High catalytic activity of magnetic Fe₃O₄@SiO₂-Schiff base-Co(II) nanocatalyst for aerobic oxidation of alkenes and alcohols and DFT study

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A R T I C L E   I N F O
Article history:
Received 30 July 2018
Received in revised form
3 November 2018
Accepted 5 November 2018
Available online 9 November 2018

Keywords:
Magnetic recovery
Molecular oxygen
Nanocatalyst
Imidazole
DFT calculation

A B S T R A C T
A new heterogeneous nanocatalyst (Fe₃O₄@SiO₂-Schiff base-Co(II)) was successfully fabricated applying silica-coated magnetite nanoparticles as a suitable and efficient support for covalent anchoring of a cobalt(II) Schiff base complex. This catalyst was characterized by FT-IR, XRD, SEM, EDX, ICP-OES, CHN, DRS, TGA, VSM techniques, and QM study. According to theoretical calculations, the Schiff base-Co(II) complex at high spin state with square planar geometry is more stable than low spin state. Also, Schiff base-Co(II)/imidazole complex has distorted square pyramidal geometry. Evaluating the activity of the nanocatalyst was performed for the oxidizing of different olefins (styrene, norbornene, α-methyl styrene, cyclohexene, and cyclooctene) and alcohols (benzyl alcohol, benzhydrol, n-butanol, n-octanol and n-heptanol). In these reactions, the influence of two various oxidants, molecular oxygen and tert-butyl hydroperoxide (TBHP), were examined. The results exhibited that the nanocatalyst was considerably effective for the aerobic epoxidation of norbornene, cyclohexene, and cyclooctene with 100% conversion and selectivity within 1 h. Also, by oxidizing of benzyl alcohol and benzhydrol, benzoic acid (conversion: 94%, selectivity: 91%) and benzophenone (conversion and selectivity: 100%) were achieved, respectively. The results suggested that the nanocatalyst has a remarkable role in oxidation reaction of olefins and alcohols. Other promising advantages of the catalyst were easy magnetic separation and recyclability for several times without significant loss of catalytic efficiency.

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1. Introduction

Over the past few decades, increasing demands from chemical industries for practical compounds, such as epoxides, aldehydes, ketones, and carboxylic acids, which are obtained from oxidation of olefins and alcohols has led to significant attempts at developing efficient catalysis systems for the oxidizing of olefins and alcohols with regard to economic and environmental aspects [1–3]. On this basis, the use of molecular oxygen which is accepted as a green, inexpensive, high atom-efficient, and readily available oxidant is extremely considered [4]. It is well known that many Schiff base transition metal complexes such as Cu(II) [5–7], Co(II) [8–10], Mo(VI) [11–14], V(IV) [15–17], Mn(III) [18–20], and Ni(II) [21,22], complexes are useful catalysts for oxidation reactions because of the similarity of their structure to that of the porphyrin ring, high ability to load oxygen and mimicking enzymes [23]. Among these catalysts, various homogeneous and heterogeneous cobalt compounds have attracted great attention for the oxidizing of olefins [24,25] and alcohols [26,27] not only because of their low cost and eco-friendly nature but also for their selective performance. Besides efficiency of catalysts, stability and recyclability constitute serious factors for catalysis systems. Therefore, separation and reuse of the homogeneous catalysts is a challenging subject in a lot of catalytic research. In this regard, an efficient strategy to overcome these drawbacks is immobilization of homogeneous complexes onto/in solid supports, including activated carbon [28,29], clays [30–32], zeolites [33–35], graphene oxide [36,37], and polymers [38–41]. Recently, promising advancement in this area is achieved by using magnetic nanoparticles as solid supports. Some advantages of them are high specific surface area and simple separation from reaction media by an external magnet. Despite the benefits of magnetic nanoparticles, the major problems of them are agglomeration and
decomposition during catalytic reactions. To avoid these problems, synthesis of magnetic core-shell structure is widely suggested. Among the variety of inert materials such as carbon, silica and polymer for coating the surface of magnetite core, silica is selected as a suitable material that not only modifies the surface with silanol groups for further functionalization but also improves surface stability and reduces aggregation [42–44].

During the last years, impressive advances have been achieved in the epoxidation of olefins [45–47] and oxidation of alcohols [48,49] by using magnetic immobilized Schiff base cobalt(II) complexes. Although using aldehydes in agriculture and fine chemicals has led to the focus of many researches on the slight oxidizing of primary alcohols and acquiring aldehydes, because of the wide application of carboxylic acids in industry, great attention has also been paid to the full oxidizing of primary alcohols, which led to obtaining carboxylic acids [50–52]. Thus, there is a considerable demand to design effective catalysts for the oxidizing of alcohols to carboxylic acids. Also inspired by the function of imidazole of histidine or thiolate of cysteine in natural metalloproteines [53–55], the utilization of N-donor axial ligands such as imidazole and pyridine bases has been a subject of growing interest in the catalytic epoxidation reactions. Based on the literature, employment of nitrogen donors can be enhanced the catalytic efficiency of bimimetic Schiff base transition metal complexes in the epoxidation reactions [56–58].

In this study, efforts are made to synthesize and characterize a new heterogeneous cobalt(II) nanocatalyst (Fe3O4@SiO2–Schiff base-Co(II)). Also, the optimized geometry of Schiff base-Co(II) and Schiff base-Co(II)/imidazole complexes are theoretically determined. To know the behavior of the nanocatalyst in the oxidation reaction, the oxidation of a series of olefins and alcohols in the presence of O2 and TBHP as oxidants is studied.

2. Experimental

2.1. Chemicals and methods

Chemicals were purchased from Sigma-Aldrich, Merck and Acros Organics. All of them were applied without further purification. FT-IR spectra were obtained with a Bruker FTIR model Tensor 27 spectrometer using KBr discs in the range of 500–4000 cm−1. X-ray diffraction peaks were collected from a Philips X’Pert diffractometer (λ = 1.54 Å (Cu Kα radiation), step size = 0.02/°, voltage = 40 kV, current = 30 mA, 2θ range = 10–70°). To acquire magnetic properties, a vibration sample magnetometer (VSM) was utilized (BHV-55, Riken, magnetic field range: 8000 Oe to +8000 Oe, room temperature). The CHN analysis was carried out with a Perkin-Elmer elemental analyzer (2400 Series II system). Diffuse reflectance spectra (DRS) were registered with an Ava Spec 2048 TECH spectrometer, using BaSO4 as the reference. To take the transmission electron microscopy (TEM) and scanning electron microscopy (SEM) images, Zeiss EM10C electron microscope and KYKY-EM3200 microscope were used, respectively. Thermal experiments (TGA) were registered on a TGA/DSC1 (Mettler Toledo). To determine the amount of cobalt of the catalyst, ICP-OES analysis was performed with a Varian Vista-Pro instrument. GC and GC–mass analysis were carried out by applying an Agilent 6890 Series with a FID detector, HP-5% phenylmethylsiloxane capillary and an Agilent 5973 Network, mass selective detector, HP-SMS 6898 Network GC system, respectively.

2.2. Synthesis of nanocatalyst

Firstly, based on the reported procedure, co-precipitation method was applied to synthesize the Fe3O4 nanoparticles (1) [59]. Then, core-shell structure of Fe3O4@SiO2 (2) was prepared by coating of Fe3O4 core with tetraethyl orthosilicate under alkaline conditions. In the next step, refluxing 0.8 mmol of 3-aminopropryltrimethoxysilane with the 15 mL of toluene suspension of compound (2) (100 mg) under N2 atmosphere for 48 h leads to the attachment of amine groups on the silica-coated magnetic surface. The obtained compound designated as Fe3O4@SiO2–NH2 (3). Afterwards, the processes of washing with ethanol and anhydrous toluene and drying the compound (3) within 10 h at 60 °C were carried out [60]. Thereafter, Fe3O4@SiO2–Schiff base (4) was synthesized by the addition of 2’-hydroxypropyrophene (150 mg, 1 mmol) to the 15 mL of anhydrous toluene suspension of compound (3) (100 mg). The resulting mixture was refluxed under N2 for 48 h. After rinsing the obtained solid with anhydrous toluene, the compound (4) was dried at 60 °C in oven during 10 h. Finally, by refluxing a mixture which consists of 15 mL of an ethanolic solution of CoCl2·6H2O (237 mg, 1 mmol) and 100 mg of (4) during 18 h and under N2, Fe3O4@SiO2-Schiff base-Co(II) nanocatalyst (5) was constructed (Scheme 1). Then, after magnetic isolation of (5), unreac- ted cobalt was removed from the surface by being washed with EtOH, and then nanocatalyst (5) dried at 60 °C within 10 h.

2.3. Catalytic experiments for the oxidation of olefins

To perform the oxidation reactions, a round bottom flask which is equipped with a cooling condenser was applied. Through a general procedure, a reaction mixture of the nanocatalyst (10 mg), olefin (5 mmol), solvent (acetonitrile: 3 mL), imidazole (mole ratio of imidazole to catalyst: 5), and oxidant (TBHP, 70% in H2O (20 mmol) or O2 flow) was refluxed for a suitable period of time (6 h when TBHP was used as the oxidant and 1 h when O2 flow was used). It should be noted that when O2 was used as the oxidant, isobutyraldehyde (20 mmol) as co-reductant was added to the mixture of the reaction. After finishing the reaction, isolation of the nanocatalyst was done with an external magnetic net, and then analyzing the reaction mixture was carried out using GC and GC–MS. To calculate the conversion of substrate, GC data was used, and GC–MS results were used to identify the oxidation products.

2.4. Catalytic experiments for the oxidation of alcohols

A typical reaction mixture for the alcohol oxidation consisted of catalyst (10 mg), alcohol (5 mmol), solvent (acetonitrile: 3 mL) and oxidant (TBHP (20 mmol) or O2 flow). Moreover, in the presence of O2 as the oxidant, isobutyraldehyde (20 mmol) was added to the mixture. The reaction mixture was heated at reflux for an appropriate time (10 h when TBHP was used as the oxidant and 6 h when O2 flow was used). When the reaction was completed, the nanocatalyst was isolated by an external magnetic field. Then, to analyze the filtrate, GC and GC–mass analysis were performed.

3. Theoretical

3.1. Computational details

The calculation of energetics, as well as geometry optimizations of Schiff base-Co(II) complex were performed at the density functional theory (DFT) method [61] without any symmetry constrains. The hybrid of Beck’s nonlocal three parameter exchange and correlation theory (DFT) method [62] for the close shell system and UB3LYP for open shell system have been used. All calculations have been performed with standard 6-311 + C** basis set. DFT as a suitable and popular method can be used for calculations of compounds including metals. The most expressive benefit of DFT methods is a considerable increase
in computational accuracy without the additional increase in time of calculations. The frequencies calculations were computed to confirm that an optimized structure refers to a local minimum that has only real frequencies. Afterwards, the effect of solvent on conformational equilibrium of studied compounds have been investigated using polarized continuum model (PCM) of Tomasi and coworkers [63] at the above mentioned level of calculations. It is noticeable that the solvation calculations were performed for ethanol (ε = 40) with the geometries optimization for this solvent. Generally, the PCM method presents good reliability, accuracy, adaptability and more reduced computational effort to describe the solvent effect [64–66]. Because of the sensitivity of the calculated energy to spin contamination in an open shell system, the spin contamination of studied compounds with unpaired electrons was found 0.77→0.79. After annihilating the first spin contaminant, they decreased to correct value 0.76. The model of Quantum mechanical calculations which was used in the present research was carried out with the Gaussian program series 2003 [67].

4. Results and discussion

4.1. Preparation and characterization of the nanocatalyst

Scheme 1 shows the multistep procedure of preparing the catalyst. Initially, to synthesize the Fe3O4 magnetic nanoparticles (1), the reported co-precipitation technique was applied. Then, synthesis of Fe3O4@SiO2 (2) was done via coating the surface of magnetite core with tetraethyl orthosilicate. Compound (2) was further modified with 3-aminopropyltrimethoxysilane to obtain Fe3O4@SiO2-NH2 (3). In the next step, treating compound (3) with 2’-hydroxypropiophenone caused condensation of carbonyl group with the surface amino group, which produced Schiff base groups on the support (compound 4). Finally, the reaction of Co(II) chloride with compound (4) led to the construction of Fe3O4@SiO2-Schiff base-Co(II) nanocatalyst (5).

The FT-IR spectra of (1), (2), (3), (4), and (5) are shown in Fig. 1. As indicated in Fig. 1a, the bands due to Fe–O vibrations of Fe3O4 core appear at 587 and 631 cm⁻¹. Also, the vibration bands which are attributed to the surface Fe–OH or adsorbed H2O are seen at 3417 and 1616 cm⁻¹ [68]. After Fe3O4 nanoparticles were coated with silica, new peaks appeared at 1086 (Si-O-Si asymmetric) and 816 cm⁻¹ (Si-O-Si symmetric). As displayed in Fig. 1c, functionalization of compound (2) with 3-aminopropyltrimethoxysilane leads to the appearance of new bands at around 2860 and 2920 cm⁻¹ that are related to CH stretching modes [69]. In the spectrum of (4)
which is observed below 200°C in both curves of compounds (11.7, 13.1 and 13.7 nm, respectively. Being used as the catalyst (Fig. 4a), the TEM image verify the spherical morphology of them. The average estimated anchored organic substances is 0.78 mmol g⁻¹/C.t. The X-ray diffraction analysis of (1), (2), and (5) before and after being used as the catalyst are illustrated in Fig. 2. Comparison of the XRD patterns of the prepared Fe₃O₄ (1) with that of standard Fe₃O₄ (JCPDS No. 75-0033) shows not only their peak positions but also their relative intensities are in accordance with each other. Since the peak positions of compounds (2) (Fig. 2b) and (5) (Fig. 2c) in comparison to those of (1) (Fig. 2a) are similar, no destruction occurred in the crystal structure of the Fe₃O₄ core during surface modification of it. Change in the intensity of diffraction peaks of compound (2) and nanocatalyst (5) relative to Fe₃O₄ (1) may be ascribed to the effect of the non-magnetic covering layer which coated Fe₃O₄. To determine the average crystallite size of the nanoparticles, the Debye-Scherrer formula was utilized. The results exhibited that the approximate sizes of (1), (2), and (5) are about 11.7, 13.1 and 13.7 nm, respectively.

The TEM micrograph of nanocatalyst (5) is presented in Fig. 3. It is evident that most of the nanoparticles are in quasi-spherical shape and have an average size of around 16 nm. The average sizes obtained from TEM and XRD are in agreement with each other. Also, the appearance of the magnetite cores as dark spots surrounded by bright non-magnetic shells clearly proved the structure of the nanocatalyst (5) is core-shell. Moreover, SEM was used to study the morphologies of [(1), (2), and (5)] before and after being used as the catalyst (Fig. 4a–d). As can be seen, the SEM images verify the spherical morphology of it.

TGA results of (2) and (5) are depicted in Fig. 5. As illustrated in Fig. 5, in both curves of compounds (2) and (5), the first change which is observed below 200°C may be corresponded to loss of physically adsorbed H₂O on the surface of these compounds. Moreover, the decomposition of organic substances of (5) was confirmed by observing the weight loss (16.53%, 0.75 mmol g⁻¹/C.t) in the temperature region from 280°C to 600°C. Since the nitrogen content of nanocatalyst (5) determined from CHN result is 1.1%, the estimated anchored organic substances is 0.78 mmol g⁻¹/C.t. The results obtained from CHN and TGA are in accordance with each other.

Also, tow analyses, EDX and ICP-OES, which are further confirmation for the anchoring of the cobalt complex on the surface of Fe₃O₄@SiO₂, were carried out. According to the EDX analysis (Fig. S1 (see Supplementary data)), the existence of Co, Fe, Si, and O elements in the nanocatalyst (5) was confirmed. The amount of cobalt which was loaded on the surface of (5) was measured by ICP-OES and the obtained data revealed that the cobalt content was 3.4 wt % (0.53 mmol g⁻¹/C.t).

Magnetic properties of Fe₃O₄ (1) and nanocatalyst (5) were measured by applying vibrating sample magnetometry (VSM) at room temperature (Fig. 6). Based on these curves, the super-paramagnetic behavior of (1) and (5) is verified. Comparison of the curves indicates that the saturation magnetization of (5) (35 emu/g) decreases relative to (1) (74 emu/g), which validates the coating of magnetic core with some organic matter.

4.2. Optimization of Schiff base-Co(II) complex

UB3PW91/6-311 + G** method without any initial symmetry restrictions and by assumption of C₁ point group has been applied to geometry fully optimized of Schiff base-Co(II) as a model of Fe₃O₄@SiO₂-Schiff base-Co(II) catalyst. Two various spin states of cobalt, including high spin (S = 3/2) and low spin (S = 1/2) states, are possible. To re-optimize the completely optimized geometries at high and low spin states in gas phase, the PCM method in ethanol was used by taking into account the solvent effect. The calculated results demonstrated that high spin and low spin states of Schiff base-Co(II) complex are stabilized about 37.64 kcal/mol in the solvent. Table 1 and Fig. 7 represented some geometrical factors and relative energies, respectively. As seen in Fig. 7, the stability energy of Schiff base-Co(II) complex at high spin state is about 11.27 kcal/mol more than its low spin state in solvent media. According to Fig. 7, the average of O₄-Co₁-N₃ and O₁₅-Co₁-N₂ bond angles is about 91.94° and 86.52° in high and low spin states, respectively. Therefore, both spin states of Schiff base-Co(II) complex have square planar geometry. Calculation of vibrational frequencies has confirmed stationary point with no negative eigenvalue observed in the force constant matrix.
4.3. Details of charge analysis for Schiff base-Co(II) complex in high spin state

Net atomic charges of Schiff base-Co(II) complex in high spin state have been calculated. These partial charges are derived from natural bond orbital (NBO) calculation. The net atomic charge on the Co is about 1.3 when cobalt atom is coordinated to Schiff base N2, N3, O4, and O15 positions. By considering the charge of Schiff base interacting atoms, N2 ($-0.54$), N3 ($-0.54$), O4 ($-0.78$), and O15 ($-0.77$), an electrostatic interaction could be evidenced.

After optimizing the Schiff base-Co(II) complex, we focused on the interaction between Schiff base-Co(II) complex and imidazole ring to form a new complex. The theoretical results revealed that the structure of Schiff base-Co(II)/imidazole complex is distorted square pyramidal. The optimized geometry and some structural details (bond lengths and bond angles) of it are given in Fig. 8 and Table S1, respectively.

| Connected atoms | Low spin | High spin |
|-----------------|----------|-----------|
| Bond distance (Å) |          |           |
| Co1N2           | 1.93     | 1.86      |
| Co1N3           | 1.94     | 1.85      |
| Co1O4           | 1.87     | 1.82      |
| Co1O15          | 1.87     | 1.82      |
| O15C16          | 1.35     | 1.43      |
| Bond angle (°)  |          |           |
| O4Co1N3         | 86.57    | 91.93     |
| O4Co1N2         | 170.21   | 179.93    |
| O15Co1N3        | 170.21   | 179.93    |
| O15Co1N2        | 86.46    | 91.96     |
4.4. Catalytic properties

Activity of the nanocatalyst (5) in the oxidation reaction of olefins and alcohols was assayed. To explore the reaction conditions, the effect of different factors, such as reaction time, axial ligand, solvent, amount of catalyst and oxidant, and the nature of oxidant were evaluated. Additionally, Tables S2 and S3 showed the data of some control tests, which proved the necessity of using the nanocatalyst (5).

4.5. Oxidation of olefins

By selecting the oxidation of styrene as a model reaction, the application of the nanocatalyst (5) in the oxidation reaction of olefins was tested. As seen in Table S4, when TBHP was used as an oxidant (entries 1a, 2a, and 3a), the result of oxidation of styrene was not acceptable. Thus in this reaction, the effect of imidazole as co-catalyst was investigated. The influence of different amounts of imidazole on the oxidation of styrene is given in Table S4.

Table S4 (entry 4), when O2 is used as the oxidant in the presence of imidazole, benzaldehyde (20%) and benzoic acid (10%) were also identified.

In the optimal conditions, the study of catalytic application of (5) in the oxidation reaction of olefins including styrene, norborne, α-methyl styrene, cyclooctene, and cyclohexene exhibits the considerable role of the catalyst in the oxidation reaction. The results are given in Table 2 (O2 is used as the oxidant) and Table S6 (TBHP is used as the oxidant).

With the purpose of exploring the mechanism of the oxidation reaction, a model reaction was designed by oxidizing the styrene under optimized reaction conditions and in the existence of a radical scavenger such as diphenylamine. Based on the results obtained from GC, adding diphenylamine leads to the inhibition of the reaction. Thus, this reaction proceeded via a radical mechanism [72,73]. There is extensive literature that reports the epoxidation reaction which is catalyzed by cobalt(II) compounds in the presence of O2 and isobutyraldehyde [74,75]. According to the literature, the reaction mechanism is depicted in Scheme 2. It seems that reaction between Fe3O4@SiO2-Schiff base-Co(II) and isobutyraldehyde firstly affords the intermediate I (LnCo(I)O4/5/CR) via the removal of a proton from isobutyraldehyde and the conversion of Co(II) to Co(I). Subsequently, the intermediate II (LnCo(IO4/5/0OCR) is generated through the adsorption of molecular O2 on the intermediate I. Then, regeneration of LnCo(II) is occurred following the release of RCOOO− from an intermediate II. In the next step, intermediate III (isobutyrpoxycacid) is formed and then reaction of intermediate III as an

![Fig. 7. Presentation of optimized geometry of Schiff base-Co(II) complex in solution phase.](image)

![Fig. 8. Presentation of optimized geometry of Schiff base-Co(II)/imidazole complex.](image)

| Entry | Olefins | Conversion (%) | Selectivity of epoxide (%) | TONd/c | TOFe | h−1 |
|-------|--------|----------------|---------------------------|--------|-------|-----|
| 1     | Styrene| 100            | 70                        | 858/868|       |     |
| 2     | Norborne| 100           | 100                       | 858/868|       |     |
| 3     | α-Methyl styrene| 73 | 68                        | 634/634|       |     |
| 4     | Cyclohexene| 100        | 100                       | 858/868|       |     |
| 5     | Cyclooctene| 100         | 100                       | 858/868|       |     |

a Reaction conditions: nanocatalyst (10 mg), olefin (5 mmol), oxidant (O2), isobutyraldehyde (20 mmol), mole ratio of imidazole to catalyst (5), acetonitrile (3 mL) time (1 h), and reflux.

b To determine conversion, GC was applied.

c To determine products, GC-MS was applied.

d TON = (mmoles of product)/mmoles of metal in the catalyst.

e TOF = TON/react time.

f Benzaldehyde (20%) and benzoic acid (10%) were also identified.
g Acetophenone (32%) was also identified.
An oxidant with LnCo(II) gives rise to LnCo(IV)O (intermediate IV) and isobutyric acid. Finally, the interaction of alkenes with LnCo(IV)O leads to epoxide products according to the suggested mechanism by Sheldon [1]. Also, the formation of benzaldehyde and benzoic acid in addition to styrene epoxide was depicted in Scheme 2.

To assess the recyclability of the nanocatalyst, the activity of it for oxidation of styrene was tested for 5 subsequent cycles. When finishing each cycle, the processes of magnetic isolation, washing with acetonitrile and drying the nanocatalyst were performed. After that, the recycled nanocatalyst was utilized for subsequent run under optimal reaction conditions. GC results show that after 5 cycles, the conversion declined from 100% to 90% (Fig. 9). Data obtained from ICP-OES exhibited the amounts of cobalt of the fresh and recycled nanocatalyst were 3.4 and 3.1 wt%, respectively. By considering ICP-OES results, the reason of slight decline in the performance of the recycled nanocatalyst can be ascribed to some release of the cobalt complex which adsorbed on the surface.

Further evidences to verify the reusability and stability of the catalyst were obtained by comparing the FT-IR spectra (Fig. 1), XRD patterns (Fig. 2), and DR spectra (Fig. S4) and SEM images of fresh nanocatalyst (5) for the oxidizing of styrene under optimized conditions.
and reused nanocatalyst (5). Since the similarity of the results obtained from recycled and fresh catalysts is clear, the reusability and stability of the catalyst is proven.

A comparison of the nanocatalyst (5) with other heterogeneous cobalt catalysts [47, 76–80] is reported in Table 3. It is found that our catalytic system has some advantages involving short reaction time (1 h), high conversion and selectivity.

### 4.6. Oxidation of alcohols

To optimize the reaction conditions for oxidizing of alcohols, efforts were made by selecting benzyl alcohol as a model substrate in the presence of TBHP as the oxidant. By considering the experimental data, the optimal reaction conditions are described as follows: 10 h (Fig. S5) and 10 mg (Fig. S6) were required for reaction time and amount of catalyst, respectively. The ratio of 1:4 was determined as a desired mole ratio of benzyl alcohol:TBHP (Table S7, entries 1–3). Also, replacing TBHP by O2 leads to decrease the reaction time from 10 h to 6 h (Table S7, entry 4).

It is revealed that the use of the nanocatalyst (5) in the oxidation reaction of primary alcohols leads to the formation of their relevant carboxylic acids, but the main products obtained from oxidation reaction of secondary alcohols are their corresponding ketones (Table 4). Also, the aliphatic alcohols exhibit less reactivity than the aromatic alcohols. As reported in the literature, there are some studies including cobalt complexes that oxidize primary alcohols to the corresponding carboxylic acids [81–83]. A comparison of our nanocatalyst (5) with other catalytic systems [81–87] is summarized in Table 5. Based on these observations, the efficiency of the nanocatalyst in the oxidation reaction of alcohols including primary and secondary types is proved.

### 5. Conclusions

A new magnetically separable nanocatalyst was constructed via covalent grafting of Schiff base ligand onto core-shell structured
Fe₃O₄@SiO₂, followed by complexation with cobalt(II) chloride. The optimized geometry of Schiff base-Co(II) and Schiff base-Co(II)/imidazole complexes were theoretically determined. Based on the theoretical calculations, Schiff base-Co(II) complex at high spin state with square planar geometry is more stable than low spin state and Schiff base-Co(II)/imidazole complex has distorted square pyramidal geometry. This nanocatalyst was known to successfully oxidize various olefins and alcohols. The oxidants used in these reactions were TBHP and O₂. Molecular oxygen in comparison to TBHP not only acted as a green oxidant but also significantly decreased the reaction time. Experimental results revealed that by employing 10 mg of the catalyst and acetonitrile as the reaction medium, the highest efficiency of the nanocatalyst were achieved. It is noteworthy that aerobic oxidation of norbornene, cyclohexene, and cyclooctene gave corresponding epoxides with 100% conversion and selectivity. Also, oxidation of benzyl alcohol and benzylhydroxyl showed the formation of benzoic acid (conversion: 94%, selectivity: 91%) and benzophenone (conversion and selectivity: 100%), respectively. Overall, some promising benefits of the catalyst such as convenient separation, recyclability, using an environmental oxidant, and rather high yield and selectivity make it an efficient catalyst for oxidation of olefins and alcohols.

Acknowledgement

The financial support from Alzahra University is acknowledged.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.molstruc.2018.11.016.

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