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## Unraveling the role of water in catalytic glycolysis of PET

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The chemical recycling of polyethylene terephthalate (PET) *via* glycolysis is a promising route for recovering the monomer bis(2-hydroxyethyl) terephthalate (BHET), which can be used for virgin-grade PET production. However, the influence of water—an inevitable impurity and potential byproduct—on this process is complex and not fully elucidated. This study systematically investigates the effect of water content (0–22.2 vol%) on PET glycolysis using selected heterogeneous catalysts (ZnO and Mn<sub>2</sub>O<sub>3</sub>) and homogeneous catalysts (zinc acetate (ZnAc<sub>2</sub>), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)). Product distribution and reaction kinetics were quantified by HPLC and *in situ* IR spectroscopy, respectively. The heterogeneous catalysts (ZnO and Mn<sub>2</sub>O<sub>3</sub>) and homogeneous ZnAc<sub>2</sub> retained high PET conversion (>95%) even at elevated water concentrations. Nevertheless, the BHET yield and selectivity for these systems decreased significantly due to a competing hydrolytic side reaction, promoted by water, which yields terephthalic acid (TPA). Notably, ZnAc<sub>2</sub> exhibited a more rapid decline in BHET selectivity compared to ZnO. Conversely, the organic base catalysts TBD and DBU experienced complete deactivation in the presence of water, resulting in a drastic reduction in both PET conversion and BHET yield, with DBU showing greater susceptibility. *In situ* IR experiments corroborated that the deactivation mechanism for TBD involves protonation by water. These results emphasize that water's influence is a function of the catalyst's chemical nature, modulating product selectivity for metal-based systems while causing the deactivation of organic bases. Understanding these divergent effects is critical for the optimization of industrial PET glycolysis and the rational design of water-tolerant catalytic systems.

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### Sustainability spotlight

The majority of plastic materials do not break down naturally and instead continue to pose a threat to the environment. At present, only a small proportion of plastic waste is recycled, often for energy generation or the manufacturing of lower-grade goods. The goal of this review is focused on the concept of upcycling, which involves utilizing PET waste as a raw material for the production of value-added products such as monomers, fine chemicals, and hydrogen or carbon materials. Chemical recycling coupled with rational design and optimization of catalysis provides a necessary addition to current recycling methods. Our work emphasizes the importance of the following UN sustainable development goals: industry, innovation, and infrastructure (SDG 9), and ensure sustainable consumption and production patterns (SDG12).

## 1 Introduction

The increasing ubiquity of polyethylene terephthalate (PET)—a prevalent thermoplastic used extensively in packaging, textiles, and consumer goods—has created significant environmental concerns due to its chemical stability and insufficient recycling rates.<sup>1–3</sup> Traditional mechanical recycling

processes often diminish PET's physical properties, restricting its applicability in high-value products.<sup>4,5</sup> As a result, chemical recycling methods,<sup>6–9</sup> especially catalytic glycolysis,<sup>10,11</sup> have emerged as a viable solution to break down PET into its constituent monomers, such as bis(2-hydroxyethyl) terephthalate (BHET), which can then be reprocessed into virgin-grade PET.

In the alcoholysis of PET, where alcohol acts as a solvent to produce monomers, the effectiveness of the process is largely dictated by the design of the catalyst.<sup>12</sup> Homogeneous catalysts such as zinc acetate,<sup>13</sup> titanium alkoxides, and certain ionic liquids<sup>14</sup> have demonstrated high activity due to their excellent miscibility in the reaction medium, which facilitates access to PET ester linkages. To overcome these separation issues,

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materials such as supported metal oxides,<sup>15</sup> mixed-metal oxides,<sup>16</sup> zeolites,<sup>17</sup> and metal-organic frameworks (MOFs)<sup>18</sup> offer the distinct advantage of easy recovery through simple filtration, enabling catalyst reuse and paving the way for continuous-flow processes. While significant progress has been made in optimizing catalyst efficiency and reaction kinetics,<sup>19</sup> the role of water—a ubiquitous impurity in post-consumer PET feedstocks and a potential byproduct of glycolysis—remains underexplored yet critically influential. Despite its numerous advantages, water in PET glycolysis is an unavoidable issue for practical industrial applications. Water originates from a variety of sources, including recycled ethylene glycol, the production line's ambient humidity, material handling procedures, and PET itself, which is hygroscopic (absorbing water from the environment at a rate of about 0.6%);<sup>20</sup> moreover, water can be formed in specific side reactions, present as water of crystallization in specific catalysts (such as zinc acetate dihydrate), or even purposefully added in later BHET purification steps.<sup>21</sup>

Water may act as a double-edged agent in this process: trace amounts could enhance proton transfer and catalyst activity, whereas excess moisture may hydrolyze ester bonds competitively, shifting reaction pathways or deactivating catalysts.<sup>22,23</sup> The presence of water may exert complex and sometimes contradictory influences on the glycolysis process of PET. Water may participate in side reactions (e.g., hydrolysis<sup>24</sup>) leading to the formation of unwanted byproducts (e.g., TPA), thereby reducing the yield and purity of BHET while increasing separation costs; alternatively, it may influence catalytic activity and stability or reaction medium properties, thereby altering the kinetics and mass transfer in reactions. Since PET is known to require stringent drying prior to melt processing to avert hydrolytic degradation, it is important to have a clear understanding of the independent action mechanisms and the degree of influence of water in this specific chemical recycling process of glycolysis. This knowledge is required for process design optimization, reaction efficiency improvement, product quality assurance, and assessing the industrial viability of technology.

Sensitivity to water, a common industrial impurity, may be an important yet underappreciated factor hindering the transition of laboratory achievements to industrialization. Therefore, developing water-tolerant catalytic systems is crucial for reducing the energy-intensive pre-drying steps, lowering purification costs, and improving the overall process efficiency and economic viability of PET chemical recycling. Although water is a known impurity in PET glycolysis, its influence on the process is complex and not yet fully elucidated. This study aims to examine the influence of water content on PET catalytic glycolysis over different heterogeneous ( $\text{ZnO}$  and  $\text{Mn}_2\text{O}_3$ ) and homogeneous ( $\text{ZnAc}_2$ ,  $\text{TBD}$ , and  $\text{DBU}$ ) catalysts.

## 2 Experimental

### 2.1 Materials

Materials included polyethylene terephthalate (PET) from abandoned Nongfushan spring mineral water bottles (relative molecular mass 18 000–22 000). PET was pretreated by washing with deionized water (50 °C), dicing into 3 × 3 mm fragments,

ultrasonically cleaning, and then drying (50 °C, 12 h). Tianjin Kemio Chemical Reagent Co., Ltd supplied the analytical grade ethylene glycol ( $(\text{CH}_2\text{OH})_2$ , anhydrous, ≥99.8% purity), which was used as a solvent without further purification. Standards for analysis, namely BHET (98%), methyl-(2-hydroxyethyl) terephthalate (MHET, ≥97%), and DMT (>99%), were sourced from Aladdin. The catalysts,  $\text{ZnO}$  (nanopowder, <100 nm particle size),  $\text{Mn}_2\text{O}_3$  (nanopowder, 30 nm avg. part. size),  $\text{Zn}(\text{CH}_3\text{CO}_2)_2$  ( $\text{ZnAc}_2$ , 99.9%),  $\text{TBD}$  (1,5,7-triazabicyclo[4.4.0]dec-5-ene, 98%), and  $\text{DBU}$  (1,8-diazabicyclo[5.4.0]undec-7-ene, 98%), were purchased from Sigma-Aldrich.

### 2.2 Equipment and procedures

A continuously stirred batch reactor (Parr Instrument Company, USA) was employed for the experiments. The reactor operates at a temperature range of –10 to 350 °C up to 130 bar pressure.

PET glycolysis was investigated by reacting 5.0 g of PET flakes with 25 mL of ethylene glycol and a catalyst (1 wt%) in a Parr reactor featuring temperature/pressure sensors, magnetic stirring, cooling, and control systems. Reactions proceeded at a given temperature under atmospheric pressure for 0.5–3 hours, with stirring at 500 rpm. Key experiments were repeated at least three times. Post-reaction, the hot solution was transferred to a beaker, and ~150 ml of 100 °C deionized water was added. After vigorous stirring, the mixture was immediately filtered to separate solids (catalyst and unreacted PET). These solids were dried at 80 °C overnight and weighed, allowing PET conversion to be calculated *via* eqn (1).

$$\text{Conversion of PET}(\%) = \frac{W_1 - W_2}{W_1} \times 100\% \quad (1)$$

where  $W_1$  represents PET initial weight and  $W_2$  represents the weight of unreacted PET. For heterogeneous catalysts, the initial weight of the catalyst was subtracted from the final solid weight to determine the weight of the unreacted PET  $W_2$ . For homogeneous catalysts, the catalyst remains in the liquid phase, so the filtered solid is assumed to be only unreacted PET.

Meanwhile, the filtrate was stored in a refrigerator at 4 °C for 20 hours. At this point, white crystalline flakes can be seen forming in the filtrate. The solution was subsequently filtered and separated to obtain solid products which were dried in an oven at 70 °C for 8 hours.

The yield of the monomer is defined using eqn (2):

$$\text{Yield of monomer}(\%) = \frac{W_{\text{mon}} \times \text{MW}_{\text{mon}}}{W_1 \times \text{MW}_{\text{PET}}} \times 100\% \quad (2)$$

where  $W_{\text{mon}}$  is the weight of the obtained monomer (BHET, MHET, or TPA),  $\text{MW}_{\text{mon}}$  is the molecular weight of the respective monomer,  $W_1$  is the initial weight of PET, and  $\text{MW}_{\text{PET}}$  is the molecular weight of the PET repeating unit.

### 2.3 Qualitative and quantitative methods

Sample preparation for HPLC analysis involved several steps. First, the solid phase product from PET depolymerization was dried at 50 °C overnight, weighed, and then ground. Next,



a stock solution (at maximum achievable concentration) was made by dissolving 0.004 g of the ground sample in a solvent composed of methanol and water (7 : 3 v/v). Finally, this solution was clarified by filtration through a 0.2  $\mu\text{m}$  HPLC-certified Nylon filter before injection into the HPLC system.

An Agilent 1100 Reversed-Phase HPLC system, equipped with a C8 column (4.6 mm  $\times$  150 mm) and an SPD-1 UV detector set to 254 nm, was used for analysis. The separation utilized a methanol/water (7 : 3 v/v) mobile phase at room temperature, with a 5  $\mu\text{L}$  injection volume after a 20-minute column equilibration. Standard substances were employed for both qualitative and quantitative assessments. The presence of DMT, BHET, and MHET was qualitatively determined by matching retention times of sample components with standards (Fig. 1S).

*In situ* infrared spectroscopy detection was conducted using a ReactIR 702 L *in situ* infrared spectrometer from METTLER TOLEDO (Switzerland), with the probe interface being an AgX 9.5 mm  $\times$  1.5 m fiber (silver halide), and the probe tip being made of DiComp (diamond).

### 3 Results and discussion

#### 3.1 Effect of $\text{H}_2\text{O}$ content

Fig. 1 illustrates the influence of water content (vol%) on PET conversion and the yield of bis(2-hydroxyethyl) terephthalate (BHET) when using five different catalysts: ZnO (zinc oxide),  $\text{Mn}_2\text{O}_3$  (manganese(III) oxide),  $\text{ZnAc}_2$  (zinc acetate), TBD (1,5,7-triazabicyclo[4.4.0]dec-5-ene), and DBU (1,8-diazabicyclo[5.4.0]undec-7-ene). The heterogeneous catalysts, *e.g.* ZnO and  $\text{Mn}_2\text{O}_3$ , (squares and circles, respectively) retained very high PET conversion (close to 100%) across the entire range of water content depicted. However, there was a significant decrease in PET conversion at the highest water content (ranging from 15% to 30%). These Lewis acid catalysts (ZnO and  $\text{Mn}_2\text{O}_3$ ) are also found to be very stable and to retain high activity for PET depolymerization even in the presence of high amounts of water. This is indicative of their catalytic mechanism being minimally affected by water, or of water playing a beneficial role (*e.g.*, by facilitating proton transfer or by participating in a hydrolytic depolymerization pathway in combination with glycolysis). Since PET conversion remains high (as evident from Fig. 1), the decreasing BHET yield with increasing water content shows that even for these catalysts, water promotes the side reaction of hydrolysis of PET at the expense of glycolysis. This means that while the ester linkages are still being broken, they are not exclusively reacting by reaction with ethylene glycol to yield BHET. The formation of TPA and other products of hydrolysis would lower the BHET yield.

$\text{ZnAc}_2$ , TBD, and DBU are highly effective homogeneous catalysts for low-water-content PET depolymerization, exhibiting high PET conversion and BHET yield; however, their efficiency is greatly reduced at a high water content. In particular, the organic bases TBD and DBU suffer from a steep decline in both PET conversion and BHET yield as the amount of water increases, with DBU being highly sensitive—stable to catalyst deactivation most probably due to protonation ( $\text{DBU} + \text{H}_2\text{O} \rightleftharpoons \text{DBUH}^+ + \text{OH}^-$ ).<sup>25</sup> For comparison,  $\text{ZnAc}_2$  is seen to retain high PET conversion even at high water levels, which mirrors its stability towards PET degradation; however, its yield of BHET drops progressively, which mirrors that increasing water shifts the reaction pathway from the desired glycolysis (BHET formation) to PET hydrolysis (formation of other degradation products like TPA), thereby lowering selectivity to BHET despite the maintenance of overall depolymerization activity.

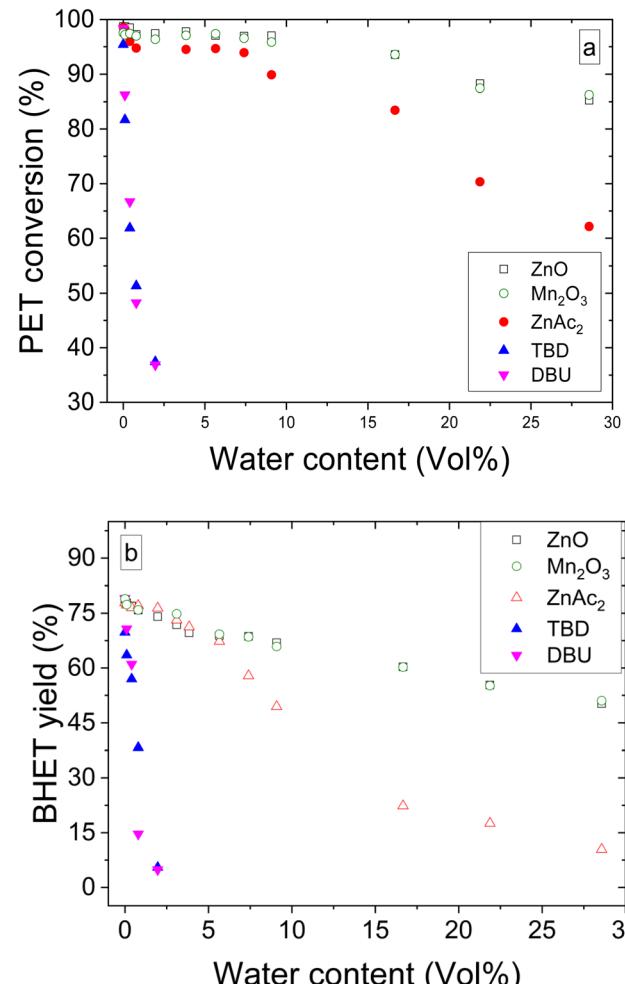


Fig. 1 The influence of water content (vol%) on PET conversion (a) and the yield of BHET (b) when using five different catalysts: ZnO (zinc oxide),  $\text{Mn}_2\text{O}_3$  (manganese(III) oxide),  $\text{ZnAc}_2$  (zinc acetate), TBD (1,5,7-triazabicyclo[4.4.0]dec-5-ene), and DBU (1,8-diazabicyclo[5.4.0]undec-7-ene). (Operating conditions: temperature = 190 °C, reaction time = 2 h, catalyst loading = 1 wt%, EG volume = 25 mL, water content = 0–30 vol%).

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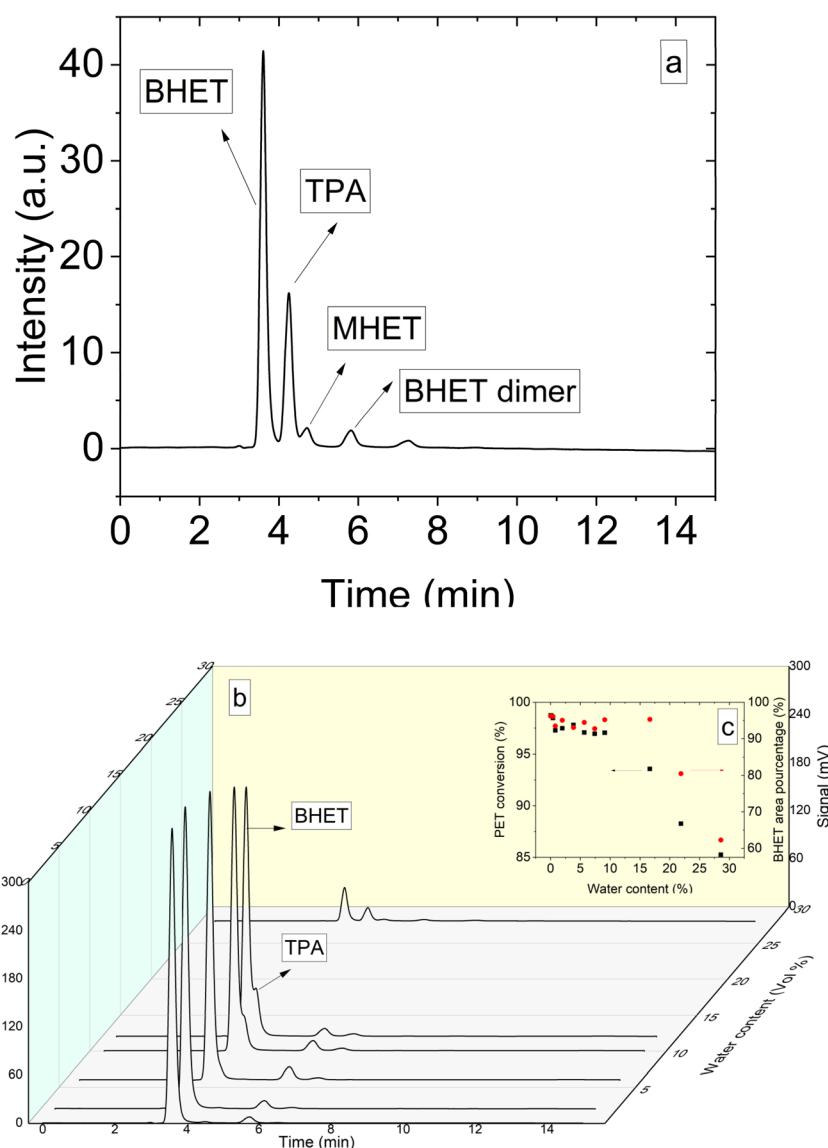
To summarize, for homogeneous organic base catalysts like TBD and DBU, increasing water content leads to severe deactivation, primarily through protonation, resulting in a sharp decrease in both overall PET conversion and, consequently, a dramatic fall in BHET yield. For heterogeneous catalysts, more water reduces BHET selectivity by promoting competing hydrolysis to byproducts (like TPA) over BHET, lowering its yield.



### 3.2 Byproduct formation

To better understand the effect of hydrolysis and catalyst deactivation induced by water, the byproducts of glycolysis were analyzed by HPLC (HPLC chromatograms of standard products and calibration data could be found in Fig. S1 and Table S1). Fig. 2a displays a HPLC chromatogram of the product mixture obtained from the ZnO-catalyzed PET depolymerization with 28 vol% water. The most prominent peak corresponds to BHET (~3.40 min), confirming that the intended glycolysis reaction was successful in producing the target monomer. However, the presence of a significant secondary peak for terephthalic acid-TPA (~4.25 min) and MHET (~4.68 min) provides clear evidence of a competing hydrolysis reaction, which occurs in the presence of water. The BHET dimer (~5.82

min), likely consisting of two BHET units linked together, indicates that the depolymerization process did not go to 100% completion, leaving some larger chain fragments behind. Fig. 2b displays a series of HPLC chromatograms illustrating the PET depolymerization process catalyzed by ZnO under varying water content conditions. Under anhydrous conditions, following an initial solvent front before 3 minutes, the most prominent peak is identified as BHET, eluting at approximately 3.40 minutes, indicating it is the major component in this sample. Subsequently, two smaller peaks appear: TPA at 4.25 min and MHET at ~4.68 minutes. A smaller, distinct peak corresponding to the BHET dimer is observed later at ~5.82 minutes, signifying it as a minor byproduct. As the initial water content increases from 0 vol% to 22.2 vol%, the primary



**Fig. 2** (a) Chromatogram of products from the ZnO-catalyzed PET depolymerization with 28 vol% water, (b) a series of HPLC chromatograms illustrating the PET depolymerization process catalyzed by ZnO under varying water content conditions (0, 2, 6, 10, 12, and 28 vol%) and (c) the corresponding peak area percentage of BHET among all products and PET conversion. (HPLC conditions: C8 column, UV detector 254 nm, mobile phase = methanol/water (7:3 v/v), temperature = 25 °C).



glycolysis product, BHET, progressively diminishes, while the hydrolysis product, TPA, correspondingly increases to become a prominent byproduct.

This shift in product distribution is quantitatively supported by Fig. 2c, which plots the corresponding peak area percentage of BHET as a measure of selectivity. As mentioned above, the fundamental ability of ZnO to facilitate the cleavage of ester bonds in PET is not significantly hindered by the presence of water. However, the selectivity toward the target glycolysis product (BHET) has a significant dependence on the water content. At a low water content (starting from 0 vol% to about 5.5–9 vol%), the selectivity towards BHET is very high, generally in the 90–95% range. This signifies that in conditions where water is scarce, the depolymerized PET is predominantly transformed into BHET. The small amount of MHET observed is likely due to trace amounts of moisture present in the system, even under rigorously controlled anhydrous conditions. It is extremely difficult to achieve a completely moisture-free environment. This residual moisture, even in parts per million, can facilitate a very low level of the hydrolysis reaction, leading to the formation of a small MHET peak.<sup>26</sup> But as soon as the concentration of water exceeds this specified range, the selectivity towards BHET decreases progressively. For example, when the volume percentage of water is 11.1%, the yield of BHET is reduced to slightly more than 80% and is further lowered to approximately 60–65% when the water concentration reaches 22.2%. This is due to two competing reactions: glycolysis (where ethylene glycol reacts to produce BHET) and hydrolysis (where water reacts to produce terephthalic acid (TPA) and other products like MHET). Both reactions need ZnO to take place. Under low water conditions, glycolysis is the favored pathway. But with water in excess (>10% vol%), it acts as a competing nucleophile, and this speeds up the hydrolysis rate. More of the PET then transforms into TPA and its precursors and less into BHET. To maximize the production of BHET using this catalytic system, it is critical to manage and reduce the content of water.

This will help ensure that high activity for PET degradation translates to a high yield of the desired glycolysis product.

Fig. 3 shows data on PET depolymerization using ZnAc<sub>2</sub>, TBD, and DBU as homogeneous catalysts. The plot illustrates the effect of different water contents (vol%) on the overall PET conversion (%) (right Y-axis, circular red points) and the selectivity for bis(2-hydroxyethyl) terephthalate (BHET), which is represented as the BHET peak area percentage (%), left Y-axis, square black points). When ZnAc<sub>2</sub> is used as the catalyst, the PET conversion rate is maintained at a nearly quantitative level (close to 100%), across the entire range of water content tested, from 0 vol% to approximately 22.2 vol%. This behavior closely resembles that of the ZnO catalyst.

When comparing the two metal-based catalysts, both ZnO and ZnAc<sub>2</sub> retain excellent PET conversion across a range of water concentrations. However, their BHET selectivity profiles differ significantly. At 0 vol% water, ZnO exhibited a slightly higher BHET selectivity (about 90–95%) and demonstrated greater tolerance to low water concentrations (up to ≈5.5–9 vol%). Its BHET selectivity remained relatively stable before beginning a more noticeable decline. However, ZnAc<sub>2</sub> exhibits a more rapid and ongoing decline in BHET selectivity immediately upon the addition of water. Additionally, ZnAc<sub>2</sub> produces a lower BHET selectivity (~40–45%) than ZnO (~60–65%) at higher water concentrations (e.g., 22.2 vol%). As compared to ZnO, this implies that although both catalysts are active for depolymerization, ZnAc<sub>2</sub> may be more prone to promoting the hydrolysis pathway over glycolysis or that its selectivity for glycolysis decreases more quickly as the water content rises. ZnO may therefore provide marginally better performance for optimizing BHET yield, especially in systems with unavoidable trace amounts of water.

In contrast to metal-based systems, the homogeneous organocatalysts TBD and DBU exhibit markedly different phenomena (or behavior) from zinc acetate, as shown in Fig. 3b and c. Under anhydrous conditions, TBD and DBU exhibit high

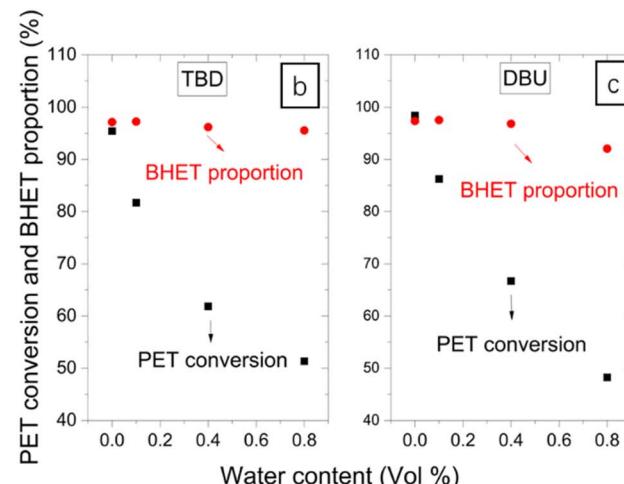
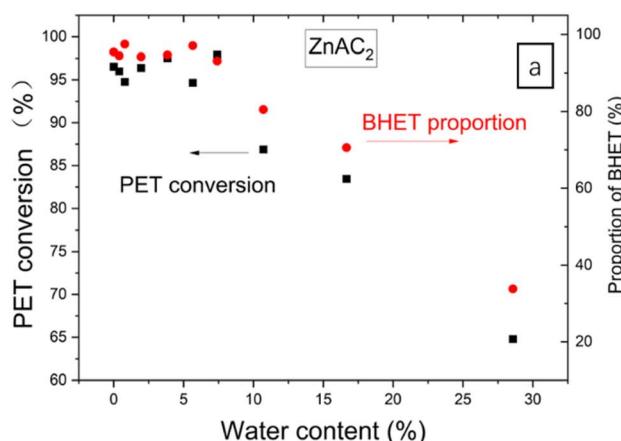


Fig. 3 The influence of water content on PET conversion and BHET peak area percentage using three different catalysts: ZnAc<sub>2</sub> (a), TBD (b) and DBU (c). (Operating conditions: temperature = 190 °C, reaction time = 2 h, catalyst loading = 1 wt%, EG volume = 25 mL, water content = 0–30 vol%).



catalytic activity, with PET conversion around 90–95% and a correspondingly high BHET selectivity of approximately 80–85%. As the water content increases, both PET conversion and BHET selectivity show a steady and significant decline. These trends observed for TBD and DBU highlight their significant susceptibility to deactivation by water, which directly impacts both the overall PET depolymerization and the production of BHET. This behavior contrasts with that of ZnO and ZnAc<sub>2</sub>, for which water primarily affects product selectivity by promoting hydrolysis as a competing pathway while overall PET depolymerization activity remains high. For TBD and DBU, water causes a more fundamental issue by deactivating the catalysts themselves, leading to a sharp decline in both the overall ability to depolymerize PET and, as a result, the production of BHET.

### 3.3 In situ IR study

Fig. 4 presents a comparative kinetic study of PET depolymerization by tracking the normalized height of the C=O infrared absorption band at 1720 cm<sup>-1</sup> (representing BHET concentration)<sup>27</sup> as a function of reaction time for four distinct catalysts: ZnO (a), ZnAc<sub>2</sub> (b), TBD (c), and DBU (d). The BHET formation kinetics is defined using eqn (3):

$$[C](t) = [C]_{\max} (1 - e^{-kt}) \quad (3)$$

For ZnO, a negligible difference was observed between anhydrous conditions and the presence of 1 vol% water (as shown *in situ* IR spectroscopy in Fig. S3 and S4). In the case of zinc acetate, the addition of water slightly reduced the formation rate of BHET. However, for TBD and DBU, in the absence of added water (black curve), BHET formation exhibits a relatively

rapid initial rate, reaching a maximum concentration (approximately 0.7–0.8 arbitrary units) around 60–80 minutes. After this peak, the BHET concentration remains largely stable or shows only a very slight decline over the 180-minute observation period. In contrast, when 1 vol% water is introduced (red curve), the initial rate of BHET formation is significantly suppressed.

Fig. 5 presents two kinetic profiles tracking the absorbance of an infrared peak at 1570 cm<sup>-1</sup>, which corresponds to the C=N stretching vibration of the TBD catalyst<sup>28</sup> (representative IR spectra are displayed in Fig. S5 and S6). In the absence of water, the intensity remains relatively stable throughout the reaction duration. In contrast, when 0.75 vol% water is present

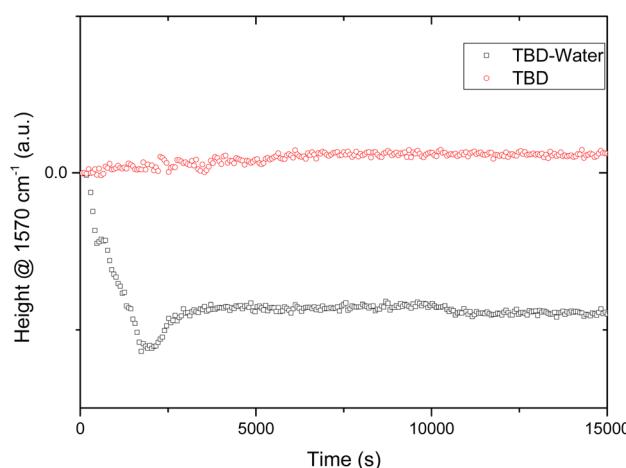


Fig. 5 Kinetic profiles tracking the height of an infrared peak at 1570 cm<sup>-1</sup>, which corresponds to the C=N stretching vibration of the TBD catalyst.

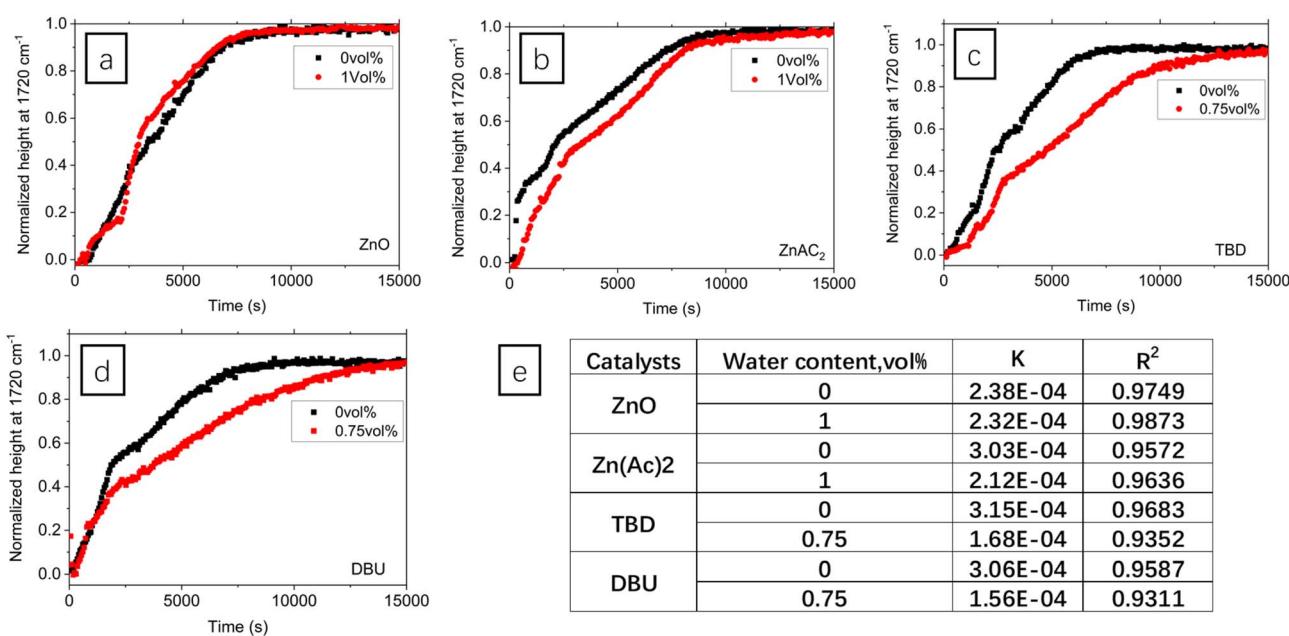


Fig. 4 A comparative kinetic study of PET depolymerization by tracking the normalized height of the C=O infrared absorption band at 1720 cm<sup>-1</sup> (representing BHET concentration) as a function of reaction time for four distinct catalysts: ZnO (a), ZnAc<sub>2</sub> (b), TBD (c), and DBU (d) and the corresponding K value for different conditions (e).



in the reaction system (black curve), the peak height undergoes a rapid decrease at the onset of the experiment. This observation is consistent with the deactivation of the TBD catalyst *via* protonation by water, where the C=N bond character of the guanidine core changes upon forming the  $\text{TBDH}^+$  cation, leading to a diminished signal at the wavenumber characteristic of the neutral TBD.

### 3.4 Mechanism discussions

The glycolysis of polyethylene terephthalate (PET) is a chemical recycling process that breaks down the polymer into its monomer, bis(2-hydroxyethyl) terephthalate (BHET). This is achieved through a transesterification reaction with excess ethylene glycol (EG) at high temperatures. The depolymerization of polyethylene terephthalate (PET) *via* glycolysis is predominantly facilitated by two distinct catalytic pathways (shown in Fig. 6): the Lewis acid mechanism, typical of metal-based catalysts (*i.e.*  $\text{ZnAC}_2$  or  $\text{ZnO}$ ), and the nucleophilic mechanism, characteristic of strong organobase catalysts (TBD or DBU).

**3.4.1 Lewis acid mechanism.** Metal-containing catalysts, including zinc acetate ( $\text{Zn(OAc)}_2$ ),<sup>29</sup> zinc oxide ( $\text{ZnO}$ ),<sup>30</sup> and manganese(III) oxide ( $\text{Mn}_2\text{O}_3$ ),<sup>31</sup> operate primarily through a Lewis acid mechanism.<sup>32</sup> The catalytic cycle is initiated by the coordination of the electrophilic metal cation (*e.g.*,  $\text{Zn}^{2+}$  or  $\text{Mn}^{3+}$ ) to the carbonyl oxygen of an ester linkage within the PET polymer backbone.<sup>33</sup> This interaction polarizes the carbonyl group, which significantly enhances the electrophilicity of the adjacent carbon atom. The now-activated carbonyl center

undergoes nucleophilic attack from a hydroxyl group of an ethylene glycol molecule, leading to the formation of a transient tetrahedral alkoxy intermediate. This unstable intermediate subsequently collapses, resulting in the scission of the C-O ester bond and cleavage of the polymer chain. The final step involves proton transfer and the release of the product—either the monomer bis(2-hydroxyethyl) terephthalate (BHET) or a shorter oligomeric chain<sup>34</sup>—which regenerates the active metal center for subsequent catalytic cycles.

The addition of water to the reaction mixture would introduce a competing nucleophile. While the primary mechanism involves the nucleophilic attack of a hydroxyl group from ethylene glycol on the activated carbonyl carbon, water molecules can also act as nucleophiles. This competing reaction, known as hydrolysis, would cleave the ester bond and result in the formation of a carboxylic acid and an alcohol.<sup>35</sup> This side reaction would divert the catalytic cycle from producing the desired monomer, bis(2-hydroxyethyl) terephthalate (BHET), and instead lead to the formation of terephthalic acid and other byproducts. This was confirmed by the study by Güçlü *et al.*<sup>35</sup> who investigated the simultaneous glycolysis and neutral hydrolysis of waste PET, focusing on how these two competing reactions influence the final products. The addition of water, which drives the hydrolysis reaction, had a significant impact on the final product yield. At very high water concentrations, the yield of the desired water-soluble products, primarily BHET and MHET, decreased. This decrease was attributed to the conversion of BHET and MHET into water-insoluble terephthalic acid (TPA).

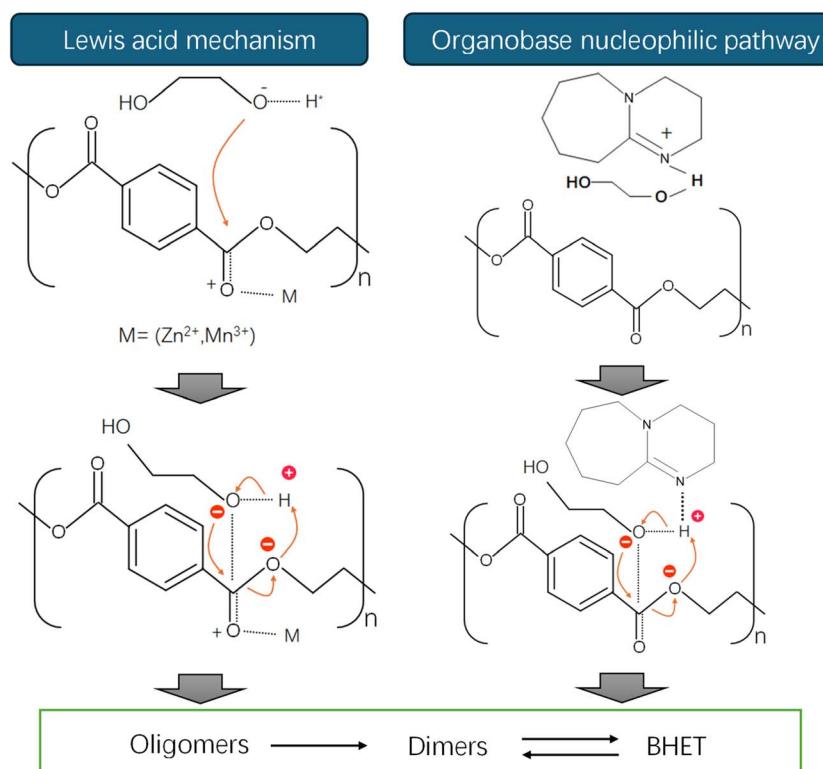


Fig. 6 Comparison of Lewis acid and organobase nucleophilic pathways for PET depolymerization.

Furthermore, the presence of water could interact with the Lewis acid catalyst itself. Water molecules, with their lone pairs of electrons on the oxygen atom, can coordinate to the electrophilic metal center (e.g.,  $Zn^{2+}$  or  $Mn^{3+}$ ).<sup>36</sup> This coordination would effectively “poison” the catalyst<sup>37</sup> by blocking the active site and reducing its ability to coordinate with the carbonyl oxygen of the PET ester linkage. Stoski *et al.*<sup>38</sup> showed that water content is a significant factor in the glycolysis of PET with zinc acetate catalysis. Their factorial design experiment revealed that increasing the water content to 2.0% (v/v) relative to ethylene glycol resulted in a 17.3% decrease in the extent of depolymerization. The negative effect of water was so significant that the researchers concluded that to achieve a higher degree of glycolysis, the reaction should be conducted at higher temperatures (170 °C or more) and in the absence of water. The competition between the PET polymer and water for coordination to the metal cation would therefore decrease the overall efficiency of the catalyst, slowing down the depolymerization reaction and lowering the yield of the desired products.

**3.4.2 Organocatalytic mechanism.** In contrast, strong organobases such as TBD and DBU catalyze the reaction *via* a nucleophilic pathway. This mechanism involves the activation of the nucleophile (ethylene glycol) rather than the electrophile (PET). The cycle begins when the organobase deprotonates an ethylene glycol molecule to generate a highly reactive glycolate anion. This potent nucleophile then attacks the carbonyl carbon of a PET ester linkage, again forming a tetrahedral intermediate. The subsequent collapse of this intermediate cleaves the polymer backbone. The catalytic cycle is completed upon protonolysis of the resulting polymer alkoxide fragment with the protonated organobase, which regenerates the active catalyst and terminates the polymer fragment with a hydroxyl group. This process repeats until the polymer is fully converted to BHET.

However, the presence of water introduces complications and can significantly hinder the efficiency of these organocatalytic systems. In the case of TBD, which is a superbase, meaning it is an extremely strong base that functions by deprotonating weak acids, the catalytic mechanism relies on TBD deprotonating the hydroxyl group of ethylene glycol (EG) to create a highly reactive glycolate anion. However, water is a much stronger Brønsted acid (lower  $pK_a$ ) than ethylene glycol. When water is present, TBD will preferentially react with it, deprotonating the water molecule to form a hydroxide ion ( $OH^-$ ) and a protonated TBD species ( $TBD^+$ ). According to Olazabal *et al.*,<sup>39</sup> water causes the hydrolysis of PET, which generates terephthalic acid (TPA). The TPA then reacts with the TBD catalyst, forming a TBD : TPA complex that deactivates the catalyst. This deactivation significantly lowers the yield of the desired product, BHET. For instance, a reaction with one equivalent of water saw the BHET yield drop from 84% to 42%. The paper by Nunes *et al.*<sup>40</sup> also supports the negative effect of water, but in a different catalytic system. Their research on using the ionic liquid [Bmim][BF<sub>4</sub>] as a catalyst for PET depolymerization under supercritical ethanol (scEtOH) found that water “poisoned” the catalyst.

## 4 Conclusions

This work critically examined the influence of water content on PET catalytic glycolysis over different heterogeneous ( $ZnO$  and  $Mn_2O_3$ ) and homogeneous ( $ZnAc_2$ , TBD, and DBU) catalysts. The results demonstrate that water has a profound, though catalyst-dependent, influence on the overall conversion of PET as well as selectivity towards targeted monomer BHET.

The metal-based catalysts,  $ZnO$ ,  $Mn_2O_3$ , and  $ZnAc_2$ , retained high PET conversion levels (close to 100%) despite high water contents. However, for all three, increasing the water content resulted in a drastic drop in the yield as well as selectivity of BHET. This was explained by the role of water as a competing nucleophile, promoting the hydrolysis of PET and the production of TPA and other byproducts and resulting in a divergence of the reaction pathway from the intended glycolysis. Among these metal catalysts,  $ZnAc_2$  showed a greater drop in BHET selectivity with a rise in water compared to  $ZnO$ .

In contrast, the organic base catalysts TBD and DBU were highly susceptible to water deactivation. Both catalysts exhibited a steep decline in PET conversion and BHET yield upon increasing water content, with DBU being more sensitive. *In situ* infrared spectroscopy provided unequivocal evidence of the deactivation of TBD, manifested in the pronounced reduction of its diagnostic C=N absorption band upon contact with water, in accordance with protonation of the catalyst. This demonstrates that, for organic bases, the major detrimental effect of water is a reduction in catalytic activity, and not simply a change in the selectivity of the reaction pathway.

The results highlight the paramount importance of water level control in PET glycolysis processing. The mechanism of water interference differs fundamentally between metal catalysts (where it is primarily a competitive reactant) and organic base catalysts (where water acts as a deactivating agent). This understanding is critical for the industrial operation of PET chemical recycling, for the choice of catalysts, for process design to minimize water impact, and for the development of more stable, water-tolerant catalytic systems for efficiently producing high-purity BHET from PET waste.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

The data that support the findings of this study are available on request from the corresponding author, Zixian JIA (jiazixian.f-shy@sinopec.com), upon reasonable request.

Data are contained within the article and the SI including (i) HPLC chromatograms for standards of BHET, MHET, DMT, and TPA, (ii) table detailing the composition of samples, their corresponding retention times from HPLC analysis, and calibration curves for quantitative analysis, (iii) an HPLC chromatogram illustrating the depolymerization process of PET catalyzed by  $ZnAc_2$  under various water content conditions, (iv)



*in situ* IR spectra recorded during the PET depolymerization process. See DOI: <https://doi.org/10.1039/d5su00528k>.

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