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Sulfide oxidation to sulfoxide using acidic catalysts assisted by MNPs

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ABSTRACT

A large number of pharmaceuticals and physiologically active compounds have sulfoxide derivatives as a structural theme. One of the most effective ways to prepare sulfoxides is by oxidizing sulfides. The oxidation of sulfides to sulfoxides has recently been shown using a series of acids supported by magnetic nanoparticles. This work primarily aims to discuss the production of acidic catalysts supported by MNPs and their catalytic usage in the oxidation of sulfides to sulfoxides.

Keywords:

Sulfoxides Oxidation
MNPs-supported acidic catalysts Biologically molecules

1. Introduction

Because the catalysts used in these processes may be rather costly or the compounds they produce might have significant monetary or therapeutic value, most current catalytic methods place a premium on easy catalyst recovery and reusability. 1-3 Due to their great catalytic potential and several biomedical uses, magnetic nanoparticles (MNPs)—an essential class of separable materials—have lately emerged as a popular study subject in organic synthesis chemistry and the material sciences. 4-5 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, Fe₃O₄ nanoparticles have garnered more special attention in modern catalysis research compared to other magnetic MNPs used as core supports, according to numerous recent studies published in the literature. 6-13 Fe₃O₄ nanoparticles have recently emerged as a viable substitute for traditional catalytic supports due to their appealing and

beneficial features. 14 An essential step in organic synthesis is the oxidation of sulfides to sulfoxides. The sulfoxides are a highly esteemed group of sulfur compounds that have several useful uses in organic synthesis, both as a precursor and an intermediate. 15 A large number of pharmaceuticals and physiologically active compounds have sulfoxide derivatives as a structural theme. 15 Modafinil, Adrafinil, CRL-40,941 (also known as fladrafinil), Fipronil, xydemeton-methyl, Omeprazole, Pantoprazole, Lansoprazole, and Rabeprazole are all part of a wonderful class of useful pharmacological and biological compounds that contain S=O linkages (Figure 1.15-23). as an external magnet makes quick work of removing the catalyst from the reaction liquid. 27 The oxidation of sulfides to sulfoxides has recently been shown using a series of acids supported by magnetic nanoparticles. We will provide a concise overview of the oxidation of sulfides to sulfoxides using acids assisted by magnetic nanoparticles in this post.

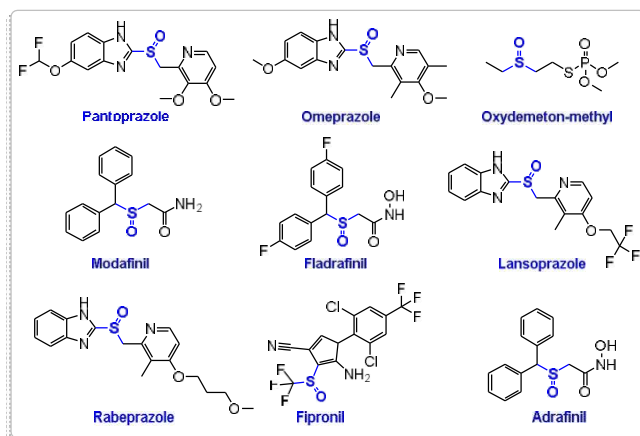
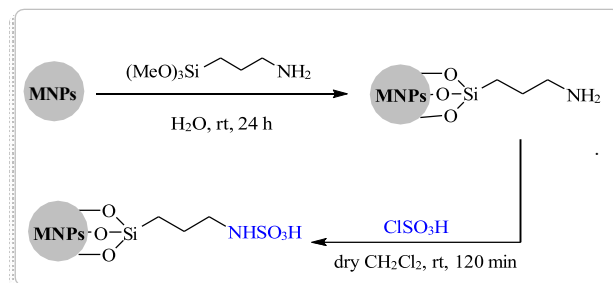


Fig 1. Pharmaceutical and biological active molecules containing sulfoxide scaffolds.

2. Sulfoxidation of sulfides

The production of N-propylsulfamic acid supported by magnetic Fe₃O₄ nanoparticles was documented by Rostami et al. in 2013. An intriguing and crucial area of study in organic synthesis is the catalysis of chemical reactions by acids. Separating the acids from the reaction environment is the primary focus of synthetic chemists due to the fact that the acids are often costly and liquid. pages 24-26 One way to get around this problem is to immobilize acidic substances on magnetic nanoparticles. catalyst for the oxidation of sulfides to sulfoxides, and its use in this process (MNPs-PSA). Scheme 1 shows the procedures involved in synthesizing this catalyst. Several spectroscopic methods, including XRD, FT-IR, and SEM, were used to analyze the structure of the as-fabricated catalyst. Sulfoxides were efficiently and actively produced by oxidizing a variety of aromatic and aliphatic sulfides using the resulting nanocomposite. H₂O₂ was present throughout the sulfoxidation processes, which were conducted in an environment devoid of solvents (Scheme 2). You can reuse the magnetic nanocatalyst for at least 10 reaction cycles without significantly reducing its reactivity. It can be retrieved simply using an external magnet device.

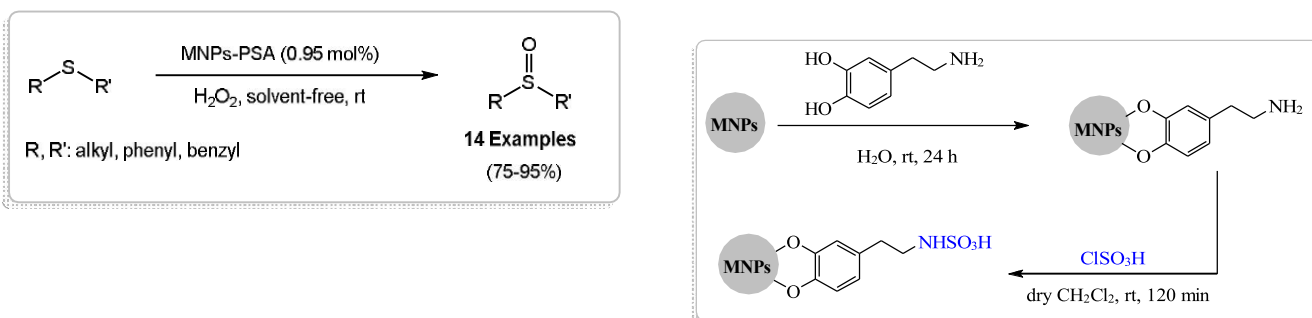
In 2016, Ghorbani-Choghamarani et al. reported the preparation of sulfamic acid immobilized on magnetic nanoparticles functionalized with dopamine (Scheme 5).



Scheme 1. General route for the synthesis of *N*-propylsulfamic acid supported on magnetic Fe₃O₄ nanoparticles (MNPs-PSA).

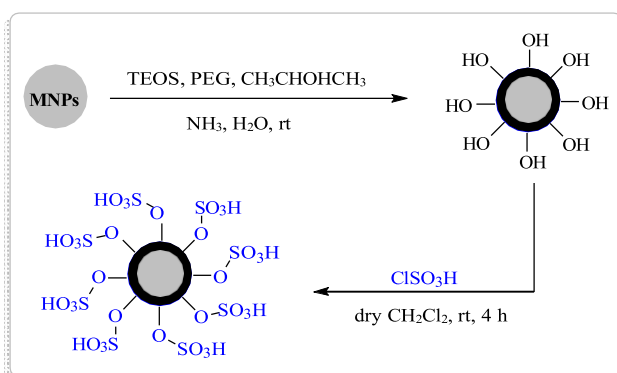
The catalytic activity of dopamine sulfamic acid-functionalized magnetic Fe₃O₄ nanoparticles (DSA@MNPs) was evaluated in the oxidation of sulfides to the sulfoxides. The structure of as-prepared catalyst was characterized by a series of spectroscopic

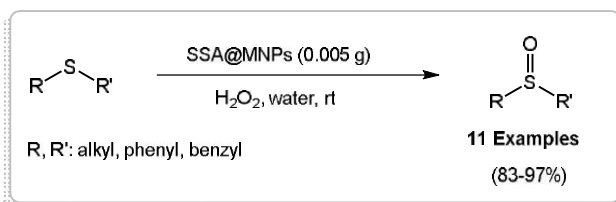
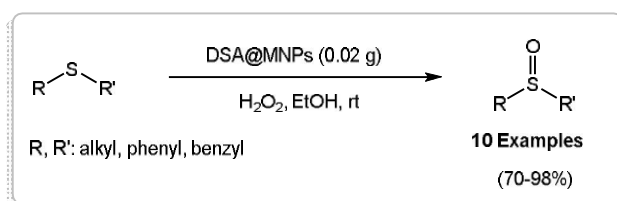
techniques such as XRD, FT-IR, TGA, SEM, VSM, TEM and EDX. The sulfoxidation reactions were carried out in the presence of hydrogen peroxide in ethanol at ambient temperature (**Scheme 6**). The catalyst was readily separated by external magnet and can be reused 4 cycles without significant loss in catalytic activity.²⁹



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

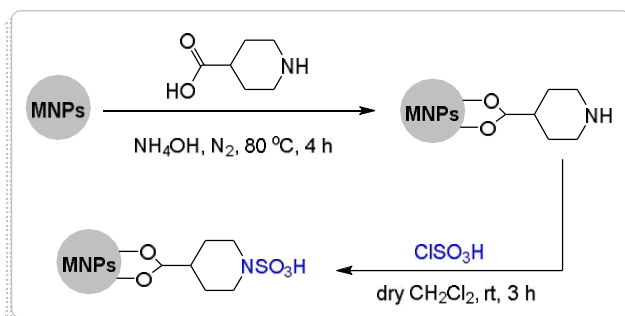
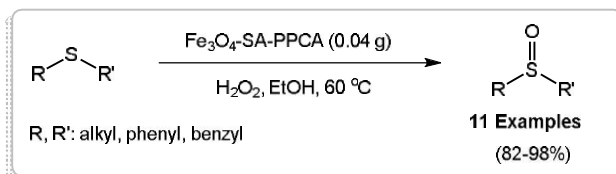
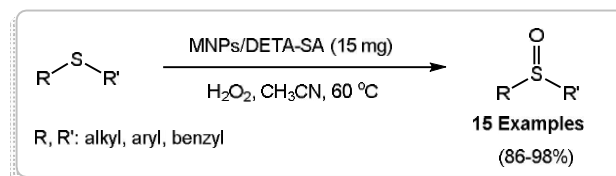
In another report, Rostami and co-workers fabricated silica sulfuric acid-coated Fe₃O₄ nanoparticles (**Scheme 3**) and examined the catalytic activity in the oxidation of sulfides to the sulfoxides. The magnetic nanocatalyst was characterized by FT-IR spectroscopy, TGA, XRD and SEM techniques. Reactions 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 Fe₃O₄ nanoparticles (SSA@MNPs).**Scheme 4.** Oxidation of sulfides to the sulfoxides catalyzed by SSA@MNPs**Scheme 5.** General route for the synthesis of dopamine sulfamic acid- functionalized magnetic Fe₃O₄ nanoparticles (DSA@MNPs).**Scheme 6.** Oxidation of sulfides to the sulfoxides catalyzed by DSA@MNPs.

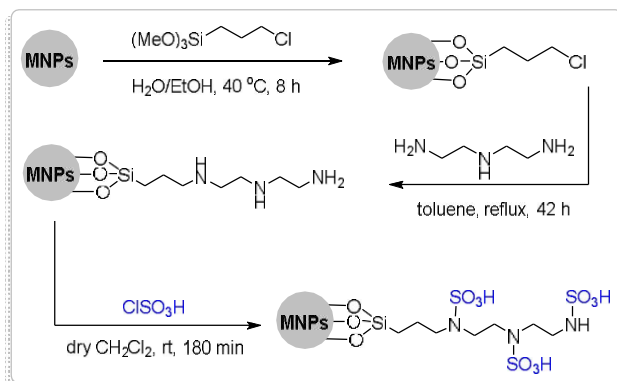
Ghorbani-Choghamarani and co-workers have also prepared a magnetically recoverable catalyst by immobilizing sulfamic acid on magnetic nanoparticles functionalized with Piperidine-4- carboxylic acid (Fe₃O₄-SA-PPCA) (**Scheme 7**). The nanostructure of the catalyst was characterized by FT-IR spectroscopy, thermogravimetric (TGA) analysis, powder X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscope (TEM). The scope of Fe₃O₄- SA-PPCA was investigated for the oxidation of sulfides to the sulfoxides 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 10.** Oxidation of sulfides to the sulfoxides catalyzed by MNPs/DETA-SA.

Scheme 8. Oxidation of sulfides to the sulfoxides catalyzed by Fe_3O_4 -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

Many organic materials, medicines, and natural products include sulfoxides, and there are a plethora of functional molecules that contain them as well. Particularly significant to the chemical and medicinal sectors are sulfoxides. Sulfoxide preparation is best accomplished via oxidation of sulfides. In this work, we detailed the production of acidic catalysts supported by MNPs and their catalytic activity in reducing sulfides to sulfoxides. A more effective catalyst is one that is magnetic acidic, as it can be retrieved with ease using a simple magnet. Future developments in heterogeneous catalysis, green chemistry, and ecologically friendly procedures will benefit greatly from these magnetically recoverable catalysts, which will serve as a sturdy and reliable foundation.

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