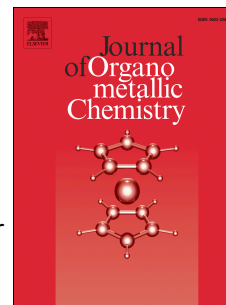


Accepted Manuscript

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PII: S0022-328X(19)30229-3

DOI: <https://doi.org/10.1016/j.jorganchem.2019.05.030>

Reference: JOM 20812

To appear in: *Journal of Organometallic Chemistry*

Received Date: 18 April 2019

Revised Date: 28 May 2019

Accepted Date: 31 May 2019

Please cite this article as: M. Kazemnejadi, B. Mahmoudi, Z. Sharafi, M.A. Nasser, A. Allahresani, M. Esmaeilpour, Synthesis and characterization of a new poly α -amino acid Co(II)-complex supported on magnetite graphene oxide as an efficient heterogeneous magnetically recyclable catalyst for efficient free-coreductant gram-scale epoxidation of olefins with molecular oxygen, *Journal of Organometallic Chemistry* (2019), doi: <https://doi.org/10.1016/j.jorganchem.2019.05.030>.

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Synthesis and characterization of a new poly α -amino acid Co(II)-complex supported on magnetite graphene oxide as an efficient heterogeneous magnetically recyclable catalyst for efficient free-coreductant gram-scale epoxidation of olefins with molecular oxygen

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Abstract

A novel magnetic nanocomposite was prepared by immobilization of a cobalt complex of a synthetic poly α -amino acid on Fe₃O₄-doped graphene oxide (GO/Fe₃O₄@PAA Co(II)) and was demonstrated to be a highly efficient catalyst for the epoxidation of olefins in mild conditions. PAA was synthesized through a multi-step synthesis, first by a poly condensation reaction of salicylaldehyde followed by the Strecker synthesis. The synthesized nanocomposite was characterized by various analytical and spectroscopic methods including FTIR, ICP, XRD, EDX, XPS, FE-SEM, TEM, TGA, VSM and DLS analyses. A wide variety of olefins could be tolerated toward epoxidation in the presence of molecular oxygen without the need for any co-reductant. The magnetic nanocomposite could be readily separated by a magnet from the mixture and reused for several times without any significant reactivity loss, which represents its potential for practical and industrial application. Also, the scalability of the process was investigated in this work.

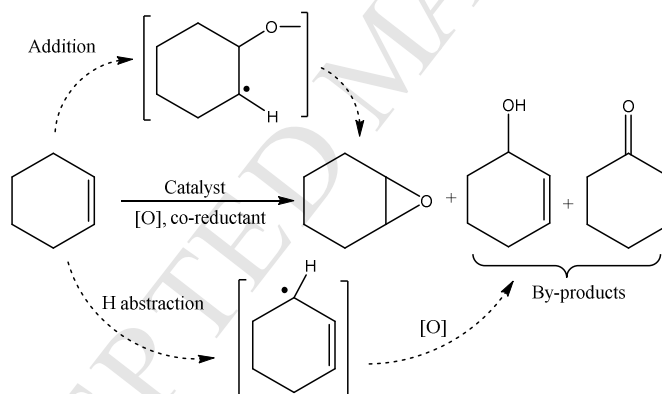
Keywords: Graphene oxide, Epoxidation, Fe₃O₄, Nanocatalyst, Magnetically recyclable, Gram-scale

1. Introduction

Epoxides are one of the key and versatile intermediates for manufacture of fine chemicals including plasticizer, perfumes, cosmetics, epoxy resins, pharmaceuticals, etc. [1]. Traditionally, epoxides are synthesized by stoichiometric amount of oxidizing reagent such as potassium monoperoxysulfate [2] and organic peracids [3]. These peroxides are not only toxic, corrosive and harmful, but also generate toxic waste products, which limited their application in industrial aspects as well as in laboratory due to the safety issues. So, the researches were conducted to use more convenient, easily handling and environmentally friendly oxidants such as molecular oxygen, TBHP, air and hydrogen peroxide [3,4]. In order to exploit the advantage of these oxidants for epoxidation, as the easily accessible and green oxidants, there is a need for a transition metal in order to oxygen transfer [5]. Various catalytic systems based on transition metals have been developed recently such as: (1) Fe₂/mpg-C₃N₄ (mesoporous carbon nitride) [6], (2) mesoporous cobalt oxide [7], (3) zeolites [8], (4) nickel complexes [9], (5) Mn(II) and (III) complexes [10], (6) Mn-porphyrin [11], (7)

$\text{Cu}_2(\text{oxalate})(1,10\text{-phen})_2\text{Cl}_2$ [12], (8) $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)\text{Br}(\text{CO})_2\{\text{iPrN}=\text{C}(\text{H})\text{C}_5\text{H}_4\text{N}\}]$ [13], and (9) $\text{Rh}_2(\text{tpa})_4$ (tpa = triphenylacetate) [14].

Despite various progress in this topic, however, most of the reported methods involve expensive reagents, unsatisfactory yield, low selectivity, non-environmentally benign, using co-reductant, harsh reaction conditions, etc. It worth noted that two excess possible products could be obtained in result of the epoxidation of an olefins bearing $\text{H}\alpha$ (Scheme 1) [15], which is not suitable for practical aspects. So, finding a highly efficient catalytic system with high selectivity and toxicity, which involves green chemistry considerations seems essential. Application of nanomaterials as a solid support due to their high ratio of surface to volume are well known for decades [16,17]. Among them, graphene oxide (GO) with the interesting properties such as sheet structure, nano-size dimension with high surface area, high thermal/chemical stability and possibility of functionalization with various organic compounds become as one of the most suitable solid supports for organic synthesis [3,4,18]. Further improvement in heterogeneous catalysts led to the preparation of magnetic nanoparticles that facilitates the separation of catalyst with an external magnetic field [19]. Fe_3O_4 nanoparticles are one of the most applicable and popular magnetic nanoparticles due to their widespread applications in various fields of area such as catalyst and medicine [5,20]. Some advantages are associated with them including low cost, high thermal stability, non-toxic, chemical stability, strong magnetization, and high crystalline structure, which conducted them for magnetization of other solid supports; this is a smart strategy for magnetization of solid supports (in this case nano graphene oxide), which has been used extensively in the last decades [3,19].



Scheme 1. Epoxidation of cyclohexene catalyzed by the transition metal catalytic systems

Cobalt complexes and generally Co-based catalytic systems have received attention due to their well-known potential for oxidation programs, being cheap and accessible, and non-toxic nature [21]. Herein, in accordance with green chemistry considerations and also importance and application of useful epoxides in organic synthesis, we plan a multiphase nanocomposite with decoration of a Co(II) complex of a synthetic poly α -amino acid onto magnetic graphene oxide as an highly active heterogeneous magnetically recoverable catalyst for the efficient free-coreductant gram-scale O_2 -epoxidation of olefins in mild conditions. This system not only benefits from advantages of a solid nano-support with high aspect ratio (graphene oxide), but also utilizes from the presence of PAA as a strong ligand on its surface that is responsible for high durability and activity of the catalyst.

2. Experimental

2.1. Materials and apparatus

All chemicals were obtained from Sigma and Fluca supplier and used as received without further purification. All the solvents were distilled and dried before use. Progress of the reactions and purity of products were monitored by thin layer chromatography (TLC) on silica gel and/or gas chromatography (GC) on a Shimadzu-14B gas chromatography equipped with HP-1 capillary column and N₂ as carrier gas. For GC analyses, anisole was used as an internal standard. Purification of imines and oximes was achieved by recrystallization from ethanol. FTIR spectra were obtained using a JASCO FT/IR 4600 spectrophotometer using KBr pellet. The ¹H NMR (250 MHz) and ¹³CNMR (62.9 MHz) spectra were recorded on a Bruker Avance DPX-250 spectrometer in CDCl₃ and DMSO-*d*₆ as solvent. Transmission electron microscopy (TEM) images were taken on a Philips EM208 microscope and was operated at 100 kV. The presence of the elements was detected by EDX spectroscopy using field emission scanning electron microscope (FE-SEM, JEOL 7600F), equipped with a spectrometer of energy dispersion of X-ray from Oxford instruments. Size distribution of the nanoparticles were measured by dynamic light scattering (DLS) analysis on a HORIBA-LB550 instrument. TGA of the samples have been performed on a NETZSCH STA 409 PC/PG in nitrogen atmosphere with a heating rate of 10 °C /min in the temperature ranges of 25-1000 °C. The magnetic behavior of the samples was conducted on Lake Shore vibrating sample magnetometer (VSM) at room temperature. ICP experiments were accomplished using VARIAN VISTA-PRO CCD simultaneous ICP-OES instrument. Conversion and epoxide selectivity was measured according to the following equations 1,2 [1,5]:

$$\text{conversion (mol\%)} = \frac{(\text{initial mol\%}) - (\text{final mol\%})}{\text{initial mol\%}} \times 100 \quad (1)$$

$$\text{Styrene epoxide selectivity} = \frac{\text{GC peak area of styrene epoxide}}{\text{GC peak area of all products}} \times 100 \quad (2)$$

2.2. Preparation of PAA

In order to preparation of poly(α -amino acid) (PAA), firstly, poly salicylaldehyde (PSA) was prepared according to a previously reported procedure [1,5,20]. PSA (0.1 g, $\overline{M}_n = 2226$) was added to 20 mL of water, then NaCN (0.5 g, 10 mmol) and NH₄Cl (0.5 g, 10 mmol) were added to the reaction mixture. The reaction was refluxed at 50 °C for 12 h. The resultant orange product (mp > 400 °C, $\overline{M}_n = 2400$), poly(α -amino nitrile) **3**, was isolated by simple filtration followed by drying into oven (50 °C) for 5 h. Poly(α -amino nitrile) was transformed to poly(α -amino acid) by hydrolysis of nitrile groups; 0.2 g of **3** was added to 15 mL of water along with several drops of H₂SO₄, and the mixture was refluxed at 80 °C for 12 h. The mixture reaction was cooled to room temperature and neutralized with 0.5 N KOH solution. Poly(α -amino acid) **4**, was filter off, drying and isolated as a stable powder (mp > 400 °C). Scheme 2 shows the preparation of PAA **4** *via* a multistep synthesis.

2.3. Preparation of GO

Graphene oxide (GO) was prepared according to a modified Hummer's method from purified natural graphite [22,23].

2.4. Preparation of GO/Fe₃O₄ hybrids

GO-Fe₃O₄ hybrid was prepared *via* a chemical co-precipitation method according to the slightly modified literature procedure [24,25]. GO/Fe₃O₄ NPs were prepared with a mass ratio of 1: 5 (GO: FeSO₄). This premium ratio provides a suitable responsive to a magnetic field for the readily separation of the NPs [4]. In a typical process, GO (25 mg) was first sonicated

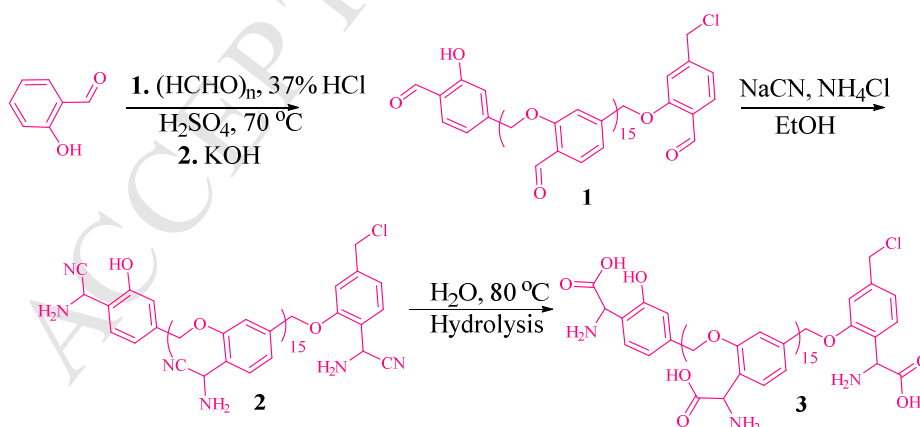
in 150 mL deionized water for 10 min. The mixture was stirred and heated to 80 °C in an oil bath. Then, NH₄OH 25% solution was added dropwise to the mentioned solution until the pH adjusted to 11. Then, FeSO₄·7H₂O (125 mg) along with sodium dodecyl sulfate (SDS) were added into the aqueous dispersion of GO solution. The resulting mixture was stirred under N₂ atmosphere for 24 h at 80 °C. The GO/Fe₃O₄ nanoparticles were collected by an external magnetic field followed by washing with deionized water several times in order to eliminate the excess iron salts. Finally, the product was separated by a simple external magnet, then dried in vacuum (40 °C) for 4 h (Scheme 2).

2.5. Preparation of GO/Fe₃O₄@PAA-Co(II) complex

For the preparation of GO/Fe₃O₄@PAA complex, 20 mg of GO/Fe₃O₄ in 50 mL DMF was ultra-sonicated for 1 h, and then 0.2 g of *N,N'*-dicyclohexylcarbodiimide (1.0 mmol, DCC) and 4-dimethylaminopyridine (DMAP) along with 0.5 g of PAA were added into the solution. The resultant mixture was stirred for 8 h at 80 °C under N₂ atmosphere. The product, GO/Fe₃O₄@PAA **7**, was separated using an external magnetic field and washed with water for several times until the pH reached to 7, and then dried into oven (60 °C). Complexation of cobalt to GO/Fe₃O₄@PAA was takes place by sonication of GO/Fe₃O₄@PAA (1.0 g) in 20 mL EtOH followed by addition of Co(OAc)₂ (10 mg) to the solution. The mixture was stirred at room temperature for 2 h. The product **8** was purified as same as the previous step using an external magnetic field.

2.6. General procedure for catalytic epoxidation of olefins by GO/Fe₃O₄@PAA-Co(II)

In a typical run, in a three-necked round-bottom flask equipped with a O₂ (g) inlet (bubbling 15 mL/min, 1.0 atm.), a condenser and a magnet stirrer bar, a mixture of styrene (10.0 mmol) and catalyst **8** (50 mg, 0.2 mol%) were stirred in CH₃CN (10 mL) at 60 °C. The reaction progress was monitored by TLC. Upon reaction completion, the catalyst was magnetically filtered, and the residue was directly subjected to GC instrument to quantify the epoxide product. Moreover, the desired epoxide product was purified by column chromatography followed by identification by ¹H NMR and ¹³C NMR spectra. Activity of the catalyst was expressed by turnover frequency (TOF) as well as turnover number (TON) [1,5].



Scheme 2. Synthesis of poly(AA)

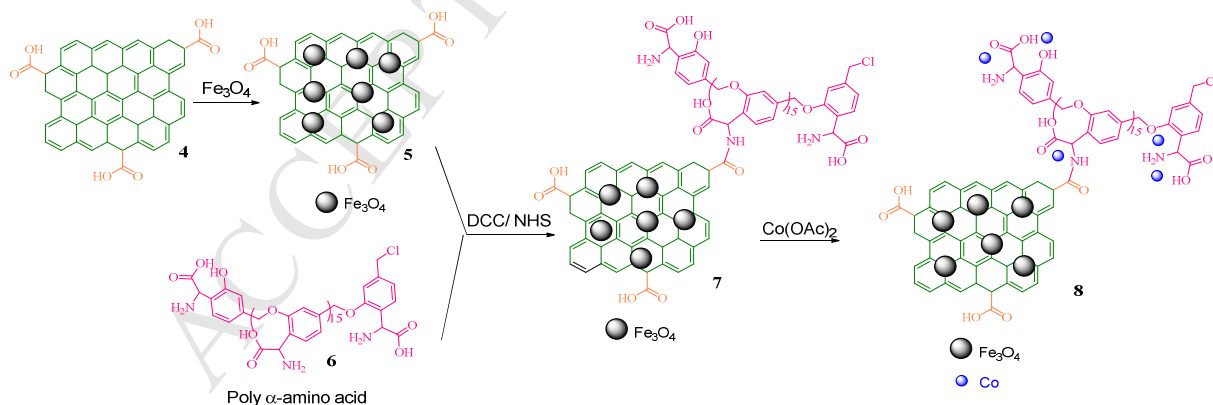
3. Results and discussion

3.1. Catalyst characterization

According to GPC analysis of the prepared poly(α -amino nitrile), $M_w = 2400$, it could be calculated that the present nitrile functions per mole of poly(α -amino nitrile) is $17/2400 = 7$

mmol. So, assuming that all of the nitrile groups are converted to acid; the poly(α -amino acid) contain 7.0 mmol acid functions per gram of PAA.

FTIR spectra of 5-chloromethyl salicylaldehyde, **2**, **3**, **4**, GO (**5**), **6**, **7**, and **8** are shown in Fig. 1. The characteristic peaks at 725 cm^{-1} , 1481 cm^{-1} , and some series vibrations at $2900\text{--}2950\text{ cm}^{-1}$ are related to C-Cl (Str.), C-H (Aliphatic, Bend.), and C-H (Aliphatic, Str.) vibrations, respectively, which completely confirmed the chloromethylation of salicylaldehyde (Fig. 1a) [1,5,20]. The polymerization of 5-chloromethyl salicylaldehyde causes to a large reduction of O-H stretching vibration intensity at 3400 cm^{-1} , confirming that the polymerization takes place through the ether bond formation (Fig. 1b) [20]. The preparation of α -amino nitrile *via* the Strecker synthesis was characterized by a strong peak at 2110 cm^{-1} related to CN (nitrile) groups (Fig. 1c). Moreover, two characteristic peaks at 3500 and 3550 cm^{-1} demonstrating the presence of primary amine groups (Stretching vibrations). Elimination of the sharp peak refer to nitrile at the spectrum of **4**, confirmed clearly their transformation to carboxylic acids (Fig. 1d). This reduction along with a red shift of the amine groups in FTIR spectrum of poly(α -amino acid), could be related to the formation of $\text{COO}^- \text{NH}_3^+$, that is characteristic for a typical amino acid [26]. Fig. 1e, shows the FTIR spectrum of graphene oxide. A peak at 1735 cm^{-1} was assigned to the stretching vibration of C=O for carboxylic groups (Fig. 1e). The intense bond at 3422 cm^{-1} is attributed to the stretching vibration of hydroxyl groups of GO surface. The peak at 1626 cm^{-1} represents C=C stretching vibrations for aromatic rings related to the non-oxidized graphene oxide framework [27]. Advent of a strong absorption at 572 cm^{-1} at GO/ Fe_3O_4 FTIR spectrum indicates the Fe-O (Str.) nanoparticles, confirming the incorporation of Fe_3O_4 NPs on the GO. Another characteristic peak was the reduction of O-H bond intensity due to the decoration of Fe_3O_4 on the graphene oxide (Fig. 1f). Fig. 1g shows the amide bond linkage in **7** at 1622 cm^{-1} . A shoulder at 1635 cm^{-1} could be attributed to free C=O carboxylic bonds. Also, vibrations about 1400 cm^{-1} represents the bending vibration of methylene groups in the polymer (Fig. 1g). Reduction in the intensity of peaks at carboxylic region, confirmed the successful coordination of cobalt cations through these functional groups as indicated in Scheme 3 (Fig. 1h). Furthermore, advent of a series of packs at $\sim 479\text{ cm}^{-1}$ shows the Co-O bond stretching vibration [28], confirming the successful coordination of Co (Scheme 3).



Scheme 3. Synthesis of GO/ Fe_3O_4 @PAA Co(II) complex

The magnetic property of the samples was studied by VSM analysis. The samples give suitable and satisfactory response to the applied magnetic field (Fig. 2A). No hysteresis phenomenon was found for the samples, which is characteristic for the superparamagnetic nanoparticles [29]. These results confirmed the incorporation of Fe_3O_4 NPs on GO. For

comparison, Fe_3O_4 NPs were separately prepared and studied by VSM. The analyses show 78 emu.g^{-1} , 65 emu.g^{-1} , and 32 emu.g^{-1} saturation magnetization for Fe_3O_4 , $\text{GO}/\text{Fe}_3\text{O}_4$, and $\text{GO}/\text{Fe}_3\text{O}_4@\text{PAA-Co(II)}$ respectively (Fig. 2A, a-c). The results indicate a large reduction in magnetization for the catalyst **8**, which represent the functionalization of GO in each step (Fig. 2A-c).

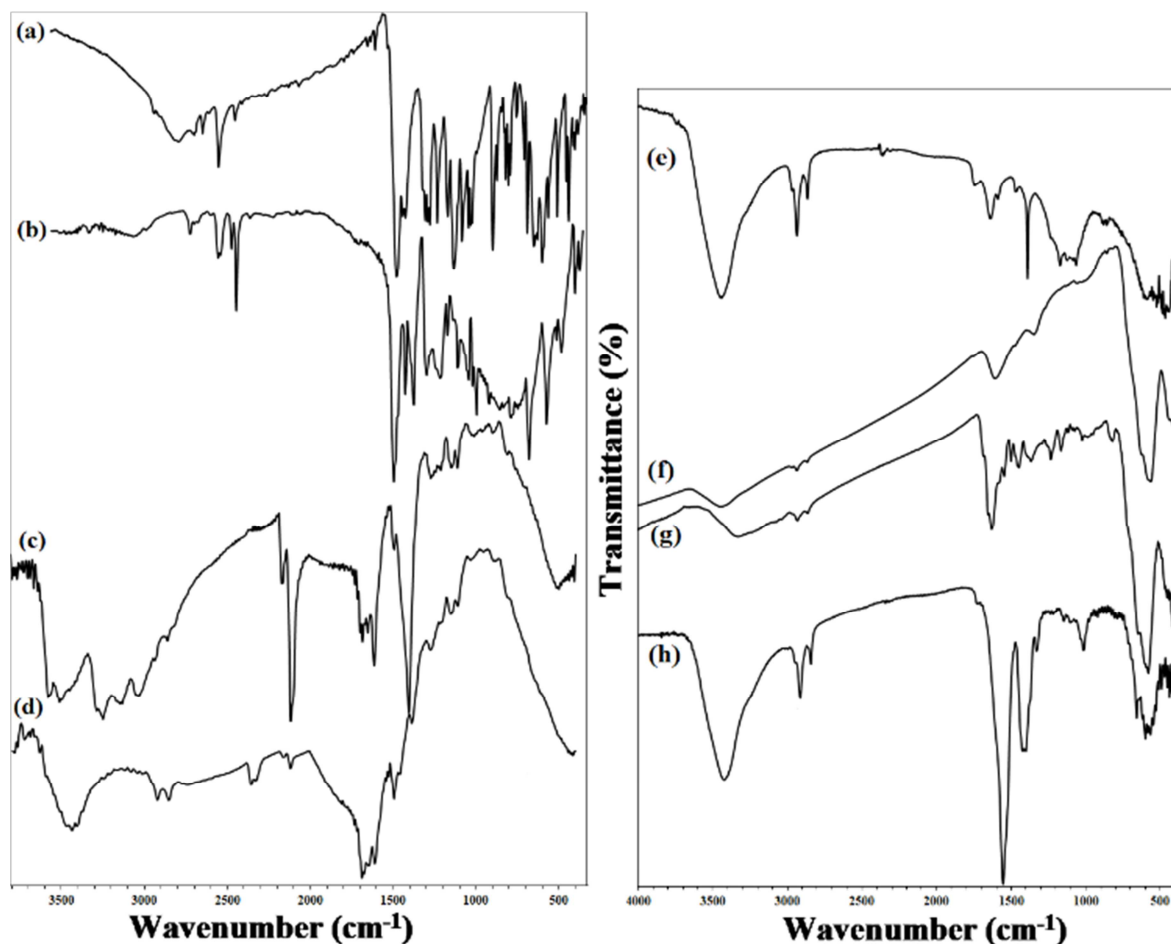


Fig. 1 FTIR spectra of (a) 5-chloromethyl salicylaldehyde, (b) poly salicylaldehyde (**2**), (c) poly(α -amino nitrile) (**3**), (d) poly(α -amino acid) (**4**), (e) GO (**5**), (f) $\text{Fe}_3\text{O}_4/\text{GO}$ (**6**), (g) $\text{GO}/\text{Fe}_3\text{O}_4@\text{PAA}$ (**7**), (h) $\text{GO}/\text{Fe}_3\text{O}_4@\text{PAA-Co(II)}$ (**8**)

The samples were further characterized by TGA analysis. TGA spectrum of $\text{GO}/\text{Fe}_3\text{O}_4$ indicates three main weight losses (Fig. 2B-a). In the first stage, a slow weight loss takes place near 80 °C correspond to 9% weight loss due to desorption of water [18]. Another weigh loss occurs around 220 ° with a mild slope, which last to 440 °C. This 18% weight loss exhibited the vaporization and decomposition of various functional groups (Fig. 1a) on GO framework (Fig. 2B-a). Finally, decomposition of $-\text{COO}^-$ groups provide 12% weight loss above 600 °C in agreement with the literature [3,18]. An enhancement in thermal stability of $\text{GO}/\text{Fe}_3\text{O}_4@\text{PAA}$ was observed, demonstrating the influence of the coated PAA on $\text{GO}/\text{Fe}_3\text{O}_4$ hybrid. Again, the small weigh loss is due to the release of water on the $\text{GO}/\text{Fe}_3\text{O}_4@\text{PAA}$ at 180 °C (10% weight loss). The main weight loss in temperature range of 550-820 °C represents the decomposition of PAA on the $\text{GO}/\text{Fe}_3\text{O}_4$ (Fig. 2B-b). This weigh loss is equal to 40% and confirming the loading amount of PAA on the NPs. Coordination of cobalt to $\text{GO}/\text{Fe}_3\text{O}_4@\text{PAA-Co(II)}$ showed an enhance in its thermal stability, which the overall weight loss was found to be 52% at 1000 °C (compared to $\text{GO}/\text{Fe}_3\text{O}_4@\text{PAA-Co(II)}$)

with 57% weight loss). This difference may be attributed to the coordinated cobalt in the GO/Fe₃O₄@PAA-Co(II) (Fig. 2B-c). Also, the peak refer to the decomposition of polymer takes place in lower temperatures with a milder slope, that could be attributed to the effect of coordinated cobalt to PAA.

XRD patterns of GO, GO/Fe₃O₄ and GO/Fe₃O₄@PAA-Co are shown in Fig. 3A. GO presents an amorphous peak at $2\theta=10.8^\circ$ related to (001) plane, that is characteristic for the graphene oxide [4]. Fig. 3A-a, shows the XRD pattern of GO/Fe₃O₄ with six characteristic peaks at $2\theta=30.3^\circ, 35.5^\circ, 43.2^\circ, 53.8^\circ, 57.5^\circ, 62.9^\circ$, which were assigned to their indices (220), (311), (440), (442), (511), and (440) respectively [3,4]. These reflections were in agreement with the crystal structure of Fe₃O₄ NPs (JCPDS no. 19-0629). As shown in Fig. 3A-b, the intensity of the peak at 10.8° is largely reduced. This behavior suggests that the Fe²⁺ ions act as a reducing agent for graphene oxide [3,19]. The crystal structure of the catalyst **8**, was also demonstrated the peaks for Fe₃O₄ crystal structure as well as a new amorphous peak at $2\theta=11.5^\circ$. This peak could be assigned to the amorphous PAA in comparison with the GO/Fe₃O₄ XRD pattern, that is coated on the GO framework. Furthermore, the results also proved that the functionalization of GO/Fe₃O₄ with PAA doesn't lead to the phase change of Fe₃O₄ NPs.

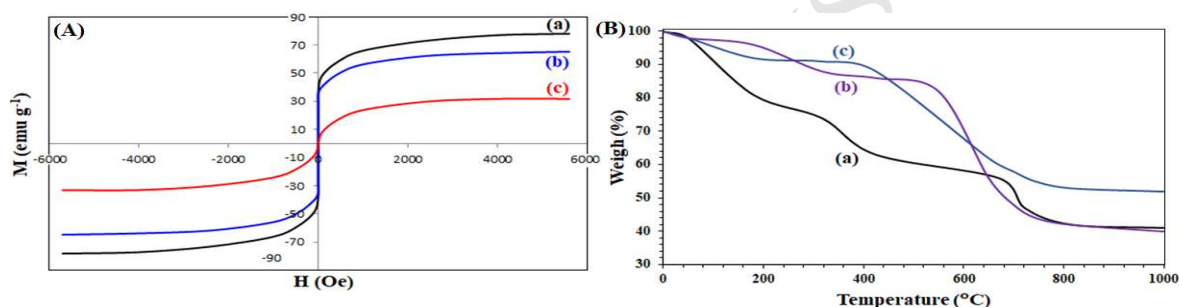


Fig. 2. (A) VSM curves of (a) Fe₃O₄, (b) GO/Fe₃O₄, and (c) GO/Fe₃O₄@PAA-Co(II). (B) TGA spectra of (a) GO/Fe₃O₄, (b) GO/Fe₃O₄@PAA and (c) GO/Fe₃O₄@PAA-Co(II).

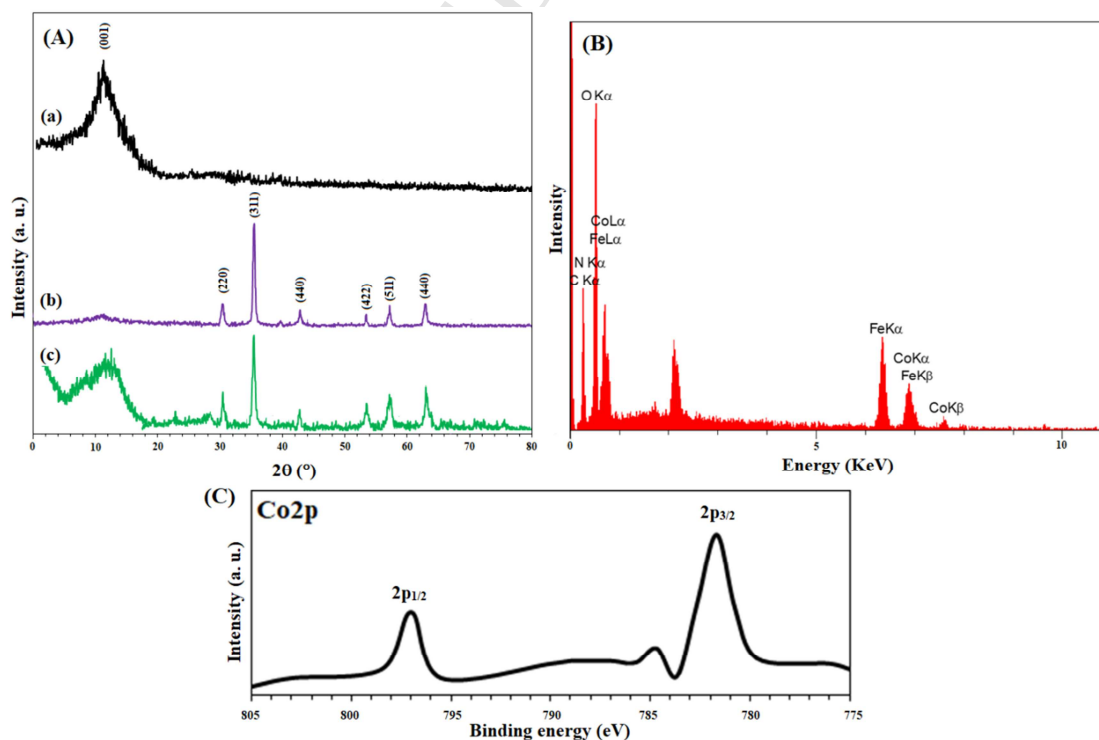


Fig. 3. (A) XRD patterns of (a) GO, (b) GO/Fe₃O₄, (c) GO/Fe₃O₄@PAA-Co. (B) EDX spectrum of GO/Fe₃O₄@PAA-Co (II). (C) High resolution normalized XPS Co2p spectrum of GO/Fe₃O₄@PAA-Co (II)

The presence of elements in the catalyst **8** was detected by EDX analysis. As shown in Fig. 3B, the elements C, O, N, Co, and Fe were detected, which confirming the structure of **8**. The high resolution XPS Co2p spectrum of GO/Fe₃O₄@PAA-Co(II) revealed the oxidation state of Co (II) ions in the catalyst. As shown in Fig. 3C, the Co2p_{1/2} and Co2p_{3/2} lines were appeared at 797.2 eV and 781 eV respectively, which confirms that Co(II) is the only component in GO/Fe₃O₄@PAA-Co(II) and all Co ions are in +2 oxidation state.

The amount of cobalt in GO/Fe₃O₄@PAA-Co(II) was also determined by ICP analysis which is 0.40 mmol.g⁻¹. This amount was completely in agreement and consistence with the results from TGA analyses (Fig. 2B-c).

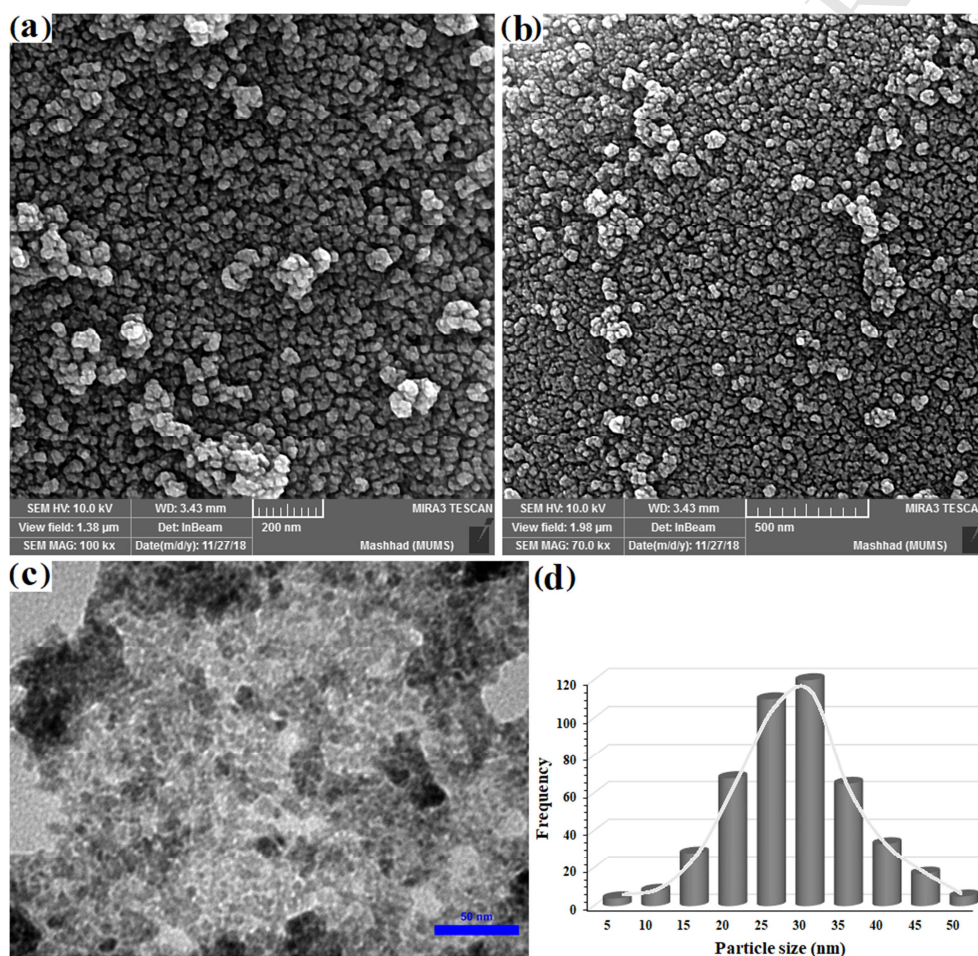


Fig. 4. (a), (b) FE-SEM images, (c) TEM image, and (d) DLS analysis of GO/Fe₃O₄@PAA-Co(II)

The morphology of the NPs was studied by FE-SEM technique. As shown in Fig. 4a,b, the images clearly demonstrated the chemical deposition of Fe₃O₄ NPs on GO framework. The results from TEM analysis, also, confirmed the preparation of GO/Fe₃O₄@PAA-Co(II) hybrid with an average size of 28 nm for the particles (Fig. 4c). The results obtained from DLS analysis (Fig. 4d), revealed that the main size distribution of the NPs are in the range of 25-30 nm. The mean size of the NPs was found to be 30 nm with a deviation of 8.2, in agreement with the corresponding TEM image.

3.2. Optimization of reaction parameters

To explore the catalytic activity of GO/Fe₃O₄@PAA-Co(II), the epoxidation reaction of olefins was conducted in the presence of GO/Fe₃O₄@PAA-Co(II). First, for optimization of the reaction conditions, effective parameters involve in the reaction such as temperature, solvent, oxygen flow rate, and catalyst amount were studied over the epoxidation of styrene as a model reaction. As shown from the spectra in Fig. 5, all mentioned parameter played a crucial role in the epoxidation reaction. Acetonitrile and DMF afforded the most efficiencies among the used solvents with 93% conversion (Fig. 5a). It seems that high dielectric constants associated with them ($\epsilon=36.46, 38.25$ for CH₃CN and DMF respectively) are responsible for this excellent efficiencies. This property is in agreement with the proposed radical mechanism in the next section involves polar substrates and intermediates. Low conversions for epoxy styrene were obtained in DEE, EtOH, and MeOH. It worth noted that the selectivity is strongly depend on the solvent. The highest selectivity was obtained for EtOH (Fig. 5a, 98%). Then, the model reaction was performed in various amount of the catalyst (Fig. 5b). The most possible efficiency was obtained when the reaction was carried out in the presence of 0.2 mol% of GO/Fe₃O₄@PAA-Co(II). Didn't found any significant influence on selectivity at other catalyst amounts. Oxygen flow rate of 15 mL/min and 60 °C (CH₃CN) give epoxy styrene with high efficiency (Fig. 5c). The selectivity linearly dropped in higher O₂ concentrations or temperatures. It may be due to promotion of side oxidation products in these conditions.

Catalytic performance of GO/Fe₃O₄@PAA-Co(II) was investigated toward a variety of olefins including aliphatic, conjugated, cyclic, and in other hand, terminal or internal types under obtained premium conditions. The results including time, conversion, epoxide selectivity and TOF were tabulated in Table 1. The method demonstrated high efficiency in terms of TOF and epoxide selectivity for all substrates (Table 1, **10a-10m**). Surprisingly, epoxidation of substrates with two alkene functionality takes place selectively on one of alkene functional groups (Table 1, **10j** and **10m**). Epoxidation of 3-methyl-1-(oxiran-2-yl)but-3-en-2-one was selectively take placed on the terminal alkene functional group (Table 1, **10l**), which represent chemoselectivity of the present method toward terminal alkenes than the corresponding conjugate types. Also, the preparation of **10i** and **10k** with high conversion demonstrated that the method is suitable for epoxidation of sterically hindrance olefins (Table 1, **10i** and **10k**). It was observed that internal alkenes afforded higher selectivity than other terminal alkenes (Table 1, **10b**, **10d**, **10e**).

3.3. Control experiments

Some control experiments were conducted to show the exclusive catalytic activity of GO/Fe₃O₄@PAA-Co(II). For this goal, PAA-Co(II) complex, graphene oxide, Fe₃O₄, and Co(OAc)₂ were used as catalyst in epoxidation reaction of styrene (10.0 mmol) in CH₃CN in the presence of molecular O₂ (15 mL/min) at 60 °C for 3 h. All the control experiments were conducted under the same conditions. Table 2 shows the corresponding results. GO and Fe₃O₄ afforded inconsiderable efficiency for styrene epoxidation. Also, the selectivity was completely loss for them (Table 2).

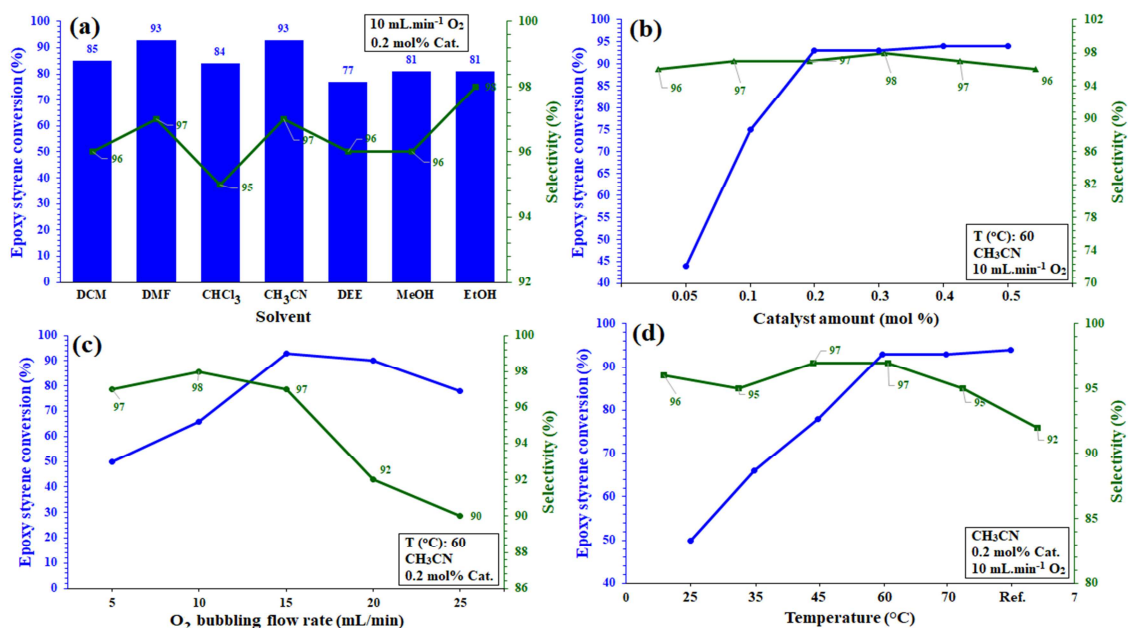
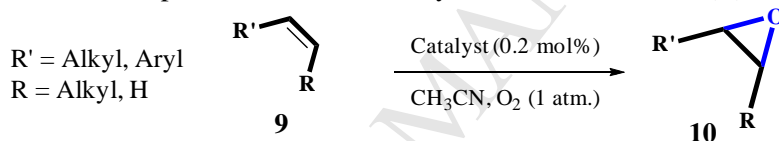
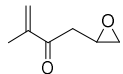
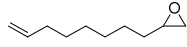


Fig. 5. Screening (a) solvent, (b) catalyst amount, (c) O₂ bubbling flow rate, and (d) temperature on the epoxidation of styrene catalyzed by GO/Fe₃O₄@PAA-Co(II) for 3 h. Green curves demonstrate epoxide selectivity for each study. Conditions: styrene (10.0 mmol), solvent (10 mL).

Table 1 Epoxidation of alkenes by GO/Fe₃O₄@PAA-Co(II)^a



Entry	Product 10	Time (h)	Conversion (%) ^b	Yield (%) ^c	Epoxide selectivity (%) ^b	TOF (h ⁻¹) ^d
1	10a	3	93	88	97	155
2	10b	3.5	96	92	97	137
3	10c	2.2	94	90	95	213
4	10d	2.5	96	93	98	192
5	10e	1	99	96	99	495
6	10f	8	96	90	95	60
7	10g	1	95	93	99	475
8	10h	7.5	98	94	79	65
9	10i	24	92	86	86	19
10	10j	1	96	93	80	480
11	10k	9	94	82	85	52

12		10l	45 min	92	88	86	613
13		10m	1	92	90	84	460

^a Reaction conditions: alkene (10 mmol), catalyst 8 (50 mg, 0.2 mol%), 60 °C, CH₃CN (10 mL), O₂ (~1 atm. bubbling 15 mL/min), time.

^b Isolated yield

^c GC analysis; using an internal standard technique (Anisole) and is based on alkenes.

^d Based on conversion

Co(OAc)₂ provides a moderate efficiency and selectivity (Table 2). Coordination of cobalt into PAA provides only 77 % conversion with low selectivity (88%). In this regard, given the presence of free Fe₃O₄ NPs on GO surface in the catalyst, a synergetic effect arising from Fe₃O₄, Co and PAA-Co complex immobilized on GO could be considered. There is not any detectable product in the absence of any catalyst. The results illustrated the advantage and superiority of the support and the designed structure on the catalytic behavior over all applied reagents, which selectively conduct the epoxidation of alkene.

Table 2 The conversions and selectivities of styrene epoxidation catalyzed by PAA-Co(II) complex, CO, Fe₃O₄, and Co(OAc)₂ along with blank experiment

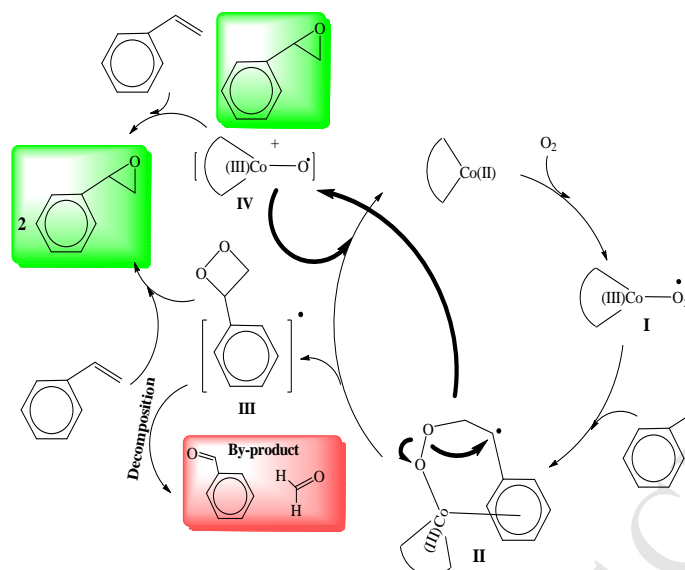
Catalyst	PAA-Co(II) complex ^a	GO	Fe ₃ O ₄ ^b	Co(OAc) ₂	Blank
Conversion (%)	77	8	38	62	Trace
Selectivity (%)	88	35	57	75	-

^a PAA-Co(II) complex was prepared by addition of CoCl₂·6H₂O (10 mg) to 1.0 g of PAA in 25 mL ethanol at reflux conditions. The reaction was stirred for 3 h, then the complex filtered, washed and dried at room temperature.

^b Fe₃O₄ was prepared according to a previously reported procedure [29]

3.4. Mechanism studies

According our observations and other researchers' work [1,30-32], a plausible mechanism was suggested for the epoxidation of olefins with molecular oxygen catalyzed by GO/Fe₃O₄@PAA-Co(II). The suggested mechanism is illustrated in Scheme 4. In first, Co-superoxo active radicals were generated by interaction of the catalyst with O₂ (Scheme 4, Int. I). This was proved by taking XPS analysis of the mixture *in situ*, which the presence of both Co(II) and Co(III) was detected to the mixture (Fig. 6A). Styrene is added to this Co-superoxo intermediate through an oxidative addition reaction, which led to the cyclic intermediate II (Scheme 4). A cyclic peroxide radical (Intermediate III) could be formed from intermediate II and the catalyst is regenerated for the next cycle. This peroxide interacts with another styrene molecule to produce the desired epoxide product. However, the active peroxide may be decomposed to form aldehyde and formaldehyde by-products (Scheme 4), that is not completely consistent with the observed high selectivity in this work for all substrates. Another rote is possible *via* the collapse of II (Scheme 4, bold arrow), which led to a Co-oxo radical (Int. IV) and a desired epoxide molecule, based on the previously reported mechanisms [33,34]. Intermediate IV could be also interacting with another styrene molecule to form epoxide product. Given that high selectivity observed for the substrates, this rote seems to be more probable. However, the formation of epoxide could be takes place through each routes and or a mixture of them. It worth noted that the Co(II) species are only species in the mixture in end of the reaction according to XPS analysis of the recovered catalyst after reaction completion (Fig. 6A-b), which corroborates that the highly active plausible intermediates III and IV are consumed and/or decomposed during reaction.



Scheme 4. A plausible reaction mechanism for catalytic epoxidation of olefins using GO/Fe₃O₄@PAA-Co(II)

To support of the suggested radical mechanism, in another control experiment, hydroquinone as a strong and efficient radical scavenger was added to the reaction mixture of styrene at beginning ($t=0$) as well as 1.5 h of the reaction. Progress of the reactions were monitored every 30 min and the results were gathered in Fig. 6B. As shown in Figure 6B, the reaction is stopped immediately after addition of hydroquinone. Furthermore, addition of hydroquinone at start of the reaction, almost suppress the reaction progress. These results completely confirm that the epoxidation reaction of olefins catalyzed by GO/Fe₃O₄@PAA-Co(II) accomplished by active radical species as shown in Scheme 4.

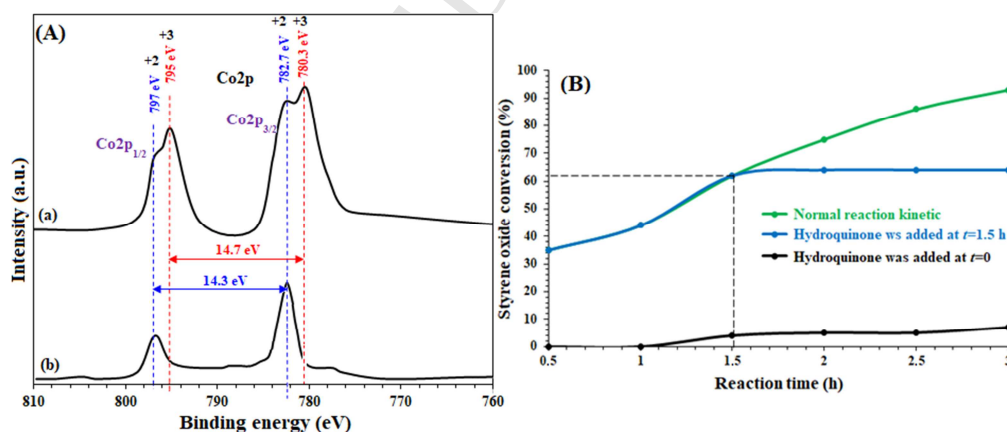


Fig. 6. (A) (a) *In situ* normalized high-resolution XPS spectrum of the epoxidation reaction mixture of styrene catalyzed by the GO/Fe₃O₄@PAA-Co(II) and (b) XPS spectrum of the recovered catalyst (first cycle). (B) Reaction kinetics (green curve) and effect of hydroquinone on reaction progress at beginning (black curve) and at 62% conversion (blue curve) for the epoxidation reaction of styrene.

The magnetic nanocatalyst **8** could be easily recovered from the mixture and reused for the subsequent reactions without any significant reactivity loss (Fig. 7a). The recyclability of the catalyst was investigated for 6 consecutive runs and as a result, didn't found any significant drop in selectivity, epoxide efficiency and catalyst yield. In addition, a small metal leaching was detected in each run that was negligible. The results clearly demonstrate the stability and durability of the catalyst during the reaction. To prove this, the recovered catalyst after 6th run

was characterized by some techniques. VSM analysis of the recovered catalyst demonstrated a similar magnetic behavior as same as the corresponding fresh catalyst. There is not any decrease in saturation magnetization. The results were also confirmed the absence of any magnetite leaching from the catalyst surface. Furthermore, the FE-SEM and TEM images from the recovered catalyst revealed that the catalyst preserves its morphology and distribution during several recycling.

It is well known that some catalytic reactions would anyway take place even if an actual catalytic species is leached off from their material [35,36]. Although, a negligible metal leaching was found for the catalyst, to gain more insight into heterogeneous nature of the catalyst, hot filtration test was applied on the model reaction. The catalyst was magnetically removed *in situ* from the epoxidation reaction of styrene in CH_3CN in the presence of molecular oxygen (15 mL/min bubbling) after 1 h of the reaction mixture (44% epoxy styrene conversion). Reaction progress was monitored every 15 min by GC instrument. Didn't observe any significant progress in epoxidation, which the conversion reached to 46 % after 3 h. These results are in agreement with leaching studies and confirm that the catalyst completely act heterogeneously during the reaction.

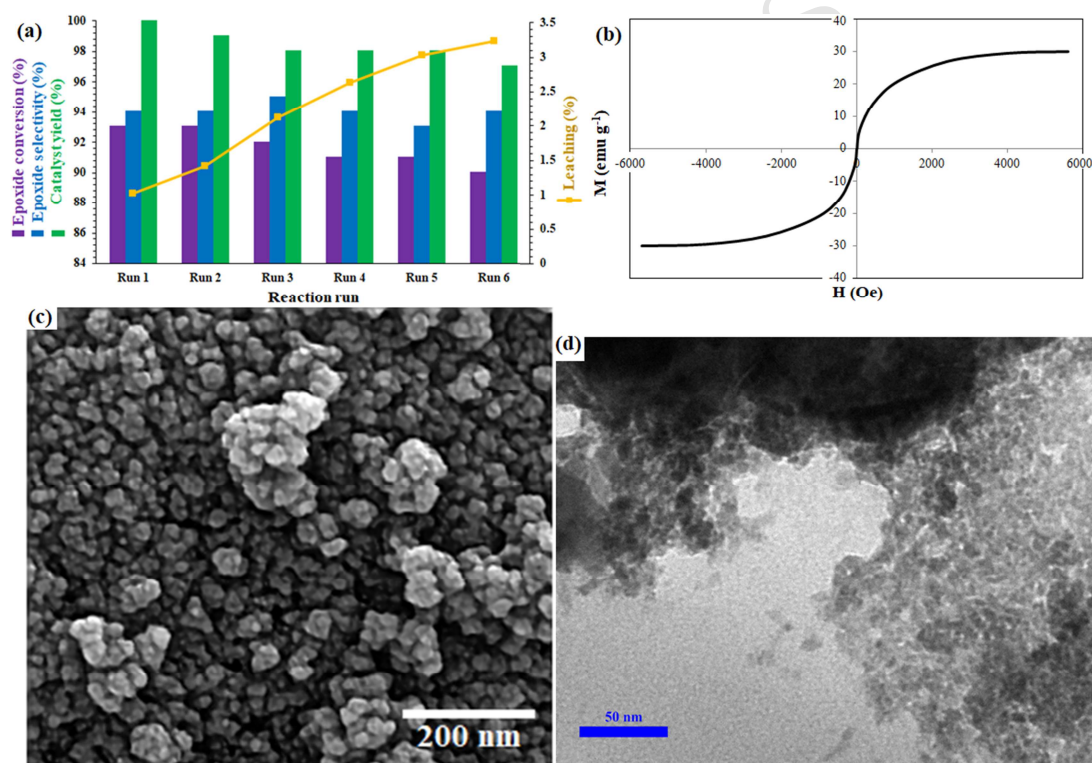


Fig. 7. (A) Recycling of $\text{GO}/\text{Fe}_3\text{O}_4@\text{PAA-Co}$ for the oxidation reaction of styrene in CH_3CN at 60°C in the presence of molecular O_2 . (B) VSM curve, (C) FE-SEM, and (D) TEM analysis of the recovered catalyst after 6th run.

3.5. Scalability of the method

To investigate the potential of the process for larger scales, the epoxidation reaction of styrene was selected as a model reaction. The reaction was performed under the obtained premium conditions with 200, 500, and 700 mmol of styrene. As presented in Table 3, the results clearly demonstrated the direct scalability of the process, which didn't found any considerable loss in efficiency in term of time, conversion or selectivity even at large quantities (Table 3). However, a reasonable insignificant loss in conversion was observed as the amount of styrene rises; nevertheless, the selectivity was independent than the scale and remained constant thoroughly.

Table 3 Gram scale production of epoxy styrene using GO/Fe₃O₄@PAA-Co^a

Entry	mmol of styrene	Time (h)	Conversion (%) ^b	Selectivity (%)
1	200	3	90	97
2	500	3	88	97
3	700	3	86	95

^aThe reactions were performed in a 1 L round bottom flask and the reactions were mechanically stirred. All experiments were performed in the presence of 15 mL.min⁻¹ O₂ bubbling (~ 1 atm.) at 60 °C. For each entry, the amounts of CH₃CN and catalyst **8** were proportional to the amount of styrene (see “General procedure for catalytic epoxidation of olefins by GO/Fe₃O₄@PAA-Co(II)”).

^bGC yield.

4. Conclusion

In conclusion, a novel synthetic poly α -amino acid-Co(II) complex was immobilized on magnetite graphene oxide (GO/Fe₃O₄@PAA Co(II)) and used as an efficient nanocatalyst for selective epoxidation of olefins. A wide variety of olefins were subjected to epoxidation using the catalyst, which high to excellent conversions and selectivities were achieved for all of them. The catalyst has a mean size of about 30 nm (from FE-SEM, DLS and TEM analyses) with saturation magnetization of 32 emu.g⁻¹ (from VSM analysis) containing 0.2 mol%Co²⁺ (from ICP and XPS analyses). Further characterization of the nanocatalyst was obtained from FTIR, TGA, EDX, and XRD analyses. Free coreductant, gram scale, mild reaction conditions (CH₃CN, 60 °C), fast performance, selectivity toward epoxide product, durability (insignificant activity loss during six consecutive recycling), thermal stability, magnetically recoverable, and high efficiency epoxide products were some of the advantages of the present protocol, which make it suitable alternative method for the epoxidation program. Furthermore, direct scalability for the process in large quantities was found that is applicable for industrial goals.

Conflicts of interest

There are no conflicts to declare.

Acknowledgment

Authors gratefully acknowledge the financial support of this work by the Research Council of University of Birjand. We also thank Roxana Nayerlou for her critical reading and comment on the manuscript.

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Highlights

- ▶ A novel Co(II)-poly α -amino acid-modified graphene oxide was used for epoxidation of alkenes
- ▶ Epoxidation of olefins was performed in absence of any co-reductant
- ▶ The catalytic system controls epoxide selectivity and provide high efficiency
- ▶ Epoxidation occurs through a radical mechanism.