

RESEARCH PAPER

Porphyrin Grafted Magnetic Nanoparticles as an Eco-friendly, Cost-effective Catalyst for Green Oxidation of Sulfides by Meta-Chloro Peroxy Benzoic Acid

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ABSTRACT

In this paper, meso-Tetraphenylporphyrin iron(III) chloride complex, Fe(TPP)Cl, supported on magnetic nanoparticles (PCMNPs) was synthesized and characterized by HRTEM, SEM, TGA, and FT-IR and VSM. The value of saturation magnetic moments of MNPs and PCMNPs are 68.5 and 60.3 emu/g, respectively. The SEM and HRTEM image were shown the uniformity and spherical-like morphology of nanoparticles with an average diameter from ~55 to 65 and 15 ± 5 nm, respectively. The synthesized catalyst was successfully applied as a magnetically recoverable heterogeneous catalyst in oxidation of sulfides to related sulfoxides in water/ethanol as green solvents by meta-Chloro peroxy benzoic acid (m-CPBA). The selectivity and chemoselectivity of this clean system were attracted so much attention. No surfactants, additives, toxic reagents or organic solvents and by-product were involved. The maximum conversion and selectivity were attained at around neutral pH, which is advantageous for full-scale application. Ten successive cycles of catalyst was shown that the catalyst was most strongly anchored to the magnetic nanoparticles.

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INTRODUCTION

The controlled and selective oxidation of sulfides to sulfoxide is one of the most important technologies for the conversion of petroleum products to valuable commodity chemicals [1-3]. Because of overoxidation of sulfides to sulfones, control of the reaction conditions such as the control of time, temperature and the relative amount of oxidants, plays an important role in avoiding the formation of oxidation side products, but this is often hard to achieve and therefore there is still considerable interest in the development of selective oxidants for this transformation [4-8]. For industrial-scale oxidation reactions, transition-metal complexes are often used as catalysts [9-11].

In the past two decades, the catalysis of sulfides by metalloporphyrins has received considerable attention [12]. Despite the high catalytic activity of these heterogeneous porphyrin catalysts, their separation techniques were energy and time consuming and caused loss of the catalyst [13]. Immobilization of porphyrins complexes on magnetic nanoparticles (MNPs) offers a solution to the problems due to the ease of catalyst separation by applying an appropriate magnetic field [14]. To benefit the valuable applications of MNPs and unique properties of porphyrins as ligands and in continues of our recent works on the development of heterogeneous catalysts, herein, we report the green and selective oxidation

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of sulfides to sulfoxides. In this work, FeTPPCL complex was immobilized on $\gamma\text{-Fe}_2\text{O}_3$ and used it as recoverable catalyst for oxidation of sulfides by m-CPBA oxidant in water. Very recently, we used immobilized different porphyrins on Fe_3O_4 and tetrabutylammonium peroxomonosulfate (TP) oxidant in the oxidation of sulfides [15-17]. While, the black Fe_3O_4 nanoparticles can be easily oxidized into yellow Fe_2O_3 when they are exposed to the air directly and their magnetism decreases significantly and TP oxidant, which was commercially unavailable, prepared from expensive reagents, very short-term shelf-stability (3 days). Therefore, $\gamma\text{-Fe}_2\text{O}_3$ Magnetic nanoparticles and m-CPBA was used as green chemistry and economic point of view.

MATERIALS AND METHODS

Purity determinations of the products were accomplished by GC on a YL instrument by using a 60m, 0.32mm ID, and 0.5 micrometer coating capillary column. Chemicals were purchased from Merck Chemical Company. NMR spectra were recorded in ppm in CDCl_3 on a Bruker Avance DPX-400 instrument using TMS as internal standard. HRTEM microscope (Philips CM30) was performed for HRTEM analysis. Hitachi Japan, model s4160 scanning electron microscopy (SEM) at accelerating voltage of 15 kV was used for the morphology of the products. A JASCO FT-IR 460 plus spectrophotometer were recorded the FT-IR spectra. A Shimadzu thermo gravimetric analyzer (TG-50) is the model of thermo gravimetric analysis (TGA). Room temperature magnetization isotherm was obtained using VSM, vibrating sample magnetometer, (LakeShore 7400).

Synthesis of $\gamma\text{-Fe}_2\text{O}_3$ (MNPs)

$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (3.98 g) and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (6.5 g) were dissolved in deionized water (70 mL) under Ar atmosphere at room temperature [18-19]. To reach the reaction pH to 11, an ammonium hydroxide solution (0.6 M, 400 mL) was added drop wise (drop rate = 1 mL min^{-1}) to the stirring mixture at room temperature. The resulting black dispersion was stirred for 1 h at room temperature, and heated to reflux for 1 h to yield a brown dispersion. The magnetic nanoparticles were subsequently separated by a magnetic bar and washed with deionized water/ethanol for three times. The synthesized sample was heated

at 2°C min^{-1} up to 250°C and then kept in the furnace for 3 h to give brown powder.

Synthesis of chloro-functionalized $\gamma\text{-Fe}_2\text{O}_3$ (CMNPs)

The prepared MNPs (3.6g) was sonicated in dry toluene (50ml) for 30 min. 3-chloropropyltrimethoxy silan (4ml) and triethylamine as a catalyst (0.4 ml) were added to the dispersed $\gamma\text{-Fe}_2\text{O}_3$ in toluene and then heated to 105°C for 48h. The resulting CMNPs was separated by an external magnet and washed with toluene /ethanol /water mixture for three times and dried under vacuum [20].

Synthesis of porphyrin immobilized on CMNPs (PCMNPs)

1.25 g of dry CMNPs powder was sonicated in 75 ml ethanol for 20 min. 0.10g Fe(TPP)Cl was added under mechanical stirring and the mixture was heated to 85°C for 7h. The unsupported porphyrins were removed through soxlet extraction with chloroform.

General procedure for oxidation of sulfides

To a mixture of 100 mg of thioanisole (1 mmol) and 0.0083 g of PCMNPs (0.01 mmol) in 2 ml bidistilled water/ethanol (1/2) was added 0.03 g (0.15 mmol) of m-CPBA. The reaction mixture was stirred under air at 10°C for 20 min that GC and TLC monitored progress of reactions. After completion of the reaction, ethanol was removed by rotary and then the mixture was washed with ethyl acetate (6 ml), and the organic phase was separated and evaporated. If necessary, further purification was performed by silica chromatography eluted with n-hexane/ethyl acetate (10:1).

Recycling procedure

After completion of the oxidation of methyl phenyl sulfide, the product was isolated by ethyl acetate (6 ml) and the reaction mixture was separated by external magnet and the solid catalyst was separated, washed with ethyl acetate (3 ml), dried and reused for the similar reaction.

RESULTS AND DISCUSSION

Catalyst synthesis and characterization

At first, by using chemical coprecipitation technique of ferric and ferrous ions in alkali solution with minor modifications, MNPs were synthesized [33,34]. The magnetic nanoparticles were then allowed to react with an appropriate concentration of 3-chloropropyltrimethoxysilane

to give CMNPs. The obtained CMNPs were reacted with Fe(TPP)Cl to obtain PCMNPs.

The size and structure of PCMNPs were evaluated using scanning electron microscopy (SEM). The SEM and HRTEM image (Fig. 1 and 2) showed uniformity and spherical-like morphology of nanoparticles with an average diameter from ~55 to 65 and 15 ± 5 nm, respectively.

The magnetization curves of PCMNPs and MNPs were measured at room temperature using a vibrating sample magnetometer (VSM). No reduced remanence and coercivity were detected, indicating both unmodified and PCMNPs are superparamagnetic (Fig. 3). The value of saturation magnetic moments of MNPs and PCMNPs are 68.5 and 60.3 emu/g, respectively.

The band at around $450-610 \text{ cm}^{-1}$ was

assigned to the stretching vibrations of Fe-O bond in these compounds (Fig. 4A) [21]. The anchoring of aminopropyl groups on MNPs was confirmed by stretching vibrations appeared at about $2800-3000$ and 3446 cm^{-1} (Fig. 4B) [22]. Other bands derived from deformation and stretching vibrations of the porphyrin complex covalently anchored to magnetic support via chloro functionality (Fig. 4C).

The thermo gravimetric analysis (TGA) of PCMNPs was used to determine the thermal stability and content of organic functional groups on the surface of magnetic nanoparticles (Fig. 5). The small amount of weight loss around 100°C was attributed to the desorption of adsorbed water. Another mass loss appeared at around 160°C and the organic parts decomposed completely at 500°C . According to the TGA profile, the amount of organic components supported on magnetic is estimated to be 0.12 mmol g^{-1} .

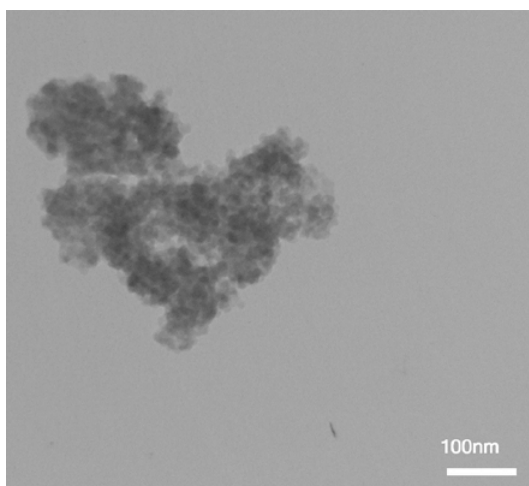


Fig. 1. HRTEM of PCMNPs

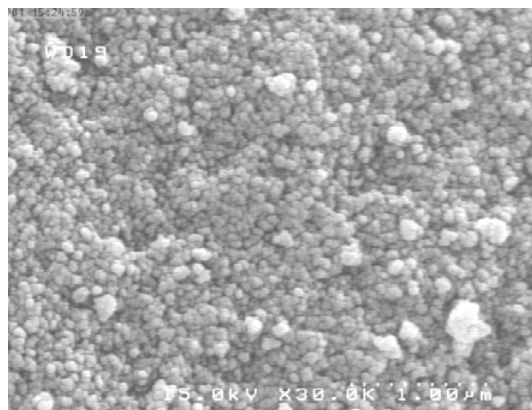


Fig. 2. The SEM image of PCMNPs

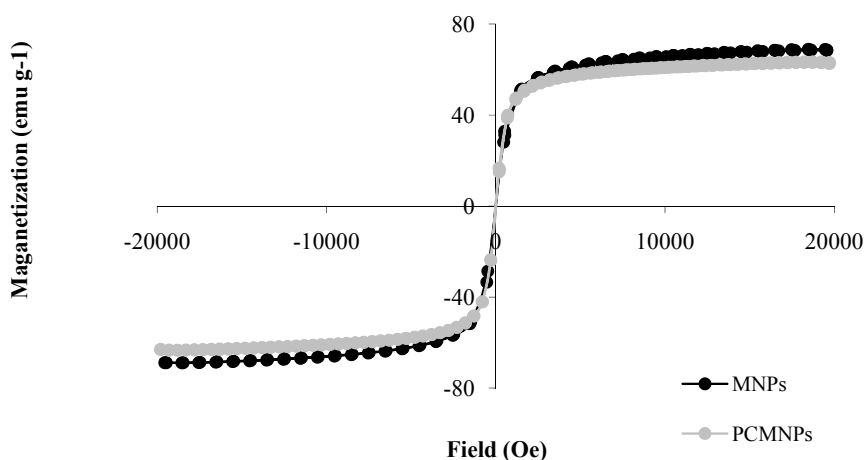


Fig. 3. Magnetization curves of MNPs and PCMNPs

Aqueous oxidation of sulfides to sulfoxides

Preliminary experiments were addressed to oxidation of thioanisole (0.1 mmol) with m-CPBA (0.15 mmol) in neat water under air that a mixture of the related sulfoxide (35%) and sulfone (5%) after 10 min according to GC analysis at room temperature. For easy recovery of catalyst, Fe(TPP) Cl was immobilized on CMNPs and evaluate its catalytic potential in heterogeneous aqueous oxidation of sulfides. When a few mounts of PCMNPs (0.001mmol) were added to the reaction mixture the conversion rate enhanced significantly and a mixture of the related sulfoxide (48%) and sulfone (52%) after 20 min according to GC analysis at 25°C. The effects of various temperatures on selectivity of product were shown that by decreasing the temperature, the selectivity and

conversion of sulfide to sulfoxide was increased. In 10°C, the methyl phenyl sulfoxide was obtained as sol product (Table 1).

The effect of different solvent was considered. The examination of different solvents such as dichloromethane(9%), chloroform(11%), toluene(1%), ethylacetate(1%), hexane(2%), ethanol (55%) and water and mixture water and ethanol showed that the mixture water/ethanol promoted the yield of sulfoxide product. The possibility to use water and ethanol as green reaction mediums is a remarkable advantage. The investigation different ratios of water/ethanol were shown very well that in ½ ratio, the complete conversion of thioanisole was obtained with the formation of the corresponding sulfoxide as the sole product (Table 2).

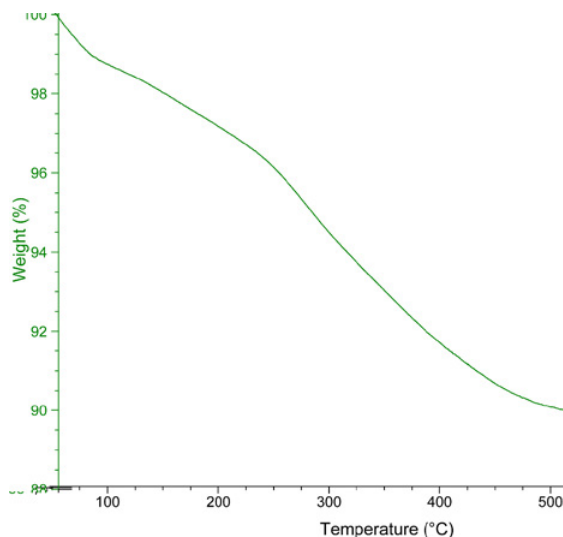


Fig. 5. The TGA of PCMNPs

Table 1. The effect of temperature on the oxidation of methyl phenyl sulfide on PCMNPs by m-CPBA^a

Entry	T/°C	Conversion%	Sulfide selectivity%
1	25	96	100
2	15	100	57
3	10	100	48

^a The reactions were run under air in water/ethanol after 20 min with a molar ratio of 100:150:1 for sulfide/m-CPBA/catalyst

Table 2. The effect of ratio of water/ethanol as solvent for oxidation of methyl phenyl sulfide catalyzed by PCMNPs and by using m-CPBA^a

Entry	H ₂ O/ethanol	Conversion%	Sulfoxide Selectivity%
1	1:0	100	60
2	0:1	55	45
3	1:1	95	63
4	2:1	90	35
5	1:2	96	100

^a The reactions were run at 10°C after 20 min with a molar ratio of 100:1500:1 for sulfide/m-CPBA/catalyst

The amount of m-CPBA oxidant could effect directly on yield of reaction. The desired reaction rate and conversion were achieved by using 0.15 mmol of oxidant. To evaluate the oxidizing potential of various oxidants, methyl phenyl sulfide was subjected to the oxidation protocol using O₂, H₂O₂, t-butyl hydroperoxide (tBuOOH), NaIO₄, and UHP. Under the catalytic influence of CMNPs, Only trace amounts of the oxidation products were observed (Fig. 6). When the reaction was carried out by using m-CPBA, full conversion of sulfide was observed at the same time.

It seems that good dispersy of PCMNPs in aqueous solution seems to be the most important factor to affect the efficiency. Two experimental were performed to confirm the effect of dispersy within 20 min and at 10°C. In the first

experimental, with magnetic stirring 60% yield of methyl phenyl sulfoxide was obtained and in the second experimental, catalyst was sonicated for 10 min and then oxidant was added and stirred magnetically, which led to 96% yield of methyl phenyl sulfoxide. Infact, by ultrasonic irradiation the mobility of nanoparticles in water is high and the whole volume can be quickly scanned with small amounts of nanomaterials due to their small size of PCMNPs.

As explored in previous studies the addition of additives (10 times vs. catalyst) within 20 min such as imidazole (52%) and pyridine (15%), sodium dodecyl sulfate at SDS condition (40%), and also performing the reaction in inert atmosphere (Ar, 72 and 83% after 20 and 40 min) did not improve the yield of sulfoxide product.

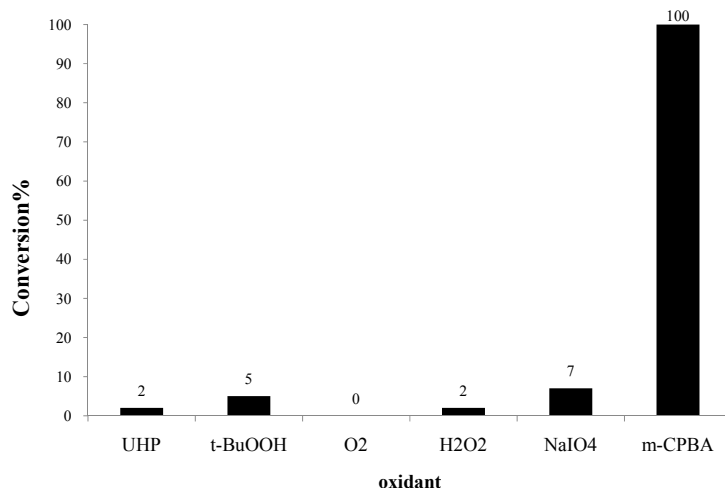


Fig. 6. The effect of different oxidant on the oxidation methyl phenyl sulfide catalyzed by PCMNPs and using by m-CPBA

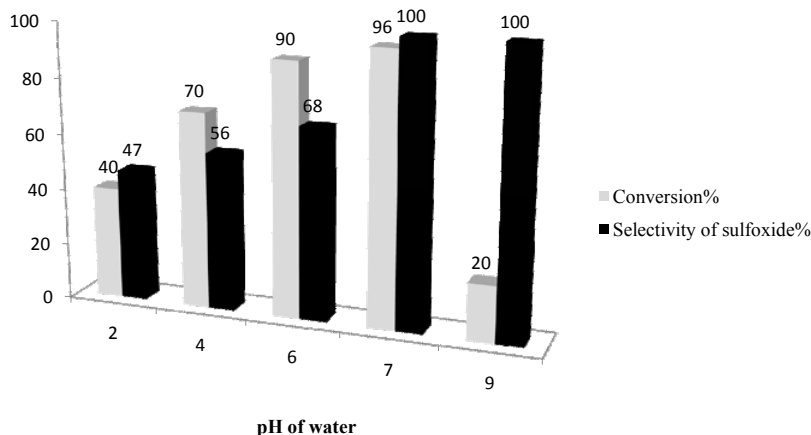
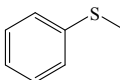
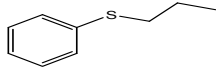
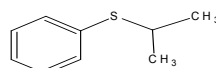
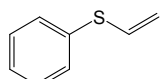
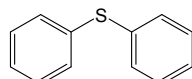
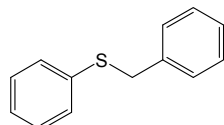
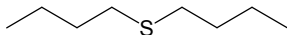
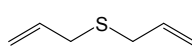


Fig. 7. The effect of pH of water on the oxidation of thioanisole catalyzed by PCMNPs and using m-CPBA as an oxidant.

Table 3. The oxidation of various sulfides catalyzed by PCMNPs and by using m-CPBA as an oxidant^a

Entry	Sulfide	sulfoxide Isolated Yield%	Sulfoxide Selectivity%
1		96	100
2		83	85
3		90	95
4		93	100
5		78	80
6		90	97
7		96	100
8		92	100

^aThe reactions were run under air at 10°C after 20 min with a molar ratio of 100:150:1 for sulfide/m-CPBA/catalyst

Next, different standard buffered solutions were used to consider the pH of water on the yield of oxidation of methyl phenyl sulfoxide (Fig. 7). The maximum conversion and selectivity were attained at around neutral pH, which is advantageous for full-scale application. This is because any necessity to changing the pH level of the water to optimum oxidation is eliminated making the process more cost effective compared to other oxidation systems that require an acidic or basic optimum pH level.

Finally, different sulfides were subjected to the reaction systems in the presence of PCMNPs and the results are listed in Table 3. All substrates could be smoothly converted to sulfoxides with high/excellent yields and excellent selectivities were obtained under mild conditions (Table 3). A salient feature of the present oxidation system

is its excellent selectivity of sulfoxide products and overoxidation was not happened. Sulfoxides and sulfones could be nearly stoichiometrically produced and very small percentages of byproduct (the related sulfone) were detected, which makes title methods good alternatives for sulfoxide. Encouraged by promising results obtained in the oxidation of sulfides, the chemoselectivity of this clean catalytic system was evaluated. Sulfides having a benzylic C-H bond (entry 6), and carbon-carbon double bond (entries 4 and 8) were cleanly transformed into the corresponding sulfoxides in excellent yield without formation of any epoxide, alcohol and carbonyl by-products.

Recovery of catalyst

The magnetic property of PCMNPs facilitates efficient recovery of the catalyst from the

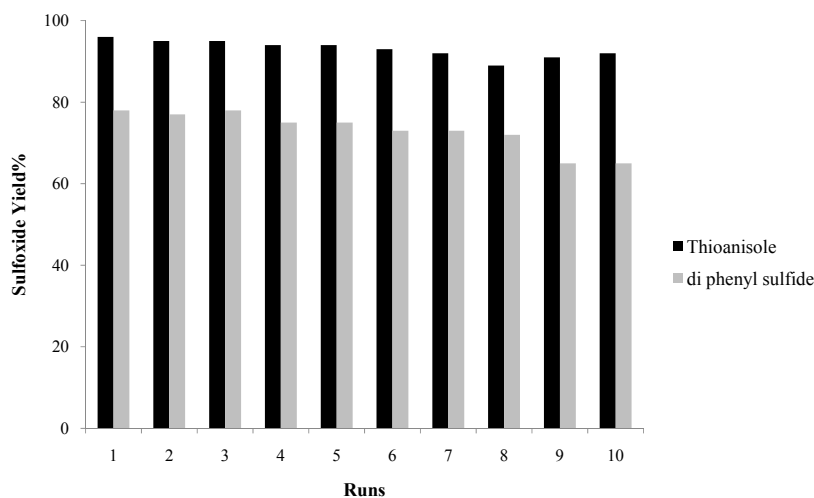


Fig. 8. Recycling of the catalytic system for oxidation of thioanisole and di phenylsulfide in water/ ethanol

reaction mixture during workup procedure. After performing the oxidation of methyl phenyl sulfide with *m*-CPBA under the present conditions, EtOAc was added to the reaction mixture. The catalyst was separated by an external magnet from the reaction mixture, washed with EtOAc as a safe solvent, dried 30 min at 100°C and reused for a consecutive run under the same reaction conditions. The average isolated yield of the product for oxidation of methyl phenyl sulfide and di phenyl sulfide for ten consecutive runs was 95 and 84%, which clearly demonstrates the practical reusability of this catalyst (Fig. 8). Therefore, title methodology is cost effective and environmentally benign because of using water as reaction media, reusing of catalyst and easy isolation of hydrophobic organic products and also lack of need to surfactants, nitrogen donors, toxic reagents or organic solvents. These advantages for this high yielding sulfoxides method offered ready scalability. The use of a semi scale-up procedure (5.00 mmol) for oxidation of methyl phenyl sulfoxide at the present of PCMNPs led to isolation of the thianisole in 91% yield.

CONCLUSION

In summary, Fe(TPP)Cl complex supported on γ -Fe₂O₃ magnetic nanoparticles as a new magnetically recyclable heterogenous catalyst for selective oxidation of sulfides to sulfoxides in water by *m*-CPBA. The catalyst was easily isolated from the reactions mixture by an external magnet and reused ten times without significant degradation in its activity. No surfactants, additives, toxic

reagents or solvents and by-product were involved and no laborious purifications were necessary.

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interests regarding the publication of this paper.

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