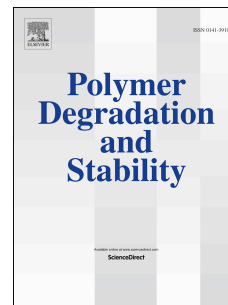


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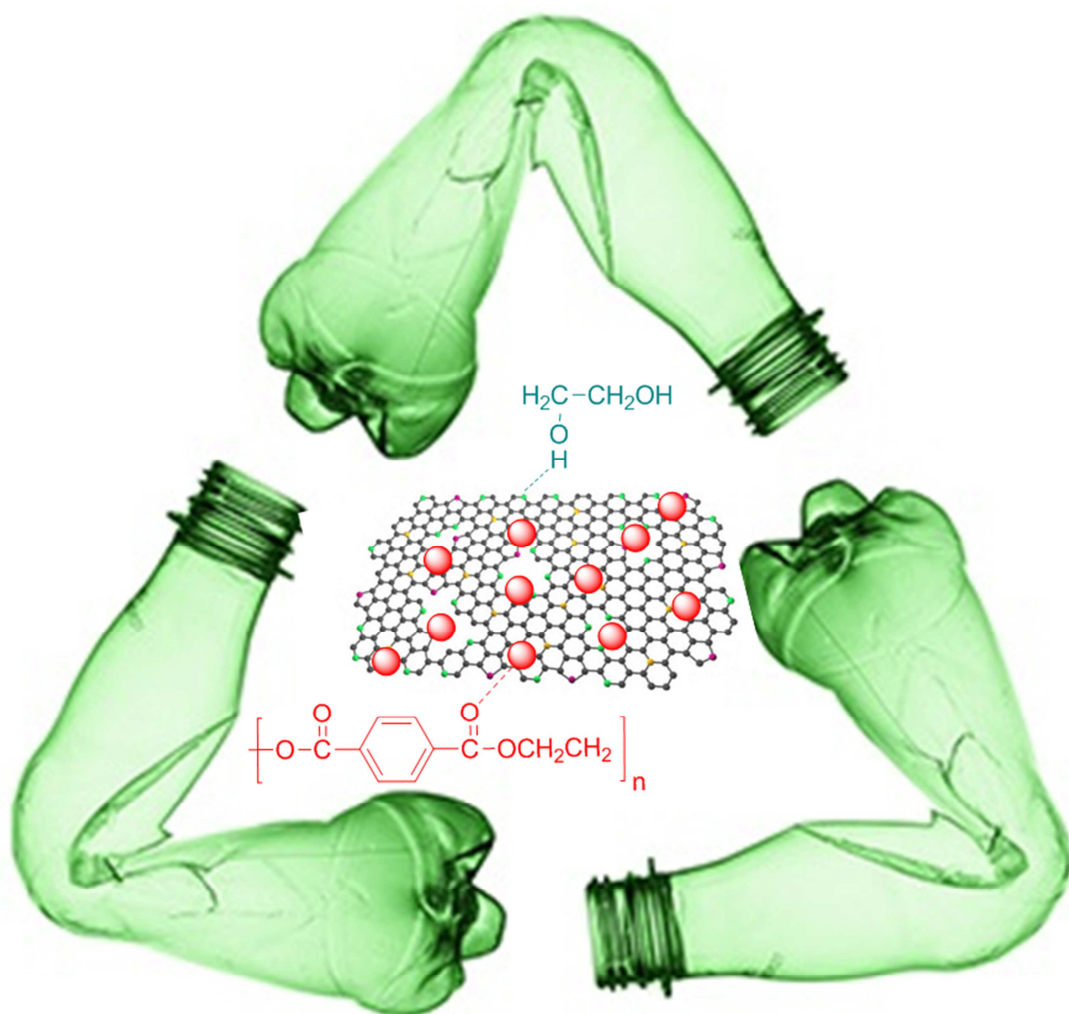
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ACCEPT 1

**Maghemite/nitrogen-doped graphene hybrid material as a reusable bifunctional catalyst
for glycolysis of polyethylene terephthalate**

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Abstract

In this paper, we present superparamagnetic γ -Fe₂O₃/nitrogen-doped graphene hybrid material as an efficient and environment-friendly bifunctional catalyst for a sustainable polyethylene terephthalate chemical recycling. The presented catalyst exhibit superparamagnetic behavior because of the infinitely small coercivity arising from the negligible energy barrier in the hysteresis of the magnetization loop. By magnetic recovering of the catalyst, the danger of releasing harmful catalyst components to the environment is reduced and the process becomes more cost-effective and sustainable. To the best of our knowledge, bifunctional catalyst including acidic and basic sites have never been used in any glycolysis reactions, particularly for polyethylene terephthalate. The catalytic activity of nitrogen-doped graphene and γ -Fe₂O₃ are also investigated which show the synergetic catalytic activity of γ -Fe₂O₃/nitrogen-doped graphene nanocomposite.

Keywords: Doped graphene; Fe₂O₃; Catalysis; glycolysis; polyethylene terephthalate.

1. Introduction

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The effective recycling of polyethylene terephthalate (PET) has attracted considerable attention in the field of sustainable technology and resource conservation [1]. PET, one of the most important industrial polymers produced today, is a semi-crystalline, thermoplastic polyester with thermal stability, clarity, transparency, light, and processability. Because of these excellent properties, PET is produced in considerable amount and is used in the manufacture of high strength fibers, X-ray films, soft drink bottles and in textile industry [2]. Increased world consumption of PET which has grown by 4.5% per year from 2010 to 2015 results in serious environmental problems [3]. Among the primary (re-extrusion), secondary (mechanical), tertiary (chemical) and quaternary (energy recovery) methods for recycling waste PET [4], chemical route is preponderant because it can reproduce virgin monomer products [5]. Several chemical recycling methods such as alcoholysis, aminolysis, ammonolysis, hydrolysis, and glycolysis have been reported [6-8]. Glycolysis offers some important advantages including milder reaction conditions, less volatility of the solvent, and giving bis(hydroxyethyl) terephthalate (BHET) which can be employed to produce dimethyl terephthalate-based or terephthalic acid-based PET production lines, textile softener, and unsaturated polyester resins [9, 10]. The glycolysis reaction is very slow in the absence of catalyst. So, various catalysts such as titanium-phosphate, carbonate, sulfate, and metal acetates are used for glycolysis reaction [11-13]. Some of the drawbacks of these catalyst includes impurity of products, existence of side reactions, and difficulty in separating product from catalyst.

Ionic liquids and metal oxides are the two recent catalysts [14, 15] which using metal oxides could be better option because of the ease of synthesis. Moreover high monomer yield, ease of recovery, reusability, high mechanical strength, and long shelf life make metal oxides unique among the catalysts [16]. Recently, various metal oxides-based heterogeneous catalysts have

been tested in the glycolysis of PET [17-19], which γ -Fe₂O₃ could be an ideal option due to the cheapness, nontoxicity, abundance, and magnetic recyclability. Imran et al. reported that the mixed-oxide spinels showed high catalytic activity for PET glycolysis at 260°C under 5.0 atm [17]. In another report, more than 90% yield of BHET was obtained after glycolysis at 300°C using γ -Fe₂O₃ nanoparticles [20]. However, the pristine metal oxides nanoparticles suffer from irreversible aggregation reducing their dispersion. Among the various methods to overcome these problems, we chose graphene as an attractive support because of the high specific surface area, unique planar structure, low density, flexibility, and thermal and chemical stability [21-23]. The metal oxide/graphene composite has been prepared through various methods. The hydrothermal reduction of metal salts and graphene oxide (GO) is widely used, owing to the simple operation and the low cost. The heteroatom doping does not only contribute to additional catalytic activity of graphene but also enhances the interaction between metal oxide or metal nanoparticles and graphene to improve the chemical stability of the composites [24]. Nitrogen doping provides additional electrons for the graphitic lattice and results in metallic or semi-conductive character [25]. N-doped graphene has been reported to be metal free catalyst for selective oxidation of benzylic alcohols and ethylbenzene [26], Knoevenagel and transesterification reactions [27] as well as the esterification of fatty acids [28].

The difficult synthesis of the catalysts, low activity as well as the need for high temperatures and high pressures limits the use of most of the previously reported catalysts in the glycolysis of PET. Therefore, development of green, efficient, easily recyclable and low-cost catalysts as well as the milder conditions and higher rates are highly desirable. In this work, for the first time a bifunctional catalyst has been introduced for glycolysis of PET.

Investigation of interaction between reactants and the catalyst is necessary to provide useful information for designing efficient catalysts. It has been found that catalysts bearing functional groups with ability to form H-bonds with EG and subsequently activation of the oxygen of the hydroxyl in EG represents high activity for glycolysis of PET. The chloride and bromine ions, carbonyls, and amines are such a groups. On the other hand, a catalyst with groups interacting with the oxygen of PET carbonyls results in more partial positive charge on the carbon of PET carbonyls and then promotes the disruption of the PET chain. So, Our approach was guided by four imperatives: (i) the catalyst should have the groups with ability to form H-bonds with EG or acting as a base (ii) the catalyst should have the groups interacting with the oxygen of PET or acting as an acid, (iii) the catalyst should be magnetic which can be easily recycled and (iv) the development of an efficient process for PET recycling under the mild conditions.

2. Experimental

2.1. Materials

Graphite powder (325 mesh), sulfuric acid (H_2SO_4), potassium peroxodisulfate ($\text{K}_2\text{S}_2\text{O}_8$), diphosphorus pentoxide (P_2O_5), potassium permanganate (KMnO_4), hydrogen peroxide (H_2O_2), iron(II) sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), and ammonia solution ($\text{NH}_3 \cdot \text{H}_2\text{O}$) were purchased from Merck Chem. All other chemicals were purchased from Aldrich or Merck companies and used as received without any further purification.

2.2. Instruments and characterization

Transmission electron microscopy (TEM) was performed by LEO 912AB electron microscope. Thermogravimetric analysis (TGA) was carried out using STA 1500 instrument at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ in air. X-ray powder diffraction (XRD) data were collected on an XD-3A diffractometer using $\text{Cu K}\alpha$ radiation. X-ray photoelectron spectroscopy (XPS) was performed

using a VG multilab 2000 spectrometer (ThermoVG scientific) in an ultrahigh vacuum. Scanning electron microscope (SEM) was performed on a Zeiss Supra 55 VP SEM instrument. AA-680 Shimadzu (Kyoto, Japan) flame atomic absorption spectrometer (AAS) with a deuterium background corrector was used for determination of the metal. The magnetization of the samples in a variable magnetic field was measured using a vibrating sample magnetometer (VSM) with a sensitivity of 10^{-3} EMU and a magnetic field of up to 8 kOe. The magnetic field was changed uniformly at a rate of 66 Oe s^{-1} . ^1H NMR spectra were recorded with a BRUKER DRX-300 AVANCE spectrometer, and $\text{DMSO-}d_6$ was used as solvent.

2.3. Synthesis of graphene oxide (GO)

Graphene oxide (GO) was prepared through a modified Hummers method [29, 30]. Graphite powders were first oxidized by sulfuric acid. Then 2.5 g of the graphite powder was treated with a solution by mixing 12.5 ml of concentrated H_2SO_4 with 2.5 g $\text{K}_2\text{S}_2\text{O}_8$ and 2.5 g P_2O_5 . The mixture was kept at 80 °C for 6 h using a hotplate. Subsequently, the mixture was cooled to room temperature and diluted with 500 mL de-ionized (DI) water and left overnight. The mixture was then filtered and washed with DI water to remove the residual acid. The product was dried under ambient conditions overnight. The pretreated graphite powder was put into cold (0 °C) concentrated H_2SO_4 (125 ml). Then KMnO_4 (15 g) was added gradually under stirring, and the temperature of the mixture was kept below 20 °C by cooling. The mixture was then stirred at 35 °C for 4 h and then diluted with DI water (250 ml). Because adding water to concentrated sulfuric acid medium releases a large amount of heat, the dilution was carried out in an ice bath to keep the temperature below 50 °C. After adding all of the 250 mL DI water, the mixture was stirred for 2 h, and then an additional 750 mL DI water was added. Shortly thereafter, 20 ml 30% H_2O_2 was added to the mixture and the color of the mixture changed into brilliant yellow and

began bubbling. The mixture was filtered and washed with 0.1 M HCl to remove metal ions, followed by 500 mL DI water to remove the acid. The resulting GO solid was dried in air.

2.4. Synthesis of γ -Fe₂O₃/nitrogen-doped graphene hybrid material

Fe₂O₃/nitrogen-doped graphene hybrid material was prepared by the following process. 125 mg of graphite oxide was dispersed in 54 mL of H₂O and sonicated for 10 min. Then, 200 mg of FeSO₄·7H₂O was added into GO suspension followed by intense agitation for 10 min. Then, 6 mL of NH₃·H₂O (30%) was added dropwise for 30 min, and then, the as-obtained brown viscous suspension was transferred into a stainless steel vessel and subjected to the hydrothermal reduction at 180 °C for 12 h. The mixture was filtered and washed with DI water and α -Fe₂O₃/nitrogen-doped graphene hybrid material was dried in oven. The as-prepared material was further mixed with ethylene glycol (EG) as an oxidant and refluxed at 200°C for 5 h to obtain γ -Fe₂O₃/nitrogen-doped graphene hybrid material [31]. For comparison purposes, pure γ -Fe₂O₃ nanoparticles and nitrogen-doped graphene were fabricated. The γ -Fe₂O₃ nanoparticles were produced by calcining Fe₃O₄ nanoparticles prepared through the traditional co-precipitation method [32, 33]. Nitrogen-doped graphene was synthesized with a combined hydrothermal and freeze-drying process [34].

2.5. General procedure for the glycolysis of PET

A round-bottom flask equipped with a reflux condenser was loaded with 0.3 g of PET, 4 g of EG, and a certain amount of catalyst. The glycolysis reaction was carried out under atmospheric pressure at 195 °C. The flask was immersed in an oil bath at a specific temperature for the required time. After the reaction, the glycolysis product was dissolved in water at 90 °C, in which BHET, its dimers, and EG are soluble. From this solution, the catalyst was recovered via simple magnetic decantation. The recovered catalyst was washed with deoxygenated DI water

three times, dried, and reused. BHET from the glycolysis product was also recovered for further characterization. After the catalyst was recovered, the solution was kept at 90 °C for 45 min under vigorous stirring. The PET residual was separated from the mixture through filtration. When the resulting filtrate reached 60 °C, it was refiltered to remove the dimers from the BHET monomers. The resulting filtrate from the second filtration was refrigerated for 24 h, and then filtered to recover the monomer BHET. The recovered BHET crystals were dried, and characterized by NMR.

3. Results and discussion

3.1. Synthesis and recognition of the catalyst

Owing to the abundant oxygen-containing functional groups on the surface of GO comprising carboxyl, hydroxyl and epoxy groups, GO is negatively charged. After stirring Fe^{2+} with GO suspension, the oxidation by GO and air lead to the formation of Fe^{3+} on GO sheets. Adding ammonia solution gives $\text{Fe}(\text{OH})_3$ nanoparticles on GO which undergoes hydrothermal reaction to produce Fe_2O_3 /nitrogen-doped graphene. To prepare $\gamma\text{-Fe}_2\text{O}_3$ /nitrogen-doped graphene, the as-prepared material was further mixed with EG as an oxidant and refluxed. According to the amount of Fe determined by AAS, Fe_2O_3 content in the as-obtained catalyst was estimated to be 4.6 mmol/g.

Morphological structure of the resulting $\gamma\text{-Fe}_2\text{O}_3$ /nitrogen-doped graphene hybrid material has been verified by SEM and TEM as shown in Figure 1. Fe_2O_3 nanoparticles with sphere-like morphology in the size of 20–70 nm and well dispersed on the surfaces of N-doped graphene can be observed from both SEM (Figure 1A) and TEM (Figure 1B) images.

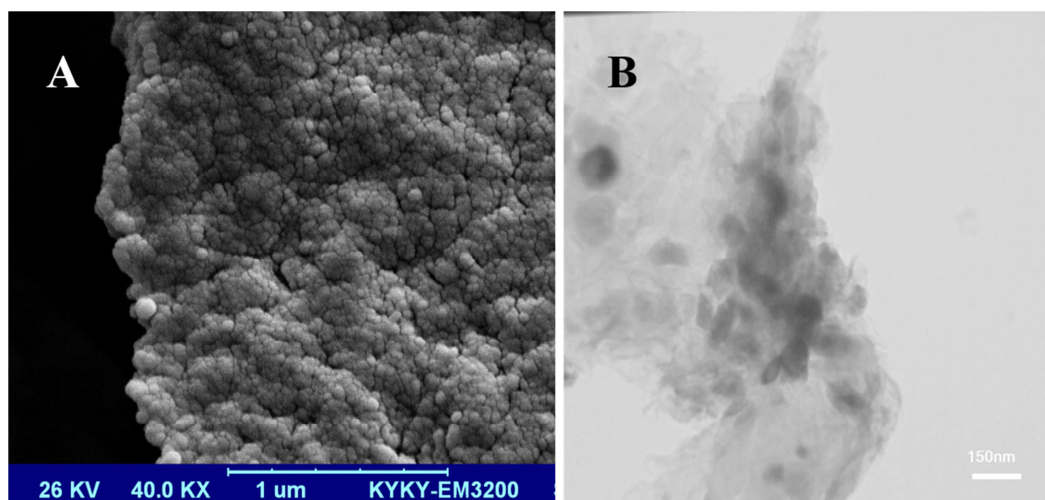


Fig. 1. SEM and TEM images of γ -Fe₂O₃/N-doped graphene hybrid material (A and B).

X-ray powder diffraction (XRD) has been used to determine the crystalline structure of the resulting α and γ -Fe₂O₃/N-doped graphene hybrid material as shown in Figure 2. For α -Fe₂O₃/N-doped graphene, it exhibits a series of peaks at 24, 33.0, 35.5, 40.7, 49.3, 53.9, 57.3, 62.3, 63.9, 71.7, and 75.4° which respectively be related to (012), (104), (113), (024), (116), (018), (214), (300), (101), and (220) crystal planes of synthesized hematite (namely α -Fe₂O₃, JCP DS no. 33-0363). XRD data also indicated that α -Fe₂O₃ of the as-obtained material had an orthorhombic structure. There was no indication of any other additional phases, demonstrating its high purity and crystallinity. GO has been converted to graphene in the hydrothermal process, but the peak of graphene at \sim 24° almost overlaps with the main peak of Fe₂O₃ (012). There are six peaks at 30.3, 35.6, 43.3, 53.8, 57.2 and 62.8° ascribed to (220), (311), (400), (422), (511) and (440) planes of the standard XRD data for the cubic spinal crystal of the bulk maghemite (namely γ -Fe₂O₃, JCPDS NO. 04-0755). The major broad peak of N-doped graphene is observed at \sim 24.0°. The XRD peaks of two samples show good broadening, indicating the ultrafine nature of the Fe₂O₃ particles.

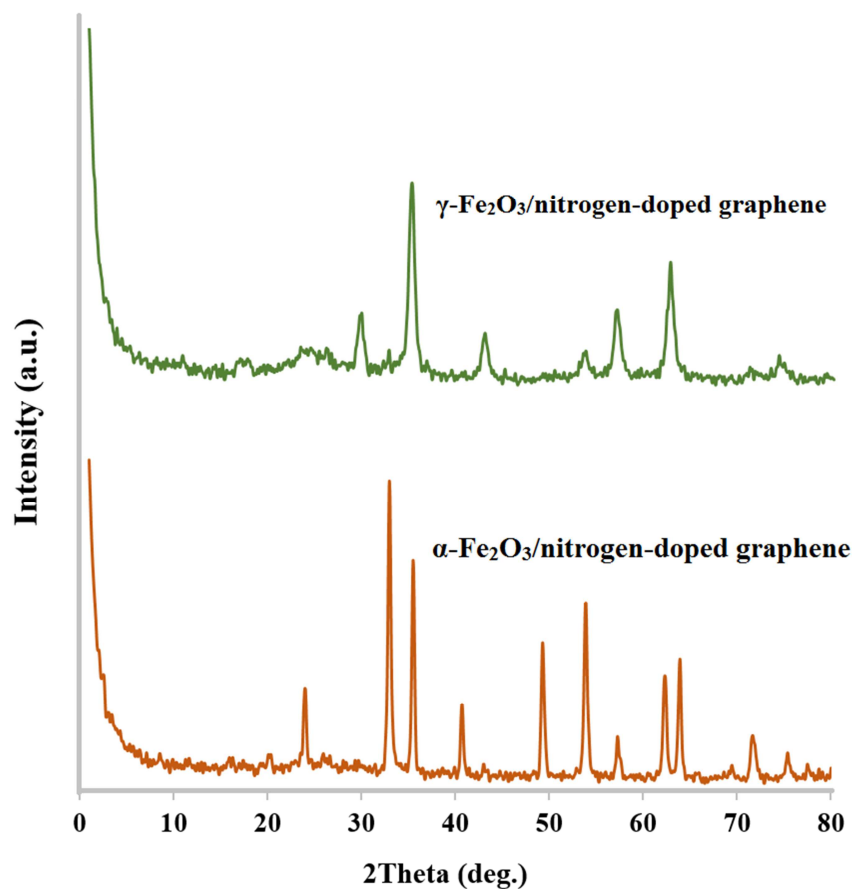


Fig. 2. XRD patterns of α -Fe₂O₃/N-doped graphene hybrid material (A) and γ -Fe₂O₃/N-doped graphene hybrid material (B).

TGA and DTA curves of γ -Fe₂O₃/N-doped graphene were obtained and presented in Figure 3. TGA measurement was used to determine the loading amount of Fe₂O₃ in the hybrid material. In this experiment, the sample is heated to 780°C under air atmosphere at a heating rate of 10 °C/min and a change in mass loss was recorded. The weight loss between 220–550 °C can be ascribed to the combustion of graphene. Therefore, the content of Fe₂O₃ in the as obtained hybrid material was calculated to be 75 wt%.

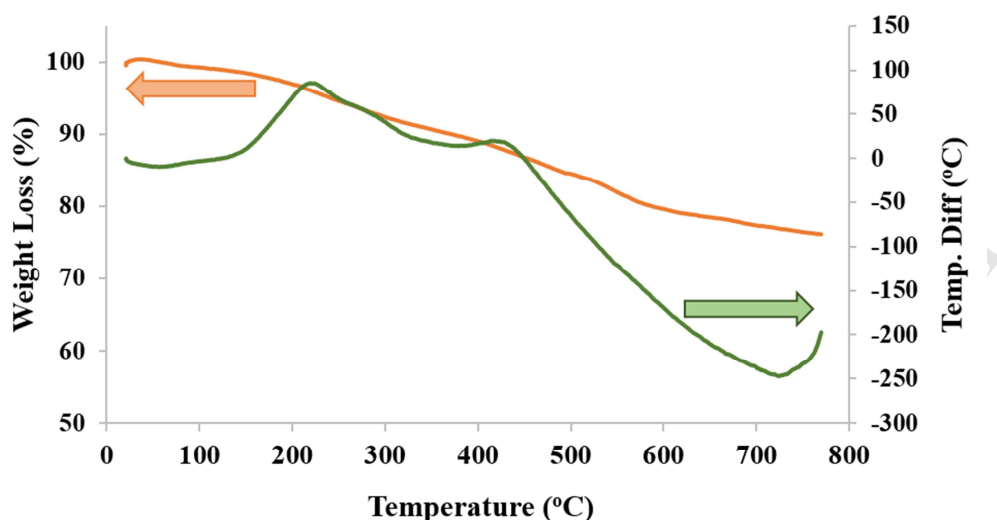


Fig. 3. TGA and DTA curves of γ -Fe₂O₃/N-doped graphene hybrid material.

To investigate the electronic structure and composition of the as-prepared hybrid material in detail, the XPS study was carried out. The XPS survey scan of γ -Fe₂O₃/N-doped graphene (Figure 4A) shows four key elements, C, O, N, and Fe, in the sample. The presence of nitrogen with the atom percentage of 3.1% confirms the successful doping of nitrogen into graphene sheets. The high resolution XPS C 1s spectrum (Figure 4B) can be deconvoluted into three subpeaks, indicating the existence of three types of carbon. The peaks at 284.6, 285.4, and 286.5 eV are assigned to graphite-like sp² C (C-C linkage), C-N, and C=O linkages. The presence of the peak at 285.4 eV attributed to C-N confirms the substitution of the nitrogen atoms within graphene sheets [35, 36]. It is noteworthy that the lower intensity of C=O linkage peak at 286.5 eV means that the GO was well reduced to graphene. The high-resolution spectrum of Fe 2p in Fig. 4C obviously shows two peaks at 711.9 eV and 726.0 eV related to Fe 2p_{3/2} and Fe 2p_{1/2}, respectively, with a satellite peak at 720.8 eV, characteristic of Fe₂O₃ [37].

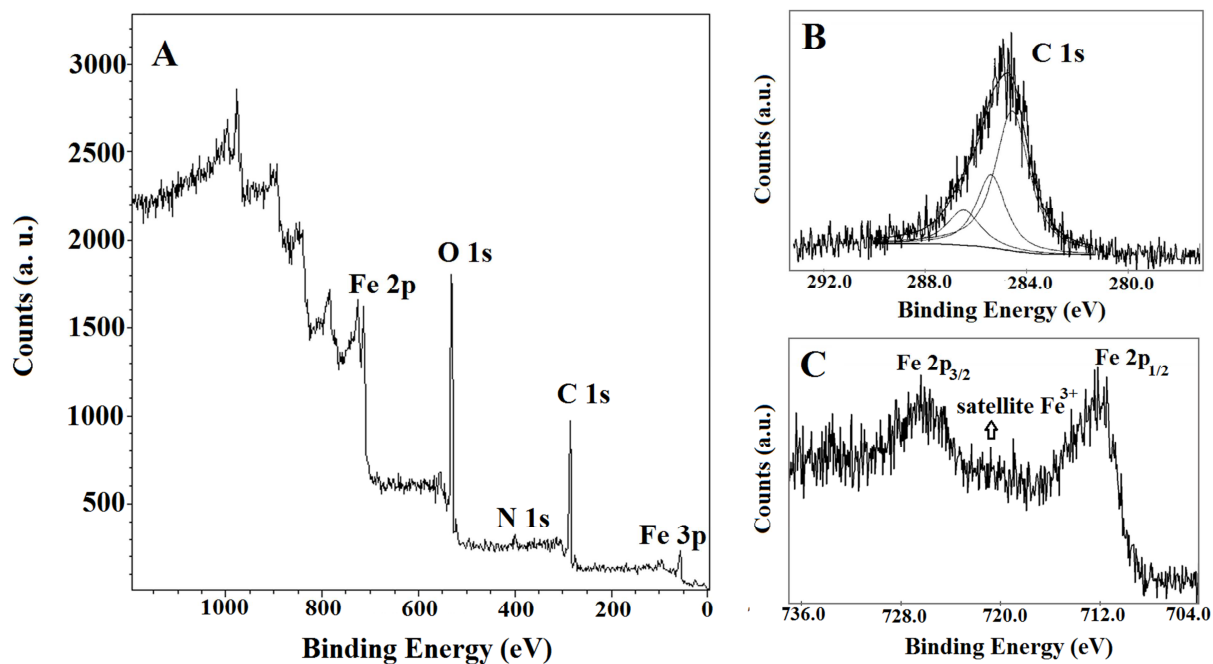


Fig. 4. XPS spectrum of γ -Fe₂O₃/N-doped graphene hybrid material, and high resolution XPS spectra of C 1s and Fe 2p.

The magnetic properties of the γ -Fe₂O₃/N-doped graphene hybrid material was studied by VSM. Figure 5 shows the magnetization as a function of applied magnetic field, measured at room temperature. It shows the magnetization saturation at relatively low external field (~2500 Oe) which indicates a narrow particle-size distribution and a good crystallinity of the maghemite nanoparticles. The as-prepared hybrid material exhibited a value of saturation magnetization as high as 39.4 emu/g which is far from the value expected for bulk γ -Fe₂O₃ crystallite (i.e., 73.5 emu/g). The results show no hysteresis at room temperature and zero values for both retentivity and coercivity corresponded to the superparamagnetic behavior expected from the Mössbauer results.

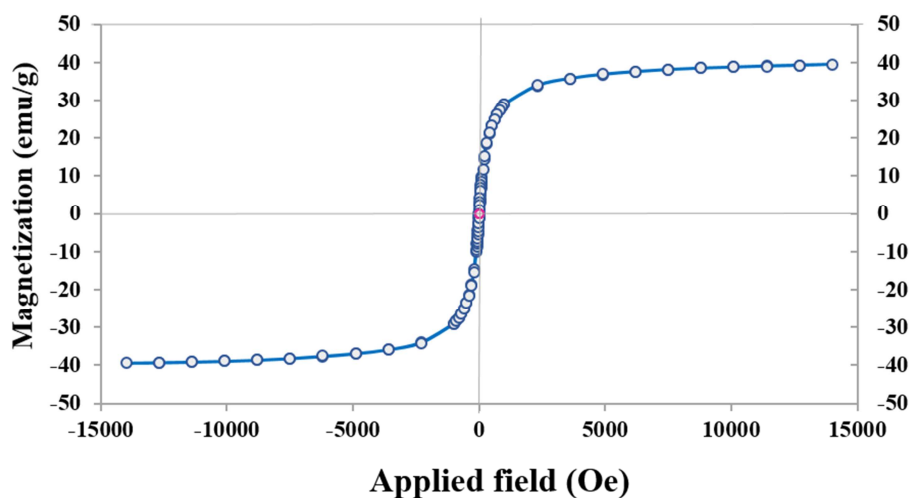


Fig. 5. The field-dependent magnetization of γ -Fe₂O₃/N-doped graphene hybrid material.

3.2. Catalytic activity

We employed γ -Fe₂O₃/N-doped graphene hybrid material as catalyst for PET glycolysis and the effect of different parameters such as catalyst amount, time and amount of EG on the BHET yield were investigated (Fig. 6).

The PET conversion, BHET monomer yield, and selectivity of BHET were calculated using the equations 1-3, respectively:

$$\text{Conversion of PET (\%)} = \frac{\text{initial weight of PET} - \text{weight of undepolymerized PET}}{\text{initial weight of PET}} \times 100 \quad (1)$$

$$\text{Yield of BHET (\%)} = \frac{\text{moles of BHET produced}}{\text{moles of PET units}} \times 100 \quad (2)$$

$$\text{Selectivity of BHET (\%)} = \frac{\text{moles of BHET produced}}{\text{moles of glycolyzed PET units}} \times 100 \quad (3)$$

At first, different amounts of γ -Fe₂O₃/N-doped graphene catalyst including 0.01, 0.02, 0.03 and 0.035 g were tested for PET glycolysis at 195°C with 4 g EG. According to the results, the yield of BHET increases upon the augmentation of catalyst amount from 0.01 to 0.03 g which may be due to preparation of more active sites and consequently acceleration of the reaction. With 0.03 g

of catalyst the yield of BHET reached a maximum value of 100% retaining constant also with 0.035 g catalyst (Fig. 6A). Moreover, the reaction time was also optimized (Fig. 6B), since the reaction yield rises until an equilibrium between the monomer and remaining dimer. After this point, the yield reduces due to the polymerization of BHET as a side reaction. The optimized time was obtained after 3 h for a glycolysis reaction containing 0.03 g catalyst at 195°C. When the amount of EG increases from 2 to 4 g, the BHET yield increases which 100% yield was obtained in the presence of 4 g EG under the above mentioned conditions (Fig. 6C). The yield of BHET without catalyst was only 4.1%. The significant difference between the BHET yields with and without γ -Fe₂O₃/N-doped graphene displaying the catalytic activity of this material. We also evaluated the performance of catalyst at 250°C in a stainless steel batch-type reactor which this reaction gave 100% BHET yield in only 80 min.

To examine if γ -Fe₂O₃ and N-doped graphene have a dramatic effect on the catalytic performance, these materials together with the as-synthesized γ -Fe₂O₃/N-doped graphene were evaluated as catalysts for PET glycolysis under the same conditions (Fig. 6D). The γ -Fe₂O₃/N-doped graphene clearly exhibits a much better activity than γ -Fe₂O₃ and N-doped graphene catalysts. That is, γ -Fe₂O₃/N-doped graphene exhibits much higher PET conversion, BHET yield, and BHET selectivity which is due to the synergetic effect of γ -Fe₂O₃ and N-doped graphene in the catalytic glycolysis of PET.

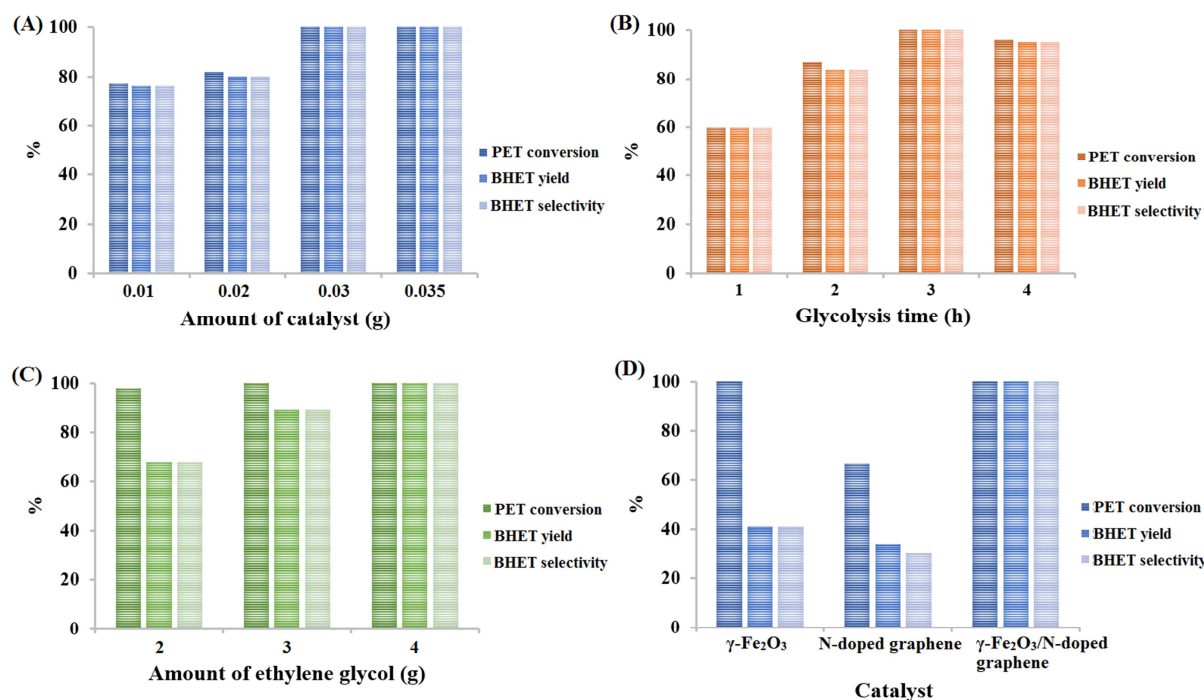
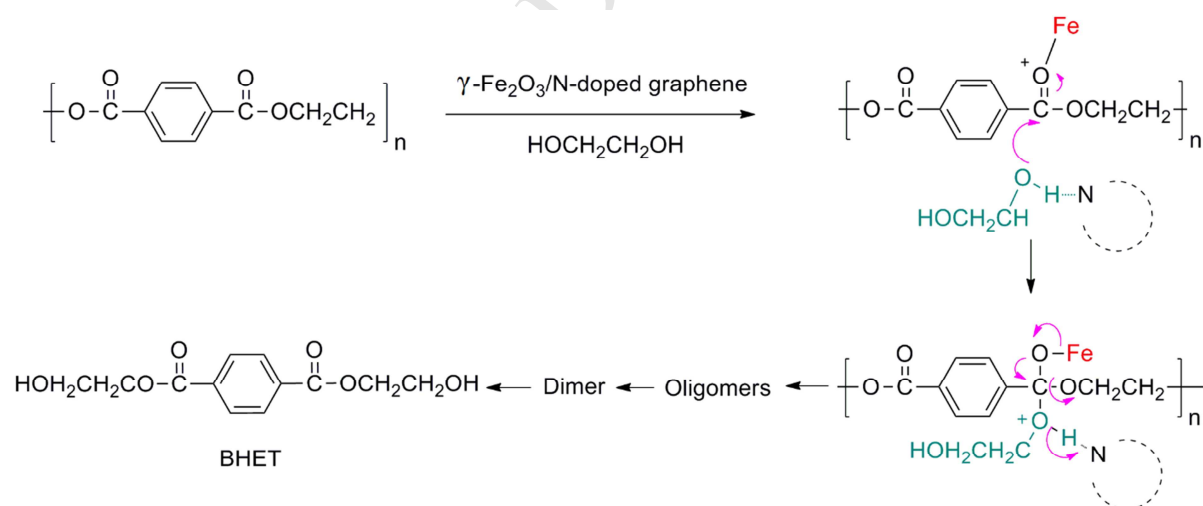


Fig. 6. (A) Effect of the amount of γ -Fe₂O₃/N-doped graphene on the PET glycolysis. Reaction conditions: PET (0.3 g), EG (4 g), 195°C, 180 minutes. (B) Effect of glycolysis time. Reaction conditions: PET (0.3 g), EG (4 g), γ -Fe₂O₃/N-doped graphene (0.03 g), 195°C. (C) Effect of the amount of EG. Reaction conditions: PET (0.3 g), γ -Fe₂O₃/N-doped graphene (0.03 g), 195°C, 180 minutes. (D) Effect of different catalysts. Reaction conditions: PET (0.3 g), EG (4 g), catalyst amount (0.03 g), 195°C, 180 minutes.

Previous studies show that in a transesterification reaction as in PET glycolysis, nitrogen doped graphene can act as an efficient catalyst. For example, Porwal et al. described a successful application of nitrogen doped graphene as a non-acidic catalyst for the esterification of fatty acids. Kannari et al. prepared nitrogen-doped carbon materials by ammoxidation of commercial carbon sources and used as base catalysts for Knoevenagel and transesterification reactions [27]. In this work, for the first time, we employed nitrogen doped graphene providing dual role in adsorption ability to PET as well as activating EG to promote PET recycling. Because of the

strong π - π interactions, graphene shows strong adsorption ability toward chemicals bearing with one or more benzene rings. Moreover, the basic sites (electron rich) on the nitrogen doped graphene may abstract proton from EG to promote the nucleophilicity. Therefore, we believed that nitrogen doped graphene not only strongly adsorbed, but also degraded the adsorbed PET.

We used γ -Fe₂O₃/N-doped graphene hybrid material which possess the advantages of both N-doped graphene and metal oxide. In the case of metal oxides, the positive metal ions and negative oxygen ions can act as Lewis acid and Brønsted base, respectively. As mentioned before, these basic sites can promote the nucleophilic attack of EG through the abstract of hydrogen from hydroxyl groups. On the other hand, basic sites protonate the carbonyl groups and enhance their electrophilic character. Therefore, the carbonyl carbon will be more vulnerable to the attack of nucleophile EG, resulting in the breaking of the PET chain and efficient PET glycolysis. So, the glycolysis reaction mechanism for PET glycolysis with N-doped graphene acting as basic catalyst and γ -Fe₂O₃ acting as acidic catalyst can be suggested (Scheme 1).



Scheme 1. Proposed mechanism for PET glycolysis with γ -Fe₂O₃/N-doped graphene as a bifunctional catalyst.

^1H NMR was employed to confirm the main product of glycolysis was BHET monomer (Fig. 7). The signals at 3.7 and 4.3 ppm are related to the methylene protons of $\text{CH}_2\text{-OH}$ and COO-CH_2 , respectively. The triplet signal at 4.9 ppm represents the protons of the hydroxyl. The single signal at 8.1 ppm is ascribed to the four aromatic protons of the benzene ring. Moreover, the ^1H NMR spectrum is in good accordance with those reported in the literature [38].

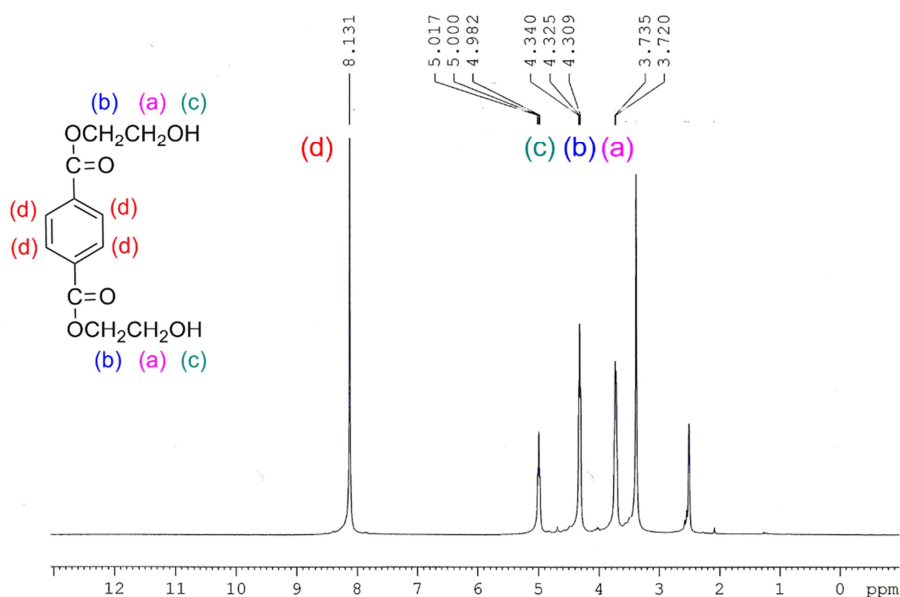


Fig. 7. ^1H NMR spectrum of BHET.

3.3. Catalyst recycling

The sustainable catalysts which decrease the cost and required time for replacing the spent catalyst with the fresh one are always highly desirable in chemical industries. The presence of $\gamma\text{-Fe}_2\text{O}_3$ provides the possibility for magnetic isolation of the catalyst from the reaction mixture which is very important for complete catalyst recovery and also eliminating the need for time-consuming filtration or centrifugation. We investigated the reusability of the $\gamma\text{-Fe}_2\text{O}_3/\text{N-doped}$ graphene catalyst in PET glycolysis. For this purpose, when the glycolysis reaction was complete, the resulting solution containing the suspended catalysts was subjected to a magnet to

recover the catalyst. The catalyst was used for the next run under similar conditions of the first one. The results showed that after five runs the catalyst giving practically no considerable change in activity as that of the first run (Figure 8). The SEM image and XRD pattern of the recovered catalyst have been presented in Figure 9 exhibiting no considerable change compared to the original catalyst. This suggests high stability and reusability of the catalyst.

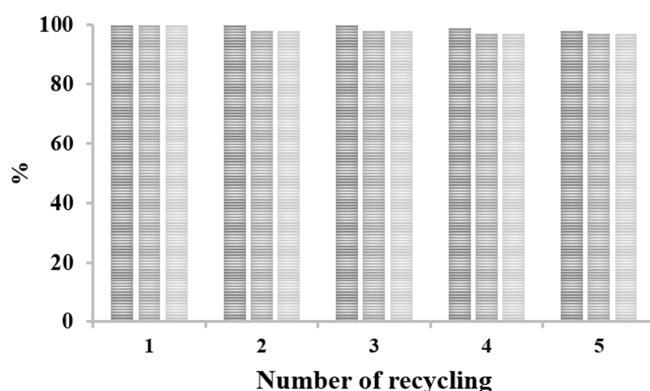


Fig. 8. Effect of recycling on the catalytic activity of γ -Fe₂O₃/N-doped graphene.

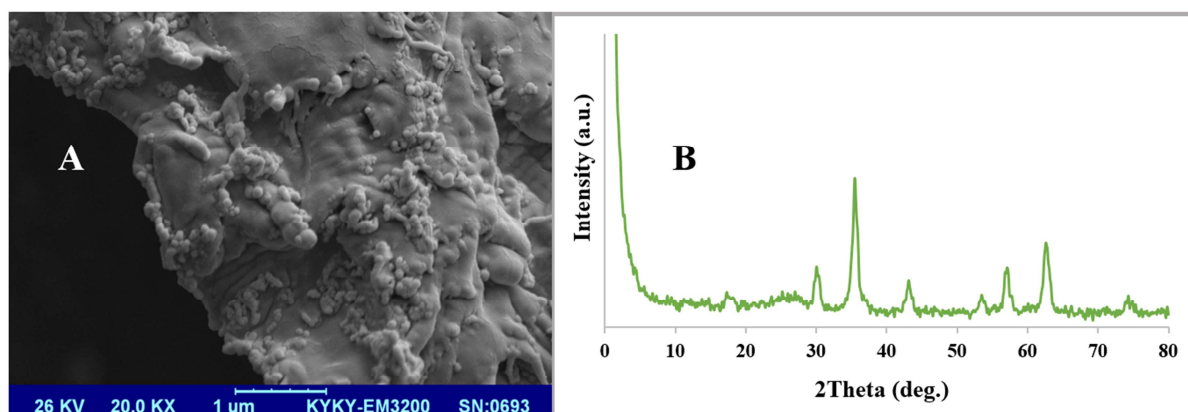


Fig. 9. SEM image and XRD pattern of recovered γ -Fe₂O₃/N-doped graphene.

4. Conclusion

For the first time, a bifunctional catalyst was introduced for glycolysis of PET. For this purpose γ -Fe₂O₃/N-doped graphene was synthesized which γ -Fe₂O₃ acts as acidic sites and N-doped

graphene as basic site for PET glycolysis. The BHET yield of 100% was obtained under relatively mild conditions in the presence of a small amount of the catalyst at short reaction time. The role of Fe_2O_3 and N-doped graphene were discussed and a possible reaction mechanism was suggested. The enhanced catalytic activity for $\gamma\text{-Fe}_2\text{O}_3/\text{N-doped graphene}$ was observed compared to Fe_2O_3 and N-doped graphene suggesting their synergistic effect for PET glycolysis. Moreover, the catalyst could be easily recycled by magnetic isolation and showing no significant loss in activity for five runs. The high monomer yield, possibility of magnetic recycling, low cost, and ease of applicability are some advantages of the $\gamma\text{-Fe}_2\text{O}_3/\text{N-doped graphene}$ catalyst compared to traditional catalysts. These properties made the presented catalyst unique and suitable for practical large scale and sustainable applications.

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