Journal of Molecular Liquids 214 (2016) 1–6

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

# (Mg–Zn)–Al layered double hydroxide as a regenerable catalyst for the catalytic glycolysis of polyethylene terephthalate

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A R T I C L E I N F O

*Article history:*
Received 4 August 2015
Received in revised form 14 October 2015
Accepted 27 November 2015
Available online xxxx

*Keywords:*
Degradation
Glycolysis
Catalysis
Layered double hydroxide
Polyethylene terephthalate

A B S T R A C T

(Mg–Zn)–Al layered double hydroxide (LDH) was prepared by the coprecipitation method at low super saturation conditions. The prepared (Mg–Zn)–Al LDH was analyzed using XRD, FTIR, $N_2$ adsorption–desorption, TGA and DSC, confirming the formation of pure LDH phase. The extent of polyethylene terephthalate (PET) degradation by the glycolysis process was studied using the prepared (Mg–Zn)–Al LDH. The glycolysis process was optimized in terms of catalyst concentration, temperature, time, ethylene glycol dosage. Under the optimal conditions of 1.0 wt.% of catalyst with 20 g of ethylene glycol (EG) in the presence of 2.0 g of PET at 196 °C after 3 h of glycolysis, complete PET conversion was achieved and the yield of bis (2-hydroxyethyl) terephthalate (BHET) reached 75%.

## 1. Introduction

Poly(ethylene terephthalate), more commonly known as PET, is an indispensable material due to its excellent physical and chemical properties. It is an important material in the textile industry, and in food packaging where it has noticeably become the choice for beverage containers [1]. The escalating production of PET today is, however, still leading to a global concern over the treatment of PET waste products and their destructive impact to the environment [2]. PET does not create a direct hazard to the environment, but due to its substantial fraction by volume in the wastes stream and because it is a non-degradable material in normal conditions, it is seen as a noxious material. Commonly practiced mechanical recycling has been considered as a temporary solution because the recycled PET, which is often used for secondary materials other than beverage bottles, ends up in landfills [3,4]. Great attention is currently being paid to chemical recycling, which basically involves the recovery of monomers and produces interesting value-added chemicals or intermediates from the PET waste [5]. Chemical recycling processes for PET are divided as follows: (i) glycolysis, (ii) methanolysis, (iii) hydrolysis, and (iv) other processes such as aminolysis or ammonolysis. Glycolysis can be described as a molecular depolymerization process by transesterification between PET ester groups and a diol, usually ethylene glycol (EG) in excess, to obtain the monomer bis(2-hydroxyethyl) terephthalate (BHET) [6–8]. Studies on the kinetics show that without catalysts, PET glycolysis is very slow, and complete conversion of PET to monomer BHET is almost impossible [9,10]. Metal acetates were the first reported catalysts for PET glycolysis [11–14]. Later on, researchers developed more environment-friendly alternatives like mild alkalies, sulfates, metal chlorides, and zeolites; however, PET glycolysis using these catalysts still required long reaction times, and gave low BHET monomer yields [15–19]. Wang et al. [20, 21] have reported that various ionic liquid catalysts for PET glycolysis could be recovered, then used repeatedly; however, the conversion of PET and selectivity toward BHET were very low, and the process was very slow. They also studied the glycolysis of PET using an Fe-containing magnetic ionic liquid, which exhibited higher catalytic activity than conventional ILs. However, the monomer produced was very easily stained by the Fe-containing ILs [22]. Recently, Al-Sabagh et al. [23] reported that 1-butyl-3-methylimidazolium acetate ([Bmim][OAc]) exhibited excellent catalytic activity and reusability when used as a catalyst in the glycolysis of PET, compared with 1-butyl-3-methylimidazolium chloride ([Bmim][Cl]). They also reported that Cu- and Zn-acetate-containing ionic liquids could act as efficient catalysts in PET glycolysis [24]. The catalytic activity with these homogeneous catalysts is high. However, they cannot be easily separated from the reaction mixture. More recently, three series of solid catalysts including $SO_4^{2-}/ZnO$, $SO_4^{2-}/TiO_2$ and $SO_4^{2-}/ZnO\text{-}TiO_2$ have been tested in PET glycolysis. The $SO_4^{2-}/ZnO\text{-}TiO_2$ exhibited a catalytic activity with 100% conversion of PET and 72% selectivity of BHET after 3 h at 180 °C under atmospheric pressure [25]. Imran et al. reported that the mixed-oxide spinels exhibited better catalytic performance than the single metal oxides in PET glycolysis at 260 °C and 5.0 atm [26]. Bartolome et al. studied the glycolysis of PET using easily recoverable

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http://dx.doi.org/10.1016/j.molliq.2015.11.049
0167-7322/

superparamagnetic γ-$Fe_2O_3$ nanoparticles and the results showed that the catalyst exhibited an excellent activity with 100% conversion of PET and more than 90% yield of BHET after 1 h at 300 °C [27] However, these catalysts have several drawbacks, such as the need for high temperatures and high pressures. Therefore, it is necessary to develop new catalysts for the glycolysis of PET.

Layered double hydroxides are also termed as hydrotalcites or anionic clays. The charge on the layer and intercalated ions in these compounds are reverse of those found in cationic clays such as smectite. Layered double hydroxide structure is derived from the mineral brucite, in which magnesium is octahedrally surrounded by hydroxyl ions, and different octahedra share edges to form infinite sheets [28]. When some divalent ions are substituted by trivalent cations, a positive charge is created on the layers, which is compensated by anions and water molecules in the interlayers [29]. Chen et al. [30] reported that Mg–Al hydrotalcites and their corresponding mixed oxides catalysts act as efficient catalysts in PET glycolysis. Using the hydrotalcites as a glycolysis catalyst can be a great opportunity to explore a new set of catalysts, which opens new horizons for the recycling of PET. To the best of our knowledge, no article has been published regarding the use of (Mg–Zn)–Al LDH as a catalyst for the glycolysis of polyethylene terephthalate. In this study, (Mg–Zn)–Al LDH was prepared, characterized and tested in the PET glycolysis. The PET glycolysis mechanism was proposed.

## 2. Experimental

### 2.1. Materials

$Al(NO_3)_3.9H_2O$, $K_2CO_3$, ethylene glycol (EG) and KOH were obtained from Sigma–Aldrich. $Mg(NO_3)_2.6H_2O$ and $Zn(NO_3)_2.6H_2O$ were obtained from Acros Organics. 1,1,2,2-Tetrachloroethane and phenol were obtained from Merck. PET pellets (3.2 × 2.8 × 4 mm) were purchased from Hangzhou Zhenghan Biological Technology Co. Ltd. The intrinsic viscosity of PET was measured in a 60:40 (*w*/*w*) phenol/1,1,2,2-tetrachloroethane solution at 25 °C and found to be 0.64 $dLg^{-1}$. Using the Mark–Houwink method, the weight average molecular weight ($4.08 \times 10^4$ $gmol^{-1}$) and number-average molecular weight ($2.7 \times 10^4$ $gmol^{-1}$) was calculated from this intrinsic viscosity. The polydispersity index was calculated using the values of the weight average molecular weight and number-average molecular weight, and found to be 1.51.

### 2.2. Catalyst preparation

The layered double hydroxides containing (Mg–Zn)–Al with 15 wt.%. of zinc were prepared by co-precipitation method at low super saturation conditions and at constant pH [31,32]. A 1 M aqueous solution (1097.7 mL) containing the dissolved salts of $Mg(NO_3)_2.6H_2O$ (182.5 g), $Zn(NO_3)_2.6H_2O$ (68.13 g) and $Al(NO_3)_3.9H_2O$ (117.7 g) (solution A) was prepared. Separately, a 2 M aqueous solution containing $K_2CO_3$ and KOH (solution B) was prepared. Solutions (A) and (B) were added concurrently to a glass reactor, containing deionized $H_2O$ (100 mL), at a controlled pH of 9. The slurry was kept under vigorous stirring, at a temperature of 80 °C for 18 h. Thereafter, the obtained precipitate was entirely washed with hot deionized water to eliminate excess ions, and dried at 100 °C for 24 h.

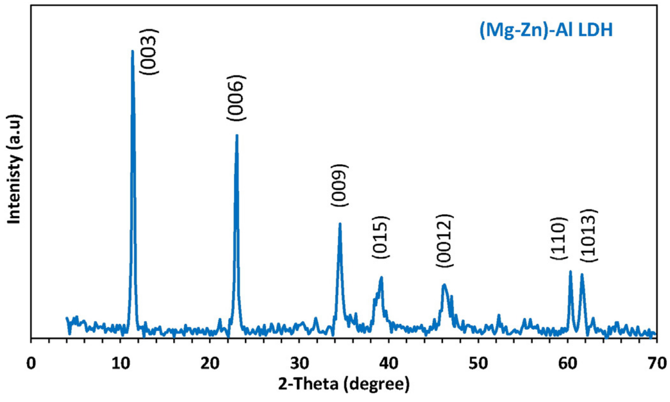


**Fig. 1.** XRD of (Mg–Zn)–Al LDH as described in [34].

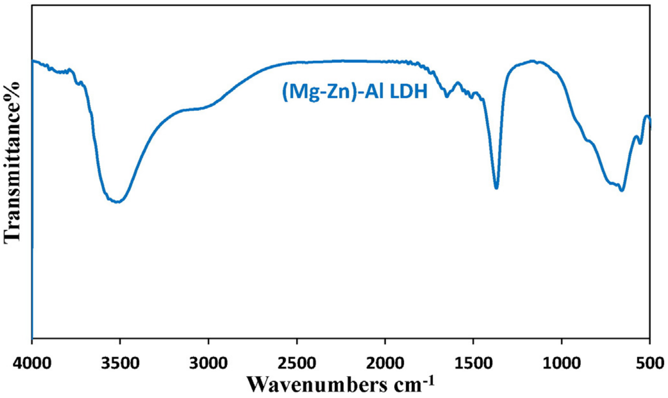


**Fig. 2.** FTIR spectrum of (Mg–Zn)–Al LDH as described in [34].

### 2.3. General procedure for the PET glycolysis

A 50-mL round-bottom three-necked flask equipped with a thermometer and a reflux condenser was loaded with 2.0 g of PET, 20.0 g of ethylene glycol, and a certain amount of catalyst as described in [23]. The glycolysis reactions were performed under atmospheric pressure in the reaction temperature range of 170–196 °C for a glycolysis time of 1–4 h. The flask was immersed in an oil bath at a specific temperature for the required time. When the glycolysis reaction was complete, the undepolymerized PET pellets were quickly separated from the liquid phase before the products precipitated. An excess amount of cold distilled water was used to wash the undepolymerized PET pellets, and the water was subsequently mixed with the product fraction. The undepolymerized PET was collected, dried, and weighed. The PET conversion is defined in Eq. (1):

$$\text{Conversion of PET}(\%) = \frac{W_0 - W_1}{W_0} \times 100\% \tag{1}$$

where $W_0$ is the initial weight of PET and $W_1$ is the weight of undepolymerized PET. Meanwhile, the glycolysis product mixture was

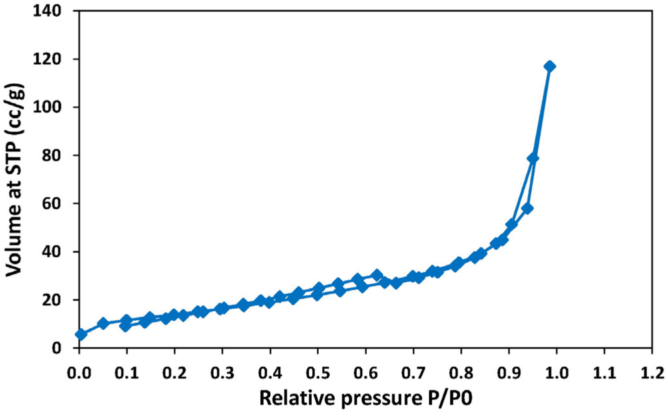


**Fig. 3.** $N_2$ adsorption–desorption isotherm of (Mg–Zn)–Al LDH as described in [34].

**Table 1**
Surface data of the prepared (Mg–Zn)–Al LDH as described in [34].

| Sample | $A_{BET}$ ($m^2$/g) | Vp (mL/g) | r = Vp/$A_{BET}$ (Å) | C-value in BET equation |
|---|---|---|---|---|
| (Mg–Zn)–Al LDH | 51.04 | 0.069 | 12 | 114.87 |

vigorously agitated (cold distilled water would dissolve the remaining ethylene glycol and monomer) and then the catalyst was separated by centrifugation. The collected filtrate was concentrated to approximately 150 mL using a vacuum rotary evaporator at 50 °C. The concentrated filtrate was stored in a refrigerator at 0 °C for 24 h. White crystalline flakes formed in the filtrate and were subsequently separated and dried. This product was the bis(hydroxyethyl) terephthalate (BHET) monomer. The insoluble fraction in cold water was a mixture of the dimer and oligomers. The selectivity and yield of the BHET monomer are defined in Eqs. (2) and (3), respectively:

$$\text{Selectivity of BHET}\,(\%) = \frac{W_{BHET}\,/MW_{BHET}}{W_{PET,D}/MW_{PET}} \times 100\% \qquad (2)$$

$$\text{Yield of BHET}(\%) = \frac{W_{BHET}\,/MW_{BHET}}{W_{PET,I}/MW_{PET}} \times 100\% \qquad (3)$$

where $W_{PET,\,D}$, $W_{PET,\,I}$ and $W_{BHET}$ are the weight of depolymerized PET, initial weight of PET and weight of BHET at a specific reaction time, respectively. $MW_{BHET}$ and $MW_{PET}$ are the molecular weights of BHET (254 $gmol^{-1}$) and the PET (192 $gmol^{-1}$) repeating unit, respectively.

### 2.4. Characterization

The layered double hydroxides containing (Mg–Zn)–Al and the main product were analyzed with FTIR using a Nicolet FTIR IS-10 spectrometer (Waltham, MA, USA) with KBr disks. X-ray diffraction (XRD) patterns of the samples were recorded in the range 2θ = 4–80° using a Philips powder diffractometer with Cu Kα radiation (k = 0.154 nm). The instrument was operated at 40 kV and 40 mA. The spectra were recorded with a 2θ step of 0.02° at a scanning rate of 2° θ/min. Surface area, pore volume and average pore size were obtained from the $N_2$ adsorption–desorption isotherms determined at 196 °C using a Quantachrome Nova 3200 instrument (USA). Prior to measurements, the samples were perfectly degassed at 100 °C for 12 h under vacuum (10–5 mmHg). Differential scanning calorimetry (DSC) and thermo gravimetric analysis (TGA) were carried out using the differential thermal analyzer DTA-7, Perkin-Elmer apparatus. The main degradation product was analyzed using an HPLC system equipped with a pump Waters 515, a sample injector and a Waters 2489 UV–detector set at 254 nm. Column Waters (X Bridge Tm C18 5 μm 4.6 × 250 mm) was used. The mobile phase was methanol/water of 70:30 with a flow rate equal to 1 mL/min.

## 3. Results and discussion

### 3.1. Catalyst characterization

#### 3.1.1. X-ray diffraction

The XRD pattern of (Mg–Zn)–Al LDH (Fig. 1) shows that the peaks located at lower 2θ are more intense than those located at higher 2θ values where they exhibit the Bragg reflections of basal planes. The high crystalline brucite-like layer is characterized by the presence of basal and in-plane spacing with sharp and symmetric peaks at the basal (0 0 3), (0 0 6) and (1 1 0) reflections as shown at Fig. 1. In addition, the d003 spacing (7.8 Å) is within the accepted values for a LDH structure Table S1 lists the unit cell parameters c and a, which are calculated using Bragg's law. The unit cell parameters c and a are defined as the cation–cation distance within the brucite-like layer and the thickness of the brucite-like layer, respectively [33]. Table S1 also presents the crystal sizes, which are calculated using Scherrer's equation.

#### 3.1.2. Fourier transform infrared spectroscopy analysis

The Fourier transform infrared spectrum of the prepared (Mg–Zn)–Al LDH is shown in Fig. 2. The broad absorption at 3445–3500 $cm^{-1}$ is assigned to the O-H stretching vibration of the water molecule in the brucite-like layers [35]. The peak at 1640 $cm^{-1}$ is assigned to the bending mode of O–H in water molecule [36]. The weak shoulder peak occurs at approximately 3000 $cm^{-1}$ is assigned to the OH stretching mode of interlayer water molecules hydrogen-bonded to interlayer anions. A characteristic band in the low frequency region, corresponding to

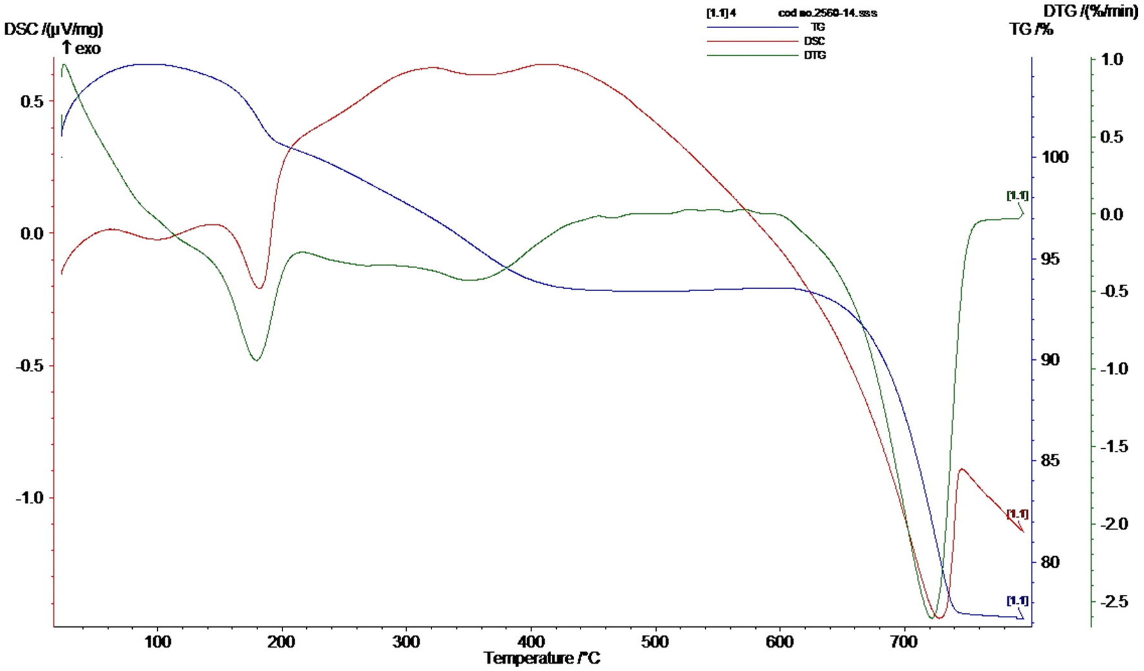


**Fig. 4.** DSC, TGA and DTG curves of (Mg–Zn)–Al LDH as described in [34].

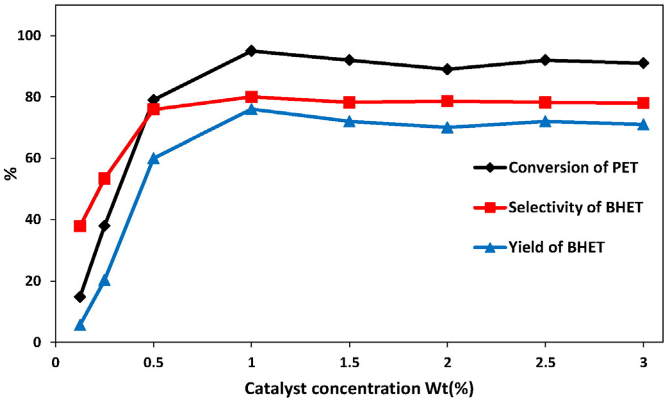


**Fig. 5.** Effect of the amounts of (Mg–Zn)–Al on the PET glycolysis. Reaction conditions: PET (2 g), EG (20 g), 1 atm, 196 °C, 2 h.

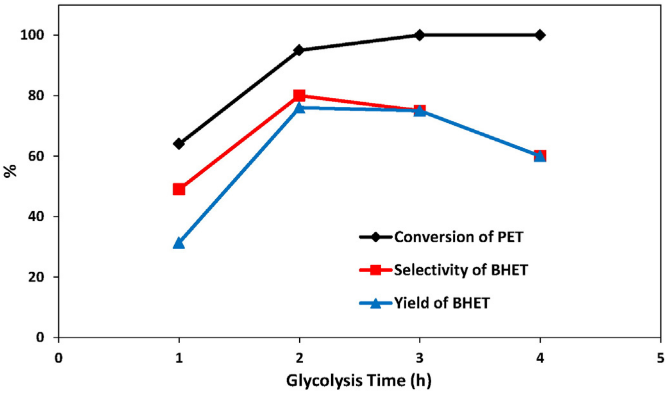


**Fig. 7.** Effect of the reaction time on the PET glycolysis. Reaction conditions: PET (2.0 g), EG (20 g), (Mg–Zn)–Al (1.0 wt.%), 1 atm, 196 °C.

vibration modes and ascribed to M–O vibration at 1000 cm$^{-1}$ [37]. In addition, a strong band at 1370 cm$^{-1}$ indicates the presence of $CO_3^{2-}$ anions in the interlayer region [36]. The weak shoulder at 788 cm$^{-1}$can be attributed to A–O– bond vibrations.

### 3.1.3. Nitrogen adsorption–desorption

The adsorption–desorption isotherm of the prepared (Mg–Zn)–Al LDH is shown in Fig. 3. According to IUPAC classification, the adsorption–desorption isotherm seems to be a type II where hysteresis is lacking, which indicates the presence of cluster of particles (plate-like) that gives rise to non-uniform pores with a slit shape [38,39]. The average pore radius (r) is calculated using the equation $r = (Vp/A_{BET})$, where Vp is the total pore volume taken at $P/Po \approx 1.0$, and $A_{BET}$, is the specific surface area obtained using the BET equation, taken at $P/Po = 0.98$ [38,40]. Using the values listed in Table 1, the full width of pores of the prepared (Mg–Zn)–Al LDH was calculated and found to be 24 Å. This value indicates that the pores size of the prepared (Mg–Zn)–Al LDH lies in the range of pore sizes that assigned to mesoporosity [34].

### 3.1.4. Thermal analysis and morphological structure

The phase transformations of the prepared catalyst were investigated using thermogravimetric analysis as shown in Fig. 4. The DSC-DTG curve shows endothermic peaks at approximately 190 °C, 370 °C and over 700 °C. The first endothermic peak at approximately 190 °C corresponds to the elimination of physically adsorbed water molecules on the surface and interlayer space. The second one, at approximately 370 °C is due to the dehydroxylation of the brucite-like sheets as well as the decomposition of the carbonate anions (partial overlap) [41]. The third one, over 700 °C is due to the elimination of the volatile anions [42]. The TGA curve presents a gradual weight loss in the range of 40–700 °C. The first weight loss is ascribed to external surface water and to interlamellar water molecules. The second weight loss is ascribed to the dehydroxylation of the brucite-like layers along with anion decomposition. Finally, the third weight loss is ascribed to a progressive elimination of the volatile anions [42].

## 3.2. Qualitative analysis of the main degradation product

The DSC curve in Fig. S1(a) shows a sharp endothermic peak at 110 °C; furthermore, the melting onset temperature and peak temperature of BHET are 110.9 and 110 °C, respectively. Fig. S1(b) presents the FTIR spectrum of the BHET material. The FTIR spectrum of the BHET monomer clearly showed an OH band at 3447 cm$^{-1}$ and 1134 cm$^{-1}$, C=O stretching at 1715 cm$^{-1}$, alkyl C–H at 2880 and 2963 cm$^{-1}$ and aromatic C–H at 1411–1506 cm$^{-1}$, all of which are present in BHET [43]. The HPLC chromatogram is shown in Fig. S1(c). The presence of a single peak in the HPLC chromatogram indicates that the purity of the main product in the glycolysis of PET is very high.

## 3.3. Effect of reaction conditions on the glycolysis reaction of PET

### 3.3.1. Effect of catalyst concentration

Fig. 5 presents the influence of the catalyst concentration on the glycolysis of PET. The conversion of PET and the selectivity and yield of BHET increases sharply with increasing the weight ratio of catalyst to PET from 0.125 to 1.0%. This trend is the result of the increase in the catalyst weight accelerating the reaction and shortening the equilibration time. Beyond the weight ratio (catalyst to PET) of 1.0%, the added catalyst has no significant effect on the conversion of PET and the selectivity and yield of BHET.

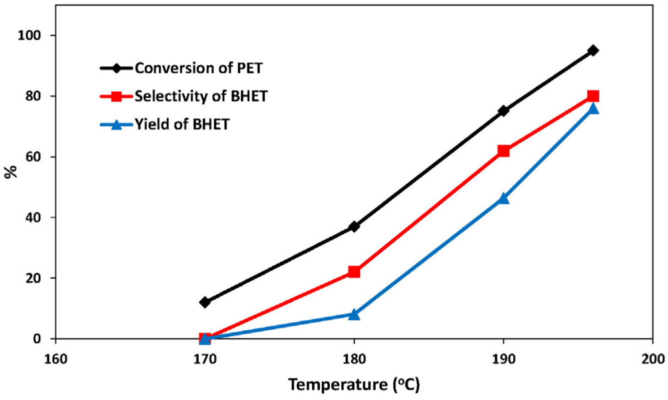


**Fig. 6.** Effect of the reaction temperature on the PET glycolysis. Reaction conditions: PET (2 g), EG (20 g), (Mg–Zn)–Al (1.0 wt.%), 1 atm, 2 h.

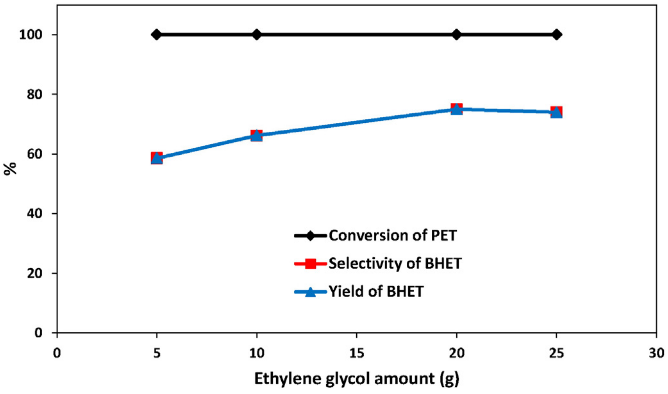


**Fig. 8.** Effect of the ethylene glycol amount on the PET glycolysis. Reaction conditions: PET (2 g), (Mg–Zn)–Al (1.0 wt.%), 1 atm, 196 °C, 3 h.

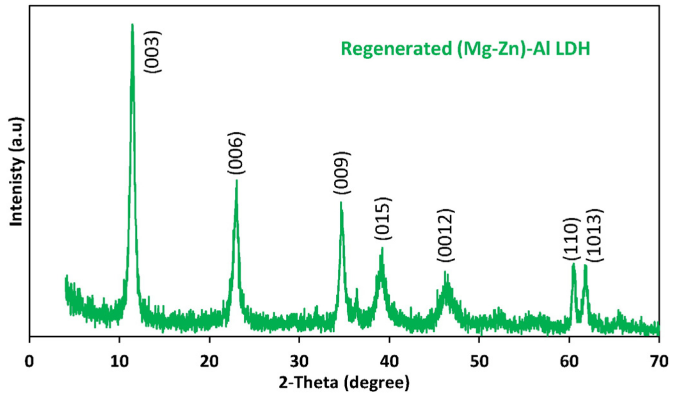


**Fig. 9.** XRD of the regenerated (Mg–Zn)–Al LDH (reused 4 times).

### 3.3.2. Effect of reaction temperature

The effect of reaction temperature on the conversion of PET and the yield of BHET was investigated, and the results are shown in Fig. 6. The results reveal that the conversion of PET and the yield and selectivity of BHET are greatly enhanced with increasing reaction temperature. When the temperature was 170 °C, the PET conversion was only 12%, and there was no BHET yield. However, with increasing glycolysis temperature, the conversion of PET increased markedly. The conversion of PET and the selectivity and yield of BHET reach a maximum value of 95%, 80% and 76%, respectively, when the glycolysis temperature is 196 °C.

### 3.3.3. Effect of reaction time

It is obvious that the conversion of PET and the selectivity and yield of BHET increases distinctly with increasing glycolysis time as shown in Fig. 7. When the reaction time was 3.0 h, the PET conversion was 100% and the selectivity and yield of BHET were 75%. However, when the reaction time was more than 3.0 h, the yield of BHET decreased, and the conversion of PET remained 100%. The selectivity and yield of BHET were decreased by prolonging the reaction time. This may be attributed to the polymerization of BHET carried out as a side reaction during the glycolysis of PET with increasing reaction time, which would account for the decrease in the selectivity and yield of BHET [23].

### 3.3.4. Effect of ethylene glycol (EG) dosage

The effect of ethylene glycol (EG) dosage on the glycolysis reaction is shown in Fig. 8. The PET conversion and BHET yield and selectivity increases with increasing the EG dosage from 5.0 g to 20 g. Beyond the EG dosage of 20 g, the added catalyst has no significant effect on the conversion of PET and the selectivity and yield of BHET.

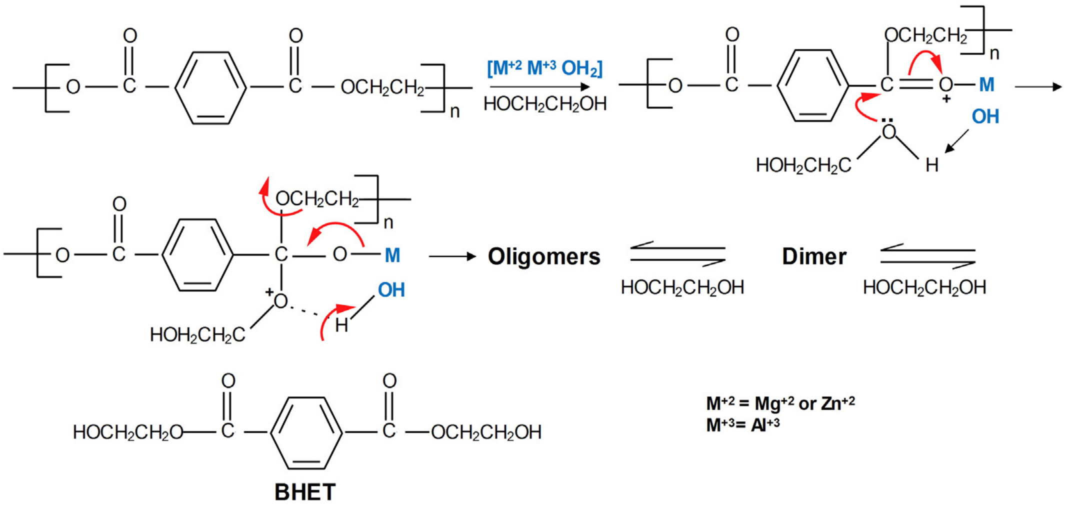
### 3.4. Catalyst stability and reusability

To determine whether the catalyst lost activity or not, the reusability of the prepared (Mg–Zn)–Al LDH was studied in PET glycolysis. After the reaction, the catalyst was separated by centrifugation and reused without any further purification. Fig. S2 shows that the (Mg–Zn)–Al LDH can be reused up to four times without apparent decrease in the PET conversion and the selectivity and yield of BHET under the given conditions. Fig. 9 shows the XRD pattern of the regenerated (Mg–Zn)–Al LDH. It is obvious that the structure of (Mg–Zn)–Al LDH withstands even after reusing the catalyst up to four times. The TGA and DSC curves support this data, where the catalyst is thermally stable within the range of the reaction temperature. Moreover, the memory effect of hydrotalcite has a key role in retrieving the structure of hydrotalcite even if the structure is altered at very high working temperatures. The catalyst may lose the physically adsorbed water molecules on the surface and interlayer space during the glycolysis reaction at 190 °C. However, when the catalyst is regenerated and washed several times with deionized water, the catalyst retrieves the eliminated water.

### 3.5. Mechanism of glycolysis

The mechanism and proposed pathway of the glycolysis of PET catalyzed by the (Mg–Zn)–Al LDH are illustrated in Scheme 1. Di Cosimo et al. [44] reported that three different types of basic sites exist in Mg-Al LDH: isolated $O^{2-}$ ions, $Mg^{2+}$–$O^{2-}$ pairs, and OH groups; their relative concentration depends on the Al content. In contrast, the surface Lewis acidic sites are provided by $Mg^{2+}$, $Al^{3+}$ and/or others cations (substitution of Mg or incorporation of $Zn^{2+}$).

The metal cations of the hydrotalcites catalyst interact with the oxygen of the carbonyl group, thus creating more partial positive charge on the carbon in the carbonyl group. Meanwhile, the basic sites on the catalyst interact with the hydrogen in the hydroxyl group of ethylene glycol, resulting in the oxygen of ethylene glycol becoming more negative and better able to attack the carbon cation of the ester group, breaking the C–O bond in PET. Afterwards, the hydrogen in ethylene glycol leaves. Then, the acyl-oxygen is cleaved, and the $-OCH_2CH_2-$ group leaves and combines with $H^+$ to form $HOCH_2CH_2-$. Thus, longer PET chains decompose to shorter chains: oligomers, dimers, and finally monomers.



**Scheme 1.** Mechanism of the PET glycolysis.

## 4. Conclusion

In conclusion, (Mg–Zn)–Al LDH, as a regenerable and low-cost catalyst, can effectively degrade PET wastes into monomer BHET under mild conditions. It is found that 3 h of glycolysis at 190 °C is sufficient for the conversion of PET to reach 100% and the yield of BHET to reach 75% using 1.0 wt.% of catalyst with 20 g of EG and 2.0 g of PET. The presence of Lewis acidic sites and basic sites on the catalyst facilitates the attack of the oxygen in ethylene on the carbon cation of the ester group.

## Acknowledgments

Financial support by the Egyptian Petroleum Research Institute is gratefully acknowledged.

## Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.molliq.2015.11.049.

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