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The Glycolysis of Poly (ethylene terephthalate) Waste: Recovery of Terephthalic Acid by Magnetic Fe_3O_4@APTS Nanoparticle

Mir Mohammad Alavi Nikje*, **Elmira Ghamari, Lida Sarchami, Seyedeh Leila Rahmani Andabil**

Chemistry Department, Faculty of Science, Imam Khomeini International University, Qazvin, Iran

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Abstract

In this research, the chemical recycling of terephthalic acid from PET waste by using nano Fe_3O_4@Py-APTS as solid support was reported. The performance of organically modified nano magnetic was examined in detail and the results were compared with unsupported reactions as the model. By using the solid support, the required time for complete glycolysis, consumption of solvent and catalyst, decreased up 95 %, 37.5 % and 30 % respectively. Results showed that nano Fe_3O_4@Py-APTS delivered good performance as the reagent as well as the solid support in depolymerizing of PET to the terephthalic acid.

Keywords: *Poly (ethylene terephthalate), Recycling, Nano Fe_3O_4@Py-APTS, Terephthalic acid.*

Introduction

Poly (ethylene terephthalate) (PET) is one of the most important plastics, showing superb thermal and mechanical properties. Although its main application was by far the textile industry, large quantities of this material are consumed in the manufacture of video and audio tapes, photographic films and especially of soft-drink bottles. The World consumption of PET is approximately 26 million tons a year [1]. By increasing in PET production and since this polymer is not biodegradable, big waste stream create a serious environmental problem each year. Chemical recycling of PET has been attracting attention for both environmental and economic reasons [2].

In order to recovery TPA monomers, the hydrolysis of PET in presence of acid and base using convent solvents was reported by several scholars. Alkaline Hydrolysis of PET was carried out with the use of an aqueous alkaline solution of KOH or NaOH [3]. Wan

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****Corresponding author:*** *Mir Mohammad Alavi Nikje, Chemistry Department, Faculty of Science, Imam Khomeini International University, P.O. Box: 288, Qazvin, Iran. E-mail: drmm.alavi@gmail.com.*

Hydrolyzed PET in Potassium Hydroxide Solution [4]. Also alkaline hydrolysis of PET has been reported by Spaseska. His process was carried out with sodium hydroxide and trioctyl methyl ammonium bromide (TOMAB) as catalyst [5]. In another report PET was glycolized by using several ionic liquids and basic ionic liquids as catalysts [6]. Also PET was Hydrolyzed by 1-n-butyl-3-methylimidazolium chloride ([Bmim][Cl]) as solvent and acid-functionalized ionic liquid 1-methyl-3-(3-sulfopropyl)-imidazolium hydrogen sulfate as catalyst [7]. In addition the efficiency of Benzalkonium chloride (BKC) as phase transfer catalyst, on hydrolyzed PET waste has been surveyed [8]. Tabekh hydrolyzed PET by using commercial sulfuric acid produced by the Syrian Chemical Corporation in order to obtain TPA yield [9]. In another report PET was glycolized by using EG as solvent and NaOH as catalyst [10]. Oku glycolized PET with Sodium Hydroxide in Nonaqueous Ethylene Glycol [11].

In order to improve recycling conditions and reduce energy and time consumption other updated methods are cited. Chemical recycling of PET through phase transfer-catalyzed alkaline hydrolysis under microwave irradiation [12], glycolysis of PET by using DEG as solvent and NaOH as catalyst under microwave irradiation [13] and degradation of PET under influence of microwave irradiation in presence charcoal as catalyst [14].

In continuation of our previous work on PET chemical recycling [13, 15] we decided to examine the performance of nano-Fe_3O_4@Py-APTS as the reagent-solid support in order to recovery TPA from the bottles wastes. By using of this reagent-solid support required time to access to high recovery yield significantly decreases so that is comparable with microwave method.

Experimental

Instruments

The magnetite NPs (Fe_3O_4) and (Fe_3O_4@APTS) were characterized for particle size and morphology using field emission scanning electron microscopy (Hitachi model LEO 1430VP). Fourier transform infrared spectroscopy (FT-IR) spectra were done on a Brucker Tensor 27 spectrophotometer. TGA was performed with Perkin- Elmer Pyris Diamond TG/DTA under N2 atmosphere at a heating rate of 7.5°C/min and NMR spectra were recorded by an Avance 300 Bruker.

Materials

The iron (II) chloride tetrahydrate ($FeCl_2{\cdot}4H_2O$, 99.7%), iron (III) chloride hexahydrate ($FeCl_3{\cdot}6H_2O$, 99.0%), ammonia ($NH_3.H_2O$, 25%-28%), ethanol (C_2H_5OH 99.7%),aminopropyl-triethoxysilane (APTS), 2-chloropyridine and citric acid, were purchased from Merck and were used as received without further purification. PET flakes were prepared from used clear colorless PET bottles. Sodium hydroxides purchased from Merck, Germany. Moreover, diethylene glycol and HCl (37 %) solution were purchased from Iranian Petrochemical Company.

Synthesis of the well-dispersed Fe_3O_4 nanoparticles

The magnetite nanoparticles were synthesized through co-precipitation method by the reaction of ferric and ferrous (2/1 in mol/mol) precursors using reported method [16].

Preparation of Fe_3O_4@APTS nanoparticles

Fe_3O_4@APTS nanoparticles were prepared by using presentation method in previously works [17]. First magnetite nanoparticles (500 mg) was dispersed in 600 ml of ethanol/water (5/1) and sonicated for 20 min by addition of acetic acid and regulating of pH at 4. Then, APTS (4 ml) was added to the solution and the mixture was stirred mechanically at room temperature for 4 h. Finally, the core-shell nanoparticle was separated and washed with distilled water for four times and then dried at 45°C in oven overnight and characterized.

Preparation of nano-Fe_3O_4@Py-APTS

The obtained Fe_3O_4@APTS was mixed with 2-chloropyridine (0.8 ml) and acetonitrile (35 ml). The reaction mixture was allowed to stir for overnight under reflux conditions. The material was obtained by magnetic separation followed by two times washing with acetonitrile (30 ml).

IR spectroscopy analysis of obtained Fe_3O_4 and nano-Fe_3O_4@Py-APTS

Modification of magnetite nanoparticle with APTS and 2-chloropyridine was confirmed by FT-IR spectroscopy. The vibrations at 400 cm^{-1} and 580 cm^{-1} are attributed to the Fe–O functional groups of magnetite nanoparticle. By the way, Fe–O–Si band vibration appeared at around 584 cm^{-1} what overlaps with Fe–O bands. The vibrations at 1457 cm-1 and 3519 cm-1 refer to C=C and N-H respectively. Alkyl C–H stretches is found at 2854 and 2924 cm^{-1}. The Si-O-Si bond is found at 1150 cm^{-1}. The vibrations at 3400-3600 cm^{-1} are attributed to adsorbed O-H by Fe_3O_4.

PET glycolysis using nano-Fe_3O_4@Py-APTS and NaOH:

In this section we use a two-necked flask, 50 ml round-bottom glass equipped with a condenser, thermometer and magnetic stirrer. PET flakes (1 g) were treated with diethylene glycol using different PET: DEG molar ratios (1:4 to 1:8) at 160˚C. The used catalyst and support were NaOH (0.2 - 0.5 g) and Fe_3O_4@Py-APTS (0.01 - 0.3 g), respectively. After a certain time, reaction mixture was cooled by adding distilled water with intensive agitation. Then the TPA in the mixture was precipitated by bringing the pH to 2-3 by addition of HCl and dried at 80°C in the oven for 1 h and finally characterized.

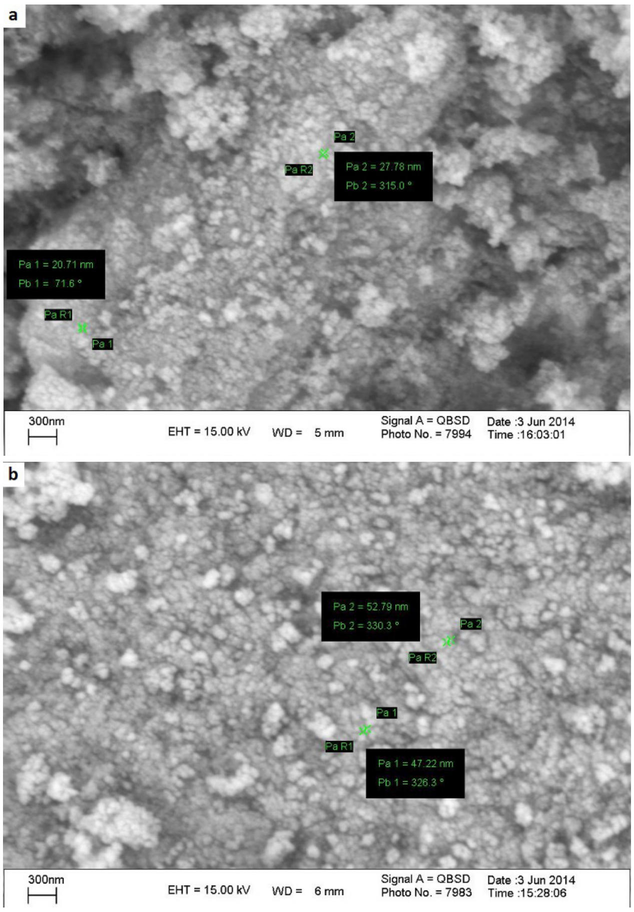
IR spectroscopy analysis of obtained TPA

In the IR spectrum of obtained TPA from glycolysis reaction, revealed frequencies at 2500-3250 cm^{-1}, 1685 cm^{-1} and 1574-1425 cm-1 are related to the C-H, carbonyl and aromatic ring functional vibration stretching, respectively and data was matched with an authentic sample data.

Results and discussion

Nano-Fe_3O_4@Py-APTS solid support characterization

The FE-SEM image of synthesized magnetite nanoparticles is shown in the figure 1. From the figure, Fe_3O_4 nanoparticles and Fe_3O_4@Py-APTS have spherical shape with average size of 30-40 and 50-60 nm, respectively.



Figures 1. FE-SEM images of synthesized a Fe_3O_4 and b Fe_3O_4@Py-APTS nanoparticles.

Figure 2 shows the thermal gravimetry analysis curves (TGA) of Fe_3O_4 and Fe_3O_4@Py-APTS nanoparticles, respectively. In samples there is an insignificant weight loss stage (below 130°C) that can be imputed to the evaporation of water and ethanol. In addition in modified sample, weight loss started at 200 to 800°C and correspondent to the thermal decomposition of (Py-APTS) coating on magnetite nanoparticles. Actually weight loss, the coated Py-APTS on the surface Fe_3O_4 NPs is calculated as 8%.

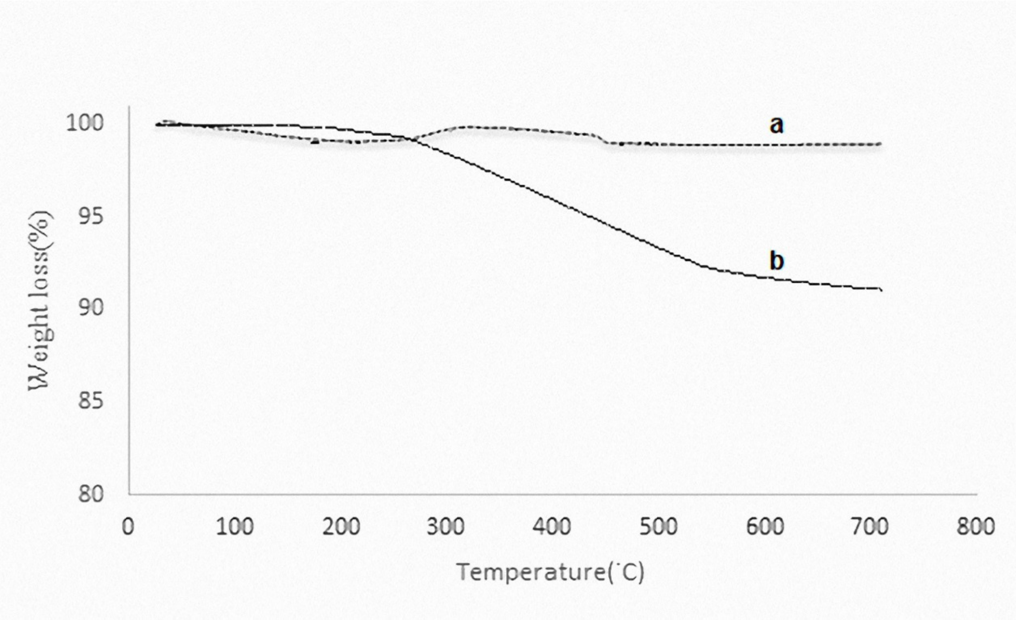


Figure 2. TGA curves for a Fe_3O_4 and b Fe_3O_4@Py-APTS nanoparticles.

The role of reagent-solid support on TPA recovery

The results of performance of Fe_3O_4@Py-APTS as solid support in recovering of TPA collected in figures 3-4 and tables 1-2, respectively and data were compared with our previously reported data without using this solid support [14]. In the present of Fe_3O_4@Py-APTS (0.02 g) the required recovery time to access high recovery yield decreases up 95% which is comparable with microwave conducted reaction (Figure 3). This can be related to the Fe_3O_4@Py-APTS capability to increase surface area rendering more active sites and thermal stability. In the other hand hydroxyl and amine functional groups of Fe_3O_4@Py-APTS may react as the reagent.

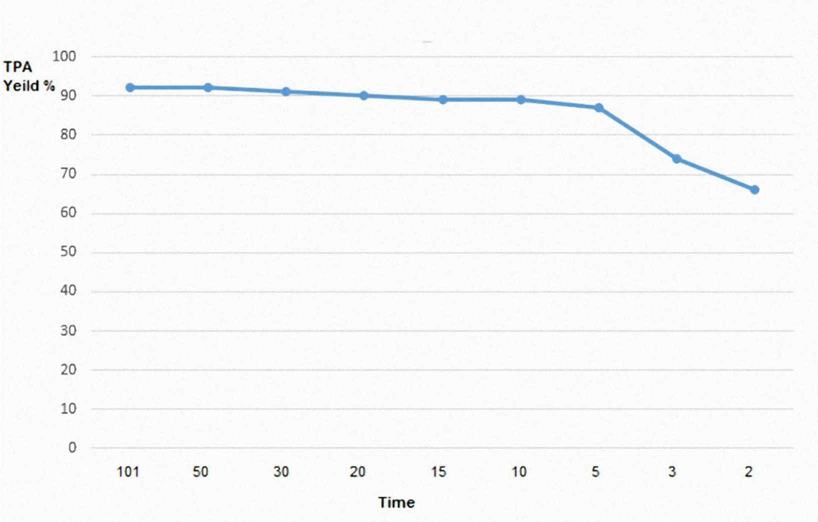


Figure 3. The effect of time on the glycolysis of PET in the present of Fe_3O_4@Py-APTS (0.02).

The results of changing concentration of Fe_3O_4@Py-APTS are collected in Table 1. In entry 3 maximum amount of terephthalic acid yield (90%) was obtained, that is related to presence of Fe_3O_4@Py-APTS (0.03 g) in the reaction mixture.

Table 1. The effect of solid support concentration on the glycolysis of PET (1 g) in the present of NaOH (0.5 g) and DEG (7 ml).

TPA yield %	Unreacted PET (g)	Time (min)	Fe_3O_4@Py-APTS (g)	Entry
81	0.00	5	0.01	**1**
84	0.00	5	0.02	**2**
90	0.00	5	0.03	**3**
89	0.00	5	0.05	**4**
90	0.00	5	0.08	**5**
84	0.00	5	0.10	**6**
80	0.00	5	0.20	**7**
78	0.00	5	0.30	**8**

In order to studying of catalyst role, six sets of reactions were handled in the same reaction times and data collected in the Table 2. As shown on entry 4 of Table 2, by decreasing NaOH concentration to 30% sightly value of reaction (entry 1), the TPA recovery yield will remain constant.

Table 2. The effect of catalyst concentration on the glycolysis of PET (1g).

TPA yield %	Unreacted PET (g)	Time (min)	Fe_3O_4@Py-APTS (g)	NaOH (g)	DEG (ml)	Entry
90.2	0.00	101	0.00	0.50	7	**1**
90	0.00	101	0.03	0.50	7	**2**
89	0.00	101	0.03	0.40	7	**3**
87	0.00	101	0.03	0.35	7	**4**
79	0.11	101	0.03	0.30	7	**5**
41	0.50	101	0.03	0.20	7	**6**

In order to finding the optimum PET: DEG molar ratios, we decrease this ratio (Figure 4). As shown in this figure, in present of Fe_3O_4@Py-APTS (0.03 g) and by altering PET: DEG molar ratios from 1:8 to 1:4, the slight decrements in TPA recovery yield are observed and suddenly drop in 1:4 molar ratio and this means we have 37.5% saving energy.

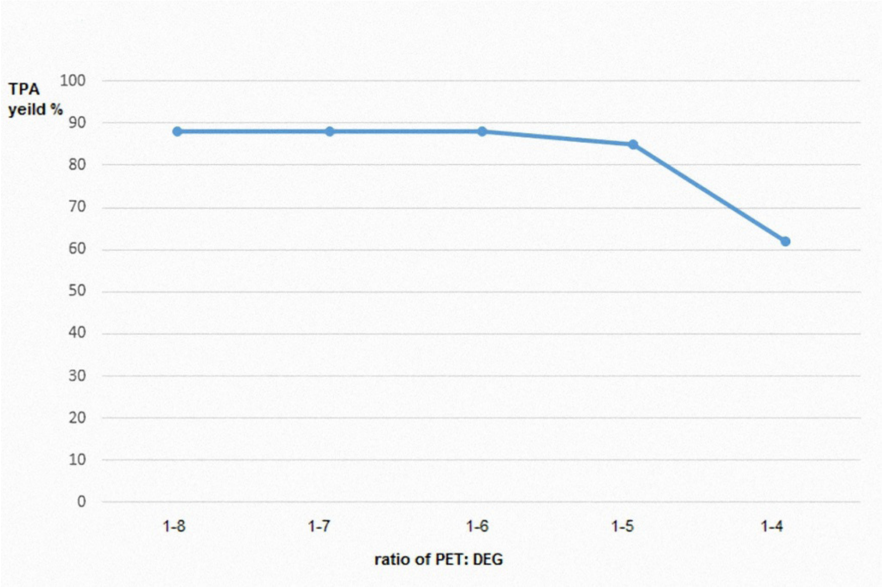


Figure 4. The effect of PET: DEG molar ratios on the glycolysis of PET in the present of Fe_3O_4@Py-APTS (0. 03 g) and NaOH (0.35 g).

^{1}*HNMR analysis*

Figure 5 shows 1HNMR spectrum of obtained TPA. The revealed bands at 8.02 ppm and 13.2 ppm are related to protons of aromatic ring and acidic proton respectively.

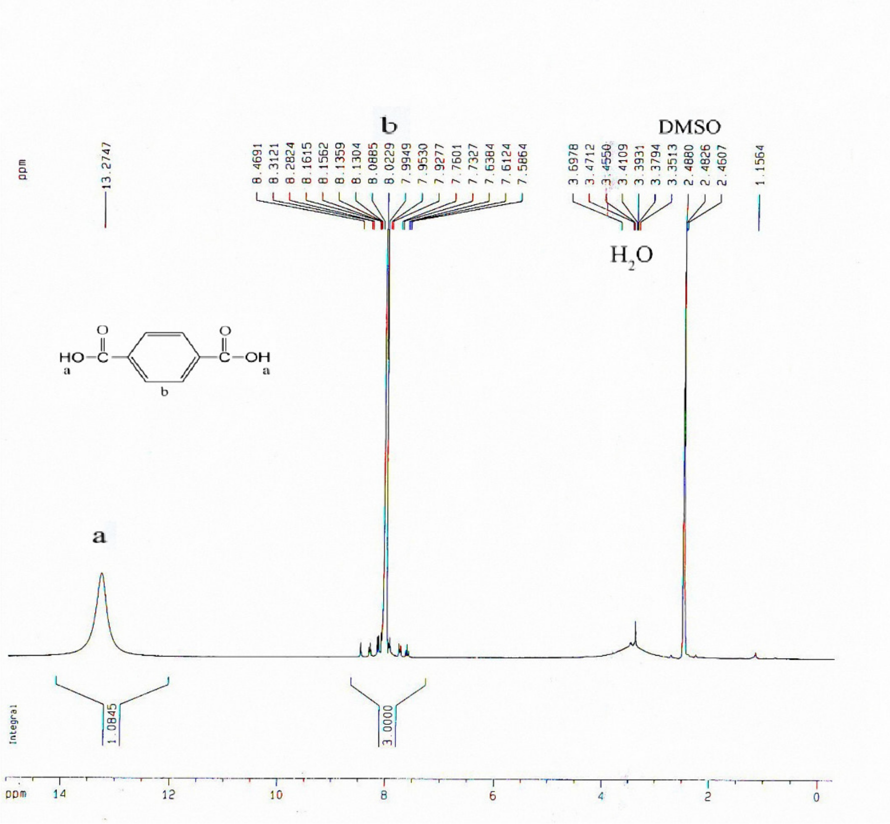


Figure 5. 1HNMR spectra of obtained TPA from Glycolysis.

Conclusion

The effect of nano Fe_3O_4@Py-APTS as a solid support in the recovery of terephthalic acid from PET waste was evaluated and the obtained results led to successful recovering of TPA at the short reaction times, Low consumption of solvent and catalyst and high yields.

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