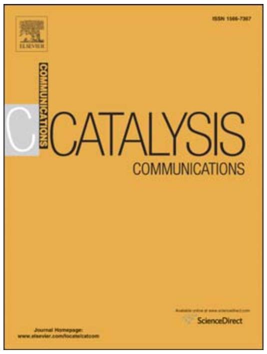


DABCO tribromide immobilized on magnetic nanoparticle as a recyclable catalyst for the chemoselective oxidation of sulfide using H_2O_2 under metal- and solvent-free conditions

Amin Rostami, Yahya Navasi, Darush Moradi, Arash Ghorbani-Choghamarani

PII: S1566-7367(13)00334-8
DOI: doi: 10.1016/j.catcom.2013.08.025
Reference: CATCOM 3629

To appear in: *Catalysis Communications*

Received date: 12 June 2013
Revised date: 31 July 2013
Accepted date: 26 August 2013

Please cite this article as: Amin Rostami, Yahya Navasi, Darush Moradi, Arash Ghorbani-Choghamarani, DABCO tribromide immobilized on magnetic nanoparticle as a recyclable catalyst for the chemoselective oxidation of sulfide using H_2O_2 under metal- and solvent-free conditions, *Catalysis Communications* (2013), doi: 10.1016/j.catcom.2013.08.025

DABCO tribromide immobilized on magnetic nanoparticle as a recyclable catalyst for the chemoselective oxidation of sulfide using H_2O_2 under metal- and solvent-free conditions

Amin Rostami*[,a,b], Yahya Navasi[a], Darush Moradi[a], Arash Ghorbani-Choghamarani[c]

[a]*Department of Chemistry, Faculty of Science, University of Kurdistan, Zip Code 66177-15175, Sanandaj, Iran.*

[b]*Research Centre for Medicinal Plant Breeding and Improvement, University of Kurdistan, Sanandaj, Iran.*

[c]*Department of Chemistry, Faculty of Science, Ilam University, Ilam, Iran.*

(E-mail: a_rostami372@yahoo.com, Tel: +989183730910; Fax: +988716624004)

ABSTRACT

Magnetic nanoparticle-supported the 1,4-diazabicyclo[2.2.2] octane tribromide (MNPs-DABCO tribromide) as a bromine source was readily prepared and characterized by X-ray diffraction (XRD), thermogravimetric analysis (TGA), fourier transform infrared spectroscopy (FT-IR), Energy dispersive X-ray spectroscopy (EDX), the scanning electron microscopy (SEM), and vibrating sample magnetometer (VSM) techniques. The catalytic activity of MNPs-DABCO tribromide was investigated in the chemoselective oxidation of sulfides to sulfoxides using 30% H_2O_2 as an oxidant at room temperature under solvent-free conditions. The heterogeneous catalyst could be recovered easily and reused 15 times without significant loss of its catalytic activity.

Keywords: Magnetic nanoparticles, 1,4-Diazabicyclo[2.2.2] octane tribromide, Nanocatalyst, Hydrogen peroxide, Sulfides, Sulfoxides

1. Introduction

Catalyst recovery and reusability are the two most important features for many catalytic processes; most heterogeneous systems require a tedious workup of the final reaction mixture to recover the catalyst [1].

Magnetic nanoparticles (MNPs) have recently appeared as a new type of catalyst support because of their easy preparation and functionalization, large surface area ratio, facile recovery and recyclability via magnetic force as well as low toxicity and price [2]. These fascinating features have made MNPs a promising alternative to other catalyst supports [3-5].

In order to decrease the toxicity of molecular bromine, a wide variety of bromine source reagents were designed and applied in organic synthesis [6-8]. The main disadvantage of reagents based on bromine is their separation from the products which needs solid-liquid or liquid-liquid techniques in many reactions. This drawback can be overcome by immobilizing these reagents or catalysts on magnetic nanoparticle (MNPs), which can be easily removed from the reaction mixture by magnetic separation.

Sulfoxides are valuable synthetic intermediates for the synthesis of chemically and biologically important and significant molecules [9]. The main synthetic route for the preparation of these valuable materials is oxidation of the corresponding sulfides. Although a wide variety of reagent systems available for this key transformation, the major disadvantages of these methods include removal or recovery of the expensive catalyst, metal residues in the products, and the formation of large amounts of toxic waste [10-14]. Hence there is a need to develop new catalysts which can overcome these drawbacks.

In continuation of our studies on application of *N*-bromo reagents and magnetically separable catalysts in organic reactions [15-17], herein, we report the magnetic nanoparticle-supported DABCO tribromide as a novel, eco-friendly, and reusable organic-inorganic hybrid catalyst for the chemoselective oxidation of sulfides to corresponding sulfoxides using H_2O_2 as a green oxidant. Two major novelties of this work are: (1) this is the first report of a magnetic-nanoparticle-supported DABCO tribromide for use as bromine source reagent or catalyst and (2) this is the first time that a magnetically recyclable nanocatalyst has been used for the oxidation of sulfide to sulfoxide in the absence of any transition-metal.

2. Experimental

2.1. General procedure for the oxidation of sulfides

The sulfide (1 mmol) was added to a mixture of 30% H_2O_2 (2.4 equiv, 1 g) and MNPs-DABCO tribromide (10 mg), and the mixture was stirred at room temperature for the time specified. The progress was monitored by TLC (EtOAc/*n*-hexane, 1/10). After completion of the reaction, the catalyst was separated from the product by an external magnet (within 5 seconds) and the mixture was washed with Et_2O (2×5 mL) and decanted. The combined organics were dried over anhydrous Na_2SO_4 and then evaporation of diethyl ether under reduced pressure gave the pure products in 80-97% yields.

3. Results and discussions

3.1. Preparation and Characterization of MNPs-DABCO tribromide

DABCO tribromide successfully was immobilized over MNPs by using the surface modification strategy as descripted in Scheme 1.

<Scheme 1>

Magnetic Fe_3O_4 nanoparticles were prepared by chemical coprecipitation method and coated with 3-chloropropyltrimethoxysilane (CPTMS) by covalent bonds. The reaction of the supported CPTMS with DABCO in dry acetone under reflux conditions for 36 h produced the DABCO functionalized magnetic nanoparticles (MNPs-DABCO) [18]. Ultimately, the reaction of DABCO group with bromine in $CHCl_3$ led to the corresponding DABCO tribromide supported on magnetic nanoparticles (MNPs-DABCO tribromide) [19-20]. Experimental details were provided in the Supplementary data.

The catalyst has been characterized by XRD, TGA, EDX, FT-IR, SEM and VSM techniques. The position and relative intensities of all peaks in the XRD pattern of MNPs-DABCO tribromide confirm well with standard XRD pattern of Fe_3O_4, indicating retention of the crystalline cubic spinel structure during functionalization of MNPs (Supplementary data, Fig. S1) [21].

One indication of bond formation between the nanoparticles and the catalyst can be inferred from TGA. The TGA curves of the MNPs-CPTMS and MNPs-DABCO tribromide are presented in Fig. 1. The weight loss at temperatures below 200 ºC is due to the removal of physically adsorbed solvent and surface hydroxyl groups [22]. Organic groups have been reported to desorb at temperatures above 260 °C. The weight loss of CPTMS-modified magnetite NPs appears about 2.5% at 270-480ºC which is contributed to the thermal decomposition of the 3-chloropropyl silane groups. For MNPs-DABCO tribromide, there is a well-defined mass weight loss of 7.5 % between 250 and 500 ºC related to the breakdown of the DABCO tribromide moieties. On the basis of this result a loading of 0.22 mmol/g was obtained.

<Figure 1>

EDX spectrum shows the elemental composition (Fe, Si, Br and Cl) of the MNPs-DABCO tribromide (Supplementary data, Fig. S2).

Successful functionalization of the MNPs can be inferred from FT-IR techniques. The FT-IR spectra for the MNPs (black), MNPs-CPTMS (green), MNPs-DABCO (red), and MNPs-DABCO tribromide (blue) samples are shown in Figure 2. The FTIR spectrum for the magnetite nanoparticles alone shows a stretching vibration at 3381 cm^{-1} which incorporates the contributions from both symmetrical and asymmetrical modes of the O-H bonds which are attached to the surface iron atoms. The presence of an adsorbed water layer is confirmed by a stretch for the vibrational mode of water found at 1626 cm^{-1}. The absorption bands at 574 cm^{-1} and 623 are attributed to the Fe-O bonds. The band formation between MNPs and 3-chloropropylsilica group is confirmed by Fe-O-Si absorption band that appear at 999 cm^{-1}. The presence of DABCO moiety on the surface of MNPs can be inferred from both FT-IR spectra of MNPs-DABCO and MNPs-DABCO tribromide. There are four characteristic peaks include CH_2 starching and bending bonds at 2954 cm$^{−1}$ and 1462 cm$^{−1}$ respectively, C-N$^+$ starching at 1615 cm$^{−1}$ and C-N starching at 1386 cm$^{−1}$ [18, 23-24]. Compared with the spectrum of MNPs-DABCO, the MNPs-DABCO tribromide exhibits a characteristic broad band in the region 1107-991 cm^{-1}. Br_3 exhibits a signal between 180 and 200 cm^{-1} which is not detectable with the FT–IR spectrum [25].

<Figure 2>

The SEM image of MNPs-DABCO tribromide was confirmed that the catalyst was made up of uniform nanometer-sized particles less than 26 nm (Supplementary data, Fig. S3).

The magnetic property of MNPs and MNPs-DABCO tribromide were characterized by VSM (Supplementary data, Fig. S4). As expected, the bare MNPs, showed the higher magnetic value (saturation magnetization, *Ms*) of 74.3 emug^{-1} [26], the *Ms* value of MNPs-DABCO tribromide is decreased due to the silica coating and the layer of the grafted catalyst (56.0 emu g^{-1}). It has been reported that the Fe_3O_4 nanoparticles with a value of coercivity (Hc) lower than 20 Oe could be called superparamagnetic. MNPs and MNPs-DABCO tribromide have an Hc of 16.09 and 14.15 Oe, respectively. As a result, the modified MNPs have a typical superparamagnetic behavior [27-28] and can be efficiently attracted with a small magnet.

Unfortunately, due to the magnetic properties of MNPs-DABCO tribromide it is actually impossible to further characterize this material by using solid-state NMR spectroscopy.

3.2. The catalytic applications of MNPs-DABCO tribromide in the oxidation of sulfides to sulfoxides

The catalytic activity of MNPs-DABCO tribromide was investigated in the selective oxidation of sulfides to sulfoxides using 30% H_2O_2 as a green oxidant (Scheme 2).

<Scheme 2>

In order to optimize the reaction conditions, we evaluated the influence of different amounts of catalyst and hydrogen peroxide on the oxidation of methyl phenyl sulfide as a model compound under solvent-free conditions at room temperature (Table 1). As shown in Table 1, the reaction was incomplete in the absence of a catalyst even after 24 h. The optimum amount of H_2O_2 (2.4 equivalent) in the presence of MNPs-DABCO tribromide (10 mg) is ideal for complete conversion of methyl phenyl sulfide sulfides to methyl phenyl sulfoxide.

<Table 1>

In order to generalize the scope of the reaction, a series of structurally diverse sulfides was subjected to oxidation under the optimized reaction conditions, and the results are presented in Table 2. The reactions went on well to afford products in short times and good to high yields. It is important to note that thiantrene was homoselectively oxidized to thianthrene monosulfoxide without the formation of the disulfoxide product.

To show the chemoselectivity of this method, the sulfides containing oxidation-prone and acid-sensitive functional groups such as OH, CHO and $COOCH_3$ were subjected to the sulfoxidation reaction; these functional groups remained intact during the conversion of sulfides to sulfoxides (Table 2, entries 8-10).

<Table 2>

The ability to easily recover and recycle of MNPs-DABCO tribromide was investigated. We have found that this catalyst was rapidly recovered and demonstrated remarkably excellent recyclability; after the first use of catalyst in oxidation of methyl phenyl to give methyl phenyl sulfoxide, the catalyst was separated by an external magnet (Fig. 3), washed thoroughly with ether, and reused as such for subsequent experiments under similar reaction conditions. As shown in Fig. 4, catalyst was reusable without any significant loss of activity for the 15th recycling.

<Figure 3>

<Figure 4>

On the basis of the literature [14], a plausible mechanism for this transformation is outlined in scheme 3.

<Scheme 3>

In summary, we have designed the first MNPs-DABCO tribromide as a source of bromin that catalyze oxidation of sulfides to sulfoxides using H_2O_2 with remarkably high activity and chemoselectivity. The heterogenized catalyst can be readily recycled by magnetic decantation and used for oxidation for up to 15 times without any significant loss of activity. Studies to further explore the potential of this powerful immobilization strategy for the preparation of magnetically recoverable chiral catalysts are underway.

Acknowledgment

We are grateful to the University of Kurdistan Research Councils for the partial support of this work.

References

[1] A. P. Wight, M. E. Davis, Chem. Rev. 102 (2002) 3589-3614.

[2] S. Shylesh, V. Schunemann, W.R. Thiel, Angew. Chem. Int. Ed. 49 (2010) 3428-3459.

[3] Y. Zhu, L. P. Stubbs, F. Ho, R. Liu, C. P. Ship, J. A. Maguire, N. S. Hosmane, Chem. Cat. Chem. *2* (2010) 365-374.

[4] V. Polshettiwar, R. Luque, A. Fihri, H. Zhu, M. Bouhrara, J-M. Basset, Chem. Rev. 111 (2011) 3036-3075.

[5] R. B. Nasir-Baigand, R. S. Varma, Chem. Commun. 49 (2 013) 752-770.

[6] G. R. Dake, M. D. B. Fenster, P. B. Hurley, B. O. Patrick, J. Org. Chem. 69 (2004) 5668-5675.

[7] E. Kolvari, A. Ghorbani-Choghamarani, P. Salehic, F. Shirini, M.A. Zolfigol, J. Iran. Chem. Soc. 4 (2007) 126-174.

[8] H. Veisi, R. Ghorbani-Vaghei, Tetrahedron 66 (2010) 7445-7463.

[9] I. Frenanez, I. Khiar, Chem. Rev. 103 (2003) 3651-3706.

[10] O. Shigeru, O. Yutaka, K. Seizi, T. Waichiro, Bull. Chem. Soc. Jpn. 39 (1966) 364-366.

[11] K. Sato, M. Hyodo, M. Aoki, X. Q. Zheng, R. Noyori, Tetrahedron 57 (2001) 2469-2476.

[12] B. M. Choudary, B. Bharathi, C. V. Reddy, M. L. Kantam, J. Chem. Soc. Perkin Trans. 1, (2002) 2069-2074.

[13] M. A. Zolfigol, K. Amani, A. Ghorbani-Choghamarani, M. Hajjami, R. Ayazi-Nasrabadi, S. Jafari, Catal. Commun. 9 (2008) 1739-1744.

[14] D. Habibi, M. A. Zolfigol, M. Safaee, A. Shamsian, A. Ghorbani-Choghamarani, Catal. Commun. 10 (2009) 1257-1260.

[15] A. Khazaei, A. Rostami, M. Mahboubifar, Catal. Commun. 8 (2007) 383-388.

[16] B. Atashkar, A. Rostami, B. Tahmasbi, Catal. Sci. Technol., 2013, 3, 2140-2146.

[17] A. Rostami, B. Atashkar, H. Gholami, Catal. Commun. 37 (2013), 69-74.

[18] A. Hasaninejad, M. Shekouhy, N. Golzar, A. Zare, M. M. Doroodmand, Appl. Catal. A: Gen. 402 (2011) 11-22.

[19] M. M. Heravi, F. Derikvand, M. Ghassemzadeh, B. Neumuller, Tetrahedron Lett. 46 (2005) 6243-6245.

[20] J. A. Struss, W. D. Barnhart, M. R. Velasco, A. Bronley-DeLancey Tetrahedron Lett. 47 (2006) 6635-6636.

[21] F. Brackmann, H. Schill, A. Meijere, Chem. Eur. J. 11 (2005) 6593-6600.

[22] M. Z. Kassaee, H. Masrouri, F. Movahed, Appl. Catal. A: Gen. 395 (2011) 28-33.

[23] S. Luo, X. Zheng, H. Xu, X. Mi, L. Zhang, J.-P. Cheng, Adv. Synth. Catal. 349 (2007) 2431-2434.

[24] C. Dálaigh, S. A. Corr, Y. Gunko, S. J. Connon, Angew. Chem. Int. Ed. 46 (2007) 4329-4332.

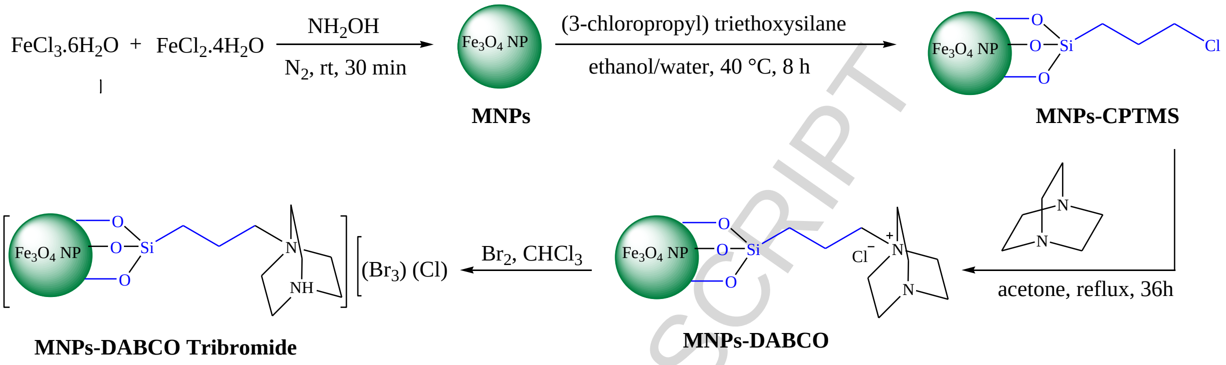
[25] B. S. Ault, L. Andrews, J. Chem. Phys. 64 (1976) 4853-4859.

[26] K. Naka, A. Narital, H. Tanakal, Y. Chujo, M. Morita, T. Inubushi, I. Nishimura, J. Hiruta, H. Shibayama, M. Koga, S. Ishibashi, J. Seki, S. Kizaka-Kondoh, M. Hiraoka, Polym. Adv. Technol. 19 (2008) 1421-1429.

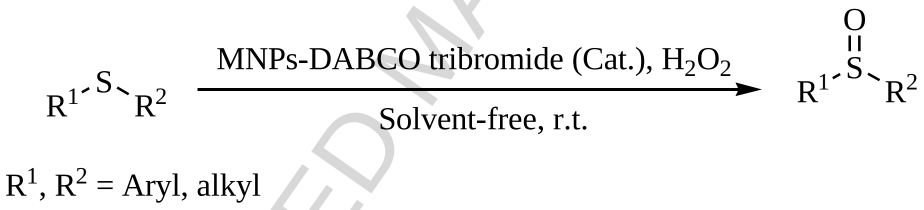
[27] R. C. Ohandley, Modern Magnetic Materials: Principles and Applicat Ions; Wiley: New York, 2000

[28] R. H. Iida, K. Takayanagi, T. Nakanishi, T. J. Osaka, Colloid Interface Sci. 314 (2007) 274-280.

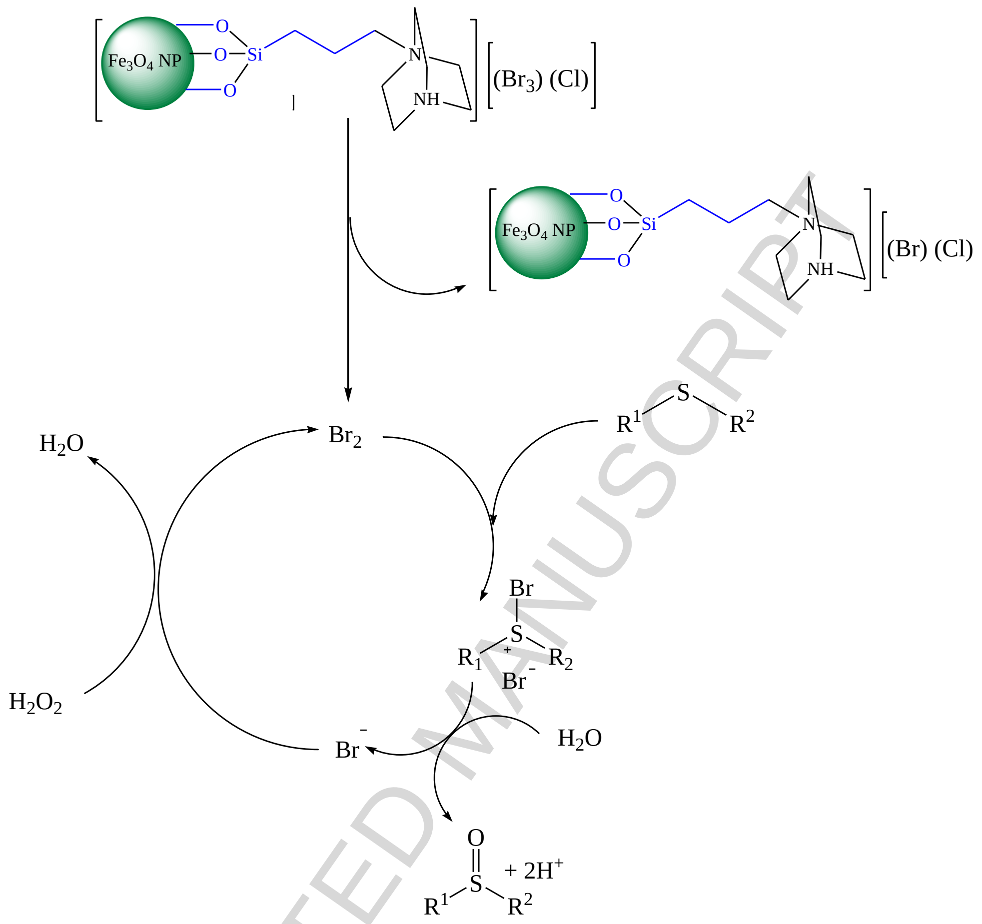
Schemes



Scheme 1. Synthesis of MNPs-DABCO Tribromide



Scheme 2. MNPs-DABCO tribromide catalyzed the oxidation of sulfides to sulfoxides using H_2O_2



Scheme 3. A possible mechanism for the oxidation of sulfides to sulfoxides using H_2O_2 catalyzed by MNPs-DABCO tribromide

Figures

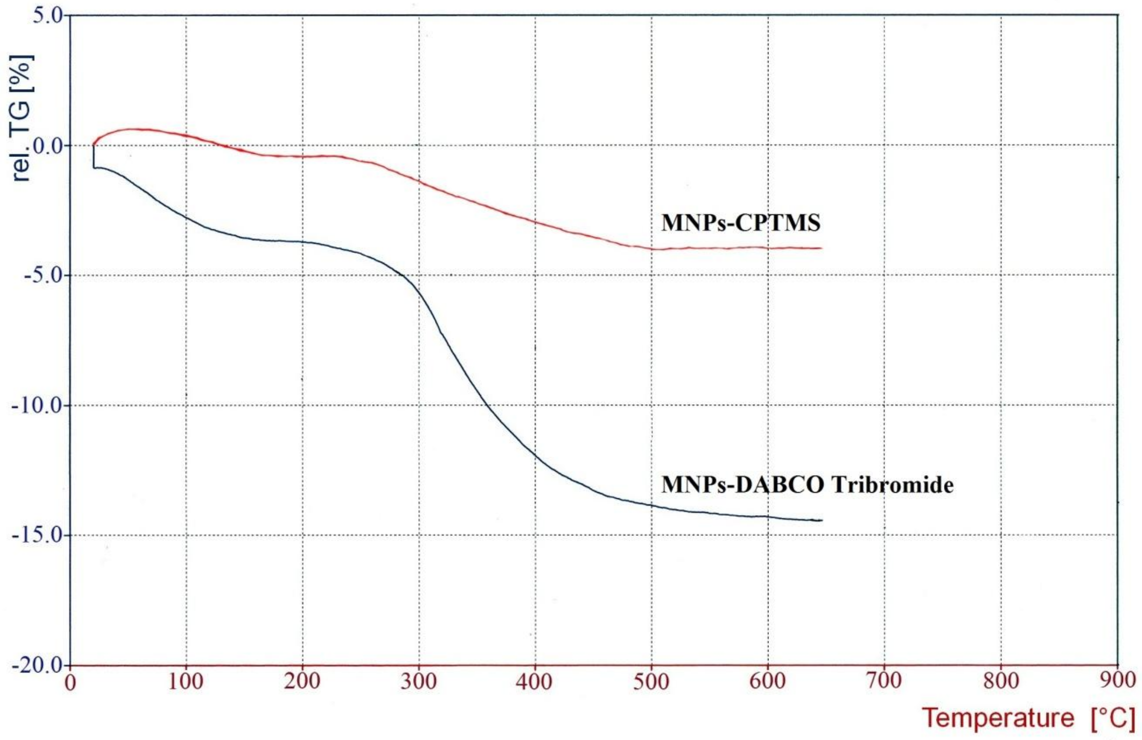


Fig. 1. TGA profile of the MNPs-CPTMS and MNPs-DABCO Tribromide

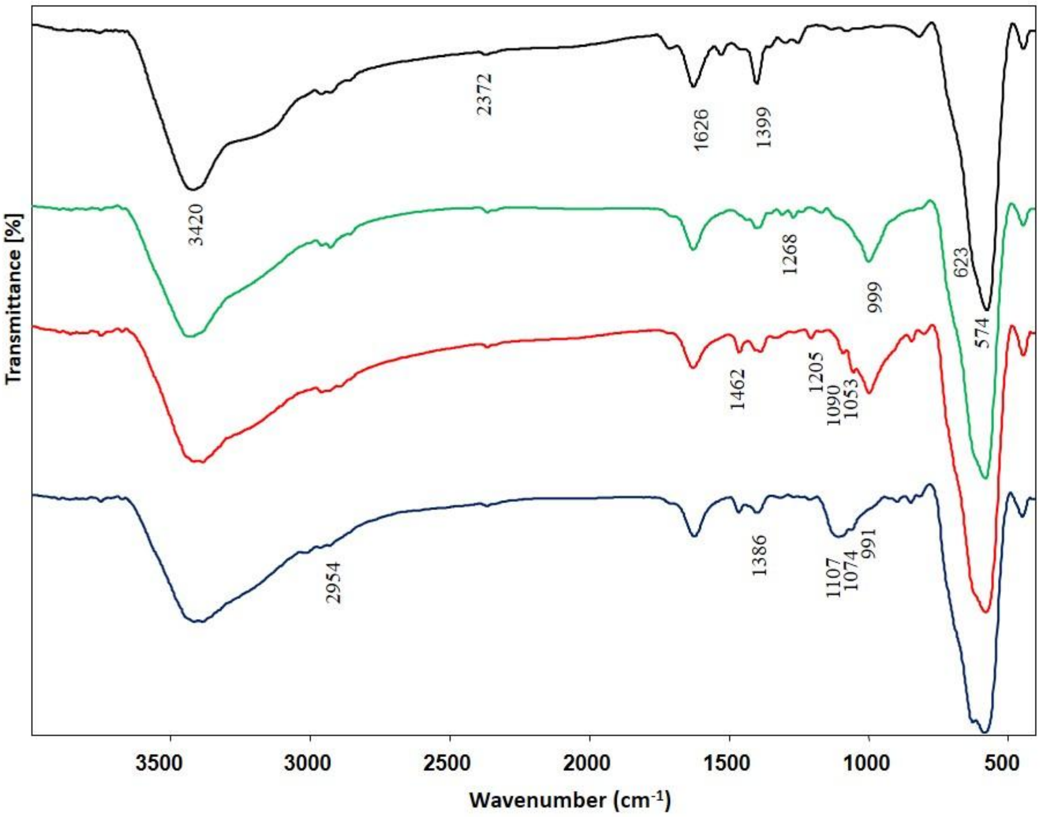


Fig. 2. FTIR spectra of MNPs (black), MNPs-CPTMS (green), MNPs-DABCO (red) and MNPs-DABCO tribromide (blue)

Fig. 3. A reaction mixture in the absence (left) or presence of a magnetic field (right)

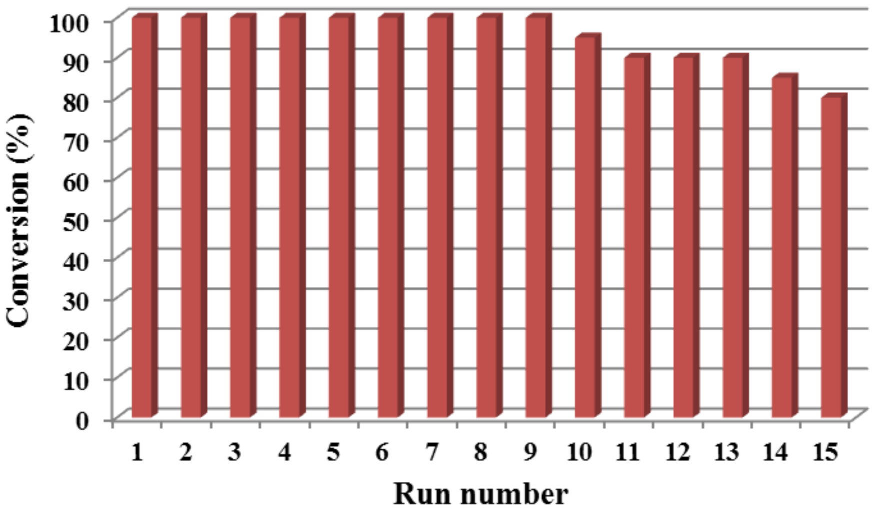


Fig. 4. The recycling experiment of MNPs-DABCO tribromide for oxidation of methyl phenyl sulfide (1 mmol) using H_2O_2 at room temperature for

20 min

Tables

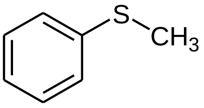
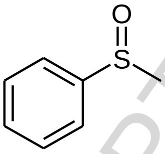
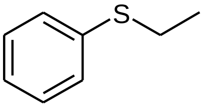
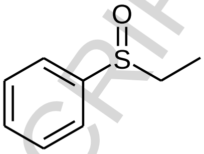
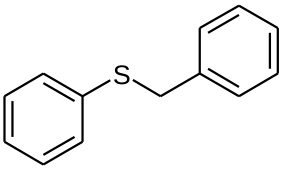
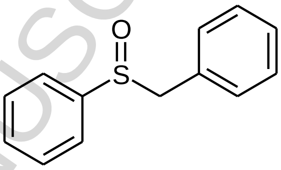
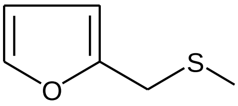
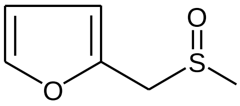
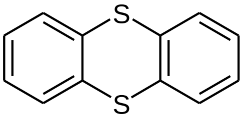
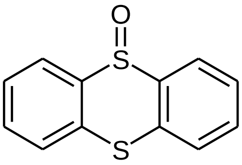
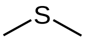
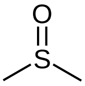
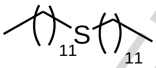
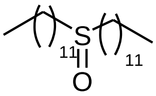
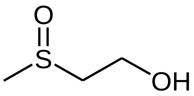
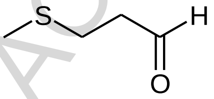
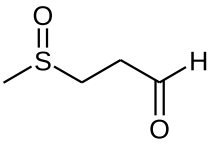
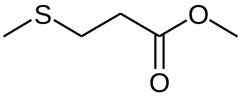
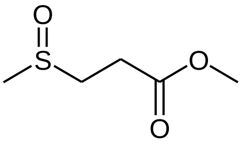
Table 1

The selective oxidation of methyl phenyl sulfide to methyl phenyl sulfoxide under different conditions

Entry	Catalyst (mg)	H_2O_2 (equiv.)	Time/min	Converted yield (%)[a]
1	Catalyst-Free	2.4	24h	80
2	Fe_3O_4 NP (5)	2.4	24h	80
3	MNPs-DABCO tribromide (5)	2.4	20	100
4	MNPs-DABCO tribromide (10)	2.4	5	100
5	MNPs-DABCO tribromide (15)	2.4	5	100
6	MNPs-DABCO tribromide (30)	2.4	3	100
7	MNPs-DABCO tribromide (10)	0.6	20	100
8	MNPs-DABCO tribromide (10)	1.2	15	100

[a] Conversion of sulfide to sulfoxide was determined by GC

Table 2
MNPs-DABCO tribromide (10 mg) catalyzed selective oxidation of sulfides (1 mmol) to sulfoxides using 30% H_2O_2 (2.4 equiv.) under solvent-free conditions at room temperature

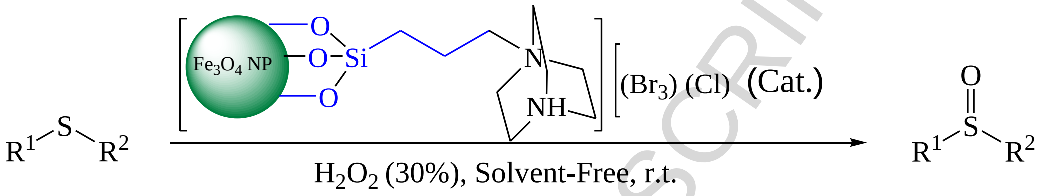
Entry	Sulfide	Time (min)	Sulfoxide[a]	Yield (%)[b]
1		20		97
2		20		95
3		25		97
4		5		90
5		70		92
6		15		80
7		5		93
8		5		83
9		5		82
10		5		82

[a]All the products are known and were characterized by IR, ^{1}H NMR, and by melting point comparisons with those of authentic samples [10-14].

[b]Isolated yield

Graphical Abstract

DABCO tribromide immobilized on magnetic nanoparticle as a recyclable catalyst for the chemeselective oxidation of sulfide using H_2O_2 under metal- and solvent-free conditions



R^1, R^2 =Aryl, Heterocyclic, Benzylic and Alkyl

Highlights

- MNPs-DABCO tribromide as a source of bromine was synthesized and characterized.
- MNPs-DABCO tribromide catalyzed highly efficient the chemoselective oxidation of sulfides.
- H_2O_2 was used as a green, commercially available, cheap, and chemically stable oxidant.
- The catalyst was easily recovered and reused without any significant loss in catalytic activity.