https://doi.org/10.1002/aoc.3726

FULL PAPER

Copper(II) Schiff Base Complex Immobilized on Superparamagnetic Fe₃O₄@SiO₂ as a Magnetically Separable Nanocatalyst for Oxidation of Alkenes and Alcohols

Marzieh Sarkheil | Maryam Lashanizadegan

Department of Chemistry, Faculty of Physics and Chemistry, Alzahra University, PO Box 1993893973, Tehran, Iran

Correspondence

Maryam Lashanizadegan, Department of Chemistry, Faculty of Physics and Chemistry, Alzahra University, PO Box 1993893973, Tehran, Iran. Email: m_lashani@alzahra.ac.ir A new heterogeneous catalyst containing a copper(II) Schiff base complex covalently immobilized on the surface of silica-coated Fe₃O₄ nanoparticles (Fe₃O₄@SiO₂-Schiff base-Cu(II)) was synthesized. Characterization of this catalyst was performed using various techniques. The catalytic potential of the catalyst was investigated for the oxidation of various alkenes (styrene, α -methylstyrene, cyclooctene, cyclohexene and norbornene) and alcohols (benzyl alcohol, 3-metho-xybenzyl alcohol, 3-chlorobenzyl alcohol, benzhydrol and *n*-butanol) using *tert*-butyl hydroperoxide as oxidant. The catalytic investigations revealed that Fe₃O₄@SiO₂-Schiff base-Cu(II) was especially efficient for the oxidation of norbornene and benzyl alcohol. The results showed that norbornene epoxide and benzoic acid were obtained with 100 and 87% selectivity, respectively. Moreover, simple magnetic recovery from the reaction mixture and reuse for several times with no significant loss in catalytic activity were other advantages of this catalyst

KEYWORDS

Alcohol, alkene, copper(II) Schiff base complex, magnetic nanoparticles, oxidation catalyst

1 | INTRODUCTION

Catalytic oxidation of organic substrates into useful products is a fundamental synthetic method in chemical industries and laboratory researches.^[1] Among the oxidation catalysts, Schiff base transition metal complexes represent a very useful class of compounds because their structures are similar to that of the porphyrin ring and they are good at loading oxygen and mimicking enzymes.^[2] Therefore, homogeneous or heterogeneous catalytic activities of various Schiff base transition metal complexes such as Cu(II),^[3-5] Co(II),^[6-8] V(V),^[9,10] Mo(VI),^[11,12] Mn(II)^[13,14] and Ni(II)^[15,16] complexes in the oxidation of organic substrates have been extensively investigated. Although homogeneous catalysts often show high catalytic performances, they are associated with some drawbacks including difficulty of separation from products, deactivation of catalyst via dimerization and instability at high temperatures. These drawbacks are in contrast with economic and environmental concerns in industrial applications. So,

many strategies involving entrapment of homogeneous catalysts inside the pores of solid supports^[17,18] or grafting them on the surface of $\operatorname{organic}^{[19-21]}$ or $\operatorname{inorganic}^{[22-24]}$ supports have been employed to heterogenize the homogeneous catalysts. One of the best solid supports are magnetic nanoparticles which enable a catalyst to be readily separated from reaction media by means of an external magnet.^[25] Since magnetic nanoparticles tend to aggregate in a liquid due to the anisotropic dipolar attraction and being unstable under acidic conditions, the magnetic core is usually protected with an outer shell such as silica^[26,27] or polymers.^[28] Among them, silica is a suitable candidate which provides appropriate properties such as preventing aggregation and improving thermal and chemical stability. Also, its surface contains silanol groups that can be modified by various coupling agents and consequently specific ligands can be covalently anchored on the surface of the magnetic support.^[29]

In the past few decades, great interest has been paid to catalytic oxidation of alkenes for the production of several important products such as epoxides, aldehydes, ketones and alcohols, which are essential intermediates in pharmaceutical and chemical industries.^[30] The catalytic oxidation of alcohols into corresponding carbonyl or acid compounds has also been attracting the attention of chemical researchers. Although the partial oxidation of primary alcohols to aldehydes is of great importance owing to the application of aldehydes in agricultural and fine chemicals, the complete and direct oxidation of them to carboxylic acids also is also of great importance in industry.^[31–33] Thus to date, many efforts have been made to design clean, reusable and efficient catalysts for the oxidation of alkenes and alcohols. In this regard, many articles that focus on the catalytic role of Schiff base complexes immobilized on magnetic nanoparticles in the oxidation of alkenes^[34–38] and alcohols^[39–42] have been published.

Herein, we report the synthesis, characterization and catalytic application of a copper(II) Schiff base complex covalently anchored on the surface of silica-coated Fe_3O_4 nanoparticles ($Fe_3O_4@SiO_2$ -Schiff base-Cu(II)) for the oxidation of various alkenes and alcohols.

2 | EXPERIMENTAL

2.1 | Materials and instrumentation

Solvents and starting materials were purchased from Acros Organics, Merck or Sigma-Aldrich and were used without further purification. Fourier transform infrared (FT-IR) spectra (KBr discs, 500–4000 cm^{-1}) were recorded using a Bruker FT-IR Tensor 27 spectrometer. X-ray diffraction (XRD) patterns were collected using a Philips X'Pert diffractometer using Cu K α radiation ($\lambda = 1.54$ Å). Elemental analyses were realized with a 2400 Series II CHN analyser (PerkinElmer, USA). Scanning electron microscopy (SEM) images were obtained using a KYKY-EM3200 microscope. Transmission electron microscopy (TEM) images were obtained with a Philips CM120 electron microscope. Magnetic properties were determined using a vibrating sample magnetometer (BHV-55, Riken, Japan) in the magnetic field range of -8000 to +8000 Oe at room temperature. The amount of copper in the catalyst was determined using an inductively coupled plasma optical emission spectroscopy (ICP-OES) instrument (Varian, Vista-Pro, Australia). Thermogravimetric analysis (TGA) was conducted with a TGA/DSC1 (Mettler Toledo). The oxidation products were analysed by GC and GC-MS using an Agilent 6890 Series with a flame ionization detector, an HP-5% phenylmethylsiloxane capillary and an Agilent 5973 Network, mass selective detector, HP-5MS 6989 Network GC system, respectively.

2.2 | Preparation of Fe₃O₄@SiO₂-Schiff base-Cu(II) Catalyst

Fe₃O₄ magnetic nanoparticles were prepared by the coprecipitation method according to a reported procedure.^[43] Also, coating of magnetic nanoparticles with silica $(Fe_3O_4@SiO_2)$ was performed based on a literature method.^[44]

To functionalize Fe₃O₄@SiO₂ with amine groups, a mixture of Fe₃O₄@SiO₂ (0.1 g) with 3-aminopropyltrimethoxysilane (APTMS; 0.8 mmol, 0.14 ml) was refluxed in dry toluene under nitrogen atmosphere for 48 h. The obtained solid (Fe₃O₄@SiO₂-APTMS) was washed with 30 ml of toluene and ethanol and dried at 60 °C for 10 h. Afterwards, to synthesize the Schiff base on the surface of Fe₃O₄@SiO₂-APTMS, 2'-hydroxypropiophenone (0.75 g, 1 mmol) was added to a suspended solution of Fe₃O₄@SiO₂-APTMS (0.1 g) in dry toluene (15 ml). After refluxing under nitrogen atmosphere for 48 h, the resultant material (Fe₃O₄@SiO₂-Schiff base) was washed with toluene and dried at 60 °C for 10 h. Finally, Fe₃O₄@SiO₂-Schiff base-Cu(II) was prepared by adding an ethanolic solution (20 ml) of $Cu(CH_3COO)_2 \cdot H_2O$ (0.19 g, 1 mmol) to $Fe_3O_4@SiO_2$ -Schiff base (0.1 g). The resulting mixture was sonicated and then refluxed under nitrogen atmosphere for around 17 h (Scheme 1). Then, the catalyst was recovered by magnetic decantation, washed several times with absolute ethanol to remove unreacted copper and dried at 60 °C for 10 h.

2.3 | General procedure for oxidation of alkenes and alcohols

All oxidation reactions of alkenes and alcohols were performed in a 10 ml round-bottom flask equipped with a water condenser. In a typical run, to a solution of catalyst (0.01 g) and substrate (5 mmol) in CH₃CN (3 ml), *tert*-butyl hydroperoxide (TBHP; 20 mmol) was added. The resulting mixture was refluxed for an appropriate time (2 h for alkenes, 6 h for alcohols). At the end of the reaction, the catalyst was collected using an external magnet and the reaction mixture was subjected to GC and GC–MS analyses. Conversion of substrates was calculated from GC data and the oxidation products were identified from GC–MS results.



SCHEME 1 Preparation of Fe₃O₄@SiO₂-Schiff base-Cu(II)

3 | RESULTS AND DISCUSSION

3.1 | Characterization of Fe₃O₄@SiO₂-Schiff base-Cu(II) Catalyst

The FT-IR spectra of Fe₃O₄, Fe₃O₄@SiO₂, Fe₃O₄@SiO₂-APTMS, Fe₃O₄@SiO₂-Schiff base and Fe₃O₄@SiO₂-Schiff base-Cu(II) are presented in Figure 1. In the FT-IR spectrum of Fe_3O_4 (Figure 1a), the bands appearing at 587 and 631 cm $^{-1}$ correspond to Fe–O vibrations. Also, the bands seen at 3417 and 1616 cm^{-1} should be related to the stretching and bending vibrations of adsorbed water or FeOH groups of the surface.^[45,46] The FT-IR spectrum of Fe₃O₄@SiO₂ (Figure 1b) shows two peaks at around 1086 and 816 cm⁻¹ corresponding to Si-O-Si asymmetric and symmetric vibrations, respectively. This observation confirms the coating of silica on the surface of the Fe₃O₄ nanoparticles. As shown in Figure 1(c), two peaks at 2920 and 2860 cm^{-1} due to the C-H stretching vibrations corroborate the presence of anchored propyl groups in Fe₃O₄@SiO₂-APTMS.^[47] After the reaction of 2-hydroxypropiophenone with Fe_3O_4 @SiO₂-APTMS, a band is observed at 1609 cm⁻¹ in its FT-IR spectrum (Figure 1d) due to C=N vibration. The C=N vibration of Fe₃O₄@SiO₂-Schiff base-Cu(II) (Figure 1e) shows a lower frequency in comparison to the corresponding vibration in the spectrum of Fe₃O₄@SiO₂-Schiff base. This indicates the involvement of azomethine nitrogen in coordination to the metal centre.

The XRD patterns of Fe_3O_4 , $Fe_3O_4@SiO_2$ and $Fe_3O_4@SiO_2$ -Schiff base-Cu(II) are exhibited in Figure 2. As seen in Figure 2(a), the position and relative intensities of all diffraction peaks of prepared Fe_3O_4 match with the standard Fe_3O_4 XRD pattern (JCPDS no. 75–0033). After



FIGURE 1 FT-IR spectra of (a) Fe_3O_4 , (b) $Fe_3O_4@SiO_2$, (c) $Fe_3O_4@SiO_2@APTMS$ and (d) $Fe_3O_4@SiO_2-Schiff$ base; and $Fe_3O_4@SiO_2-Schiff$ base-Cu(II) (e) before use and (f) after use as catalyst



FIGURE 2 XRD patterns of (a) Fe₃O₄, (b) Fe₃O₄@SiO₂, (c) fresh Fe₃O₄@SiO₂-Schiff base-Cu(II), (d) Fe₃O₄@SiO₂-Schiff base-Cu(II) recovered after first cycle and (e) Fe₃O₄@SiO₂-Schiff base-Cu(II) recovered after fourth cycle

coating the magnetite with silica and immobilizing the copper(II) complex on the silica-coated Fe_3O_4 (Figure 2a– c), the similar characteristic peaks of Fe_3O_4 with change in intensity are observed. This indicates the retention of the magnetite phases during surface modification of Fe_3O_4 . However, the change in the peak intensities can be related to the shielding effect of shell on magnetite core.^[37] Based on the XRD results, the average crystallite size of Fe_3O_4 , $Fe_3O_4@SiO_2$ and $Fe_3O_4@SiO_2$ -Schiff base-Cu(II) is calculated to be around 11.7, 13.1 and 13.2 nm, respectively, by applying the Debye–Scherrer equation.

The TEM image of $Fe_3O_4@SiO_2$ -Schiff base-Cu(II) (Figure 3a) indicates that most of the nanoparticles have an almost spherical shape. Also, the core–shell structure of the catalyst is confirmed by revealing the Fe_3O_4 cores as dark spots embedded in bright SiO₂-Schiff base-Cu(II) shells. The size of each nanoparticle is around 15 nm which is in accordance with the value obtained from XRD analysis. The surface morphologies of Fe_3O_4 , $Fe_3O_4@SiO_2$ and $Fe_3O_4@SiO_2$ -Schiff base-Cu(II) were further studied using SEM. As seen in Figure 3(b)–(d), these compounds have spherical morphology and aggregation causes an increase of the nanoparticle sizes.

TGA curves of $Fe_3O_4@SiO_2$ and $Fe_3O_4@SiO_2$ -Schiff base-Cu(II) are illustrated in Figure 4. In the TGA curve of $Fe_3O_4@SiO_2$ (Figure 4a), the weight loss around 200 °C is 4 of 8 WILEY-Organometallic Chemistry



FIGURE 3 (a) TEM image of $Fe_3O_4@SiO_2$ -Schiff base-Cu(II). SEM images of (b) Fe_3O_4 , (c) $Fe_3O_4@SiO_2$ and (d) $Fe_3O_4@SiO_2$ -Schiff base-Cu(II)



FIGURE 4 TGA curves of (a) $Fe_3O_4@SiO_2$ and (b) $Fe_3O_4@SiO_2$ -Schiff base-Cu(II)

related to removal of physically adsorbed water molecules and surface hydroxyl groups on the magnetic surface.^[44] As seen in Figure 4(b), the TGA curve of Fe₃O₄@SiO₂-Schiff base-Cu(II) shows a weight decrease below 200 °C, which is ascribed to loss of physically adsorbed water molecules of the catalyst. Also, the weight loss (17.79%, 0.9 mmol g ⁻¹) in the range 250–600 °C can be attributed to destruction of organic groups. Elemental analysis of Fe₃O₄@SiO₂-Schiff base-Cu(II) was performed and the amount of nitrogen is obtained as 1.14%. Thus, based on the obtained nitrogen, the amount of grafted organic groups is estimated to be 0.8 mmol g⁻¹, these data being consistent with the TGA results.

The copper content of $Fe_3O_4@SiO_2$ -Schiff base-Cu(II) was determined using ICP-OES. The result shows the amount of copper is 5.1 wt%. Moreover, the energy-dispersive X-ray analysis of $Fe_3O_4@SiO_2$ -Schiff base-Cu(II) (Figure S1 in the supporting information) indicates the existence of Cu, Si, Fe and O in the catalyst. These are other data that indicate the copper complex was successfully immobilized onto $Fe_3O_4@SiO_2$.

The magnetization curves of Fe_3O_4 and $Fe_3O_4@SiO_2$ -Schiff base-Cu(II) are depicted in Figure 5. Both types of nanoparticles have good magnetic properties and show no remanence effect (superparamagnetic property). Comparison of the magnetic saturation value of Fe_3O_4 (74 emu g⁻¹) with that of $Fe_3O_4@SiO_2$ -Schiff base-Cu(II) (39 emu g⁻¹) shows a decrease in the catalyst magnetic saturation value. This observation provides clear evidence of the existence of some organic matter on the surface of the magnetic core. Although the magnetic saturation value of $Fe_3O_4@SiO_2$ -Schiff base-Cu(II) is decreased, it can still be efficiently separated from solution with an external magnet and also can be rapidly redispersed after removal of the external magnet.

3.2 | Catalytic activity studies

The catalytic performance of $Fe_3O_4@SiO_2$ -Schiff base-Cu(II) for the oxidation of alkenes and alcohols with TBHP was studied. In search of optimum reaction conditions, the



FIGURE 5 Magnetization curves of (a) Fe_3O_4 and (b) $Fe_3O_4@SiO_2$ -Schiff base-Cu(II)

influence of various factors, such as reaction time, solvent and amount of oxidant and catalyst, were investigated. Also, a series of blank experiments (Table S1) were carried out and the results indicate that the presence of both catalyst and oxidant is necessary for an effective catalytic performance.

3.2.1 | Oxidation of alkenes

The catalytic activity of the catalyst in the oxidation of styrene, as a model substrate, with TBHP as oxidant was evaluated. This reaction was monitored in various solvents such as acetonitrile, ethanol, chloroform and dichloromethane (Figure 6). The results show that the highest styrene conversion is obtained in acetonitrile within 2 h. The higher catalytic performance in acetonitrile may be attributed to its high dielectric constant and boiling point.^[48] The effects of different mole ratios of TBHP to styrene (Table 1) and catalyst amounts (Table 2) were also investigated. According to the experimental results, the best catalytic performance is achieved using TBHP and styrene in a mole ratio of 4:1 and in the presence of 0.01 g of the catalyst during 2 h.

To determine the general applicability of $Fe_3O_4@SiO_2$ -Schiff base-Cu(II) in the oxidation reaction, the oxidation



FIGURE 6 Effect of time and solvent on styrene oxidation. (Reaction conditions: styrene (5 mmol), catalyst (0.01 g), TBHP (15 mmol), solvent (3 ml) and reflux)



TABLE 1 Effect of mole ratio of TBHP to styrene on styrene oxidation^a

	Mole ratio		Selectivity (%)		
Entry	(TBHP:styrene)	Conversion (%) ^b	Benzaldehyde ^c	Styrene epoxide ^c	
1	2	68	50	50	
2	3	85	44	56	
3	4	95	63	37	

^aReaction conditions: catalyst (0.01 g), styrene (5 mmol), acetonitrile (3 ml), 2 h under reflux.

^bDetermined by GC.

^cDetermined by GC-MS.

TABLE 2 Effect of amount of catalyst on styrene oxidation^a

	Catalyst		Selectivity (%)		
Entry	amount (g)	Conversion (%) ^b	Benzaldehyde ^c	Styrene epoxide ^c	Others
1	0.005	91	59	41	—
2	0.01	95	63	37	—
3	0.02	97	54	35	11

^aReaction conditions: styrene (5 mmol), acetonitrile (3 ml), 2 h. ^bDetermined by GC.

^cDetermined by GC-MS.

of various alkenes, namely norbornene, styrene, α -methylstyrene, cyclohexene and cyclooctene, was carried out under the optimized conditions (Table 3). Based on the obtained data, the catalyst shows high catalytic performance in the alkene oxidation reaction.

In order to study the reaction mechanism, the oxidation of styrene was performed in the presence of diphenylamine as an efficient radical scavenger. It is found that the addition of diphenylamine inhibits the styrene oxidation and the reaction proceeds via a radical mechanism.^[49,50] So, it seems that decomposition of TBHP to tert-butoxyl and tert-butylperoxyl radicals is catalysed by Cu²⁺ in one-electron transfer processes.^[51] According to the radical mechanism operation, the behaviour of the alkenes used is depicted in Scheme 2. The main reason for different product selectivity in the oxidation of cyclic alkenes is due to competition between oxidation of the double bond and the allylic site. In the case of alkenes with double bonds attached to benzene ring, the oxidation may predominantly occur through the double bond because no allylic hydrogen is present. Styrene oxidation gives styrene epoxide and benzaldehyde. In this reaction, styrene epoxide is firstly formed and production of benzaldehyde may be due to the ring opening of styrene epoxide followed by cleavage of C-C bond^[52] (Scheme 2a). Significantly, the sole product of norbornene oxidation is norbornene epoxide. The high selectivity of epoxide reveals that only double bond undergoes oxidation. Since the allylic site oxidation through abstraction of α -hydrogen leads to formation of unstable bridgehead radical, the oxidation via this route may not occur^[53] (Scheme 2b). In the case of cyclooctene and cyclohexene, both undergo epoxidation and allylic oxidation concomitantly (Scheme 2c,d). The selectivity towards

TABLE 3 Oxidation of alkenes in the presence of Fe₃O₄@SiO₂-Schiff base-Cu(II)^a

Entry	Alkene	Conversion (%) ^b	Major product ^c (selectivity, %)	$TON^d/TOF^e (h^{-1})$
1	Norbornene	82	Norbornene epoxide (100)	494/247
2	Styrene	95	Benzaldehyde ^f (63)	572/286
3	α-Methylstyrene	100	Acetophenone ^g (54)	602/301
4	Cyclohexene	64	2-Cyclohexene-1-one ^h (65)	386/193
5	Cyclooctene	65	Cyclooctene epoxide ⁱ (77)	392/196

^aReaction conditions: catalyst (0.01 g), alkene (5 mmol), TBHP (20 mmol), acetonitrile (3 ml), 2 h under reflux.

^bDetermined by GC.

^cDetermined by GC-MS

^dTON: moles of product converted per mole of metal in the catalyst.

^eTOF: moles of product converted per mole of metal in the catalyst per unit time.

^fBenzaldehyde (37%) was also identified as by-product.

^g2-Phenyl-1,2-propanediol (36%) was also identified as by-product.

^hCyclohexene epoxide (26%) was also identified as by-product.

ⁱ2-Cyclooctene-1-one (23%) was also identified as by-product.



SCHEME 2 Proposed mechanism for oxidation of (a) styrene, (b) norbornene, (c) cyclooctene and (d) cyclohexene

epoxide in cyclooctene oxidation is higher than in cyclohexene oxidation. Such behaviour may be attributed to cyclooctene chair conformation in which the double bond lies in a different plane from all other carbons,^[54] whereas cyclohexene has half-chair conformation and its double bond lies in the plane of allylic hydrogens.^[55] Thus, less reactivity is observed for allylic hydrogens of cyclooctene in comparison to those of cyclohexene.

The reusability of the catalyst in the oxidation of styrene was investigated for five consecutive runs (Figure 7). After each run, the catalyst was separated by magnetic decantation, washed with acetonitrile and dried. Then it was reused for subsequent reactions under optimized conditions. As seen in Figure 7, the conversion of styrene oxidation decreases



FIGURE 7 Reusability of $Fe_3O_4@SiO_2$ -Schiff base-Cu(II) for oxidation of styrene under optimized conditions

from 95 to 85% after five runs. Also, ICP-OES analysis shows that the copper content of used catalyst (3.9 wt%) is less than that of fresh catalyst (5.1 wt%). This is may be attributed to the release of surface-adsorbed copper complex. So, the partial decrease in the activity may be due to some leaching and chiefly inevitable loss of the catalyst during the catalyst collection process. Based on the obtained results, the catalyst has good reusability and stability in the optimized reaction conditions. Also, the similarity of the FT-IR spectra (Figure 1) and XRD patterns (Figure 2) of Fe₃O₄@SiO₂-Schiff base-Cu(II) before and after use as a catalyst confirms the stability of the catalyst.

3.2.2 | Oxidation of alcohols

In order to evaluate the catalytic performance of $Fe_3O_4@SiO_2$ -Schiff base-Cu(II) in the oxidation of alcohols, the oxidation of benzyl alcohol as representative substrate with TBHP as oxidant was investigated. In this study, the experimental results show that the best catalytic performance of this system is achieved under the following conditions: 6 h is estimated as reaction time (Figure S2), TBHP and benzyl alcohol in a mole ratio of 4:1 (Table S2) and amount of catalyst is determined as 0.01 g (Table S3). The influence of

TABLE 4 Oxidation of alcohols in the presence of Fe₃O₄@SiO₂-Schiff base-Cu(II)^a

Entry	Alcohol	Conversion (%) ^b	Major product ^c (selectivity, %)	TON/TOF (h ⁻¹)
1	Benzyl alcohol	100	Benzoic acid (87)	602/100
2	3-Methoxybenzyl alcohol	86	3-Methoxybenzoic acid (85)	518/86
3	3-Chlorobenzyl alcohol	63	3-Chlorobenzoic acid (84)	380/63
4	Benzhydrol	100	Benzophenone (100)	602/100
5	<i>n</i> -Butanol	47	Butanoic acid (100)	283/47

^aReaction conditions: catalyst (0.01 g), alcohol (5 mmol), TBHP (20 mmol), acetonitrile (3 ml), 6 h under reflux.

^bDetermined by GC.

^cDetermined by GC-MS.

various solvents such as acetonitrile, methanol, ethyl acetate and chloroform on the benzyl alcohol oxidation was also studied. The results are listed in Table S4 and the best conversion and selectivity are obtained in acetonitrile.

The results of the oxidation of various alcohols, namely benzyl alcohol, 3-methoxybenzyl alcohol, 3-chlorobenzyl alcohol, benzhydrol and *n*-butanol, under the optimized conditions are presented in Table 4. The major products for oxidation of primary and secondary alcohols are the corresponding carboxylic acid and ketone, respectively. Also, the least reactivity is shown by the aliphatic alcohol, and the presence of electron-withdrawing and electron-donating substituents on the benzene ring may affect the reactivity of the aromatic alcohols.^[41]

4 | CONCLUSIONS

A new magnetic catalyst (Fe₃O₄@SiO₂-Schiff base-Cu(II)) was synthesized by reacting copper(II) acetate with silicacoated magnetite nanoparticles functionalized with Schiff base groups. The catalytic activity of this catalyst was evaluated for the oxidation of various alkenes (styrene, α -methylstyrene, cyclooctene, cyclohexene and norbornene) and alcohols (benzyl alcohol, 3-methoxybenzyl alcohol, 3-chlorobenzyl alcohol, benzhydrol and *n*-butanol) with TBHP as oxidant. Based on the optimized results, the best catalytic performances were obtained in acetonitrile using 0.01 g of catalyst. It was found that the catalyst successfully catalysed the epoxidation of norbornrne with 82% conversion and 100% selectivity during 2 h. Also, catalytic oxidation of benzyl alcohol gave 100% conversion with 87% selectivity for benzoic acid within 6 h. Some advantages including rather high yield and selectivity, easy separation and recyclability demonstrate that Fe₃O₄@SiO₂-Schiff base-Cu(II) is an efficient heterogeneous catalyst.

ACKNOWLEDGEMENTS

Financial support from Alzahra University is acknowledged.

REFERENCES

 R. G. Sheldon, B. J. Kochi, Metal-Catalyzed Oxidations of Organic Compounds, Academic Press, New York 1981.

- [2] M. P. Doyle, D. C. Forbes, Chem. Rev. 1998, 98, 911.
- [3] H. Hosseini-Monfared, E. Pousaneh, S. Sadighian, S. Weng Ng, E. R. T. Tiekink, Z. Anorg. Allg. Chem. 2013, 639, 435.
- [4] P. Gogoi, M. Kalita, T. Bhattacharjee, P. Barman, *Tetrahedron Lett.* 2014, 55, 1028.
- [5] A. Ghorbani-Choghamarani, B. Ghasemi, Z. Safari, G. Azadi, Catal. Commun. 2015, 60, 70.
- [6] S. Menati, H. Amiri-Rudbari, B. Askari, M. Riahi-Farsani, F. Jalilian, G. Dini, C. R. Chim. 2016, 19, 347.
- [7] L. Chen, B.-D. Li, Q.-X. Xu, D.-B. Liu, Chin. Chem. Lett. 2013, 24, 849.
- [8] S. Shit, D. Saha, D. Saha, T. N. Guru Row, C. Rizzoli, *Inorg. Chim. Acta* 2014, 415, 103.
- [9] G. Romanowski, J. Kira, M. Wera, J. Mol. Catal. A 2014, 381, 148.
- [10] G. Romanowski, J. Kira, Polyhedron 2013, 53, 172.
- [11] G. Romanowski, J. Kira, Polyhedron 2016, 117, 352.
- [12] J. Zhang, P. Jiang, Y. Shen, W. Zhang, X. Li, *Micropor. Mesopor. Mater.* 2015, 206, 161.
- [13] O. Erdem, B. Guzel, Inorg. Chim. Acta 2014, 418, 153.
- [14] A. Mavrogiorgou, M. Papastergiou, Y. Deligiannakis, M. Louloudi, J. Mol. Catal. A 2014, 393, 8.
- [15] S. Bhunia, S. Koner, Polyhedron 2011, 30, 1857.
- [16] F. Heshmatpour, S. Rayati, M. Afghan-Hajiabbas, B. Neumüller, Z. Anorg. Allg. Chem. 2011, 637, 1224.
- [17] G. Willingh, H. S. Abbo, S. J. J. Titinchi, Catal. Today 2014, 227, 96.
- [18] D. R. Godhani, H. D. Nakum, D. K. Parmer, J. P. Mehta, N. C. Desai, J. Mol. Catal. A 2016, 415, 37.
- [19] K. C. Gupta, A. K. Sutar, C.-C. Lin, Coord. Chem. Rev. 2009, 253, 1926.
- [20] R. Antony, S. T. D. Manickam, K. Saravanan, K. Karuppasamy, S. Balakumar, J. Mol. Struct. 2013, 1050, 53.
- [21] A. K. Sutar, T. Maharana, Y. Das, P. Rath, J. Chem. Sci. 2014, 126, 1695.
- [22] A. Mavrogiorgou, M. Baikousi, V. Costas, E. Mouzourakis, Y. Deligiannakis, M. A. Karakassides, M. Louloudi, J. Mol. Catal. A 2016, 413, 40.
- [23] M. J. Taghizadeh, H. Karimi, H. Sadeghi-Abandansari, Res. Chem. Intermed. 2016, 42, 8201.
- [24] Z. Li, S. Wu, H. Ding, D. Zheng, J. Hu, X. Wang, Q. Huo, J. Guan, Q. Kan, New J. Chem. 2013, 37, 1561.
- [25] M. B. Gawande, P. S. Brancoa, R. S. Varma, Chem. Soc. Rev. 2013, 42, 3371.
- [26] M. Mohammadikish, M. Masteri-Farahani, S. Mahdavi, J. Magn. Magn. Mater. 2014, 354, 317.
- [27] X. Li, Y. Fang, X. Zhou, J. Ma, R. Li, Mater. Chem. Phys. 2015, 156, 9.
- [28] X. Cai, H. Wang, Q. Zhang, J. Tong, Z. Lei, J. Mol. Catal. A 2014, 384, 217.
- [29] M. B. Gawande, Y. Monga, R. Zboril, R. K. Sharma, Coord. Chem. Rev. 2015, 288, 118.
- [30] B. Fredrich, W. Gerhartz, Ullmann's Encyclopedia of Industrial Chemistry, Vol. A3, Wiley-VCH, Weinheim 1985.



8 of 8 WILEY-Organometallic Chemistry

- [31] M. B. Smith, J. March, Advanced Organic Chemistry: Reactions, Mechanisms and Structure, Wiley-Interscience, New York 2001.
- [32] R. C. Larock, Comprehensive Organic Transformations: A Guide to Functional Group Preparations, Wiley-VCH, New York 1999.
- [33] R. A. Sheldon, H. Van Bekkum, Fine Chemicals through Heterogeneous Catalysis, Wiley-VCH, New York 2001.
- [34] A. Bezaatpour, S. Khatami, M. Amiri, RSC Adv. 2016, 6, 27452.
- [35] M. Afshari, M. Gorjizadeh, S. Nazari, M. Naseh, J. Magn. Magn. Mater. 2014, 363, 13.
- [36] M. Zare, Z. Moradi-Shoeili, M. Bagherzadeh, S. Akbayrak, S. Ozkar, New J. Chem. 2016, 40, 1580.
- [37] M. Ghorbanloo, A. Mohamadi, M. Amini, J. Tao, *Transition Met. Chem.* 2015, 40, 321.
- [38] J. Sun, G. Yu, L. Liu, Z. Li, Q. Kan, Q. Huo, J. Guan, *Catal. Sci. Technol.* 2014, 4, 1246.
- [39] A. R. Judy-Azar, E. Safaei, S. Mohebbi, Mater. Res. Bull. 2015, 70, 753.
- [40] A. R. Judy-Azar, S. Mohebbi, J. Mol. Catal. A 2015, 397, 158.
- [41] Q. Zhou, Z. Wan, X. Yuan, J. Luo, Appl. Organometal. Chem. 2016, 30, 215.
- [42] P. B. Bhat, R. Rajarao, V. Sahajwall, B. R. Bhat, J. Mol. Catal. A 2015, 409, 42.
- [43] X. Liu, Z. Ma, J. Xing, H. Liu, J. Magn. Magn. Mater. 2004, 270, 1.
- [44] M. Tajbakhsh, M. Farhang, R. Hosseinzadeh, Y. Sarrafi, RSC Adv. 2014, 4, 23116.
- [45] H. Cao, J. He, L. Deng, X. Gao, Appl. Surf. Sci. 2009, 255, 7974.
- [46] M. Yamaura, R. L. Camilo, L. C. Sampaio, M. A. Macdo, N. Nakamura, H. E. Toma, J. Magn. Magn. Mater. 2004, 210, 217.
- [47] M. Esmaeilpour, A. R. Sardarian, J. Javidi, Appl. Catal. A 2012, 445–446, 359.

- [48] J. Rydberg, C. Mussikas, G. R. Choppin, Principles and Practices of Solvent Extraction, Marcel Dekker, New York 1992.
- [49] L. M. Slaughter, J. P. Collman, T. A. Eberspacher, J. I. Brauman, *Inorg. Chem.* 2004, 43, 5198.
- [50] F. Farzaneh, J. Taghavi, R. Malakooti, M. Ghandi, J. Mol. Catal. A 2006, 244, 252.
- [51] U. Junghans, C. Suttkus, J. Lincke, D. Lässig, H. Krauyscheid, R. Gläser, *Micropor. Mesopor. Mater.* 2015, 216, 151.
- [52] R. Ghosh, Y.-C. Son, V. D. Makwana, S. L. Suib, J. Catal. 2004, 224, 288.
- [53] J. March, Advanced Organic Chemistry, John Wiley, New York 1985.
- [54] U. Neuenschwander, I. Hermans, J. Org. Chem. 2011, 76, 10236.
- [55] E. L. Eliel, S. H. Wilen, Stereochemistry of Organic Compounds, John Wiley, New York 1994.

SUPPORTING INFORMATION

Additional Supporting Information may be found online in the supporting information tab for this article.

How to cite this article: Sarkheil M, Lashanizadegan M. Copper(II) Schiff base complex immobilized on superparamagnetic $Fe_3O_4@SiO_2$ as a magnetically separable nanocatalyst for oxidation of alkenes and alcohols. *Appl Organometal Chem.* 2017;e3726. https://doi.org/10.1002/aoc.3726