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Schiff base complexes of Ni, Co, Cr, Cd and Zn supported on magnetic nanoparticles: As efficient and recyclable catalysts for the oxidation of sulfides and oxidative coupling of thiols

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ABSTRACT

Oxidation of sulfides to sulfoxides and oxidative coupling of thiols into their corresponding disulfides were carried out using hydrogen peroxide (H_2O_2) as oxidizing agent in the presence of immobilized Ni, Co, Cr, Zn or Cd complexes on Fe_3O_4 magnetic nanoparticles (M-Salen-MNPs) as stable, heterogeneous, efficient and magnetically recoverable nanocatalysts under mild reaction conditions. These supported complexes were characterized by FT-IR spectroscopy, thermogravimetric analysis (TGA), powder X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS). A variety of aromatic and aliphatic sulfides and thiols with different functional groups were successfully oxidized with short reaction times in good to excellent yields. Recovery of the catalyst is easily achieved by magnetic decantation and reused for several consecutive runs without significant loss of its catalytic efficiency.

1. Introduction

The immobilization of homogeneous catalysts on various support materials to facilitate catalysts separation and recycling is of great importance in catalyst science [1,2]. However, immobilization of homogeneous catalysts usually decreases the catalytic activity or selectivity [3]. This could be solved using nanoparticles (NPs) as catalyst supports. Nanoparticulate supports form a "semi-homogeneous" system and can serve as an intermediate between homogeneous and heterogeneous catalysis [4]. However, nanoparticles are difficult to separate by filtration techniques [5]. This drawback can be overcome by magnetic nanoparticles (MNPs), which can be easily removed from the reaction mixture by magnetic separation. More important, magnetic separation of the MNPs is easier and more effective than filtration or centrifugation, simple, economical and promising for industrial applications [3,6]. One of the most promising MNPs supports for the development of high-performance catalyst supports is superparamagnetic iron oxide [6,7]. The notable advantages of Fe_3O_4 MNPs are simple in synthesis, readily available, low cost, high surface area, low toxicity and superparamagnetism properties [8]. Therefore, Fe_3O_4 MNPs are considered as ideal supports for the heterogenization of homogeneous catalysts [9].

Recently, metal complexes of Schiff-bases have been emerged for the development of efficient variety of catalysts [7,10] however, to clean and facilitate catalysts separation, Schiff-base compounds have been supported onto heterogeneous materials [11,12]. Among them, salicylidene Schiff-base (salen) can be easily prepared using condensation of salicylaldehyde and amine groups. On the other hand, salen complexes of transition metals are stable compounds that have been used as catalysts for various organic reactions. Among transition metals, Ni, Co, Cr, Cd and Zn Schiff-base complexes are amongst the most versatile catalysts known for organic transformations [13,14].

The selective oxidation of organosulfur compounds is of great importance in synthetic, biological, and industry [14]. Disulfides are important in both biological (including DNA cleavage, stabilisation of peptides in proteins), and industrial processes (e.g. applications in vulcanization of rubbers and elastomers) [14]. Furthermore, disulfides are important reagents in organic synthesis, and can be used as a protecting group for thiol [15], sulfonylation of enolates and other anions [16], synthesis of organo-sulfur compounds *via* C—S bond formation [17] and they are also important starting materials in the preparation of sulfenyl and sulfinyl reagents [18].

Likewise, the selective oxidation of sulfides to sulfoxides is an important transformation in organic chemistry [19] Some of biologically active sulfoxides play an important role as therapeutic agents such as antifungal, antibacterial, anti-atherosclerotic, anti-

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ulcer, antihypertensive and anti-atherosclerotic as well as psychotropics and vasodilators [20,21]. Furthermore, Omeprazole and the pesticide Fipronil are two typical examples of the extensive application of these intermediates in pharmaceutical and fine chemical industries [22,23]. Additionally, sulfoxides are also valuable in the C—C bond-formation and molecular rearrangements [24].

Therefore, many methods including different catalysts (homogeneous and heterogeneous catalysts) and various oxidants (e.g. metal oxidants, organic oxidant, peroxides, halogens, and air) have been used for the selective oxidation of organic sulfides and thiols [15–25]. Concerning the green oxidant, H_2O_2 (with only H_2O as a byproduct) in particular have received attention because of their environmental implications, readily available, high atom efficiency and lower costs involved than when using other oxidizing agents [26].

Owing to the context of green chemistry and reuse of catalyst, herein Ni, Cd, Co, Cr and Zn-based heterogeneous catalysts have been reported for oxidative coupling of thiols into corresponding disulfides and also oxidation of sulfides to sulfoxides under mild condition.

2. Experimental section

2.1. Materials

Chemicals and solvents used in this work were purchased from Sigma–Aldrich, Fluka or Merck chemical companies and used without further purification.

Table 1
Oxidation of sulfides into sulfoxides using H_2O_2 in the influence of M-salen-MNPs at 35 °C under solvent-free condition.

Entry	Sulfide	Catalyst [Time (min)]	Catalyst [Yield[a] (%)]	Mp (°C) found [Reference]
1	Ph-S-Me	**I** [20] **II** [15] **III** [20] **IV** [60] **V** [60]	**I** [95] **II** [95] **III** [95] **IV** [96] **V** [96]	30–32 [19]
2	*p*-MePh-S-Me	**I** [25] **II** [40] **III** [20] **IV** [30] **V** [30]	**I** [92] **II** [95] **III** [94] **IV** [94] **V** [99]	119–123 [30]
3	Ph-S-CH_2CH_2OH	**I** [5] **II** [5] III [5] **IV** [5] **V** [5]	**I** [94] **II** [94] **III** [94] **IV** [94] **V** [94]	Oil [31]
4	Methyl furfuryl sulfide	**I** [10] **II** [15] **III** [10] **IV** [10] **V** [10]	**I** [95] **II** [96] **III** [96] **IV** [96] **V** [96]	Oil [19]
5	Tetrahydrothiophene	**I** [5] **II** [5] III [5] **IV** [5] **V** [5]	**I** [92] **II** [88] **III** [90] **IV** [91] **V** [90]	Oil [19]
6	$CH_3(CH_2)_2CH_2$-S-$CH_2(CH_2)_2CH_3$	**I** [30] **II** [30] **III** [30] **IV** [30] **V** [30]	**I** [94] **II** [92] **III** [96] **IV** [95] **V** [94]	Oil [32]
7	$CH_3(CH_2)_{10}CH_2$-S-CH_3	**I** [30] **II** [60] **III** [15] **IV** [120] **V** [60]	**I** [97] **II** [96] **III** [95] **IV** [99] **V** [96]	60–65
8	$CH_3CH_2CH_2$-S-$CH_2CH_2CH_3$	**I** [10] **II** [10] **III** [10] **IV** [5] **V** [10]	**I** [95] **II** [93] **III** [94] **IV** [93] **V** [93]	Oil [14]
9	CH_3-S-CH_2CH_2OH	**I** [5] **II** [5] III [5] **IV** [5] **V** [5]	**I** [97] **II** [95] **III** [91] **IV** [96] **V** [94]	Oil [14]
10	CH_3-S-$CH_2CH_2CO_2CH_3$	**I** [5] **II** [5] III [5] **IV** [5] **V** [5]	**I** [94] **II** [95] **III** [93] **IV** [91] **V** [93]	Oil [19]

[a] Isolated yields.