

Schiff Base Complex Coated Fe₃O₄ Nanoparticles: A Highly Recyclable Nanocatalyst for Selective Oxidation of Alkyl Aromatics

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Received: 3 January 2014 / Accepted: 16 March 2014 / Published online: 30 March 2014
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Abstract In this work, a new magnetically separable nanocatalyst was developed by covalent binding of a Schiff base ligand, *N,N'*-bis(3-salicylidenaminopropyl)amine (salpr), on the surface of silica coated magnetic nanoparticles (Fe₃O₄/SiO₂) and followed complexation with Cu(OAc)₂. Characterization of the prepared nanocatalyst (Fe₃O₄/SiO₂/Cu(II)salpr) was performed with different physicochemical methods such as FT-IR, X-ray diffraction, X-ray photoelectron spectroscopy, scanning electron microscopy, transmission electron microscopy and vibrating sample magnetometry. The prepared Fe₃O₄/SiO₂/Cu(II)salpr catalyst presented high activity for selective oxidation of various alkyl aromatics with *tert*-butyl hydroperoxide as oxidant. After the reaction, the catalyst was easily separated by simply applying an external magnetic field.

Keywords Schiff base complex · Magnetic · Oxidation

1 Introduction

The selective oxidation of alkyl aromatic compounds into the corresponding ketones is one of the most important and challenging transformations in the chemical industry, since the oxidation products are essential intermediates for the manufacture of high-value fine chemicals, agrochemicals,

pharmaceutical and high-tonnage commodity chemicals [1, 2]. Traditionally, a stoichiometric amount of oxidant such as manganese dioxide, chromic acid, potassium dichromate, or selenium dioxide was employed for these transformations [2]. These processes lead to the formation of large volumes of toxic and corrosive wastes, and suffer from tedious workup procedures. Green chemistry teaches us that there is a need for non-toxic and clean methods for carrying out organic reactions [3, 4]. Therefore, development of environmentally friendly methods for the oxidation of alkyl aromatic compounds is the subject of interest. *N*-hydroxyphthalimide (NHPI) as a radical generator has been employed for the oxidation of various types of organic compounds with O₂ as oxidant [5–7]. It is believed that the phthalimide *N*-oxyl (PINO) radical generated in situ from the reaction of O₂ and NHPI, abstracts the hydrogen atom from a sp³ (saturated) carbon, forming the corresponding alkyl radical. Under aerobic conditions, these radicals subsequently react with O₂, to give various types of oxygen-containing compounds such as alcohols and ketones [8]. In order to promote this pathway, some inorganic or organic compounds such as transition metal salt (specifically Co(II)) [9], MnO₂ [10], NaOH [11], dimethylglyoxime (DMG) [12], some substituted quinines and anthraquinones (AQ) [13, 14] have been utilized. Although exhibit excellent activity and selectivity, these catalysts are generally homogeneous and are not easily recoverable after oxidation. Also, the work up procedure is not convenient and generates a lot of waste. Recently, Gutmann et al. [15] developed a modification of the MC (Co–Mn–Br system) catalytic protocol for benzylic oxidations in Continuous Flow Mode, an increasing popular technology in organic chemistry. Despite of high heat and mass transfer, good safety, but high cost and catalyst recycling problems still limits its development. In the search to minimize these

Electronic supplementary material The online version of this article (doi:10.1007/s10562-014-1244-2) contains supplementary material, which is available to authorized users.

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disadvantages, the heterogenization of homogeneous catalysts has emerged as a focus of research.

Hence, the use of heterogeneous catalysts in liquid-phase oxidation, particularly of neat substrate, is a subject of considerable interest from the standpoint of green chemistry and environmental consciousness, because losses of both solvent and catalyst on separation can lead to unacceptable levels of waste. For the oxidation of alkyl aromatic compounds, some heterogeneous catalysts such as metal complexes supported on alumina/silica [16, 17], metalloporphyrins supported on chitosan [18], M-APO-11 (M = Co, Mn and V) [19], Mn-MCM-41 [20], M-SBA-15 (M = Cu, Mn–Ti, Ag) [21–23], polymer-anchored complexes [24, 25], zeolite encapsulated metal complexes [26], and Pd nanocatalysts [27] have been reported in recent years. These heterogeneous catalysts can be separated from reaction system by simple filtration.

Recently, some nanoparticles that have magnetic properties have been used as supported materials to immobilize homogeneous catalysts, and the obtained heterogenized catalysts can be quickly and easily recovered in the presence of external magnetic fields [28–32]. So herein we presented a heterogeneous copper Schiff base complex catalyst (Scheme 1, $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{Cu(II)salpr}$), which was modified by magnetic silica nanoparticles and used for oxidation of various alkyl aromatic compounds with *tert*-butyl hydroperoxide (TBHP) as the oxidant without the need of any solvent. To the best of our knowledge there is no any report about preparation of such magnetically recoverable nanocatalyst for the oxidation of alkyl aromatics.

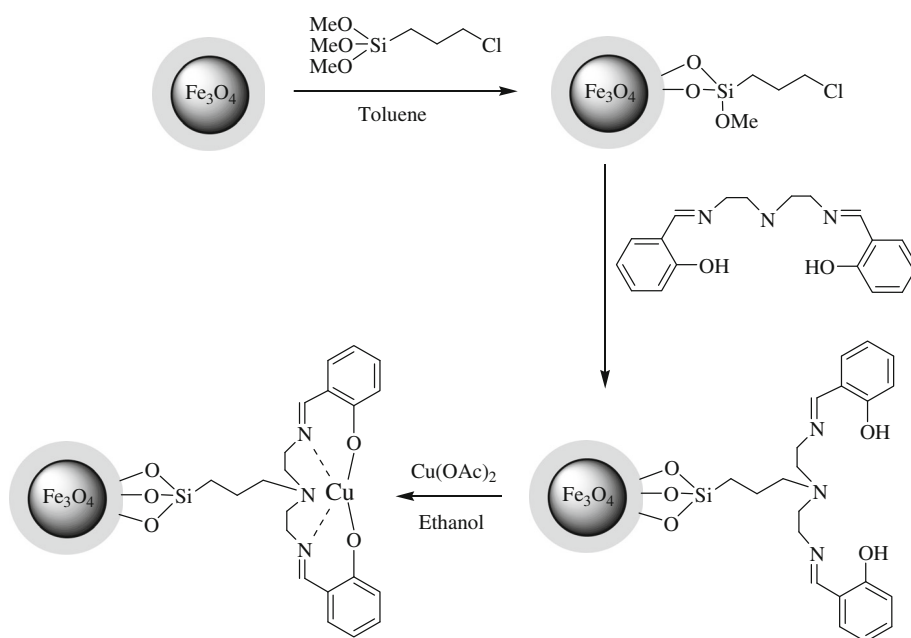
2 Experimental

2.1 Materials and Instrumentation

Ferrous chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), chloropropyl trimethoxysilane, tetraethyl orthosilicate (TEOS), ammonia (25 wt%) were purchased from commercial sources and used for the reaction without further purification. The salpr ligand was prepared according to the reported method [33].

Fourier transform infrared spectra were recorded on NICOLET NEXUS870. The transmission electron micrographs (TEM) of the nanoparticles were recorded using a JEM-2100 instrument with an accelerating voltage of 100 kV. Samples were prepared for TEM by placing droplets of a suspension of the sample in ethanol on a polymer microgrid supported on a Cu grid. Scanning electron micrographs (SEM) of the samples were taken with ZEISS-DSM 960A microscope with attached camera. Magnetic susceptibility measurements were carried out using a vibrating sample magnetometer (VSM) (BHV-55, Riken, Japan) in the magnetic field range of $-8,000$ to $8,000$ Oe at room temperature. XRD data were collected with Cu $K\alpha$ radiation on Bruker C8 ADVANCE. The XPS analysis was made on a photoelectron spectrometer (ESCALAB 250, Thermo, America) with Al $K\alpha$ radiation (1,486.6 eV). Chemical analyses of samples were carried out with VARIAN VISTAMPX ICP-AES atomic absorption spectrometer. Products were identified using a 6820 gas chromatograph (GC) with an Agilent Technologies HP-Innowax ($30 \text{ m} \times 0.32 \text{ mm} \times 0.5 \mu\text{m}$).

Scheme 1 The synthesis of $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{Cu(II)salpr}$



2.1.1 Preparation of Silica Coated Magnetic Nanoparticles (Fe₃O₄/SiO₂, SCMNP) and Chloropropyl Modified SCMNP (ClpSCMNP)

Magnetic nanoparticles (bare MNPs) were prepared according to reported chemical coprecipitation method [34]. Modification of the prepared MNPs was performed as followed [35]: An amount of 1 g of the synthesized Fe₃O₄ was suspended in 35 ml ethanol and 6 ml deionized water and sonication for 15 min was carried out to maintain proper dispersion. Tetraethyl orthosilicate (TEOS) (1.5 ml) was added slowly to the mixture and sonicated for another 10 min. Then aqueous ammonia (10 %, 1.4 ml) was added slowly over 10 min under mechanical stirrer. The reaction was allowed to proceed at 40 °C for 12 h. After the reaction, the silica coated magnetic nanoparticles (SCMNP) was separated from the reaction mixture using a permanent magnet and washed several times with distilled water and methanol. The obtained SCMNP (2 g) were suspended in toluene (100 ml) with sonication and then chloropropyl trimethoxysilane (2 ml, Merck) was added under dry nitrogen atmosphere. The mixture was refluxed for 12 h and the resulted solid was magnetically separated, washed with ethanol to remove the unreacted residue of silylating reagent and then vacuum dried at 353 K.

2.1.2 Preparation of salpr/SCMNP (Fe₃O₄/SiO₂/salpr)

The obtained ClpSCMNP (2 g) was suspended in 100 ml of acetonitrile with sonication. To the mixture, excess of salpr ligand (1 g, 3.2 mmol) and triethylamine (0.5 ml) were added and the resulted mixture was refluxed for 12 h. The resultant solid was separated magnetically and then washed with ethanol several times to remove the unreacted residue of the salpr ligand and dried under vacuum at 353 K.

2.1.3 Preparation of Cu(II)salpr Modified SCMNP (Fe₃O₄/SiO₂/Cu(II)salpr)

For the preparation of target material, excess of Cu(OAc)₂·H₂O (300 mg, 1.5 mmol) was dissolved in ethanol (50 ml). Salpr/SCMNP (1 g) were then added to this solution and after sonication the mixture was refluxed for 12 h. After separation with an external magnet, the product was washed with methanol to remove unreacted Cu(OAc)₂. The resulted Cu(II)salprSCMNP (Fe₃O₄/SiO₂/Cu(II)salpr) material was then dried under vacuum at 353 K and characterized with FT-IR spectroscopy, X-ray diffraction, scanning and transmission electron microscopies and vibrating sample magnetometry.

2.2 Catalytic Oxidation of Alkyl Aromatics in the Presence of Fe₃O₄/SiO₂/Cu(II)salpr

Oxidation of alkyl aromatics was carried out in a 25 ml round bottomed flask equipped with a condenser and a mechanical stirrer. *Tert*-butylhydroperoxide (TBHP) (80 % in di-tertiary butyl peroxide) was used as oxidants. In a typical procedure, to a mixture of catalyst (100 mg) and alkyl aromatic (20 mmol) was added oxidant (30 mmol) and *n*-decane as internal standard in turn. The flask was immersed in an oil bath in order to make the working temperature constant at 80 °C for a predetermined time (12 h) with continuous stirring. Samples were withdrawn periodically and analyzed using a gas chromatograph (HP, Agilent 6,820) equipped with a capillary column and a FID detector. GC–MS of products were recorded using a Shimadzu-14A fitted with a capillary column (CBP5-M25). The copper content of recycled catalyst was measured with above mentioned atomic absorption spectrometer after dissolution of the solid in hydrogen fluoride solution.

3 Results and Discussion

3.1 Preparation of Fe₃O₄/SiO₂/Cu(II)salpr

Scheme 1 shows the sequence of events in the functionalization of MNPs with copper Schiff base complex. The bare MNPs were synthesized by chemical coprecipitation method under alkaline condition according to the literature [34], which was not shown in Scheme 1. Then, the external surface of MNPs was coated with a silica shell to yield SCMNP, followed by treatment of silanol groups of SCMNP with chloropropyl trimethoxysilane to obtain chloropropylated silica coated magnetic nanoparticles (ClpSCMNP). The second step involves substitution reaction of ClpSCMNP chloro groups with secondary amine group of salpr Schiff base to yield the salpr/SCMNP, a tetradentate Schiff base ligand supported on SCMNP. Addition of triethylamine in this step facilitates the substitution reaction. Finally, complexation of the salpr/SCMNP was performed with excess of Cu(OAc)₂·H₂O to afford Cu(II)salpr/SCMNP (Fe₃O₄/SiO₂/Cu(II)salpr). The resulted material was washed with methanol in order to remove the unreacted Cu(OAc)₂ and dried under vacuum at 353 K.

3.2 Characterization of the Prepared Nanocatalyst

In order to confirm the modification of the magnetite surface, the FT-IR spectra of the prepared materials were obtained and have been shown in Fig. 1. The strong absorption bands related to Si–O–Si stretching vibrations was

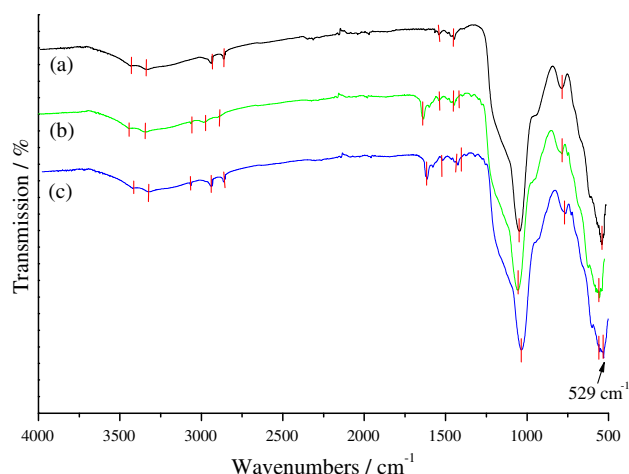


Fig. 1 FT-IR spectra of *a* chloropropyl modified SCMNP (ClpSCMNP), *b* $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{salpr}$ MNP and *c* $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{Cu(II)salpr}$ MNP

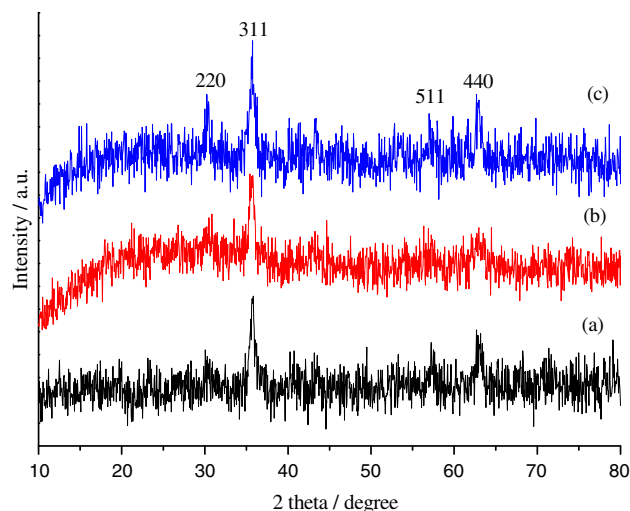


Fig. 2 XRD patterns of *a* Fe_3O_4 , *b* $\text{Fe}_3\text{O}_4/\text{SiO}_2$ MNP and *c* $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{Cu(II)salpr}$ MNP

observed in all three spectra at $1,000\text{--}1,100\text{ cm}^{-1}$, and it is possible to suggest that there is formation of a silica shell. The FT-IR spectrum of ClpSCMNP (Fig. 1a) showed several signals originating from chloropropyl-groups, which are related to C–H stretching modes of the propyl groups, appeared in the area of $1,450\text{--}1,560$ and $2,935\text{--}2,860\text{ cm}^{-1}$. By observing the spectrum mentioned, it was concluded that the $\text{Fe}_3\text{O}_4/\text{SiO}_2$ was modified by chloropropyl-groups successfully. In the FT-IR spectrum of salpr/SCMNP (Fig. 1b) a band at $1,630\text{ cm}^{-1}$, assigned to C=N stretching vibration of salpr ligand [16], and some weak bands at $3,066\text{--}3,040$ and $1,400\text{--}1,500\text{ cm}^{-1}$ assigned to stretching vibrations of aromatic rings of salpr

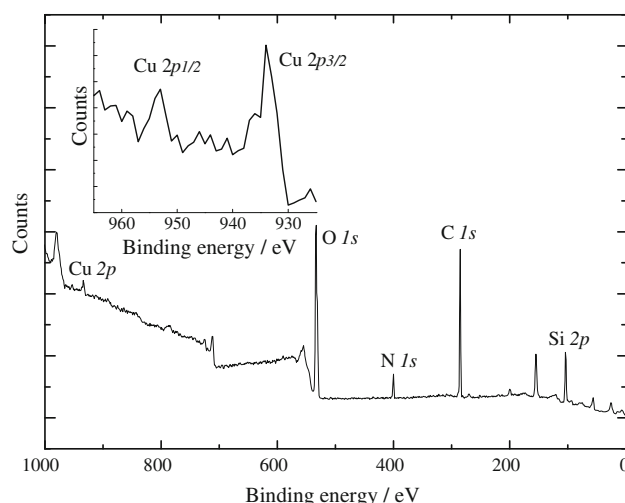


Fig. 3 XPS spectrum of $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{Cu(II)salpr}$ MNP

ligand were observed that were not present in parent SCMNP. These bands confirmed the anchoring of salpr ligand on chloropropyl-groups modified support. The band at $1,630\text{ cm}^{-1}$ upon reaction of salpr ligand with Cu(OAc)_2 shifted to lower frequency ($1,615\text{ cm}^{-1}$) (Fig. 1c) indicating complexation of C=N group of supported ligand with copper. Also, a new absorption band at 529 cm^{-1} was assigned to Cu–N band [36].

Copper content of the prepared nanomaterial was found to be 0.62 wt% on the basis of ICP-AES chemical analysis.

Figure 2 depicts the XRD pattern of prepared nanomaterial. The coating process of silica shell has been confirmed by IR spectrum in Fig. 1 and as shown in Fig. 2, a diffuse peak in (b) and (c) at about 20 degree that belong to it are also exhibited. Furthermore, the diffraction peaks can be assigned to the planes of inverse cubic spinel structured Fe_3O_4 (JCPDS no. 19-0629), and the coating process did not induce any phase change of Fe_3O_4 .

X-ray photoelectron spectrum of copper Schiff base coated Fe_3O_4 catalyst is shown in Fig. 3. The O 1s peak at 532.6 eV and Si 2p peak at 103.2 eV are as expected for SiO_2 -type material. The peaks for N 1s at 400.2 eV and C 1s at 284.8 eV confirms the immobilization of copper Schiff base complex onto $\text{Fe}_3\text{O}_4/\text{SiO}_2$ surface. The intense and broad photoelectron peak at 934.5 eV ($\text{Cu } 2p_{3/2}$) and 954.3 eV ($\text{Cu } 2p_{1/2}$) along with the presence of the characteristic shakeup satellite peaks suggests that the copper oxidation state is +2 in the surface of the $\text{Fe}_3\text{O}_4/\text{SiO}_2$ support [37].

To study the magnetic properties of magnetite nanoparticles before and after silica coating we investigated the hysteresis loops of magnetite and functionalized magnetite nanoparticles at room temperature using vibrating sample magnetometry (VSM). Magnetization curves of prepared

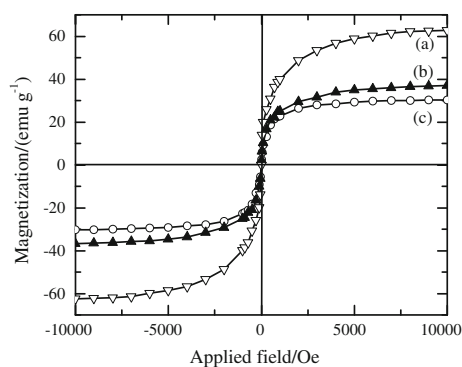


Fig. 4 Magnetization curves of (a) Fe₃O₄, (b) Fe₃O₄/SiO₂ MNPs and (c) Fe₃O₄/SiO₂/Cu(II)salpr MNPs

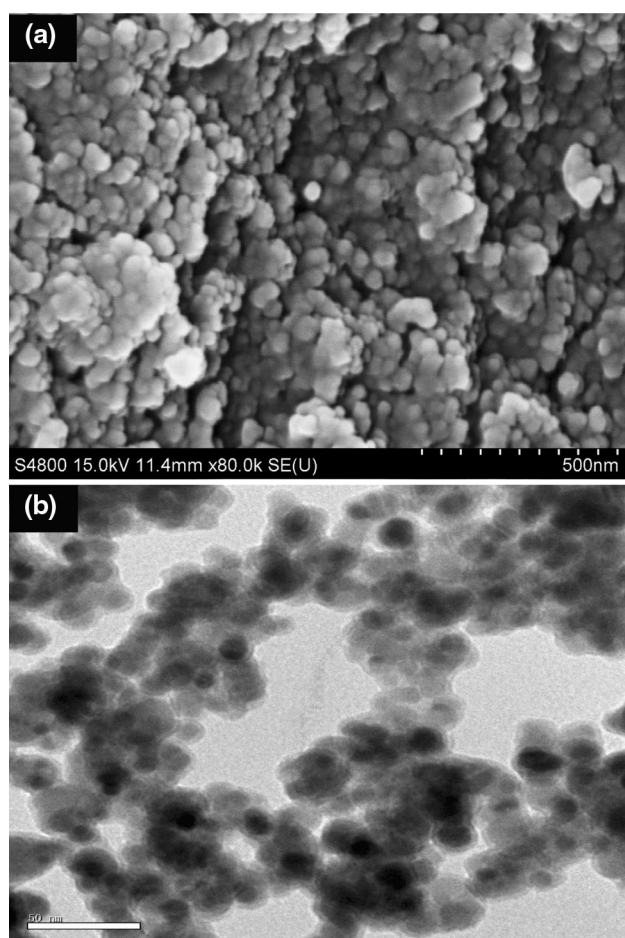


Fig. 5 a SEM and b TEM images of prepared Fe₃O₄/SiO₂/Cu(II)salpr MNPs

Scheme 2 Formed products over Cu nanocatalyst

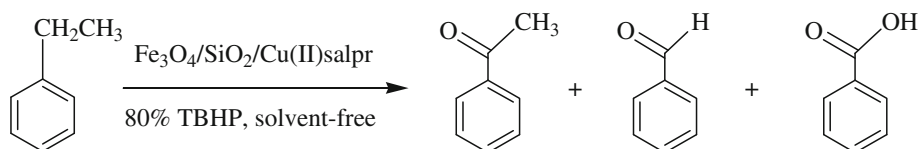


Table 1 Catalytic oxidation of ethylbenzene with TBHP over Cu(II)salpr/SMNPs

Entry	Time (h)	T (°C)	Conversion (%)	Selectivity (%) ^a	TOF (h ⁻¹) ^b
1	2	80	24	75	247
2	4	80	38	83	196
3	8	80	59	90	152
4	12	80	85	93	146
5	16	80	86	88	111
6	12	50	43	76	74
7	12	60	58	81	100
8	12	70	74	85	127
9	12	90	84	92	144
10	12	100	81	91	139
11 ^c	16	80	14	54	—
12 ^d	16	80	15	52	—

Reaction conditions: catalyst (100 mg), ethylbenzene (20 mmol), TBHP (30 mmol), solvent free

^a Selectivity toward the acetophenone

^b Calculated as mmol of product formed per mmol of copper in the catalyst per hour

^c Reaction was carried out in the presence of SCMNPs

^d Reaction was carried out without catalyst

materials are shown in Fig. 4. As shown in Fig. 4, saturation magnetizations for Fe₃O₄, Fe₃O₄/SiO₂ and Fe₃O₄/SiO₂/Cu(II)salpr are 62.66, 37.08 and 30.38 emu g⁻¹, respectively. The order is due to the increasing amount of nonmagnetic material (organic ligands) on the particle surface, which makes up a larger percentage of the non-magnetic fraction. A direct result of this effect is that it takes longer time to separate Fe₃O₄/SiO₂ and Fe₃O₄/SiO₂/Cu(II)salpr than bare Fe₃O₄ nanoparticles from particle solution.

To further characterize the catalyst, SEM and TEM images were obtained as shown in Fig. 5. As can be seen in TEM images, the synthesized catalysts are well dispersed, the particle size is about 10 nm, and most of the nanoparticles are almost spherical in shape.

3.3 Catalytic Oxidation of Alkyl Aromatics in the Presence of Fe₃O₄/SiO₂/Cu(II)salpr

The catalytic activity of prepared nanomaterial was first tested in the oxidation of ethylbenzene using TBHP as an

Table 2 Oxidation of various alkyl aromatics

Entry	Substrate	Conversion (%)	Selectivity (%) ^a	TOF (h ⁻¹) ^b
1		90	95	155
2		76	90	131
3		75	91	129
4		64	85	110
5		60	82	103
6		82	90	141
7		80	89	138
8		78	91	134
9		78	91	134
10		80	88	138
11		77	89	132

Reaction conditions: catalyst (100 mg), alkyl aromatics (20 mmol), TBHP (30 mmol), solvent free, 80 °C for 12 h

^a Selectivity toward the corresponding benzylic ketone

^b Calculated as mmol of product formed per mmol of copper in the catalyst per hour

oxidant without any solvent. Different reaction conditions including reaction time and temperature were investigated. The oxidation results as well as turnover frequencies (TOFs), i.e. mmol of product formed per mmol of copper in the catalyst per hour are given in Table 1. The oxidation took place on the α -carbon of the ethylbenzene, acetophenone was found to be the main product, along with minor quantities of benzaldehyde and benzoic acid (Scheme 2). The formation of other products viz. benzaldehyde may arise from the cleavage in the C–C bonds while the presence of benzoic acid may results from the oxidation of benzaldehyde formed. No oxidation was observed in the aromatic ring of the ethylbenzene.

Interestingly, the conversion was higher in solvent free condition than in the presence of solvents (Fig. S1), which might be attributed to the blocking of active sites by solvent molecules or may be explained by the diffusion competition of the solvent and the substrate [16, 34].

As seen in Table 1, catalytic activities increased sharply in a period of 2–12 h, while the TOF value decreased from 247 to 146 (entries 1–4). This indicates that the rate of side reaction has gradually decreased with the progress of the reaction. When the reaction was carried out for 16 h, 86 % conversion and 88 % selectivity was observed (entry 5), which has no obvious increase than the results obtained for 12 h (85 % conversion and 93 % selectivity). This is

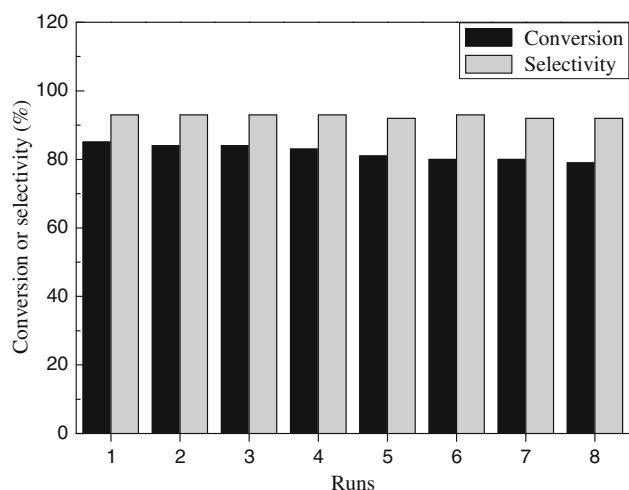


Fig. 6 Recycling study of Fe₃O₄/SiO₂/Cu(II)salpr MNPs

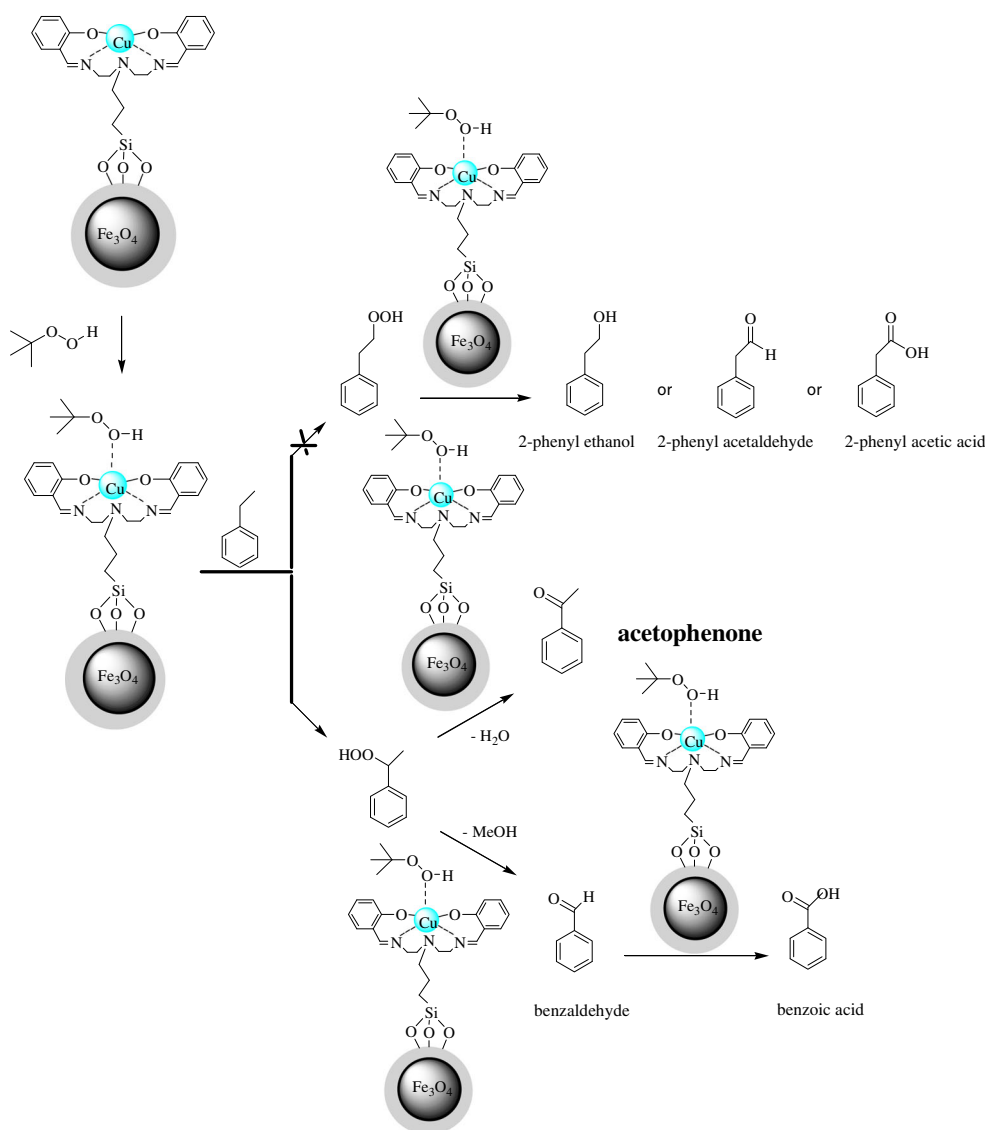
because that the formation of benzaldehyde may arise from the cleavage of the C–C bond with the increase of the reaction time, while the formation of benzoic acid may result from the oxidation of benzaldehyde. It is reported that high temperature favored the oxidation process [35], but lead to the formation of byproducts at the same time. When the reaction was carried out at 80 °C for 12 h, best result was achieved. Further increase of temperature showed no benefit and on the contrary few decrease on conversion and selectivity as well as TOF was observed (entries 4, 6–10). Low catalytic activity was found when the reaction was carried out using SMNPs as catalyst (entry 11) or without any catalyst (entry 12), which confirms the role of copper Schiff base as catalytic active species. As a result, 12 h and 80 °C were chosen as a suitable reaction condition for the following reactions.

To examine the utility and generality of this methodology for the oxidation of alkyl aromatics, we applied the present catalyst system to a variety of alkyl aromatics as shown in Table 2. Reactions took place on the α -carbon and all alkyl aromatics are oxidized to corresponding ketone as main products. As can be seen in Table 2, the oxidations of some ethylbenzene derivatives proceed smoothly and show good selectivity to acetophenone. Interestingly, an electron donating substituent (e.g. methoxy group, entry 1) at the *para*-position of ethylbenzene has a positive effect on the oxidation yield while an electron withdrawing substituent including the NO₂ or Cl group at the *para*-position suppresses the oxidation (entries 2, 3). Due to steric effects, all substituents at the *ortho*-position have a negative effect on the oxidation reaction (entries 4, 5). Diphenylmethane is oxidized to benzophenone effectively and selectively, which gives 82 % conversion and 90 % selectivity (entry 6). Cycloalkylarenes such as indane

and tetralin are readily oxidized to their corresponding carbonyl compounds 1-indanone and 1-tetralone, the oxidation took place selectively at the benzylic C–H bond and few oxidation by-products were observed during the reaction (entries 7, 8). The aromatics containing two benzene rings such as fluorene also underwent oxidation to the corresponding ketones with good conversions and selectivity (entry 9). Alkylbenzenes containing open chain alkyl group such as *n*-propylbenzene and *n*-butylbenzene underwent the reaction with 80 and 77 % conversion providing corresponding benzylic ketones with 88 and 89 % selectivity (entries 10, 11). These results show the substrate compatibility of this protocol. It is worth mentioning that no oxidation occurred on the aromatic ring of all the substrates.

Due to the magnetic nature of the Fe₃O₄/SiO₂ support, the nanocatalyst was separated simply by applying an external magnet to the reaction vessel in 10 s and the resulting clear supernatant can be decanted. After being washed by methanol, it was subjected to another reaction with identical substrate. In the ethylbenzene experiment, the recovered nanocatalyst can be reused for at least 8 times at the same reaction conditions without great loss of activity (Fig. 6). The coated SiO₂ ensured the stability of Fe₃O₄ core against oxidation in the reaction, so as to achieve a high recyclability. After 8 times of reuse, SiO₂ may be dropped off. The Fe₃O₄, losing the protection of SiO₂ was easy to be oxidized. As the principal part of magnetism was destroyed, the catalyst would be lost in the solution and recovery decreased gradually [35].

Based on the previous studies [16], a possible mechanism for the oxidation of ethylbenzene in the system was proposed as shown in Scheme 3. The oxidation of the ethylbenzene with TBHP is supposed to occur by free radical mechanism, yielding primarily ethylbenzene hydroperoxide. Firstly, TBHP is activated by coordinating with the immobilized Cu nanocatalyst to form the co-coordinated TBHP. Then, the activated distant oxygen of co-coordinated TBHP reacted with ethylbenzene to yield the products. Abstraction of alcoholic OH hydrogen and the CH hydrogen by the activated TBHP oxygen yields acetophenone. Similar abstraction of OH hydrogen of 1-phenyl ethanol by the activated oxygen yields benzaldehyde. The formation of benzaldehyde may arise from the cleavage of C–C bond, while the formation of benzoic acid may result from the oxidation of benzaldehyde. More detail mechanism of oxidation of ethylbenzene was shown in Scheme S1 in the Supplementary Information (SI) section. It is worth mentioning that in the reaction mixture, no byproducts such as 2-phenyl ethanol, 2-phenyl acetaldehyde and 2-phenyl acetic acid were detected by GC-Mass (unfavored path in Scheme 3).



Scheme 3 A possible mechanism for the oxidation of ethylbenzene

4 Conclusion

In this work, we have shown that functionalization of silica coated magnetic nanoparticles with a tetradentate salpr Schiff base ligand and subsequent complexation with copper affords an easily recoverable truly heterogenized copper nanocatalyst which is active and selective in catalytic oxidation of alkyl aromatics. The nanocatalyst can be reused for at least 8 times without great loss of activity.

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