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Nanostructured micro particles as a low-cost and sustainable catalyst in the recycling of PET fiber waste by the glycolysis method

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ABSTRACT

Magnetic Mg-Al-O@Fe$_3$O$_4$ micro particles were synthesized by coating nanosized Mg-Al double oxides onto Fe$_3$O$_4$ micro particles. The formed hierarchical structure gave Mg-Al-O@Fe$_3$O$_4$ micro particles a high active surface area, which enabled these micro particles to work efficiently as a catalyst in the glycolysis of poly(ethylene terephthalate) (PET). The bis(hydroxyethyl) terephthalate (BHET) yield reached above 80 mol% in the presence of 0.5 wt% of Mg-Al-O@Fe$_3$O$_4$ micro catalyst in the reaction system within 90 min at 240 °C. After the reaction, Mg-Al-O@Fe$_3$O$_4$ micro catalyst was easily retrieved by a magnetic decantation and can be repetitively used for two times with a high catalytic efficiency. After that, the deactivated Mg-Al-O@Fe$_3$O$_4$ micro catalyst can be regenerated by heat treatment. The regenerated Mg-Al-O@Fe$_3$O$_4$ micro catalyst displays a comparable catalytic performance as that of the virgin catalyst. In addition, the Mg-Al double oxides and Fe$_3$O$_4$ micro particles are low-cost and environmentally benign. Therefore, the Mg-Al-O@Fe$_3$O$_4$ micro catalyst may contribute to an economically and environmentally improved large-scale circular recycling of PET fiber waste.

1. Introduction

Since 2016, the global textile production is over 100 million tons every year (The fiber year consulting, 2017). Among all types of textile fibers, poly(ethylene terephthalate) (PET) fibers are the most common fibers in the textile industry due to their excellent mechanical properties and their economic prices. In 2018, the consumption of PET fibers was 55.1 million tons which accounted for more than 50% of the world fiber consumption (The fiber year consulting, 2019). However, these synthetic fibers have a very poor biodegradability in nature. It is estimated that around 39 million tons of post-consumer textile wastes are generated worldwide each year (Fashion and Waste: An Uneasy Relationship). Therefore, the tremendous amount of PET fiber wastes has caused serious environment problems. To preserve our resources and living environment, a sustainable and economic feasible way to recycle PET fiber wastes is urgent.

To achieve this goal, glycolysis is believed to be a very promising recycling method since it is a low-cost process and consumes a low amount of energy (Lorenzetti et al., 2006; Sinha et al., 2010). The generated bis(hydroxyethyl) terephthalate (BHET) monomer can be directly integrated into the existing industrial PET production lines. However, the glycolysis of PET is an extremely slow process in the absence of catalysts (Al-Sabagh et al., 2016a,b). To accelerate the glycolysis process, catalysts are often added into the reaction system. The most common catalysts are metal acetates, such as zinc acetate (Al-Sabagh et al., 2016a,b; Ghaemy and Mossaddegh, 2005; Lopez-Fonseca et al., 2010). Most metal acetates are soluble in ethylene glycol (EG), which makes catalysts homogenously dispersed in the reaction system resulting in a homogenous glycolysis of PET. Therefore, this type of catalysts usually shows a very good catalytic performance. However, the recovery of catalysts is an energy-intensive process and means that an excessive amount of EG must be removed by distillation. In addition, some metal acetates contain heavy metal ions which might cause a secondary pollution to the environment (Tchounwou et al., 2012; Zaman et al., 2012).

Nanosized heterogenous catalysts is another type of catalysts being intensively studied. For example, Wi et al. used silica nanoparticles doped with zinc oxide (ZnO) and cesium dioxide (CeO$_2$) in the glycolysis of PET (Wi et al., 2011). They found that the monomer yield reached maximum when the catalyst size was 60 nm. Lima et al. prepared titanate nanotubes and applied them as catalyst in the same glycolysis process (Lima et al., 2017). Compared with zinc acetate, the reaction showed a higher

yield of BHET in the presence of titanate nanotubes. A graphene oxide-manganese oxide nanocomposite was synthesized by Park et al. (Park et al., 2012). A monomer yield of 96.4% was obtained in the presence of this nanocomposite. Even though nanosized heterogenous catalysts provide a good catalytic performance in the glycolysis of PET, they still face the same problem as that of the homogenous catalysts, i.e. difficult recovery and heavy metal pollutions. Considering a scale-up process, it will take a long time and consume a significant amount of energy to recover the catalysts by high-speed centrifugation or cumbersome filtrations.

Ionic liquids (ILs) have been investigated as a green option as catalyst in the glycolysis of PET (Yue et al., 2013; Wang et al., 2015). Different from heterogeneous nanoparticle catalysts, ILs could be easily recycled and reused several times. However, high catalyst concentration and long reaction time are the challenges for its application in the large-scale glycolysis of PET (Al-Sabagh et al. 2014). Furthermore, the synthesis of IL catalysts is complicated and expensive, which is another obstacle that hinders its application in a scale-up process.

To realize closed-loop recycling of PET in a sustainable and economical feasible way, a cheap and easily recoverable catalyst is crucial. Bartolome et al. have reported the application of magnetic γ-Fe$_2$O$_3$ nanoparticles as a recoverable catalyst in the glycolysis of PET (Bartolone et al., 2014). The γ-Fe$_2$O$_3$ nanocatalyst was easily recovered by a magnetic decantation. However, the catalytic performance of γ-Fe$_2$O$_3$ in the glycolysis process seems to be relatively low since the reaction temperature has to be as high as 300 °C with a nanocatalyst concentration of 5 wt% (corresponding to PET) in order to get a good catalytic performance. Al-Sabagh et al. deposited magnetic Fe$_3$O$_4$ particles onto the surface of multiwall carbon nanotube (MWCNT) and it formed a Fe$_3$O$_4$ boosted MWCNT catalyst (Al-Sabagh et al., 2016a,b). The 100% of BHET yield was reported at the reaction temperature of 190 °C for 2 h. However, a high cost of MWCNT component will make the final Fe$_3$O$_4$ boosted MWCNT catalyst very expensive which then lead to an increase of the recycling cost of PET wastes considering a scale-up process. Recently, Cano et al. synthesized ionic liquid-coated SiO$_2$@Fe$_3$O$_4$ nanoparticles as nanocatalyst in the glycolysis of PET (Cano et al., 2020). A 100% yield was reported in the presence of 15 wt% of catalyst at a reaction temperature of 180 °C for 24 h. From an industrial point of view, the expensive synthetic procedures and long reaction time might however hinder the application of such a catalyst in a scale-up process. Therefore, there is still a great interest and urgent need to develop catalysts which have high catalytic efficiency and sustainability, while keeping the production cost low.

In our group, we found that a synthetic nanoclay based on Mg-Al double oxides gave a very high catalytic efficiency in the depolymerization of PET. Different from conventional catalysts, this synthetic nanocatalyst is low-cost and environmentally benign since it is based on Mg-Al double oxides. However, to recycle this catalyst from a pilot scale reaction was found to be difficult due to its small dimensions. Even worse, unremoved catalyst residues in the obtained monomer generated negative effects in the repolymerization process, which reduce the quality of the regenerated PET fiber.

Inspired by the previous work on magnetic nanoparticles, we coated nanosized Mg-Al double oxides onto the surfaces of micrometer-sized Fe$_3$O$_4$ particles. The fabricated Mg-Al-O@Fe$_3$O$_4$ micro catalyst combines a high catalytic activity with an easy magnetic recoverability. We here demonstrate that a cheap, efficient, environmentally benign and easy recoverable catalyst in the chemical recycling of PET is synthesized. In addition, the catalyst is easy to fabricate, and may contribute to an economically and environmentally improved large-scale circular recycling of PET fiber waste.

2. Materials and methods

Raw materials for the catalyst synthesis are ACS grade of Mg (NO$_3$)$_2$, Al(NO$_3$)$_3$, NaOH and Na$_2$CO$_3$ with all purity above 98% (Sigma Aldrich Sweden AB). Industrial grade Fe$_3$O$_4$ micro particles (F100b) were kindly supplied by NEOSID. Fiber grade PET pellets (RT 20) was bought from Invista. The intrinsic viscosity (IV) of the virgin PET is 0.64.

2.1. Preparation of catalyst

2.1.1. Pre-treatment of magnetic Fe$_3$O$_4$ particles

The magnetic Fe$_3$O$_4$ particles were obtained as industrial products. Before using the Fe$_3$O$_4$ particles, they were heat treated at 1200 °C to improve the crystallinity followed by ball milling for 48 h to remove agglomerates. After that, the Fe$_3$O$_4$ particle slurry was sieved into particle sizes >50 μm, 50–30 μm, 30–10 μm, and <10 μm. The finest particle fraction with a size below 10 μm was further exposed to a sedimentation procedure for different time intervals (1, 5 and 15 min). This allowed the finest particles to be removed and two particle fractions with a narrow size distribution to be obtained. From the sedimentation procedures, the particles that were sedimented for 1 min were selected to be used as the magnetic support due to the suitable material characteristics of magnetic properties and particle size.

2.1.2. Preparation of Mg-Al-O@Fe$_3$O$_4$ micro catalyst

To begin with, two stock solutions (A and B) were prepared. Solution A was prepared by dispersion of Fe$_3$O$_4$ particles into the solution containing Mg(NO$_3$)$_2$ and Al(NO$_3$)$_3$. The molar ratio of Fe$_3$O$_4$ to Mg(NO$_3$)$_2$ was 1:20 and the molar ratio of Mg(NO$_3$)$_2$ to Al(NO$_3$)$_3$ was 3:1. Solution B was prepared by dissolving of sodium hydroxide and sodium carbonate in deionized water. The molar concentration of NaOH and NaCO$_3$ in solution B was 0.4 M and 0.12 M, respectively. Then, solution B was dropwise added into solution A under vigorous stirring until the pH value of the solution reached 10. Thereafter the magnetic stirrer was turned off, and the final suspension was left to age for 24 h at 60 °C. The formed suspension was washed with deionized water until the pH value of the suspension became 6. The magnetic catalyst precursor was concentrated in the water phase using a magnet and the formed particle slurry was collected and frozen. The water was removed by freeze drying to avoid the formation of hard agglomerates which are usually formed when water-particle systems are dried by vaporization. To convert the solid catalyst precursor to actual catalyst, a heat treatment was applied. The temperature in the heat treatment was increased with a heating rate of 5 °C per minute until 1000 °C, holding at 1000 °C for 2 h and then cooled with 5 °C per minute to room temperature.

2.2. Depolymerisation of PET and preparation of BHET monomer

5 g of PET pellets, a certain amount of catalyst and 25 g of EG was put into a 150 ml reactor. The reaction system was heated to the desired reaction temperature. After a certain reaction time, the reaction was cooled to around 140 °C and then a vacuum distillation system was applied to the reactor to recycle the excess EG. The distilled EG was collected and reused. When no EG came out from the distillation system, some boiling water was added to the reactor to dissolve the reaction products. From this solution, the catalyst was recovered by a simple magnetic decantation and washed several times with hot water. The remaining solution was filtered to remove oligomers and unreacted PET. The collected oligomers and unreacted PET were dried at 80 °C overnight.

Thereafter the resulting liquid was put in a fridge at 4 °C overnight to crystallize the monomer.

The BHET monomer crystals were filtered and re-dissolved in hot water and re-crystallized. The second crystallization process aimed to further purify the monomer. After the second crystallization process, the BHET crystals were filtered and dried at 70 °C overnight.

The BHET yield was calculated according to Eq. (1)

$$\text{BHET yield (mol.\%)} = \frac{\frac{W_{BHET}}{M_{BHET}}}{\frac{W_{PET}}{M_{PET}}} \times 100\% \quad (1)$$

where M_{BHET} is 245 g/mol and M_{PET} for the repeating unit is 192 g/mol.

The depolymerization efficiency was expressed according to Eq. (2)

$$\text{Depolymerization efficiency} = \frac{W_{PET-}W_1}{W_{PET}} \times 100\% \quad (2)$$

where W_1 is weight of the oligomers and unreacted PET.

2.3. Regeneration of catalyst

After the depolymerization process, the catalysts were collected and regenerated through a heat treatment procedure, where the catalysts were exposed to 1000 °C for 2 h with a heating and cooling rate of 5 °C per minute.

2.4. Characterization section

X-ray diffraction (XRD) measurements were performed on a Bruker D8 Advance X-ray diffractometer equipped with Cr X-ray source (λ = 2.2897 Å) in the Bragg-Brentano setup. CrK_β is filtered out by vanadium (V) filter. System geometry was aligned with a standard quartz (SiO_2) sample which gave the main diffracted peak from CrK_α diffraction at 40.05° with the peak resolution finer than 0.10° (i.e. full-width at half maximum (FWHM)). The diffracted peaks from $K_{\alpha 1}$ and $K_{\alpha 2}$ were distinguished with a separation of 0.06°. Scanning range in the measurements was set between 25.00° and 150.00° in the step size of 0.05°. The step time was 0.80 s. Prior to data analysis in the DIFFRAC.EVA software (Version 4.1.1), the $K_{\alpha 2}$ contribution were stripped and the background noise levels were reduced. Fourier smooth was applied to all diffractograms. Structural evaluation was carried out by means of Bragg's law calculation together with crystal geometry equations. Phase identification was conducted with reference to the powder diffraction file (PDF) database, i.e. PDF4 + 2020 (Version 4.20.0.1). Semi-quantitative analysis was conducted to evaluate the composition of the identified phases. Rietveld refinement was conducted using FullProf Suite (The version published in July 2017) through the Match! Software (Version 3.11.2.188). The morphology analysis of synthesized particles was analyzed by scanning electron microscopy (SEM), which was performed on the JEOL JSM-6610LV scanning electron microscope. The samples were pasted onto a carbon tape on the sample holder and measured without coating of a conductive layer. The surface area of catalyst was measured by Gemini VII 2390, which employs BET nitrogen adsorption technique. ^1H NMR spectra were obtained from a Bruker Advance
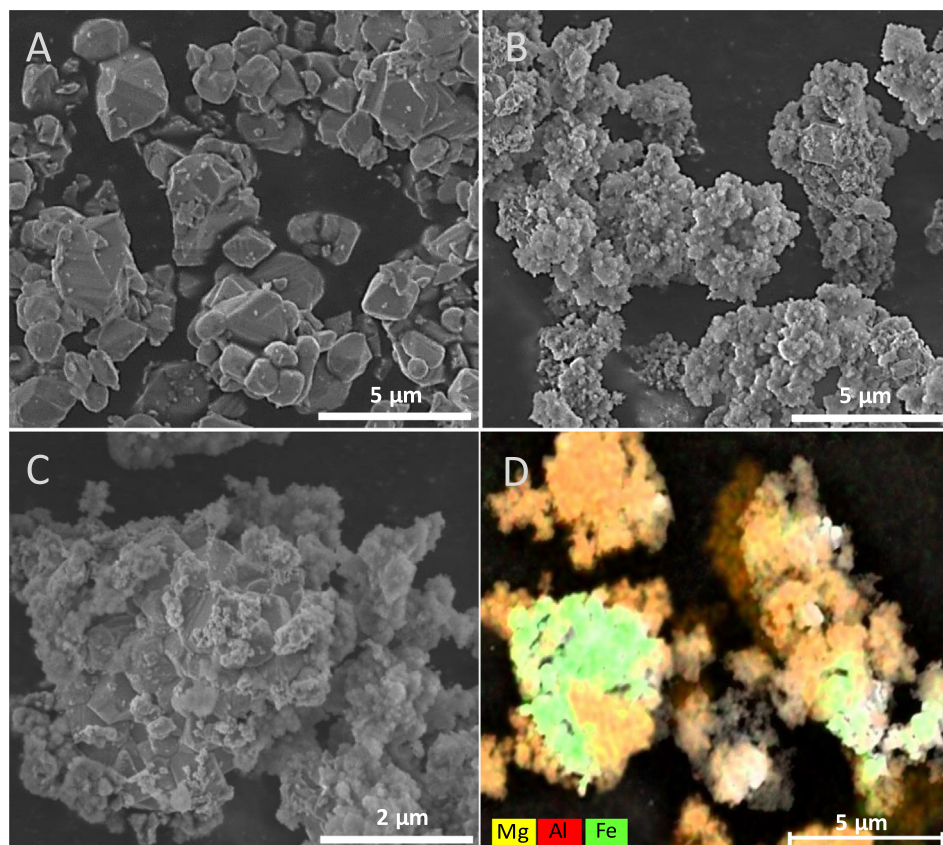

Fig. 1. SEM images of raw Fe_3O_4 micro particles and synthesized Mg-Al-O@Fe_3O_4 micro particles. A is the raw Fe_3O_4 micro particles; B is the synthesized Mg-Al-O@Fe_3O_4 micro particles; C is the synthesized Mg-Al-O@Fe_3O_4 micro particles with a higher magnification; D is an EDX image of synthesized Mg-Al-O@Fe_3O_4 micro particles.

400 spectrometer operating at 400 MHz. The solvent used to dissolve BHET was DMSO d_6.

3. Results and discussion

3.1. Characterization of the synthesized Mg-Al-O@Fe₃O₄ micro particles

As shown in Fig. 1A, the raw Fe_3O_4 micro particles are well crystallized and each crystal plane has a very smooth surface. When the Fe_3O_4 particles are coated with Mg-Al double oxides, the surface morphology is significantly changed. It is clearly seen that some nanoparticles coat on the surfaces of Fe_3O_4 particles (Fig. 1C). These nanoparticles agglomerate together and form a layer structure on the Fe_3O_4 micro particles (Fig. 1B). The coating of Mg-Al double oxides onto the Fe_3O_4 micro particles is also confirmed by an energy dispersive X-ray (EDX) mapping analysis as shown in Fig. 1D. The BET surface measurements reveal that the surface area of Mg-Al-O@Fe₃O₄ micro particles is 72.1 ± 0.0 7 m²/g which is much higher than that of Mg-Al double oxides (27.2 ± 0.09 m²/g) and Fe_3O_4 micro particles (1.24 ± 0.09 m²/ g). Therefore, the rougher surface morphology formed on the particles contributes to an increased surface area of the Mg-Al-O@Fe₃O₄ micro particles which will be beneficial for the application as catalyst.

The formed coating layer of Mg-Al double oxides is not just physically absorbed on the surface of Fe_3O_4 micro particles. The diffractogram of the synthesized Mg-Al-O@Fe₃O₄ micro particles indicates that the Mg-Al double oxides are sintered into the structure of Fe_3O_4 micro particles (Fig. 2, compare the black and green patterns). The basic structure of the raw Fe_3O_4 micro particles is determined to have a $Fe_{2.66}O_{4.00}$-like (PDF: 04-006-2472, a = 8.32 00 Å) face-centered cubic (FCC) structure with the lattice parameter of 8.3178 Å through the calculation with a crystal geometry equation for an FCC structure, but not the expected Fe_3O_4 (PDF: 04-005-4319, Fd-3 m, a = 8.3958 Å). Semi-quantitative analysis shows that $Fe_{2.66}O_4$ dominates 98.5% of the structure and only 1.5% is Fe_3O_4 (see Table S1 in support information). The raw Mg-Al double oxides are found to have three phases. They are periclase (MgO, PDF: 00-045-0946, Fm-3 m, a = 4.211 Å), brucite ($Mg(OH)_2$, PDF: 00–007-0239, P-3 m1, a = 3.147 Å; c = 4.769 Å) and spinel ($MgAl_2O_4$, PDF: 04–007-2712, Fd-3 m, a = 8.086 Å), in which the Mg-phases consists of 80% of the structure and the spinel is 20% (See Table S1 in support information). With these two diffractograms as references, the main peaks in the pattern of the particles mixture without heat treatment actually has a very similar structure as the Fe_3O_4 microparticles, but the lattice parameter is slightly smaller, i.e. 8.3108 Å. Diffractogram from the synthesized Mg-Al-O@Fe₃O₄ micro particles, indeed, shifts slightly to the left (subfigure in Fig. 2), which refers to lattice expansion after heat treatment. With this shift and the change of d-spacing of this peak, the calculated lattice parameter, a, becomes 8.3284 Å. The lattice expansion of the synthesized Mg-Al-O@Fe₃O₄ micro particles was considered to be due to the diffusion of Mg^{2+} and Al^{3+} ions into the magnetic Fe_3O_4 structure. A new spinel structure of $(Mg_{0.22}\text{-}Fe_{0.78})(Mg_{0.78}Al_{0.40}Fe_{0.82})O_4$ (PDF: 01-079-5407, Fd-3 m, a = 8.329 0 Å) is matched with this diffractogram. In addition, the small peaks at 35°, 53° and 98° which are observed in the diffractogram of mixed particles disappear in the diffractogram of synthesized Mg-Al-O@Fe₃O₄ micro particles. The transformation of these minor features also reveals the structural change of the particles during heat treatment.
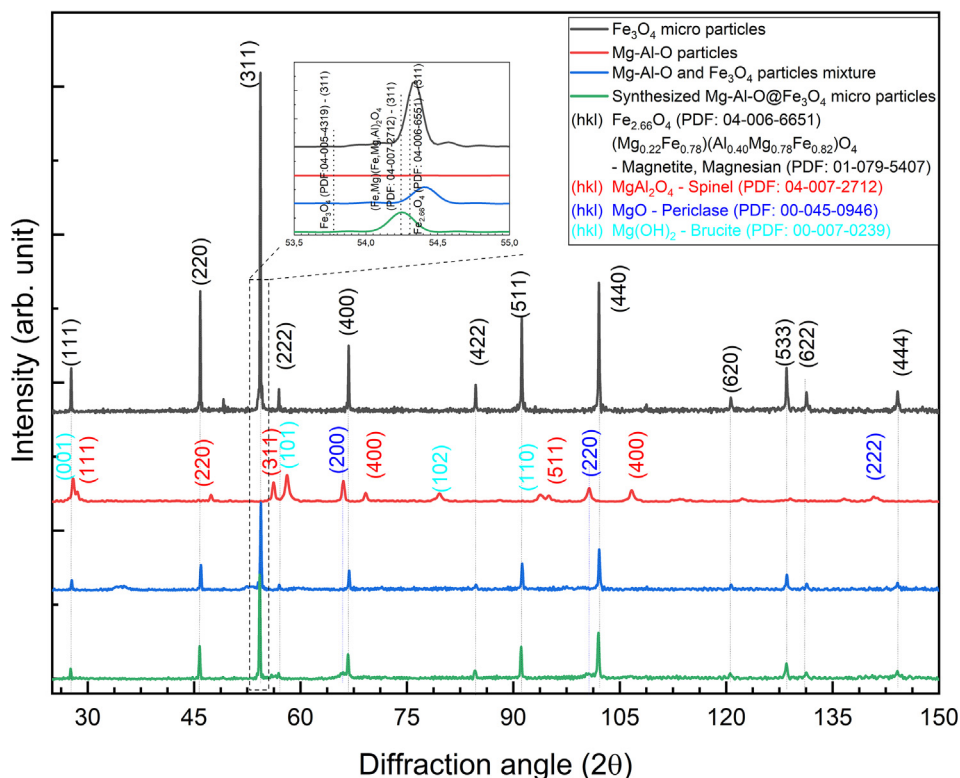

Fig. 2. Diffractograms of the raw Fe_3O_4 micro particles, the raw Mg-Al double oxides particles, the mixture of Mg-Al double oxides and Fe_3O_4 particles, and the synthesized Mg-Al-O@Fe₃O₄ micro particles. The mixture of Mg-Al double oxides and pure Fe_3O_4 was prepared by a dry mixing procedure where particles of Mg-Al double oxides and Fe_3O_4 was mixed without any additional heat treatment. The subfigure shows the zoomed-in region between 53.5° and 55°. It illustrates the position difference of the (3 1 1) peaks among the Fe_3O_4, the mixture of Mg-Al double oxides and Fe_3O_4 particles and the synthesized Mg-Al-O@Fe₃O₄ micro particles, as well as the corresponding positions for relevant PDF patterns from the database.
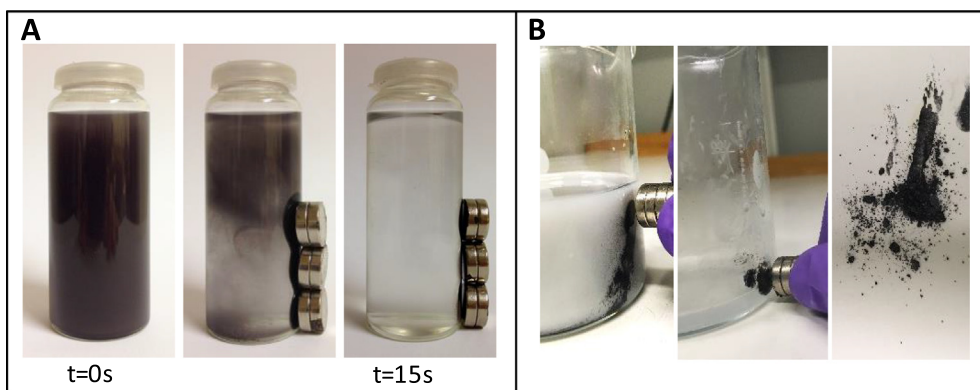
Fig. 3. A magnetic field was used to retrieve the Mg-Al-O@Fe_3O_4 micro particles from A: water and B: the reaction system.

Even though the lattice dimension of Fe_3O_4 is changed in the process when coated with Mg-Al double oxides, the magnetic properties is not lost. This allows the synthesized Mg-Al-O@ Fe_3O_4 micro particles to be retrieved from both water and the reaction system through the application of a magnetic field as shown in Fig. 3.

3.2. Mg-Al-O@ Fe_3O_4 micro catalyst performance

The synthesized Mg-Al-O@Fe_3O_4 micro particles were investigated as a catalyst in the glycolysis of PET. As comparison, the glycolysis of PET in the presence of raw Fe_3O_4 micro particles and Mg-Al double oxides were also conducted separately.

The depolymerization of PET in the absence of a catalyst does not occur. There is no BHET monomer collected within 120 min at 240 °C. When Fe_3O_4 micro particles are added into the reaction, the glycolysis starts to occur. However, the yield of monomer BHET is only around 1.6 mol%. Compared with Fe_3O_4 micro particles, Mg-Al double oxides show a much higher catalytic performance as the yield of BHET reaches 76 mol%. The high catalytic activity of Mg-Al double oxides is consistent with the literature (Chen et al., 2013). When Fe_3O_4 micro particles are coated with Mg-Al double oxides, a synergetic effect is clearly observed in the glycolysis of PET. The BHET yield reaches to 82 mol% in the presence of Mg-Al-O@Fe_3O_4 micro particles in the reaction, which is the highest value in all the tests. The enhanced catalytic performance of the synthesized Mg-Al-O@Fe_3O_4 micro particles in the glycolysis process is probably due to the creation of hierarchical structure by coating nanosized Mg-Al double oxide particles onto the Fe_3O_4 micro particles, which results in an increase of active surface area.

In addition, the catalytic stability of Mg-Al-O@Fe_3O_4 micro particles is also studied since the catalyst has to be immersed in water during the purification of BHET monomer. The water molecules may deactivate the catalyst. To study this, the virgin Mg-Al-O@Fe_3O_4 micro particles were put in deionized water overnight and then collected by the magnetic decantation. The collected particles were dried at 90 °C for 120 min. The Mg-Al-O@Fe_3O_4 micro particles retrieved from the water still show a very high catalytic performance with a BHET yield of around 80 mol%, which is comparable to the BHET yield in the presence of the virgin Mg-Al-O@Fe_3O_4 micro particles. Thus, it can be concluded that the catalytic properties of Mg-Al-O@Fe_3O_4 micro particles are not influenced by the exposure to water.

3.3. Optimization of glycolysis process

The glycolysis process catalyzed by Mg-Al-O@Fe_3O_4 micro particles is optimized in terms of catalyst concentration, reaction temperature and reaction time, respectively.

3.3.1. Catalyst concentration

As presented in Fig. 4A, Mg-Al-O@Fe_3O_4 micro particles work very efficient in catalyzing the glycolysis of PET. In the absence of Mg-Al-O@Fe_3O_4 micro particles, no glycolysis occurs. However, when there is 0.1 wt% of Mg-Al-O@Fe_3O_4 micro particles in the reaction system, the yield of BHET increases from 0 to 70 mol%. As the concentration of Mg-Al-O@Fe_3O_4 micro particles increases, the yield of BHET continues to increase, until it reaches the maximal value when the concentration of Mg-Al-O@Fe_3O_4 micro
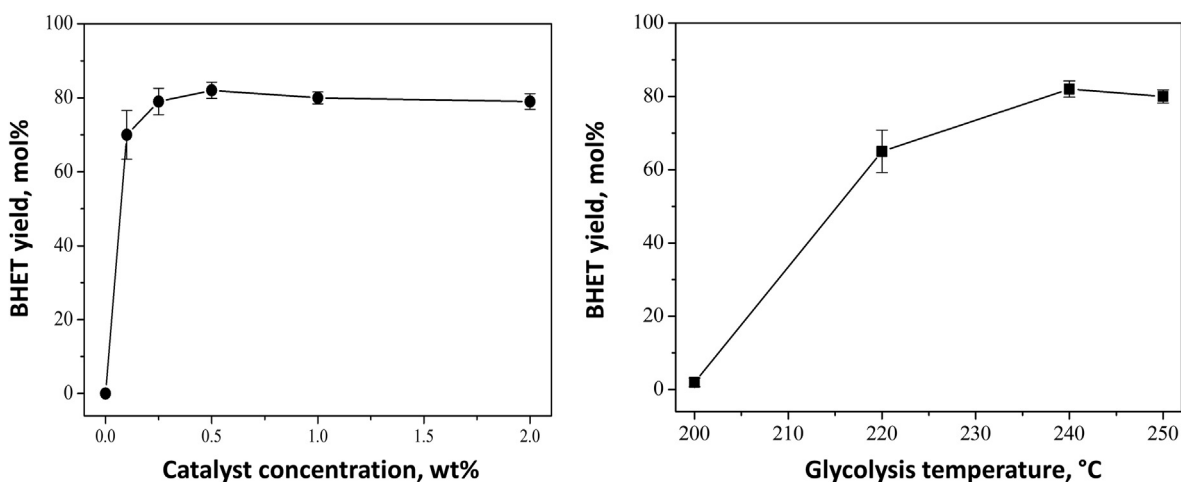

Fig. 4. Mg-Al-O@Fe_3O_4 micro catalyst performance. A is the BHET yield as a function of catalyst concentration; B is the BHET yield as a function of glycolysis temperature.
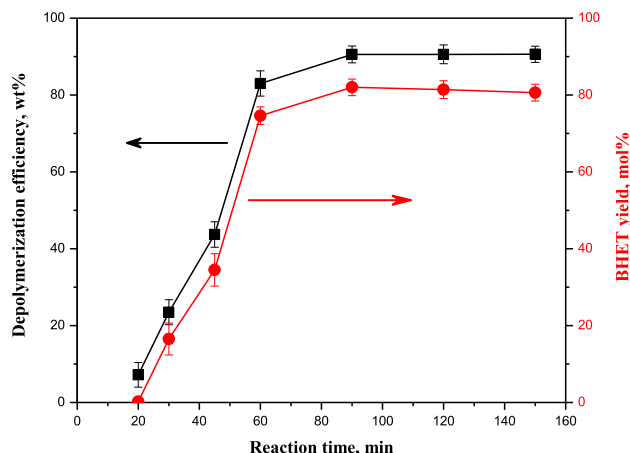
Fig. 5. Catalyst efficiency as a function of reaction time.

particles is 0.5 wt%. A further increase of the concentration of Mg-Al-O@Fe_3O_4 micro particles does not lead to an improvement of BHET yield. On the contrary, a slight decrease of the BHET yield is obtained when catalyst concentrations above 0.5 wt% is used. The decrease of BHET is probably due to the reformation of oligomers from BHET (Imran et al., 2010).

3.3.2. Reaction temperature

The reaction temperature is a very critical parameter in the glycolysis of PET since the glycolysis of PET is an endothermic reaction (Imran et al., 2010; Chen et al., 2013). The high reaction temperature favors the generation of BHET monomer. In our previous work, it was also found that the glycolysis reaction in the presence of catalyst is temperature dependent (Guo et al., 2018). In this study, the glycolysis of PET was carried out in a temperature range between 200 °C and 250 °C to investigate the influence of the reaction temperature on the catalytic performance of Mg-Al-O@Fe_3O_4 micro particles. As shown in Fig. 4B, the micro catalyst is not able to trigger the reaction at the temperature of 200 °C. However, the glycolysis shows a significant increase in the BHET yield when the temperature is raised to 220 °C. A yield of 82 mol% is reached at 240 °C, while a further increase of the temperature leads to a slight decrease of the BHET yield. This might be due to that high temperatures also can contribute to the formation of oligomers (Imran et al., 2010).

3.3.3. Reaction time

As shown in Fig. 5, Mg-Al-O@Fe_3O_4 micro catalyst shows a high depolymerization rate in the glycolysis of PET. After 20 min, already around 7 wt% of PET is depolymerized even though no BHET is collected. This is probably because BHET is still soluble

in water at the low temperatures. Thus, the generated BHET, which dissolves in water, is lost during the purification process. When the reaction time increases to 30 min, 16.5 mol% of BHET is collected. Under this reaction condition, the depolymerization efficiency reaches up to 23.5 wt%. As the reaction time further increases, both depolymerization efficiency and BHET yield continue to improve. The maximum depolymerization efficiency and BHET yield are achieved at the reaction time of 90 min with the maximal values of 90.5 wt% and 82 mol%, respectively. A further increase of the reaction time does not improve the depolymerization efficiency and BHET yield. Thus, it reveals that the glycolysis of PET in the presence of 0.5 wt% of Mg-Al-O@Fe_3O_4 micro catalyst reaches a depolymerization equilibrium after a reaction time of 90 min.

3.4. Recycling of catalyst

One of the key objectives of this study was to design and synthesize a catalyst which is easy to recover and reuse. The application of such a sustainable catalyst would reduce the consumption of new resources to manufacture the catalyst and decrease the overall cost of the glycolysis process. To test the recyclability of Mg-Al-O@Fe_3O_4 micro catalyst in the glycolysis process, the micro catalyst was collected by magnetic decantation after each glycolysis reaction, washed by deionized water and dried for the next run. As presented in Fig. 6A, the Mg-Al-O@Fe_3O_4 micro catalyst shows a high catalytic activity in the glycolysis reaction the first two times they are used consecutively. After that, the Mg-Al-O@Fe_3O_4 micro catalyst shows an obvious decrease in its catalytic activity. For the fourth time, the micro catalyst almost loses its catalytic effect. However, the loss of catalytic activity is not due to stripping of the coating layer of Mg-Al double oxides. As revealed in Fig. 6B, the magnetic Mg-Al-O@Fe_3O_4 micro catalyst still keeps its intact structure with a dense coverage of Mg-Al double oxides around Fe_3O_4 micro particles. The temporary loss of catalytic activity is probably due to the absorption of organic PET oligomers and monomer which block the active sites of catalyst. The deactivated Mg-Al-O@Fe_3O_4 micro catalyst can however be regenerated by heat treatment at 1000 °C. As can be seen in Experiment R in Fig. 6A (green column), the regenerated catalyst shows again a high catalytic performance, and is comparable to the virgin catalyst.

3.5. BHET monomer

The recovered monomer was analyzed by NMR. A high purity of the recovered BHET is confirmed by NMR analysis. As shown in Fig. 7, the signal at δ 3.7 ppm (peak 2) represents the protons of the methylene of —CH_2—OH group, the signals at δ 4.3 ppm (peak 3) and 4.9 ppm (peak 1) indicate the protons of the methylene
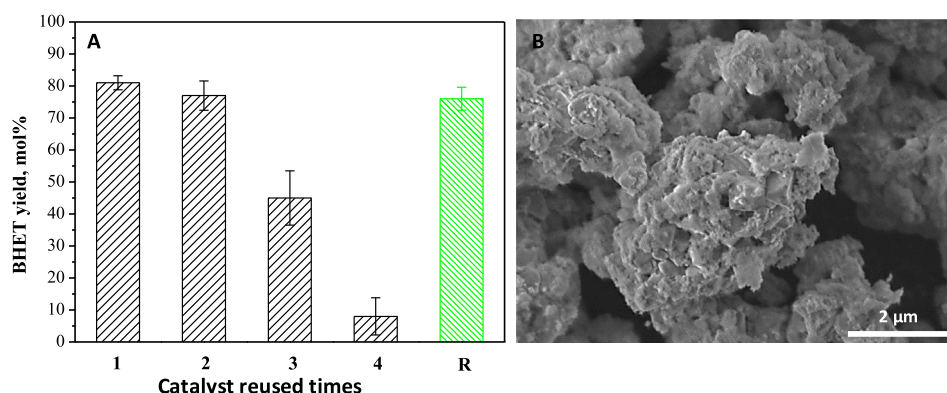

Fig. 6. The catalytic efficiency of the Mg-Al-O@Fe_3O_4 micro particles in the glycolysis of PET when the catalyst was reused up to 4 times and R represents the regenerated catalyst. B is the SEM image of deactivated Mg-Al-O@Fe_3O_4 micro catalyst after reusing for 4 times.
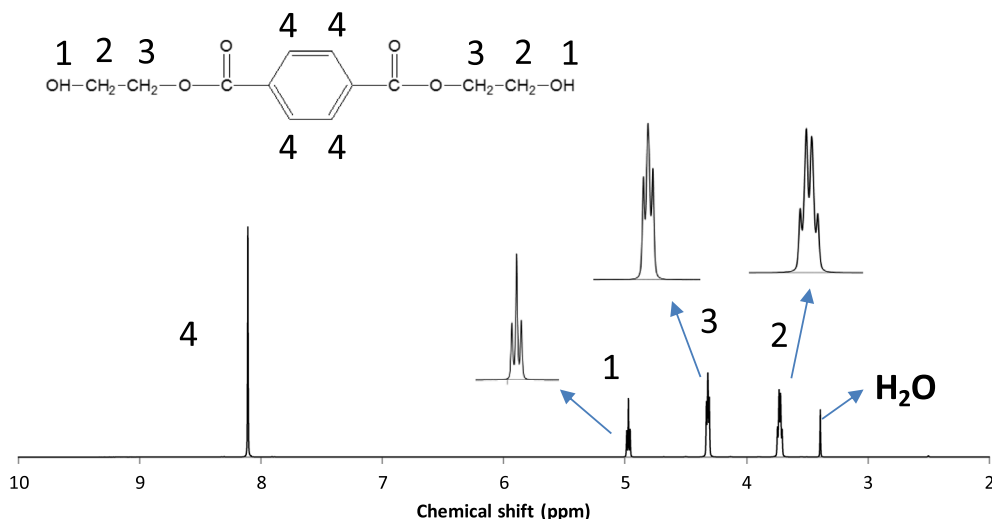
Fig. 7. NMR analysis of recovered BHET monomer.

Table 1
Comparison of different catalysts in the glycolysis of PET.

Catalyst	Catalyst concentration wt%	Reaction temperature °C	Reaction time, min	BHET yield, mol%	Recyclability	Cost, $/kg
Zinc acetate	0.5–1	198	480	75	difficult	2.1
γ-Fe_2O_3 nanoparticles	5–10	255–300	60–80	80–90	easy	10–65
Fe_3O_4-boosted MWCNT	5	190	120	100	easy	550–1200
Mg-Al-O@Fe_3O_4	0.5	240	90	82	easy	3.2

close to COO— group and the proton in hydroxyl group. The signal at δ 8.1 ppm (peak 4) is characteristic of the four aromatic protons. The NMR spectrum is consistent with those reported in the literature (Imran et al., 2010).

According to our previous work, the presence of unremoved catalysts can influence the subsequent re-polymerization and thus reduce the quality of the regenerated PET fibers. To investigate presence of unremoved catalyst in the recovered BHET monomer, inductively coupled plasma mass spectrometry (ICP-MS) analysis was conducted. As comparison, the commercial BHET from Sigma-Aldrich was used as a refence. As summarised in Table S2 (see support information), all three ions are present in very low concentrations in both the commercial BHET and the recovered BHET, and are below the detection limit of ICP-MS. The result indicates that the catalyst is totally removed after the reactions.

3.6. Comparison Mg-Al-O@Fe_3O_4 with other different catalysts

The Mg-Al-O@Fe_3O_4 micro catalyst developed in this study was compared with other catalysts, to estimate their potential application in a scale-up recycling process. Table 1 shows the estimated cost of the catalyst developed in this study. As comparison, the estimated costs of other catalysts which are reported in the literature are also included in the table (the cost calculations are presented in supporting information).

Furthermore Table 1 summarizes that Fe_3O_4-boosted MWCNT catalyst is the best catalyst in the glycolysis of PET in terms of the BHET yield. A 100% of BHET yield is reported to be achieved in the presence of 5 wt% of catalyst at 190 °C for 120 min. However, the high cost of Fe_3O_4-boosted MWCNT catalyst and high catalyst concentration will probably limit the application of this catalyst in a large-scale recycling process. The Mg-Al-O@Fe_3O_4 micro catalyst developed by us, however, seems to be a very promising recyclable catalyst in the glycolysis of PET. Compared with Fe_3O_4-boosted MWCNT catalyst, Mg-Al-O@Fe_3O_4 micro catalyst shows a relatively lower BHET yield but still over 80 mol%. While, the esti-

mated cost of Mg-Al-O@Fe_3O_4 micro catalyst is only 3.2 $/Kg which is much cheaper than Fe_3O_4-boosted MWCNT catalyst. In addition, a very low catalyst concentration (0.5 wt%) is needed to achieve a high catalytic performance. Therefore, we believe that Mg-Al-O@Fe_3O_4 micro catalyst may be a very promising catalyst in the large-scale chemical recycling of PET fiber waste.

4. Conclusions

Here we demonstrate nanosized Mg-Al double oxides that are sintered onto magnetic Fe_3O_4 micro particles. The formed hierarchical structure attributes a high active surface area to the synthesized Mg-Al-O@Fe_3O_4 micro particles, which renders these micro particles a high catalytic performance in the glycolysis of PET. A BHET yield of over 80 mol% is achieved in the presence of 0.5 wt% of Mg-Al-O@Fe_3O_4 micro particles at 240 °C for 90 min. The synthesized Mg-Al-O@Fe_3O_4 micro catalyst displays good magnetic property which can be easily retrieved and reused. After the first two times they are used consecutively, the deactivated catalyst can be regenerated by heat treatment. The regenerated catalyst shows similar catalytic performance as virgin catalyst. In addition, the Mg-Al double oxides and Fe_3O_4 micro particles are low-cost and environmentally benign. Therefore, this synthesized Mg-Al-O@Fe_3O_4 micro catalyst may contribute to an economically and environmentally improved large-scale circular recycling of PET fiber waste.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.wasman.2021.03.049.

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