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1. Introduction

Selective catalytic oxidation of alcohols to carbonyls is one of the most important chemical transformations in industrial chemistry. Carbonyl compounds such as ketones and aldehydes are the precursors for many drugs, vitamins, and fragrances and they are also important intermediates for many complex syntheses.^{1,2} Numerous methods are available for alcohol oxidation. Conventional methods for these transformations generally involve the use of stoichiometric or more than stoichiometric quantities of inorganic oxidants such as chromium(v1) and permanganates and also the use of toxic, corrosive and expensive oxidants.³ The search for new oxidation catalysts is one of the most important topics connected with both industrial and academic research.

Manganese Schiff base complexes are known as powerful homogeneous catalysts for oxidation of organic compounds and various single oxygen atom donors such as NaClO, PhIO, KHSO₅, H_2O_2 and NaIO₄ have been used in these reactions. But, the catalytic activity of manganese Schiff base complexes in homogeneous conditions usually decreases with time due to the oxidation of ligand or formation of dimeric oxo- and peroxobridged complexes. The heterogenization of these homogeneous catalysts on solid supports displayed high recyclability and stability, and also decreased the possibility of dimerization, and formation of undesired mono-oxo manganese($_{IV}$).^{4,5}

Direct covalent attachment of Mn(III) salophen complex to the hydroxyapatite-encapsulated γ -Fe₂O₃ nanocrystallites: an efficient magnetic and reusable catalyst for oxidation of alcohols

Ali Saffar-Teluri

In the present work, the highly efficient oxidation of alcohols catalyzed by manganese(III) salophen acetate, [Mn(salophen)OAc], supported on hydroxyapatite coated magnetite nanoparticles, HAp–Fe₂O₃, is reported. First, the HAp–Fe₂O₃ nanoparticles were modified with 5-chloromethyl-2-hydroxybenzaldehyde and then using 1,2-diamino benzene, 2-hydroxybenzaldehyde and Mn(CH₃COO)₂·4H₂O, [Mn(salophen)OAc] was synthesized and attached to the support *via* covalent linkages. The prepared catalyst was characterized by FT-IR spectroscopy, X-ray diffraction, diffuse reflectance UV-Vis spectrophotometry and scanning electron microscopy. This new heterogeneous catalyst was used for efficient oxidation of alcohols with NalO₄ at room temperature. This new heterogeneous catalyst is of high reusability in the oxidation reactions, in which the catalyst was reused several times without significant loss of its catalytic activity.

The use of nanostructured materials as support for different versions of catalyst immobilization is increasing. In spite of the advantages of supported catalysts, the tedious recycling of catalysts by filtration and the inevitable loss of some solid catalyst in the separation process, especially with air sensitive materials, are some of the drawbacks of the traditional procedures. Therefore, there is more interest to introduce more efficient manners for catalyst recovery, especially from the standpoint of green chemistry. Magnetic nanoparticles are receiving increasing interest in recent years.⁶⁻⁸ The magnetic nature of these particles allows for easy recovery and recycling of the catalysts by an external magnetic field, which may optimize operational cost and enhance product's purity.

Hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂, HAp) is a principal component of animal bones and its synthetic form finds many applications in bioceramics, chromatographic adsorbents, lighting materials, powder carriers, chemical sensors, retardant of cancer cells, drug delivery agent, catalyst supports, catalysts for dehydration and dehydrogenation of alcohols, methane oxidation, ion conductors and powders for artificial teeth and bones paste germicides.⁹⁻¹⁴ These properties relate to various surface characteristics of HAp. It has been found that HAp surface possesses P–OH groups acting as sorption sites.¹⁵ The sorption properties of HAp are of great importance for both environmental processes and industrial purposes.

Covalent surface modification of inorganic materials using organic compounds is an efficient way to obtain materials having specific properties. Recently, the reaction between phenyl phosphonic dichloride ($C_6H_5P(O)Cl_2$) and calcium hydroxyapatite has been investigated. From their results, a

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Fig. 1 Covalent surface modification of hydroxyapatite using $C_6H_5P(O)Cl_2$.



Fig. 2 Oxidation of alcohols with NaIO_4 catalyzed by $\gamma\text{-Fe}_2\text{O}_3\text{@HAp}/\text{Mn}(salophen)\text{OAc}.$

mechanism has been proposed for the formation of covalent P–O–P bonds as the result of a reaction between the $C_6H_5P(O)$ Cl_2 organic reagent and HPO_4^- and/or OH^- ions of the hydroxyapatite (Fig. 1).^{16–22}

Herein, we report the attachment of Mn(salophen)OAc on HAp-coated γ -Fe₂O₃ *via* a strong covalent interaction and investigate its catalytic activity in alcohols oxidation as a magnetically recyclable oxidation catalyst (Fig. 2).

2. Experimental

All materials were commercial reagent grade. These materials were obtained from Merck or Fluka chemical companies and used without further purification. The diffuse reflectance UV-Vis spectra were recorded by a solid UV-Vis JASCO model V-670 spectrophotometer. FT-IR spectra were obtained with potassium bromide pellets in the range 400–4000 cm⁻¹ with a JASCO 6300 spectrophotometer. A scanning electron micrograph of the catalyst was taken on a Philips XL 30 SEM instrument. Information about the phase of catalyst was obtained by the X-ray powder diffractometer (Cu Ka, k = 1.54178 Å; Philips) in the Bragg angle ranging between 10° and 80°.

2.1 Synthesis of HAp-encapsulated- γ -Fe₂O₃ (γ -Fe₂O₃@HAp)

Preparation of HAp-encapsulated- γ -Fe₂O₃ was according to the previously reported method.^{23,24} FeCl₂·4H₂O (1.85 mmol) and FeCl₃·6H₂O (3.7 mmol) were dissolved in deionized water (30 ml) under Ar atmosphere at room temperature, and the resulting solution was added to a 25% NH₄OH solution (10 ml) with vigorous mechanical stirring. A black precipitate Fe₃O₄ was produced instantly. After 15 min, 100 ml of Ca(NO₃)₂·4H₂O (33.7 mmol, 0.5 M) and (NH₄)₂HPO₄ (20 mmol, 3.0 M) solutions adjusted to pH 11 were added drop-wise to the obtained precipitate over 30 min with mechanical stirring. The resultant milky solution was heated to 90 °C. After 2 h, the mixture was

cooled to room temperature and aged overnight. The dark brown precipitate formed was filtered, washed repeatedly with deionized water until neutral, and air dried under vacuum at room temperature. The as-synthesized sample was calcined at 300 °C for 3 h, giving a reddish-brown powder.

2.2 Synthesis of manganese(m) salophen acetate supported on hydroxyapatite coated Fe₂O₃ [γ -Fe₂O₃@HAp/Mn(salophen) OAc]

The procedures of the catalyst synthesis is shown in Fig. 3.

The HAp-encapsulated- γ -Fe₂O₃ nanoparticles (3.0 g) were dispersed in ethanol (50 ml) for 1 h. Then, 5-chloromethyl-2hydroxybenzaldehyde (30 mmol) was added and the reaction mixture was refluxed for 24 h. At the end of this time, the mixture was cooled to room temperature and a solution of 1,2diamino benzene (10 mmol) in ethanol (20 ml) was added dropwise to the above solution. After stirring for 12 h, 2hydroxybenzaldehyde (10 mmol) was added to mixture. The resulted mixture was heated under reflux for 12 h. In order to synthesize Mn(III) complex, Mn(CH₃COO)₂·4H₂O (10 mmol) was added to the suspension and stirred at reflux temperature under Ar for 8 h. After this time, the precipitate was collected with a permanent magnet, and rinsed with ethanol three times. The product was dried and stored under vacuum conditions.

The manganese(III) salophen loading on γ -Fe₂O₃@HAp support, determined by ICP analysis, was calculated from the manganese content in the heterogenized catalyst.

2.3 Typical procedure for oxidation of alcohols with NaIO₄ catalyzed by γ -Fe₂O₃@HAp/Mn(salophen)OAc

All of the reactions were carried out at room temperature under air in a 25 ml flask equipped with a magnetic stirrer bar. A solution of NaIO₄ (1 mmol) in H₂O (5 ml) was added to a mixture of alcohol (0.5 mmol) and γ -Fe₂O₃@HAp/Mn(salophen) OAc (130 mg) in CH₃CN (5 ml). Progress of the reactions was monitored by thin layer chromatography (TLC) technique. At the end of the reaction, the catalyst was removed by a magnet. The catalyst was thoroughly washed with Et₂O and combined washings and filtrates were purified on a silica gel plate or a silica gel column to give the pure product. All of the products are known compounds and were identified by comparison of their physical data with those of authentic samples. Blank experimental with using the same experimental conditions in the absence of catalyst or in the absence of oxidant were also performed.

2.4 Catalyst reuse and stability

The reusability of the γ -Fe₂O₃@HAp/Mn(salophen)OAc catalysts was investigated in the multiple sequential oxidation of 4methoxybenzyl alcohol as described above. At the end of each reaction, the catalyst was separated from the reaction mixture by a permanent magnet, washed and dried carefully before using it in the next run.



Fig. 3 Synthesis of γ -Fe₂O₃@HAp/Mn(salophen)OAc.

3. Results and discussion

3.1 Preparation and characterization of the catalyst, γ -Fe₂O₃@HAp-Mn(salophen)OAc

For identification of the structure of γ-Fe₂O₃@HAp-Mn(salophen)OAc, we studied FT-IR spectra of γ -Fe₂O₃@HAp and γ -Fe₂O₃(a)HAp-Mn(salophen)OAc (Fig. 4). It was found that all characteristic bands of y-Fe2O3@HAp appeared in the FT-IR spectrum of γ -Fe₂O₃@HAp-Mn(salophen)OAc. For example, PO₄-derived bands at 481, 607, 641, 970, 1043, 1104 cm⁻¹,^{25,26} are observed in these spectra. Stretching mode of Fe-O appears at 573 cm⁻¹. The band at 1644 cm⁻¹ reflecting OH stretching is also observed.27 In addition, it was noted that a new band at 1610 cm⁻¹ appeared in the FT-IR spectrum of γ -Fe₂O₃@HAp-Mn(salophen)OAc, which was attributed to the vibration of the azomethine group (C=N) of the salophen complex. The vibration of the azomethine group (C=N) of the free ligand was observed at 1627 cm⁻¹. In the complex this band is shifted to the lower frequency, indicating that the nitrogen atom of the azomethine group is coordinated to the metal ion. Coordination of azomethine nitrogen is confirmed with the presence of a new band at 422 cm⁻¹ region assignable to υ_{Mn-N} for Mn(salophen)OAc complex. The FT-IR bands of γ -Fe₂O₃@HAp-Mn(salophen)OAc at 1450–1550 cm⁻¹ are due to the stretching vibrations of C=C bonds of the phenyl ring. The presence of a new band at 1360 cm⁻¹ region assignable to the acetate ion



Fig. 4 FT-IR spectra of (a) $\gamma\text{-}Fe_2O_3@HAp$ and (b) $\gamma\text{-}Fe_2O_3@HAp-Mn(salophen)OAc.}$



(OAc) for this complex. Due to overlapping by the framework of hydroxyapatite, some of vibration of the groups were absent in the spectrum of γ -Fe₂O₃@HAp-Mn(salophen)OAc.

The above results are confirmed by the FT-IR spectrum of the homogeneous Mn(salophen)OAc in Fig. 5.

The diffuse reflectance spectra provide further evidence for the presence of the Mn(salophen) complex on the support. The diffusion reflection UV-Vis spectra of γ -Fe₂O₃@HAp and γ -Fe₂-O₃@HAp-Mn(salophen)OAc are shown in Fig. 6. The diffusion reflection UV-Vis spectrum of γ -Fe₂O₃@HAp shows three bands at 225, 270 and 345 nm which could be due to the ligand (O) to metal (Fe³⁺) charge transfer transitions and the excitation of an Fe³⁺-Fe³⁺ pair. The absorption spectrum of γ -Fe₂O₃@HAp-



Fig. 6 Diffusion reflection UV-Vis spectra of (a) γ -Fe_2O_3@HAp and (b) γ -Fe_2O_3@HAp-Mn(salophen)OAc.



Fig. 7 UV-Vis spectrum of Mn(salophen)OAc.



Fig. 8 XRD patterns of (a) $\gamma\text{-}Fe_2O_3@HAp$ and (b) $\gamma\text{-}Fe_2O_3@HAp-Mn(salophen)OAc.}$

Mn(salophen)OAc exhibits three new bands near 220, 295 and 380 nm. The two bands near 220 and 295 nm are attributed to the π - π * transition of the benzene ring of salicylaldehyde, and the n- π * transition of the azomethine chromophore, respectively,²⁸ while the third band near 380 nm, as the most characteristic adsorption band of Mn(m)salophen complex, is due to metal to ligand charge transfer (MLCT),²⁹ indicating that γ -Fe₂O₃@HAp-Mn(salophen)OAc have been successfully *in situ* synthesized by consecutive reactions. In this spectrum two bands near 225 and 345 nm are attributed to support. The band 270 nm in spectrum was absent due to overlapping by adsorption band of Mn(m)salophen complex.



Fig. 9 SEM image of the γ -Fe₂O₃@HAp-Mn(salophen)OAc.

Table 1 Optimization of the γ -Fe₂O₃@HAp-Mn(salophen)OAc amount in the oxidation of 4-methoxybenzyl alcohol with NalO₄^{*a*}

Entry	Catalyst amount (mg)	Aldehyde yield ^b (%) after 1 h
1	0	10
2	90	45
3	110	63
4	130	95
5	145	95
5	145	95

 a Reaction conditions: 4-methoxy benzyl alcohol (0.5 mmol), NaIO_4 (1 mmol), catalyst, CH_3CN/H_2O (5/5 ml). b Isolated yield.

Table 2 The effect of oxidant on the oxidation of 4-methoxybenzyl alcohol catalyzed by $\gamma\text{-}Fe_2O_3@HAp-Mn(salophen)OAc at room temperature^{\alpha}$

Entry	Oxidant	Aldehyde yield ^{b} (%) after 1 h
1	NaIO	05
1	(KUSO)	95
2	$Oxolie (KHSO_5)$	85
3	H_2O_2	80
4	H ₂ O ₂ /urea	35
5	tert-BuOOH	20
6	Bu_4NIO_4	50
7	NaOCl	45
8	No oxidant	10

 a Reaction conditions: 4-methoxy benzyl alcohol (0.5 mmol), NaIO4 (1 mmol), catalyst (130 mg), CH_3 CN/H_2O (5/5 ml). b Isolated yield. For further investigation, the UV-Vis spectrum of homogeneous Mn(salophen)OAc is shown in Fig. 7. Mn(salophen)OAc shows an absorption peak at 380 nm. Since the γ -Fe₂O₃@HAp did not show any peak at 380 nm in its diffuse reflectance spectrum, therefore, it is confirmed that Mn(salophen)OAc has been supported on γ -Fe₂O₃@HAp.

The characterization of γ -Fe₂O₃@HAp and γ -Fe₂O₃@HAp-Mn(salophen)OAc was further carried out byXRD patterns (Fig. 8). There was no obvious difference between the support (γ -Fe₂O₃@HAp) and the catalyst (γ -Fe₂O₃@HAp-Mn(salophen)) OAc). This result indicates that supporting of Mn(salophen)) OAc on γ -Fe₂O₃@HAp does not change the support structure.

Fig. 9 depicts the SEM image of the γ -Fe₂O₃@HAp-Mn(salophen)OAc nanocatalyst. The catalyst nanospheres show a smooth surface and mean diameter of catalyst is less than 100 nm.

3.2 Catalytic experiments

The prepared catalyst was used for the oxidation of alcohols with sodium periodate at room temperature. First, the reaction parameters, such as catalyst amount, type of solvent and oxidant, were optimized in the oxidation of 4-methoxybenzyl alcohol.

3.2.1 The effect of catalyst amount on the oxidation of 4methoxybenzyl alcohol catalyzed by γ -Fe₂O₃@HAp-Mn(salophen)OAc. In order to optimize the catalyst amount, different amounts of γ -Fe₂O₃@HAp-Mn(salophen)OAc were used in the



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Fig. 10 The proposed intermediates for formation of manganese-oxo intermediate from t-BuOOH, NaIO₄ and H₂O₂.

Table 3 The effect of solvent on the oxidation of 4-methoxybenzyl alcohol with NaIO₄ catalyzed by γ -Fe_2O_3@HAp-Mn(salophen)OAc at room temperature

Entry	Solvent	Aldehyde yield ^{ab} (%) after 1 h
1	CH ₃ CN/H ₂ O	95
2	CH ₃ OCH ₃ /H ₂ O	50
3	CH ₃ CH ₂ OH/H ₂ O	45
4	CCl_4/H_2O	10
5	CH_2Cl_2/H_2O	30
6	$CHCl_3/H_2O$	20

 a Reaction conditions: 4-methoxy benzyl alcohol (0.5 mmol), NaIO₄ (1 mmol), catalyst (130 mg), solvent/H₂O (5/5 ml). b Isolated yield.

oxidation of 4-methoxybenzyl alcohol (0.5 mmol) with $NaIO_4$ (1 mmol). The best results were obtained with 130 mg of the catalyst (Table 1).

3.2.2 The effect of oxidant on the oxidation of 4-methoxybenzyl alcohol. The ability of different single oxygen donors, such as NaIO₄, H₂O₂, UHP (urea–H₂O₂) and *tert*-BuOOH, was investigated in the oxidation of 4-methoxybenzyl alcohol. The results, which are summarized in Table 2, showed that NaIO₄ is the best oxygen source because of its good oxidation conversion, inertness in the absence of catalyst and its high solubility in CH₃CN/H₂O. Also, the high activity of NaIO₄ can be attributed to the high tendency of this oxidant for formation of manganeseoxo intermediate from the proposed intermediate because of the steric hindrance of the bonds (Fig. 10).

3.2.3 The effect of solvent on the oxidation of 4-methoxybenzyl alcohol. In order to choose the reaction media, different solvents were checked in the oxidation of 4-methoxybenzyl alcohol with NaIO₄. Among the different mixtures of acetonitrile, acetone, ethanol (single phase systems), dichloromethane, chloroform (two phase systems with n-Bu₄NBr as a phase transfer catalyst) and water, a 1 : 1 mixture of acetonitrile/water was chosen as the reaction medium, because a higher catalytic activity was observed (Table 3). The higher catalytic activity in the acetonitrile/water mixture is attributed to the polarity of solvent and solubility of NaIO₄ in it. For six solvents acetonitrile, acetone, ethanol, dichloromethane, chloroform and water, the dielectric constants are 37.5, 20.7, 24.5, 8.93, 4.81 and 80.1, respectively.

3.3 Oxidation of alcohols with NaIO4 catalyzed by $\gamma\text{-}$ Fe2O3@HAp-Mn(salophen)OAc

First, in order to show the effect of Mn(salophen) in the oxidation of alcohols, blank experiments in the presence of γ -Fe₂O₃ or γ -Fe₂O₃@HAp were carried out and the results showed that only negligible amounts of oxidation products were detected. Also, the same reaction was designed for the oxidation 4-methoxybenzyl alcohol in the presence of Mn(salophen)OAc. The results showed that only 50% of the corresponding aldehyde is produced after 60 min, while, by γ -Fe₂O₃@HAp-Mn(salophen)OAc, the reaction is almost completed (95% yield). This can be related to the nanoparticle nature of γ -Fe₂O₃@HAp, with a high isolation of catalytic active sites, which in turn increases the catalytic activity. Therefore, γ -Fe₂O₃@HAp-Mn(salophen)OAc was found as an efficient catalyst for the oxidation of alcohols with NaIO₄ at room temperature under air (Table 4).

Table 4	Oxidation of alcohols with NaIO ₄	catalyzed by γ-Fe ₂ O ₃ @	aHAp-Mn(salophen)OAc at room	temperature
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Entry	Alcohol	Product ^a	$\mathrm{Yield}^{b}\left(\%\right)$	Time (min)
1	C ₆ H ₅ -CH ₂ OH	C ₆ H ₅ -CHO	92	80
2	o-NO ₂ -C ₆ H ₄ -CH ₂ OH	o-NO ₂ -C ₆ H ₄ -CHO	85	150
3	m-NO ₂ -C ₆ H ₄ -CH ₂ OH	$m-NO_2-C_6H_4-CHO$	86	135
4	p-NO ₂ -C ₆ H ₄ -CH ₂ OH	p-NO ₂ -C ₆ H ₄ -CHO	90	120
5	o-Br-C ₆ H ₄ -CH ₂ OH	o-Br-C ₆ H ₄ -CHO	92	85
6	<i>p</i> -Br-C ₆ H ₄ -CH ₂ OH	<i>p</i> -Br–C ₆ H ₄ –CHO	94	80
7	o-Cl-C ₆ H ₄ -CH ₂ OH	o-Cl-C ₆ H ₄ -CHO	90	80
8	p-Cl-C ₆ H ₄ -CH ₂ OH	<i>p</i> -Cl-C ₆ H ₄ -CHO	90	78
9	p,o-Cl ₂ -C ₆ H ₃ -CH ₂ OH	p,o-Cl ₂ -C ₆ H ₃ -CHO	92	75
10	o-F-C ₆ H ₄ -CH ₂ OH	o-F-C ₆ H ₄ -CHO	93	78
11	o-H ₃ C-C ₆ H ₄ -CH ₂ OH	o-H ₃ C-C ₆ H ₄ -CHO	95	75
12	p-H ₃ C-C ₆ H ₄ -CH ₂ OH	p-H ₃ C-C ₆ H ₄ -CHO	95	65
13	o-H ₃ CO-C ₆ H ₄ -CH ₂ OH	o-H ₃ CO-C ₆ H ₄ -CHO	95	70
14	p-H ₃ CO-C ₆ H ₄ -CH ₂ OH	p-H ₃ CO-C ₆ H ₄ -CHO	95	60
15	PhCH ₂ CH ₂ OH	PhCH ₂ CHO	85	140
16	PhCH(OH)CH ₂ CH ₃	PhCOCH ₂ CH ₃	89	100
17	PhCH ₂ CH ₂ CH ₂ OH	PhCH ₂ CH ₂ CHO	84	150
18	$CH_3(CH_2)_6CH_2OH$	$CH_3(CH_2)_6CHO$	78	155
19	CH ₃ (CH ₂) ₅ CH(OH)CH ₃	$CH_3(CH_2)_5COCH_3$	76	140
20	CH ₃ CH ₂ CH ₂ CH ₂ OH	CH ₃ CH ₂ CH ₂ CHO	75	145
21	CH ₃ CH ₂ CH(OH)CH ₃	CH ₃ CH ₂ COCH ₃	78	140

^a Isolated yield. ^b All of the products are known compounds and were identified by comparison of their physical data with those of authentic samples.

This heterogeneous catalyst was applicable for the oxidation of a wide variety of primary and secondary alcohols to corresponding aldehydes and ketones. As shown in Table 4, benzyl alcohol and substituted benzyl alcohols are converted to their corresponding aldehydes efficiently. The electron donor substituted groups on benzene ring of alcohols, accelerate the reaction and acceptors groups have the opposite effect. In this oxidation process, the aromatic primary alcoholic groups were oxidized with faster rate and higher yields than the aliphatic groups.

3.4 Proposed mechanism for oxidation of alcohols with NaIO₄ catalyzed by γ -Fe₂O₃@HAp-Mn(salophen)OAc

The exact mechanism for oxidation of alcohols with NaIO₄ in the presence of Schiff bases was not reported in the literatures. However, based on the solvents and substituents effects, a plausible mechanism is that the manganese salophen **1** is first transformed to the manganese-oxo intermediate **5** in the presence of NaIO₄. The oxo compound reacts with alcohol to afford intermediates **7** and **8** by electrophilic oxygen of the oxo compound. The intermediate **9** can be formed from **7** and **8** and is finally converted to the desired product by elimination of water and releases the catalyst for the next catalytic cycle (Fig. 11).

3.5 Catalyst reuse and stability

The reusability of a heterogeneous catalyst is of great importance from synthetic and economical points of view. The homogeneous Mn(salophen)OAc cannot be recovered even

Table 5 The results of catalyst recovery and the amounts of manganese leached in the oxidation of 4-methoxybenzyl alcohol with sodium periodate^a

Run	$\mathrm{Yield}^{b}\left(\%\right)$	Mn leached ^{c} (%)	
1	95	0.28	
2	95	0.10	
3	92	0	
4	90	0	
5	90	0	
6	87	0	

 a Reaction conditions: 4-methoxy benzyl alcohol (0.5 mmol), NaIO₄ (1 mmol), catalyst (130 mg), CH₃CN/H₂O (5/5 ml). b Isolated yield. c Determined by ICP.



Fig. 11 The proposed mechanism for the oxidation of alcohols.



Fig. 12 (A) Catalyst dispersed in CH_3CN/H_2O , (B) γ -Fe₂O₃@HAp-Mn(salophen)OAc nanoparticles adsorbed on the magnetic stirring bar and (C) catalyst separation by a magnet.

Table 6 Comparison of the results obtained for oxidation of alcohols catalyzed by γ -Fe₂O₃@HAp-Mn(salophen)OAc with some of those reported in the literature

Entry	Catalyst	Oxidant/time(min)/yield(%)	Ref.
1	Co@SiO ₂ @Schiff base nickel complex	H ₂ O ₂ /50/94	30
2	[Co(salophen)]/bentonite	tert-BuOOH/480/44	31
3	Cobalt salophen encapsulated in zeolite Y	O ₂ /180/33	32
4	$CoFe_2O_4$ (a) SiO_2 (a) SiO_2 (b) SiO_2 (b) SiO_2 (b) SiO_2 (c)	H ₂ O ₂ /120/95	33
5	Sulphonato-salen-chromium(III) hydrotalcites	H ₂ O ₂ /120/66	34
6	Mn(salen)OAc	NaIO ₄ /30/91	35
7	By γ -Fe ₂ O ₃ @HAp-Mn(salophen)OAc	NaIO ₄ /80/92	This work

once, in contrast, the γ -Fe₂O₃@HAp magnetic nanoparticles supported catalyst can be separated and reused several times without significant loss of its activity. The reusability of γ -Fe₂-O₃@HAp-Mn(salophen)OAc was investigated in the multiple sequential oxidation of 4-methoxybenzyl alcohol with NaIO₄. At the end of the each reaction, the catalyst was separated by a permanent magnet, washed with Et₂O and dried carefully before using it in the next run. After using the catalyst for six consecutive times, the aldehyde yield was 87% (Table 5) (Fig. 12). The filtrates were collected for determination of Mn leaching. The results showed that after two first runs, no remarkable manganese was detected in the filtrates by ICP analysis.

The results obtained by this method were compared with some of previously reported methods for the oxidation of alcohols with different catalysts. As can be seen in Table 6, the presented method is more efficient and more acceptable in term of yield, reaction time and reusability.

4. Conclusion

A novel catalytic system by direct covalent attachment of Mn(III) salophen complex to the hydroxyapatite-encapsulated magnetic γ -Fe₂O₃ nanocrystallites was synthesized. This heterogenized

catalyst showed excellent catalytic capability in the oxidation of alcohols and could be reused for at least 6 times without loss of its activity.

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