

# 废弃聚对苯二甲酸乙二醇酯化学升级回收研究进展

戴瑞红<sup>1,2†</sup>, 林航青<sup>3†</sup>, 詹佳慧<sup>1</sup>, 丛容非<sup>3</sup>, 罗虎<sup>1\*</sup>, 魏雪梅<sup>4</sup>, 夏林<sup>1</sup>, 王慧<sup>1,3\*</sup>

1. 中国科学院上海高等研究院, 低碳转化科学与工程中心, 上海 201210

2. 中国科学院大学, 北京 100049

3. 上海科技大学物质科学与技术学院, 上海 201210

4. 脂溶性维生素浙江省工程研究中心(绍兴文理学院), 绍兴 312000

† 同等贡献

\* 联系人, E-mail: [luoh@sari.ac.cn](mailto:luoh@sari.ac.cn); [wanghh@sari.ac.cn](mailto:wanghh@sari.ac.cn)

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**摘要** 塑料的工业生产为人们日常生活带来了极大便利, 然而, 快速增加的废弃塑料对生态环境造成了巨大压力, 使得废塑料的回收利用成为全球关注的热点. 聚对苯二甲酸乙二醇酯(PET)是一种性能优异的热塑性聚酯材料, 广泛应用于纺织、包装、电子器件等行业. 目前, 废弃PET化学回收主要采用水解与醇解等方法, 将其转化为单体或低聚物等用于合成新的PET或其他高附加值化学品. 在此基础上, 本文综述了近年来PET热解、水解、醇解、氢解、光/电催化、微波强化等化学升级回收的研究进展, 介绍了产物选择性调控的反应机理, 分析了各类方法面临的挑战并展望了未来PET化学升级回收的发展方向, 旨在为开发高效的工业回收技术提供技术参考, 推动塑料循环经济的发展.

**关键词** 聚对苯二甲酸乙二醇酯, 化学升级, 催化剂, 反应机理

塑料为社会生活提供了便利, 但其逐年增加的废弃物对生态环境和人类健康造成了巨大威胁<sup>[1-3]</sup>. 聚对苯二甲酸乙二醇酯(polyethylene terephthalate, PET)是对苯二甲酸和乙二醇缩聚或对苯二甲酸(2-羟乙基)酯缩聚生成的半结晶热塑性聚酯, 被广泛应用于纺织、包装和电子等行业, 年产量超过3000万吨<sup>[4]</sup>. 然而, 随着PET需求量的增加, 其废弃物总量达到世界固体废物总量的12%<sup>[5]</sup>. PET具有稳定的化学性质, 在自然条件下的降解周期长达200~400年, 常用的处理方法如填埋会导致土地资源浪费和土壤、水源污染; 焚烧会导致空气污染并产生大量温室气体. 此外, 废弃的PET也可能进入食物链, 威胁人类健康<sup>[6]</sup>.

化学回收作为一种有前景的废塑料处理方法正受

到广泛关注, 可以将塑料废弃物转化为单体原料或高附加值化学品, 实现塑料的循环利用和升级再造. 目前PET回收的研究重点多集中在原料的转化率和产物收率上, 缺乏对PET降解过程的总结和反应机理的描述. 因此, 从化学升级回收角度出发, 本文对PET热解、水解、醇解和氢解的反应过程进行了综述和分析, 探讨了光/电催化和微波辅助对PET选择性解聚的促进和强化作用, 以期对PET的高效回收提供新的研究方向与思路.

## 1 热解

PET的热解通常是在无氧或缺氧的条件下, 利用高温加热将PET转化成小分子产物(酸类、酯类、酮类、

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Dai R, Lin H, Zhan J, et al. Research progress on chemical upcycling of waste polyethylene terephthalate (in Chinese). Chin Sci Bull, 2025, 70: 2825–2837, doi: [10.1360/TB-2024-0920](https://doi.org/10.1360/TB-2024-0920)

芳烃等)的过程<sup>[7-10]</sup>, 产物分离后可应用于新的化工生产过程. 目前, PET热解主要生成对苯二甲酸(TPA)和苯甲酸乙烯酯, 苯甲酸乙烯酯不稳定会发生重排和脱羰基反应生成苯乙酮, 如图1(a)所示. TPA与苯乙酮在催化剂上可以进一步转化, 比如发生脱氧反应如图1(b)所示<sup>[11-13]</sup>. 热解温度、压力、停留时间等反应参数会影响产物的组成, 不同的催化剂也影响着热解产物的选择性. 金属氧化物<sup>[14,15]</sup>(如CaO、NiO、Fe<sub>2</sub>O<sub>3</sub>等)、金属盐<sup>[16]</sup>(CuCl<sub>2</sub>、Zn(OAc)<sub>2</sub>等)、分子筛(ZSM-5<sup>[17]</sup>、MCM-41<sup>[18]</sup>)等在PET热解中均有应用, 其中ZSM-5和CaO具有较为优异的催化性能. ZSM-5分子筛具有独特的孔结构以及丰富的酸位点, 广泛应用于脱氧反应(尤其是脱羧和脱羰基反应), PET的初级裂解产物在ZSM-5的酸位点上发生烷基化和氢转移反应生成单芳烃和多环芳烃<sup>[15]</sup>; Nasution等人<sup>[19]</sup>发现HZSM5-70(Si/Al = 70的HZSM-5催化剂)和NiO/HZSM5-70能将PET热解产物中C<sub>5</sub>-C<sub>12</sub>汽油范围烃类的收率分别提高到66.48%和85.05%(无催化剂时C<sub>5</sub>-C<sub>12</sub>收率为33.39%). HZSM5-70的酸位点不仅具有优异的裂化/重整能力, 可将长链烃转化为短链烃, 还可以促进含氧化合物脱氧转化成脂肪族和芳香族化合物; 而负载NiO增加了Lewis和Brønsted酸位点的总量, 从而提升了催化剂的活性, 并且NiO/HZSM5-70在循环5次后仍保持较好活性. CaO

参与的水汽裂解中, PET会先水解形成TPA, TPA脱羧形成苯和CO<sub>2</sub>, 如图1(b)所示<sup>[12]</sup>. 此外, Diaz-Silvarrey等人<sup>[20]</sup>将硫化氧化锆用于PET的热解中, 在450~600℃和20 s的停留时间下, 可回收27 wt%~32 wt%的苯甲酸, 硫化氧化锆上具有丰富的Lewis酸位点(Zr原子)和Brønsted酸位点(表面的羟基氢), 这些活性位点会促进热分解产物形成碳正离子, 进而裂解成更小的分子. 何品晶团队<sup>[13]</sup>等利用KOH活化将废PET热解升级为富含CH<sub>4</sub>的热解气和分级多孔炭. 该过程中废PET初步分解后, 含氧组分完全热解脱氧形成芳烃, 芳烃进一步缩聚成不同分子量的多环芳烃, 分子量小的转化成碳球, 大的则转化成碳块, 热解所得碳材料具有微孔和介孔结构, 可用作超级电容器的电极.

## 2 水解

PET的水解根据水相中pH的不同可分为酸性水解、碱性水解和中性水解. 水解过程的机理如图2所示, OH<sup>-</sup>或H<sub>2</sub>O作亲核试剂进攻酯键促进PET的解聚, 生成TPA与乙二醇(EG), 其反应速率与PET颗粒大小、温度、压力、催化剂、反应介质对表面的润湿程度等因素有关<sup>[21]</sup>. 废PET水解所得的TPA和EG不仅可作为新PET合成的原料, 还可广泛应用于医药、阻燃剂、染料等领域.

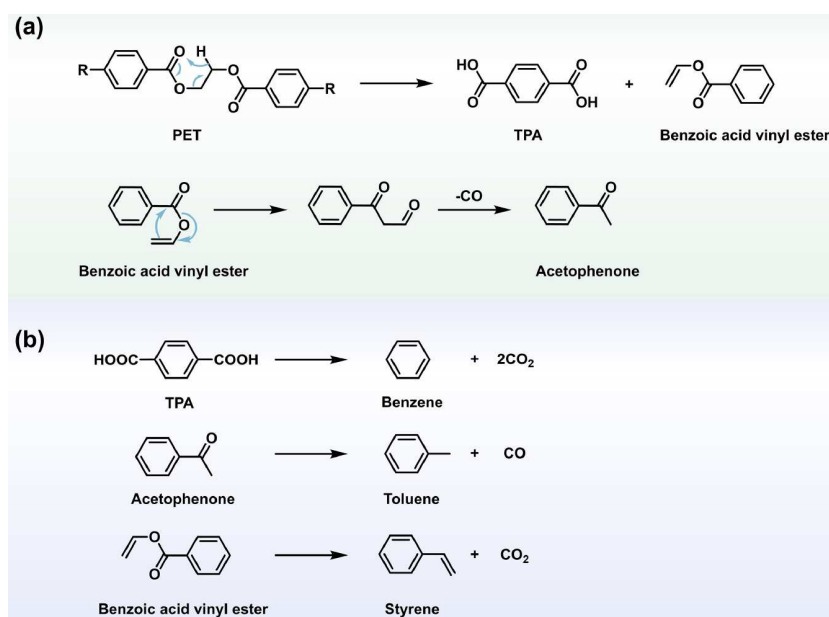


图1 (网络版彩色)PET热解反应示意图<sup>[15]</sup>. (a) PET热解的主要过程; (b) PET热解过程可能发生的脱氧反应

Figure 1 (Color online) Schematic diagram of PET pyrolysis reaction. (a) The main process of PET pyrolysis; (b) possible deoxidization reaction during PET pyrolysis

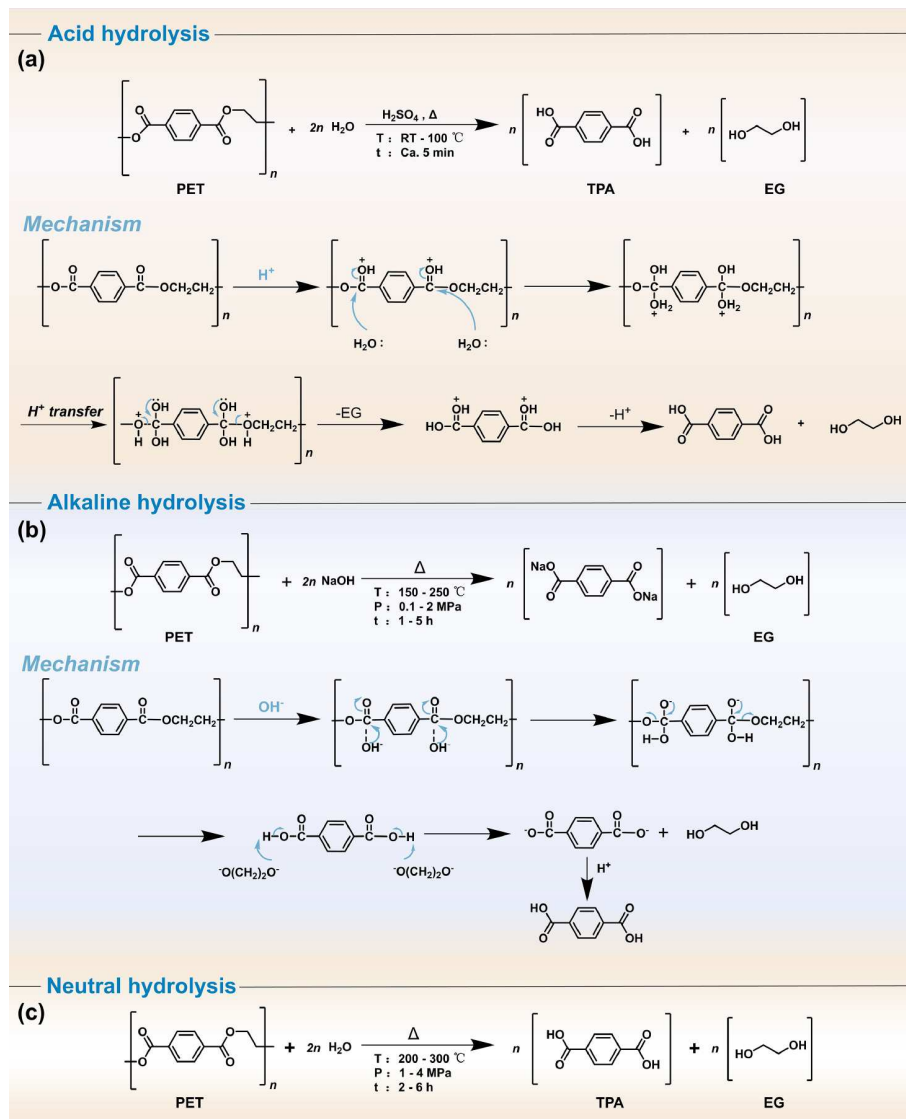


图2 (网络版彩色)PET水解反应与机理示意图<sup>[22,23]</sup>。(a) 酸性水解；(b) 碱性水解；(c) 中性水解

Figure 2 (Color online) Schematic diagram of PET hydrolysis reaction and mechanism<sup>[22,23]</sup>。(a) Acidic hydrolysis; (b) alkaline hydrolysis; (c) neutral hydrolysis

PET的传统酸解一般使用硫酸、硝酸或磷酸作催化剂，如图2(a)所示，酸解中H<sub>2</sub>O作亲核试剂进攻质子化后的PET，形成四面体正离子，再经质子转移、消除醇和质子后得到TPA<sup>[21,23]</sup>。2021年，Abedsoltan等人<sup>[24]</sup>利用聚4-苯乙烯磺酸主链的疏水性改善了PET表面的润湿性，增加了PET表面的局部Brønsted酸位点浓度，从而提高了催化降解效率，在16 h内解聚了超过90%的PET。有机弱酸TPA<sup>[25]</sup>和有机强酸对苯磺酸<sup>[26]</sup>均可在水溶液中电离出H<sup>+</sup>催化PET完全降解成TPA，收率分别为95.5%和96.2%；相比之下，TPA水解PET的温度更高，而

对苯磺酸也面临着强腐蚀性的问题。固体酸催化剂也广泛应用于PET的催化水解，如SO<sub>4</sub><sup>2-</sup>/TiO<sub>2</sub><sup>[27]</sup>和WO<sub>x</sub>/TiO<sub>2</sub><sup>[28]</sup>均可在超临界CO<sub>2</sub>下解聚PET，通过CO<sub>2</sub>溶胀PET提供更多反应空间，并利用其流动性增加H<sub>2</sub>O与酯基的接触以促进水解。SO<sub>4</sub><sup>2-</sup>/TiO<sub>2</sub>催化剂中，由于SO<sub>4</sub><sup>2-</sup>离子与TiO<sub>2</sub>框架以双齿整合形式相连，因此SO<sub>4</sub><sup>2-</sup>/TiO<sub>2</sub>比纯TiO<sub>2</sub>拥有更大的表面积可提供更多的Lewis酸位点，钛阳离子的空轨道接受H<sub>2</sub>O分子的电子对后，H<sup>+</sup>离开H<sub>2</sub>O分子进入反应体系中催化反应的进行，完成Lewis酸位点到Brønsted酸位点的转化；WO<sub>x</sub>/TiO<sub>2</sub>中，高

电负性的 $\text{WO}_x$ 物种在 $\text{TiO}_2$ 载体上产生 $\text{Ti}^{4+}$ 作为Lewis酸位点,  $-\text{OH}$ 与 $\text{Ti}^{4+}$ 或 $\text{W}^{6+}$ 连接作为Brønsted酸中心, 超临界 $\text{CO}_2$ 携带 $\text{H}_2\text{O}$ 和有效的Brønsted酸渗透到PET基体中催化反应的进行.  $\text{Ni}/\gamma\text{-Al}_2\text{O}_3$ <sup>[29]</sup>在水热条件下即可实现100%的PET降解, PET先在水中解聚成低聚物, 吸附在催化剂表面并且与Ni形成不饱和键, Ni与PET中的O原子形成强烈的相互作用可诱导O原子与C原子的分离, 断裂C—O键生成TPA, 但该催化剂对反应器和降解条件要求更高.

PET的碱性水解通常采用2 wt%~20 wt%的NaOH或KOH水溶液在200℃以上实现PET催化降解. 如图2(b)所示, 碱解中 $\text{OH}^-$ 作为亲核试剂直接进攻酯羰基碳发生亲核加成反应, 形成四面体中间体后再进行 $-\text{O}(\text{CH}_2)_2\text{O}^-$ 的消除反应, 生成的TPA上的氢转移到 $-\text{O}(\text{CH}_2)_2\text{O}^-$ 中最终形成EG和对苯二甲酸盐<sup>[21,23]</sup>. 2023年, 梅清清团队<sup>[30]</sup>利用废弃香蕉皮煅烧所得的碱性提取物BPE(Banana Peel Extract), 有效活性成分是 $\text{K}_2\text{CO}_3$ ,  $\text{CO}_3^{2-}$ 水解生成 $\text{OH}^-$ 解聚PET, 在150℃、4 h内实现PET的完全水解; 使用两亲性季铵盐(如四丁基碘化铵<sup>[31]</sup>、三辛基甲基溴化铵<sup>[32]</sup>)做相转移催化剂可使PET在较温和的条件下进行水解, 原因在于相转移催化剂兼具亲水性和亲脂性, 其中具有亲脂性的阳离子可将 $\text{OH}^-$ 离子运输到相界面处并进攻PET的酯键. 牛志强团队<sup>[33]</sup>开发的罗布森型双核锌催化剂 $\text{Zn}_2\text{L}(\text{NO}_3)_2$ 可在30~340℃和pH 8~14的范围内解聚PET, 反应速率提高的关键是催化反应遵循分子内水解途径, 即 $\text{Zn}_2\text{L}(\text{NO}_3)_2$ 经初始诱导期所生成的中间体的Zn位点在与PET酯羰基结合的同时, 也会受到相邻Zn位点上 $-\text{OH}$ 的进攻. 此外, 以正戊基替换双核催化剂中的取代基可适当增加活性中心的电子密度来提升催化效率<sup>[34]</sup>, 所得的 $\text{Zn}_2\text{L}-n\text{-pentyl}(\text{NO}_3)_2$ 在0.1 mol/L的NaOH和90℃下达到传统强碱体系23倍以上的比活性.

PET的中性水解往往在高于200℃和1~4 MPa压力下进行, PET与 $\text{H}_2\text{O}$ 的质量比范围为1:2~1:12<sup>[35]</sup>. 中性水解不使用腐蚀性试剂且不产生酸碱废水, 被视为一种环境友好的方法. 张东团队<sup>[36]</sup>提出PET中性水解的反应速率是关于TPA浓度的1/2级的自催化模型, 水解产物TPA所电离的 $\text{H}^+$ 会进一步催化PET水解, 机理如图2(a)所示. 在超临界(385℃、30 MPa)或亚临界(300℃、30 MPa)状态下, PET在1 min内完全水解得到TPA(收率分别为83.46%和93.46%)<sup>[37]</sup>.  $\text{Zn}(\text{Ac})_2$ <sup>[38]</sup>和海水<sup>[39]</sup>也可作为中性水解催化剂,  $\text{Zn}(\text{Ac})_2$ 的催化过程中,

$\text{Zn}(\text{Ac})_2$ 水解生成的HAc进一步电离出 $\text{H}^+$ 催化反应的进行, 提高反应速率; 海水中的金属离子( $\text{Na}^+$ 、 $\text{Mg}^{2+}$ 等)使聚合物链中产生不稳定的酯键, 导致PET随机解聚并缩短链长, 最终得到TPA和EG等产物. 此外, Sabde等人<sup>[40]</sup>在2023年发现相转移催化剂(PEG 400)在240℃的条件下中性水解0.5 h, 即可将PET转化成TPA, 收率达到90%, PET在240℃下开始熔化所形成的低聚物PET被PEG 400转移到水相中发生水解生成TPA和EG.

### 3 醇解

PET的醇解可分为甲醇醇解和乙二醇醇解, 生成对苯二甲酸二甲酯(DMT)或对苯二甲酸乙二醇酯(BHET)等产物, 机理如图3所示, 在高温和酸碱催化下, PET聚合物发生酯交换反应, 断裂聚合物中的酯键, 最终转化为DMT或者BHET, 其反应速率与温度、时间、催化剂等因素有关<sup>[22]</sup>.

PET的甲醇醇解是以甲醇为溶剂, 在180~220℃和2~7 MPa条件下将PET废弃物解聚为对苯二甲酸二甲酯和乙二醇的过程, 如图3(a)所示. 降解产物DMT在化学市场上有着广泛的使用, 它可广泛用于聚酯塑料的生产, 或加氢生产具有良好工业潜力的1,4-环己烷二甲醇<sup>[42]</sup>. 在PET的降解过程中, 催化剂的种类如离子液体和固体催化剂有着显著的影响.

吕兴梅团队<sup>[43]</sup>采用1-乙基-3-乙基咪唑乙酸酯和丙烯酸金属盐合成的离子液体催化剂 $\text{PIL-Zn}^{2+}$ , 该催化剂能够在170℃条件下反应1 h后将PET高选择性地转化为DMT, 收率可达89.1%. 调控离子液体中的金属, 会影响金属-氧键的强弱, 最终影响催化剂的活性<sup>[44]</sup>. 在最佳条件下, 催化剂中带正电的 $\text{Zn}^{2+}$ 直接攻击PET上的C=O键, 同时带负电荷的阴离子 $\text{Ac}^-$ 作用于甲醇羟基上的氢, 促使氧带更多的负电荷, 更易与聚酯C=O上的碳结合, 形成新的酯键并断裂聚酯分子链. 然而, 这种离子液体只有一种类型的酸, 会限制其活性, 而Brønsted-Lewis二元酸离子液体可解决此问题<sup>[45]</sup>. 刘仕伟等人<sup>[46]</sup>合成一种新型的Brønsted-Lewis二元酸离子液体催化剂 $[\text{HO}_3\text{S}-(\text{CH}_2)_3\text{-NEt}_3]\text{Cl}-[\text{ZnCl}_2]_{0.67}$ , 该催化剂使得PET在195℃反应0.5 h后, DMT收率达到78.4%. 研究发现由于 $[\text{HO}_3\text{S}-(\text{CH}_2)_3\text{-NEt}_3]\text{Cl}-[\text{ZnCl}_2]_{0.67}$ 结合了 $\text{ZnCl}_2$ 和 $[\text{HO}_3\text{S}-(\text{CH}_2)_3\text{-NEt}_3]\text{Cl}$ 的优点, 生成了更多的酸性位点, 与Brønsted-Lewis酸产生协同作用, 最终得到较好的结果.

相比于离子液体催化剂, 固体催化剂制备过程较

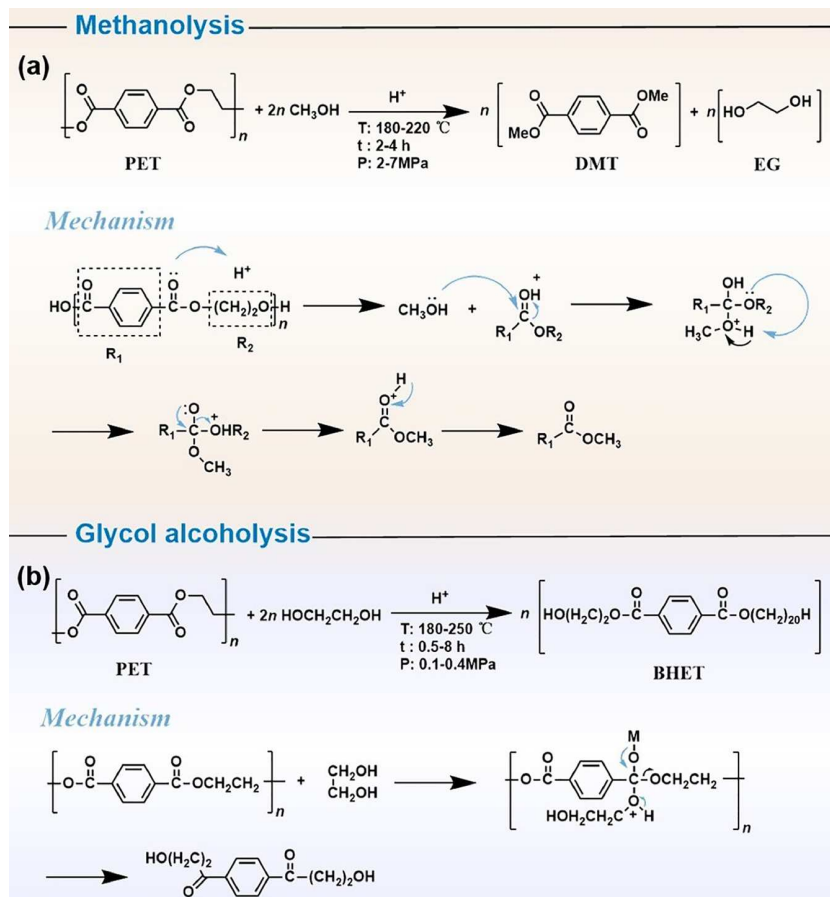


图3 (网络版彩色)PET醇解反应以及机理示意图<sup>[22,41]</sup>。(a) 甲醇醇解; (b) 乙二醇醇解

Figure 3 (Color online) Schematic diagram of PET alcoholysis reaction and mechanism. (a) Methanolysis; (b) glycol alcoholysis

为简单且有毒元素含量更少。张士成团队<sup>[47]</sup>通过研究不同催化剂的制备方法对催化剂活性的影响,发现通过浸渍法制备的催化剂比氨蒸发法和水热法制备的催化剂的催化性能好,浸渍法制备的Cu/SiO<sub>2</sub>催化剂,在200℃条件下反应1.5 h,得到的PET转化率和DMT选择性分别为92.3%和99.0%。通过浸渍法制备的催化剂具有更小的Cu颗粒,更高的比表面积,更高比例的Brønsted酸位点与Lewis酸位点以及更加平衡的Cu<sup>+</sup>和Cu<sup>0</sup>活性位点,因此能够表现出较好的催化性能。吕建华团队<sup>[48]</sup>采用浸渍法合成催化剂,探究催化剂中MgO含量对催化活性的影响。随着催化剂总碱量的增加,PET的转化率和DMT的收率均有所增加。NaY型沸石负载MgO后弱碱性位点数量变化不大,而强碱性位点数量则随着MgO含量的增加而明显增加,负载量为21 wt%时总碱量最高,而当负载量增加至24 wt%时,催化剂总碱量有所降低,因此21% MgO/NaY催化效果最佳,

在200℃条件下反应0.5 h后,PET转化率和DMT收率分别达到99%和91%。在上述反应过程中阳离子攻击PET羧基,而阴离子从甲醇的-OH基团中提取质子,生成亲核甲氧基离子并进而攻击PET的C=O键,从而实现PET的解聚<sup>[47~50]</sup>。

PET的乙二醇醇解是工业上重要的降解方法,主要是将PET和过量EG在常压、180~240℃条件下进行反应,PET解聚为合成单体BHET或低聚物,可用作PET或作为其他产品的原材料,如图3(b)所示。BHET作为一种新兴的单体,在各种产品中发挥着巨大潜力,包括再合成的PET、不饱和聚酯、聚氨酯和复合材料,应用领域广泛,包括纺织工业、电化学器件和生物相容性材料领域<sup>[51]</sup>。

钛金属是一类具有高度生物相容性的过渡金属元素,被许多学者作为催化剂金属活性中心的首选。中国石油大学沈国良团队先后使用具有八面体结构的苯甲

酸钛催化剂<sup>[52]</sup>、乙酰丙酮钛氧化物<sup>[53]</sup>、邻苯二甲酸钛催化剂<sup>[54]</sup>进行PET的醇解反应, BHET收率分别达到90.01%、96.41%、81.98%, 发现在PET醇解等酯交换反应中Ti离子呈Lewis酸性, 其与乙二醇的羟基形成配位结构, 形成Ti-O-R结构, 攻击PET分子结构中的C=O基团, 导致C=O裂解为C-O. PET分子经过持续的化学键断裂, 逐渐解聚形成低聚物, 最终形成BHET.

同样, Javed等人<sup>[55]</sup>使用乙醇钠(EtONa)作为催化剂降解废弃后的PET, 发现在最佳条件下(190℃, 5 h, PET: EtONa = 64(mol/mol), EG:PET = 5.28 (mol/mol), 粒径0.25 mm), PET转化率为77%, BHET收率为68%. 由于乙醇钠的碱强度较强, EG去质子化后通过亲核取代被加到PET聚合物链羰基的缺电子碳原子上, 最后, 聚合物链上Na<sup>+</sup>最终被乙二醇羟基中的H<sup>+</sup>取代, 形成BHET.

## 4 氢解

PET的氢解是指在催化剂作用下, PET的酯键发生断裂, H<sub>2</sub>被解离并与反应中间产物发生氢化, 生成短链饱和烷烃产物(苯、甲苯、二甲苯(BTX)等)的过程<sup>[56]</sup>. PET氢解多采用均相钌基催化剂<sup>[57]</sup>, 反应需要较高的H<sub>2</sub>压力、较长的反应时间且催化剂分离困难, 多相催化剂由于其温和的反应条件、易回收、高稳定性等优点逐渐获得关注<sup>[58]</sup>. 2020年, 高彦山团队<sup>[59]</sup>首次报道了C/MoO<sub>2</sub>催化的高效无溶剂PET解聚工艺, 在24 h,

260℃, 0.1 MPa H<sub>2</sub>的条件下, 将PET解聚为PTA, 收率为87%. 催化剂C/MoO<sub>2</sub>能够高效地识别PET的C-O键并使其发生β断裂, 得到苯甲酸以及苯甲酸乙烯醇酯, H<sub>2</sub>与C/MoO<sub>2</sub>反应生成C/Mo(=O)H(OCH=CH<sub>2</sub>), 作用于乙烯基苯甲酸酯中间体的氢解形成PTA. 蔡春团队<sup>[60]</sup>利用CoMo@NC催化剂(图4(a)), 在260℃、常压H<sub>2</sub>下, 反应10 h内将PET转化为更有价值的PTA, 收率高达91%. Co具有较强的氢的吸附和活化能力, Mo对氧具有强亲和力, 从XRD结果可知双金属CoMo@NC中的Mo和Co位与Mo@NC的Mo位和Co@NC的Co位相同, 说明Co与Mo的结合显著增加了催化剂的酸性和活性位点, 有利于酯基的吸附. 同时, CoMo@NC中平均孔径为3.85 nm, 且高度集中分布在平均值附近, 这种均匀的介孔结构有利于活性位点的暴露, 促进氢的活化, 从而表现出优异的催化性能.

王艳芹团队<sup>[61]</sup>以Ru/Nb<sub>2</sub>O<sub>5</sub>为催化剂, 在无外加氢源条件下, 首次将PET转化为BXT(图4(b)), 发现零价Ru物种越多越有利于脱羧, 而Ru和Nb<sub>2</sub>O<sub>5</sub>之间的强相互作用可以暴露更多的Ru<sup>δ+</sup>物种, 削弱了不需要的脱羧反应, 生成较少低级的苯, 提高BTX中甲苯和对二甲苯的选择性; 同时Nb<sub>2</sub>O<sub>5</sub>具有较强的氢解能力, 而氢解和脱羧是整个过程中的控速步骤, 因此该反应实现了PET转化为BTX的优异反应性. 张晶团队<sup>[62]</sup>发现通过调控Ru配位环境可以实现PET到BTX的有效转化

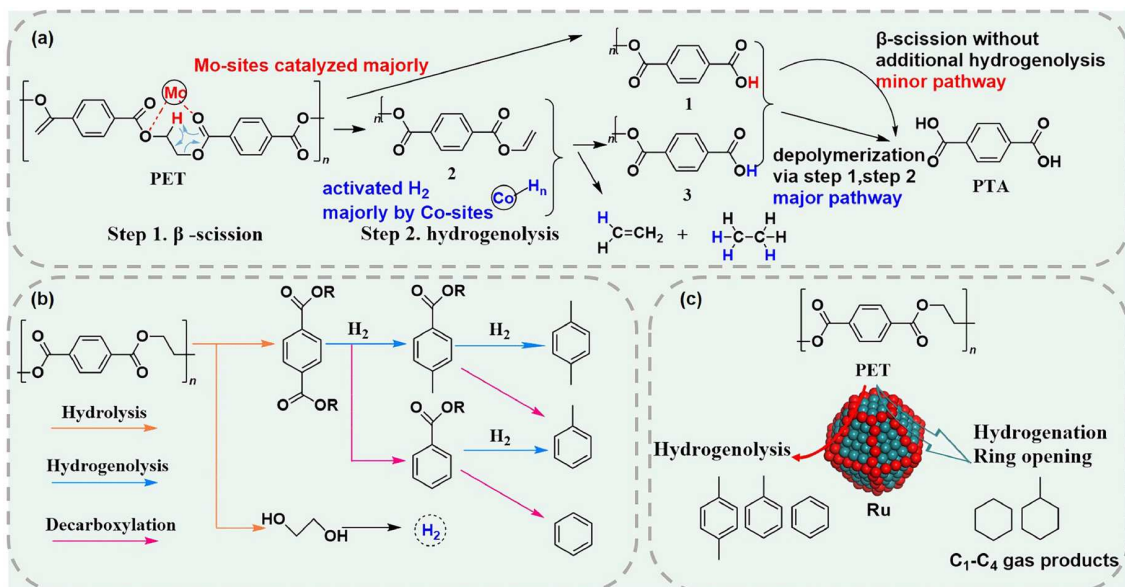


图4 (网络版彩色)PET氢解反应途径. (a) CoMo@NC催化PET氢解<sup>[60]</sup>; (b) PET氢解转化为BTX<sup>[61]</sup>; (c) Ru配位环境决定的PET氢解<sup>[62]</sup>

Figure 4 (Color online) Reaction pathway for hydrogenolysis of PET. (a) CoMo@NC catalyzed hydrogenolysis of PET<sup>[60]</sup>; (b) conversion of PET to BTX<sup>[61]</sup>; (c) PET hydrogenolysis at different Ru coordination environment<sup>[62]</sup>

(图4(c)). 研究和实验发现, 随着Ru尺寸的减小, Ru的配位数和平台与边/角位点的比例明显降低. 当Ru颗粒尺寸大于1 nm时, 芳烃产量随Ru尺寸的减小而增加; 其他尺寸的Ru/TiO<sub>2</sub>形成更多的环饱和产物和气体产物; 而在1 nm以下, Ru/TiO<sub>2</sub>会使PET发生过度氢解从而生成更多的甲烷. 在所有配位环境中, 当Ru的平均尺寸为1.1 nm, 配位数为5.0的Ru/TiO<sub>2</sub>催化剂, BTX总收率值达到最高, 为77%. 上述研究为设计用于转化含有芳香族单体的塑料的高选择性Ru基催化剂揭示了一条新途径, 使得废旧PET转化成以烷基芳烃为主要产物的BTX成为可能, 为解决PET废弃物的持久性积累和对化石能源的过度依赖提供可能的解决方案.

## 5 光/电催化

光催化是一种清洁的新兴催化方式, 可实现塑料的温和降解, 如图5(a)所示<sup>[63]</sup>. 半导体催化剂在光激发下产生光生电子和光生空穴, 价带中的光生电子激发到导带中发生还原反应(通常将H<sub>2</sub>O还原成H<sub>2</sub>), 而光生空穴留在价带中将塑料氧化成高价值的有机小分子.

Reisner等人<sup>[64]</sup>报道了基于CdS/CdO<sub>x</sub>量子点将预处理PET所得的EG升级为甲酸盐、乙酸盐等高价化学品的重整策略. Uekert等人<sup>[65]</sup>合成了无毒价廉的CN<sub>x</sub>/Ni<sub>2</sub>P催化剂, 可以将EG转化成甲酸盐、乙二醛等有机物; Ni<sub>2</sub>P助催化剂与CN<sub>x</sub>的强结合增强了电子向Ni<sub>2</sub>P的转移并减少电荷复合, 促进了电荷分离和催化效率. 元素的掺杂改性可以提高光催化剂的电导率并抑制载流子复合, 从而提升光催化剂的性能. 2023年, 邱博诚团队<sup>[66]</sup>利用O掺杂的CuIn<sub>5</sub>S<sub>8</sub>纳米片将EG升级为乙酸盐、乙醇酸盐和甲酸盐, 发现O的掺杂显著提高了电子空穴的分离效率和电子传输的性能. 2024年, 张胜波团队<sup>[67]</sup>以Pt修饰C<sub>3</sub>N<sub>4</sub>纳米球(Pt/g-C<sub>3</sub>N<sub>4</sub>)为光催化剂将EG选择性氧化成HCOOH(图5(b)). Pt的引入增大了C<sub>3</sub>N<sub>4</sub>的比表面积, 为光催化反应提供更多的活性位点; 同时, C<sub>3</sub>N<sub>4</sub>纳米球的超小尺寸( $d=2$  nm)缩短了电子传递路径和光氧化还原反应时间, 从而加速了反应过程. 光催化重整策略具有较好的环保意义, 目前的研究主要集中在设计和合成高效率、高选择性、可再生的光催化剂.

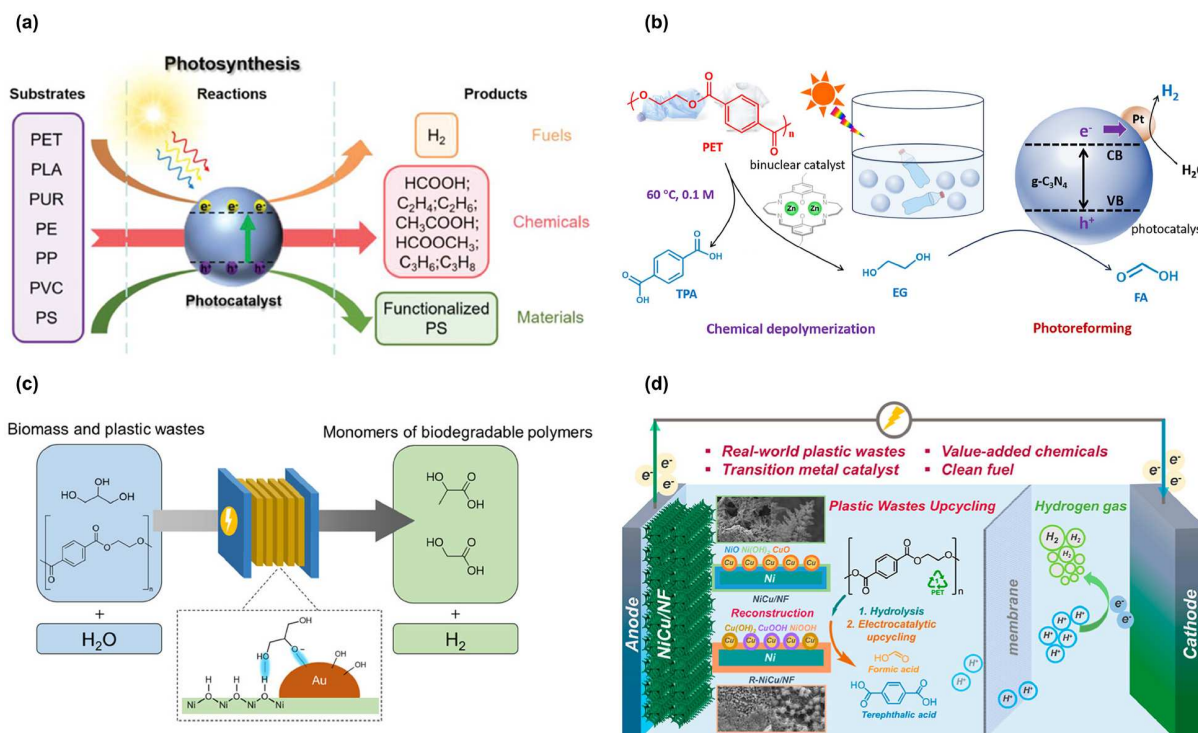


图5 (网络版彩色)PET光/电催化反应示意图. (a) 不同塑料的光催化作用示意图<sup>[63]</sup>; (b) 废PET的化学解聚与光催化串联反应示意图<sup>[67]</sup>; (c) Au/Ni(OH)<sub>2</sub> 电催化作用示意图<sup>[69]</sup>; (d) NiCu/NF 电催化示意图<sup>[71]</sup>

Figure 5 (Color online) Schematic diagram of PET photocatalysis and electrocatalysis reaction. (a) Schematic diagram of photocatalysis of different plastics<sup>[63]</sup>; (b) schematic illustration of the tandem chemical depolymerization and photocatalytic of waste PET plastics<sup>[67]</sup>; (c) schematic diagram of Au/Ni(OH)<sub>2</sub> electrocatalysis<sup>[69]</sup>; (d) schematic diagram of NiCu/NF electrocatalysis<sup>[71]</sup>

PET电催化升级包括PET的水解和产物乙二醇氧化生成高附加值化学品等过程(如对苯二甲酸、甲酸盐、乙醇酸盐等),串联反应较为复杂,在不同催化剂上会生成多种C<sub>1</sub>/C<sub>2</sub>产品。

段昊泓团队<sup>[68]</sup>开发了CoNi<sub>x</sub>P/NF催化剂将PET转化为甲酸盐(选择性>80%),发现反应过程中催化剂会发生重构并原位转化成低结晶度的CoNi<sub>0.25</sub>O<sub>x</sub>(OH)<sub>y</sub>;并利用Au/Ni(OH)<sub>2</sub>催化剂<sup>[69]</sup>,在1.15 V vs. RHE(可逆氢电极)下保持326.2 mA cm<sup>-2</sup>的电流密度,将PET水解所得的EG转化成乙醇酸(选择性为91%),工作原理如图5(c)所示。EG可通过与Ni(OH)<sub>2</sub>中的-OH相互作用富集在Au/Ni(OH)<sub>2</sub>表面,从而增加局部反应物浓度以提高催化活性。除了将EG转化成甲酸盐和乙醇酸,还可以利用WO<sub>3</sub>催化剂在常温常压下共氧化EG和NH<sub>3</sub>制备甲酰胺<sup>[70]</sup>,在100 mA cm<sup>-2</sup>的电流密度下法拉第效率为43.2%,反应速率达到537.7 μmol cm<sup>-2</sup> h<sup>-1</sup>,其中WO<sub>3</sub>中的W原子表现出对NH<sub>3</sub>的良好吸附行为,吸附在WO<sub>3</sub>上的NH<sub>3</sub>原位转化成-NH<sub>2</sub>亲核进攻EG在WO<sub>3</sub>上的吸附态乙醇醛,促进了C-C键的断裂并发生C-N偶联反应,最终生成甲酰胺,WO<sub>3</sub>的性能优于其他甲酰胺的电催化剂。

Kang等人<sup>[71]</sup>将铜电沉积在泡沫镍上合成NiCu/NF电催化剂并用于PET的解聚升级,工作原理示意如图5(d)所示。其中Cu的加入不仅促进催化剂生成关键活性物NiOOH和CuOOH/Cu(OH)<sub>2</sub>,还加快了电荷转移,增加电化学活性面积,以及显著降低乙二醇氧化反应中决速步骤的吉布斯自由能变ΔG,促进C-C的断裂。NiCu<sub>60s</sub>/NF在EGOR中具有最佳的甲酸盐法拉第效率

(FE=95.8%)和产率(0.70 mmol cm<sup>-2</sup> h<sup>-1</sup>)。PET的电催化升级具有较好的经济前景,需进一步研究和设计适用于工业化应用的高效电催化剂。

## 6 微波辅助解聚

PET化学利用一直面临着成本高和效率低的挑战,微波辅助解聚可以利用微波选择性加热的优势,作用并活化极性化学键,降低反应的活化能,从而使解聚反应更容易发生<sup>[72]</sup>。微波能够穿透PET作用于内部的极性键,产生热量并加剧分子运动,减弱大分子间的相互作用力;同时,微波的非热效应会影响PET分子链的构象、电荷分布以及反应活性位点。微波热效应和非热效应的协同作用会促进聚合物分子链的断裂,从而在较为温和条件下将PET解聚为单体。

Mohsin等人<sup>[73]</sup>使用甲醇和二甲基亚砜(DMSO)为溶剂,在微波照射下采用甲氧基钠原位水解的方法对PET进行化学回收,相较于传统的加热方法,微波辅助可在70℃将PET完全降解的反应时间缩短至5 min,转化率为100%,TPA收率为73.93%。

Azeem等人<sup>[74]</sup>研究了微波辐照对PET绿色快速乙二醇解聚过程的影响,采用顺序解聚技术,在3 min内将99%的PET转化为TPA,对苯二甲酸一羟乙基酯和BHET单体,产率分别为62.79%~80.66%、17.22%~34.79%和0.54%~0.59%。

唐军旺团队<sup>[75]</sup>采用0.4 wt%的Mn/ZnO催化剂,以EG作为溶剂,结合微波辐射在175℃下,仅需5 min即可将PET完全降解成单体BHET,并且选择性高达88%。

Scé等人<sup>[76]</sup>对比了传统加热和微波辅助加热条件

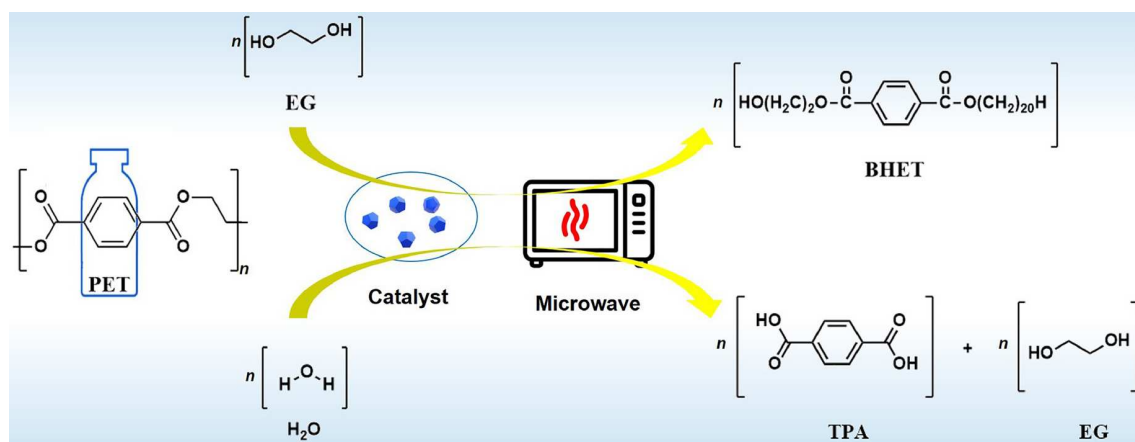


图6 (网络版彩色)微波辅助PET解聚示意图

Figure 6 (Color online) Schematic diagram of microwave-assisted depolymerization of PET

下,咪唑阳离子(dimim)[FeCl<sub>4</sub>]和(dimim)<sub>2</sub>[Fe<sub>2</sub>Cl<sub>6</sub>(m-O)]两种卤金属酸盐配合物对PET乙二醇解的催化活性,发现微波强化在效率和反应时间上具有明显优势.在常规加热条件下,反应24 h后,双核铁配合物的产率略低于(dimim)[FeCl<sub>4</sub>] (74% vs. 77%).而微波辅助工艺在2 h内即可获得类似反应结果,使用偶极体[Fe<sub>2</sub>Cl<sub>6</sub>(m-O)]配合物的PET降解产物收率为77%,高于非偶极体[FeCl<sub>4</sub>]阴离子配合物的69%.

Ha等人<sup>[77]</sup>开发了一种高效节能的微波辅助深度共晶溶剂(ChCl-Zn(OAc)<sub>2</sub>),用于强化PET的乙二醇解聚,在最佳反应条件下,反应9 min即可得到99%的BHET收率,同时,该方法具有较低的比能量消耗(45 kJ/g),并最大限度地减少废物的产生.微波辐射可以强化PET的解聚过程,缩短反应时间,在温和条件下生成高附加值产物,有助于实现循环经济.

## 7 总结与展望

近年来,PET的化学升级回收已获得工业界的关注,SABIC公司利用回收的rPET生产LNP ELCRIN IQ复合树脂-聚对苯二甲酸乙二醇酯,截至2022年底已转化4亿个0.5 L的PET瓶.瑞士PET化学回收公司Gr3n与西班牙Intecsa Industrial工程公司合作,基于微波辅助解聚技术共同建造了一座工业规模的塑料回收工厂,旨在将PET分解成对苯二甲酸和乙二醇两种单体,再重新生产塑料瓶和纺织品等.尽管PET的化学升级回收技术已经取得了一些进展,但其大规模应用过程中仍面临着挑战.

PET热解工艺简单,反应温度较高,产物组成相对

复杂,往往需要进一步的分离与纯化.水解中,酸性水解反应速率快且产物纯度高,但是酸度低的有机酸需更为严苛的反应条件,而强酸会导致设备腐蚀;碱解条件温和且催化剂廉价易得,在工业中应用较多,但会排放大量的碱性废水;中性水解清洁环保,目前面临着反应速率较慢、反应条件严苛等诸多问题.PET甲醇解具有高转化率和产物纯度高等优点,但甲醇的挥发性需要更加严格的安全措施;乙二醇解相对安全环保、反应条件温和,但产物转化率不高且产物分离提纯能耗大.PET氢解可发生在无溶剂体系中、产物的附加值高,需要进一步提高催化剂的活性和稳定性.

光/电催化作为环境友好型的催化方式,目前缺乏工业电流密度下高效稳定的电催化剂,同时光/电催化过程都需经过碱性水解的预处理步骤后再重整升级,因此克服PET的低溶解性直接实现解聚仍具有挑战性<sup>[78]</sup>.微波辐照可以提高反应速率,极大加快PET的解聚速率,但是微波强化反应过程的作用机制尚不明确.

因此,废弃PET的化学升级回收需要进一步设计能够生成高附加值产品的反应路线,构建高效的催化剂并利用先进表征手段阐明PET降解和活性位点的构效关系;深入揭示不同催化剂对PET的活化、C-C/C=O断裂以及产物调控的作用机制;加强聚合物链的动态解聚过程和反应动力学研究;考虑微波强化与水解/醇解的过程耦合,在温和条件下实现PET的选择性降解;拓展光/电催化技术路线在塑料转化中的应用范围,并考虑反应过程和环境/成本之间的平衡,结合回收与清洗过程推动废塑料化学升级技术实现大规模工业利用.

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Summary for “废弃聚对苯二甲酸乙二醇酯化学升级回收研究进展”

# Research progress on chemical upcycling of waste polyethylene terephthalate

Ruihong Dai<sup>1,2†</sup>, Hangqing Lin<sup>3†</sup>, Jiahui Zhan<sup>1</sup>, Rongfei Cong<sup>3</sup>, Hu Luo<sup>1\*</sup>, Xuemei Wei<sup>4</sup>, Lin Xia<sup>1</sup> & Hui Wang<sup>1,3\*</sup>

<sup>1</sup> CAS Key Laboratory of Low-Carbon Conversion Science and Engineering, Shanghai Advanced Research Institute, Chinese Academy of Sciences, Shanghai 201210, China

<sup>2</sup> University of Chinese Academy of Sciences, Beijing 100049, China

<sup>3</sup> School of Physical Science and Technology, ShanghaiTech University, Shanghai 201210, China

<sup>4</sup> Zhejiang Engineering Research Center of Fat-soluble Vitamin, Shaoxing University, Shaoxing 312000, China

† Equally contributed to this work

\* Corresponding authors, E-mail: [luoh@sari.ac.cn](mailto:luoh@sari.ac.cn); [wanghh@sari.ac.cn](mailto:wanghh@sari.ac.cn)

The industrial production of plastics has greatly enhanced our daily life, but the rapid accumulation in waste plastics now places immense pressure on the ecological environment, making recycling and reuse a global priority. Polyethylene terephthalate (PET) is an excellent thermoplastic polyester, which is widely used in textiles, packaging, electronic devices, and other industries. Currently, chemical recycling of waste PET primarily involves hydrolysis and alcoholysis, converting it into monomers or oligomers that can be used to synthesize new PET or other high-value chemicals. This review summarizes and analyzes recent advancements in the pyrolysis, hydrolysis, alcoholysis, and hydrogenolysis of PET, aiming to elucidate the reaction mechanisms that govern product selectivity. PET pyrolysis involves the breaking down of PET into small molecular products, such as acids, esters, ketones, and aromatics under oxygen-free or oxygen-deficient conditions with high-temperature heating. The product composition is influenced by the choice of catalysts. PET hydrolysis can be classified into acidic hydrolysis, alkaline hydrolysis, and neutral hydrolysis based on the pH of the aqueous phase. OH<sup>-</sup> or H<sub>2</sub>O acts as a nucleophile to attack the ester bonds, facilitating PET depolymerization into terephthalic acid (TPA) and ethylene glycol (EG). The reaction process of PET hydrolysis is mainly controlled by increasing the concentration of OH<sup>-</sup> or H<sup>+</sup>. PET alcoholysis is typically conducted in methanol and ethylene glycol, with acidic sites influencing the reaction pathway. Under high temperature and acid-base catalysis, PET undergoes ester exchange reactions, breaking the polymer's ester bonds, and ultimately converting it into dimethyl terephthalate (DMT) or bis(2-hydroxyethyl) terephthalate (BHET). PET hydrogenolysis, on the other hand, involves breaking the ester bonds of PET using H<sub>2</sub> to produce short-chain saturated hydrocarbons (such as benzene, toluene, and xylene (BTX)). The catalytic active centers are designed and optimized to enhance the efficiency of PET hydrogenolysis.

Additionally, this review explores photocatalytic, electrocatalytic and microwave-assisted depolymerization of PET to improve the product selectivity. Photocatalysis is a clean, emerging catalytic method in which semiconductor catalysts generate photogenerated electrons and photogenerated holes under light excitation. The photogenerated electrons are excited from the valence band to the conduction band, enabling reduction reactions (such as reducing H<sub>2</sub>O to H<sub>2</sub>), while the holes in the valence band oxidize plastics into valuable small organic molecules. This approach enables mild plastics degradation. PET electrocatalytic upgrading includes processes like the PET hydrolysis and the oxidation of product ethylene glycol to high-value chemicals (such as terephthalic acid, formate, and glycolate). These processes include complex cascade reactions that produce various C<sub>1</sub>/C<sub>2</sub> products depending on the catalyst used. Microwave-assisted depolymerization leverages the selective heating properties of microwaves, activating polar chemical bonds and reducing the activation energy of the reaction. Besides, this process enhances PET depolymerization, shortens reaction times and generates high-value products under mild conditions, supports the circular economy goals.

This review also summarizes the difficulties and challenges associated with various recycling methods and outlines the future directions for PET chemical upcycling. The development of efficient catalysts and in-depth exploration of reaction mechanisms to control product selectivity is recommended to advance the understanding of PET selective depolymerization process. Integrating new technologies, such as microwave-assisted processes and photo/electrocatalysis, could further enhance the reaction rates and efficiency at mild reaction conditions, which accelerates their application in real waste plastic scenarios. This review provides technical references for advancing the industrial recycling technologies and promotes the progress in plastic waste upcycling.

**polyethylene terephthalate (PET), chemical upcycling, catalyst, reaction mechanism**

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