REVIEW ARTICLE

Recent progress in catalytic glycolysis of waste polyethylene terephthalate with ethylene glycol: Catalyst, mechanism and kinetics

Jiawei Li[*]

Department of Chemistry, University College London, London WC1E 6BT, United Kingdom

Due to the large consumption of polyethylene terephthalate (PET), the accumulated PET wastes have already become an issue to the environment. Research groups focus on the degradation of PET wastes for recycling in the last two decades, and several chemical methods have been investigated including glycolysis, alcoholysis, hydrolysis, aminolysis, and ammonolysis. The studies are faced with the challenges in catalyst development and mechanism insights. Therefore, the achievements are worth reviewing for future exploration and application. This review systematically summarized the catalysts used in PET glycolysis with ethylene glycol (EG), which were categorized into 4 groups including metal oxide, ionic liquid, deep eutectic solvent (DES), and others. The effects of reaction conditions on catalytic performance, reaction mechanism, and kinetics were also analyzed.

[*]**Corresponding author:** Jiawei Li, Department of Chemistry, University College London, London WC1E 6BT, United Kingdom. Email: Vera-ljw@outlook.com.

Introduction

Polyethylene terephthalate (PET) is a well-known polymeric material, which is widely used in soft drink bottles, packaging, film material, and textiles [1]. These uses are made possible thanks to its light weight, high strength, low toxicity, and transparency properties [2]. However, the discarded PET is hard to degrade by itself. The most common ways people use to degrade PET nowadays are still incineration and landfill [3], which may cause serious air pollution. Therefore, the reuse of waste PET has become a key issue, not only to solve the environmental problems it causes but also to alleviate the pressure of overuse of basic resources [4]. In previous studies, it was found that the fastest way to degrade PET was to convert it from polymer to monomer. In this case, glycolysis with ethylene glycol (EG) [5], hydrolysis with acid or base [6], aminolysis with amine [7], and alcoholysis with

alcohol [8] become the mainstream approach. In terms of cost and efficiency, glycolysis with EG has greater advantages than the others, and it will degrade PET into bis(2-hydroxyethyl) terephthalate (BHET) and other oligomers. Of these, metal oxide [9], metal acetates [10], DES [11], and ionic liquids [12] are the dominant catalysts for this approach and have achieved high recoveries of PET in laboratory pretests. Despite all the efforts, problems still exist for various applications. Therefore, the summarization of the recent achievements is necessary and meaningful as the basis for the following research. The aim of this review is to analyze and discuss in detail the catalytic performance and structure-activity relationship of the reported catalysts, the catalytic mechanism, and the kinetics of glycolysis of EG with waste PET, and to make suggestions for prospective studies.

Catalysts and their effects on PET degradation

The production of BHET from PET and EG *via* catalysed glycolysis is performed under a condition of 190 - 240°C. Although the raw materials are the same, the reaction times, temperatures, and product yield vary with the catalyst properties such as crystal phase, acidity, basicity, and stability, which affect the reaction rate. The catalysts that have been studied so far can be broadly classified into metal oxides, metal acetates, DES, and ionic liquids.

1. Metal oxides
The metal oxides are traditional catalysts that has been researched for many years and used by scholars and companies because the metal oxides can provide Lewis acid sites, and the metal cation can strip electrons from the oxygen atom of carbonyl group of PET, thus breaking the ester bond [13]. During these years, the researchers tried to modify the catalyst including the bulk metal oxide, supported metal oxide, and metal oxide nanosheet, as summarized in Table 1.

(1) Bulk metal oxide
In 2022, Mohammadi *et al*. utilized the Sb_2O_3, which showed a dual catalytic performance on PET degradation. The BHET yield could reach up to 97.5% by glycolysis of PET using EG at the conditions of 200°C, 2.1 bar, EG/PET of 5.0 (weight ratio), and catalyst loading of 0.5 wt% [14]. From H-NMR spectra, it was found that the purity of BHET could be controlled by the modulation of reaction condition, which was supported by the disappearance of a small singlet peak in H-NMR spectra and weight loss of recrystallized BHET in TGA curve. Stimulated by this discovery, they successfully degraded PET catalysed by Sb_2O_3 under microwave irradiation, generating a 96.7% yield of PET oligomers at 240°C and 400 W, among which only 3.3% BHET was achieved using 0.25 wt% Sb_2O_3 at an EG/PET weight ratio of 2.5 [15]. It was confirmed by HPLC analysis that the Sb2O3 favoured the production of oligomers rather than complete cleavage of ester bond, attributed to the weak Lewis acidity of Sb_2O_3. Lin *et al*. carried out the glycolysis of PET

over Ni-doped MgO catalyst, having a Mg/Ni molar ratio of 75/1 at 185°C, the yield of BHET climbed to 93.7% after 50 minutes [16]. It was observed from XPS that the Ni showed a greater electronegativity than Mg, resulting in a stronger Ni-O bonds and the substitution of Ni^{2+} by Mg^{2+}. These interactions induced the slight lattice distortion that weakened the Mg-O bonds, creation of oxygen vacancies, suggesting that the catalysts had rich chemisorbed oxygen species considered as the active sites. Yunita *et al*. conducted the PET glycolysis with the catalysis of CaO, having ostrich eggshell structure at the reaction conditions of 192°C and EG/PET weight ratio of 15, the yield of BHET reached 76.4% after 2h [17]. The XRD patterns confirmed that the crystallinity of CaO would increase linearly with the calcination temperature up to 1,000°C, which consequently improved the catalytic efficiency.

(2) Supported metal oxides
Yao *et al*. utilized the traditional ZnO in combination with mesoporous SBA-15 for the glycolysis of PET at the reaction conditions of 197°C, EG/PET mass ratio of 4/1. 100% conversion of PET and 91% yield of BHET were obtained within 1 h [18]. The high performance of catalyst was contributed to the strong chemical interaction between the catalyst and oxygen in the carbonyl group of PET, which was revealed by *in situ* IR spectra, decreasing the activation energy. Zhang *et al*. designed a kind of porous Mn_3O_4-$MgAl_2O_4$ spinel combined material (Mn_3O_4/p-spMgAl800), which was prepared from calcined MgAl-layered double hydroxide (LDH) support and Mn_3O_4 [19]. The highest BHET yield of 97.6 % could be achieved at the conditions of 190°C and EG/PET ratio of 20 in a reaction time of 3 h. The redistribution of $MgAl_2O_4$ spinel nanoparticles, dispersion of Mn_3O_4, and surface defects in the acid-base pairing of Al^{3+}-O_2-Mg^{2+}, which were confirmed by TEM and TPD, could promote catalytic activity. Zangana *et al*. reported a fast glycolysis process within 3.5 min using 5 wt% activated carbon supported CaO catalyst and 95% PET conversion with 75% BHET yield could be attained at the reaction conditions of 197°C, 800 W and EG/PET weight ratio of 10/1

Table 1. Metal oxide catalysts for PET glycolysis.

Catalyst	Temperature (°C)	Time (mins)	PET conversion	BHET yield	EG/PET ratio	Reference
Bulk metal oxide catalysts						
Sb_2O_3	200	-	-	97.50%	5	[14]
Sb_2O_3 under microwave	240	-	96.70%	3.30%	2.5	[15]
Ni-dopped MgO	185	50	-	93.70%		[16]
CaO	192	120	-	76.40%	15	[17]
Supported meta oxide catalysts						
ZnO and mesoporous SBA-15	197	60	100%	91%	4	[18]
porous Mn_3O_4-p-spMgAl800	190	180	-	97.60%	20	[19]
activated carbon supported CaO	197	3.5	95%	75%	10	[20]
CaO-supported MCF	190	-	100%	80.10%	20	[22]
Metal oxide nanomaterials						
Mo dopped ZnO	180	60	100%	94.50%	4	[23]
2D holey MnO_2/HGO	200	10	100%	100%	18.5	[24]
Fe_2O_3@MoS_2	225	180	97%	90%	-	[25]
CeO_2 with KH550	196	15	98%	90.30%	7	[26]

[20]. The addition of the activated carbon would promote the absorption of microwave irradiation and inhibit the loss of calcium element [21]. Zhao *et al.* synthesized a CaO-supported mesocellular siliceous foam (MCF) catalyst for the glycolysis of PET to BHET. 100% conversion of PET together with 80.1% yield of BHET could be achieved at the optimal condition of 190°C and n(EG):n(PET) of 20:1 [22]. The high catalytic activity depended on the basicity, good dispersion of CaO in both bulk and surface of MCF, and porous structure, which were supported by CO_2-TPD, XRD, and TEM analysis.

(3) Metal oxide nanomaterials
Cao *et al.* discovered that the d-electron showed a strong correlation with the active sites of metal oxide catalysts, and thus developed a type of heteroatom-doped ZnO nanosheet. A 94.5% yield of BHET monomer and 100% conversion of PET could be achieved over Mo/ZnO catalyst at the conditions of 180°C and a PET/EG molar ratio of 1/4 after 1 h [23]. The HRTEM, XRD, and XPS characterization results unravelled that the defective state, the molecular adsorption activation, and transfer of electron in the catalytic reaction could be regulated by the

replacement of Zn by Mo or Co at the defective sites. Jin *et al*. carried out the glycolysis of PET on 2D holey MnO_2/graphene oxide (MnO_2/HGO) nanosheets at the conditions of 200°C and EG/PET weight ratio of 18.5. 100% yield of HBET and 100% PET conversion were achieved after 10 min reaction [24]. The researcher credited the high catalytic performance of MnO_2/HGO to the abundance of nanopores smaller than 20 nm and large specific surface area of HGO, which enabled the uniform and compliant deposition of MnO_2, as determined by TEM and XRD. Cha *et al*. designed a hydrodynamic system for synthesis of Fe_2O_3@MoS_2 0D/2D nanocomposite catalyst, which had a Fe/Mo ratio of 7/3. 97% PET conversion and 90% BHET yield could be obtained at 225°C for 3 h reaction [25]. According to the Raman spectroscopic analysis results, there was a shift in binding energy of Fe_2O_3@MoS_2, which indicated the MoS_2 nanosheet effectively bound to Fe_2O_3 nanoparticles and low formation energy. Yun *et al*. developed CeO_2 nanoparticle using 3-aminopropyltriethoxysilane (KH550) for the glycolysis of PET with EG. In a reaction time of 15 min, a 98% conversion of PET could be achieved together with 90.3% yield of BHET at 196°C and

Table 2. Ionic liquid catalysts for PET glycolysis.

Catalyst	Temperature (°C)	Time	PET conversion	BHET yield	EG/PET ratio	Reference
Catalyst with metal element						
[C$_6$TMG]Cl/2ZnCl$_2$	195	70 min	100%	92.70%	5	[28]
CoFe$_2$O$_4$ with [C$_{10}$COOHBIM]OAc	196	2.5 h	100%	95.40%	-	[29]
[HMIM]Cl/ZnCl$_2$ with [HMIM]Cl/CoCl$_2$	190	2 h	100%	87.10%	-	[30]
rGO/[TESPMI]$_2$CoCl$_4$	190	3 h	100%	95.20%	-	[31]
Fe$_3$O$_4$@SiO$_2$@[MIM]FeCl$_4$	180	24 h	100%	100%	1/100	[32]
Fe$_3$O$_4$@PMIM-SbBr$_4$	200	1 h	100%	96.40%	-	[33]
(DIMIM)$_2$[Fe$_2$Cl$_4$(μ-ox)]	170	3 h	99%	99%	-	[34]
Catalyst without metal element						
[Ch][Gly]	93.5	125 min	100%	88.70%	-	[35]
[Ch]$_3$[PO$_4$]	180	3 h	100%	60.60%	4	[36]
[Ch][OAc]	180	4 h	-	85.20%	4	[37]
[EMIM]$_2$TPA	195	106 min	100%	83.60%	3.6	[38]
DBN with 2-methylphenol	190	30 min	100%	87.30%	-	[39]

EG/PET mass ratio of 7 [26]. The high capability of catalyst was contributed to the KH550, which promoted the exposure of more active sites and prevented the agglomeration of catalyst as confirmed by XRD. In addition, the formation of oxygen defects induced by the lattice strain of Ce^{3+} also enhanced the catalytic efficiency.

2. Ionic liquid

Due to the unique properties of ionic liquid such as great thermal stability, uniformity, and low vapor pressure, it had been widely studied and used in electrochemistry and catalysis. Previous studies proposed the p-p interaction between the PET and aromatic solvents, hydrogen bond, and significant role of anion and cation [27]. Ionic liquid can be classified into two categories: with and without metal element, as summarized in Table 2.

(1) Ionic liquid with metal element

Wang *et al*. introduced [C$_6$TMG]Cl/2ZnCl$_2$ as catalyst for the glycolysis of PET. 100% conversion of PET and 92.7% yield of BHET could be achieved under the conditions of 195°C, 70 min, and EG/PET ratio of 5 [28]. The catalytic productivity was improved by not only the Zn^{2+}, which had stronger acidity thus was a better Lewis acid site than other metal ions, but also the positive effect of electron donation group in

cation, overcoming the influence of steric hindrance. Wang *et al*. performed the glycolysis with EG catalysed by CoFe$_2$O$_4$ magnetic nanoparticle (MNP) with [C$_{10}$COOHBIM]OAc as ionic liquid surfactant at 195°C for 2.5 h, which attained a full conversion of PET and BHET yield of 95.4% [29]. The surfactant modified the size of CoFe$_2$O$_4$ MNP, which promoted the good dispersion of catalyst and enhanced catalytic performance, denoted by TEM. Chen *et al*. synthesized a [HMIM]Cl/ZnCl$_2$ and [HMIM]Cl/CoCl$_2$ mixture with a ratio of 2. 100% PET conversion and 87.1% BHET yield could be obtained at 190°C within 2 h [30]. NMR analysis showed that the high catalytic activity was due to the synergetic catalytic effects between the [HMIM]Cl/ZnCl$_2$ and [HMIM]Cl/CoCl$_2$ for unconventional broken chain product and selective chain scission. Najafi-Shoa *et al*. reported a cobalt-based ionic liquid catalyst which frauded on graphene surface (rGO/[TESPMI]$_2$CoCl$_4$) to carry out the glycolysis of PET at 190°C. After 3 h, 100% conversion of PET and 95.2% yield of BHET were achieved [31]. The excellent catalyst performance was owed to the synergetic effects between the anion and cation, the hydrogen bond established between the graphene and EG, π-π interactions, and the contribution of nitrogen doped graphene. Cano *et al*. designed a silica-coated magnetic Fe$_3$O$_4$

nanoparticle with an iron-containing ionic liquid $Fe_3O_4@SiO_2@[MIM]FeCl_4$, which generated a 100% PET conversion and BHET yield at 180°C, 24 h, and EG/PET ratio of 1/100 [32]. The enhanced activity and selectivity were due to the hydrogen bond interaction of EG and PET with the imidazolium cation and metal complex which played a key synergic role. Mohammadi *et al*. proceeded the glycolysis of PET on $Fe_3O_4@PMIM-SbBr4$ catalyst. The PET conversion was 100%, and the BHET yield could climb up to 96.4% after 1 h at 200°C and 0.6 bar [33]. The presence of $SbBr_4^-$ functionalized ionic liquid catalyst allowed the crystallization of BHET at room temperature, which promoted the catalytic efficiency, as confirmed by FTIR analysis. In addition, the monodispersed and geometrically uniformed size distribution induced by paramagnetic nature of Fe_3O_4 also enhanced the catalytic performance. Cot *et al*. discovered a $(DIMIM)_2[Fe_2Cl_4(\mu-ox)]$ catalyst to obtain a 99% PET conversion and BHET yield in 3 h under microwave radiation at 6 W and 170°C [34]. Specifically, PET should be smashed into a size of 6 mm. The dielectric vibration property of catalyst absorbed energy efficiently from microwave irradiation, resulting in the decrease of reaction temperature, so less energy was needed to maintain the heating, thus improved the catalytic rate and efficiency.

(2) Ionic liquid without metal element
Liu *et al*. explored a [Ch][Gly] catalyst for the glycolysis of PET with EG. Within 125 min, a complete conversion of PET and 88.7% BHET yield could be obtained at 93.5°C [35]. The high catalyst performance was attributed to the relatively small activation effect of amino acid anion on the hydroxyl hydrogen of EG, which was presented by H-NMR. Sun *et al*. introduced $[Ch]_3[PO_4]$ in the glycolysis of PET and achieved BHET in approximately 60.6% yield with a 100% conversion of PET under optimal conditions of EG/PET ratio of 4 at 180°C after 3 h reaction [36]. The good miscibility of $[Ch]_3[PO_4]$ with EG presumably formed a eutectic solvent, which was consistent with the strong hydrogen bond interaction between them, leading to high

catalytic activity. Liu *et al*. investigated a [Ch][OAc] catalyst that had a satisfactory performance on glycolysis of PET. An 85.2% yield of BHET could be generated at EG/PET ratio of 4, 180°C, and 4 h [37]. The catalytic efficiency was enhanced by the electron-deficient structure caused by the alkyl group in OAc^- and the small size of Choline, through the increasing hydrogen interaction between PET and the catalyst, as discovered by DFT. In addition, the cation and anion's synergistic interaction also contributed. Zhang *et al*. processed the glycolysis using $[EMIM]_2TPA$ catalyst at an EG/PET ratio of 3.6 and 197°C, the PET conversion and BHET yield could climb up to 100% and 83.6% within 106 min [38]. The hydrogen bond, which strengthened the nucleophilicity of hydroxyl bond of EG, and catalyst diminished the need of post-processing by reducing the introduction of impurities to the system, enhancing the production efficiency. Wang *et al*. synthesized 1, 5-diazabicyclo [4.3.0] -5-nonene (DBN) mixed with 2-methylphenol catalyst to carry out the glycolysis with EG. 100% PET conversion could be achieved together with a BHET yield of 87.3% under 190°C and 30 min [39]. The high reactivity of catalyst was benefit from the inductive and conjugated effect of methyl group at ortho-position of benzene ring and the high electron density would lead to the strong interaction between the catalyst and EG.

3. Deep eutectic solvent (DES)
The use of DES as catalyst in PET depolymerization stimulated a faster and higher selectivity than conventional solvents, as summarized in Table 3. Because the carbonyl group was activated by the hydrogen bond network, hence decreased the activation energy [40]. Liu *et al*. conducted the glycolysis of PET using $[Betaine]/Zn(OAc)_2$ as catalyst [41]. 95% PET conversion and 85% yield of BHET could be achieved at the conditions of 190°C and EG/PET of 5 after 45 min. The high catalytic effect was due to the three substituents on the nitrogen atom of Betaine, which showed the strongest synergistic effect with EG through the attack of Zn^{2+}, leading to the activation of C=O bonds in PET, as proved by H-NMR and *in situ* IR. Liu *et al*.

Table 3. DES catalysts for PET glycolysis.

Catalyst	Temperature (°C)	Time	PET conversion	BHET yield	EG/PET ratio	Reference
[Betaine]/Zn(OAc)$_2$	190	45min	100%	85.00%	5	[41]
1, 3-DMU/Zn(OAc)$_2$	190	20min	100%	82.00%	4	[42]
ChCl-Zn(OAc)$_2$	180	3h	-	91.60%	8	[43]
HTBD-OAc/Zn(OAc)$_2$	190	3h	100%	88.50%	5	[44]
acetamide/ZnCl$_2$@ ZIF-8	195	25min	100%	83.50%	5	[45]
DBU with DMU	180	70min	-	83.00%	3	[46]
ethlene glycol/K$_2$CO$_3$	180	2h	100%	88.00%	15	[47]
FeCl$_3$·6H$_2$O/MSA	120	3h	100%	100.00%	-	[48]

reported a 1, 3-Dimethlurea/Zn(OAc)$_2$ (1, 3-DMU/Zn(OAc)$_2$) catalyst for the glycolysis of PET [42]. 100% PET conversion and 82% BHET yield were obtained at the conditions of 190°C and EG/PET of 4 after 20 min. As illustrated by H-NMR, the synergistic effect of 1, 3 DMU and Zn(OAc)$_2$ together with the basicity and steric hindrance of active sites of urea made a contribution to the high catalytic performance. Ha *et al*. utilized a ChCl-Zn(OAc)$_2$ catalyst to improve the PET glycolysis with EG [43]. The BHET yield would reach 91.6% at the optimal condition of 180°C and EG/PET of 8 after 3 h. The high selectivity of BHET monomer was achieved by giving an appropriate amount of DES to inhibit the competition of the excessive hydrogen atom. The high yield was ensured by the small particle size of PET, which enhanced the mass transfer at the liquid-solid interface and the synergistic effect of catalyst. Zhu *et al*. introduced 1, 5, 7-triazabicyclo [4.4.0] decium acetate/Zn(OAc)$_2$ (HTBD-OAc/Zn(OAc)$_2$) in the glycolysis of PET at the condition of 190°C, and EG/PET of 5. Full conversion of PET and 88.5% BHET yield were obtained in 3h [44]. The new hydrogen bond which was formed between the amino group of DES and EG, and the hydrogen bond between the OAc- and [HTBD]+ played a predominant role in the high catalytic activity. Wang *et al*. performed the PET glycolysis with EG on acetamide/ZnCl2@ ZIF-8 [45]. A completed conversion of PET and 83.5% BHET yield was obtained in 25 min under 195°C with an EG/PET ratio of 5. The Zn^{2+} ion showed strong Lewis acid and formed strong interaction with carbonyl oxygen in PET. In addition, the amino group in acetamide exhibited low steric hindrance and formed hydrogen bonds with EG. Both parts enhanced the catalytic performance. Li *et al*. combined 1, 8-diazabicyclo [5.4.0] undec-7-ene (DBU) with dimethylurea (DMU) to synthesize a catalyst used for the glycolysis of PET [46]. An 83% yield of BHET could be attained at 180°C and a DBU/DMU ratio of 1 after 70 min. The high catalytic activity was due to the increased electronegativity of the nitrogen atoms, which in turn was due to the substitution of methyl groups for hydrogen atoms in the DMU. The lower steric hindrance, formation of hydrogen bond, and synergetic effect of catalyst also favoured the PET glycolysis, as proposed by NMR and DFT calculation. Sert *et al*. proceeded the glycolysis of PET using ethylene glycol/K$_2$CO$_3$ as catalyst [47]. A 100% conversion of PET and 88% yield of BHET was reached at the optimal condition of 180°C and EG/PET of 15/1 after 2 h. The DES showed a higher catalytic efficiency owing to the relatively high basicity (pKa = 14) and low viscosity. Rollo *et al*. carried out the glycolysis of PET using EG over FeCl$_3$·6H$_2$O/methane sulfonic acid (MSA) [48]. After 3 h, the conversion of PET and yield of BHET could climb to 100% and 99.7% at 120°C. The synergetic effect between the Lewis and Brønsted acid sites was crucial for the catalytic efficiency, which likely involved a simultaneous "double activation" of ester group by these two different active sites.

4. Other catalysts

Table 4. Other catalysts for PET glycolysis.

Catalyst	Temperature (°C)	Time	PET conversion	BHET yield	EG/PET ratio	Reference
ultrasmall cobalt nanoparticle	180	3h	96%	77.00%	-	[49]
cyanamide	190	2.5h	100%	95.21%	10	[50]
S/Zn-Ti	180	3h	100%	72.00%	-	[51]
Na12 [WZn$_3$(H$_2$O)$_2$(ZnW$_9$O$_{34}$)$_2$]	190	4h	100%	84.50%	4	[52]
Si-TEA	190	1.7h	-	88.50%	12.6	[53]
EtONa	196	2.97h	98%/93%	75.00%	-	[54]
TBD with MSA	180	2h	-	91.00%	-	[55]

As summarized in Table 4, Veregue *et al.* reported an ultrasmall cobalt nanoparticle to carried out the glycolysis of PET without water. 96% PET conversion and a 77% yield of HBET were achieved at 180°C after 3 h reaction [49]. The high catalytic performance was attributed to the tannic acid (TA) molecule which enabled EG promote into the active sites. Also, the good dispersity of cobalt nanoparticles formed by TA molecule played an important role. Wang *et al.* investigated a cyanamide catalyst that had good performance on glycolysis of PET. A complete PET conversion and 95.21% yield of BHET could be achieved at the conditions of EG/PET ratio of 10 and 190°C after 2.5 h [50]. The hydrogen interaction between PET, EG, and cyanamide enhanced the catalytic efficiency which was proved by H-NMR and DF. Zhu *et al.* introduced S/Zn-Ti in the glycolysis of PET at the condition of 180°C. After 3 h, full conversion of PET and 72% BHET yield were obtained [4]. The binary oxide characteristic of catalyst played an elementary role in the high catalytic activity. It ensured the large surface area and medium acid sites could expose more active sites at low calcination temperature. Fang *et al.* designed a polyoxometalate catalyst with sandwich structure and two active sites for glycolysis of PET with EG [3]. Under the optimal condition of 190°C and EG/PET ratio of 4, a series of metal used in the catalyst were tested and the zinc showed the best performance, which led to 100% PET conversion and 84.5% BHET yield after 4 h. The catalytic efficiency was enhanced by the exposure of multiple transition metal active sites in each crystal structure, which allowed the reciprocity of EG and catalyst. In addition, each active sites exhibited activity and jointed the alcoholysis of PET, as confirmed by SC-XRD. Fehér *et al.* conducted PET glycolysis on Si-TBD and the Si-TEA catalyst, separately [51]. The optimal condition was 190°C and EG/PET ratio of 12.6. The BHET yield could be obtained as 88.5% within 1.7 h when use Si-TEA. Compared to Si-TBD, Si-TEA showed relatively higher thermal stability, which promoted a better catalytic efficiency, as measured by TG-DSC. Javed *et al.* developed MeONa and EtONa as catalysts for the glycolysis of PET [52]. A coloured PET conversion of 98% and white PET conversion of 93% could be attained with catalysis of 2.97 h, BHET yield of 75% under the condition of 196°C. Both catalysts showed an appropriate tolerance while processing large amount of waste PET, indicating they had outstanding catalytic performance. However, with the evidence of HPLC analysis, MeONa was better than EtONa. Jehanno *et al.* explored a catalyst which combined TBD and MSA with a ratio of 1:1 to perform glycolysis with EG [53]. After reaction time less than 2 h, a BHET yield of 91% was achieved at 180°C. The prominent catalytic performance was due to the complete transfer of acidic proton of MSA to the basic nitrogen of TBD, thus an ionic pair was created between these two compounds. In addition, the hydrogen bond was also formed to enhance the thermal stability of protic ionic salt, leading to good catalytic activity proved by TGA and H-NMR.
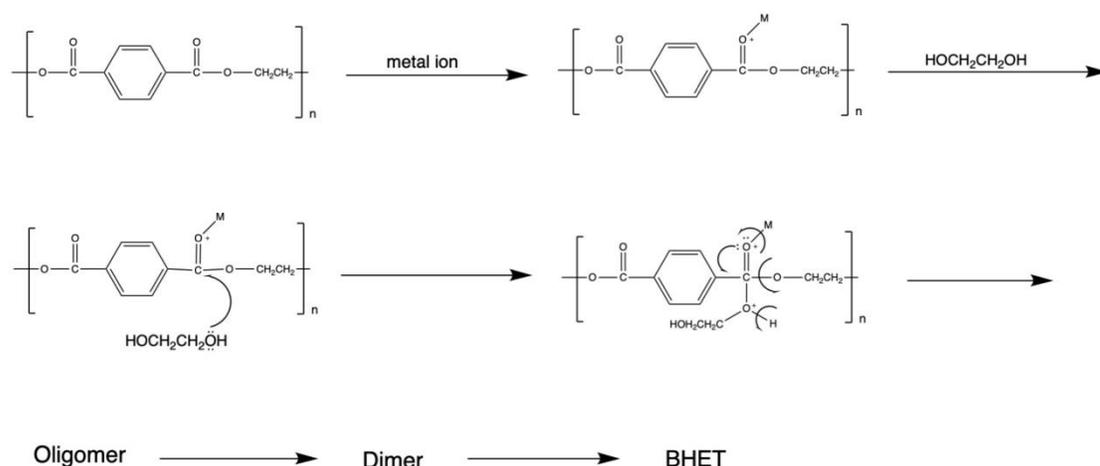
Mechanism and kinetics

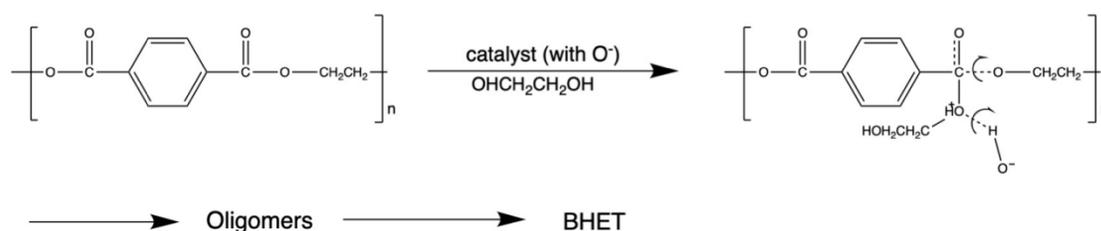**Figure 1.** Mechanism 1 of metal oxide catalyzed reaction system.

Figure 2. Mechanism 2 of metal oxide catalysed reaction system.

The proposed mechanism was different in metal oxide catalysed reaction system and ionic liquid/DES catalysed reaction system. BHET generation was a reversible step-by-step reaction, maintaining the equilibrium among oligomers, dimers, and BHET by optimal reaction conditions [54].

1. Metal oxide catalyzed reaction system

When the reaction was on the metal oxide, the vacancy orbital on the Lewis acid center would deprive the lone pair of electrons from the carbonyl oxygen in PET to form M-O$^+$=C which caused electrons dissipate and enhanced the electrophilicity of the carbonyl carbon, which indicated that the double bond was activated (Figure 1) [13]. Then the oxygen on EG hydroxyl group attacked the electron deficient carbon on PET and dehydrogenated, forming a tetrahedral intermediate. The repeating reactions would continue to yield oligomers, dimers, and BHET as products [17].

When catalyst acted as Bronsted base site, it attacked hydrogen on the EG hydroxyl group, affording the formation of EG- intermediate which was more nucleophilic [16]. Then the nucleophilic EG- attacked the carbonyl carbon on PET to form a tetrahedral intermediate [55], and the corresponding ester group would be cleaved. The reactions would be repeated until the final product BHET was obtained (Figure 2).

As for kinetics, the reaction order was first order. So, the rate equation was:

$$\frac{d(Cpc)}{dt} = -kC_{pc} \qquad (1)$$

where k was the rate constant of the reaction and Cpc was the concentration of polycarbonate at t.
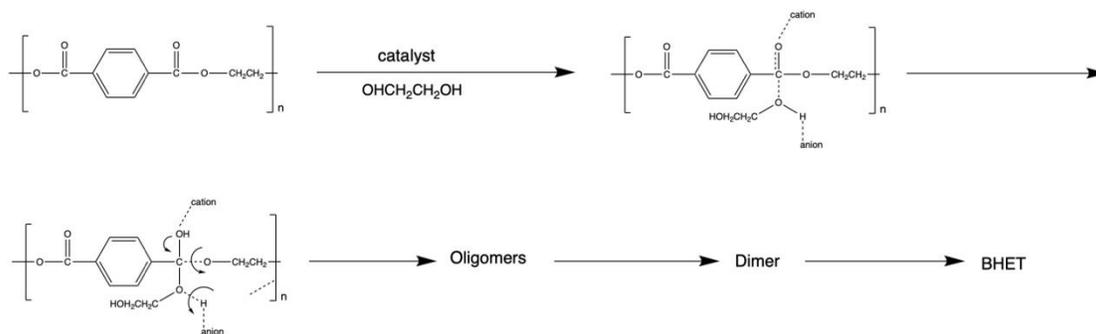
$$C_{pc} = C_{pc}(1-X) \qquad (2)$$

Figure 3. Mechanism of metal oxide catalyzed reaction system.

where X was the PET conversion. Then equation1 could be written as:

$$\frac{dy}{dt} = k(1\text{-}X) \tag{3}$$

Equation 3 could be integrated against time to give:

$$ln\frac{1}{1-X} = kt \tag{4}$$

The effects of temperature and time were proportional to the rate of PET glycolysis. [22]

2. Ionic liquid/DES catalyzed reaction system
Anion could strongly interact with EG hydroxyl group and PET carbonyl group by forming hydrogen bonds, increasing the O-H bond length to facilitate the loss of hydrogen in EG, and increase the electronegativity of oxygen in PET carbonyl group making the carbonyl carbon more positively charged (Figure 3) [55]. The cation/metal ion mostly attacked the carbonyl oxygen in PET, and a four-membered ring transition state was formed to disintegrate the PET chain. This synergic effect contributed to the catalytic performance. Then the process was repeated to decompose PET into oligomers, dimers, and finally the BHET.

Conclusion and prospects

Up to now, glycolysis of PET with EG had been intensively investigated and studies had been carried out to develop new catalyst. The catalysts can mainly be classified into 4 categories including metal oxides, ionic liquids, DES, and others. The high catalytic performance can be attributed to the metal active sites, hydrogen interactions, synergetic effects, size, and the dispersion of active sites. With the understanding of reaction mechanism, the activation of carbonyl group of PET is the rate-determining step, which depends on the interaction of catalyst with EG and/or PET, as proved by kinetic calculation. In future studies, the following aspects deserves great efforts:

1). The process using non-metal contained catalysts are expected to reduce the environmental pollution.

2). More efforts should be put in developing simple structured and highly active catalysts.

3). As the glycolysis temperature is still relatively high, new method or technique is needed to improve catalytic stability.

4). Methods for recovery of catalysts are required.

5). The systematic research on mechanism-based kinetic calculation is deserved.

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