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Aerobic oxidation of olefins in the presence of a new amine functionalized

core-shell magnetic nanocatalyst

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Abstract

study *meso*-tetrakis(4-carboxyphenyl)porphyrinatomanganese(III) In this acetate was immobilized onto the surface of amine functionalized Fe₃O₄ magnetic nanoparticles through covalent linkage. The new magnetic nanocatalyst [Fe₃O₄@SiO₂@NH₂@MnTCPP(OAc)] was characterized using Fourier infrared spectroscopy (FT-IR), X-ray powder diffraction (XRD), electronic and atomic absorption spectroscopy, vibrating sample magnetometry (VSM), thermogravimetric analysis (TGA) and scanning electron microscopy (SEM). The prepared catalyst was used for the oxidation of alkenes with molecular oxygen as standard green oxidant excellent results achieved. The hetero genized and were new [Fe₃O₄@SiO₂@NH₂@MnTCPP(OAc)] oxidation catalyst could be readily reused at least five times without significant decrease in the activity, which displays potential for practical applications.

Keywords: Magnetic nanoparticles, Molecular oxygen, Aerobic oxidation, Heterogenized catalyst, Metalloporphyrin.

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1. Introduction

Oxidation of organic compounds is considered as a starting point for the synthesis of valuable pharmaceutical chemicals in the presence of various catalytic systems. Epoxides as the most important intermediate, which play a significant role in various chemical and biological reactions such as preparation of glue, ethylene glycol, amino alcohols and resin, can usually produce by oxidation of olefins [1-3].

Cytochrome P450 as a powerful enzyme for the oxidation of different types of substrates consists of an iron porphyrin serving as an active catalytic site [4]. Considerable attentions has been paid to the role of porphyrin-based complexes in the oxidation reaction as biomimetic systems, especially for laboratory use [4-6]. In the past decades, due to an ever-increasing environmental pollution, special attention was paid to the use of green oxidants in oxidation reactions [7-9] and great attention has been devoted to the molecular oxygen because of its important advantages such as high active oxygen content, low cost, fast kinetic and available amount [10-12]. Moreover, use of heterogeneous catalyst in the oxidation reactions is another way of approaching green chemistry. Beside the importance of green chemistry in process research, heterogenization of metal complexes help to overcome the problems of oxidative degradation of catalysts. In this aspect, various types of solid support such as mesoporous materials, activated carbons, clays and zeolites were applied to produce hybrid catalysts. The immobilization of transition metal complexes onto the surface of nanomaterials is of widespread interest [13-15]. Large-scale application of Fe_3O_4 nanoparticle as solid support is due to their super paramagnetic property, simple separation, large surface area to volume ratio and easy functionalization [16-18].

In this study, a highly efficient nanocatalyst for the aerobic oxidation of olefins was introduced by immobilization of manganese porphyrin onto the surface of amine functionalized magnetic nanoparticles via amide bond.

2. Experimental

2.1. Preparation of nanocatalyst

A multistep procedure was applied to prepare the magnetic nanocatalyst $[Fe_3O_4@SiO_2@NH_2@MnTCPP(OAc)]$ as illustrated in scheme 1.



Scheme 1. Schematic preparation of magnetic nanocatalyst.

 Fe_3O_4 nanoparticles, $Fe_3O_4@SiO_2$ and $Fe_3O_4@SiO_2@NH_2$ were prepared and characterized using precipitation method as reported previously [18-22] (see supporting information).

Meso-tetrakis(4-carboxyphenyl)porphyrin (H₂TCPP) and MnTCPP(OAc) were prepared and characterized by Adler's method (see supporting information, S1).

MnTCPP(OAc) was anchored onto the surface of amine-functionalized magnetic nanoparticles ($Fe_3O_4@SiO_2@NH_2$) through covalent linkage. The carboxyl group of the MnTCPP(OAc) was attached to the -NH₂ group of magnetic nanoparticles ($Fe_3O_4@SiO_2@NH_2$) using 2-(1H-benzotriazole-1-yl)-1,1,3,3-tetramethyluronium tetraflouroborate (TBTU) as a highly effective uranium salt in the presence of N,N'-diisopropylamine (DIPEA) [23-24] (see supporting information, S1).

2.2. Catalytic test

In a typical procedure, catalytic experiments were carried out in a 5 mL test tube containing 1.06×10^{-3} mmol of nanocatalyst, 0.19 mmol of alkene and 0.96 mmol isobutyraldehyde (IBA) in acetone (1mL). The oxidation reaction initiated under O₂ atmosphere (oxygen balloon) and allowed to stir for 30 min at room temperature. After completion of the reaction, the heterogeneous nanocatalyst was magnetically recovered, organic phase was analyzed by GC-FID and the oxidation product was identified by comparison with authentic samples.

3. Results and Discussion

3.1. Catalyst preparation

Chemical formation of amide bond is one of the most challenging organic transformations, especially for the activity of many peptide hormones. In this aspect, carboxylic acid usually

activated by a coupling reagent and subsequently, the activated form of carboxylic acid react with amine group to produce amide bond.

The surface of amine functionalized silica coated magnetic nanoparticles $(Fe_3O_4@SiO_2@NH_2)$ were modified via the attachment of Mn-porphyrin to prepare porphyrin based magnetic nanocatalyst (Scheme 1). To promote formation of amide bonds between carboxyl group of metalloporphyrin and the amine group of Fe₃O₄@SiO₂@NH₂, basic coupling reagents (TBTU/DIPEA) were used as reported previously [25-27]. The resultant catalyst [Fe₃O₄@SiO₂@NH₂@MnTCPP(OAc)] were fully characterized by different standard methods.

3.2. Catalyst characterization

The amount of loaded manganese porphyrins center onto the surface of amine-functionalized magnetic nanoparticles was determined by atomic absorption spectroscopy (AAS) revealed that each gram of the magnetic nanocatalyst contains 500 µmol of manganese porphyrin.

Immobilization of MnTCPP(OAc) on the surface of amine functionalized magnetic evaluated with FT-IR nanopartic les spectra. The was FT-IR spectrum of [Fe₃O₄@SiO₂@NH₂@MnTCPP(OAc)] (see supporting information, Figure S4) showed a detectable absorption band at around 1650 cm⁻¹ which confirmed the formation of amide bond between -COOH groups of Mn-porphyrins and -NH₂ groups of the support. In addition, other signals at about 1392, 1540 and 1595 cm⁻¹ corresponding to the vibrations of metalloporphyrin are present in the FT-IR spectra. The absorption band at 2854-2923 cm⁻¹ ascribed to the C-H stretching of the propyl group in the pendent APTS can be clearly observed in the FT-IR spectrum of Fe₃O₄@SiO₂@NH₂ which confirms that APTS has been successfully bonded to the silica coated magnetic nanoparticles. The wide absorption peak at about 3400 cm^{-1} is due to hydroxyls (OH) present in water and the amine groups are obscured [28-29].

Fig. 1 shows the XRD pattern of $[Fe_3O_4@SiO_2@NH_2@MnTCPP(OAc)]$ to investigate the crystalline structure of the prepared magnetic nanocatalyst. In the XRD pattern of $[Fe_3O_4@SiO_2@NH_2@MnTCPP(OAc)]$, some characteristic peaks centered on the 20 values of 30.6, 35.7, 43.8, 54.2, 57.3, 63.6, 71.5 and 74.8 correspond to (220), (311), (400), (422), (511), (440), (620) and (533) plans of cubic inverse spinel Fe₃O₄. These diffraction peaks are in good agreement with the database in JCPDS file (PCPDFWIv.2.02, PDF no. 85-1436) and shows that Fe₃O₄ nanoparticles were synthesized without impurity phases and also indicated that the crystalline structure of Fe₃O₄ did not changed after coating with silica shell [30]. Based on the Scherrer's equation, the average particle size of $[Fe_3O_4@SiO_2@NH_2@MnTCPP(OAc)]$ were 22





The SEM images of $Fe_3O_4@SiO_2$ and the prepared nanocatalyst $[Fe_3O_4@SiO_2@NH_2@MnTCPP(OAc)]$ clearly show uniformity and the smooth spherical morphology of magnetic nanoparticles (see supporting information, Figure S5). After porphyrin incorporation, magnetic nanoparticles slightly aggregated and average particle sizes increased,

suggesting immobilization of a huge amount of Mn-porphyrins onto the surface of amine functionalized solid support ($Fe_3O_4@SiO_2@NH_2$).

The magnetic properties of amine functionalized solid support (Fe₃O₄@SiO₂@NH₂), and the prepared nano-catalyst [Fe₃O₄@SiO₂@NH₂@Mn(TCPP)OAc] were characterized by a vibrating sample magnetometer (VSM) under an applied field of -10000 to 10000 Oe at room temperature and the results are illustrated in Fig. 2. A ferromagnetic behavior evidenced through the S-Shaped hysteresis loop and the prepared magnetic nano-catalyst shows strong magnetization, which can be easily separated by an external magnet. According to the magnetization curves, the reduced saturation magnetization values observed for the prepared nanocatalyst in comparison with Fe₃O₄@SiO₂@NH₂ nanoparticles, which was predictable and were due to the diamagnetic surface coating and surface functionalization of Fe₃O₄ nanoparticles [31-32].





The UV-Vis spectrum of magnetic nanocatalyst confirmed the presence of metalloporphyrin on the surface of the synthesized magnetic solid support ($Fe_3O_4@SiO_2@NH_2$) (see supporting information, Figure S6). According to the literature, manganese porphyrins show a characteristic peak at about 475 nm (Soret band) which is clearly detectable in the UV-Vis spectrum of

MnTCPP(OAc) in ethanol (see supporting information, Figure S6, a). No absorption peak was observed in this region in the UV-Vis spectrum of dispersed $Fe_3O_4@SiO_2@NH_2$ in ethanol (Figure S6, b). After deposition of MnTCPP(OAc) onto the surface of magnetic solid support, the UV-Vis spectrum of $[Fe_3O_4@SiO_2@NH_2@MnTCPP(OAc)]$ which has been dispersed in ethanol (by using an ultrasonic bath) shows the typical Soret band of Mn-porphyrins at 481 nm (see supporting information, Figure S5, c). Based on the results, the UV-Vis spectrum of magnetic nanocatalyst exhibited a slight red shift compared to the spectrum of pure MnTCPP(OAc), which could be because of the coordination and aggregation of metalloporphyrins onto the surface of $Fe_3O_4@SiO_2@NH_2$. Moreover, these data confirmed that the structure of Mn-porphyrin remain unchanged after deposition onto the surface of magnetic solid support.

Thermal behavior of $Fe_3O_4@SiO_2@NH_2$ and $[Fe_3O_4@SiO_2@NH_2@Mn(TCPP)OAc]$ were analyzed by thermo-gravimetric analysis (TGA) under N₂ atmosphere (100 mL/min) at a heating rate of 10 °C/min (see supporting information, Figure S7). The TGA curves showed high thermal stability of both Mn-porphyrin coated and uncoated magnetic nano-spheres and no significant degradation of support and separation of the catalyst from the surface of support was observed. The first weight loss step (3.9%) in the temperature range of 100 °C could be related to the loss of physically adsorbed water molecules on the surface of the $Fe_3O_4@SiO_2@NH_2$, and the second weight loss step of 4% between 170 °C and 280 °C is due to the loss of water molecules which are either free-existent at the compound level or bonded to SiO_2 . The last weight loss observed in the temperature range between 500 °C and 900 °C could be related to the loss of NH₂ functional groups attached to the surface of the $Fe_3O_4@SiO_2$. The comparison of two thermograms showed that the weight loss between temperature 260 °C and 470 °C is likely to be due to the separation

of metalloporphyrins from the surface of solid support, which is a very modest reduction and only 2% weight loss could be detectable in this step.

3.3. Catalytic experiments

In order to investigate the catalytic activity of the prepared magnetic nanocatalyst $[Fe_3O_4@SiO_2@NH_2@MnTCPP(OAc)]$ for the aerobic oxidation of olefins, oxidation of styrene (as a model substrate) has been studied under magnetic stirring and different parameters were taken under consideration such as solvent, reaction time, amount of catalyst and reductant (isobutyraldehyde).

In order to find an appropriate solvent for the oxidation of styrene with molecular oxygen and isobutyraldehyde (IBA) in the presence of $[Fe_3O_4@SiO_2@NH_2@MnTCPP(OAc)]$, different solvents such as methanol, ethanol, dichloromethane, chloroform, acetonitrile and acetone were applied and based on the results, the highest conversion in the relatively short time obtained in acetone (Table 1). Epoxy styrene was the major product (acetophenone and benzaldehyde were other products which are detected by GC) and no product was detectable by GC in the absence of the catalyst.

Entry	Solvent	Time (min)	Conversion%	Selectivity%
1	CH ₂ Cl ₂	90	41	100
2	CH ₃ CN	90	43	78
3	CHCl ₃	90	23	68
4	CHCl ₃	120	47	65
5	$CO(CH_3)_2$	60	>99	76
6	CH ₃ OH	120	0	-

Table 1. Effect of solvent on the oxidation of styrene with O_2 in the presence of $[Fe_3O_4@SiO_2@NH_2@MnTCPP(OAc)]$ at room temperature ^a.

7	EtOH	120	0	-

^a The molar ratios for Catalyst:Styrene:IBA are (1:90:450) under an oxygen atmosphere.

Different catalyst concentrations were used in the range of 0.001 g to 0.003 g (see supporting information, Figure S8). The obtained data showed superior catalytic efficiency for aerobic oxidation of styrene in the presence of 0.002 g (0.55 mol%) of catalyst after 30 min (see supporting information, Figure S8, b); however, more catalyst concentration applied caused less efficiency in the same reaction time (see supporting information, Figure S8, c).

Previous reports have been shown that aerobic oxidation of hydrocarbons in the presence of metallo-complexes for the best efficiency needs a reducing agent (such as light aldehydes) to reduce dioxygen at the beginning of the reaction [33-34]. In this research, isobotylaldehyde (IBA) was selected as effective reducing agent for the aerobic oxidation of styrene in the presence of [Fe₃O₄@SiO₂@NH₂@MnTCPP(OAc)] and in order to achieve the highest product yields, the effect of molar ratio of IBA/styrene was studied (see supporting information, Figure S9). Based on the results, no product was observed in the absence of isobutyraldehyde and the highest conversion (100%) was achieved at molar ratio 1:5 of IBA:styrene in acetone at room temperature.

To prove the activity of $[Fe_3O_4@SiO_2@NH_2@MnTCPP(OAc)]$ in the model reaction, aerobic oxidation of a range of olefins under optimized condition were studied and the results have been presented in Table 2.

Based on the results, excellent conversions and desired selectivity to epoxide were achieved for all olefins. This catalytic system led to complete conversion of α -methyl styrene, *trans*stilbene and cyclohexene after 30 min and styrene, 4-methyl styrene and 4-chloro styrene in 1 hour. Cyclooctene was converted to its epoxide in 83% yield after 30 min, 4-methoxy styrene

and indene converted to the corresponding epoxides by 96% and 80% respectively after 60 min. Less activity was observed in the case of terminal olefins (1-octene, 48%).

Table 2. Aerobic oxidation of various olefins in the presence of $[Fe_3O_4@SiO_2@NH_2@MnTCPP(OAc)]$ at room temperature.^a

Entry	Alkene	Product	Conversion% ^b	Selectivity% ^b
1			83	87
2	\bigcup		100	80
3	Ph	Ph	100	100
4		Ph O	85(100) ^b	97(90) ^b
5	CI		56(100) ^b	57(80) ^b
6	Me		(100) ^b	70
7	MeO	Me O	(96) ^b	98
8	Me	MeO MeO	100	67
9			80 ^b	85
10	$()_{5}$	\sim	21(48) ^b	100

^a Reaction conditions: the molar ratios for Catalyst:Olefin:IBA is 1: 180:900, reaction time:30 min under an oxygen atmosphere, acetone: 1mL. ^b Reaction time: 60 min.

A plausible mechanism for the oxidation of styrene with O_2 in the presence of $[Fe_3O_4@SiO_2@NH_2@MnTCPP(OAc)]$ has been reported (Scheme 2). Isobutyraldehye used as a

useful reducing agent for aerobic oxidations and based on the literature [33-36]; free radicals are involved in the catalytic oxidation of olefins with molecular oxygen/IBA. In this mechanism, two parallel pathways could be possible. In the first step, Mn-por reacts with IBA to generate an acyl radical (Scheme 2, (a)). In the second one, the generated acyl radical reacts with dioxygen to give an acylperoxy radical (Scheme 2, (b)) which can oxidize styrene directly (Scheme 2, pathway (A)). Acylperoxy radical can also act with another aldehyde to give peroxyisobutyric acid (Scheme 2, (c)), resulting the production of another acyl radical. Formation of epoxy styrene is assumed by the presence of an active intermediate (high-valent Mn-porphyrin species) which are formed by the reaction of the peroxyisobutyric acid with Mn(II) porphyrin (Scheme 2, pathway (B)).



The reusability of heterogeneous catalysts is one of the most important ability, which make them useful for various applications. The magnetic property of core-shell magnetic nonocatalysts can facilitate recovery and reusability of the heterogenized catalyst. The reusability of the prepared porphyrin based nanocatalyst investigated in the multiple sequential oxidation of styrene with O_2 in acetone at room temperature. After each catalytic cycle, when the magnetic stirring stopped, the catalyst easily separated from the reaction media by an external magnet (see supporting information, Figure S10), washed with acetone (2 mL, 2×2 time), completely dried and used in the subsequent run without further purification.

[Fe₃O₄@SiO₂@NH₂@MnTCPP(OAc)] was reused for at least five consecutive cycle and the amounts of Mn leached after each run were determined by AAS analysis as illustrated in Table 3. The results show that after each catalytic cycle, trace amount of Mn was leached; only after more reaction time, proper conversion and high selectivity was achieved (Table 3, column 3). AAS, FTIR and UV-Vis spectra were employed to prove the stability of magnetic nano-catalyst after five catalytic cycle; the results show that the structure of the recovered catalyst remain unchanged (see supporting information, S4".

Table 3. The result of the reusability of nano-catalyst for the oxidation of styrene with O_2 at room temperature.

Run	Time (min)	Conversion % ^a (Selectivity%)	Mn-leaching%
1	60	100 (90)	0
2	60	97 (90)	0.04
3	80	86 (90)	0.15
4	80	86 (88)	0.21
5	90	80 (88)	0.47

^a The molar ratios for Catalyst:Styrene:IBA are (1:180:900) under an oxygen atmosphere, acetone: 1 mL. To evaluate the catalytic efficiency of $[Fe_3O_4@SiO_2@NH_2@MnTCPP(OAc)]$, the obtained results of this catalytic system for the aerobic oxidation of styrene were compared with some earlier reported studies and the results proved the efficiency of our proposed model especially in the case of the reaction time and temperature (see supporting information, Table S1).

4. Conclusions

In conclusion, manganese porphyrin was successfully immobilized onto the surface of amine functionalized silica coated Fe_3O_4 . The magnetically separable catalyst is highly efficient for green oxidation of alkenes with O_2 in the mild condition. This super magnetic nanoparticle can

be used for several times without detectable leaching of the catalyst and decreasing the catalytic activity and selectivity.

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- Preparation of a new porphyrin based magnetic nanocatalyst [Fe₃O₄@SiO₂@NH₂@MnTCPP(OAc)].
- Aerobic oxidation of olefins at room temparature and in the short reaction time.
- Excellent activity and high stability of magnetic nanocatalyst.

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