the catalysts and the domain-limiting effect of the spatial structure of porous carriers, which play a pivotal role in mimicking the catalytic process of enzymes. However, existing catalysts may not be able to catalyze all types of plastics efficiently and may produce undesired by-products. In future research on hydrotreating, the use of more economical metal catalysts, such as Co and Ni, is being explored to reduce costs, working on the development of inexpensive catalysts that are both highly efficient and selective to achieve the desired product distributions under milder reaction conditions.

5. Oxidative Cleavage

Oxidative cleavage is a stochastic method of breaking chemical bonds. It has been observed that in landfills or other natural environments, plastics exhibit a yellow color and brittle physical properties due to the deterioration of the polymer chains, a process also known as “plastic aging” or “autoxidation” [99]. The utilization of oxidation catalysts, together with the exothermic reactions that frequently accompany oxidation, serves to reduce the temperature requirements of the reaction process. Consequently, oxidation can facilitate the depolymerization of plastic waste under mild conditions. With the addition of oxygen, the plastic waste undergoes functionalization during the degradation process, resulting in the formation of degradation products rich in functional groups such as -OH and -COOH. The functionalization step increases the value of the degradation products. Commonly used catalytic oxidation techniques include Fenton reaction, Fenton-like reaction and photocatalysis, which provide a diverse portfolio of technologies for the catalytic degradation of plastic wastes [100]. However, the majority of plastics are insoluble macromolecules that are unable to undergo degradation under typical conditions. To achieve effective degradation of plastic waste, it is necessary to either improve existing oxidation techniques or combine them with other methods according to their structural characteristics. The mechanism of degradation of plastics or polymers in the reaction is generally investigated by analytical techniques, including gel permeation chromatography (GPC), mass spectrometry (MS), viscometry, NMR spectroscopy and FTIR spectroscopy [100–102].

5.1. Mechanism of Oxidative Cleavage

The process of oxidative cleavage is initiated by the trigger of free radicals. Researchers have employed external stimuli and catalysts to promote effective oxidative cleavage [103]. Oxidative cleavage typically requires high energy (e.g., UV light (254 nm) [104] or high temperature (>200 °C)). The formation of monoclinic O, peroxides, superoxides, and so forth, results in the breakdown of polymer bonds within the polymer backbone, thereby accelerating the rate of degradation. The oxidizing radicals can follow two principal pathways [14]. The first of these, designated “pathway A”, undergoes hydrogen atom transfer (HAT), whereby they abstract a hydrogen atom from the C-C bond in the polymer backbone, resulting in the creation of peroxy groups. Upon the cleavage of the O-O bond, oxygen-centered radicals are generated [102]. Pathway B is initiated by a Russell-type mechanism, whereby two peroxy radicals couple to form four consecutive oxygen atoms [105]. The oxygen-centered radicals can undergo β-cleavage to form ketone and alkyl radicals, or HAT to form alcohols.

The introduction of a catalyst permits the reaction to occur at lower temperatures, thereby yielding more selective products [10]. The catalysts most commonly employed in catalytic oxidation processes are organic compounds or transition metals. These may be either homogeneous or heterogeneous catalysts. These catalysts promote the generation of ROS or excited state species that directly degrade the polymer backbone under mild conditions and accelerate the reaction process [106].

5.2. Chemical Catalysed Oxidation

The oxidation processes typically follow a free radical mechanism, which is a chain reaction involving highly reactive radical species. Heat is a condition that is easily regulated and significantly promotes chemical reactions. Experiments have demonstrated that the rate of oxidation and the degradation process of polymers can be effectively regulated by controlling the temperature [107]. When exposed to elevated temperatures in air or oxygen environments, air, O_2 and oxygen-enriched air, when used as oxidants, result in the formation of oxidative radicals on polymer, oxidative cleavage and the subsequent conversion of plastic waste into small molecule oxidation products. However, elevated temperatures in the presence of oxygen increase the risk of explosion, underscoring the paramount importance of safety [14]. An effective method for the oxidation of polyolefins is metal-catalyzed C-H bond functionalization, introducing oxygen-containing functional groups (carboxyl, hydroxyl, carbonyl, aldehydes and esters) into polymer chains. For instance, the compatibility, adhesion, permeability and surface wettability of polymers can be enhanced [108].

John’s group has developed a method for the hydroxylation of PE based on the Ni-catalysed($[Ni(Me_4Phen)_3](BPh_4)_2$) oxidation of the C-H bond. The introduction of functional groups (including alcohols, ketones, and alkyl chlorides) per 100 monomer units was observed to occur between 2.0 and 5.5 times, with alcohol-to-ketone or chlorine selectivity reaching as high as 88% [108]. Subsequently, the C-H bonds in PE were subjected to selective catalytic oxidation using Ru catalysts. Even at a lower degree of functionalization, functionalized materials can exhibit physical properties, such as stronger adhesion, that are not present in unmodified polyolefins [109]. It was demonstrated that transition metals, particularly Co(II) and Mn(II) acetylpyruvates, serve as effective catalysts for the oxidation of HDPE. This occurs through the reaction of these metals in aqueous dispersions at 120 °C under 8 bar O_2. The reaction time was reduced by a factor of two to three in comparison to the non-catalytic process [101].

5.3. Photocatalysis

Given the low solubility of the majority of non-biodegradable plastics, there are few reports on reactions below 200 °C. Instead, light can be considered a sustainable energy source. In the case of oxidative cleavage, the excitation of free radicals by light irradiation is a key mechanism underlying the breaking of polymer bonds [110]. It can excite to achieve various chemical transformation processes, including energy transfer, bond breaking, single electron transfer, and hydrogen atom transfer.

In recent years, the development of photocatalysts as a green and sustainable substance has become a pivotal area of research. Currently, the most prevalent photocatalysts are semiconductor materials, including titanium dioxide (TiO_2) [111], zinc oxide, and others. Additionally, graphitic carbon nitrides (g-C_3N_4), graphene-based photocatalytic materials, bismuth vanadates, cadmium sulfides (CdS), tantalum oxides (TaON), and niobium pentoxide (Nb_2O_5) [112] are also in use. These semiconductor photocatalysts, which display high reactivity and stability, are capable of generating electron-hole pairs under light irradiation. They can be effectively used in various applications, including water separation, solar energy capture and the abatement of pollutants through heterophase photocatalysis [113]. This section mainly focuses on the oxidative cleavage of plastics catalyzed using photochemical methods, including homogeneous and heterogeneous catalysis (Table 5).

Table 5. Summary of experimental oxidative cleavage data.

Feed	Temperature/°C	Pressure	Catalyst	Time/h	Major Products	Yield/%	Ref.
PE/PP/PVC	RT	Air	Nb_2O_5	40	CO_2	main	[112]
PE	RT	Air	Goethite	300	Mass loss	16	[114]
PS	RT	0.1 Mpa O_2	PSA-TiO_2	4	Benzoic acid	44.5	[115]
PS	150	10 bar O_2	g-C_3N_4	24	Benzoic acid	74	[116]
PS	RT	2 bar O_2	g-C_3N_4	8	Acetophenone	86.2	[117]
PVC	RT	Air	CDs/Zr-MOF	60	CH_3COOH	14	[118]
Phenoxy resins	RT	Air	Ir-based	4–10	Dimethyl bisphenol A	60	[119]

5.3.1. Heterogeneous Photocatalysis

In natural environments, the weathering rate of plastics is accelerated under solar exposure. In particular, the corrosion rate of plastics is accelerated when they are exposed to high-intensity sunlight for long periods in air circulation [114]. Consequently, numerous researchers have enhanced this process in laboratory settings by employing high-energy photons (such as gamma or UV light [120]) to initiate photo-induced oxidative cleavage on plastic surfaces. For example, Doğan et al. calculated and compared the doses of UV lamps and solar UV after irradiating PE films with UV lamps and sunlight using Philips TUV 15 W/G15T8 UV lamps. Following a 14-day exposure to UV-C irradiation, a 13% reduction in PE film thickness was observed, accompanied by a 9.4% increase in weight per square centimeter.

Heterogeneous catalysts have the advantage of easy separation, and heterogeneous catalytic systems are also promising for the conversion of chemicals. TiO_2 is currently reported to be one of the most common and effective heterogeneous semiconductor photocatalysts, with a band gap energy of approximately 3.2 eV. It is activated in the UV region to break C-C and C-H bonds during photocatalysis [121]. The optimization of the photocatalytic activity of TiO_2 can be achieved through many different methods, including alternating its crystalline structure, particle size and introducing defects. Furthermore, the electronic structure and optical properties of the catalysts can be modified through doping and surface modification to enhance their response efficiency in the visible region, thereby improving their photocatalytic performance. For instance, researchers examined the photocatalytic degradation performance and mechanism of LDPE-TiO_2 in NaCl-free water, NaCl-containing water, and air [121]. The modification of organic amine ligands on the TiO_2 surface resulted in enhanced degradation activity of PS. The alkaline modifiers significantly improved the initial alkyl C-H oxidation and C-C cleavage processes, with the primary products being benzoic acid in yields up to 43.5% [115].

Graphitic carbon nitride (g-C_3N_4), as a non-metallic organic polymer photocatalyst with an appropriate band gap width. The catalyst can be readily prepared through the calcination of a range of inexpensive and accessible precursors, including monocyanamide, dicyanamide, thiourea, melamine, and urea [122]. To illustrate, Wang demonstrated a photocatalytic method to oxidize PS to aromatic oxygenated compounds under visible light irradiation using a g-C_3N_4 catalyst prepared by thermal condensation of urea [116]. The conversion of 0.5 g of PS plastic waste at 150 °C yielded 0.36 g of aromatic oxygenates, with benzoic acid, acetophenone and benzaldehyde identified as the main products in the liquid phase. The conversion rate was found to be >90%. Furthermore, high surface area g-C_3N_4 was synthesized with high selectivity for the conversion of PS to acetophenone under visible light by employing a variety of stripping techniques, including chemical stripping (C-g-C_3N_4), thermal stripping (T-g-C_3N_4) and ultrasound-assisted stripping (S-g-C_3N_4) [117,123]. In addition, the immobilization of various metals onto g-C3N4 also enhances its photocatalytic properties. Ru is a low-cost and biocompatible metal that promotes C-H bond cleavage, and enhances light absorption and electron injection. Ru was doped into graphitic phase carbon nitride (g-C_3N_4) to investigate its radical reaction mechanism in the photocatalytic degradation of LDPE and to explore the synergistic effects of pH and reaction temperature on the photocatalytic efficiency [113].

Nb_2O_5 is abundantly stored and has good environmental friendliness and strong oxidation ability. Due to its valence band maximum of +2.5 V and conduction band minimum of −0.9 V, it is widely employed in photocatalysis. Nb_2O_5 with unique Lewis acid sites (LASs) and Brønsted acid sites (BASs) can be synthesized by different methods, and these properties are crucial for the activity of photocatalysis. Xie proposed a photocatalysis strategy that is capable of achieving complete photodegradation of PE with 100% conversion under simulated natural environmental conditions using a single atomic layer catalyst of Nb_2O_5 [112]. Furthermore, it was discovered that the generated CO_2 could be transformed into acetic acid (CH_3COOH) through selective photocatalysis. Despite the successful conversion of a diverse range of waste plastics into C2 fuels through light-induced sequential C-C bond cleavage and coupling reactions, the current conversion process with CO_2 as an intermediate product has resulted in a relatively low yield of acetic acid.

As a porous photocatalyst, metal-organic frameworks (MOFs) have tailored structures and tunable properties, combining the advantages of both homogeneous and heterogeneous catalysts. They are typically formed by metal ions or metal clusters (metal nodes) and organic ligands through a process known as self-assembly. Therefore, MOFs show great potential and application in photocatalysis [124]. To date, various effective methods have been proposed to enhance the degradation performance of MOFs, including surface photosensitization, heterostructure building, noble metal modification and elemental doping. Among various types of MOF materials, the light absorption ability of MOFs can be enhanced by complexing with metal nanoparticles (Au, Ag, Pd, Fe), particularly in the visible and near-infrared regions, thus improving photocatalysis efficiency. The photocatalysis efficiency of Fe-based MOF photocatalysts has been widely documented, with their strong absorption of sunlight and superior pollutant removal capabilities [125]. The composite photocatalyst (Cu_1Pd_2)z@PCN-222(Co) was constructed by integrating cobalt and ultrafine CuPd nanocluster catalysts into a porphyrin-based metal-organic framework. In the presence of visible light, the excited porphyrin transfers electrons to both the Co sites and the CuPd nanoclusters [126]. On this basis, Dou synthesized a bimetallic MOF (FeAg-MOF) and then converted the unstable Ag sites in FeAg-MOF into stable Ag_2O nanoparticles by light [127]. The proper matching of the conduction and valence bands of Ag_2O and Fe-MOF has the effect of extending the light absorption range and promoting efficient electron-hole separation in the Ag_2O/Fe-MOF photocatalysts. A variety of plastics such as PEG, PE, and PET were converted into small hydrocarbon molecules and produced H_2. Subsequently, the group attempted to transform unstable metal sites in MOF into ultra-small semiconductors. Zn-UiO66-NH_2 was selected as the precursor and uniformly encapsulated in MOF pores for photocatalytic reactions in plastics [128]. The amine (-NH_2) group in it provides a coordination effect to Zn^{2+} and helps to enrich Zn sites in the MOF pores. Furthermore, the prepared photocatalyst CDs/Zr-MOF, which combines carbon nanodots with metal-organic frameworks, was employed for the upcycling of photocatalytic PVC. The maintenance of the MOF structure not only facilitated charge and mass transfer but also improved the surface-to-volume ratio of the carbon nanodot active sites [118].

5.3.2. Homogeneous Photocatalysis

Homogeneous photocatalysts are uniformly dispersed at the molecular level, and their active centers are uniformly distributed throughout the reaction system. This makes homogeneous photocatalysts exhibit high selectivity and activity in photocatalytic reactions. However, it often gives rise to difficulties in recycling. Han [129] et al. employed vanadium(V) photocatalyst for the selective conversion of small molecule alcohols, poly(ethylene glycol) (PEG) copolymers and poly(ethylene monohydric alcohols) to formic acid and formate by a visible light-driven C-C bond oxygenation method using a low-power white light-emitting diode (LED) as the energy source. Subsequently, an optically-driven recycling method utilizing inexpensive metals was reported via a C-H bond oxidation/C-C bond cleavage tandem reaction method [130]. The majority of conventional plastics (e.g., PS, PVC, PE, PVA) were recycled with up to 77% carbon recovery and the selective formation of valuable, separable products, including formic acid, acetic acid and benzoic acid. The successful application of optimized reaction conditions to copolymers, multilayer packaging and actual plastic waste also validated the continuous flow g-stage process. Robert [119] concentrated his research efforts on organocatalytic reactions based on proton-coupled electron transfer (PCET). They reported a catalytic method to depolymerize commercial phenoxy resins and high molecular weight hydroxylated polyolefin under visible light irradiation at ambient temperature. Using Ir-based molecular catalysts, PCET activates C-H to generate alkoxyl radicals, which trigger β-cleavage of the C-C bond. The degradation process yields separable product mixtures, which are also readily converted to condensation monomers.

Zeng reported a highly practical and selective reaction for the efficient oxidation of alkyl aromatics to carboxylic acids, which addresses the issue of selective degradation of PS [131]. The reaction was catalyzed by inexpensive and readily available $FeCl_3$ with visible light (blue LED light) at room temperature in an oxygen environment. Subsequently, through optimization of the conditions, the system can facilitate the selective degradation of PS to benzoic acid, providing a practical approach for the generation of high-value chemicals from PS waste [132]. Erin employed $FeCl_3$ as a catalyst for the upgrading of PS to benzoyl groups under white light irradiation and an oxygen-enriched environment [133]. The homolytic cleavage of $FeCl_3$ generates chlorine radicals, which facilitate the degradation process through hydrogen atom extraction (Figure 7). Eventually, the high molecular weight PS (>90 kg/mol) was degraded to a molecular weight of less than 1 kg/mol, with the production of 23% benzoyl products. Subsequently, the disparity in reactivity between chlorine and bromine radicals was employed to elucidate the degradation mechanism of PS [134]. The disparity in reactivity between chlorine and bromine radicals was employed to elucidate the degradation mechanism of PS. An exogenous bromine source was introduced to elevate the concentration of HBr, which augmented the yield of acetophenone as the principal degradation product.

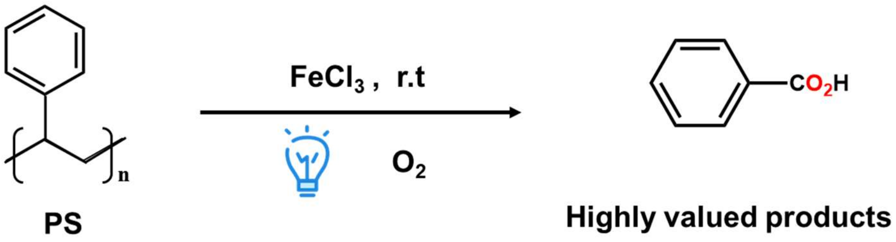

Figure 7. Upcycling of PS with metal catalysts ($FeCl_3$) and oxygen.

5.4. Electrocatalysis

The field of electrochemistry has witnessed a period of significant growth in recent years, with the application of electrochemistry to plastic degradation processes representing an emerging area of technological development. The provision of electrons through an externally applied potential enables a diverse range of chemical reactions that may not be feasible through conventional thermochemistry or photochemistry [135]. The single-electron oxidation and reduction reactions promoted by electrochemical processes achieve the transformation of free radical intermediates. Electrocatalysis depends on the electrode material, electrolyte, and physicochemical properties of the material. Electrodes represent the core components of electrochemical systems, facilitating the conduction of electricity, the activation of reactants, the acceleration of electron transfer rates and the selective promotion of electrochemical reactions [136]. Electrocatalysis can utilize either a molecular medium as a catalyst (transition metal complexes or organic compounds) or the electrode itself as a catalyst [137]. The initiation or acceleration of redox reactions is facilitated by the electrode in the presence of an external potential, which can be generated by an electric field. Such electrodes include metal oxide electrodes (Ti/PbO_2, SnO_2-based, RuO_2 [138]), as well as carbon-based electrodes.

Moreover, the catalyst plays a crucial role during electrocatalysis. A nickel-supported NiOOH catalyst was synthesized via a two-step method for the electrocatalytic conversion of PBAT alkaline hydrolysis products to higher-value chemicals (succinate), with a current density of up to 100 mA cm^{-2} at 1.43 V and a Faraday efficiency of 97.6% [139].

5.5. Chemical-Biological Cascades Catalytic Oxidation

The degradation of polyolefin plastics by chemical methods results in a diverse range of product distributions due to the absence of functional sites within their pure hydrocarbon structure. These sites are necessary to direct the catalyst to the specific cleavage site within the polymer. A new method for developing chemical-biological upcycling techniques is currently being proposed. To illustrate, a cascade method of $Co(acac)_2$-catalyzed radical oxidation reaction with *Bacillus velezensis C5*, which can degrade LDPE, resulted in a 2.32-fold increase in the degradation rate compared to direct biodegradation [102]. Sullivan et al. [140] co-authored a breakthrough publication on the catalytic oxidation of

HDPE, PS, and PET mixed plastics (Figure 8). It was discovered that metal-catalyzed autoxidation could occur through C-H bond oxidation and C-C bond cleavage, with Co and Mn catalysts. The cleavage of O-O bonds to form alkoxyl radicals was observed, which could subsequently undergo C-C cleavage via a β-cleavage step. The mixed plastics were depolymerized into a mixture of oxygenated small molecules which are favorable substrates for biotransformation. Moreover, the researchers devised a *Pseudomonas aeruginosa* to biotransform the acid mixture into a single product, β-ketoadipate or polyhydroxystreptanoates. The mixing process establishes a strategy for the selective conversion of mixed plastic wastes into useful chemical products.

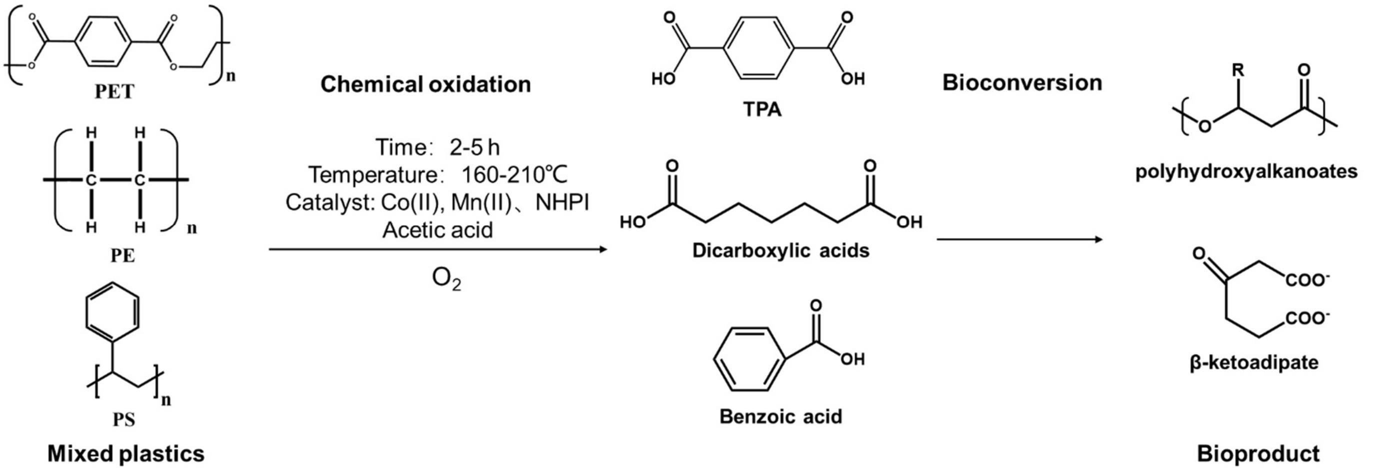

Figure 8. Upcycling of mixed plastic waste through chemical oxidation and bioconversion.

Wang et al. [141] described a comparable chemical-biological cascade method for the expeditious conversion of PE into structurally intricate and pharmacologically active compounds (Figure 9). The aerobic catalysis of PE collected from post-consumer and marine waste streams resulted in oxidative cleavage, producing carboxylic dicarboxylic acids that could be used as a carbon source by the *Aspergillus*. The modified Aspergillus niger was observed to synthesize a range of fungal secondary metabolites, including *Aspergillus* benzaldehyde, citrulline, virulence factors and mutagens when grown using these oxidation products. Subsequently, a similar cascade approach was employed to oxidatively cleave PS, resulting in the production of benzoic acid. This was then utilized by *Aspergillus* constructus strains for the synthesis of fungal secondary metabolites [142]. This biochemical cascade approach has greatly expanded the range of recyclable products from various types of plastics.

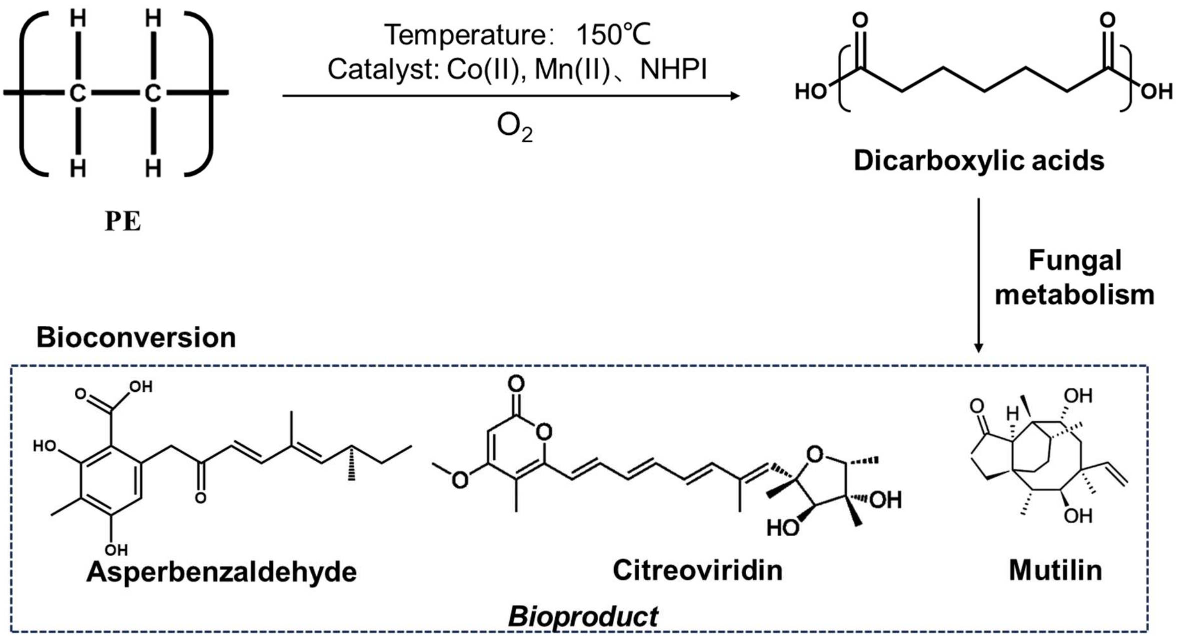

Figure 9. Upcycling of PE with metal catalysts and oxygen.

5.6. Summary

Homogeneous photocatalysis is typically highly active and can achieve the cleavage of C-C linked plastics such as PE and PS through C-H activation and C-C cleavage. Heterogeneous photocatalysis selective oxidative cleavage consists of three reaction processes: direct photocatalysis of PLA/PVC/PE to acetic acid; conversion of plastics to CO_2 as an intermediate for reduction to CH_3COOH; and oxidative cleavage of PS to benzoic acid by a C-H activation/C-C cleavage process similar to that in homogeneous photocatalysis. To address the current challenges, future researches focus on the development of novel catalysts designed to efficiently catalyze the degradation of plastics, as well as the exploration of new photocatalytic mechanisms for the efficient conversion of these challenging plastics. The reaction conditions should also be optimized to reduce CO_2 generation and improve the selectivity of the target products.

6. Conclusions

Over many years, extensive research has been conducted into the degradation and recycling of waste plastics. This encompasses a range of techniques, including pyrolysis, solvolysis (such as hydrolysis, alcoholysis ammonolysis, and alkene metathesis), hydrogen degradation, and oxidation. In the past, researchers concentrated their efforts on the practical applications of pyrolysis of waste plastics. To accelerate the degradation rate under mild conditions, researchers have also developed varieties catalysts, including metal, non-metal, bifunctional composite, and MoF materials for hydrotreating, oxidative treatment, and other methods. In the past, researchers concentrated their efforts on the practical applications of pyrolysis of waste plastics. To accelerate the degradation rate under mild conditions, researchers have also developed varieties catalysts, including metal, non-metal, bifunctional composite, and MoF materials for chemical degradation and recycling methods.

Notwithstanding the recent advancements in this field, numerous challenges and avenues for enhancement persist. Firstly, it is necessary to expand the scope of research concerning polymer plastics. While polyester plastics, such as PET, have been the subject of considerable research, comparatively little attention has been devoted to polyolefin plastics, including PE, PP, and PVC. Furthermore, the selectivity of the small molecule products in the degradation process should be enhanced to facilitate the generation of a greater quantity of high-yield, high-value products to enhance the potential and competitiveness of the commercialization process. For example, in the ongoing degradation process of PS to C2 compounds, an excess of intermediate product CO_2 is converted, resulting in a diminished yield of the desired target product, acetic acid. In addition, most of the oxidative cleavage described in this paper still utilizes high concentrations of oxygen. Such elevated oxygen levels can potentially lead to explosive issues. Therefore, if waste plastics are processed in large quantities, large reactors should be designed with this in mind to minimize safety issues while effectively degrading the polymer. Waste plastics can also be recycled in mixed chemical-biological cascades. Beckham illustrates a study on the valorization of polymer waste through oxidative cleavage and biotransformation. The upcycling of waste plastics into valuable chemicals is achieved through the alteration of the bacterial or fungal mechanism.

In conclusion, future research into the recycling and degradation of waste plastics should prioritize the reduction of the difficulty of the reaction. It is recommended that the degradation rate is increased under mild conditions, while simultaneously improving product selectivity to obtain high-value products. It is essential to guarantee the commercial viability and environmental friendliness of the technology route to facilitate the advancement of plastic recycling technology.

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Author Contributions

Z.T.: Writing—Original draft, Visualization, Investigation, Formal analysis. Z.W.: Investigation. Y.Z.: Writing—review & editing. G.X.: Writing—Review & editing, Project administration, Methodology, Funding acquisition. H.S.: Writing—Review & editing, Supervision, Resources, Project administration, Methodology, Funding acquisition, Conceptualization.

Ethics Statement

Not applicable.

Informed Consent Statement

Not applicable.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Nomenclature

PE: Polyethylene; LDPE: low-density polyethylene; HDPE: high-density polyethylene; PP: Polypropylene; PVC: Polyvinyl chloride; PET: Polyethylene terephthalate; PS: Polystyrene; Mw: weight-average molecular weight; Mn: number-average molecular weight; PU: Polyurethane; PLA: Polylactic acid; BTX: Benzene, toluene, ylene; BHET: 2-hydroxyethyl methyl terephthalate; TPA: terephthalic acid; EG: Ethylene glycol; PCA: protocatechuic acid; GLA: glycolic acid; UV: Ultravioletray. MAP: Microwave-assisted pyrolysis; CMP: Chlorine-containing mixed plastic.

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