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Efficient oxidative coupling of thiols and oxidation of sulfides using UHP in the presence of Ni or Cd salen complexes immobilized on MCM-41 mesoporous as novel and recoverable nanocatalysts

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ABSTRACT

Oxidation of sulfides to sulfoxides and oxidative coupling of thiols into their corresponding disulfides were carried out using urea-hydrogen peroxide (UHP) as oxidizing agent and immobilized Ni or Cd complexes on MCM-41 as stable, heterogeneous, efficient and recoverable catalysts under mild reaction conditions. These supported complexes were characterized by FT-IR spectroscopy, thermogravimetric analysis (TGA), powder X-ray diffraction (XRD) and N_2 adsorption–desorption isotherms. 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 at room temperature. Catalysts were easily recovered and reused for several consecutive runs without significant loss of their catalytic activity and efficiency.

1. Introduction

In the last few years, immobilization of homogeneous catalysts on various solid supports with the advantage of catalysts separation and recycling have been widely studied in many divergent areas of research [1,2], because the reactions are carried out under mild conditions and the organic products are easily isolated. However, immobilization of homogeneous catalysts usually decreases the catalytic activity or selectivity [3,4]. This drawback can be overcome using nanomaterials as ideal heterogeneous supports. Because nano-sized catalysts can serve as efficient bridge and fill the gap between homogeneous and heterogeneous catalysts [5]. Among different nanoparticles, mesoporpus silica, especially MCM-41, is commonly employed as a heterogeneous support for the immobilization of homogeneous catalysts. Compared to traditional silica materials, mesoporous silica have several advantages, such as thermal and mechanical stability, large specific surface area for catalyst loading, high dispersion of the active phases, non-toxic content, ease of surface modification and tunable pore size [6]. Additionally, the supported catalyst on mesoporous silica can be reused for several runs without significant loss of its catalytic efficiency [7]. The large surface area and high-density surface silanol sites could be functionalized with different compounds containing active sites [8] such as amine and subsequently various ligands containing Schiff base metal complexes. Therefore, covalent anchoring of the Schiff base complexes onto a functionalized siliceous mesoporous material with large pore diameters is fascinating [9]. Recently, Schiff base metal complexes have found wide applications in efficient catalytic reactions [10]. For example, chromium, copper or cobalt salen compounds have been grafted on the surface of MCM-41 trough aminosilane linkers and these heterogeneous catalysts were found to be active for different organic functional group transformations [11,12]. Among transition metals, Ni and Cu complexes of salen type have been recently used as efficient catalysts [13,14].

The oxidation of organosulfur compounds such as sulfides and thiols into their corresponding sulfoxides and disulfides are useful in the synthesis of new products, which may play an important role in various medical, biological, and nanotechnological applications [15–17]. In particular, sulfoxides are valuable synthetic intermediates for the production of a range of chemically and biologically active molecules including therapeutic agents such as

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anti-ulcer, antifungal, antibacterial, anti-atherosclerotic, antihypertensive and anti-atherosclerotic, as well as psychotropic and vasodilators [18,19]. Furthermore, Omeprazole and the pesticide Fipronil are two typical examples of the extensive application of these intermediates in the pharmaceutical and fine chemical industries [20,21]. Likewise, disulfides are used in sulphenylation of enolates and other anions [22], and they are also essential moieties of biologically active compounds for peptide and protein stabilization anions [23] while some disulfides have also found industrial applications as vulcanizing agents [22]. Furthermore, disulfides are relatively more stable to organic reaction conditions such as oxidation, alkylation and acylation compared to the corresponding free thiols; also the thiol group can be conveniently protected as a disulfide [23]. For this reason, many methods have been developed over the years to increase the efficiency of these kinds of oxidation reactions. For example, oxidation of sulfides and thiols have been reported in the presence of various catalysts and using different oxidants (e.g. metal oxidants, organic oxidants, peroxides, halogens, and air) [24,25]. Hydrogen peroxide (H_2O_2) is one of the most widely used oxidant that has been applied for the oxidation of sulfides and thiols as an inexpensive and environmentally benign oxidant, because it produces only water as a side-product [26]. However, the handling of its concentrated solutions is not desirable for safety problems. In order to avoid the problems associated with the use of concentrated solution of H_2O_2 (such as, handling difficulties and hydrolysis of the desired product), this compound has been adducted with some carrier such as urea. Therefore, urea hydrogen peroxide (UHP) as a cheap, commercially available, stable solid and anhydrous source of H_2O_2 has been used instead of aqueous H_2O_2 [27,28].

Therefore, this work focused on the immobilization of Ni and Cd salen complexes onto MCM-41 and their catalytic applications in the oxidation of sulfides into sulfoxides as well as in the oxidative coupling of thiols into their corresponding disulfides using UHP at room temperature under mild conditions.

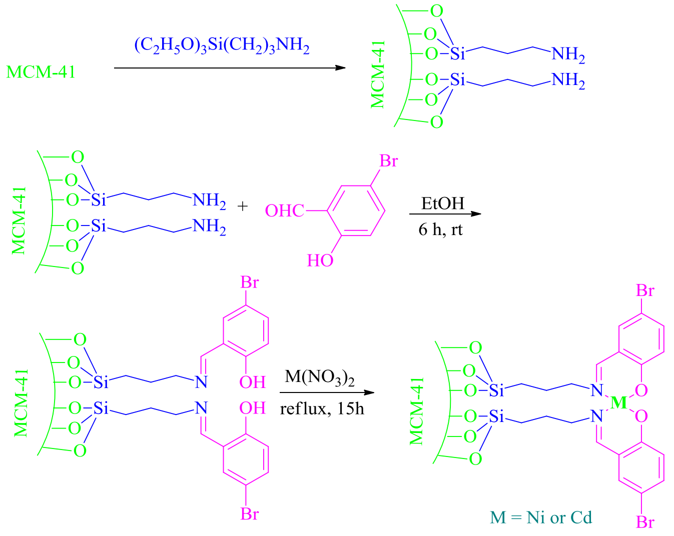
2. Experimental

2.1. Synthesis of siliceous MCM-41

MCM-41 was synthesized according to the literature method [29]. The source of silicon was tetraethyl orthosilicate (TEOS) and the structure directing agent was cetyltrimethylammoniumbromide (CTAB). A typical synthesis gel was prepared by adding 5.78 g of TEOS to an aqueous solution containing 1.01 g of CTAB, 0.34 g of NaOH and 30 mL of deionized water. After stirring about 1 h at room temperature, the resulting homogeneous mixture was crystallized under static hydrothermal conditions at 383 K in a teflon lined autoclave for 96 h. After cooling to room temperature the resulting solid was obtained by filtration, washed with deionized water and, dried in air at 353 K. In order to remove the CTAB surfactants, the collected product was calcined at 813 K for 24 h. This mesoporous material is designated as Si-MCM-41.

2.2. Synthesis of Ni or Cd-Salen-MCM-41

Post synthesis organic modification of the mesoporous material was performed by stirring 4.8 g of MCM-41 with 4.8 g of (3-amino propyl)-triethoxy silane (APTES) in n-hexane (96 mL) at 353 K for 24 h under nitrogen atmosphere. The resulting white solid MCM-41-($SiCH_2CH_2CH_2NH_2$)$_x$ was filtered, washed with n-hexane and dried under vacuum and then this solid (1 g) was refluxed with 5-boromo salicyl aldehyde (1 mmol, 0.201 g) under N_2 atmosphere in ethanol at 353 K for 3 h. The resulting solid salen was washed with ethanol, collected by filtration and dried under vacuum. Finally, the silylated Ni or Cd-Salen-MCM-41 was prepared by stirring the above mentioned solid (1 g) with $Ni(NO_3)_2.2H_2O$ or $Cd(NO_3)_2.4H_2O$ (1 mmol), in ethanol for 12 h. Eventually, the resulting green solid was filtered, washed with ethanol using Soxhlet for 12 h and dried under vacuum.



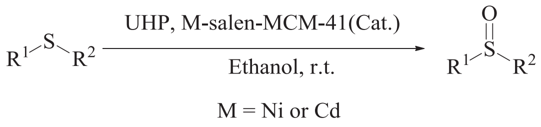
Scheme 1. Procedure for the preparation of M-Salen-MCM-41 catalyst.

2.3. General procedure for the oxidation of sulfides to sulfoxides using UHP in the presence of Ni or Cd-Salen-MCM-41

A mixture of sulfide (1 mmol), UHP (5 mmol) and Ni or Cd-Salen-MCM-41 (0.02 g) was stirred at room temperature in ethanol and the progress of the reaction was monitored by TLC. After completion of the reaction, catalyst was separated by simple filtration and washed with dichloromethane (4 × 5 mL). Finally, the organic solvents were evaporated, and products were obtained in good to high yields.

2.4. General procedure for the oxidative coupling of thiols into disulfides using UHP in the presence of Ni or Cd-Salen-MCM-41

Ni or Cd-Salen-MCM-41 (0.02 g) was added to a mixture of thiol (1 mmol) and UHP (6 mmol) in ethanol (4 mL). Then the mixture was stirred for the appropriate time at room temperature (Scheme 3). The progress of reaction was monitored by TLC. After completion of the reaction, the catalyst was separated by simple filtration and the mixture was washed with CH_2Cl_2 (5 × 2 mL). Dichloromethane was evaporated under reduced pressure to afford



$$R^1{-}S{-}R^2 \xrightarrow[\text{Ethanol, r.t.}]{\text{UHP, M-salen-MCM-41(Cat.)}} R^1{-}S(=O){-}R^2$$

M = Ni or Cd

Scheme 2. The Oxidation of sulfides into sulfoxides using UHP.

$$R{-}SH \xrightarrow[\text{Ethanol, r.t.}]{\text{UHP, M-salen-MCM-41(Cat.)}} R{-}S{-}S{-}R$$

M = Ni or Cd

Scheme 3. The oxidative coupling of thiols into disulfides using UHP.