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ORIGINAL ARTICLE

Silica sulfuric acid-coated Fe_3O_4 nanoparticles as high reusable nanocatalyst for the oxidation of sulfides into sulfoxides, protection and deprotection of hydroxyl groups using HMDS and Ac_2O

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Acetylation

Abstract Oxidation of sulfides, acetylation of alcohols and phenols and selective trimethylsilylation of primary and secondary benzyl alcohols are carried out using silica sulfuric acid-coated Fe_3O_4 magnetic nanoparticles (SSA@MNPs) as a stable, efficient and magnetically recoverable nanocatalyst. Also, deprotection of silyl ethers was reported in ethanol at room temperature in the presence of SSA@MNPs as a magnetic nanocatalyst. The magnetic nanocatalyst was characterized by FT-IR spectroscopy, TGA, XRD and SEM techniques. 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.

1. Introduction

During the past two decades, a great deal of attention has been paid to developing methods for heterogenizing homogeneous catalysts in order to combine the advantages of both homogeneous and heterogeneous catalyses [1,2]. Nanoparticulate supports can serve to bridge the gap between these two traditional disciplines [3]. However, the nanocatalyst supported can be separated from products by conventional filtration or centrifugation techniques. But, it is difficult, time consuming and expensive to separate fine particles from a reaction mixture [4]. Therefore, magnetic nanoparticles (MNPs) based on iron oxides have emerged in the organic reactions, which can be easily and rapidly isolated from the reaction mixture using external magnet [5]. More importantly, magnetic separation of the MNPs is easier and more effective than filtration or centrifugation [6,7]. However, bare nanoparticles of iron oxides tend to aggregate into large clusters and lose their catalyst

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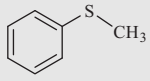
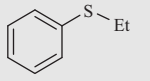
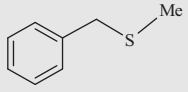
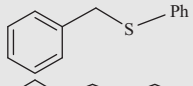
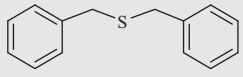
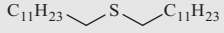
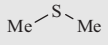
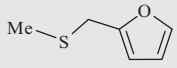
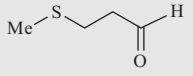
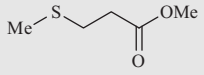
Table 1 Optimization of the reaction conditions for the oxidation of benzyl methyl sulfide (1 mmol) as a model compound.

Entry	Solvent	Catalyst (mg)	H_2O_2 (mmol)	Time (min)	Conversion (%)
1	CH_3CN	5	1.2	24	100
2	CH_2Cl_2	5	1.2	10	100
3	Ethanol	5	1.2	25	100
4	*n*-Hexane	5	1.2	8	100
5	Solvent free	5	1.2	35	100
6	THF	5	1.2	60	Trace
7	Ethyl acetate	5	1.2	5	100
8	H_2O	15	1.2	5	100
9	H_2O	10	1.2	5	100
10	H_2O	5	1.2	13	100
11	H_2O	3	1.2	20	–[a]
12	H_2O	5	1.4	5	100
13	H_2O	5	1	30	100

[a] The reaction was not complete.

Table 2 Oxidation of sulfides into sulfoxides using H_2O_2 under the influence of SSA@MNPs in water and at room temperature.

Entry	Sulfide	Product	Time (min)	Yield (%)[a]
1		2a	5	87
2		2b	5	90
3		2c	13	87
4		2d	5	85
5		2e	5	92
6		2f	20	86
7		2g	10	91
8		2h	20	83
9		2i	10	87
10		2j	2	80
11		2k	15	97

[a] Isolated yield.

loading capacity when compared to many conventional single-nanoparticles [8]. On the other hand, it is also difficult to graft the surface of Fe_3O_4 MNPs with organic materials since there are few hydroxyl groups on the surface of Fe_3O_4 MNPs. Also to prevent the antioxidation of MNPs, the modification and surface coating for Fe_3O_4 MNPs is necessary [9]. Silica is commonly employed as the coating layer for the surface of MNPs because it is stable, inert, has a high specific surface area, non-toxic, surface modification is easy, cheap and resistant under catalytic conditions [10,11].

Table 3 Optimization of reaction conditions for trimethylsilylation of benzyl alcohol (1 mmol) with HMDS (1.5 mmol) as a model compound.

Entry	Solvent	Catalyst (mg)	Time (min)	Conversion (%)
1	CH_2Cl_2	10	100	–[a]
2	Solvent free	10	100	–[a]
3	THF	10	80	100
4	*n*-Hexane	10	100	–[a]
5	Ethyl acetate	10	100	–[a]
6	CH_3CN	15	10	100
7	CH_3CN	10	15	100
8	CH_3CN	5	20	100

[a] The reaction was not complete.

The selective oxidation of sulfides to sulfoxides is an important transformation in organic chemistry [12] because of their extensive applications as synthetic intermediates for the construction of various chemically, biologically active molecules and drug metabolism [13]. For example, omeprazole and the pesticide fipronil are two typical examples of the extensive application of these intermediates in pharmaceutical and fine chemical industries [14,15].

Besides, the protection–deprotection steps of active protic functional groups are frequently required in the multistep synthesis as well as in the chemistry of drug design and food or cosmetic industries [16]. Acetylation and trimethylsilylation of hydroxyl groups are the most widely used transformations for the protection of alcohols and phenols. Because acetylation and trimethylsilylation of hydroxyl groups are carried out under mild conditions, acetates and silyl ethers can also be easily deprotected into the parent hydroxyl groups [17,18]. On the other hand, silyl ethers have a good stability for most non-acidic reagents and non-polar solvents [19]. Furthermore, trimethylsilylation is also extensively used for the derivatization of hydroxyl compounds to increase their volatility for gas chromatography and mass spectrometry [19]. Respectively, acetylation and trimethylsilylation of hydroxyl groups are performed employing Ac_2O and 1,1,1,3,3,3-hexamethyldisilazane (HMDS) in the presence of protonic acids, Lewis acids, heteropoly acids, clays or amine bases [20–22].

2. Experimental

2.1. Preparation of catalyst

First, the Fe_3O_4 MNPs were prepared according to the very recently reported method [5–7]. Then the obtained Fe_3O_4 MNPs (2 g) were dispersed in 20 mL of water by sonication for 30 min, and then 2-propanol (200 mL) was added to the reaction mixture. The reaction mixture was stirred using a