DIFFERENT METHODS OF CATALYTIC DEGRADATION OF WASTE POLYMER

A MSC DEGRADATION REPORT BY:

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DIFFERENT METHODS OF CATALYTIC DEGRADATION OF WASTE POLYMER

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CERTIFICATE

This is to certify that the dissertation entitled **"Different Methods of Catalytic Degradation Of Waste Polymer**" is a Bonafide work carried out by Ms. Krutika Umesh Gawde under my supervision in partial fulfillment of the requirement for the award of the degree of Masters of Science in Chemistry at the School of Chemical Sciences, Goa University.

Prof. Dr. Rohan Kunkalekar

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ABSTRACT

Various recycling technologies have been developed to deal with plastic problems, but they face considerable economic and technological challenges in practice. An attractive alternative is upcycling, which aims to dig out the embedded value to encourage large-scale valorization of plastic wastes. The degradation of non-recoverable plastic wastes is another necessity to treat the widespread pollution. This review presents an overview on brief assessment on possible options to address the plastic problems. In combination with the development of recycling technologies, we summarize recent advances in upcycling to valuable chemicals, fuels, and materials. Subsequently, we highlight the advances in catalytic degradation of plastics to environmentally benign or degradable products and mineralization into carbon dioxide and water. We conclude with our perspective on the ongoing challenge and opportunities.

INTRODUCTION

Since the appearance of the first synthetic polymer in 1907, various plastics have been increasingly manufactured and used in ever-expanding fields because of their low cost, durability, safety, and processability. Nowadays, plastics-based materials have become ubiquitous and indispensable in modern society, with a wide scope and range of applications that cannot currently be displaced by other materials. Along with an excessive dependence on plastic products, the end-of-life treatment of post-consumer plastic wastes has become a huge problem because plastics are designed to be robust and durable. As of now, 6,300 Mt of plastic wastes had been cumulatively generated; of which, 79% entered landfills or accumulated in the natural environment, and 12% was incinerated. Only 9% of plastic wastes have been recycled, and most of the recycled plastic is down-cycled toward less recyclable and low-value products, such as plant pots and garden furniture[1].

Because of this, global plastic pollution, as a planetary threat, had already formed before people began to realize its seriousness, complexity, and urgency. Plastic wastes are widely and increasingly observed in oceans, lakes, rivers, soils, sediments, the atmosphere, and animal biomass. Microplastic (%5 mm) and nanoplastic (%100 nm) pollution originated from both direct emission of ‘‘microbeads’’ and ‘‘micro-exfoliates’’ (primary microplastics) contained in household cosmetic products into household wastewater and from the breakdown of larger plastic waste into small plastic pieces (secondary microplastics) via photooxidation under solar irradiation, physical crushing, and biodegradation in the natural environment. Microplastics and nanoplastics can be ingested by various organisms, and nanoplastics can even accumulate in plants ultimately resulting in heigher enrichment via food webs. Plastic debris can function as a medium to compile and spread hydrophobic organic pollutants, heavy metals, and diseases.

Although the direct toxicological effect of plastics on human health has not been substantiated, the ever-increasing emission of plastics is destined to generate multiple harmful effects. For example, microplastics have increasingly entered into the human food system, such as seafood, tea, and vegetables, as a nonnegligible threat to food safety and agricultural sustainability. Moreover, microplastics have been detected in human organs and have identified chemical traces of plastic in tissue. In addition, global greenhouse gas (GHG) emissions from the plastic life-cycle is expected to rise from 1.7 Gt of carbon dioxide (CO2) equivalent in to 6.5 Gt in 2050 under current trends, contributing significantly to climate change.

The improper management of plastic wastes not only contaminates the environment but also signifies an immense loss of economic value. Allthough several recycling technologies have been investigated, they suffer universally from low benefits, high costs, and secondary pollution, leading to limited practical applications.Therefore, the development of cost-effective, environmentally friendly, and efficient approaches to valorize plastic wastes into value-added products is indispensable to prevent their dissemination into natural environment. In addition, the development of effective catalytic-degradation technologies is essential for treating nonrecoverable plastic wastes^{2}.

Most plastic wastes fall into four top categories polyester, polyolefin, polyvinyl chloride (PVC), and polystyrene (PS). Polyethylene terephthalate (PET) is the most widely used polyester, with a global annual production of 70 million tons (Mt) for use in textiles, packaging, carpeting, and single-use beverage bottles. Polyolefins, including polyethylene (PE) and polypropylene (PP), with annual production of approximately 138 and 80 Mt, respectively, account for 57% of the plastic content of municipal solid waste. Among PEs, high-density polyethylene (HDPE) is used extensively for electrical insulators, toys, bottles, pipes, and films, whereas low-density polyethylene (LDPE) is mainly used in devices, food packaging, and plastic wrap. As the cheapest plastic, PVC is one of the most problematic wastes for the environment because of the emission of phthalate plasticizers and chlorine-containing hydrocarbons (dioxins) during its end-of-life treatment. Among the various plastic wastes, only PET and HDPE are routinely recycled, but the reclamation rate is far from satisfactory.

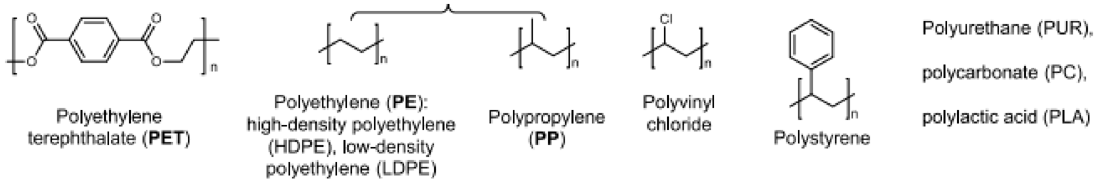


Figure: 1

Both recycling and upcycling process are designed for the valorization of post-consumer plastic, but they cannot deal with nonrecoverable plastic wastes. Commercially, running-water treatment technologies can remove microplastics from wastewater via skimming, sedimentation, and tertiary filtration, but most plastics without substantial degradation are still retained in sewage sludge. Environmental degradation of plastic wastes, including abiotic degradation and biodegradation behaviors, depends on many complex factors, including physical properties and molecular structures, and generally suffers from low efficiency[3].

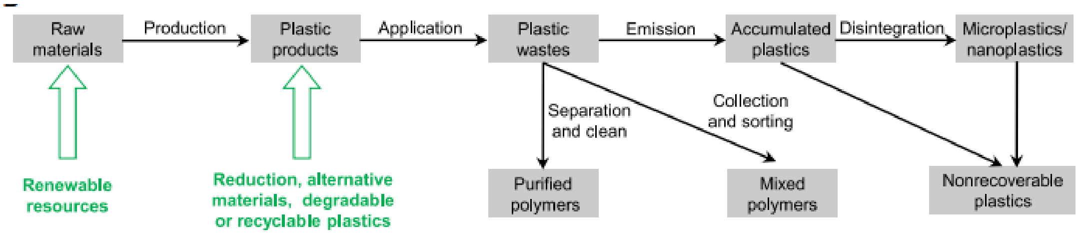


Figure: 2

LITERATURE REVIEW

Plastic polymers properties

Plastic degradation process is influenced by both environmental conditions and physicochemical properties of polymeric substances. The physicochemical properties of plastic play an important role in the degradation process. Plastic susceptibility to abiotic and biotic degradation depends on backbone composition and chain length, with long carbon chain such as PP, making polymers resistant to degradation. However, the incorporation of heteroatoms, such as in PET and PU (oxygen-containing polymers) constitutes plastic susceptible to biodegradation and thermal degradation. Also, the polymer hydrophobicity affects the degradation efficiency, where the degradation rate increases with increasing hydrophilicity. Furthermore, the degradation rate depends on the polymer crystallinity. The more crystalline the polymeric structure, more water and oxygen are needed for degradation. Therefore, an increase in either molecular weight or degree of crystallinity reduces degradation rate. On the other hand, the amorphous polymeric structure can be attacked by water and oxygen. The polymer amorphous regions are also considered more suitable for thermal oxidation. In this concern, the polymer MW can affect the degradation rate, while high MW polymers exhibit a slower degradation rate because of their lower relative surface area.[1]

Because of the strong chemical inertness of plastic wastes, natural degradation can take decades and continue to emit hazardous organic pollutants. Therefore, the development of effective catalytic degradation technologies, which could completely mineralize nonrecoverable plastic waste into CO2 and water or degrade them to environmentally benign or degradable intermediates is of high importance for the remediation of plastic pollution.

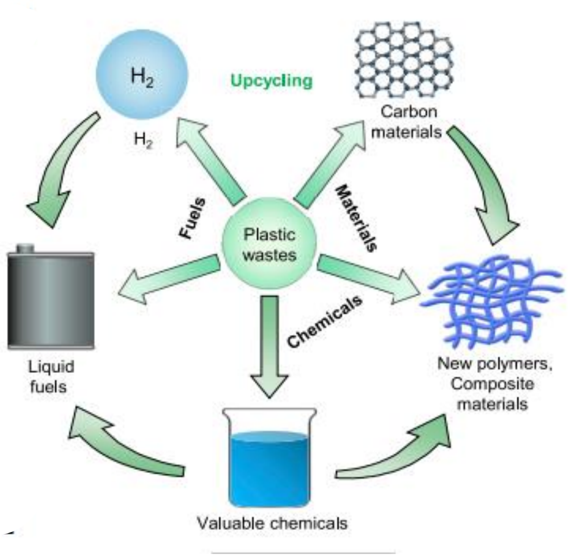


Figure 3: Upcycling toward value-added products

UPCYCLING TO CHEMICALS

Various catalytic depolymerization methods have been investigated for the conversion of PET to monomers.

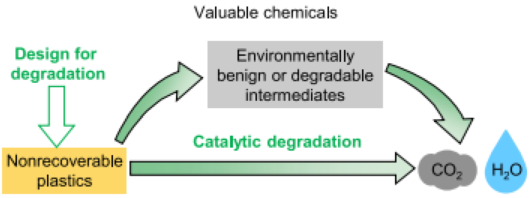


Figure 4: Degradation of plastic wastes

Catalytic depolymerization to monomers

Methanolysis: PET methanolysis is based on the treatent of PET with methanol at relatively high temperatures (180−280 °C) and pressures (20−40 atm), which leads to the formation of DMT and EG. The reaction is catalyzed by typical transesterification catalysts such as zinc acetate, magnesium acetate, cobalt acetate, and lead dioxide.

In Methanolysis of polyethylene terephthalate (PET) Aluminium triisopropoxide (AIP) promoted the methanolysis of polyethylene terephthalate (PET) to form monomers, dimethyl terephthalate (DMT) and ethylene glycol (EG), in an equimolar ratio. The methanolysis at 200 C in methanol with an AIP catalyst gave DMT and EG in 64% and 63% yields, respectively. The yields were increased by using a toluene/methanol mixed solvent containing 20–50 vol.% toluene; maximum yields, 88% for DMT and 87% for EG, were obtained at 20 vol.% toluene. These results indicate that the rate of methanolysis strongly depends on the solubility of PET. The results of GPC analysis suggest that the methanolysis of PET in the absence of the catalyst includes three steps. In the first step, the depolymerisation occurred at a tie molecule of bis(hydroxyethyl)terephthalate [BHET] monomer (O75%) which was effectively separated from dimer in quite pure crystalline form.[4]

These methods can also be used for the depolymerization of other polyester plastics, such as polybutylene terephthalate (PBT). Glycolysis is also the predominant catalytic depolymerization method for polyurethanes (PUR). The harsh reaction conditions, the use of excess solvents and depolymerizing agents, as well as the formation of by-products are the main obstacles to commercial deployment of these processes connecting PET crystals and the chain length was shortened to about 1/3. The shortened chain was depolymerized to oligomers in the second step. The GPC curve of the oligomers tailed to low molecular weight, clearly indicating that the depolymerization took place at random positions on the polymer chain. The third step, the depolymerisation from the oligomers to the monomers, was promoted only in the presence of the AIP catalyst.

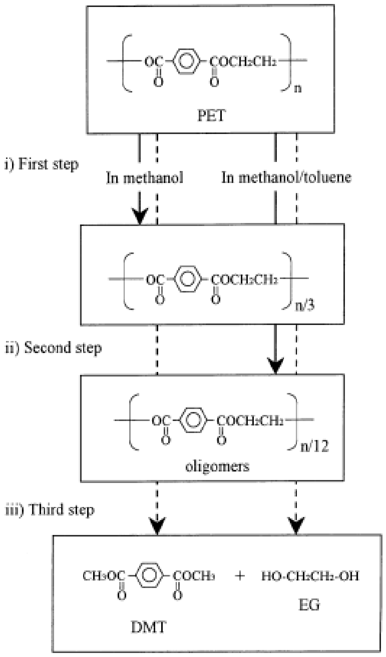


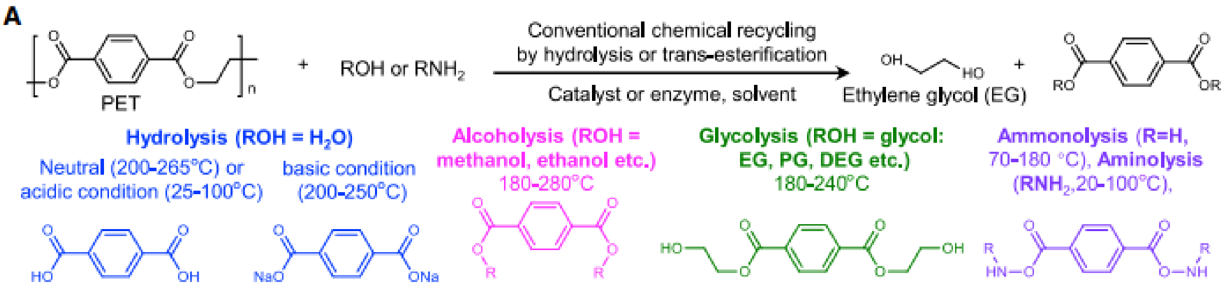
Figure 5: Reaction scheme of PET methanolysis. Solid line: without catalyst; broken line: with catalyst.

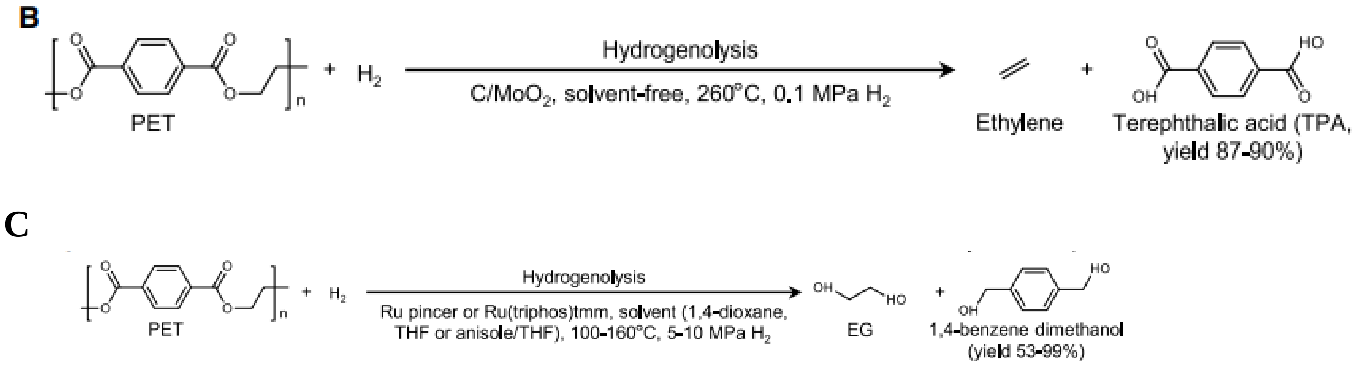
Glycolysis: Glycolysis is the simplest and oldest method of PET depolymerization. The method involves a transesterification reaction of PET with an excess of glycol at temperatures in the range of 180–240 °C, promoting the formation of BHET (a substrate for PET synthesis). Different glycols, such as EG, diethylene glycol (DEG), propylene glycol (PG), polyethylene glycol (PEG), 1,4-butanediol, and hexylene glycol, are used for the glycolysis of PET.

Poly(ethylene terephthalate) [PET] fibre wastes was depolymerised using excess ethylene glycol[EG] in the presence of metal acetate as a transesterification catalyst. The glycolysis reactions were carried out at the boiling point of ethylene glycol that is at 198°C under nitrogen atmosphere up to 10 h. Influences of the reaction time, volume of EG, catalysts and their concentrations on the yield of the glycolysis products were investigated. The glycolysis products were analysed for hydroxyl and acid values and identified by different techniques, such as HPLC, 1H NMR and 13C NMR, mass spectra, and DSC. It was found that the glycolysis products consist mainly

Hydrolysis: Reaction of PET with water under neutral, acidic, or basic conditions at high temperature and pressure breaks the polyester chains into TPA and EG. Acid hydrolysis is performed most frequently using concentrated sulfuric acid though the application of other concentrated mineral acids (e.g., phosphoric or nitric acid) is permissible. Low purity of TPA is the major drawback of this method. Hydrolysis is comparatively slow because water is a weak nucleophile.[5]

In a recent study report depolymerization of high-density PE was conducted in various liquid-phase solvents with the Ru/C catalyst under relatively mild conditions. The maximum yields of the jet-fuel- and lubricant range hydrocarbons were 60.8 and 31.6wt %, respectively. After optimization of the reaction conditions (220°C and 60 bar of H2), the total yield of liquid hydrocarbon products reached approximately 90 wt % within only 1 h. The product distribution could be tuned by the H2 partial pressure, the active-metal particle size, and the solvents.[6]



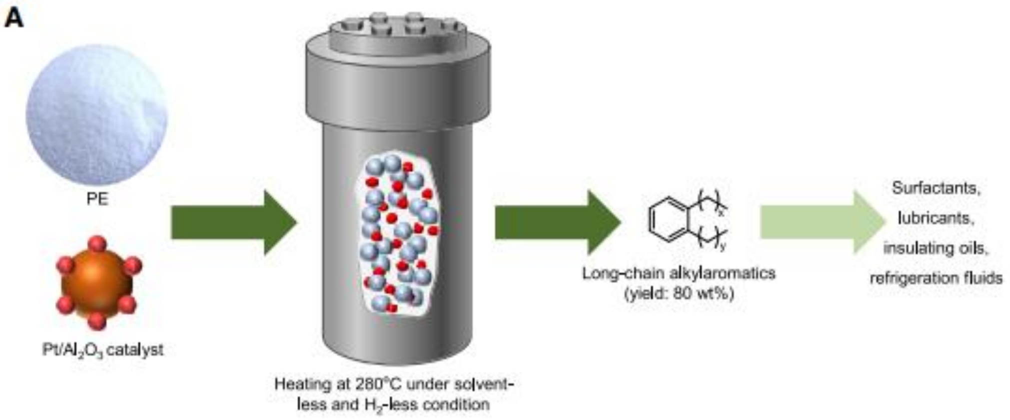


(A) Depolymerization of PET via hydrolysis or trans-esterification.(B and C) Hydrogenolysis of PET over (B) C/MoO2 and (C) Ru catalyst

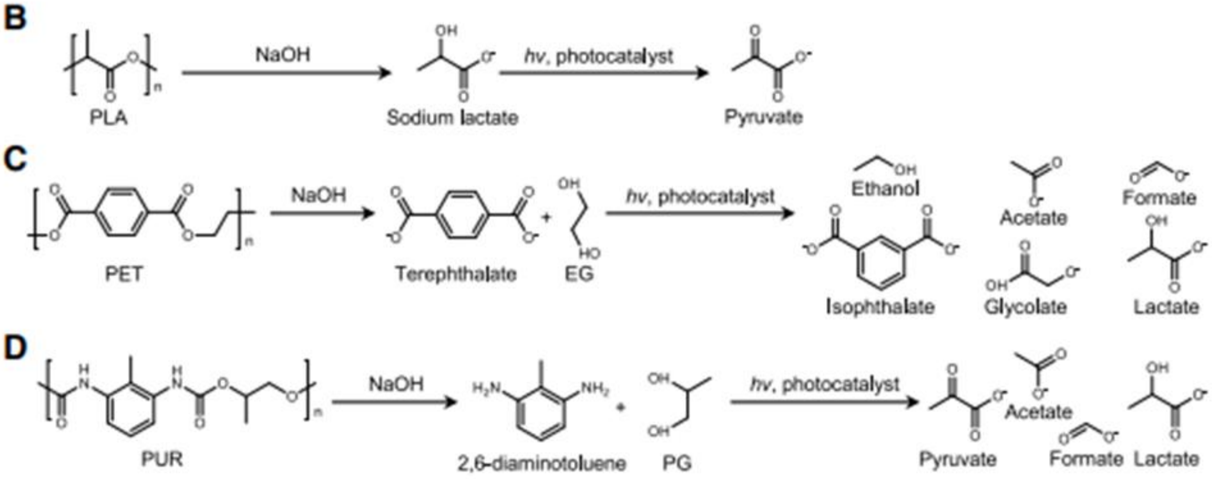
Other routes to useful chemicals

Direct hydrogenolysis of polyolefins, including PE and PP, **generally** produce mixed alkanes with a wide molecular distribution, instead of well-defined monomers, even when elaborately designed catalytic systems are used. The consumption of expensive H2, which essentially originates from non-renewable fossil fuel resources, is a primary barrier to the application of hydrogenolysis technologies. Tandem catalysis, which refers to integrating multiple reaction steps into one-pot catalytic systems in an appropriate sequence through precise regulation of active sites, the chemical environment, and the reaction conditions, offers a promising strategy to inhibit unwanted side reactions to tailor a reaction pathway and then achieve selective, efficient conversion of plastic waste to target products. Recently, upcycling of PE to long-chain alkyl aromatics has been achieved by tandem hydrogenolysis/aromatization over a commonly used heterogeneous catalyst, platinum nanoparticles supported on g-alumina (Pt/ Al2O3), without consuming the external hydrogen.[7]

In contrast to pyrolysis, which generates complex, low-value mixtures under harsh condition (>400C), the tandem catalytic system produces high yields (up to 80 wt%) of low-molecular-weight liquid/ wax products with high selectivity for valuable long-chain alkylaromatics and alkylnaphthenes (average carbon atom number of 30, dispersity [Đ] = 1.1) from various PE grades under solvent-less conditions at a moderate temperature (280C). The conversion of two commercial-grade PE samples with higher molecular-weight, LDPE plastic bag and HDPE water-bottle caps produces overall liquid yields of 69 wt% and 55 wt% with alkylaromatic selectivities of 44 mol% and 50 mol%, respectively, validating its applicability to real-world plastic wastes. During the reaction, hydrogenolysis of PE chains can consume H2 and then reduce the thermodynamic values (DG and DH) of aromatization, whereas aromatization generates H2 to induce the hydrogenolysis (Figure 3B). The liquid alkylaromatics can be used as feedstocks to produce various products of daily life, such as surfactants, lubricants, refrigeration fluids, and insulating oils. In addition, theoretical simulation suggests that the tandem olefin metathesis and double-bond isomerization may selectively convert PE waste with excess ethylene into propylene products.[8]



A **Figure 6**: PE upcycling to long-chain alkylaromatic



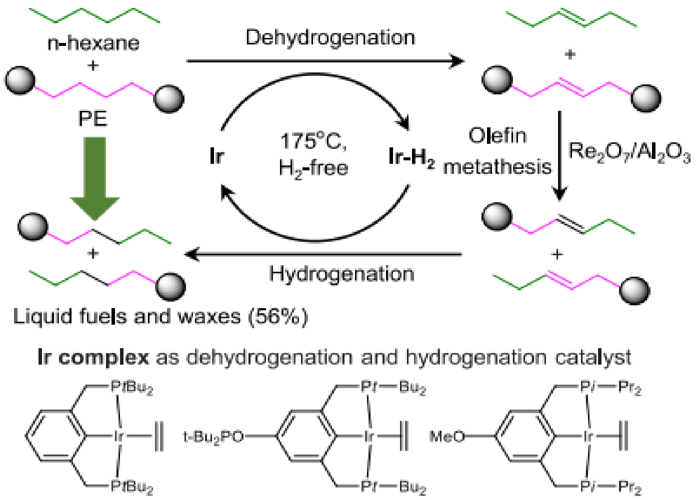
B C,D: **Photoreforming of plastics to H2-** (B–D) Conversion of PLA (B), PET (C), and PUR (D) to organic products.

A tandem-catalysis strategy has also been successfully used for the conversion of PET to benzene, p-xylene, and methylbenzene (BTX) without using external hydrogen sources (Figure 3C), as an alternative approach to hydrogenolysis. Compared with the hydrogenolysis of PET over a Ru/Nb2O5 catalyst at 200C in the presence of 0.3 MPa H2, H2-free conversion of PET back to BTX in the same catalytic system was achieved by unearthing hidden structural hydrogen under relatively harsh reaction conditions (220C), affording total monomer yields up to

91.3% with quantitative selectivity to BTX (>99.9%). The Ru/Nb2O5 catalyst could catalyze three tandem steps, including PET hydrolysis, EG reforming to H2, and hydrogenolysis of C–O/C–C bonds, along with partial decarboxylation reaction.[9]

The application of other catalytic technologies in plastics upcycling may also produce useful products. For example, PE waste can be used to synthesize plasticizers for PLA. Under microwave radiation, both HDPE and LDPE are selectively oxidized by HNO3 to dicarboxylic acid mixtures, including succinic, glutaric, and adipic acid.[9] The reaction of dicarboxylic acid mixtures with 1,4-butanediol and crotonic acid delivers plasticizers. The resulting plasticizers can be covalently attached to PLA by a reactive extrusion process, improving the strain at break to 142% and decreasing the glass-transition temperature by 10C. The integrated processing of12 polyoxymethylene polymer waste with biomass-derived diols, such as 1,3-propanediol over an acid catalyst, affords cyclic acetals as promising solvents, fuel additives, pharmaceutical intermediates, and polymeric monomers.[10]

As discussed above tandem catalysis has provided an effective strategy for the upcycling of PE and PET to value-added chemicals without consuming external hydrogen. Tandem catalytic cross-alkane metathesis (CAM) using low-value and widely available short alkanes as crossmetathesis partners enables the efficient conversion of different types of PE to liquid fuels and waxes under relatively mild conditions (175°C).40 During the reaction, the iridium (Ir) complex catalyzes the dehydrogenation of both PE and short alkane, generating unsaturated alkenes and Ir–H2. Next, the Re2O7/Al2O3 catalyst breaks down the PE chains by scrambling the double bond. Finally, Ir–H2 hydrogenates the newly formed alkenes to saturated alkanes. PE fragments with long chains can react with the light alkane via multiple CAM processes, eventually leading to short hydrocarbons.



Tandem catalytic cross alkane metathesis of PE

Plastic wastes can also be valorized to more-valuable fuel products, such as jet fuel, with the rapid development of accurate and selective depolymerization and hydrogenolysis technologies. For example, hydrogenolysis of HDPE over a Ru/C catalyst can provide jet-fuel and lubricant-range hydrocarbons with yields as high as 60.8 and 31.6 wt%, respectively.96 Theoretically, the chemical composition of plastic wastes is close to that of oxygen-containing liquid fuels, which have distinct advantages over current alkane fuels. Compared with lignocellulosic biomass, the upcycling of plastic wastes to oxygen-containing liquid fuels will consume less, or even zero, external hydrogen if desired reaction pathway can be reached[9].

UPCYCLING TO FUELS

The elementary compositions of many plastics, in particular the C and H content in polyolefins are close to petroleum-derived hydrocarbons. As a consequence, the calorific values of plastic wastes are comparable to currently used liquid fuels. In addition, plastic wastes are also considered as alternative hydrogen-rich energy feedstock because of the relatively high hydrogen content (approximately 8–14 wt %). In contrast, upcycling to high-performance fuels, including H2 and liquid alkanes with a narrow molecular-weight distribution has shown great promise for the valorization of plastic wastes.

Catalytic pyrolysis to hydrocarbon fuels

This focuses on the pyrolysis of polyethylene (PE) over Fe-modified Pt/Al_2O_3 catalysts in the absence of external H_2 to produce hydrocarbon fuels at a mild condition (330°C). The critical interest is to achieve the mild conversion of PE by using the bimetallic catalyst to generate in-situ H instead of external H_2 for hydrogenolysis. Results show that a slight impregnation of Fe on Pt/Al_2O_3 (Fe/Pt=0.25) can improve the oil yield and light oil selectivity as well as promote the formation of aromatics and alkenes in oil after PE pyrolysis in a batch reactor. Multiple active sites including Pt, Fe and Lewis acid site of Al_2O_3 work systematically to drive the tandem catalysis without H_2. The Pt plays the major role in PE pyrolysis via hydrogenolysis assisted by in-situ generated H, but shows the mutual inhibition with the acid site of Al_2O_3 that is contributive to PE cracking via a traditional carbocation chemistry. Fe modification on Pt/Al_2O_3 plays multiple roles in catalysis: promotes cyclization reaction, benefits the hydrogenolysis activity of Pt by providing active H during aromatic formation, and decreases catalyst acidity to reduce gas production. However, an over-impregnation of Fe (Fe/Pt=1) partially covers the Pt sites, resulting in the decrease of fuel oil production but an increase in residue yield due to the deactivation of Pt sites. The post-reaction catalyst can be almost completely regenerated after combustion and reduction.[11]

The thermal degradation of different municipal plastic wastes containing polyethylene, polypropylene, ethylene-propylene copolymer, polystyrene, polyamide and polyurethane rubber was investigated in a horizontal tube reactor using different cracking parameters. The further utilization of volatile products, i.e fuel-like utilization was investigated; moreover, the effects of the cracking parameters (temperature, residence time) on the yields and properties of products were determined. It was found that the chemical structure of polymers greatly affected the qualitative and quantitative properties of volatile products. The yields of volatile products increased both with temperature and residence time. The yields of liquids of 10-25% separated from the gases leaving the reactor could be increased further by 10-15% by distilling the residue. When polystyrene was also in the polymer blend, a significant aromatic content was observed, mainly ethyl-benzene, styrene, toluene and benzene. After distillation, the aromatic content was concentrated mostly in the lighter fractions (F1), which is an advantageous property for further fuel-like utilization. Similar to the aromatic content, the heteroatom content of product liquids was also influenced by the structure of the raw material. Cracking the MPW-2 sample yielded a liquid with high sulphur and nitrogen content.[12]

Degradation of polyethylene over various microporous materials—zeolites, zeolite-based commercial cracking catalysts as well as clays and their pillared analogues— in a semi-batch reactor. The liquid products formed had a boiling point distribution in the range of motor engine fuels. From the zeolites, ZSM-5 resulted mostly in gaseous products. Commercial cracking catalysts fully degraded the polymer resulting in higher liquid yield and lower coke content than their parent ultrastable Y zeolite. This confirmed the suitability of such catalysts for a polymer recycling process and its commercialisation potential, as it confirmed the potential of plastic waste being co-fed into a refinery cracking unit. Clays, saponite and Zenith-N, a montmorillonite, and their pillared analogues were less active than zeolites, but could fully degrade the polymer. They showed enhanced liquid formation, due to their mild acidity, and lower coke formation.[13]

UPCYCLING TO POLYMER

Incorporation of plastic-derived monomers, oligomers, or even polymer fragments into new materials through copolymerization with external building blocks. One-pot upcycling of BPA-PC into high-value poly(aryl ether sulfone)s (PSUs) (Figure 7A), a type of high-performance engineering thermoplastics that can be used for reverse-osmosis and water-purification membranes, medical equipment, and high-temperature applications, has been achieved by depolymerization of BPA-PC into active phenoxides, which are then in situ polycondensed with daryl fluorides.

The depolymerization of BPA-PC with aliphatic diols produces bisphenol A and the corresponding carbonate-containing diols (Figure 7A), which can be polymerized into a series of value-added aliphatic polycarbonates with ionic conductivity as potential polymer electrolytes for solidstate batteries[14].

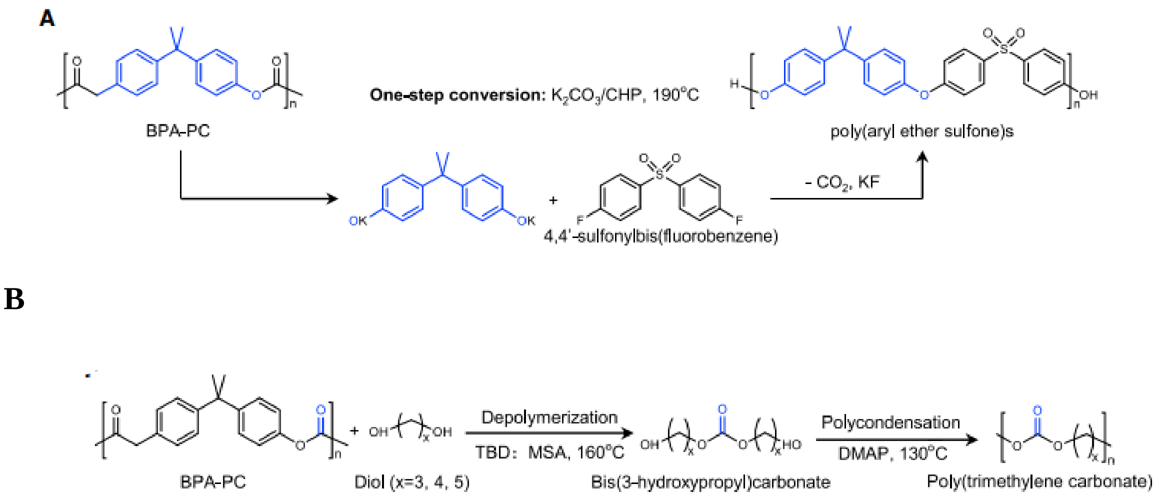
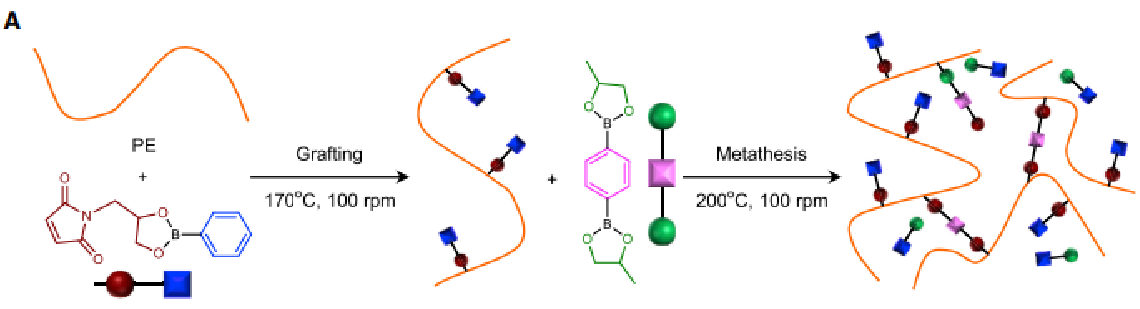


Figure 7A: One-step conversion of BPA-PC into poly(aryl ether sulfones. **B:** Conversion of BPA-PC to aliphatic polycarbonates.

Commercial HDPE, a typical thermoplastic, has been converted to high-performance vitrimers through grafting of maleimides bearing dioxaborolane functionalities onto HDPE, followed by cross-linking of functional polymers containing pendant dioxaborolane units, via metathesis with a bis-dioxaborolane (Figure 7B)[15]. Compared with the original HDPE, the resulting vitrimers exhibit markedly improved melt strength, dimensional stability at elevated temperatures, and solvent and environmental stress-cracking resistance. Analogously, conversion of polyolefins, including PP and PE, to high-performance vitrimers (Figure 7B) has been achieved by grafting maleic anhydride (MA) using dicumyl peroxide (DCP) as a free-radical initiator, followed by epoxy-anhydride curing with a difunctional epoxy (DGEBA)[16].



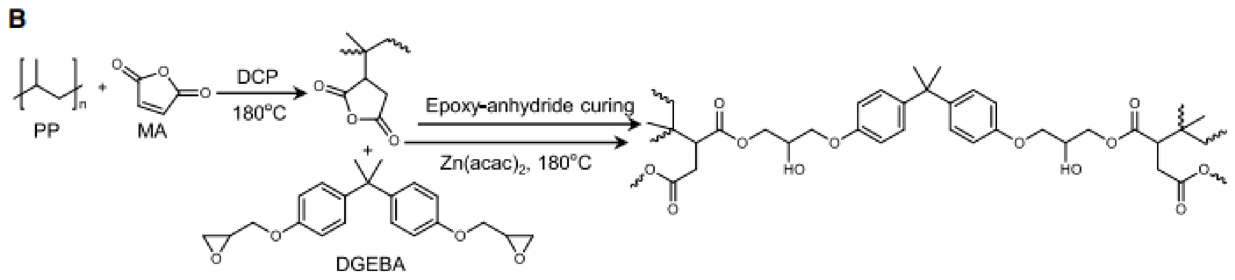
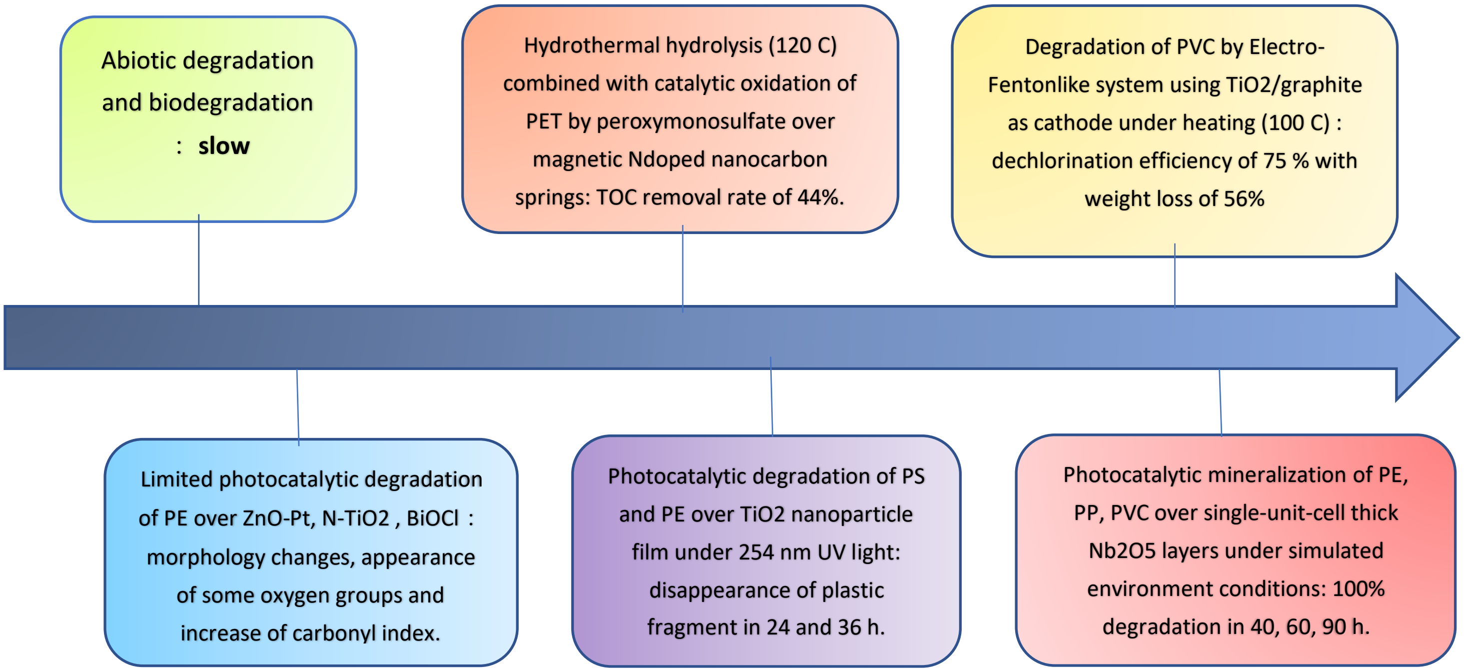


Figure 8: (A) Conversion of commercial HDPE to vitrimers via metathesis with dioxaborolane.130 Adapted with permissions,130 (B) Conversion of PP to vitrimers by grafting MA.

CATALYTIC DEGRADATION

Advanced oxidation processes (AOPs), including Fenton reactions, Fenton-like reactions, and photocatalytic oxidation have offered a potential portfolio for the catalytic degradation of plastic waste (Figure 9). These technologies were primarily designed and developed for the degradation of soluble organic pollutants with low molecular weights



Abiotic degradation and biodegradation : **slow**

Limited photocatalytic degradation of PE over ZnO-Pt, N-TiO2 , BiOCl : morphology changes, appearance of some oxygen groups and increase of carbonyl index.

Hydrothermal hydrolysis (120 C) combined with catalytic oxidation of PET by peroxymonosulfate over magnetic Ndoped nanocarbon springs: TOC removal rate of 44%.

Photocatalytic degradation of PS and PE over TiO2 nanoparticle film under 254 nm UV light: disappearance of plastic fragment in 24 and 36 h.

Degradation of PVC by Electro-Fentonlike system using TiO2/graphite as cathode under heating (100 C) : dechlorination efficiency of 75 % with weight loss of 56%

Photocatalytic mineralization of PE, PP, PVC over single-unit-cell thick Nb2O5 layers under simulated environment conditions: 100% degradation in 40, 60, 90 h.

Figure 9: Trend of the development of catalytic degradation technologies.

Complete mineralization of PE, PP, and PVC into CO2 (Figure 10) has been achieved via photocatalytic degradation using single-unit-cell-thick Nb2O5 layers as photocatalyst under simulated natural environment conditions[17]

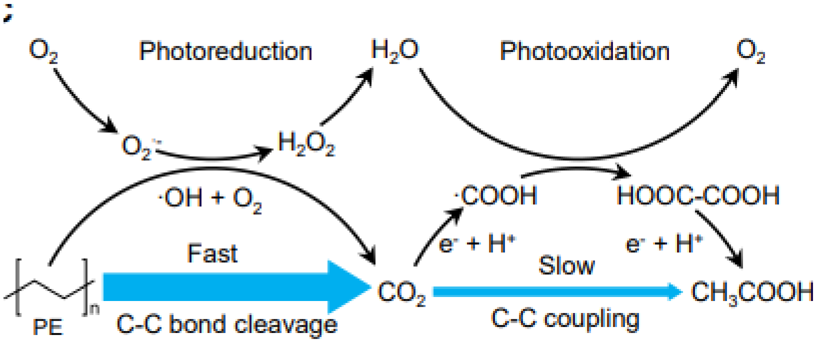


Figure10: Mechanism of Degradation of PE, PP, and PVC under simulated natural environment conditions using single-unit-cell-thick Nb2O5 layers as photocatalyst

Solid phase photocatalytic degradation of PE

In Solid-phase photocatalytic degradation of polyethylene (PE) plastic with TiO2 in the ambient air under solar and ultraviolet light irradiation is carried out and compared with that of pure PE through weight loss monitoring, scanning electron microscopic (SEM) analysis, gas chromatography (GC), FT-IR spectroscopy and X-ray photoelectron spectroscopy (XPS). PE-TiO2composite plastic can be efficiently decomposed and the main products are CO2 and water. The weight-loss of PE-TiO2 (1 wt%) film reached 42% under solar irradiation for 300 h. The degradation rate can be controlled by changing the content of TiO2 nanoparticles in PE plastic. The degradation of composite plastic initiated on PE-TiO2 interface and then extended into polymer matrix induced by the diffusion of the reactive oxygen species generated on TiO2 particle surface. The present study demonstrates that the polymer-TiO2 compositing is a practical and promising way to degrade the plastic waste under solar light without any pollution.[18]

Solid phase photocatalytic degradation of polystyrene plastic with goethite

Photodegradable polyethylene-boron-goethite (PE-B-goethite) composite film is prepared by embedding the boron-doped goethite into the commercial polyethylene. The goethite catalyst is modified by boron in order to improve its photocatalytic efficiency under the ultraviolet and visible light irradiation. Solid phase photocatalytic degradation of PE-B-goethite composite film is carried out in an ambient air at room temperature under ultraviolet and visible light irradiation. Weight loss monitoring is performed scanning electron microscope (SEM) analysis, FT-IR spectroscopy and X-ray photoelectron spectroscopy (XPS). The results observed through this method is photo-induced degradation of PE-B-goethite composite films is higher than that of the pure PE films and the PE-goethite composite films while there has been observed little change under the visible light irradiation. The weight loss of the PE-B-goethite (0.4 wt.%) composite film under the UV-irradiation for 300 hr reached 12.6%.[19]

Solid-phase photocatalytic degradation of PVC–TiO2 polymer

In The solid-phase photocatalytic degradation of poly(vinyl chloride) (PVC)–TiO2 composite films was investigated under the ambient air in order to assess the feasibility of developing photodegradable polymers. The photodegradation of the composite films was compared with that of pure PVC films through performing weight loss monitoring, scanning electron microscopic (SEM) analysis, gel permeation chromatography (GPC), FT-IR and UV–VIS spectroscopy, and X-ray photoelectron spectroscopy (XPS). TiO2-embedded PVC showed highly enhanced photodegradation. Irradiating the composite film for 300 h under air reduced its average molecular weight by two-thirds and weight by 27% while the irradiation under nitrogen atmosphere induced little degradation. The photocatalytic degradation of the composite film accompanied the increase in the FT-IR carbonyl peak intensity, the evolution of CO2 and H2O, and the whitening due to the visible light scattering from growing cavities.[20]

Photocatalytic degradation

The solid-phase photocatalytic degradation of polyvinyl chloride (PVC) films by tungstophosphoric acid (HPW) was carried out based on the unique redox property of heteropolyacid. PVC films doped with HPW (1.5, 2.0 wt.%) were prepared and their photocatalytic degradation was carried out under the irradiation of UV with wavelength 254 nm and visible light above 300 nm. The photocatalytic activity was determined by weight loss monitoring and scanning electron microscopic (SEM) analysis. HPW-doped PVC showed highly enhanced photodegradation. Irradiating the composite film for 250 h by visible light reduced its weight up to 70%.

The photocatalytic degradation of PVC films embedded with semiconductor nanomaterials TiO2 and CdS was also investigated and compared with that of HPW–PVC. It was noticed that TiO2–PVC and CdS–PVC induced less degradation. The SEM images of PVC composite films further confirmed the above results. The photodegradation of PVC by boric acid and such acid catalysts implied that the high photocatalytic activity of HPW-doped PVC film was due to the unique redox property of HPW, rather than the acidity. FT–IR and UV–vis spectroscopic studies provided some preliminary results about the structure of the HPW–PVC composite system and will lay some foundations for further studying the photocatalytic mechanism. The advantages for

PVC photodegradation by heteropoly compound were assessed. They show that this method possesses feasibility and, from the point of view of plastics assorting with environmental protection, provides a new way to develop photodegradable plastics.[21]

Degradation of polystyrene using clinoptilolite catalysts

Several solid acids such as silica–alumina, HZSM-5, HY, mordenite and clinoptilolite (natural and synthesized) are screened for their performances in the catalytic degradation of polystyrene (PS). The clinoptilolites showed good catalytic activity for the degradation of PS with very high selectivity to aromatic liquids. The increase of contact time and surface acidity enhanced the production of ethylbenzene. High degradation temperature favored the selectivity to styrene monome.[22]

Depolymerisation of poly(ethylene terephthalate) fibre wastes using ethylene glycol

Poly(ethylene terephthalate) [PET] fibre wastes was depolymerised from industrial waste using excess ethylene glycol [EG] in the presence of metal acetate as a transesterification catalyst. The glycolysis reactions were carried out at the boiling point of ethylene glycol under nitrogen atmosphere up to 10 h. Influences of the reaction time, volume of EG, catalysts and their concentrations on the yield of the glycolysis products were investigated. The glycolysis products were analysed for hydroxyl and acid values and identified by different techniques, such as HPLC, 1 H NMR and 13C NMR, mass spectra, and DSC. It was found that the glycolysis products consist mainly of bis(hydroxyethyl)terephthalate [BHET] monomer (O75%) which was effectively separated from dimer in quite pure crystalline form[23].

CONCLUSION

Upcycling and catalytic degradation map out two important routes toward the vision of a sustainable and zero-pollution future. Some upcycling processes and products have already been shown to have distinct advantages in both high-value areas and basic applications. Ascertaining the embedded value in plastic waste, which is present in the form of carbon, hydrogen, chemicals, energy, and macromolecular structures, might not only reduce the generation of undesired side-products and the consumption of energy and other external resources but also contribute to the improvement of conversion efficiency, eventually elevating the overall benefits.

Advanced catalytic methods must be established to improve reaction efficiency. Generally, both upcycling and recycling processes are restrained by limited solid-solid contact efficiency between the recalcitrant plastic substrate and heterogenous catalysts, intricate reaction networks, and undesired degradation of the target products. This catalytic degradation techniques have been successful in carrying out degradation as well as converting plastic into more chemical products such as hydrocarbon fuel etc. However, this techniques require not only high temperature and cost, but also appropriate catalysts to guarantee narrow distribution of hydrocarbon. Pyrolysis and gasification have been extensively investigated to convert plastic wastes to fuel, they yield only complicated mixtures, which require tedious separation, purification, and upgrading process to providing commercial fuel product. Hence, the development of quantum dot catalysts, homogeneous catalysts, enzyme-mimetic catalysts, tandem catalysis strategies, stabilization chemistry, and the coupling of different catalytic technologies is a potential option for solving these bottlenecks. In addition, the catalysts should have a high tolerance for air, moisture, and organic or metal salt contaminants. Few of catalytic processes have already showed the possibility of degrading plastic waste under artificially optimized harsh conditions.

Another pivotal environmental concern associated with plastics is the exhaustion of non-renewable fossil resources. The most hopeful solution to this problem is to develop more ‘‘sustainable’’ polymers from CO2 and renewable resources, in particular, plant-based feedstocks, such as cellulose, lignin, other polysaccharides, deoxyribonucleic acid, polyhydroxyalkanoates, sugars, vegetable oils, and terpenes; however, most current routes toward renewable feedstocks are far from cost effective relative to conventional routes. Although several recyclable and degradable polymers from renewable sources have been successfully designed in the laboratory, the ideal integration of sustainability, degradability (or recyclability), usability, and low-cost, in practice, is still a huge challenge. Biobased, fossil- based, and in a natural conditions biodegradable polymers can be developed for sustainable environment. In principle, cutting down the use of plastic material and substituting alternative material for the plastic would prevent the generation of plastic wastes and, in addition, relieve that excessive dependence on depletable resources. But this alone won’t solve the problem as years and years of plastic has been accumulated in the environment and is deteriorating quality of life on earth. For future prospect degradation process can be improved by modifying the natural polymers, by combining catalytic and biodegradation process, by developing biodegradable and durable polymer, replacing this artificial polymers with more sustainable ones.

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