

MNP-supported acidic catalysts in oxidation of sulfides to sulfoxides

Ali Mirzaie *

Young Researchers and Elite Club, Ilam Branch, Islamic Azad University, Ilam, Iran

ARTICLE INFO

ABSTRACT

Article history:

Received 5 May 2018

Revised 17 May 2018

Accepted 17 May 2018

Available online 17 May 2018

Keywords:

Sulfoxides

Oxidation

MNPs-supported acidic catalysts

Biologically molecules

Sulfoxide derivatives are also prevalent structural motifs in many drugs and biologically active molecules. Oxidation of sulfides is the best strategy for the preparation of the sulfoxides. In recent times, a series of acids supported on magnetic nanoparticles have been reported for the oxidation of sulfides to the sulfoxides. In this paper, attention is focused on the fabrication of MNPs-supported acidic catalysts and their catalytic applications in the oxidation of sulfides to the sulfoxides.

1. Introduction

Easy recovery of catalysts and their reusability are two prominent characteristics in most of modern catalytic processes because either the employed catalysts are often very expensive or the targeted products are often very valuable from the economical and medicinal points of view.¹⁻³ In this respect, as an important class of separable materials, magnetic nanoparticles (MNPs) have recently become a hot research topic in organic synthetic chemistry and material sciences, because of their high potential in catalysis and numerous applications in biomedicine.⁴⁻⁵ Numerous recent studies reported in literature clearly demonstrated that among the various employed magnetic MNPs as the core magnetic support, Fe₃O₄ nanoparticles have received more special attention in modern catalysis research due to their tremendous properties such as simple synthesis and fictionalization, abundance and unique activities, high stability, high surface area, low toxicity and price and simple separation by magnetic forces.⁶⁻¹³ These attractive and valuable properties have caused that Fe₃O₄ nanoparticles have been emerged as a promising alternative to other catalyst supports.¹⁴

Oxidation of sulfides to the sulfoxides is an important reaction in organic synthesis. Sulfoxides are an important class of organic sulfur compounds that their applications as precursor or intermediate in organic synthesis are highly regarded among chemists.¹⁵ Sulfoxide derivatives are also prevalent structural motifs in many drugs and biologically active molecules.¹⁵

A nice category of valuable pharmaceutical and biological molecules containing S=O bonds, Modafinil, Adrafinil, CRL-40,941 or fladrafinil, Fipronil, Oxydemeton-methyl, Omeprazole, Pantoprazole, Lansoprazole and Rabeprazole is listed in **Figure 1**.¹⁵⁻²³

Catalysis of chemical reactions by acids is always an important and fascinating research target in organic synthesis. Since the acids are often liquid and expensive, their separation from reaction media is the most important concern of synthetic chemist.²⁴⁻²⁶ The immobilization of acidic on magnetic nanoparticles is a good solution to overcome this drawback,

because the catalyst can be readily separated from the reaction medium by external magnet.²⁷

In recent times, a series of acids supported on magnetic nanoparticles have been reported for the oxidation of sulfides to the sulfoxides. In this paper, we will briefly summarize the application of on magnetic nanoparticles- supported acids in the oxidation of sulfides to the sulfoxides.

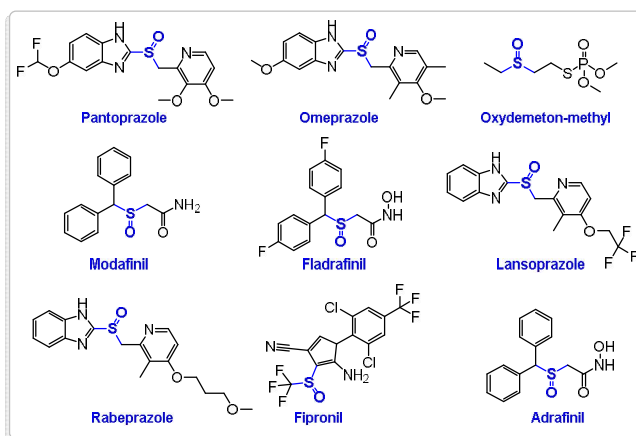


Fig 1. Pharmaceutical and biological active molecules containing sulfoxide scaffolds.

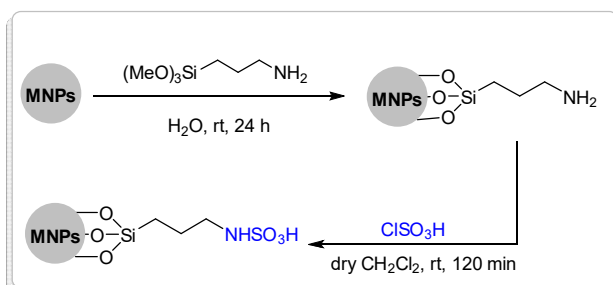
2. Sulfoxidation of sulfides

In 2013, Rostami et al. reported the fabrication of *N*-propylsulfamic acid supported on magnetic Fe₃O₄ nanoparticles (MNPs-PSA) and its catalytic activity in the oxidation of sulfides to the sulfoxides. Synthesis steps of this catalyst depicted in **Scheme 1**. The structure of as-fabricated catalyst was characterized by a series of spectroscopic techniques such as XRD, FT-IR and SEM.²⁷

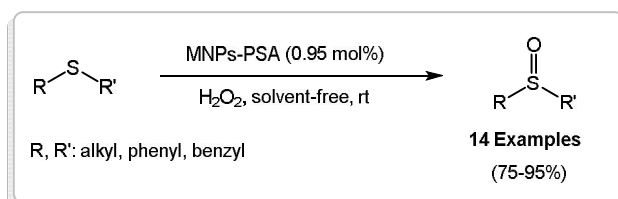
* Corresponding Author:

E-mail address: a.mirzaie@gmail.com (A. Mirzaie)

The resultant nanocomposite was highly active and efficient for oxidation of various aromatic and aliphatic sulfides to obtain the sulfoxides. The sulfoxidation reactions were performed in the presence of H_2O_2 under solvent-free conditions (Scheme 2). The magnetic nanocatalyst can be readily recovered easily by applying an external magnet device and reused for at least 10 reaction runs without considerable loss of reactivity.

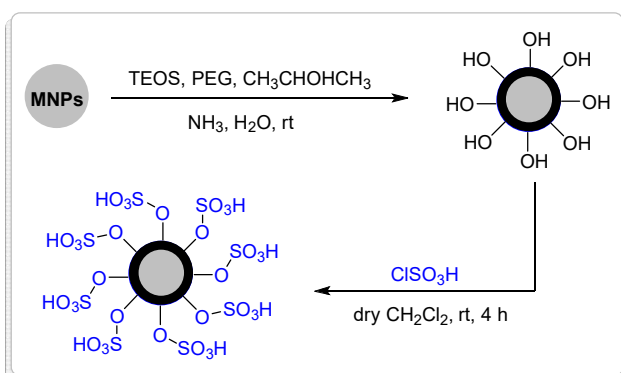


Scheme 1. General route for the synthesis of *N*-propylsulfamic acid supported on magnetic Fe_3O_4 nanoparticles (MNPs-PSA).



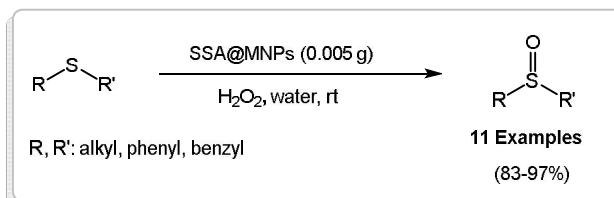
Scheme 2. Oxidation of sulfides to the sulfoxides catalyzed by MNPs-PSA.

In another report, Rostami and co-workers fabricated silica sulfuric acid-coated Fe_3O_4 nanoparticles (Scheme 3) and examined the catalytic activity in the oxidation of sulfides to the sulfoxides. The magnetic nanocatalyst was characterized by FT-IR spectroscopy, TGA, XRD and SEM techniques. Reactions could be then conducted under aqueous medium at ambient temperature, good to excellent yields of the target products were obtained in less than 20 min (Scheme 4). The catalyst was easily separated with the assistance of an external magnetic field from the reaction mixture and reused for several consecutive runs without significant loss of its catalytic efficiency.²⁸



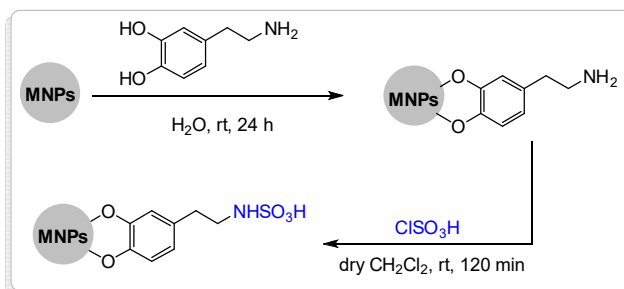
Scheme 3. General route for the synthesis of silica sulfuric acid-coated Fe_3O_4 nanoparticles (SSA@MNPs).

In 2016, Ghorbani-Choghamarani et al. reported the preparation of sulfamic acid immobilized on magnetic nanoparticles functionalized with dopamine (Scheme 5).

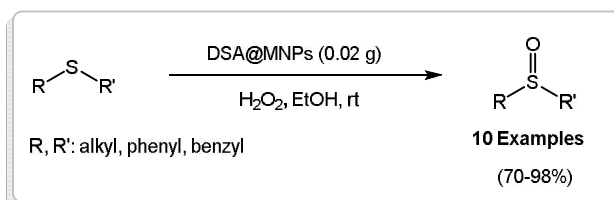


Scheme 4. Oxidation of sulfides to the sulfoxides catalyzed by SSA@MNPs.

The catalytic activity of dopamine sulfamic acid-functionalized magnetic Fe_3O_4 nanoparticles (DSA@MNPs) was evaluated in the oxidation of sulfides to the sulfoxides. The structure of as-prepared catalyst was characterized by a series of spectroscopic techniques such as XRD, FT-IR, TGA, SEM, VSM, TEM and EDX. The sulfoxidation reactions were carried out in the presence of hydrogen peroxide in ethanol at ambient temperature (Scheme 6). The catalyst was readily separated by external magnet and can be reused 4 cycles without significant loss in catalytic activity.²⁹



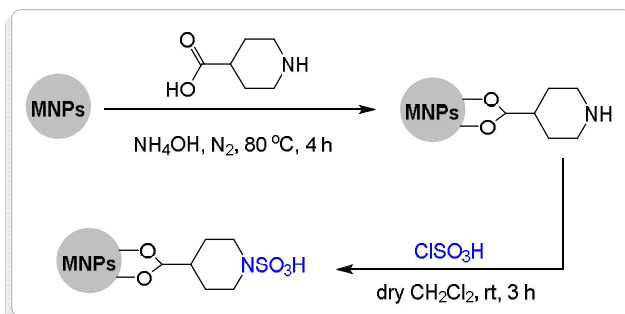
Scheme 5. General route for the synthesis of dopamine sulfamic acid-functionalized magnetic Fe_3O_4 nanoparticles (DSA@MNPs).



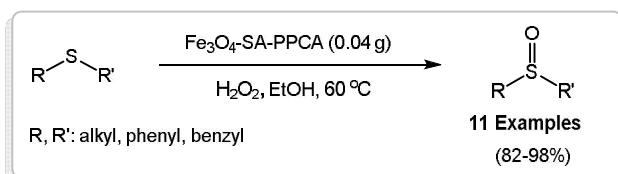
Scheme 6. Oxidation of sulfides to the sulfoxides catalyzed by DSA@MNPs.

Ghorbani-Choghamarani and co-workers have also prepared a magnetically recoverable catalyst by immobilizing sulfamic acid on magnetic nanoparticles functionalized with Piperidine-4-carboxylic acid (Fe_3O_4 -SA-PPCA) (Scheme 7). The nanostructure of the catalyst was characterized by FT-IR spectroscopy, thermogravimetric (TGA) analysis, powder X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscope (TEM). The scope of Fe_3O_4 -SA-PPCA was investigated for the oxidation of sulfides using hydrogen peroxide, in ethanol at room temperature (Scheme 8).

The catalyst was reused up to 10 runs and no significant loss of activity was observed.³⁰

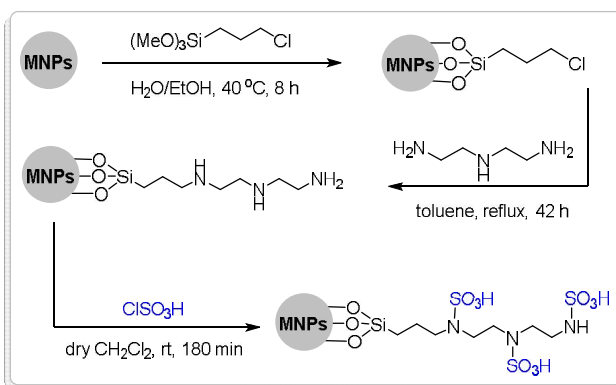


Scheme 7. General route for the synthesis of Fe₃O₄-SA-PPCA.



Scheme 8. Oxidation of sulfides to the sulfoxides catalyzed by Fe₃O₄-SA-PPCA.

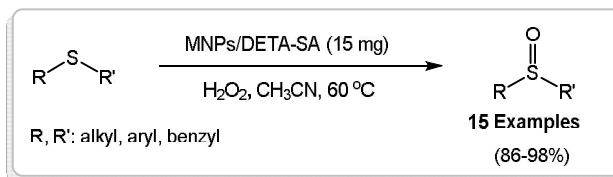
More recently, Shiri et al. reported the synthesis of sulfamic acid supported on magnetic nanoparticles functionalized with diethylenetriamine (MNP/DETA-SA) (Scheme 9) and its catalytic activity in the oxidation of sulfides to the sulfoxides. As-prepared nanosolid was characterized by FT-IR, SEM, VSM, XRD and TGA spectroscopic techniques. Under the optimized conditions, a variety of sulfides were successfully oxidized to the corresponding sulfoxides in high yields (Scheme 10). The nanosolid catalyst could be easily recovered by a simple magnetic separation and reused for many cycles without deterioration in catalytic activity.³¹



Scheme 9. General route for the synthesis of MNP/DETA-SA.

3. Conclusion

Sulfoxides are found in many natural products, pharmaceuticals, organic materials, and in numerous functional molecules. Sulfoxides are especially important in chemical and pharmaceutical industries.



Scheme 10. Oxidation of sulfides to the sulfoxides catalyzed by MNP/DETA-SA.

Oxidation of sulfides is the best strategy for the preparation of the sulfoxides. This paper focused on the fabrication of MNPs-supported acidic catalysts and their catalytic activity in the oxidation of sulfides to the sulfoxides. Magnetic acidic catalysts can be easily recovered by simple magnet; therefore it makes the catalyst more efficient. These magnetically recoverable catalysts will provide a solid and stable platform for heterogeneous catalysis, green chemistry, and environmentally benign protocols in the near future.

Acknowledgements

This work was supported by the research facilities of Islamic Azad University of Ilam, Iran.

References

1. L. Shiri, A. Ghorbani-Choghamarani, M. Kazemi, *Res. Chem. Intermed.* **2017**, 43, 2707.
2. L. Shiri, S. Rahmati, Z. Ramezani-Nejad, M. Kazemi, *Appl. Organomet. Chem.* **2017**, 31, e3687.
3. L. Shiri, A. Ghorbani-Choghamarani, M. Kazemi, *Aust. J. Chem.* **2016**, 69, 585.
4. L. Shiri, A. Ghorbani-Choghamarani, M. Kazemi, *Monatsh Chem.* **2017**, 148, 1131.
5. L. Shiri, A. Ghorbani-Choghamarani, M. Kazemi, *Appl. Organometal. Chem.* **2017**, 31, e3596.
6. S. Shylesh, V. Schunemann, W.R. Thiel, *Angew. Chem. Int. Ed.* **2010**, 49, 3428.
7. Y. Zhu, L. P. Stubbs, F. Ho, R. Liu, C. P. Ship, J. A. Maguire, N. S. Hosmane, *Chem. Cat. Chem.* **2010**, 2, 365.
8. V. Polshettiwar, R. Luque, A. Fihri, H. Zhu, M. Bouhrara, J-M. Basset, *Chem. Rev.* **2011**, 111, 3036.
9. D. Wang, D. Astruc, *Chem. Rev.* **2014**, 114, 6949.
10. B. Karimi, F. Mansouri, H. M. Mirzaei, *Chem. Cat. Chem.* **2015**, 7, 1736.
11. R. B. Nasir-Baig, R. S. Varma, *Chem. Commun.* **2013**, 49, 752.
12. M. A. Zolfigol, R. Ayazi-Nasrabadi, S. Bagheri, *Appl. Organometal. Chem.* **2016**, 30, 500.
13. M. A. Zolfigol, R. Ayazi-Nasrabadi, S. Bagheri, *Appl. Organometal. Chem.* **2016**, 30, 273.
14. L. Shiri, A. Ghorbani-Choghamarani, M. Kazemi, *Aust. J. Chem.* **2017**, 70, 9.

15. M. Kazemi, M. Ghobadi, *Nanotechnol Rev.* **2017**, 6, 549.
16. C. Mareker, *Liebigs. Ann. Chem.* **1865**, 136, 75.
17. J.G. Rowlands, *Synlett.* **2003**, 2, 236.
18. A.M. Khenkin, R. Neumann, *J. Am. Chem. Soc.* **2002**, 124, 4198.
19. R. Bentley, *Chem. Soc. Rev.* **2005**, 34, 609.
20. R.N. Rao, D.D. Shinde, M.V. Talluri, S.B. Agawane, *J. Chromatogr. B.* **2008**, 873, 119.
21. H. Tan, Y. Cao, T. Tang, K. Qian, W.L. Chen, J. Li, *Sci. Total Environ.* **2008**, 407, 428.
22. T. Shimatani, M. Moriwaki, J. Xu, S. Tazuma, M. Inoue, *Dig. Liver Dis.* **2006**, 38, 802.
23. S. Strobel, M. Kist, *Helicobacter.* **2000**, 5, 41.
24. N. Koukabi, E. Kolvari, M.A. Zolfigol, A. Khazaei, B.S. Shaghasemi, B.A. Fasahati *Adv. Synth. Catal.* **2012**, 354, 2001.
25. S. Rostamnia, A. Nuri, H. Xin, A. Pourjavadi, S.H. Hosseini, *Tetrahedron Lett.* **2013**, 54, 3344.
26. J. Safari, Z. Zarnega, *J. Mol. Catal. A. Chem.* **2013**, 379, 269.
27. A. Rostami, B. Tahmasbi, F. Abedi, Z. Shokri, *J. Mol. Catal. A. Chem.* **2013**, 378, 200.
28. A. Rostami, A. Ghorbani-Choghamarani, B. Tahmasbi, F. Sharifi, Y. Navasi, D. Moradi, *J. Saudi. Chem. Soc.* **2017**, 21, 399.
29. A. Ghorbani-Choghamarani, H. Rabiei, B. Tahmasbi, B. Ghasemi, F. Mardi, *Res. Chem. Intermed.* **2016**, 42, 5723.
30. A. Ghorbani-Choghamarani, G. Azadi, *Croat. Chem. Acta.* **2016**, 89, 49.
31. L. Shiri, H. Narimani, M. Kazemi, *Appl. Organometal. Chem.* **2018**, 32, e3927.

❖ **How to cite this paper:** A. Mirzaie, MNPs-supported acidic catalysts in oxidation of sulfides to sulfoxides. *J. Med. Chem. Sci.* **2018**, 1, 5-8.
Link: http://jmchemsci.com/article_63160.html