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Magnetic nanoparticles containing Manganese salophen complex as an selective and recyclable catalyst for epoxidation of alkenes

Mozhgan Afshari,[1]* Maryam Gorjizadeh, [1]Simin Nazari[2]

[1]*Department of Chemistry,* Shoushtar *Branch, Islamic Azad University,*
Shoushtar, *Iran*

[2]*Department of Chemistry, Sousangerd Branch, Islamic Azad University,*
Sousangerd, Iran

Abstract

A magnetically recoverable catalyst consisting of Mn (III) salophen complex was prepared. The synthesized catalyst was characterized by X-ray powder diffraction (XRD), transmission electron microscopy (TEM), vibrating sample magnetometry (VSM), inductively coupled plasma atomic emission spectroscopy (ICP-AES) and Fourier transform infrared (FT-IR). The immobilized catalyst was shown to be an efficient heterogeneous catalyst for the epoxidation of various alkenes using hydrogen peroxide (H2O2) as oxidant. The catalyst could be easily and efficiently isolated from the final product solution by magnetic decantation and be reused for 5 consecutive reactions without showing any significant activity degradation.

Keywords: Cobalt ferrite, Epoxidation, Magnetic nanoparticles, Surface functionalization, Mn (III) salophen complex.

Introduction

Schiff base complexes have been widely described as excellent catalysts for oxygen transfer reactions, such as epoxidation. In spite of efficiency of these compounds in homogeneous catalysis systems [1-3], we would like to avoid the loss of the catalyst during the products isolation and simplify the step of the separation of the catalyst from the reaction mixture. One of the solutions of this problem is the immobilization of the catalyst on the solid support. Several insoluble solid materials either organic polymers or inorganic porous have been frequently applied as heterogeneous catalytic support for Schiff base complexes [4-7]. Inorganic matrices show some advantages over organic supports such as high thermal, chemical and mechanical stability. Covalent grafting of a homogeneous catalyst on an inorganic matrices insoluble porous solid support allows catalyst recovery by filtration. [8-11] However, due to the diffusion of substrates and products through the pores of the support materials, a substantial decrease in reaction rate is frequently observed compared to the homogeneous system [12-15]. Thus, it is worthwhile to consider new materials as support for these homogenous catalysts.

Magnetite nanoparticles (MNPs), have attracted increasing interest because of their unique physical properties including the high surface area, magnetism, low toxicity and their potential applications in various fields. Among various MNPs, Cobalt ferrite ($CoFe_2O_4$) nanoparticles are easily prepared and surface functionalized and they can be recycled from the solution by external magnetic field. So, the catalyst supported on $CoFe_2O_4$ nanoparticles can be easily separated from the reaction system and reused [16, 17]. However, cobalt ferrite tends to aggregate in liquid media which leads to the reduction of its surface area. It has been demonstrated that the formation of a passive coating of inert materials such as polymers, carbons, and silica on the surfaces of iron oxide nanoparticles could help prevent their aggregation in liquid and improve their chemical stability [18, 19]. Among them, silica is the most prominent material for coating because it is chemically inert and the surface is often terminated using a silanol group that can react with various coupling agents to covalently attach specific ligands to the surfaces of these magnetic nanoparticles [20].

In this study, we wish to present a novel method for the immobilization of a Mn(III) salophen complex on imidazole functionalized silica coated cobalt ferrite nanoparticles

(Mn(salophen)-imid-Si@Si-MNPs). The catalytic activity and reusability of this composite in the alkene epoxidation was investigated.

Experimental

General

All chemicals were purchased from Sigma-Aldrich or Merck and used as received. Cobalt ferrite MNPs were prepared using the procedure reported by Maaz et al. [21]. Silica coated $CoFe_2O_4$ nanoparticles (Si-MNPs) were made by using sol-gel method [22]. imidazole functionalized silica coated magnetic nanoparticles (imid -Si@Si-MNPs)were achieved by using the previously reported methods [16].X-ray diffraction (XRD) patterns were recorded with a Philips X-ray diffractometer (Model PW1840). FT-IR spectra were obtained using BOMEM MB-Series 1998 FT-IR spectrometer. Magnetic properties of all nanoparticles were measured with a vibrating sample magnetometer (VSM, Meghnatis Daghigh Kavir Company, Iran) at room temperature. NMR spectra were recorded in $CDCl_3$ on a Bruker Advanced DPX 400 MHz spectrometer.

Synthesis of Mn(salophen)-imid-Si@Si-MNPs

A schematic representation for the synthesis of Mn (III) salophen complex anchored on imidazole functionalized silica coated cobalt ferrite nanoparticles is shown in Scheme 1.

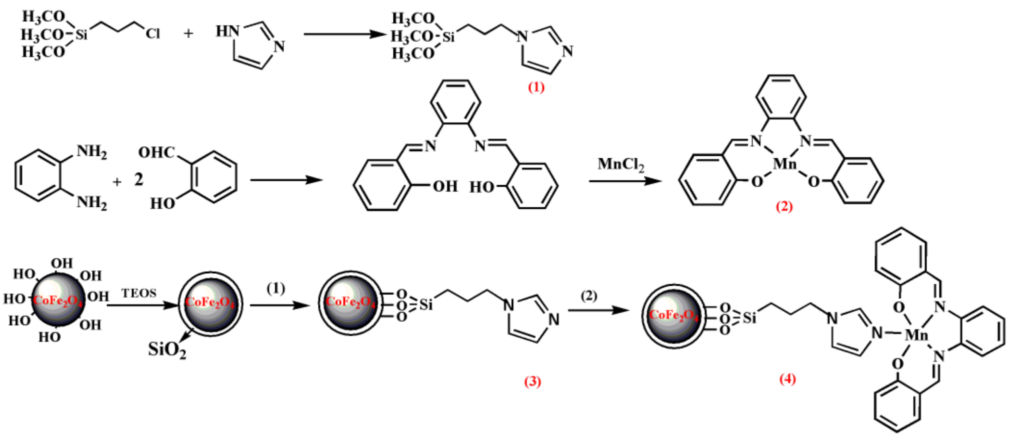


Fig 1. Schematic representation of the formation of Mn (salophen)-imid-Si@ Si-MNPs catalyst

Mn(III) complex (2) have been synthesized by the reaction of $MnCl_2$ in ethanolic solution with the Schiff base obtained by the condensation of 1, 2 -phenylenediamine (2 mmol, 0.216 g) and salicylaldehyde (4 mmol, 0.43 ml). Then Mn(III) salophen complex was dissolved to 1, 2 dichloroethane and 0.75 g of imid -Si@Si-MNPs (3) were dispersed to it and the whole mixture was refluxed for 2 days. After that, the expected final product, Mn(salophen)-imid-Si@Si-MNPs (4), was separated by magnetic decantation and washed with 1,2 dichloroethane, methanol and chloroform until the washings were colorless and left to dry in a desiccator.

Catalytic studies

In a typical run, a 25 mL flask was charged with catalyst (0.05 g), acetonitrile (5 mL), alkene (1 mmol), and H_2O_2 (2 mmol). This mixture was heated in an oil bath at 70 ˚C and the progress of the reaction was monitored by TLC. At the end of the reaction, the catalyst was simply collected using a magnetic bar and the reaction mixture was then transferred out of the flask. The decanted solution was purified on a silica-gel plate or a silica-gel column to obtain the pure product. The structures of the products were established on the basis of their spectral analysis (IR, ^{1}H NMR)

Results and discussion

Characterization of Mn (salophen)-imid-Si@Si-MNPs

The catalyst was synthesized by a procedure that shown in Scheme 1, and characterized by various techniques.

The FT-IR spectrum of heterogenised manganese salophen shows the expected principal bands for the free schiff base ligand. The C-H deformation band is visible at 1458 cm^{-1} and the band at 1621 cm^{-1} was assigned to –C=N stretching vibration of the immine group of the ligand that were not in the imidazole functionalized silica coated cobalt ferrite. The other bands at 581cm^{-1}, 819 cm^{-1} and 1100 cm^{-1} ascribed to Fe-O stretching absorption, asymmetrical and symmetrical vibrations of the Si-O-Si bond respectively (see Fig. 1) [23].

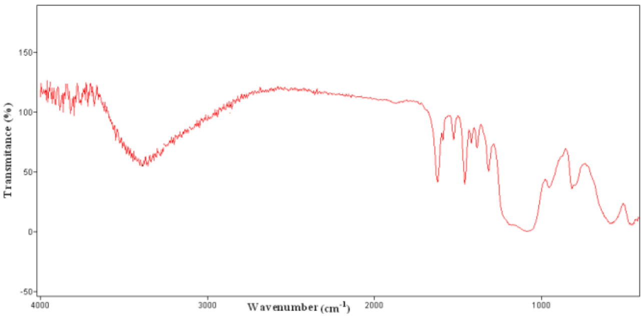


Fig.2. FT-IR spectrum Mn (salophen)-imid-Si @ Si-MNPs

XRD measurements of Mn(salophen)-imid-Si@Si-MNPs exhibit diffraction peaks corresponding to the cubic reverse spinel structure of $CoFe_2O_4$ (JCPDS PDF #221086), while the silica layered systems show an additional broad band at 2θ=20–30 (Fig. 2b and

2c) for the amorphous silica. The average crystallite size of the Mn(salophen)-imid-Si @ Si-MNPs was calculated to be ~29 nm by Debye-Scherer formula for the (311) reflection.

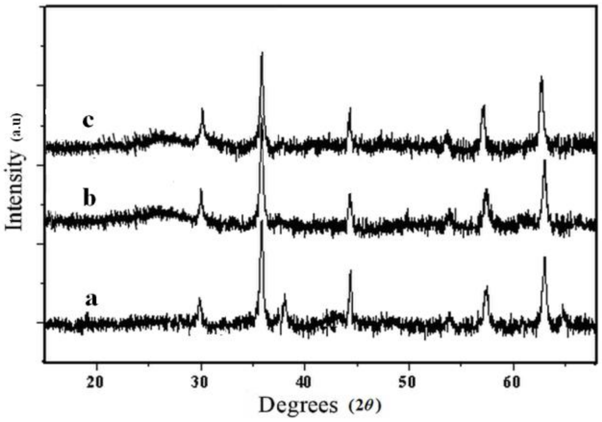


Fig. 2. XRD pattern of (a) MNPs, (b) Si-MNPs and (c) Mn (salophen)-imid-Si@Si-MNPs

The TEM micrograph of the nanoparticles is shown in Fig.3. TEM image indicated that the most of the prepared nanoparticles are spherical shaped and have size less than 30 nm which show a close agreement with the values calculated by XRD analysis. Interestingly, the magnetic core is visible as a dark spot inside the bright spherical SiO_2 thin shell in the TEM image of Mn(salophen)-imid-Si@Si-MNPs sample.

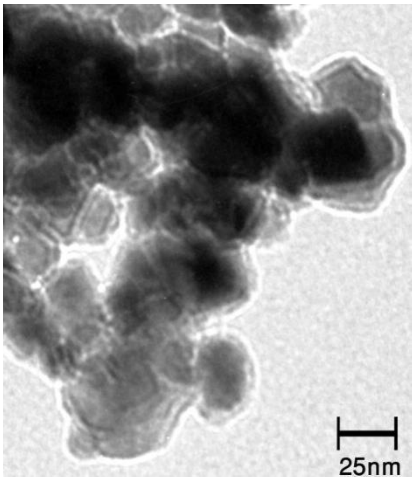


Fig. 3. TEM image of (salophen)-imid-Si @ Si-MNPs

Magnetic measurements of the samples were carried out at room temperature using a vibrating sample magnetometer (VSM). The saturation magnetization (M_s), remanence magnetization (M_r) and coercivity (H_c) values of MNPs, silica coated cobalt ferrite (Si-MNPs) and Mn(salophen)-imid-Si@Si-MNPs are given in Table 1. As clearly shown, the saturation magnetization of coated sample is slightly less than that of uncoated sample, whereas the coercivity of coated sample is significantly larger than that of uncoated one. This is probably due to the formation of non-crystalline silica on the surface of $CoFe_2O_4$ nanoparticle as well as the restriction of domain wall motion by the magnetic dilution effect of inert silica.

Table1. Magnetic property of the as-fabricated nanoparticles

compound	**H_c (Oe)**	**M_r (emu/g)**	**M_s (emu/g)**
MNPs	796.1	24.63	59.49
Si-MNPs	861.05	16.40	38.93
Mn(salophen)- imid -Si@Si-MNPs	900	5.19	17.38

The manganese content of the catalyst, as determined by ICP-AES, was 0.16 mmol/g. This is the proof for the fact that Mn salophen complex was immobilized onto the imidazole functionalized silica coated $CoFe_2O_4$.

Eepoxidation of alkenes

The performance of heterogenised manganese salophen nanocatalysts were tasted in epoxidation of alkenes. To find the optimized conditions, styrene was used as a model. The obtained optimum conditions were: catalyst 0.05 g, H_2O_2 and substrate in a molar ratio of 2:1, respectively and the reaction temperature was set at 70 ˚C. In this work, acetonitrile was selected among different solvents (acetone, chloroform, methanol and 1, 2-dichloroethane) due to high yield and good dispersibility of the catalyst in this media. Replacing H_2O_2 by*t*-BuOOH, $NaIO_4$ or H_2O_2/ Urea (UHP) cause to decrease the obtained total epoxidation yields, So H_2O_2 was selected as a best source of oxygen for this system

We have also examined bare MNPs, Si-MNPs, and imid-Si @ Si-MNPs for the epoxidation of styrene. According to the results that summarized in table 2, entries 8-11, the catalytic activity of the synthesized catalyst must be attributed to the presence of Mn salophen in this composite.

The obtained preliminary results for the epoxidation of styrene were encouraging and to extend the scope of this heterogeneous catalytic system, the epoxidation of further olefins was carried out under the optimized conditions (scheme 2).

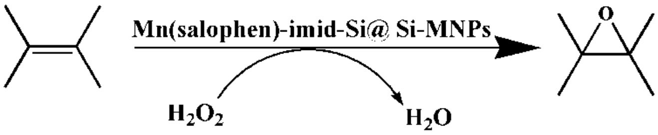
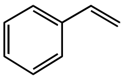
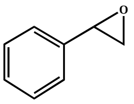
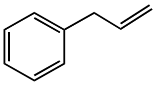
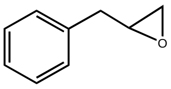
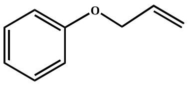
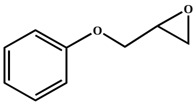
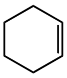
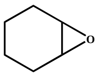
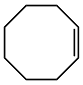
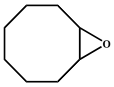
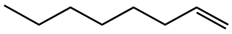
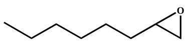
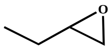
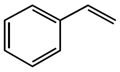
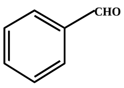
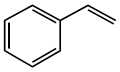
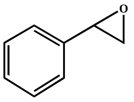
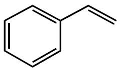
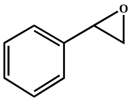
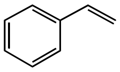
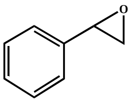


fig 3. Oxidation of alekenes using Mn (salophen)-imid-Si@ Si-MNPs catalyst

Table 2. Oxidation of alkenes by H_2O_2 using Mn (salophen)-imid-Si @ Si-MNPs catalyst [a]

Entry	Alkenes	Product	Yield % [b]
1[c]			88
2[c]			75
3[c]			90
4[c]			86
5[c]			90
6[c]			68
7[c]			60
8[d]			36
9[e]			-
10[f]			-
11[g]			83

[a] Reaction conditions: alkene(1mmol), H_2O_2(2 mmol), catalyst (0.05 g), acetonitrile (5 ml), T=70°C, time= 5 h

[b]Isolated yields

[c]catalyst: Mn(salophen) -imid-Si @ Si-MNPs, [d]catalyst: MNPs, [e]catalyst: Si-MNPs, [f]catalyst:

Si-imid@Si-MNPs
[g] Fifth recycled catalyst

As shown in Table 2, the newly designed hybrid catalyst can epoxidize cyclohexene, cyclooctene, 1-octene, 1-butene, allylbenzene and allyl phenyl ether efficiently and selectively in the presence of H_2O_2.

To evaluate the stability and level of reusability of the catalyst, we conducted experiments of epoxidiation of styrene using the recycled Mn(salophen)-imid-Si@Si-MNPs catalyst. After the completion of the first reaction, the catalyst was concentrated on the sidewall of the reaction vessel using an external magnet and the solution was removed by decantation and the left used catalyst was washed with CH_3CN. A new reaction was then conducted with fresh reactants under similar conditions. It was found that the developed catalyst could be used at least five times without any change in reactivity (see table 2, entry 11). ICP-AES analysis has shown that slight leaching of the catalyst from support occurred after the fifth run. Moreover, the FT-IR spectrum of the recovered catalyst showed no change after using it for five times.

It should be mentioned that our work in terms of both economic and environmental aspects showed much superiority for the epoxidation of alkenes compared to the similar reported catalysts [24]. The main advantages of this catalyst are that it can be easily recovered by means of an external magnet for several times and use of H_2O_2 as a green oxidant.

Conclusions

In conclusion, we have developed the novel supported manganese salophen complex using surface-modified $CoFe_2O_4$ magnetic. The synthesized catalyst was confirmed by XRD, FT-IR, TGA, TEM, ICP-AES, and VSM techniques. This catalyst has showed high catalytic activity in epoxididation some alkenes in the presence of H_2O_2 as green oxidant. It is noteworthy to highlight that the catalyst is environmentally friendly since could be magnetically recovered by an external magnetic field and reused 5 times without a significant loss of activity. These results indicated a good stability of this nano composite catalyst towards the reaction medium.

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