Calcined Zn/Al Hydrotalcites as Solid Base Catalysts for Glycolysis of Poly(ethylene terephthalate)

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ABSTRACT: In this research, glycolysis of poly(ethylene terephthalate) (PET) with ethylene glycol (EG) was carried out using Zn/Al mixed oxide catalyst. These mixed oxides were prepared by calcining crystalline Zn/Al hydrotalcites at different calcination temperatures. The samples and corresponding precursors were characterized by X-ray diffraction, BET, Fourier-transform infrared spectra, thermogravimetry/differential thermal analysis, and Hammett titration method. The experimental results showed that Zn/Al mixed oxides obtained from hydrotalcites were found to be more active than their individual oxides for glycolysis of PET. The relationship between catalytic performance and chemical–physical features of catalysts was established. In addition, a study for optimizing the glycolysis reaction conditions, such as the weight ratio of EG to PET, catalyst amount and reaction time, was performed. The conversion of PET and yield of bis(2-hydroxyethyl terephthalate) (BHET) reached about 92% and 79%, respectively, under the optimal experimental conditions. Moreover, it should be noted that Zn/Al mixed oxide not only provided an effective heterogeneous catalyst for glycolysis of poly(ethylene terephthalate), but also presented a novel method for decolorization of discarded colored polyester fabric. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 41053.

INTRODUCTION

Polyethylene terephthalate (PET) is used extensively as fibers, photographic film, food packaging, and soft drink bottles. With increasing consumption of PET, a large amount of waste PET is growing rapidly. Chemical recycling of PET waste is becoming an increasingly important method for the conversion of waste PET into valuable chemicals. Chemical depolymerization processes are divided as glycolysis, hydrolysis, methanolysis, and aminolysis.[1,2] All of these processes have both advantages and disadvantages. Hydrolysis using acid or alkaline catalysts results in terephthalic acid (TPA), along with corrosion and pollution problems. Neutral hydrolysis is usually run at high pressure and temperature. Methanolysis is the degradation of PET by methanol at high temperatures and high pressures with the products being dimethyl terephthalate (DMT) and ethylene glycol (EG). Aminolysis is the reaction of PET with different aqueous amine solutions to yield the corresponding diamides of TPA and EG. Glycolysis reaction can be described as the transesterification process between diols, usually using ethylene glycol (EG), and ester groups of PET to obtain the monomer bis(hydroxyethyl terephthalate) (BHET). The main advantage of this process is that BHET can be reused as raw material to reproduce to PET

by blending with virgin BHET. Moreover, the monomer can be used in the synthesis of unsaturated polyester, polyurethanes and the others.[3–5] The glycolysis process is chosen for further investigation.

Glycolysis of waste PET without a catalyst is an extremely sluggish process. Therefore, the challenge and disadvantage accompanied with glycolysis processes are the relatively high consumption of energy. The present work is an attempt to reduce the reaction time and save the energy consumption needed in this process. Glycolysis of PET is most frequently carried out in the presence of metal acetates (Zn, Co, Mn) as catalysts. Xi et al.[6] reported a glycolysis conversion of almost 85.6% at 196°C, reaction time of 3 h, the weight ratio (zinc acetate to PET) of 1% and the weight ratio (EG to PET) of 5. Ghaemy et al.[7] reported that the yield of BHET from glycolysis of PET fibers was 75% under the optimal conditions and purified BHET was separated from products of glycolysis by changing with temperature. Metal acetates show high catalytic activity for glycolysis PET waste. However, this type of catalyst leads to many problems such as catalyst separation and heavy metal pollution due to excellent solubility of metal acetate in EG. To eliminate these problems, attention was focused on to develop

eco-friendly catalysts for glycolysis PET. López-Fonseca et al.[8] revealed that alkali catalysts, such as sodium carbonate and sodium bicarbonate, exhibited the catalytic activity for the glycolysis of PET, and the yield of BHET was about 70% with sodium carbonate as catalyst at 196°C with PET: catalyst molar ratio of 100 : 1 in the presence of a large excess of EG. Wang et al.[9] carried out the depolymerization of PET under different kinds of ionic liquids as catalysts. The conversion of PET catalyzed by [bmim]Cl could reach to 44.7% with the amount of ionic liquid 1.0 g, reaction time of 8 h and 1 atm. The special properties of ionic liquids make it easy to separate the catalyst from glycolysis products. Series of solid catalysts including SO_4^{2-}/Co-Zn-O and SO_4^{2-}/ZnO-TiO$_2$ are investigated for the glycolysis of PET.[10,11] The SO_4^{2-}/ZnO-TiO$_2$ exhibits a catalytic activity with 100% conversion of PET and 72% selectivity of BHET after 3 h at 180°C. Moreover, the solid catalyst could be easily separated and reused for four times. Recently, the spinel type compound of solid acids metal oxides catalyst for glycolysis PET, such as $ZnMn_2O_4$, $CoMn_2O_4$, and $ZnCo_2O_4$, was reported. The yield of BHET is up to 92.2 mol% under 260°C, 5 atm and using $ZnMn_2O_4$ as the catalyst.[12]

A hydrotalcite-like compound is often used as a precursor of basic catalysts. In our early research, the glycolysis process of PET to BHET using calcined Mg/Al hydrotalcites is investigated.[13] These catalysts exhibit excellent catalytic activity of glycolysis PET, but they have not been enough stability due to easily absorb carbon dioxide and water. This work is a continuation of our initial research. Compared with the early research, this work focuses on Zn/Al mixed oxide derived from the corresponding hydrotalcites precursors. In spite of the relevant industrial interest for these catalysts, the scientific literature concerning Zn/Al hydrotalcites as solid base catalysts or catalyst precursors is relatively poor.

In this work, Zn/Al hydrotalcites is used as catalyst precursors to obtain Zn/Al mixed oxides. Structural properties of Zn/Al mixed oxide and the corresponding hydrotalcites precursors are studied by X-ray diffraction (XRD), BET, Fourier-transform infrared (FTIR) spectra, thermogravimetry/differential thermal analysis (TG/DTA), and Hammett titration method. The optimal compositions of the catalyst and optimum reaction conditions are presented. The relationship between textural properties, basicity, and catalytic activity is investigated. Furthermore, stability and regeneration of catalysts are also discussed.

EXPERIMENTAL

Preparation of Catalyst

The Zn/Al hydrotalcite-like compound was prepared by co-precipitation method and then calcined to obtain its corresponding mixed oxide. The detailed procedure was as follows: A solution was prepared by mixing solutions of Zn and Al metal nitrates at the desired molar ratio. Another solution was prepared by dissolving 0.35 mol sodium hydroxide and 0.15 mol sodium carbonate in 200 ml of distilled water. Two solutions were simultaneously added dropwise into a flask under vigorous stirring at room temperature, and the addition took nearly 1.5 h. The pH was maintained at 10 during this process. The mixture was aged in mother liquor for 1 h under stirring and then placed at 65°C for 24 h. The precipitated solid was filtered, washed with deionized water, and subsequently dried at 50°C in air to yield hydrotalcites. For convenience, the hydrotalcites obtained with different Zn/Al molar ratios of 1, 2, 3, and 4 were designated as ZnAl-HT-1, ZnAl-HT-2, ZnAl-HT-3, and ZnAl-HT-4. The Zn/Al hydrotalcite was calcined at different temperatures for 4h in a muffle furnace to obtain the corresponding mixed oxides, which were called ZnAl-1, ZnAl-2, ZnAl-3, and ZnAl-4.

Characterization of Catalysts

XRD patterns of the samples were obtained by Bruker D8 Advance, using Cu Kα radiation ($\lambda = 1.54056$Å). The operating voltage and current was 40 kV and 30 mA, respectively. The samples were step-scanned in steps of 0.04° (2θ) using a count time of 10 s/step. The phases were identified by comparing with the JCPDF files. The metal compositions of the hydrotalcites were determined with inductively couple plasma (ICP) Emission spectrometry (IRIS Advantage Radial, ThemoElemental), after dissolving the samples in nitric acid. Specific surface area of the samples were measured by nitrogen adsorption at −196°C using surface area and pore size analyzers (Autosorb-1-MP, Quantachrome), the samples were degassed at 200°C for 2 h prior to measurements. Thermal decomposition of the hydrotalcites was evaluated by TG and DTA carried out on Diamond TG/DTA instrument under nitrogen atmosphere at 10°C/min from room temperature up to 800°C. The FTIR spectrum was recorded in a Bruker Equinox 55 instrument, using KBr pellets. The range 4000–400 cm^{-1} was investigated. Hammett indicator method was used to measure the basicity of the catalyst according to the literature.[14] The calcined hydrotalcites of 0.15 g were immersed in a toluene solution of phenolphthalein and stirred for 30 min, then titrated with a toluene solution of benzoic acid (0.02 M) to determine the total basicity. A qualitative determination of the strength of basic sites in calcined solids was done by Hammett indicators. 25 mg of solid catalyst was added into the mixture of 1mL Hammett indicators and 10 mL methanol inside a test tube, and test tube was shaken. The color of the solution was matched with those of Hammett indicators after 2 h. The following Hammett indicators were used: Neutral Red ($pK_{BH+} = 6.8$), Bromothymol Blue ($pK_{BH+} = 7.6$), Phenolphthalein ($pK_{BH+} = 9.6$), Alizarin Red ($pK_{BH+} = 11.0$), and 2, 4-Dinitroaniline ($pK_{BH+} = 15.0$).[14,15]

Glycolysis of PET

Consumed PET soft drink bottles were cut into 2 × 2 mm particles for glycolysis experiments after washing and removing caps, labels, and bottom parts. PET samples were dissolved in the mixture solution (60 wt % phenol/40 wt % 1,1,2,2-tetrachloroethane). The viscosity average molecular weight of PET was 2.59 × 10^4 g/mol measured using a Ubbelohde viscometer at 30°C according to from the equation $M = 3.61 \times 10^4 [\eta]^{1.46}$.[16] All the reagents were purchased from sinopharm chemical reagent factory and used without further purification.

A 250 mL round bottom three-necked flask equipped with an electromagnetic stirrer, thermometer, and reflux condenser was loaded with 5 g of PET and a certain amount of EG and
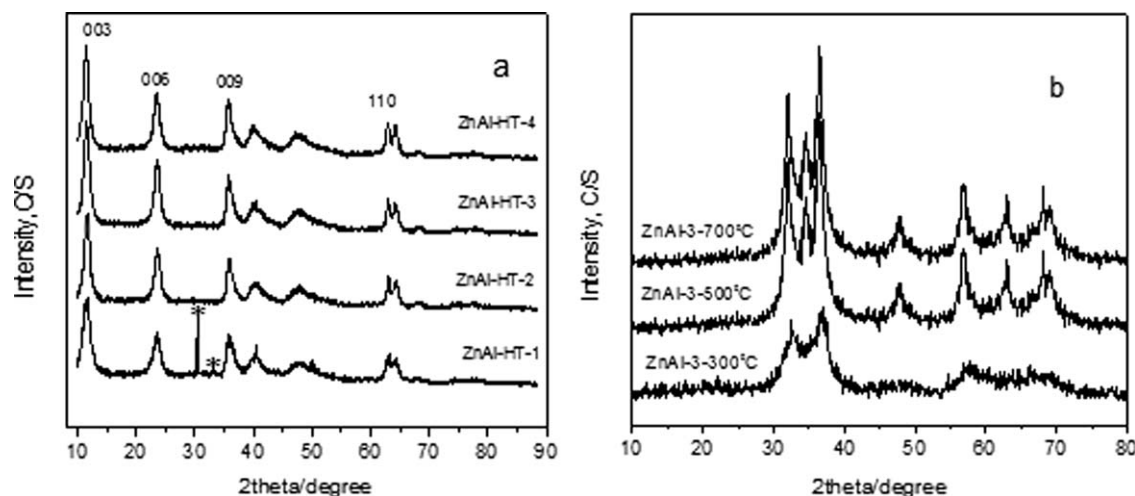
Figure 1. XRD patterns of hydrotalcite samples. (a) Uncalcined hydrotalcite samples; (b) Zn/Al-3 calcined at various calcination temperatures.

catalysts. The glycolysis reaction was carried at 196°C (the boiling point of EG) under nitrogen atmosphere. At the end of reaction, 100 mL boiling water was added to the round bottom flask and the mixture was separated into solid and liquid phases by filtration. The solid product possessed undepolymerized PET, insoluble oligomers and solid catalyst, and then was extracted with boiling water; the water was mixed with the liquid fraction. The white crystalline of BHET was obtained from the filtrate by chilling it. The BHET monomer was purified by

repeated crystallization from water, dried in an oven at 50°C and weighted to estimate the yield of BHET. The yield of BHET monomer and conversion of PET were calculated using the following equations:

$$\text{Yield of BHET} = \frac{\text{weight of BHET monomer}/M_{\text{BHET}}}{\text{weight of initial PET}/M_{\text{PET}}} \times 100 \tag{1}$$

$$\text{Conversion of PET} = \frac{\text{weight of initial PET-weight of rest PET}}{\text{weight of initial PET}} \times 100 \tag{2}$$

where M_{BHET} and M_{PET} refer to the molecular weights of BHET (254 g/mol) and repeating unit of PET (192 g/mol), respectively.

FTIR spectroscopy was used to identify the chemical structure of the products of glycolysis using KBr disc technique. Elemental analysis was performed on Elementer Vario El III apparatus by combustion analysis. Differential scanning calorimeter (DSC) was carried out STA 409 PC Luxx apparatus with the heating rate of 10°C/min from 25 to 250°C under nitrogen atmosphere. The morphology of unreacted PET samples was observed on field emission scanning electron instruments (S-4800, Japan).

RESULTS AND DISCUSSION

Characterizations of Catalysts

Figure 1(a,b) show the XRD patterns of Zn/Al hydrotalcites both uncalcined and calcined samples. These patterns of uncalcined samples are characteristic of layered materials with a hydrotalcite-like structure. XRD patterns clearly indicate that no other crystalline phase co-exists with the HT-like components, except for the pattern of the molar ratio of Zn/Al is 1, in which the residual sodium nitrate appears ($2\theta = 29.5°$ and $32.0°$).[17] The unit cell parameters a and c can be calculated using the equations: $c = 3d_{003}$ and $a = 2d_{110}$.[18] The results of calculations

are shown in Table I. The interlayer distance (d_{003}) is increased with the increasing of the molar ratio of Zn/Al. This is because the low Al^{3+} content decreases the electrostatic attraction between the excess positive charge of Al^{3+} and the negative charge of the interlayer anion and hence increases the interlayer distance.[19] During calcination, the decomposition of Zn/Al hydrotalcites results in the formation of their corresponding oxides. This fact is confirmed by the XRD patterns of samples calcined at 300°C, 500°C and 700°C [Figure 1(b)]. The characteristic diffraction peaks of the hydrotalcite-like structure vanish when the calcinations temperature reaches to 300°C. With increasing of calcinations temperature, the peaks of ZnO strengthen gradually, which demonstrate the crystallization degree of ZnO increases evidently. Compared to the previous literature,[20] $ZnAl_2O_4$ spinel peaks are not observed at 700°C. Meanwhile, the peak of Al_2O_3 phase is not found; this results show that Al^{3+} cations are dispersed in the structure of ZnO.

Chemical composition data of uncalcined Zn/Al hydrotalcites indicates that the amounts of Zn and Al for all samples are in acceptable agreement with the recipes of precipitation solution, which evidence that the co-precipitation is nearly complete.

The FTIR spectrum for ZnAl-HT-3 is presented in Figure 2. The broad peak is found at 3438.82cm^{-1} and it corresponded
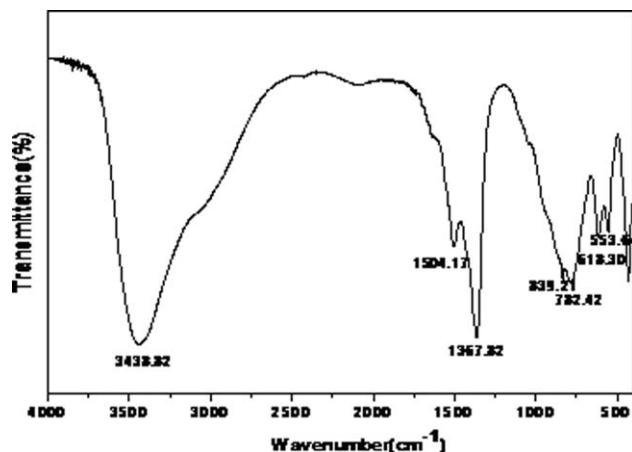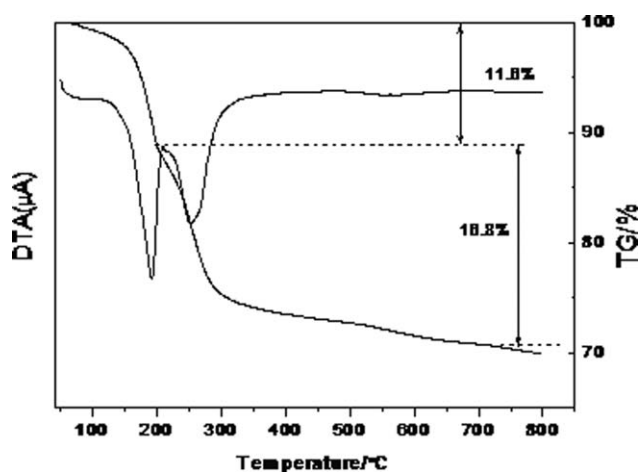
Table I. Elemental Analysis and XRD Results of Hydrotalcites with Different Zn/Al Ratio

Sample	Zn/Al (measured)	(003) 2θ (°)	d_{003} (nm)	(110) 2θ (°)	d_{110} (nm)	a (nm)	c (nm)
ZnAl-HT-1	1.02	11.64	0.760	63.12	0.147	0.294	2.280
ZnAl-HT-2	1.93	11.64	0.760	62.91	0.147	0.294	2.280
ZnAl-HT-3	2.81	11.56	0.765	63.01	0.148	0.296	2.295
ZnAl-HT-4	3.53	11.46	0.771	62.84	0.150	0.300	2.313

to the OH^-, caused by the interlayer water molecules and hydroxyl groups in the brucite-like layers.[21] The weak peak at 1504.17 cm^{-1} stands for absorption peak OH^-.[20] The stretching vibration of CO_3^{2-} appears at 1367.82 cm^{-1} and 839.21 cm^{-1}. In the low energy ranges 400 cm^{-1}–780 cm^{-1} corresponds to Zn/Al-hydrotalcites lattice vibrations, the peaks at 782.42 cm^{-1} and 553.64 cm^{-1} can be assigned to Al–O stretching mode.[22]

Thermal decomposition of ZnAl-HT-3 is investigated by the TG/DTA method, the experimental result is shown in Figure 3. The first endothermic peak appears at about 186°C, which is accompanied by a mass loss 11.6%, involves the elimination of the surface weakly bound water and interlayer water without collapse of hydrotalcite structure. The second endothermic peak at about 258°C, with mass loss of approximately 16.8%, is attributed to the decomposition of the carbonate anion in the brucite-like layers, and the deeper decomposition of brucite layer OH^- anions. This is in agreement with the previous literature.[23] Moreover, the endothermic peak, corresponds to form the $ZnAl_2O_4$ spinel phase, is absent in this temperature range, this result in accordance with the experimental results of XRD curves of calcined ZnAl-HT-3 [Figure 1 (b)].

Table II reports that the values of the BET special surface areas for the corresponding Zn/Al mixed oxides obtained from Zn/Al hydrotalcites with the different molar ratio of Zn/Al and the different calcination temperature. The surface area significantly increases with increasing calcination temperature from 300°C to 600°C. This is possibly because water and carbon dioxide are released and develops the porous structure during the calcination temperature range. However, when calcinations tempera-

Figure 3. TG/DTA curves of Zn/Al-HT-3.

ture reaches to 700°C, the metal oxides should be sintered, which lead to a strong decreased of the special surface areas.[24]

The alkalinities of mixed oxides with different Zn/Al moral ratios, pure ZnO, and pure Al_2O_3 are measured by Hammett titration (Table II). The experimental results show that Zn/Al molar ratios have a great influence on the basic strengths and base amount (described as basicity). Compared to the corresponding single metal oxide, the higher basicity of the binary metal oxides derived from Zn/Al hydrotalcites are obtained. It indicates that the surface basicity is improved through combining the two components of zinc and aluminum. According to previous reports,[25] When Al^{3+} is added into ZnO crystal,

Figure 2. FT-IR spectra of Zn/Al-HT-3.

Table II. Alkalinity and BET-Specific Area of Difference Zn/Al Mixed Oxides

Sample	Base strength	Basicity (mmol/g)	S_{BET} (m²/g)
Al_2O_3	$6.8 < pK_{BH+} < 7.6$	–	–
ZnO	$7.6 < pK_{BH+} < 9.6$	–	–
ZnAl-1-500°C	$11.0 < pK_{BH+} < 15.0$	0.23	69.4
ZnAl-2-500°C	$11.0 < pK_{BH+} < 15.0$	0.28	70.8
ZnAl-3-500°C	$11.0 < pK_{BH+} < 15.0$	0.32	72.1
ZnAl-4-500°C	$11.0 < pK_{BH+} < 15.0$	0.30	72.3
ZnAl-3-300°C	$9.6 < pK_{BH+} < 11.0$	0.13	57.3
ZnAl-3-400°C	$11.0 < pK_{BH+} < 15.0$	0.22	68.3
ZnAl-3-600°C	$11.0 < pK_{BH+} < 15.0$	0.29	73.4
ZnAl-3-700°C	$11.0 < pK_{BH+} < 15.0$	0.28	43.2

Table III. Catalytic Activity of Difference Catalyst

Sample	Conversion of PET (%)	Yield of BHET (%)
No catalyst	8.21	4.92
Al$_2$O$_3$	9.30	5.07
ZnO	65.12	52.23
Al$_2$O$_3$/ZnO[a]	56.32	43.21
ZnAl-1[b]	81.75	65.63
ZnAl-2[b]	89.21	74.80
ZnAl-3[b]	91.01	76.43
ZnAl-4[b]	89.73	75.92

[a] Mechanical mixture and Zn/Al molar ratio is 3.
[b] Calcinations temperature 500°C.

the defect of Zn^{2+} or Al^{3+} is produced in order to compensate the positive charge generated. The O^{2-} ions adjacent to the Zn^{2+} or Al^{3+} defects become coordinatively unsaturated and can provide basic sites. Among the binary oxides, the one with Zn/Al molar ratios of 3 possesses more basicity and reaches to 0.32 mmol/g. Furthermore, the basicities of mixed oxides follow the trend: ZnAl-3 > ZnAl-4 > ZnAl-2 > ZnAl-1. In fact, the calcined hydrotalcites are known to possess basic sites of weak, medium and high strength, corresponding to OH$^-$ groups, Zn-O ion pairs and surface O^{2-} ions, respectively.[26] On the other hand, the surface Lewis acidic sites are provided by coordinatively unsaturated Al^{3+} ions.[27] It was widely accepted that transesterification reaction was efficiently catalyzed by acid–base catalysts.[28] Therefore, it is reasonable to infer that Zn/Al mixed oxides derived from the corresponding hydrotalcites have high catalytic activity for the glycolysis of PET.

Catalytic Activity of Zn/Al Mixed Oxides
The effects of Zn/Al molar ratios on their catalytic activity are investigated. The experimental results are illustrated in Table III. The experiments are carried out with the weight ratio (EG to PET) of 5, the weight ratio (catalyst to PET) of 1%, 196°C, and
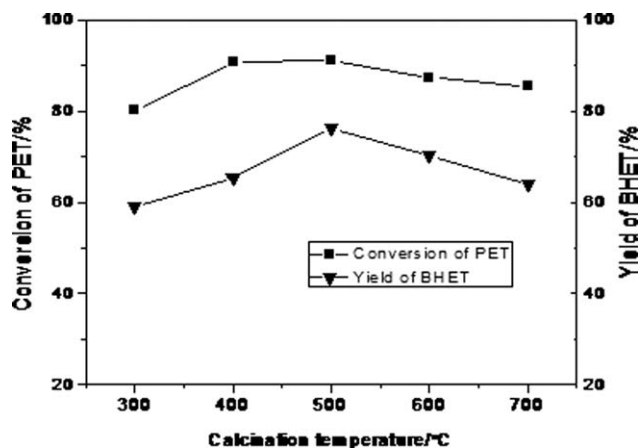

Figure 4. Effect of calcination temperature on the catalytic activity of Zn/Al-3.

Table IV. Effect of Particle Size of Catalysts on Glycolysis Reactions

Catalyst[a] (particle size)	Zn(OAc)$_2$	ZnAl-3 (50–65 mesh)	ZnAl-3 (65–100 mesh)	ZnAl-3 (100–200 mesh)
Yield of BHET	68.89%	71.21%	76.43%	77.60%
Zinc content (wt %)	0.17	0.0014	0.0051	0.042

[a] Weight ratio (catalyst to PET) is 1 wt %.

reaction time of 50 min. The results are compared with pure Al$_2$O$_3$, ZnO, and their mechanical mixture.

The results show that Al$_2$O$_3$ is inactivity and ZnO display medium catalytic activity for the glycolysis reaction, the yield of BHET is 5.07% and 52.23%, respectively. Meanwhile, the yield of BHET is 43.21% using the mechanical mixture of ZnO and Al$_2$O$_3$ (Zn/Al molar ratio is 3) as the catalyst. However, the yields of BHET using Zn/Al mixed oxides derived from the hydrotalcites are more than 65%. The catalytic activity is improved with the increase in the Zn content. When the Zn/Al ratio exceeds 3, the catalytic activity slightly decreases. Obviously, the tendency is correlated well to the variation of the basicity of Zn/Al mixed oxides (in Table II). It indicates that the basicity of mixed oxides plays an important role in the glycolysis activity. The mechanical mixture of ZnO and Al$_2$O$_3$ exhibits weaker catalytic activity than mixed oxides with the same molar ratio. It demonstrates that the basic sites should be adjacent to the acid sites in order to increasing glycolysis activity.

The influence of calcination temperature on the catalytic activity is displayed in Figure 4. From the results obtained, it is shown that calcination temperature effects significantly on the catalytic activity. With increasing calcination temperature to 500°C, the yield of BHET increased gradually and reaches the maximum of 79.2%. When calcination temperature is higher than 500°C, the yields drop considerably. This result is also correlated well with the variation of the catalyst basicity (Table II). Moreover, ZnAl-3–500°C presents higher the special surface area, therefore more active sites exposed, which is another reason to improve catalytic activity. In conclusion, mixed oxides have the highest catalytic activity when Zn/Al molar ratio is 3 and calcined at 500°C. ZnAl-3–500°C is chosen as the glycolysis catalyst for further investigation.

The effect of catalyst particles sizes on the catalytic activity is studied. The Zn/Al mixed oxide is pressed and crushed to the particles sizes ranged from 50–65, 65–100, and 100–200 meshes

Table V. Catalytic Activity of Catalyst Under Difference Solvolysis Reagent

Solvolysis reagent	Conversion of PET (%)	Reaction temperature (°C)
Propylene glycol	93.10	188
Octanol	91.13	196
Hexanol	86.71	157
Butanol	54.24	117.5
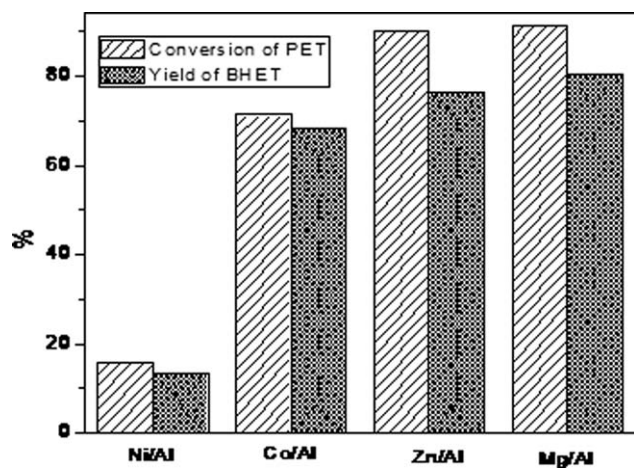
Figure 5. Comparison with catalytic activity of difference catalyst.

Figure 7. Effect of the weight ratio of EG to PET on glycolysis reactions.

through different sieves. As a result (in Table IV), the yield of BHET increases with decreasing catalyst particles sizes, it is because that glycolysis of PET is a heterogeneous reaction and glycolysis reaction proceeds at the liquid(EG)-solid(PET)-solid (catalyst) interface. Clearly, the interface area available for the reaction decreases with increasing particle size of the catalyst. On the other hand, small particles of Zn/Al mixed oxide may be transported into glycolysis products during the filtering process. So zinc element content of BHET increases with decreasing particles sizes of catalysts. After carefully considering the above factors, we use Zn/Al mixed oxide with 65–100 mesh particle size as the catalyst for glycolysis reactions in the following experiments, and the glycolysis reaction is actually a heterogeneous catalytic process under this reaction condition. Meanwhile, we also investigate zinc element content of BHET using zinc acetate as the catalyst, the experimental results show that most of the catalyst stays in glycolysis product, which maybe has a bad effect on the quality of the glycolysis products.

Catalytic activity of Zn/Al mixed oxide is further examined under various solvolysis reagents, such as propylene glycol, octanol, hexanol, and butanol. Glycolysis reaction conditions are the reaction time of 1 h, the weight ratio (ZnAl-3 to PET) of 1% and the weight ratio (solvolysis reagent to PET) of 5 and reac-
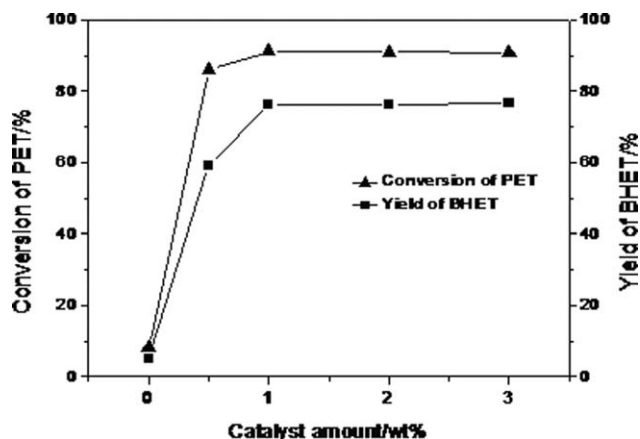
tion temperature at the boiling of solvolysis reagent. The experimental results show that the conversions of PET reach a high level in solvolysis reagent except for butanol with the lowest reaction temperature (Table V). It demonstrates that Zn/Al mixed oxide should be commonly used as the catalyst for glycolysis reaction.

Glycolysis of PET over M(II)/Al mixed oxides, when M(II) = Mg, Zn, Co, Ni, and M(II)/Al molar ratio of 3, are carried out. Glycolysis reactions are conducted with the weight ratio (EG to PET) of 5, the weight ratio (catalyst to PET) of 1%, 196°C and reaction time of 50min. Experimental data are summarized in Figure 5. Among the samples screened, Mg/Al mixed oxides have the highest catalytic activity, giving the conversion of PET is 92.3%. Zn/Al mixed oxides are also determined to be high activity, conversion of 91.0% is obtained. But low conversion of 15.7% is achieved over Ni/Al mixed oxides. The catalytic activity is in good agreement with the basic strength.[27] However, Zn/Al mixed oxides more stable than Mg/Al mixed oxides, which is beneficial for commercial applications.

Optimization of Glycolysis Reactions

Zn/Al mixed oxide with Zn/Al molar ratio of 3, calcination temperature 500°C and particles sizes ranged from 65 to 100
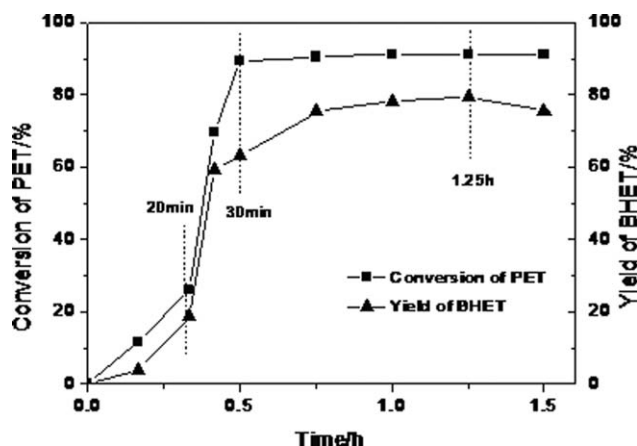

Figure 6. Effect of the catalyst amount on glycolysis reactions.

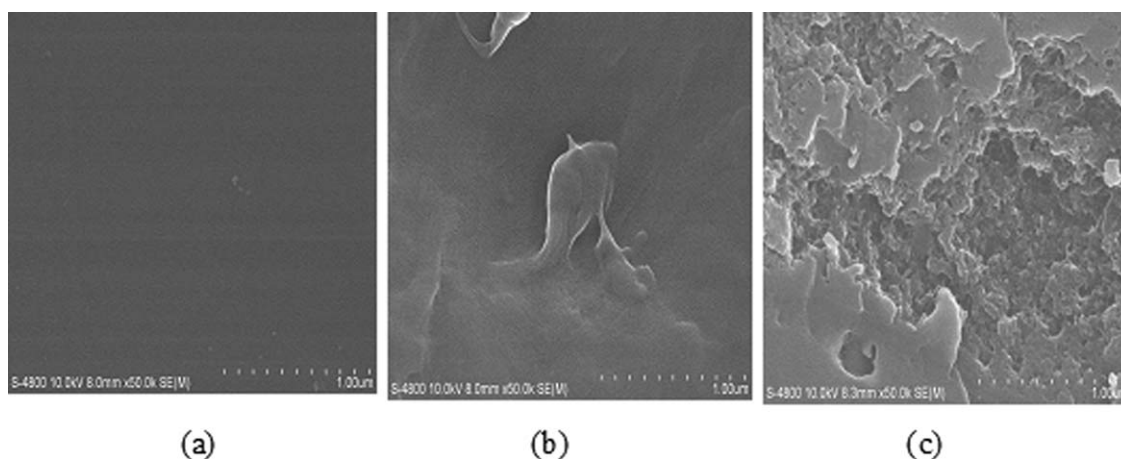**Figure 8.** Effect of reaction time on glycolysis reactions.

Figure 9. SEM photographs of the unreacted PET and residual PET: (a) unreacted PET; (b) after 20 min; (c) after 30 min.

mesh is used as the catalyst for glycolysis reactions. Further more, glycolysis reaction conditions are optimized.

The effect of the catalyst amount on glycolysis reactions is investigated. The catalyst amount is varied in the range 0–3.0 wt %. These percentages are weight fractions of PET supplied for glycolysis reaction. The results are summarized in Figure 6. The experimental results show that the yield of BHET and conversion of PET are increased with the increase of the catalyst amount from 0 to 1 wt %. Beyond the catalyst amount of 1 wt %, the added catalyst has no significant effect on the yield and conversion.

The weight ratio of EG to PET is one of the important variables, which affects conversion of PET and yield of BHET. In practice, the EG/PET ratio should be higher than that of the stoichiometric ratio in order to shift the equilibrium to the right-hand side and drive glycolysis reaction towards completion. As shown in Figure 7, the conversion of PET and yield of BHET increase considerably with increasing the weight ratio of EG to PET, and reach the maximum value. Beyond the weight ratio of 5, the excessively added EG has no enhance significantly on the conversion of PET and yield of BHET. The optimum weight ratio of EG to PET is found to be 5.
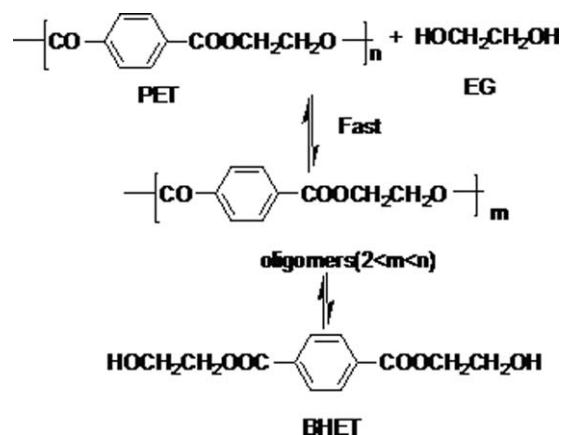
Evolution of the Glycolysis Reaction and Analysis of Glycolysis Products

To further reveal an evolution of the glycolysis of PET, the effect of reaction time on glycolysis reaction is investigated. Meanwhile, the morphological surface of residual PET particles

Table VI. Viscosity-Average Molecular Weights of Fresh and Residual PET

Time (min)	Viscosity-average molecular weight
0	25,900
10	24,250
20	18,620
30	4600
40	863

is also discussed. As seen from experimental results (in Figure 8), the rate of glycolysis reaction is low within 20 min. The glycolysis of PET occurs at the external area of PET and solid catalyst due to the surface of PET keeps smooth in this reaction stage [Figure 9(a)]. Reaction area of glycolysis is small, which results in a low reaction speed. The conversion of PET and yield of BHET are only 26% and 18% after 20 min, respectively. During the reaction time range from 20 min to 30 min, the surface of PET appears obvious porous structure [Figure 9(b,c)]; part of PET degrades into oligomers, which suspend in the ethylene glycol. Formation of porous structure not only increases the effective reaction area but also promotes penetration of EG and solid catalyst into solid PET particle. So rate of glycolysis of PET should be increased in this reaction time range. The conversion of PET reaches the maximum value after 30 min of glycolysis reaction. Meanwhile, the yield of BHET reaches only 63%. This result indicates that equilibrium should be reached between PET and the remaining amount of oligomers, but oligomers should not completely degrade into BHET in this reaction stage. With the reaction going on, the transesterification process between EG and oligomers may be further take place, the yield of BHET increases distinctly and reach

Scheme 1. Evolution of the glycolysis of PET in the presence of Zn/Al mixed oxides.
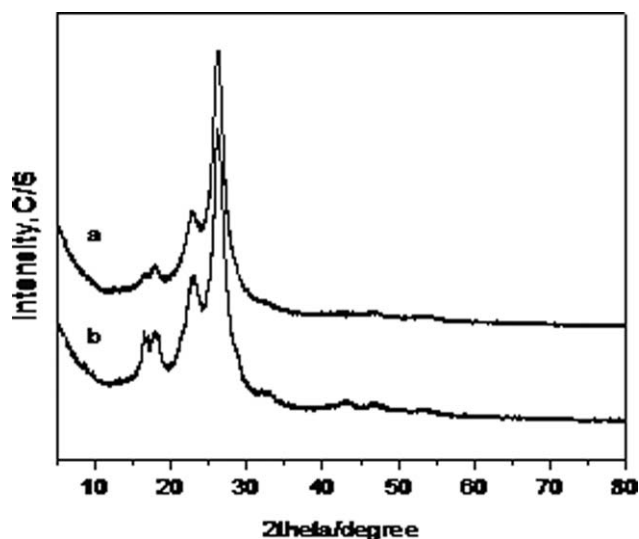
Figure 10. XRD patterns of the residual PET: (a) after 25 min; (b) after 35 min.

about 79% at 1.25 h. Further, the yield of BHET remains stable and reaches a plateau value representative of a nearly reaction equilibrium. The viscosity-average molecular weights of the fresh and residual PET are presented in Table VI. The experimental results show that the viscosity-average molecular weights of the residual PET decrease slowly in the initial phase of glycolysis reaction. However, the viscosity-average molecular weights of PET decreased sharply after 20 min, caused by the formation of a porous structure. The glycolysis reaction occurred not only at the surface, but also inside of the PET particle, resulting in the acceleration of the glycolysis reaction. The reaction of glycolysis PET can be described as follows (Scheme 1).

XRD profiles of the residual PET with various reaction times are shown in Figure 10, the XRD profiles exhibit a typical diffraction peaks of PET at $2\theta = 16.1°, 17.9°, 22.6°,$ and $26.1°$.[29] The experimental results show that the crystallinity of the residual PET is increased during the process of glycolysis reaction; this indicates that glycolysis process has easily taken place in the
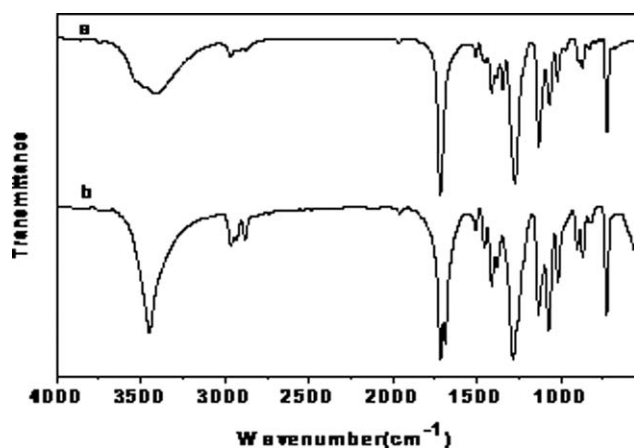

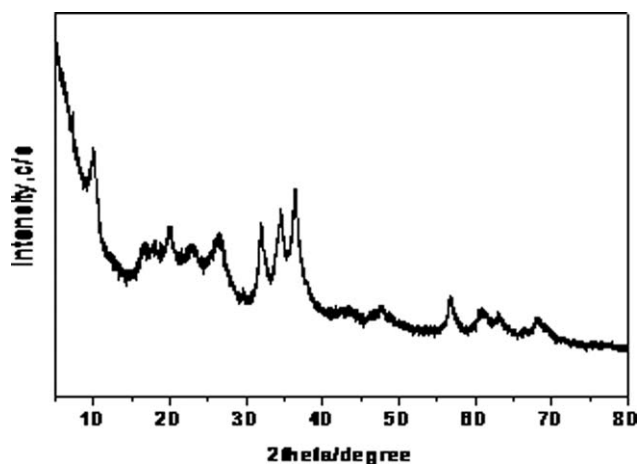**Figure 11.** IR spectra of BHET: (a) commercial BHET; (b) BHET from glycolysis reaction.

Figure 12. XRD patterns of used ZnAl-3.

amorphous region. So, the crystallinity of the residual PET should increase during the degradation process. The similar conclusion was reported by DSC.[30]

In order to confirm that glycolysis products are BHET, FTIR spectrum is performed. The FTIR spectrum (Figure 11) shows that –OH band at 3443 cm^{-1}, alkyl C–H at 2880 and 2956 cm^{-1}, C=O stretching at 1716 cm^{-1}, the C–O peak at 1136 and 1282 cm^{-1}, benzene ring peak at 1529 cm^{-1} as well as at 726, 867 cm^{-1}, present in BHET.[8] The FTIR spectrum just confirms the chemical structure of the products of glycolysis. Meanwhile, it can be seen that spectra of commercial BHET and BHET from glycolysis are quite similar, and no new peak appears in the spectrum of glycolysis product. Moreover, a definite identification could be done by DSC and elemental analysis. The DSC curve shows the sharp endothermic peak at 110°C in agreement with the known melting point of BHET.[8,30] Moreover, there are not extra peak other than BHET monomer, previous literature shows that the peak of dimer appears at 171°C.[30] The result of elemental analysis of products of glycolysis is C = 56.65%, H = 5.58 %, O = 37.77% (By difference), comparatively similar to the theoretical results of the BHET monomer. The results demonstrate that high level of purity of the monomer produced by our process.

Catalyst Deactivation and Regeneration
Another important issue concerning use Zn/Al mixed oxides as the solid catalyst is its reusability and stability. After glycolysis reactions, solid catalyst, along with unreacted PET, is remained in filter residue. In order to investigate the reusability of catalyst, solid catalyst should be separated from unreacted PET. So the filter residues are impregnated into the mixture solution (60 wt % phenol/

Table VII. Physicochemical Properties of Used Zn/Al-3

Catalyst	Actual Zn/Al molar ratio	S_{BET} (m^2/g)	Basicity (mmol/g)
ZnAl-3	2.81	72.1	0.32
ZnAl-3 (used)	2.76	38.6	0.19

Table VIII. Discoloration Properties of Zn/Al-3 and Zn/Al-HT-3

Catalyst (wt %)	Zn/Al-HT-3 (1%)[a]	Zn/Al-HT-3 (1%)	Zn/Al-HT-3 (5%)	Zn/Al-3 (1%)	Zn/Al-3 (5%)	Zn(OAc)$_2$ (1%)	Zn(OAc)$_2$ (1%) + AC[b] (1%)	Zn(OAc)$_2$ (1%) + AC[b] (5%)
L*	89.68	49.50	50.86	51.50	69.15	44.85	48.86	52.55
a*	−0.22	−2.81	−2.06	−3.31	−1.16	−4.99	−2.01	−2.03
b*	−4.11	−22.69	−25.0	−22.37	−17.66	−18.87	−28.48	−21.90
Yield BHET (%)	77.1	76.4	78.3	81.05	80.08	70.34	71.37	66.54

[a] Non-colored PET.
[b] Commercial activated carbon is used without treatment, S_{BET} is about 700 m^2/g.

40 wt % 1,1,2,2-tetrachloroethane), where most of the unreacted PET dissolves, and then solid catalyst is obtained by filtration.

It was also known that calcined hydrotalcites maybe partially reconstructed back to brucite-like layer under carbon dioxide in atmosphere and water.[31] Especially Mg/Al mixed oxides should be restored even storage in the desiccator. XRD profile of used Zn/Al mixed oxides is shown in Figure 12. The peaks at 10.8° and 20.1° are assigned to (003) and (006) planes of hydrotalcite. Meanwhile, the reflections observed at 16.1°, 17.9°, 22.6°, and 26.1° corresponded to the residual undissolved PET. The result reveals the structure of Zn/Al mixed oxides is better maintained, although the typical peak of hydrotalcites begins to appear in XRD patterns. In contrast with previous research,[13] it is demonstrated that Zn/Al mixed oxides more stable than Mg/Al mixed oxides. In this experiment, the reutilization of catalyst is investigated without any treatment and after calcining at 500°C again respectively. First, we perform glycolysis reaction using recycled catalyst after calcining at 500°C. The solid catalyst can be recycled at least five times under the optimal parameter of glycolysis reactions (the yield of BHET, 1st: 79.1%, 2nd: 72.9%, 3rd: 70.3%, 4th: 68.7%, 5th: 60.2%, 6th: 50.1%). The experimental results show that the yield of BHET is higher than 60% in the five recycle experiments. However, after five reuses, the activity of solid catalyst decreases sharply. On the other hand, the used catalyst is recycled two times under the same reaction condition without any treatment (the yield of BHET, 1st: 79.1%, 2nd: 60.1%, 3rd: 39.2%).

The metal elemental composition of used ZnAl-3 is determined by inductively coupled plasma. From the analysis results (Table VII), it can be found that the molar ratio of Zn/Al remains unchanged, which demonstrates the leach of metal ions is not the primary reason for catalyst deactivation. However, it can be noticed that the surface area of the catalyst decreases from 72.1 m^2/g to 38.6 m^2/g after glycolysis reaction and the basicity obviously deceases from 0.32 mmol/g to 0.19 mmol/g, which lead to the degradation of catalytic activity.

Glycolysis of Color PET Fiber
Color represents a limitation to the use of recycled PET fiber. In this study, glycolysis reaction of green PET fiber is investigated. Color of glycolysis of products is measured by whiteness meter (WSD-3C). The experimental results are reported using CIELab color scale. L* is a measure of brightness, a* is a measure of redness (+), and greenness (−), b* is a measure of yellowness (+) and (−).[32]

The results are shown in Table VIII. From these data, it can be proven that Zn/Al mixed oxides not only have excellent catalytic activity for glycolysis reaction but also discolor of disperse dyes in PET fiber, which reflected by increased L* (brightness), less negative a* (reduced green color). In fact, commercial activated carbon, which possesses a higher specific surface area, should have the excellent capacity of adsorbing disperse dyes. Especially, as a hydrophobic adsorbent, activated carbon has obvious advantages in adsorbing non-polar disperse dye. However, compared with activated carbon, Zn/Al mixed oxides present better capability of decolorization. So it can be concluded that the degradation of disperse dye was carried out in the presence of Zn/Al mixed oxides, the reason needs further research. However, a novel way of recycling of colored PET fiber will be put forward in the presence of Zn/Al mixed oxides.

CONCLUSIONS

Zn/Al mixed oxide, derived from Zn/Al hydrotalcites precursor, is effective catalyst for glycolysis of PET and a promising candidate to replace homogeneous catalysts. The experimental results show that the basicity of catalyst played an important role on the glycolysis activity. The catalyst with Zn/Al molar ratio of 3, 500°C calcinations possesses the best catalytic activity. The conversion of PET and yield of bis(2-hydroxyethyl terephthalate) (BHET) reach about 92% and 79%, respectively, under the optimal experimental conditions. Optimum glycolysis reaction conditions are obtained with the weight ratio (EG to PET) of 5, the weight ratio (catalyst to PET) of 1% and for 1.25 h reaction time. Moreover, the catalyst brings advantages such as easy separation and recycling, decolorization of colored polyester fiber.

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