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### Chromium containing Fe<sub>3</sub>O<sub>4</sub>/polyacrylonitrile-ethylenediamine as a

### magnetically recoverable catalyst for alcohol oxidation

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#### Abstract

A new chromium containing  $Fe_3O_4$ /polyacrylonitrile-ethylenediamine has been prepared through *in situ* polymerization of acrylonitrile onto the surface of magnetic nanoparticles. The polymer magnetic nanocomposite was utilized for the oxidation of a number of aromatic alcohols as a reusable catalyst. The corresponding aldehydes were obtained in high yields within short reaction time under mild conditions.

*Keywords:* Polymer magnetic catalyst, Cr(III), Ethylenediamine, Polyacrylonitrile, Organic-solvent-free alcohol oxidation.

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#### **1. Introduction**

In recent years, the use of nanoparticles as catalysts in organic transformations has attracted considerable interest because nanoparticles provide high surface area-to-volume ratios [1,2]. Although a significant enhancement of catalytic activity could be achieved by synthesizing a catalyst in nanometer dimensions, recovery of the catalyst from the reaction mixture is a problem as they cannot be efficiently filtered out from the reaction medium. Therefore, the design of efficient and recoverable nanoparticles has become an important issue in the case of economic and environmental aspects. In this regard, magnetic nanoparticles (MNPs) have held out significant potential as reusable catalysts because of the ease of recovery by magnetic separation, which prevents loss of catalyst and increases recyclability. Over the last decade, functionalized magnetic nanoparticles have been utilized as efficient recoverable catalyst for various organic transformations, which represent excellent catalytic activities [3-9].

Selective catalytic oxidation of benzyl alcohol to benzaldehyde is one of the most important chemical reactions in chemistry. Benzaldehyde has been widely applied in the manufacture of odorants, flavors, aniline dyes, plastic additives and pharmaceutical intermediates as an important raw material [10]. Over the last few years, many studies have been reported on the oxidation of benzyl alcohol to benzaldehyde with different catalytic systems [11–

14]. Therefore, the increasing need for efficient and selective catalysts as well as the fundamental investigations are continuously the driving forces for synthesis of new catalysts. Furthermore, from the point of view of environmentally benign and clean technologies, synthetic strategies that avoid the use of any organic solvents as well as corrosive catalysts and oxidants are becoming more attractive. Regarding sustainable systems, hydrogen peroxide is as a favorite oxidant since it can oxidize organic compounds with water as a by-product and thus avoids the

production of highly toxic wastes [15,16]. These advantages of hydrogen peroxide motivate scientists to develop new catalytic systems for  $H_2O_2$ -mediated alcohol oxidation reactions. A variety of different catalytic systems for the hydrogen peroxide promoted oxidation have been developed recently [17-21].

Chromium complexes are well-known catalysts since they have many advantages such as variable oxidation states, spin states coordination numbers and redox properties in different chromium complexes [22]. In this case, many studies have been undertaken to investigate the catalytic activity of various chromium-containing catalysts in the oxidation of alcohols [23-26].

As a continuation of our studies related to efficient heterogeneous magnetic catalysts [27,28], we became interested in immobilization of ethylenediamine onto the polyacrylonitrile coated  $Fe_3O_4$  nanoparticles through its primary amine groups, which plays as a ligand for incorporation of chromium ions. Catalytic performance of the polymer magnetic nanocomposite was examined for alcohol oxidation.

#### 2. Experimental

#### 2.1. Catalyst preparation

Preparing Cr(III)-containing Fe<sub>3</sub>O<sub>4</sub>/polyacrylonitrile-ethylenediamine includes four steps which are as follows. The schematic procedure was also illustrated in Scheme 1. First, Fe<sub>3</sub>O<sub>4</sub> nanoparticles were synthesized by a chemical co-precipitation method [29]. Afterwards, surface modification of the magnetic nanoparticles was carried out as reported in the literature [30], with some modifications. Fe<sub>3</sub>O<sub>4</sub> nanoparticles (1 g) were placed in a round bottom flask and sonicated for 10 min. Then, a solution of acrylonitrile monomer (0.5 g) in THF (15 mL) were added dropwise and sonicated for another 10 min. Benzoyl peroxide (0.05 g) was then added as

initiator, and the mixture was heated to 60 °C for 6 h while stirring. Finally, the resulting solid material was removed by a magnet and dried at 50 °C overnight to give Fe<sub>3</sub>O<sub>4</sub>-PAN. Ethylenediamine was immobilized onto the surface of Fe<sub>3</sub>O<sub>4</sub>-PAN using a simple procedure as described previously [31]. Briefly, 1 g of Fe<sub>3</sub>O<sub>4</sub>-PAN, ethylenediamine (20 mL) and deionized water (10 mL) were added to a round bottom flask and the mixture was stirred under reflux for 5 h. Then, the sample was separated by an external magnet and washed several times with warm deionized water until the pH was neutral. Finally, the nanocomposite was dried overnight under vacuum at 70 °C to yield Fe<sub>3</sub>O<sub>4</sub>-PAN-ED. Finally, the incorporation of chromium ions onto the Fe<sub>3</sub>O<sub>4</sub>-PAN-ED nanocomposite was carried out using various amounts of CrCl<sub>3</sub>.6H<sub>2</sub>O (1, 2, 3 and 4 mmol). In details, a flask containing a stirred suspension of chrome(III) chloride hexahydrate in dry methanol (15 mL) was purged with nitrogen and heated to 40 °C under a nitrogen atmosphere. Fe<sub>3</sub>O<sub>4</sub>-PAN-ED (1 g) was then added in one portion and the resulting suspension was refluxed in a nitrogen atmosphere under vigorous stirring for 6 h. Afterwards, the synthesized nanocomposite (Fe<sub>3</sub>O<sub>4</sub>-PAN-ED-Cr) was separated from the suspension by magnetic decantation, washed several times with deionized water and dry methanol, and dried under vacuum at room temperature.

The Cr content of the nanocomposite, as determined by atomic absorption spectroscopy (AAS), was found to be 0.64, 1.12, 1.58 and 1.60 mmol  $g^{-1}$  for 1, 2, 3 and 4 mmol of chrome(III) chloride hexahydrate, respectively.

#### (Space for Scheme 1)

#### 2.2. Apparatus

The crystalline structures of the samples were evaluated by X-ray diffraction (XRD) analysis on a Bruker D8 Advance diffractometer with  $CuK_a$  radiation at 40 kV and 20 mA.

Fourier transform infrared (FT-IR) spectra were recorded with a Perkin Elmer 65 spectrometer in the range of 400–4000 cm<sup>-1</sup>. Transmission electron microscopy (TEM) analysis was performed on a Phillips CM10 microscope at an accelerating voltage of 200 kV. Magnetization measurements were carried out on a BHV-55 vibrating sample magnetometer (VSM). DR UV–Vis spectroscopy was carried out with a JASCO V-670.

#### 2.3. General procedure for alcohol oxidation

In a typical reaction, a mixture of benzyl alcohol (0.2 mL, 2 mmol) and the magnetic catalyst (0.03 g) was loaded in a two-neck round bottom flask. Hydrogen peroxide (30%, 6 mmol) was then added dropwise to the mixture and stirred under organic-solvent-free condition at room temperature. The progress of reaction was monitored by thin layer chromatography (TLC). After completion of the reaction, the catalyst was separated by an external magnet and the liquid organic product was analysed by an Agilent gas chromatograph 6890 equipped with a HP-5 capillary column. Dodecane was used as the internal standard to calculate benzyl alcohol conversion and benzaldehyde selectivity.

#### 3. Results and discussion

#### 3.1. Catalyst characterization

The crystalline structures of Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>3</sub>O<sub>4</sub>/PAN–ED-Cr were evaluated by powder Xray diffraction (XRD). As displayed in Fig. 1, all the samples depict diffraction peaks at around  $30.4^{\circ}$ ,  $36.0^{\circ}$ ,  $43.3^{\circ}$ ,  $53.8^{\circ}$ ,  $57.1^{\circ}$  and  $62.5^{\circ}$  2 $\theta$  ascribing to the spinel structure of Fe<sub>3</sub>O<sub>4</sub> [32], which can be assigned to the diffractions of the (220), (311), (400), (422), (511) and (440) faces of the crystals, respectively. Furthermore, the XRD patterns show similar diffraction peaks

which indicate that the nanocomposite was synthesized without damaging the crystal structure of the Fe<sub>3</sub>O<sub>4</sub> core. Moreover, the broad diffraction peak in the range of 2 $\theta$  between 20° and 30° accounts for the amorphous polymer coated on the magnetic nanoparticles [33].

#### (Space for Fig. 1)

The FT-IR spectra of the Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>/PAN, Fe<sub>3</sub>O<sub>4</sub>/PAN–ED and Fe<sub>3</sub>O<sub>4</sub>/PAN–ED–Cr samples were recorded to confirm the modification of the magnetite surface with the organic polymer shell and metal ions (Fig. 2). The presence of magnetite nanoparticles is confirmed by the strong adsorption band at about 562  $\text{cm}^{-1}$ , corresponding to the Fe–O vibrations (Fig. 2a–d). Considering the spectrum of Fe<sub>3</sub>O<sub>4</sub>/PAN (Fig. 2b), the 2248 cm<sup>-1</sup> absorption band indicates the existence of C=N units in the nanocomposite. Moreover, the bands in the 2800-3000  $\text{cm}^{-1}$  region are attributed to the stretching of C–H bonds of the saturated alkane, which are observable in Fig. 2b-d [34]. In the case of Fe<sub>3</sub>O<sub>4</sub>/PAN-ED (Fig. 2c), it can be seen that the intensity of characteristic absorption peak of the C≡N group decreases significantly. Instead, two strong characteristic bands appeared at the region of 1654 cm<sup>-1</sup> and 1433 cm<sup>-1</sup>, which can be assigned to the amide functional group and bending vibration absorption of the N–H bond [30]. In addition, the peak at approximately  $3400 \text{ cm}^{-1}$  may be attributed the presence of the stretching vibration of the N-H groups in the structure of Fe<sub>3</sub>O<sub>4</sub>/PAN-ED. These results demonstrate that most of the  $C \equiv N$  functional groups in Fe<sub>3</sub>O<sub>4</sub>/PAN have been converted to amide groups through the immobilization of ethylenediamine, and the Fe<sub>3</sub>O<sub>4</sub>/PAN-ED was successfully obtained. In terms of Fe<sub>3</sub>O<sub>4</sub>/PAN-ED-Cr (Fig. 2d), a red shift of the band at 1654 cm<sup>-1</sup> is observed (1654 cm<sup>-1</sup>  $\rightarrow$ 1628  $\text{cm}^{-1}$ ), which is possibly due to the asymmetrical fluctuations of the carbonyl group after interaction with the metal ions [28]. The same shift also took place for the vibration absorption of the N–H bond, which shifts from 1433  $\text{cm}^{-1}$  to 1402  $\text{cm}^{-1}$  indicating the interaction between

the nitrogen donors and the metal ions. Furthermore, the characteristic band of N–H group of PAN–ED, which is located at about 3400 cm<sup>-1</sup>, reduced in the spectrum of the Fe<sub>3</sub>O<sub>4</sub>/PAN–ED–Cr (Fig. 2d), implying a strong interaction between the nitrogen donors and the metal ions [28].

#### (Space for Fig. 2)

Figure 3 depicts the TEM micrograph of the  $Fe_3O_4/PAN-ED-Cr$  nanocomposite. A continuous layer of the complex (PAN-ED-Cr) was clearly observed on the outer surface of the  $Fe_3O_4$  nanoparticles. It means that after compositing with PAN-ED-Cr, the particles were fully encapsulated by the metal-containing complex to form  $Fe_3O_4/PAN-ED-Cr$ , with the size of approximately 20 nm.

### (Space for Fig. 3)

The magnetic properties of the Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>3</sub>O<sub>4</sub>/PAN–ED–Cr nanocomposite were measured by a vibrating sample magnetometer (VSM) at room temperature (Fig. 4). It can be seen that the saturation magnetization (Ms) values of the samples are 61.2 and 42.3 emu g<sup>-1</sup> for the Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>3</sub>O<sub>4</sub>/PAN–ED–Cr, respectively. It is clear that the Ms of the nanocomposite (Fig. 4b) is significantly less than that of the magnetic nanoparticles (Fig. 4a), which may be due to the fact that the Fe<sub>3</sub>O<sub>4</sub> nanoparticles were coated completely by an inert organic shell (PAN– ED–Cr). These results from the magnetic properties are in accordance with the XRD, IR and TEM analysis.

#### (Space for Fig. 4)

The DRS UV-Vis spectroscopy of  $Fe_3O_4$ -PAN-ED and  $Fe_3O_4$ -PAN-ED-Cr was performed in order to investigate the electronic state of the transition metal ion. As illustrated in Fig. 5, there is no characteristic peak in  $Fe_3O_4$ -PAN-ED spectrum (Fig. 5a). However, in terms of

Fe<sub>3</sub>O<sub>4</sub>-PAN-ED-Cr (Fig. 5b), two absorption peaks appeared at  $\sim$ 400 and  $\sim$ 590 nm, which could be attributed to the d–d transitions of the Cr complex.

(Space for Fig. 5)

#### *3.2. Catalytic activity*

The catalytic performance of Fe<sub>3</sub>O<sub>4</sub>/PAN–ED–Cr was evaluated for the oxidation of alcohols as a new magnetic catalyst. In order to optimize the reaction conditions and obtain the best catalytic activity, the oxidation of benzyl alcohol was chosen as a model reaction. In this case, different reaction parameters such as solvent and amount of catalyst were investigated. The model reactions were carried out over the catalyst with the best metal content (reported in the experimental section, 1.58 mmol  $g^{-1}$ ) at room temperature.

As far as the effect of solvent is concerned, the model reaction was carried out in several solvents as well as organic-solvent-free condition to investigate the efficiency of the catalyst (Table 1). It can be seen, the best yield was obtained when the reaction was performed under organic-solvent-free condition (67%). Also, it is obvious that the catalytic activity of the magnetic nanocomposite significantly reduced by using water as solvent, which may be due to the possibility of blocking active sites of the catalyst by water molecular.

Moreover, the effect of catalyst amount on the oxidation of benzyl alcohol was carried out by different amounts of the catalyst (Table 1). It was observed that while the amount of catalyst increased from 0.01 to 0.03 g, the product yield raised significantly from 67% to 98%, which is probably due to the availability of more active sites ( $Cr^{3+}$ ). Since then, the percentage of yield remained stable between 0.03 g and 0.04 g, with a reduction of about 12% in benzaldehyde

selectivity, which may be due to over-oxidation of the substrate at the high amount of the catalyst.

(Space for Table 1)

In order to investigate the role  $Cr^{3+}$  in the catalyst, the model reaction was carried out under the optimized reaction conditions in the presence of Fe<sub>3</sub>O<sub>4</sub>/PAN–ED as catalyst. No reaction yield was obtained even after four hours. As a result, it can be concluded that  $Cr^{3+}$ incorporated onto the magnetic nanocomposite plays a pivotal role in the oxidation of alcohols.

Based on the experimental results, a proposed mechanism for the oxidation of alcohols by hydrogen peroxide under  $Fe_3O_4/PAN-ED$ -Cr could be summarized as the following, which is similar to the previous reported literature [35].

(1)  $\operatorname{Cr}(\operatorname{III}) + 2\operatorname{H}_2\operatorname{O}_2 \to \operatorname{Cr}(\operatorname{VI}) + 2\operatorname{HO}^{+} + 2\operatorname{HO}^{-}$ (2)  $\operatorname{HO}^{\bullet} + \operatorname{RCH}_2\operatorname{OH} \to \operatorname{RC}^{\bullet}\operatorname{HOH} + \operatorname{H}_2\operatorname{O}$ (3)  $\operatorname{RC}^{\bullet}\operatorname{HOH} + \operatorname{Cr}(\operatorname{VI}) \to \operatorname{RCHO} + \operatorname{Cr}(\operatorname{III}) + \operatorname{H}^{+}$ 

In the case of industrial aspects, reusability of the catalyst was tested by carrying out repeated runs of the reaction on the same batch of the catalyst in the case of the model reaction. In order to regenerate the catalyst, after each cycle, it was separated by a magnet and washed several times with deionized water and ethanol. Then, it was dried in oven at 60 °C and used in the oxidation reaction. The results showed that this polymer magnetic catalyst could be reused six times with no significant loss of activity/selectivity (7% in yield).

The Fe<sub>3</sub>O<sub>4</sub>/PAN–ED–Cr catalyst also represented good activity and selectivity in the oxidation of different aromatic and aliphatic alcohols (Table 2). All the investigated alcohols

were converted to their corresponding aldehydes in high yields with excellent selectivity. It can also be observed that the catalyst had high activity for the oxidation of secondary alcohols (Table 2, Entries 11 and 12).

(Space for Table 2)

#### 4. Conclusion

A facile procedure for the synthesis of Cr(III)-containing Fe<sub>3</sub>O<sub>4</sub>/polyacrylonitrileethylenediamine nanocomposite (Fe<sub>3</sub>O<sub>4</sub>/PAN–ED–Cr) was reported. This new magnetic organicinorganic nanocomposite containing  $Cr^{3+}$  represented high catalytic activity/selectivity in the oxidation of alcohols. The magnetic catalyst also showed excellent level of reusability, which make it a good candidate for industrial catalytic purposes in different oxidation reactions.

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#### **Figure captions**

- Fig. 1. XRD patterns of (a)  $Fe_3O_4$  and (b)  $Fe_3O_4$ /PAN–ED-Cr.
- Fig. 2. FT-IR spectra of (a) Fe<sub>3</sub>O<sub>4</sub>, (b) Fe<sub>3</sub>O<sub>4</sub>/PAN, (c) Fe<sub>3</sub>O<sub>4</sub>/PAN–ED and (d) Fe<sub>3</sub>O<sub>4</sub>/PAN–ED-Cr.
- Fig. 3. TEM image of the Fe<sub>3</sub>O<sub>4</sub>/PAN–ED-Cr nanocomposite.
- Fig. 4. Room temperature magnetization curves of (a) Fe<sub>3</sub>O<sub>4</sub> and (b) Fe<sub>3</sub>O<sub>4</sub>/PAN–ED–Cr.
- Fig. 5. DR UV–Vis spectra of (a)  $Fe_3O_4$ /PAN–ED and (b)  $Fe_3O_4$ /PAN–ED–Cr.
- Scheme 1. Proposed schematic figure for the structure of prepared magnetic catalyst.













Fig. 5



Solvent	Catalyst (g)	Selectivity to benzaldehyde (%)	Yield (%) <sup>b</sup>
Water	0.01	>99	49
Acetonitrile	0.01	>99	55
n-Hexane	0.01	>99	44
Solvent-free	0.01	>99	67
Solvent-free	0.02	>99	85
Solvent-free	0.03	>99	98
Solvent-free	0.04	87	98
<sup>b</sup> The main byproduct was benzoic acid. <sup>b</sup> GC yield.			

Table 1. Effect	ts of different	t solvents a	nd amount	of catalys	t on the	e benzyl	alcohol	oxidation	in the	presence	of
Fe <sub>2</sub> O <sub>4</sub> /PAN-E	D–Cr. <sup>a</sup>										

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Entry	Substrate	Product	Time (min)	Yield (%) <sup>b</sup>
1	CH <sub>2</sub> OH	Носносно	10	98
2	Br CH <sub>2</sub> OH	Вг СНО	10	93
3	CI CH <sub>2</sub> OH	СІ-СНО	10	93
4	O <sub>2</sub> N CH <sub>2</sub> OH	O <sub>2</sub> N CHO	90	59
5	MeO CHO	HO CH <sub>2</sub> OH	10	84
6	СНО	MeO CH <sub>2</sub> OH	10	90
7	сно	СН2ОН	10	98
8	H <sub>3</sub> C CH <sub>2</sub> OH	H <sub>3</sub> C — CHO	10	88
9	ОН	СНО	110	75
10	ОН	СНО	110	78
11	OH		60	80
12	ОН	20	60	82

Table 2. Organic-solvent-free oxidation of various aromatic and aliphatic alcohols over Fe<sub>3</sub>O<sub>4</sub>/PAN-ED-Cr.<sup>a</sup>

<sup>a</sup> Reaction conditions: substrate (2 mmol),  $H_2O_2$  (6 mmol), catalyst (0.03 g), room temperature, selectivity = >99. <sup>b</sup> GC yield.

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### Highlights

- 1. The synthesized nanocomposite has an excellent chemical stability.
- 2. This polymer magnetic catalyst could be prepared by a cheap and simple method.
- 3. The catalyst exhibited high catalytic activity/selectivity in the oxidation of alcohols.
- 4. The catalyst has an excellent level of reusability.

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