Sustainable chemical upcycling of waste polyolefins by heterogeneous catalysis

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Abstract
The mass production of disposable polyolefin products has led to serious plastic pollution and an imbalance between manufacturing and recycling. Given these challenges, the chemical upcycling of waste polyolefins has attracted extensive attention due to its high efficiency and economic benefits. Herein, we review the development of polyolefin chemical upcycling in heterogeneous catalysis. The status quo of polyolefin recycling is first discussed. We then introduce the advanced strategies for chemical upcycling in the view of different value-added products and discuss their challenges and prospects. Our in-depth analysis centers on the catalytic mechanism and the design principle of heterogeneous catalysts. Finally, we outlook the promising directions to facilitate the degradation process via polymer and catalyst design and optimized catalytic engineering. Innovative strategies are expected to promote the chemical upcycling of polyolefins, bringing great promise for the sustainable development of society.

KEYWORDS
chemical upcycling, heterogeneous catalysis, plastic recovery, polyolefin, value-added products
INTRODUCTION

Plastics are a crucial and indispensable component of modern society and human life,\(^1,^2\) and are widely used in agriculture, transportation, packaging, chemical, and construction industries due to their excellent physicochemical properties.\(^3,^4\) Present statistics and estimations indicated that the global plastic production reached about 360 million tons (Mt) in 2019, and the annual output of plastics by 2050 would exceed 500 Mt.\(^5\) However, the service lives of most plastics are limited and usually below 1 month due to their disposable applications. This phenomenon leads to the excessive discharge of waste plastics. Limited by low-efficiency and high energy-consuming plastic recycling technologies, more than 70% of waste plastics have not been recycled and abandoned in the landfilled and natural environment. The time of natural aging and decomposition for waste plastics is exceedingly long for decades and even centuries. This is due to the strong chemical inertness of polymers, causing serious biological damage and pollution to the atmosphere, soil, and water. Therefore, for sustainable development in the future, constructing high-efficiency, environmental friendly, and energy-saving strategies for recycling/upcycling waste plastics is extremely urgent and crucial.

Polyolefins are the most demanded and used plastics with a proportion of approximately 57% of total plastics in the world (Figure 1A).\(^6\) The conversion of waste polyolefin to value-added products via chemical upcycling has drawn tremendous attention in recent years,\(^7,^8\) which mainly includes homogeneous, enzyme, and heterogeneous catalysis.\(^9\) The homogeneous and enzyme catalysis systems can maximize the mass/heat transfer between the catalysts and polymer substrates and exhibit excellent activity and selectivity to target product. However, various additives and impurities in the commercial plastics can poison or react with the catalysts, resulting in the deactivation of catalysts.\(^10,^11\) In contrast, heterogeneous catalysts are more suitable for industrial recovery of waste polyolefins. Moreover, the poisoned or sintered catalysts can also be regenerated by some physical or chemical strategies. As a result, the superior heterogeneous catalysts are more favorable for the chemical upcycling of waste polyolefins. Notably, the design of efficient heterogeneous catalysts for polyolefin upcycling is the key, but most explorations are still in their infancy, requiring a deep understanding of the catalytic system. In particular, revealing the structure-property relationships of catalysts and the effects of various parameters on polyolefin degradation will significantly deepen the basic understanding of polyolefin
chemical upcycling. Therefore, a summary and discussion of the reported technologies and catalysts are necessary for further research.

This review will discuss the current situation of polyolefin recovery and various chemical upcycling technologies. The commercial strategies and advanced industrial technologies are first briefly summarized. Then, from the perspective of different target products, we in-depth discuss the common and advanced strategies of polyolefin chemical upcycling in recent years, and present the direction of catalyst or catalysis design based on their challenges. Finally, we proposed the potential enhancement approaches for efficient and selective recovery of polyolefins in the view of polymer modification and the design of catalysis or catalyst. Compared to other published reviews,5,12–14 we highlight more investigations on the structure-performance relationships and the design of catalysis or catalysts, which are less discussed before. In addition, the comparison and discussion on different strategies from the perspective of a specific product can give some new insights and complementation for the catalysis and catalyst design.

2 | CURRENT SITUATION OF POLYOLEFINS RECYCLING AND UPCYCLING

2.1 | Recycling approach of waste polyolefins

Polyolefins mainly include polyethylene (PE) and polypropylene (PP), and the PEs can be divided into high-density PE (HDPE), low-density PE (LDPE), and linear low-density PE (LLDPE) based on their different physicochemical properties (such as density, crystallinity, mechanical strength, etc.) (Figure 1B). Different polyolefins have significant differences in recyclability due to their specific commercial applications. For example, the plastics with long service lives, such as HDPE and PP, are widely used in the production of plastic containers, plastic bottles, plastic furniture, and other daily and industrial applications that possess low recycling frequency and are easily recycled. On the contrary, the LDPE is commonly used in producing disposable packaging and plastic bags, which have a short service life and wide distribution, resulting in the difficulty of recycling.

The commercial strategies of waste polyolefin recycling are mainly divided into the following five categories (Figure 1C): incineration treatment, primary, secondary, tertiary recycling, and landfill.15 Waste polyolefins are classified by physical and chemical properties for different treatments to achieve a recycling economy. Specifically, primary recycling generally recovers waste polyolefins through simple processing to close the loop, and the recovered polyolefins are used to produce new plastics for the same application. Different from the primary recycling, secondary recycling refers to mechanical recycling in which the recovered wastes are utilized to construct other products for different applications, achieving open-loop recycling.16 The waste polyolefins always undergo the following steps17: (1) separation and sorting on the basis of the size, shape, density, and other properties; (2) baling and transport; (3) washing to remove the contaminants; (4) grinding to form the plastic flakes; (5) compounding and pelletizing to meet the converter standard; and (6) extrusion. In the extrusion process, the polymers can be plasticized or softened by the heat and rotating screws, followed by the production of fixed cross-section extrudate via the temperature-controlled barrel sections.18 Through the thermal conduction and viscous shearing, processes, such as scission, crosslinking, branching, and thermo-oxidation, can occur in the extruder to generate the degraded materials for various applications.18–21 However, the physicochemical properties of new-produced polyolefins always get negative influences due to the existence of impurities, additives, and repetitive harsh mechanical processing. Such characteristics lead to the limited frequency of waste polyolefins and the formation of nonrecyclable polyolefins. For the nonrecyclable polyolefins, tertiary recycling (chemical upcycling) has been widely studied to convert the polyolefins to their monomers or other value-added chemicals to create higher economic benefits and meet sustainable goals.

2.2 | Industrial progress in polyolefin upcycling

In the global industry, polyolefin degradation is always driven by high temperatures. The Plastic Energy Company uses Thermal Anaerobic Conversion technology to convert waste PE, PP, PS plastics into saturated steam hydrocarbons by mechanical treatment. Diesel, naphtha, syngas, and other chemicals can be obtained after regular pressure fractionation, which are recycled in the preparation of new plastics and the operation of the factory.22 This company has now reached cooperation with others in many countries and plans to process 5 Mt of plastic waste in Europe, Asia, and the United States every year by 2030. Anellotech Company has developed a Plas-TCat technology, which can effectively convert waste and mixed plastics into value-added olefins, alkanes, and aromatic chemicals. For example, this company announced that their Plas-TCat technology successfully degraded the waste Lay’s potato chip bag into p-xylene monomers in 2020.23 In virtue of their patented pyrolysis technology and the TCat-8 pilot plant for Bio-TCat (a technology to convert
biomass into BTX [benzene-toluene-xylenes] aromatics, the Plas-TCat technology is promising to be applied on a larger commercial scale. In addition, Novoloop Company utilizes a technology of Accelerated Thermal Oxidative Decomposition (ATOD™) to degrade postconsumer polyolefin plastics into various organic acid monomers and use them to reproduce high-quality plastic products. Notably, the CO$_2$ emissions in this process are much lower than other industrial technologies.\(^{24}\) LyondellBasell Company has developed a MoReTec molecular recycling technology through cooperation with Karlsruhe Institute of Technology, which uses catalysts in the pyrolysis process to degrade waste plastic (plastic bottles, plastic packaging, etc.) into molecules, followed by the polymerization process to reproduce the plastics.\(^{25}\) In 2020, this company ran a pilot plant that can process 5–10 kg of household plastic waste per hour. Meanwhile, they are already producing and selling new plastic products obtained from waste plastics, which is planned to produce and sell 2 Mt of renewable polymers every year by 2030. In addition, DOW Company cooperated with Fuenix Company to process waste mixed plastics into high-quality liquid fuels (naphtha, paraffin, and liquefied petroleum gas) through the Fuenix Ecogy technology with low CO$_2$ emissions.\(^{26}\)

Impressively, with appeals from the Alliance to End Plastic Waste and various global organizations concerned with sustainability and environmental protection, the chemical upcycling of waste plastics has attracted much of the attention from many petrochemical companies worldwide (including BASF, SABIC, SHELL, etc.). As one of the most essential plastic products in the petrochemical industry, the recycling and upcycling of polyolefins have become an indivisible part of sustainable development.

Pyrolysis is the most applied chemical strategy in the industry for polyolefin upcycling. The pyrolysis system from Anellotech Company is taken as an example, which is commercially applied for Bio-TCat technology and further industrialized in Plas-Tcat technology (Figure 2A).\(^{27}\) In this system, plastics are fed into the fluidized bed reactor, and a separator separates the generated fluid product streams. Notably, the deactivated catalyst and char can be separated and transported to the regenerator and combustion system, followed by the regenerated catalyst and oxidation product back to the reactor for further depolymerization. In industrial polyolefin degradation, the reactor’s type, configuration, and various parameters are critical for their industrialization degree. Here, we introduce two types (pyrolysis and thermal oxidation) of reactors. As shown in Figure 2B, Plastic Energy Company designs a pyrolysis reactor,\(^{28}\) which contains a reactor chamber and contactor mounted above the reactor. The pyrolysis system first transfers the waste polyolefins to pellet or flake forms to the feed lines before entering the pyrolysis reactor. The processed pellet and flake materials are then heated in

![FIGURE 2](image-url)
After the reaction, acetone was added to the reactor to filtrate out the oligomeric resin. Next, sodium hydroxide, hydrochloric acid, and acetone were added respectively, and filtrations were used to collect the product right after each addition. As a result, the product contains various acid monomers, which could be further purified and combined with other monomers from conventional sources to become polyols.

3 | CHEMICAL UPCYLING STRATEGIES OF POLYOLEFINS

Recently, the chemical upcycling of polyolefins has achieved remarkable progress and development. Different strategies can selectively obtain various types of target products. The product types can be divided into four species including (1) oils and arenes, (2) carboxylic acids, (3) syngas, and (4) carbon materials. The recovery of waste polyolefins is a value-added economic process. According to the recovery difficulty, cost, application, and other parameters, the selective conversion of polyolefin is very crucial to enhance the product value. Taking pyrolysis as an example, the desirable products are always the oils and arenes and other high-value chemicals, rather than the relatively low-value gaseous products (e.g., CH₄ and CO₂) and char. Therefore, it is necessary to realize the tunable product distribution through chemical strategies by the development of catalyst and catalysis. In our review, from the perspective of different value-added products, we will introduce various chemical strategies and further discuss the structure-performance relationship and the design catalyst/catalysis design to achieve a maximum economic benefit.

3.1 | Oils and arenes

The structural unit of polyolefins is composed of C−C bonds and C−H bonds. To shorten the long chain of polymers, the cleavage of chemically inert C−C bonds is necessary but difficult. In the oxygen-free systems, the catalytic cleavage of C−C bonds at high temperatures can break long polymer chains to oils and arenes with high-added values. The development of polyolefin degradation to oils and arenes may alleviate the current severe consumption of fossil fuels.

3.1.1 | Thermal and catalytic pyrolysis

Pyrolysis technologies are the most commonly used strategies in the industrial chemical upcycling of polyolefins.³⁰ For the thermal pyrolysis process, polyolefins are converted into alkanes, alkenes, aromatics, and gases via random cracking of long polymer chains in inert atmospheres³¹⁻³⁵. This process follows the principle of free-radical mechanism, and the initiation reaction first occurs to crack the C−C bonds and generate the free radicals at a high reaction temperature, then the hydrogen atoms on the polymers can be rapidly captured by free radicals to form the short-chain hydrocarbons.³⁶ Despite high efficacy, the pyrolysis process always requires harsh reaction conditions of high temperatures (＞400 °C),³⁷ which always causes the preferred formation of low-value gaseous products (Figure 3A).

In contrast, catalysts during the pyrolysis process can significantly reduce the reaction temperature and time with a tunable product distribution.³⁰,³⁸ Nowadays, catalytic pyrolysis has become the primary technology in the industry to recycle polyolefins. Common catalytic pyrolysis catalysts include various acidic zeolites (ZSM-5, HZSM-5, HY, USY, etc.)³⁹⁻⁴³ and catalytic cracking (FCC) catalysts.⁴⁴ Both thermal and catalytic pyrolysis proceed together during the reaction process. Different from thermal pyrolysis, the occurrence of catalytic pyrolysis has mainly relied on the formation of carbocation intermediates.⁴⁵,⁴⁶ The Brønsted acid sites in the catalysts can introduce protons into polymer molecules at the beginning of the reaction to form active carbocation intermediates, followed by the cracking of C−C bonds and isomerization at high temperatures. Importantly, the isomerization process can rearrange the carbon skeleton to produce linear or branched chains and aromatic hydrocarbons. Then, the small molecule products enter the pores in the catalysts and undergo secondary cracking and isomerization to form smaller hydrocarbons. The activity and product distribution can be effectively tuned by adjusting the reaction temperature and time. On the other hand, the structures of catalysts also significantly affect catalytic performance. The target products can be readily achieved by tuning the specific surface area, pore size distribution, strength, and types of acid sites. Nevertheless, since the C−H bond nonoxidative activation is a thermodynamic endothermic process, the coke deposition on the catalyst surface is caused by the in-depth C−C cleavage at the high reaction temperature (300−600°C) which leads to the deactivation of catalysts.⁴⁷ Although the high-temperature oxidation regeneration process can remove the surface coke, the catalyst structures are irreparably destroyed, and the catalyst life is severely shortened. In addition, the regeneration processes also consume enormous energy, which is not conducive to sustainable recycling (Figure 3A). Therefore, developing highly efficient catalysts with superior thermal stability and anticoking property for catalytic pyrolysis of polyolefins is very crucial at present.
3.1.2 Hydrocracking

Considering the coke formation and harsh reaction conditions during the pyrolysis process, the introduction of high-pressure H₂ and hydrogenation catalysts into the reaction system would make the catalytic process thermodynamically favorable and significantly lower the reaction temperature (Figure 3A). Moreover, the generated carbon precursor can be effectively hydrogenated during the reaction, prolonging the catalyst life and reducing the high energy consumption caused by catalyst regeneration. In terms of the product value, the generated olefins would further be hydrogenated to gasoline, diesel, kerosene, lubricating oil, and other products with high economic benefits.

Bifunctional catalysts consisting of solid acidic zeolites (C−C cleavage) and dehydrogenation and hydrogenation metal catalysts (C−H activation) have been widely studied for polyolefin hydrocracking, among which the metal catalysts include the Pt, Pd, Fe, and Ni-based catalysts. In the hydrocracking process (Figure 3B) the C−H activation first occurs on metal catalysts to dehydrogenation. The intermediates desorb from the metal and diffuse to the Brønsted acid sites to form carbocation active intermediates, followed by the C−C cleavage and isomerization, which is similar to the catalytic pyrolysis reaction. The cracked and isomeric intermediates then diffuse to the metal sites for hydrogenation after completing the above reaction to form short-chain products. Compared with thermal and catalytic pyrolysis reactions, the hydrocracking can complete the high-efficiency degradation of polyolefins under mild reaction conditions (temperature: 250−375°C, H₂ pressure: 1.2−18 MPa) and shorter reaction time (<6 h). Among the various metal catalysts, Pt-based catalysts exhibit more efficient catalytic performance.
toward polyolefin hydrocracking. For example, Liu et al. utilized Pt/\(\text{WO}_3/\text{ZrO}_2\) and HY (FAU-type zeolite) composite catalysts for selective hydrocracking of LDPE under mild reaction temperature of 250°C and \(\text{H}_2\) pressure of 3 MPa (Figure 3C). When the reaction time is 2 h, the LDPE is efficiently and selectively converted into value-added liquid fuels with a conversion of approximately 94% and liquid product yield of approximately 85%, respectively.

On this basis, Vance et al. further studied the relationship between the metal-acid balance (MAB) and the mechanism of PE hydrocracking in Pt/\(\text{WO}_3/\text{ZrO}_2\) catalyst. Detailed experiment and analysis showed that the high MAB caused the rapid dehydrogenation on metal sites, while the skeleton rearrangement and C–C cleavage at the acid sites become relatively slow, leading to the in-depth isomerization of PE and concentrated product distribution with a low yield of small molecule alkanes. By contrast, when the metal loading is low, the rate-determining step is the dehydrogenation and hydrogenation process of PE molecules at the metal sites. The relatively fast reaction rates of cracking and isomerization give a wider product distribution and a decrease in the yield of isomeric products (Figure 3D and E). In summary, exploring the relationship between metal-acid and catalytic performance, as well as the internal mechanism of polyolefin hydrocracking, is an important prerequisite and basis for the design of highly active, selective, and stable hydrocracking catalysts.

3.1.3 Hydrogenolysis

Recently, polyolefin hydrogenolysis has attracted extensive attention. Unlike the hydrocracking reaction, the activation of C–H bonds and the cracking of C–C bonds in polyolefins both occur at the metal sites, suggesting that there are no isomeric products catalyzed by acidic catalysts, and the linear alkanes are the main products of the polyolefin hydrogenolysis.\(^{57}\) The reaction process of polyolefin hydrogenolysis shown in Figure 4A includes the following steps\(^ {57,58}\): (1) Dehydrogenation of polyolefin via C–H activation at the metal sites to form olefin intermediates, (2) C–C cleavage of the intermediates, (3) hydrogenation of short-chain intermediates, and finally (4) desorption. At present, Pt- and Ru-based catalysts are mainly used in the hydrogenolysis of polyolefins. Although Pt-based catalysts have high-efficiency performance in hydrocracking reactions, it is difficult for Pt metal to cleave the C–C bonds at low reaction temperature without the assistance of acid sites. Thus, the reported reaction temperatures for Pt catalysts on polyolefin hydrogenolysis are relatively high (250–300°C) and the degradation time is fairly long.\(^ {59,60}\) As a cheaper active metal for hydrogenolysis, Ru-based catalysts have drawn much attention in recent studies to catalyze polyolefins (including HDPE, LDPE, PP, waste polyolefins) to liquid fuels under mild conditions, with a reaction temperature of 200–250°C, \(\text{H}_2\) pressure of 0–6 MPa, and reaction time from 0–12 h.\(^ {56,61–64}\) However, the following challenges still exist in this reaction: (1) high yield of low-value gases (predominantly methane), generally above 10%, and (2) the long reaction time compared to the hydrocracking reaction.

To obtain more economic benefits, high-value liquid fuels are more preferred in hydrogenolysis reaction, and the inhibition of gas production should be addressed from both catalysts design and reaction engineering. Regarding the reaction engineering of polyolefin hydrogenolysis, the reaction temperature, time, \(\text{H}_2\) pressure, and mass transfer should be studied carefully. Among the above factors, the influence of \(\text{H}_2\) pressure is particularly significant. Based on the previous study about the alkane hydrogenolysis by Nakagawa et al. (Figure 4B),\(^ {65}\) the reaction orders of the side reactions for alkane methanation are negative, indicating that a higher \(\text{H}_2\) pressure is beneficial to inhibit the methanation of alkane molecules. Similarly, Wang et al.\(^ {58}\) confirmed that high \(\text{H}_2\) pressure could accelerate the rate-limiting hydrogenation reaction and desorption rate of olefin intermediates, suppressing the further hydrogenolysis and fragmentation of small molecule products at Ru sites, thereby reducing the generation of low-value methane products. In addition, Jia et al.\(^ {56}\) explored the catalytic performance of commercial 5%Ru/C on HDPE hydrogenolysis in \(n\)-hexane solvent under different \(\text{H}_2\) pressures (0–6 MPa). With a high-pressure \(\text{H}_2\), the cracking of C–C bonds in HDPE molecules is more inclined to occur at internal positions, while the Ru/C catalyst is more favorable to cleave the terminal C–C bonds to generate methane under low-pressure \(\text{H}_2\) (Figure 4C–E). In addition, the presence of solvent affects the mass and heat transfer and changes the conformation of the HDPE molecule, resulting in totally different degradation behaviors. In virtue of the presence of solvents, the commercial Ru/C catalyst exhibited a liquid fuel yield of approximately 75% within only 1 h. The reaction time in this system is much shorter than that of other solvent-free systems. Therefore, the development of more efficient polyolefin degradation systems is expected to become an emerging trend in the future.

Considering that the condition of high \(\text{H}_2\) pressure will lead to the expensive equipment cost for further industrialization, it is necessary to design high-efficiency catalysts with high selectivity toward liquid fuels to replace the high-pressure condition. For example, Wang et al. received a high liquid product yield by introducing \(\text{WO}_x\) in the Ru/WZY catalyst, which acts in a similar role as the high-pressure \(\text{H}_2\).\(^ {58}\) In the initial stage of the reaction, the spillover of adsorbed and dissociated \(\text{H}_2\) would occur from the Ru metal to the \(\text{WO}_x\), and the \(\left(\text{WO}_x\right)_n\) clusters can store \(\text{H}\) in surface hydroxyls (Figure 5A).
When the hydrogenolysis reaction occurred, the stored active H on the WOx surface would return to the Ru surface via the reverse-spillover, facilitating the hydrogenation and desorption of the olefin intermediate. The unique hydrogen spillover and reverse-spillover processes effectively suppress the in-depth hydrogenolysis and fragmentation process. Tennakoon et al. coated the surface of Pt/SiO2 with porous mSiO2 for HDPE hydrogenolysis to simulate the enzymatic deconstruction of macromolecules (Figure 5B).60 Compared with the catalysts in which the metal particles are completely exposed on the support surface, the strong interaction between the pores of mSiO2 and the long-chain HDPE can significantly facilitate their binding, and keep the HDPE in a mobile state, resulting in the continuous hydrogenolysis of HDPE on the Pt metal. Considering that the catalytic performance of the alkanes hydrogenolysis on metal catalysts is sensitive to the structure of active metals. The modifications of active metals in size, electronic structure, geometric configuration, exposed facet, and coordination environment can dramatically influence the hydrogenolysis performance to achieve the highest economic benefits in the future.

3.1.4 Tandem cross strategies

*Tandem catalytic cross alkane metathesis method (CAM).*

The CAM is a process in which the rearrangement of two alkanes is done to obtain a new distribution of carbon chains. The catalysts for the CAM are generally composed of a dehydrogenation and hydrogenation catalyst and a cross-metathesis catalyst. Two alkanes are first dehydrogenated to form olefins, then diffuse to the cross-metathesis catalyst to rearrange to obtain...
products with shortened and extended chains, which diffuse back to the hydrogenation catalyst to generate alkanes. Considering that the polyolefins are essentially ultra-long-chain alkanes, the CAM between polyolefin and short-chain alkane is regarded as a feasible strategy to shorten the polyolefins. In this system, the short-chain alkane is used as a solvent and reactant with an excessive amount. Importantly, the polyolefin degradation via CAM can occur at a low reaction temperature (<200°C), which is much lower than most strategies.

Jia et al. utilized a dual catalyst system for the PE degradation through CAM. The (t-Bu₂PO-t-BuPOCOP)Ir(C₂H₄)/γ-Al₂O₃ and Re₂O₇/Al₂O₃ were used as the dehydrogenation/hydrogenation and cross-metathesis catalyst, respectively, and the n-hexane acted the role of solvent and reactant (Figure 6A). HDPE is first converted to oils and waxes within 2 h, and the waxes are gradually converted into oils by extending reaction time. Bäckström et al. utilized PtSn catalyst as dehydrogenation and hydrogenation catalysts, which are widely used to catalyze the dehydrogenation of alkanes in the industry. The physical mixture of PtSn/Al₂O₃ and Re₂O₇/Al₂O₃ was used as catalysts to convert PE into liquid fuels at 200°C. Nevertheless, the Pt-based catalysts have a low activity toward alkane dehydrogenation at the low reaction temperature. If the reaction temperature is increased, the Re-based catalysts would be unstable, and the coke deposition may be generated on the catalysts during the reaction. Therefore, how to balance the structure-performance relationship between these two catalysts with different functions, and design a reasonable reaction system are the main challenges in the future.

**Tandem hydrogenolysis/aromatization**

The production of aromatics is very attractive in polyolefins recycling due to their high added values. In industry, the aromatics are generally produced by reforming naphtha to form a BTX mixture, followed by an alkylation reaction to obtain the high-value linear alkylbenzenes. However, this technology is strictly limited by the high operating temperature (500−600°C) and high energy consumption. In the chemical degradation of polyolefins, although the catalytic pyrolysis technology can produce the BTX with a moderate yield at 400−600°C, the coke deposition and the high yield of low-value gas products still makes this technique challenging to be commercialized. Therefore, it is crucial to develop high-efficiency strategies for converting polyolefins to aromatics at a low temperature.

Zhang et al. developed a tandem hydrogenolysis/aromatization strategy to produce alkylaromatics in the solvent- and hydrogen-free system (Figure 6B). The coupling of endothermic aromatization and exothermic hydrogenolysis can significantly decrease the reaction temperature. According to the theoretical calculation, to make the aromatization reaction thermodynamically favorable (ΔG° = 0), the H₂ generated by hydrogenolysis
is 10%. As a result, more than 90% of the generated H$_2$ can be consumed by hydrogenolysis, confirming the feasibility of the tandem reaction. The Pt/γ-Al$_2$O$_3$ catalyst efficiently converts PE to alkylaromatics at 280°C for 24 h, and the molar mass of products is in the range of 10−430 g/mol with a low gas yield. In addition, the conversion of commercial LDPE bag and HDPE water-bottle cap also shows high alkylaromatics yields of approximately 69 and 55 wt.%, respectively, indicating that this strategy can be applied to the sustainable chemical upcycling of commercial and discarded plastics to high-value alkylaromatic. This work provides more possibilities for converting olefin intermediates and has important guiding significance in the efficient and selective degradation of polyolefins into various high value-added chemicals.

3.2 Carboxylic acids

Carboxylic acids are important chemicals and raw materials for the manufacture of polymers, coatings, adhesives in the industry. In recent years, many studies have focused their attention on converting polyolefins to carboxylic acids via the advanced oxidation processes, which can occur at a relatively mild oxidation condition, and the oxygen species are incorporated into the carbon chain to form the carboxylic acids. This transformation not only
alleviates the serious pollution caused by polyolefin waste, but the manufacture of new plastics by producing carboxylic acids also realizes the open-loop recycling of polyolefin waste.

3.2.1 Fenton reaction

The structural unit of polyolefin is composed of C–C bonds and C–H bonds, but there are no hydrolyzable functional groups, leading to ultrastable property in nature. Moreover, the physicochemical properties of polyolefins (such as hydrophobicity, crystallinity, surface morphology, and molecular size, etc.) make them difficult to degrade. Therefore, to produce oxygen-containing organic chemicals, the oxidation of the structural units via introducing reactive oxygen species (ROS) are the key steps in the degradation of polyolefins. In general, ROS include hydroxyl radicals (•OH), superoxide radical anions (•O²⁻), and hydrogen peroxide radicals (•OOH). Among them, the hydroxyl radical with an oxidation potential of $E_0 = 2.73$ V versus NHE is widely used as the robust oxidant. The Fenton reaction is a method that uses Fe cations to catalyze the formation of •OH from $H_2O_2$ to decompose and mineralize polymers, resulting in the generation of low molecular weight hydrocarbons, $CO_2$ and $H_2O$. The method always shows high performance, simple process, and universal applicability to various organic polymers. Moreover, the reaction activity can be tuned by the reaction solvent, pH value, Fenton reagent, and other parameters.

The polyolefin degradation by the Fenton reaction always occurs in an aqueous solution, which is seriously limited by the hydrophobicity properties of polyolefins. Thus, the premodification of polyolefin to hydrophilic is necessary. As a classic example, Chow et al. used the sulfonation process to connect the hydrophilic sulfonic acid group to the carbon atom on the chain. The sulfonic acid group then can coordinate with Fe ions to form $PESO_3^{-}$-Fe, which accelerates the degradation of polyolefins by the Fenton reaction (Figure 7A). After reaction for 2 h, the yield of $CO_2$ and organic acids (main products were acetic acid and succinic acid) reached up to 26.7 and 64.1%, respectively, as shown in Figure 7B. In contrast, PE without sulfonation treatment did not show the degradation and mineralization behavior in the 7-h reaction time. To facilitate the formation of •OH to accelerate the Fenton reaction, various systems, such as photo-Fenton, electro-Fenton, bio-Fenton, and Sono-Fenton systems, have been studied for the decomposition of organic matter. For example, Chow et al. further shined UV light to the reaction system, effectively accelerating the degradation of PE, PP, and PVC to $CO_2$ (Figure 7A). Ghatge et al. explored...
the Bio-Fenton and Bio-Photo-Fenton degradation of PE after pretreatment (sulfonated grafted Fe\textsuperscript{3+}). As shown in Figure 7C, the glucose oxidase/TiO\textsubscript{2} (GOx-TiO\textsubscript{2}) was used as a catalyst for in-situ generating H\textsubscript{2}O\textsubscript{2} to form •OH radicals, replacing the expensive H\textsubscript{2}O\textsubscript{2}. As a result, the pretreated PE predominantly produced acetic acid and butyric acid after the Bio-Fenton reaction. When the reaction time is 48 h, the product concentrations of acetic acid and butyric acid reach 6.02 and 0.19 mM, respectively. In addition, when UV light was introduced to the reaction system, the degradation rate of PE in the Bio-Photo-Fenton system was significantly enhanced, and the product concentrations of acetic acid and butyric acid were much higher than those of the Bio-Fenton system. Furthermore, Hu et al.\textsuperscript{82} developed a strategy that couples Fenton reaction with hydrothermal reaction to mineralize the microplastics (MPs, including UHMWPE, HDPE, LDPE, PVC, PS, PP, PET). This process solves the problem of the slow degradation rate of Fenton reaction in aqueous solution (Figure 7D). The total organic carbon value can reach 104.0 mg/L, and the mineralization rate is 75.6% when the reaction time reaches 12 h. Further increasing the reaction time to 16 h, can achieve an MPs weight loss of 95.9%. In summary, the practical design of the Fenton catalytic system combined with other parameters and the origin of ROS would become the future promising focus to decompose polyolefins.

3.2.2 Microwave-assisted method

The microwave-assisted chemical recycling of waste plastics is efficient.\textsuperscript{83–85} Compared with traditional chemical upcycling methods, microwave irradiation greatly shortens the reaction time and decreases the reaction temperature. Bäckström et al.\textsuperscript{86} investigated the microwave-assisted method for efficiently degrading LDPE. In their reaction system, nitric acid and water (good absorbing ability and superheating characteristics) were utilized as oxidation agent and reaction medium, respectively. This method can efficiently convert LDPE plastic bags into water-soluble short-chain dicarboxylic acids at 180°C for 3 h. As shown in Figure 8A, the main products are malonic acid, glutaric acid, and adipic acid. Afterward, they further used this method for waste HDPE degradation to produce short-chain dicarboxylic acid as the raw materials for synthesizing polylactic acid (PLA) plasticizers, confirming that the microwave-assisted
method is a potential technology for sustainably synthesizing value-added chemicals and commodities (Figure 8B)."},

3.2.3 | Photocatalysis

Solar-driven polyolefin degradation has been in-depth investigated thanks to the low energy consumption and mild reaction conditions compared to other heat-assisted degradation processes of organic materials. This strategy generally uses oxide semiconductor materials (TiO₂, ZnO, ZrO₂, etc.) as photocatalysts for polyolefin decomposition, but their performances are always unsatisfactory. Thus, the urgent task in this field is the increase of activity. Recently, several works studied the optimized catalysts and their application in the photocatalytic degradation of polyolefins. For example, metal phthalocyanines are regarded as suitable additives for improving photocatalytic performance due to their good chemical stability and high absorption coefficient in the solar spectrum. Zhao et al. prepared a composite material of copper phthalocyanine (CuPc) and TiO₂ for decomposing PE. The TiO₂/CuPc photocatalyst had a high charge separation efficiency and produced a large number of active oxygen species. When the CuPc concentration was 0.8 wt.% and reaction time arrived at 160 h, the weight loss of PE-CuPc/TiO₂ film can reach approximately 37%, which has much higher activity than that of PE-TiO₂ (~11%) and PE (<1%). Detailed studies showed that the hydroxyl ions or water on the catalyst surface could trap the photogenerated holes and facilitate the generation of •OH radicals, accelerating the degradation rate. In addition, Jiang et al. designed ultra-thin BiOCl nanosheets with hydroxyl-rich surfaces. The surface hydroxyl content can be effectively tuned by introducing different mannitol amounts to improve the catalyst dispersion in water and adsorption capacity to polyolefins. The hydroxyl-rich BiOCl catalyst exhibited a PE microplastic weight loss of 5.38% within 5 h, which is 24 and 134 times higher than the common BiOCl (0.22%) and noncatalytic test (0.04%), respectively. Relevant characterizations confirmed that the modification of surface hydroxyl led to the larger specific surface area, more active sites, faster charge separation, and transfer rate. However, the rate of this degradation process is still too slow to completely convert polyolefins. The design and synthesis of high-efficiency catalysts remain a challenge in this field.

Compared with the photocatalytic mineralization of polyolefins, the efficient conversion of polyolefins into high value-added chemicals can maximize its economic benefits and is more in line with the sustainable development of polyolefins. Jiao et al. used Nb₂O₅ nanosheets as a bifunctional catalyst for photodegradation and CO₂ photoreduction. The Nb₂O₅ first converted PE, PP, and PVC into CO₂, which was then selectively converted into C₂ fuel (Figure 9A). In detail, the light-excited holes in the valence band of the Nb₂O₅ atomic layer can oxidize H₂O to •OH radicals, while the photo-generated electrons in the conduction band can gradually reduce O₂ to O₂•–, H₂O₂, and H₂O, followed by the oxidation of C–C bonds to CO₂. The generated CO₂ continued to interact with protons on the Nb₂O₅ catalyst and form •COOH radical intermediates, and two •COOH would couple with each other to form a HOOC–COOH intermediate. The continuous protonation of the HOOC–COOH can obtain CH₃COOH. Nevertheless, the desorption of CH₃COOH from the catalyst requires overcoming a large activation energy barrier, leading to low catalytic performance. As depicted in Figure 9B, the rates of CH₃COOH formation via degrading PE, PP, and PVC were 47.4, 40.6, and 39.5 µg/gcat/h at room temperature, respectively. The reaction time for complete decomposition was in the range of 40–60 h. The photocatalytic degradation of polyolefins to carboxylic acids is limited by the poor CO₂ reduction performance and slow CH₃COOH desorption rate of existing photocatalysts. Thus, the design of high-efficiency and bifunctional catalysts to accelerate the CO₂ reduction and C–C coupling processes is promising to enhance the yield of carboxylic acids. Moreover, the tandem reaction of photocatalysis with other efficient strategies may also boost the catalytic performance.

3.3 | Syngas

The two-step pyrolysis-gasification process is a common approach to degrade polyolefins into synthesis gas (H₂, CO, trace CO₂, and C₂–C₄ products). This process degrades polyolefins through a two-stage fixed-bed reactor, and polyolefin and catalyst are distributed separately. First, the polyolefin is pyrolyzed into gaseous hydrocarbons in the first reactor at a high temperature. A syringe pump is added between the two reactors to inject water vapor as the oxidant. The gaseous hydrocarbons, water vapor, and carrier gas flow together to the second reactor and undergoes catalytic steam reforming with the catalyst to generate syngas. In previous reports, Ru and Rh-based catalysts are highly efficient for steam reforming. In recent years, Ni-based catalysts have been widely used in polyolefin pyrolysis-gasification process because of their good catalytic performance and low cost. For instance, Wu et al. investigated the effects of CeO₂ doping, calcination temperature, and Ni loading in the Ni/CoO₂/ZSM-5 catalysts on PP gasification to produce H₂, and the
optimized H₂ concentration can reach up to 66.4 vol.%.
Yao et al. loaded Ni on different zeolite supports and studied their performance on steam reforming of waste HDPE to syngas. The experimental results showed that the highest synthesis gas yield of Ni/ZSM-30 at 850°C was 100.72 mmol/gplastic (CO:H₂ = 34.63:66.09 mmol/gplastic).
Singh et al. reported a method of substituting CO₂ for water vapor to assist the gasification process. In the initial stage of the reaction, CO₂, N₂, and Ar were introduced into two reactors to degrade cross-linked PE products efficiently (Figure 10). The produced syngas exhibited a sample-mass specific heating value of 47 MJ/kg, suggesting its potential for energy utilization. Moreover, this process consumes a large amount of CO₂, reducing the carbon emission and realizing the sustainable use of CO₂. However, the high temperature (650−900°C) in this process leads to serious metal sintering and catalyst deactivation due to the coking. In addition, the high energy consumption caused by the reaction and catalyst regeneration process also restricts this technology to be widely used in industrial applications. Therefore, designing effective catalysts with high activity, high stability, and superior resistance to carbon deposition, and upgrading the catalytic system are crucial in the future for syngas production.

### 3.4 Carbon materials

As a rich carbon source, polyolefin can be converted into various high-value carbon materials through physical and chemical methods. Some advanced and efficient studies on degrading polyolefins to prepare high-value carbon materials (such as CNTs, graphene) have been reported in recent years. Impressively, compared to the commercial material, the generated products exhibit better physicochemical properties to meet their applications. For instance, Choi et al. carbonized LLDPE into a highly ordered graphite carbon via thermal oxidation with a high polymer conversion of approximately 50%. The ordering and conductivity of the product are much better than the commercial conductive agent of super-P used for lithium-ion battery fabrication. Algozeeb et al. used the flash joule heating (FJH) method to rapidly convert waste polyolefins into high-quality flash graphene (FG) without the requirement of any catalyst. The energy consumption of converting waste plastics into FG is about 23 kJ/g or $125/t of electricity, making it very attractive in terms of economic costs and large-scale industrial applications. Jie et al. developed a microwave-initiated method to activate the FeAlO₄ catalyst to effectively degrade the crushed PE waste and produce high-yield multi-walled carbon nanotubes.
(MWCNTs) and H₂ (Figure 11). This one-step degradation process only needs 30−90 seconds, and the hydrogen yield can reach up to 55.6 mmol/g_{plastic}. In this process, the FeAlOₓ catalyst can strongly absorb the microwave energy, leading to the temperature difference between the catalyst and the polyolefin reactant being above 400°C. The heat on the catalyst can activate the C−H bonds through the heat transfer and thermal convection, followed by the rapid cracking and desorption of C−H bonds to produce H₂. The extremely rapid rate dramatically reduces the side reactions in the polyolefins pyrolysis. Meanwhile, the carbon species after the H₂ generation would diffuse to FeAlOₓ catalyst and form Fe₃C species. Finally, the MWCNTs are formed. This innovative method gives a rapid polyolefin degradation strategy. It confirms that plastic waste can be used as a precursor of high-value carbon materials and a high-quality hydrogen source, providing a new idea for the sustainable upcycling of plastics.

In the end, we summarize the catalytic performance of various chemical strategies for polyolefin upcycling (Table 1), and further evaluate the different reactors from the perspective of reaction types. For thermocatalysis, most reactions conducted in the laboratory always use batch, semi-batch and continuous-flow reactors. The reactions such as hydrocracking, hydrogenolysis, tandem hydrogenolysis/aromatization and partial pyrolysis occur in batch and semi-batch reactors. In the closed system of a batch reactor, the polyolefin can achieve a high conversion due to the extended reaction time. On this basis, the semi-batch reactor can realize the moving of reactants and products, resulting in the flexibility of catalytic performance. These two reactors are suitable for the reactions requiring high pressure, but the high equipment and labor costs limit large-scale industrial applications. By contrast, as the reactor for most thermal and catalytic pyrolysis processes, continuous-flow reactors, including the fixed bed, fluidized bed, and conical spouted bed reactors, show more flexibility than batch and semibatch reactors due to the feasibility of continuous feeding of reactants. Among them, the fluidized bed reactor exhibits a lower operating cost, making it more suitable for industrial applications. Compared to other catalytic systems, heat-driven thermocatalysis needs a higher energy consumption, but its high efficiency and moderate costs meet the industrial standard, making it the first choice for industrial polyolefin upcycling. Microwave-assisted and microwave-initiated technologies show much lower reaction time and faster heat transfer efficiency in a microwave reactor. Different from the diffusive heat transfer and thermal convection in conventional thermocatalysis, the polymer can directly receive the microwave energy through the interaction between molecules and the electromagnetic field, resulting in a rapid heating rate. Despite the fast degradation rate, the low dielectric constants of polyolefins require the presence of microwave susceptor with high dielectric constant. Moreover, the amount of polyolefin that a microwave reactor can process is small-scale, seriously restricting its industrialization. Therefore, the expansion of the microwave reactor scale and the design of microwave-susceptor/catalyst are the main directions for the rapid degradation of polyolefins. Fenton, CAM, and photocatalytic reactions have achieved many exciting advances in recent years, and their energy consumptions, costs, CO₂ emissions are much lower than those of other traditional catalysts. However, their catalytic activities are still unsatisfactory, requiring long reaction times (dozens of hours) to completely degrade waste polyolefins.
Considering the small scale of laboratory reactors with a relatively lower processing capacity, the industrialization of the advanced strategies presents many difficulties and challenges.

4 CONCLUSION AND OUTLOOKS

Plastics have played an irreplaceable role in modern society. The rapid development of society will lead to ever-increasing balance between production and waste of plastics. Several studies have focused on the synthesis and application of novel plastics, which can meet their application standards and have specific physicochemical properties to ease the degradation. However, the scrap of products is inevitable in all closed-loop and circular economy processes. The development of new plastics cannot solve the essential issues of poor sustainability. Hence, the innovation and development of highly efficient, environmentally friendly, and sustainable chemical upcycling and upcycling technologies for degrading plastics are fundamental strategies to alleviate and solve the problems caused by excessive plastics waste. As the most demanded plastic, polyolefins are difficult to be naturally degraded due to their stable chemical structure. This review expounds on the current situation of polyolefin upcycling in the world and introduces in detail the common and emerging technologies for polyolefin upcycling from different perspectives including various value-added degradation products, and discusses their challenges and potential possibilities of future commercialization. As the upcycling technologies mentioned above, we provided some suggestions and prospects for the degradation of polyolefins in the following three aspects:

1. Chemical pretreatment of waste polyolefins. The chemical inertness of polyolefins leads to more energy requirements in the degradation process than other
### Summary of catalytic performance of various chemical upcycling strategies

#### Thermal pyrolysis

| Plastic | T       | Heating rate | Liquid yield | Wax yield | Gas yield |
|---------|---------|--------------|--------------|-----------|-----------|
| HDPE    | 703 K   | 3°C/min      | 58.4%        | 26.3%     | 6.3%      |
| LDPE    | 703 K   | 3°C/min      | 75.6%        | 8.7%      | 8.2%      |

| Plastic | T       | Heating rate | Char yield | Liquid yield | Gas yield |
|---------|---------|--------------|------------|--------------|-----------|
| HDPE    | 573 K   | 5°C/min      | 2.34%      | 88.54%       | 9.12%     |
| HDPE    | 973 K   | 5°C/min      | 2.14%      | 83.86%       | 14.00%    |

#### Catalytic pyrolysis

| Catalyst | Plastic | T       | t        | P/C     | Conv. | C1-C5 sel. | C6-C12 sel. | >C13 sel. |
|-----------|---------|---------|----------|---------|-------|------------|-------------|-----------|
| HZSM-5   | LDPE    | 613 K   | 2 h      | 100     | 79.7%| 88%        | 12%         | 0%        |
| SA-2     | HDPE    | 703 K   | 10       |         | 77.4%| 0%         | 11.6%       |           |
| SA-2     | LDPE    | 703 K   | 10       | 80.2%   | 0%   | 10.8%      |             |           |

| Catalyst | Plastic | T       | t        | P/C     | C2−4 olefins | C4 alkanes | Aromatics | C5−11 | C12−20 | C21−35 |
|-----------|---------|---------|----------|---------|---------------|------------|-----------|--------|--------|--------|
| B/HZSM-5 | LDPE    | 873 K   | 40       | 65.5%   | 1.7%          | 10.2%      | 16.5%     | 5.3%   | 0.2%   |
| B/HZSM-5 | MPO     | 873 K   | 40       | 66.1%   | 1.0%          | 8.1%       | 16.1%     | 4.5%   | 3.5%   |

| Catalyst | Plastic | T       | t        | P/C     | Liquid yield | Residue yield | BTX yield |
|-----------|---------|---------|----------|---------|--------------|---------------|-----------|
| Silicalite| PE/PP   | 603 K   | 1 h      | 0.3     | 7%           | 0.7%          | 92.2%     | 0.1%    |
| Silicalite| PE/PP   | 723 K   | 1 h      | 0.3     | 38.6%        | 2.8%          | 58.2%     | 0.4%    |

#### Hydrocracking

| Catalyst | Plastic | T       | t        | P/C     | P_{42} | Solid yield | C1−4 sel. | Gasoline yield | Diesel yield |
|-----------|---------|---------|----------|---------|--------|-------------|-----------|----------------|--------------|
| Pt/WO3/ZrO2+HY | LDPE | 523 K   | 2 h      | 10      | 30 bar | 6%         | 9%        | 73%            | 20%          |
| Pt/WO3/ZrO2+HBEA | LDPE | 523 K   | 2 h      | 10      | 30 bar | 0%         | 21%       | 57%            | 6%           |

| Catalyst | Plastic | T       | t        | P_{42} | Conv. | C1−5 yield | C6−12 yield | C13−20 yield |
|-----------|---------|---------|----------|--------|-------|------------|-------------|--------------|
| SZPt0.5 | HDPE    | 648 K   | 25 min   | 8.27 MPa | 99%   | 35%        | 63.7%      | 0.3%         |
| SZNi2.0 | HDPE    | 648 K   | 25 min   | 8.27 MPa | 98%   | 30%        | 65.6%      | 2.4%         |

| Catalyst | Plastic | T       | t        | P/C     | P_{42} | C1−3 sel. | C4−6 sel. | C7−12 sel. | C13−20 sel. | C21+ sel. |
|-----------|---------|---------|----------|---------|--------|-----------|-----------|------------|-------------|-----------|
| 0.1Pt-15WZr | LDPE  | 523 K   | 2 h      | 10      | 30 bar | 2.9%      | 32.8%     | 48.9%      | 13.7%       | 1.7%      |
| 1.0Pt-15WZr | LDPE  | 523 K   | 2 h      | 10      | 30 bar | 1.0%      | 14.1%     | 52.0%      | 24.0%       | 8.9%      |

(Continues)
| Catalyst          | Plastic     | T    | t    | P\(_{\text{H}_2}\) | M\(_n\) | P/C\(_{\text{Pt}}\) | M\(_n\) after reaction | Liquid yield |
|-------------------|-------------|------|------|-------------------|--------|--------------------|--------------------------|-------------|
| Pt/SiO\(_2\)\textsuperscript{59} | PE          | 573 K | 24 h | 1.72 MPa          | 8150 Da| 50                 | 1250 Da                  | 91%         |
| Pt/SiO\(_2\)\textsuperscript{59} | PE          | 573 K | 96 h | 1.72 MPa          | 8150 Da| 50                 | 800 Da                   | >99%        |
| Pt/γ-Al\(_2\)O\(_3\)\textsuperscript{71} | LDPE        | 513 K | 8 h  | 3.5 MPa           | 34     | Conv.              | C\(_1\)− C\(_4\) yield | C\(_5\)− C\(_8\) yield | C\(_9\)− C\(_{21}\) yield |
| Pt/γ-Al\(_2\)O\(_3\)\textsuperscript{71} | HDPE        | 493 K | 1 h  | 30 bar            | 2      | n-hexane           | C\(_1\)− C\(_4\) yield | C\(_5\)− C\(_8\) yield | C\(_9\)− C\(_{21}\) yield |
| Pt/γ-Al\(_2\)O\(_3\)\textsuperscript{71} | HDPE        | 553 K | 24 h | 6 wt.%            | 69 wt.%| 15 wt.%            |                         |             |
| Pt/γ-Al\(_2\)O\(_3\)\textsuperscript{71} | HDPE        | 553 K | 24 h | 6 wt.%            | 55 wt.%| 35 wt.%            |                         |             |
| Pt/γ-Al\(_2\)O\(_3\)\textsuperscript{71} | HDPE        | 553 K | 24 h | 6 wt.%            | 69 wt.%| 15 wt.%            |                         |             |
| Pt/γ-Al\(_2\)O\(_3\)\textsuperscript{71} | HDPE        | 553 K | 24 h | 6 wt.%            | 55 wt.%| 35 wt.%            |                         |             |

**Tandem hydrogenolysis/aromatization**

| Catalyst          | Plastic     | T    | t    | H\(_2\)\(_2\) \(_2\) | Degradation efficiency | Monocarboxylic acid yield | Dicarboxylic acid yield | Yield of other acids |
|-------------------|-------------|------|------|------------------------|--------------------------|---------------------------|------------------------|----------------------|
| Fe(III)\textsuperscript{79} | SPE\textsuperscript{e} | 2 h  | 650 mmol/g | 92%/(340.6) mg/L | 19.5% | 41.8% | 26.2% |
| Fe(III)\textsuperscript{80} | SPE         | 2 h  | 650 mmol/g | 2.5 | 500 W | >99% |
| Fe(III)\textsuperscript{80} | SPP         | 2 h  | 120 mmol/g | 2.5 | 500 W | >99% |
| Free GO\(_x\)\textsuperscript{81} | SPE         | 48 h | None  | 6.02 mM | 0.19 mM | |
| TiO\(_2\)-GO\(_x\)\textsuperscript{81} | SPE         | 6 h  | 6 h   | 4.78 mM | 0.17 mM | |
| Fe\(_{3+}\)\textsuperscript{82} | UHMWPE\textsuperscript{e} | 12 h | 413 K | 200 mM | 87.7 wt.% | 104 mg/L | 75.6% |

(Continues)
### Microwave-assisted method

| Catalyst | Plastic | T    | t  | HNO₃ | Acid yield | Carbon efficiency | Succinic acid sel. | Glutaric acid sel. | Adipic acid sel. |
|----------|---------|------|----|------|-----------|------------------|-------------------|-------------------|------------------|
| HNO₃<sup>86</sup> | LDPE   | 453 K | 3 h | 0.1 g/mL | 71%       | 37%              | 36.22%            | 25.35%            | 19.82%           |
| HNO₃<sup>87</sup> | HDPE   | 453 K | 4 h | 0.15 g/mL | 49%       | 39%              | 12%               |                   |                  |

### Photocatalysis

| Catalyst | Plastic | CuPc conc. | T    | t  | Weight loss | Products |
|----------|---------|------------|------|----|-------------|----------|
| TiO₂/CuPc<sup>95</sup> | PE       | 0.8 wt.%   | 298 K | 160 h | 36.9%       | CO₂ and H₂O   |
| BiOCl<sup>196</sup> | HDPE     | P/C        | 10   | RT  | 5.38%       | CO₂ and H₂O   |

### Pyrolysis-gasification

| Catalyst | Plastic | P/C | T    | Potential H₂ production | Gas composition (vol.%) |
|----------|---------|-----|------|-------------------------|-------------------------|
| Ni/CoO₂/ZSM-5<sup>103</sup> | PP       | 2   | 773 K | 56.8 wt.%               | H₂ 66.4, CO 22.9, CH₄ 4.8, CO₂ 8.2, C₂H₄ 1.3 |
| Ni/CoO₂/ZSM-5<sup>104</sup> | PE       | 2   | 1123 K | 100.72 mmol/ｇ<sub>plastic</sub> | H₂ 56.2, CO 29.45, CH₄ 4.55, CO₂ 8.72, C₂H₄ 1.07 |
| Ni/β-zeolite-25<sup>104</sup> | PE       | 2   | 1123 K | 94.92 mmol/ｇ<sub>plastic</sub> | H₂ 55.8, CO 30.51, CH₄ 4.39, CO₂ 8.61, C₂H₄ 0.65 |

### Microwave-initiated method

| Catalyst | t | Gas yield | Solid yield | Oil yield | H₂ yield (mmol/ｇ<sub>plastic</sub>) | Evolved gas composition (Vol. %) |
|----------|---|-----------|-------------|-----------|-------------------------------------|---------------------------------|
| FeAlOₓ<sup>108</sup> | 30 s | 62.7 wt.% | 35.1 wt.% | 2.2 wt.% | 55.6 | H₂ 74.3, CH₄ 5.8, C₂H₄ 2.8, CO 1.8, C₂H₆ 15.2 |

<sup>a</sup>Mass ratio of plastic to catalyst.
<sup>b</sup> Mixed polyolefin (MPO).
<sup>c</sup>Sulfonated PE (SPE).
<sup>d</sup>Sulfonated PP (SPP).
<sup>e</sup>Ultrahigh-molecular-weight polyethylene (UHMWPE).
<sup>f</sup>Molar ratio of carbon in each plastic and Nb₂O₅ atomic layers.
polymers. Therefore, regulating the physicochemical structure of polyolefins via chemical modification is considered to be a practical approach to broaden their application and accelerate the degradation process. Recently, the functionalization of C−H bonds has been extensively studied in the polyolefin modification. The introduction of active functional groups (hydroxyl, carbonyl, amino, halogen atoms, etc.) can upgrade polyolefins with higher value and specific performance. On the other hand, the functionalization can promote the polymers to be decomposed such as the sulfonation process in the aforementioned Fenton reaction (Figure 12). In addition, other technologies are also potential strategies for pretreatment and modification of polyolefins. For example, radiation-assisted oxidation is a proven material modification technology. By irradiating polymers, crosslinking and degradation of molecular chains can be induced, and the oxygen-containing functional groups can be introduced into the carbon chains, resulting in a faster degradation rate. This type of technology is expected to be combined with other upcycling technologies in the future to degrade waste polyolefins efficiently.

(2) Design of high-efficiency catalyst. Polyolefin degradation processes always involve multiple types of catalytic processes, and the catalysts generally consist of dual or multifunctional materials. Taking the hydrocracking reaction as an example, the composite catalysts should satisfy the hydrogenation and dehydrogenation (metal catalysts) and C−C cleavage and isomerization (acid catalysts) process. The balance of these two catalysts determines the catalytic activity and selectivity to target products by tuning their concentrations, ratio, structures, spatial distance, and other parameters. For the catalytic reactions that occur on a single active site, such as hydrogenolysis and tandem hydrogenolysis/aromatization, etc., it is necessary to design and modify the structure of active sites to achieve enhanced catalytic performance. Generally, the depolymerization of polyolefins is sensitive to the catalyst structure. The electronic structure, geometric configuration, exposed crystal facets, and spatial distribution can significantly affect the catalytic performance. For this purpose, the construction of single-atom catalysts and nanoparticle catalysts, strong metal-support interaction (SMSI), the addition of promoters, and the second component for cooperative catalysis are the potential ways for the catalyst design. Summarily, the study on the structure-performance relationship plays a fundamental role in designing catalysts to produce various value-added chemicals and productions.

(3) Evolution and innovation of catalytic engineering. In the high-temperature heterogeneous catalysis system, waste plastics need to contact and react with the molten or vapor-state polyolefins. The poor mass and heat transfer and diffusion effects between catalysts and polymers severely limit the degradation. Although a higher temperature can improve the catalytic engineering, this measure is bound to be accompanied by much higher energy consumption. To reduce the viscosity and accelerate the mass and heat transfer, building and improving the microenvironment are vital. Using hydrogenolysis reaction as an example, introducing solvent in the reactor can significantly speed up the reaction rate. In addition, coupling depolymerization reaction with other reactions to accelerate the degradation process has attracted extensive attentions. Liu et al. coupled the CO2 hydrogenation, PET methanalysis, and dimethyl terephthalate (DMT) hydrogenation for converting PET into dimethyl cyclohexanedi-carboxylates. In this system, CO2 hydrogenation and PET hydrogenation were significantly boosted due to the PET presence and DMT hydrogenation, showing much higher activity than other independent reactions. From the perspective of reducing energy consumption, photothermal catalysis may be an economical and sustainable method to replace thermal catalysis. Our recent work has successfully realized the efficient degradation of polyester via photothermal catalysis (Figure 13A). The unique localized solar heating effect of CNT-PDA significantly boosts the depolymerization efficiency (Figure 13B). To evaluate the difference in energy consumption and carbon emissions between photothermal catalysis and thermal catalysis, a model for the annual processing of 100 000 tons of waste PET was established. Since solar energy is free
and clean, the energy consumption and waste emissions in photothermal catalysis are low. In comparison, thermal catalysis consumes a total of more than 370 600 GJ of electricity (approximately 5.15 million dollars) (Figure 13C). Moreover, the thermal catalysis exhausts a large amount of VOC, NOx, SOx, PM2.5, CO2, and GHG (Figure 13D and E). For example, the electricity generation in China relies heavily on thermal power technology, resulting in about 73 000 tons of CO2 emission when using thermal catalysis to treat 100 000 tons of PET. Even in developed countries, such as the United States, where electricity comes from clean energy, the thermal catalysis would also increase CO2 emissions by nearly 40 000 tons. Therefore, the low energy consumption and GHG emissions of the solar thermal upcycling technology provide a fully green strategy to resolve the environmental issues related to plastics, which is important for promoting the realization of global carbon neutrality. Recently, Zhou et al. developed an electrocatalytic strategy to convert PET into value-added potassium diformate (KDF), terephthalic acid (PTA), and H2 fuel. Waste PET was first hydrolyzed into PTA and ethylene glycol (EG), followed by the C–C cleavage of EG and H2 production, respectively, on anode and cathode over CoNi0.25P electrocatalyst. Through the precipitation, filtration, concentration, and crystallization processes, the PTA and KDF solid can be successfully collected. In summary, the design and innovation of reaction systems may become the mainstream to meet sustainable development in the future.

Notably, the current serious problem of plastic pollution cannot be solved only through recycling, but also requires comprehensive prevention and control from the aspects of synthesis, processing, application, and waste treatment. More efforts should be devoted to the government control, establishment, and improvement of laws and regulations, publicity guidance, investment of scientific research, and other aspects to tune the balance between manufacturing and waste of plastics.1

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CONFLICT OF INTEREST
The authors declare no conflict of interest.

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