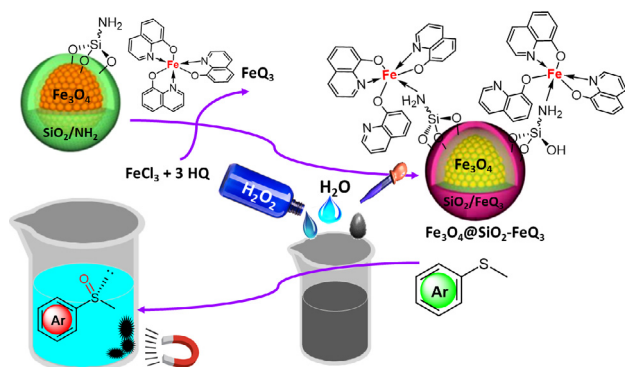


## Regular Article

# $NH_2$ -coordinately immobilized tris(8-quinolinolato)iron onto the silica coated magnetite nanoparticle: $Fe_3O_4@SiO_2-FeQ_3$ as a selective Fenton-like catalyst for clean oxidation of sulfides

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## GRAPHICAL ABSTRACT



## ARTICLE INFO

## Article history:

Received 23 June 2017

Revised 19 September 2017

Accepted 7 October 2017

Available online 10 October 2017

## Keywords:

Magnetic nanoparticle

Fenton-like catalyst

Sulfide oxidation

Sulfoxide

## ABSTRACT

A green, robust and eco-friendly procedure for the oxidation of aromatic organic sulfides to sulfones using  $H_2O_2$  catalyzed by  $NH_2$ -coordinately immobilized tris(8-quinolinolato)iron onto the silica coated magnetite ( $Fe_3SiO_6$ ) has been developed. Physicochemical properties of the resulting nanoparticles were investigated by means of techniques including X-ray diffraction, scanning electron microscopy, thermogravimetric analysis, vibrating sample magnetometer, atomic adsorption spectroscopy and FT-IR spectroscopy. The catalytic activity of sulfides oxidation showed that this atom-economical protocol provided great yields of various sulfones and allowed the sulfide function reaction conducting under the mild conditions thus to prevent the sulfide being over-oxidized to sulfoxides. The  $Fe_3O_4@SiO_2-FeQ_3$  catalysts are magnetically separable and kept stable after recycling for 7 consecutive runs without detectable activity loss.

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## 1. Introduction

Development of environmental sustainability is of primary importance for realizing green chemistry [1]. Sustainability of an organic reaction depends on the substrates, solvent, and even workup procedure for the preparation. Therefore, in the organic

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molecules oxidation process, some efforts have been devoted to the development and applied green solvent and oxidants such as  $\text{H}_2\text{O}_2$  that co-produce only water as innocuous waste [2,3]. Sulfoxides are one of the important chemical raw materials for the productions of valuable chemical compounds in biology and also play an essential role in the activation of enzymes. Thus, the generation of sulfoxides from the selective oxidation of organic aromatic sulfides has attracted tremendous attention [4]. The oxidants such as TEMPO, oxone, UHP, TBHP,  $\text{H}_2\text{O}_2$  and co-oxidant are available to perform this reaction to achieve the sulfoxides [5]. There are many studies focusing on the organic aromatic sulfides oxidation on heavy metal or Bronsted acid supported solids such as  $(\text{Zr}_4(\text{OH})_6(\text{CrO}_4)_5(\text{H}_2\text{O})_2)$ ,  $\text{Fe}_3\text{O}_4@/\text{SiO}_2/\text{Mn}(\text{III})$ ,  $\text{Fe}_3\text{O}_4/\text{PEG-SO}_3\text{H}$ ,  $\text{SBA-15}/\text{OSO}_3\text{H}$  and  $\gamma\text{-Fe}_2\text{O}_3@/\text{SiO}_2/\text{SO}_4\text{H}$ . However, one of the main challenges this reaction faced is the sulfone formation from the overoxidation of sulfides. This problem particularly occurs in the preparation of biologically relevant sulfoxides. Considering the nature of ligands in the metal complexation and its electronic properties, design, and development of novel ligand that are air and moisture stable and reusable is highly demanding [2–5]. Besides, another big concern in the supported metal complex catalyst is immobilization efficiency of the catalysts on the solid surface to guarantee the complete participant of all the active metal complex. Intensive efforts have been devoted to the development of oxidation reactions using highly atom-efficient and green reagents as well as solid catalysts which produced innocuous waste by-produce only [6]. For example, using aqueous  $\text{H}_2\text{O}_2$  as an oxidizing agent to the oxidation reaction only produce water as co-product.

In our previous study, we have developed several synthetic methods for the immobilization of various metal complexes [7]. We have found that there is desperate need for the development of efficient and rapid green selective methods [7,8]. Moreover, the synthesis of these molecules has been usually carried out in hazardous and polar solvents such as  $\text{CH}_2\text{Cl}_2$ ,  $\text{CCl}_4$ ,  $\text{C}_6\text{H}_6$ , toluene, DMF, and DMSO which has caused difficulties to the isolation and recovery of the solid. Recently, we have successfully synthesized a series of organic-inorganic hybrid heterogeneous porous material interfacial catalysts, which displayed comparable activity and selectivity to the homogenous organic reactions in a wide range of water medium [7]. To continue this research to further develop stable and highly active magnetic green solid catalyst in water, herein we have synthesized  $\text{Fe}_3\text{O}_4@/\text{SiO}_2\text{-FeQ}_3$  catalyst and applied the resulting catalysts for the oxidation of aromatic organic sulfides to produce sulfoxides, with  $\text{H}_2\text{O}_2$  as an oxidizing agent.

This system was accomplished under waste-free conditions and aiming for the sulfides oxidation with high selectivity towards sulfoxides. Owing to its heterogeneity and efficiency, it was proved recoverable and reusable after 7 recycled tests. The system has coligated simplicity, high efficiency, mild reaction conditions and ease of work-up as shown in Fig. 1.

## 2. Experimental

### 2.1. 1-Materials and apparatus

Tetraethoxysilane (TEOS), (3-aminopropyl)triethoxysilane  $[(\text{EtO})_3\text{SiPrNH}_2, \text{APTS}]$ , 8-hydroxyquinoline (oxyquinoline),  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , sulfides, oleic acid and other reagents were purchased from Aldrich, Merck (Germany) and Fluka (Switzerland) without further purifications. Melting points were measured on an Electrothermal 9100 apparatus. IR spectra were recorded on a Shimadzu IR-460 spectrometer. SEM, Electron dispersive scanning (EDS) images and EDS-mapping of the samples were recorded with a Zeiss-DSM 960A microscope. TEM images were obtained by using a Zeiss EM 900 electron microscope. Homogeneous stirring was done by

ultrasonic (Ultrasonic Homogenizer-model APU500 Advanced Equipment Engineering Company-Adecco, Iran). The crystalline phases of the nanoparticles were recognized by XRD measurements (Philips-PW1800 diffractometer). The thermo-gravimetric TGA/DTA analyses of the selected samples were performed on a Sieko TG analyzer.

### 2.2. Synthesis of $\text{Fe}_3\text{O}_4@/\text{SiO}_2\text{-FeQ}_3$

Magnetite coated silica core-shell nanoparticle ( $\text{Fe}_3\text{O}_4@/\text{SiO}_2$ ) was synthesized according to our previous reported procedure that, oleic acid was used to achieve monodispersed nanoparticle [7,9a].  $\text{NH}_2$ -functionalized  $\text{Fe}_3\text{O}_4@/\text{SiO}_2$  was synthesized by adding 1.5 mL of  $\text{C}_9\text{H}_{23}\text{NO}_3\text{Si}$  (APTES) to a sonicated suspension (5 min) of  $\text{Fe}_3\text{O}_4@/\text{SiO}_2$  (1 g) in dry toluene at  $111^\circ\text{C}$  for 24 h. The obtained magnetite nanoparticle was then incorporated with tris(8-quinolinolato)iron. The tris(8-quinolinolato)iron ( $\text{FeQ}_3$ ) was synthesized by taking 8-hydroxyquinoline (3 mmol) and  $\text{FeCl}_3$  in 3:1 M ratio by stirring at  $65^\circ\text{C}$  in anhydrous tetrahydrofuran (THF) for 4 h under nitrogen atmosphere. After the temperature had cooled down, the solid was filtered and washed 3 times with cold THF. The obtained  $\text{FeQ}_3$  was dissolved in 50 mL  $\text{CHCl}_3$  followed by addition of 1.2 g of  $\text{Fe}_3\text{O}_4@/\text{SiO}_2/\text{NH}_2$  under vigorous stirring and then the suspension was refluxed for 24 h. Finally, the solid was collected using a simple magnet and washed with  $\text{MeOH}/\text{H}_2\text{O}$  (50:50 v/v) before drying at  $60^\circ\text{C}$  at vacuum. According to AAS analyzer of the composite before and after  $\text{FeQ}_3$  immobilization, the amount of loaded  $\text{Fe}^{3+}$  was 2.6 mmol per gram of composite.

### 2.3. Characterization techniques

The fourier transform infrared spectroscopy (FTIR) spectra were collected on a Bruker-Vector 22. Homogeneous stirring was conducted by ultrasonic treatment (Ultrasonic Homogenizer-model APU500 Advanced Equipment Engineering Company-Adecco, Iran). The morphology of prepared materials was determined by transmission electron microscopy (TEM) and scanning electron microscopy (SEM) on VEGA3 TESCAN. Additionally, the nanoparticle size of catalysts was estimated based on TEM results. Powder X-ray diffraction (XRD) spectra were recorded on Philips PW1800. The atomic composition of the samples was determined by the atomic absorption analysis (AAS) analyzer.

### 2.4. General procedure for the oxidation of sulfides

The oxidation of sulfides was conducted in a round-bottomed flask (25 mL) equipped with a magnetic stirrer. 1 mmol sulfide was added into the reaction flask in the presence of 3 mmol  $\text{H}_2\text{O}_2$  (30% w/w) and  $\text{Fe}_3\text{O}_4@/\text{SiO}_2\text{-FeQ}_3$  (5 mol% based on  $\text{FeQ}_3$ ) in 1 mL water and stirred at  $25^\circ\text{C}$  for an appropriate time as shown in Table 1. When the reaction finished, the products were extracted from the suspension solution with chloroform, following by evaporation to remove chloroform and obtain the final product sulfoxide.

## 3. Results and discussion

The  $\text{Fe}_3\text{O}_4@/\text{SiO}_2\text{-FeQ}_3$  was synthesized with the typical process as follow: desired amount of 8-hydroxyquinoline and ferric chloride with a molar ratio of 3:1 in THF were stirred at  $65^\circ\text{C}$  and solid  $\text{FeQ}_3$  was separated by simple funnel filtration.  $\text{FeQ}_3$  were then mixed with amine-grafted  $\text{Fe}_3\text{O}_4@/\text{SiO}_2$  in chloroform under vigorous stirring. The suspension was then refluxed. Finally, the solid magnetic nanocomposite was collected, washed and dried. The typical synthesis process was depicted in Scheme 1.

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