



Short Communication

Selective oxidation of sulfides to sulfoxides by a molybdate-based catalyst using 30% hydrogen peroxide



Ahmad Bayat, Mehdi Shakourian-Fard, Mohammad Mahmoodi Hashemi*

Department of Chemistry, Sharif University of Technology, PO Box 11465-9516, Tehran, Iran

ARTICLE INFO

Article history:

Received 23 January 2014

Received in revised form 18 March 2014

Accepted 19 March 2014

Available online 27 March 2014

Keywords:

Selective oxidation

Magnetic nanoparticle

Molybdate anion

Highly reusable catalyst

Heterogeneous

Hydrogen peroxide

ABSTRACT

An efficient method is reported for selective oxidation of various types of sulfides to sulfoxides and sulfones in good to high yields using 30% H₂O₂ in the presence of catalytic amounts of molybdate-based catalyst in acetonitrile as solvent at room temperature. The catalyst can be easily recovered and reused for seven reaction cycles without considerable loss of activity.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

The selective oxidation of sulfides to sulfoxides is an important transformation in organic chemistry [1,2], because sulfoxides are useful synthetic intermediates for the construction of various chemically and biologically active molecules [3–5] and also they play key role in activation of enzymes. Therefore, a large number of methods, procedures and oxidizing agents have been proposed for this type of transformation. Traditional synthesis is performed by using stoichiometric amounts of oxidants which are dangerous and can create a great quantity of waste [6–8]. Moreover, over-oxidation of the sulfoxides to sulfones is a common problem during the oxidation of sulfides [9]. From an economical and environmental viewpoint, an acceptable process involving the use of molecular oxygen or hydrogen peroxide as a primary oxidant in the presence of a catalyst is particularly attractive. Hydrogen peroxide produces water as by-product and controlled partial oxidation is easier to achieve than with molecular oxygen and air [10]. This feature has stimulated the development of useful procedures for H₂O₂ oxidation with various types of catalyst systems including transition metal complexes [11–14].

In recent years, various types of molybdenum based catalyst systems have been used in selective oxidation of sulfides to sulfoxides or sulfones. For example, Na₂MoO₄·2H₂O is widely used as catalyst for hydrodesulfurization from petroleum [15–18]. This catalyst needs homogeneous reaction condition for hydrodesulfurization process and so it is difficult to recover and reuse the catalyst. Use of recycled catalysts

is required for reducing the catalytic cost and the amount of used catalyst in the reactions. One way to attain this goal is to immobilize catalytic system onto a large surface area solid carrier.

In recent years, magnetic nanoparticles (MNPs) have attracted great interest as support materials in liquid phase reactions because they have unique physical properties and can be easily separated from reaction mixture by an external magnet [19,20]. Therefore, the recovery of catalysts is much easier than by filtration or centrifuge techniques. The Fe₃O₄ core tends to be oxidized or dissolved in acidic conditions during the treatment procedure. One of the materials can be used for coating of Fe₃O₄ is SiO₂. There are several advantages of using a silica shell as the stabilizer. Silica is chemically inert, and therefore does not affect the redox reaction at the core surface. The nonmagnetic shell can suppress the particle–particle magnetic bipolar interaction and prevent them from aggregating and agglomerating. Also, the silica shell acts as a stabilizer, limiting the effect of the outside environment on the core particles so that the Fe₃O₄ cores are not prone to oxidize as a response to the lowered magnetic performance γ-Fe₂O₃. In the present work, we report our results about Fe₃O₄@SiO₂ functionalized with ammonium molybdate as a recoverable heterogeneous catalyst for selective oxidation of sulfides to sulfoxides in the presence of 30% H₂O₂.

2. Experimental

2.1. Reagents and analysis

All chemicals and solvents were purchased from Sigma-Aldrich and used without further purification. Molybdenum content of the catalyst

* Corresponding author.

E-mail address: mhashemi@sharif.edu (M.M. Hashemi).

samples was determined by X-ray fluorescence (XRF ARL8410). A TGA-Q5 thermogravimetric analyzer was used to study the thermal properties of the compounds under an inert N₂ atmosphere (at 20 mL min⁻¹) and heating at a rate of 10 °C min⁻¹. X-ray diffraction (XRD) patterns of prepared catalyst were recorded with a APD 2000, using Cu K α radiation (50 kV, 150 mA) in the range $2\theta = 10\text{--}120^\circ$. The SEM analysis was done with a KYKY-EM3200 with maximum acceleration voltage of the primary electron between 20 and 25 kV. Energy-dispersive X-ray spectroscopy (EDX) on the catalyst *I* was performed by Sirius SD. FT-IR spectra were recorded with ABB Bomem MB100 Fourier Transform Analyzer.

2.2. Preparation of magnetic nanoparticles (MNPs)

The MNPs were prepared as reported [21]. Briefly, FeCl₃·6H₂O (4.8 g, 0.018 mol) and FeCl₂·4H₂O (1.8 g, 0.0089 mol) were added to 100 mL deionized water and vigorously stirred (700 rpm) under N₂ atmosphere until the salts dissolved completely. Then, 10 mL of 25% NH₄OH was added quickly into the reaction mixture in one portion, which MNP black precipitate was formed immediately. After continuously stirring by mechanical stirrer for 1 h, the precipitate was separated by external magnet and washed with the double distilled water (five times), then vacuum-dried at 50 °C for overnight.

2.3. Fe₃O₄ magnetic nanoparticles (MNPs) coated by silica (Fe₃O₄@SiO₂)

The prepared MNPs (1 g) were homogeneously dispersed in the mixture of ethanol (80 mL) and deionized water (20 mL), and the pH of solution was adjusted to 10 by adding aqueous ammonia. Tetraethoxysilane (TEOS, 4.2 mmol) was added to the solution and stirred at 50 °C for 6 h to obtain Fe₃O₄@SiO₂ MNPs. After washing with ethanol and water for several times, Fe₃O₄@SiO₂ MNPs were dried at 60 °C for overnight.

2.4. Preparation of Fe₃O₄@SiO₂ coated by 3-aminopropyltriethoxysilane (Fe₃O₄@SiO₂-APTES)

The functionalization of Fe₃O₄@SiO₂ (1 g) was performed with 3-aminopropyltriethoxysilane (4.4 mmol, 1 mL) in dry toluene for 24 h. The solid material was washed with toluene, methanol and ethanol and then dried overnight in an oven at 60 °C. This product will be referred as Fe₃O₄@SiO₂-APTES.

2.5. Preparation of catalyst *I*

The resulting Fe₃O₄@SiO₂-APTES (1 g) was reacted with excess of HCl (1 M, 5 mL) solution for 4 h and then separated by magnet, washed with water and ethanol, and then dried in vacuum desiccator at 60 °C for overnight to afford surface bound ammonium chloride. Finally, the prepared material (1 g) was ultrasonically dispersed in water (15 mL) and then Ag₂MoO₄ (0.15 g, 0.4 mmol) was added to the dispersed material in water at room temperature. The mixture was stirred for 1 h and then was magnetically separated and washed several times with water and ethanol and then dried to afford the catalyst *I* (Scheme 1).

2.6. General procedure for the oxidation of sulfides to sulfoxides

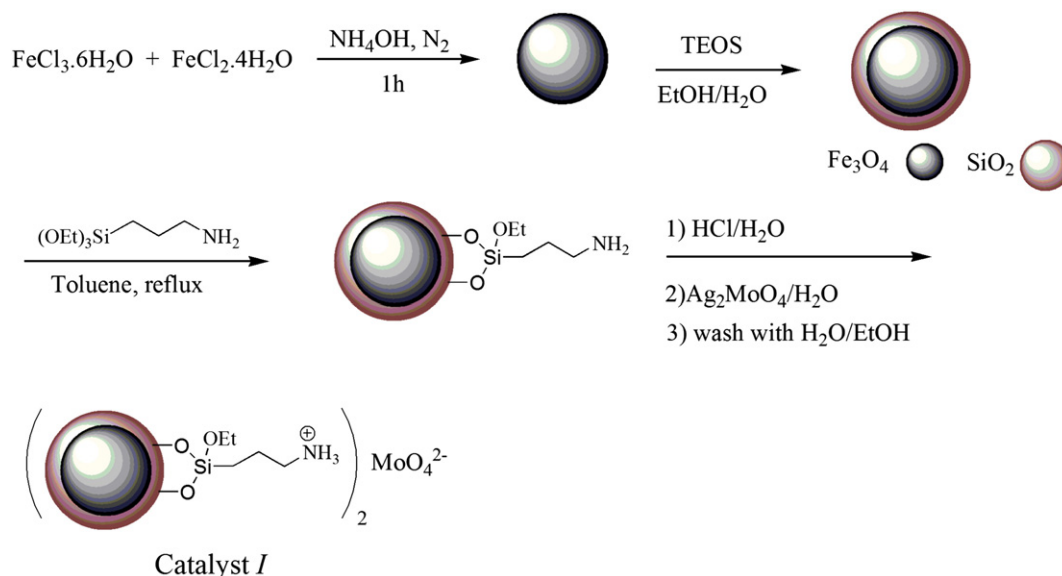
To a solution of sulfide (1 mmol) and 30% H₂O₂ (3 equivalent) in CH₃CN (10 mL), catalyst *I* (0.189 g, 3 mol% Mo) was added and the mixture was stirred at room temperature for the time specified. Completion of the reaction was indicated by Thin Layer Chromatography (TLC) (n-hexane/ethylacetate 3.5:1) and GC. After completion of the reaction, Et₂O was added and the catalyst was separated by a small magnet placed at the bottom of the flask. Finally, the excess of solvent was removed under reduced pressure to give the corresponding pure sulfoxide. Further purification was achieved by chromatography on silica gel with n-hexane/ethylacetate. All reaction products were identified by GC chromatogram, IR spectra and melting point as compared with authentic samples.

3. Results and discussion

3.1. Catalyst characterization

The IR spectrum of catalyst *I* shows peaks which are characteristic of MoO₄²⁻ anion, which clearly differs from that of Fe₃O₄@SiO₂-APTES. The absorption peaks in 884 and 939 cm⁻¹ (Fig. 1) were attributed to the Mo–O stretching frequency in MoO₄²⁻ species [22]. Also, peaks at 577 and 1101 cm⁻¹ were attributed to stretching frequency of Fe–O and Si–O, respectively [23].

The FT-IR spectrum of catalyst *I* also shows C–H stretching vibrations of APTES in around 2928 cm⁻¹ and 2850 cm⁻¹. Therefore, the presence of the organic groups on the surface of catalyst *I* was confirmed by FT-IR spectroscopy (Fig. 1).



Scheme 1. Preparation of catalyst *I*.

Download English Version:

<https://daneshyari.com/en/article/49669>

Download Persian Version:

<https://daneshyari.com/article/49669>

[Daneshyari.com](https://daneshyari.com)