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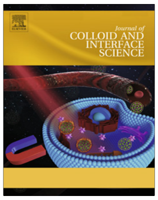

Regular Article

Diphenyl diselenide immobilized on magnetic nanoparticles: A novel and retrievable heterogeneous catalyst in the oxidation of aldehydes under mild and green conditions

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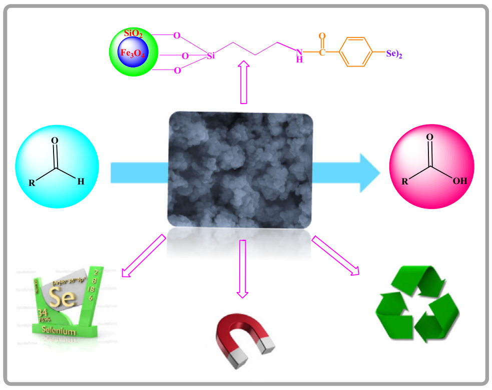
GRAPHICAL ABSTRACT

Diselenide stabilized on silica coated Fe_3O_4 nano-particle as the first magnetically recyclable diselenide catalyst, synthesized and subjected to oxidation of aldehydes to carboxylic acids.



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ABSTRACT

In the present study diselenide stabilized on silica coated Fe_3O_4 magnetic nano particles as a novel, highly efficient and magnetically retrievable heterogeneous catalyst was designed, synthesized and introduced. Full characterization of the newly prepared magnetic nanocatalyst was authenticated using several physico-chemical characterization techniques such as Fourier transform infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA), energy-dispersive X-ray spectroscopy (EDX), X-ray diffraction patterns (XRD), field-emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and vibrating sample magnetometer (VSM). Thereafter, the catalytic performance of this $(Fe_3O_4@SiO_2\text{-}Se)_2$ nanocatalyst was investigated in oxidation of aldehydes using H_2O_2 as the clean oxidant under aqueous conditions. Under the title conditions, a range of both aromatic and aliphatic aldehydes can be converted into the corresponding carboxylic acid products with excellent yields. Additionally, the magnetic nanoparticles could be conveniently recovered using an external magnetic field and reused four times without discernible decrease of efficiency. Some of the other outstanding features of this methodology are short reaction times, simple and easy work-up procedure, eco-friendly nature and cost effectiveness that make it economic, sustainable and in agreement with some green chemistry protocols.

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1. Introduction

Organoselenium compounds are very important and valuable reagents in synthetic chemistry, not only because of their very wide applications in organic and natural product synthesis [1–7], ligand chemistry [8], as precursors for the preparation of thin films in metal-organic chemical vapor deposition [9,10], and uses in materials science, but also due to many of their remarkable and interesting functions in biological and pharmaceutical activities, owing to the antiviral and antimicrobial [11], antibacterial and antifungal [12], antioxidant [13], anticancer [14], anti-HIV [15], and anti-inflammatory [16] properties of organoselenium compounds.

As selenium has an interesting chemical and biological properties [17], organoselenium catalysis has attracted much attention as a potential alternative for transition-metal-catalyzed reactions [18–20]. Selenium is much cheaper in comparisons to noble metals and it is abundant, readily transportable, and can be stored for a long period of time without any change in its chemical properties [21]. Organoselenium catalysts are utilized under benign and neutral conditions with green procedures, which are free of ligands or additives [22–24]. Therefore, research on organoselenium catalysis provides additional opportunities to develop novel green, synthetic methods with industrial potential.

Catalytic methodologies, such as the use of hydrogen peroxide as an oxidant are a leading field of interest. Hydrogen peroxide is regarded as carbon-free with a high content of active oxygen; it is an inexpensive, commercially available, green and environment-friendly oxidant that generates water as its only by-product [25,26].

In the past decade, diselenide reagents accompanied by H_2O_2 have been successfully employed as effective and practical catalysts in many useful transformations such as in the dehydration of aldoximes to nitriles [27], the oxidation of isatin [28], the epoxidation of alkenes [29], the Baeyer-Villiger (BV) oxidations of α, β-unsaturated ketones to vinyl esters [30], the oxidation of amines [31], and the dihydroxylation of cyclohexene to *trans*-1,2-cyclohexanediol [32], as a result of their mild reaction conditions, good functional group tolerance, and excellent regioselectivity. In spite of these notable achievements, the study of this field is still in its infancy, and there have only been a very limited number of reports on the use of organoselenium compounds as heterogeneous catalysts [33–37].

Although homogenous catalysts display high catalytic activities with excellent selectivities, in comparison to heterogeneous catalyst, it is difficult for these types of catalysts to be easily separated from the reaction medium and to be reused in subsequent reactions [38]. Magnetic nanoparticles-supported (MNPs-supported) catalysts have been made to bridge the gap between homogeneous and heterogeneous catalysis, preserving the desirable attributes of both systems.

Magnetite Fe_3O_4 nanoparticles have widely emerged as excellent and ideal supports for immobilization because MNP-supported catalysts are readily available, they are thermally and chemically stable, and can be prepared by simple methods. Furthermore, other important features of these nanoparticles include large specific surface areas, low toxicity, cost-effective, and a benign character. In addition, they can be easily separated from the reaction medium by an external magnet, which achieves simple separation of the catalyst without filtration [39,40].

The oxidation of aldehydes into the corresponding carboxylic acids is a very useful and prominent chemical transformation in organic chemistry [41].

Despite the large number of available and effective methods for this oxidation process, most of these processes are not without drawbacks. These processes require stoichiometric amounts of toxic, hazardous, or expensive oxidants (such as potassium permanganate, chromates and chlorite) as well as organic solvents (such as benzene, formic acid, and methylene chloride) [42] that lead to serious ecological and safety problems. Developing a clean oxidation procedure would, therefore, be beneficial for various applications. Diselenides are thus efficient catalysts for this purpose.

During our continuous investigation of the synthesis and application of heterogeneous catalytic systems [43–48], for the first time, we designed and prepared a diselenide-based catalyst supported on magnetite nanoparticles (Fe_3O_4) as a new, green, retrievable, and potent heterogeneous catalyst. It could be easily separated by external permanent magnetite and reused with little deactivation. This novel synthesized catalyst has been successfully employed for rapid and clean oxidation of aldehydes into carboxylic acids in aqueous media. A few of the marvelous specifications of this newly designed catalyst are its short reaction time, superb yield, affordability, viability, great catalytic activity, simple recovery, easy work-up of the product, and the unnecessity of operating in perilous conditions in favor of accessing carboxylic acids under mild condition.

2. Experimental section

2.1. General remarks

All the commercially available reagents and solvents in this work were purchased from Merck and Aldrich and were used without any further purification. The reaction monitoring was accomplished by thin layer chromatography (TLC) on commercial aluminum-backed plates of silica gel 60 F254, visualized, using ultraviolet light. Fourier transform infrared (FT-IR) spectra were recorded on a spectrometer (Shimadzu 8400s) using potassium bromide pellets in the range 400–4000 cm^{-1} under atmospheric conditions with a resolution of 1 cm^{-1}. The NMR spectra were measured with a Bruker Avance 500 spectrometer (^1H NMR 500 MHz and ^{13}C NMR 125 MHz) in pure deuterated chloroform with tetramethylsilane (TMS) as the internal standard. X-ray diffraction (XRD) measurement was performed by a Philips instrument with applying Cu Kα radiation with a wavelength of 1.54 Å. Field-emission scanning electron microscopy (SEM) was acquired using a Tescanvega II XMU digital scanning microscope. In order to performing the SEM analysis, a small amount of sample was placed on a carbon tape and then coated with a thin layer of gold at 10 mA for 2 min. Besides SEM, Energy-dispersive X-ray spectroscopic (EDX) analysis (equipped with the SEM instrument), was also carried out for the elemental mapping of the nanocatalyst. The magnetic properties were measured with vibrating sample magnetometer (VSM; Lakeshore7407) (Meghnatis Daghigh Kavir Co., Kashan, Iran) at room temperature. Transmission electron microscopy (TEM) was carried out using a CM30 300 kV digital transmission microscope. Thermogravimetric analyses (TGA) was done) using a LINSEIS model STS PT 16,000 thermal analyzer under air atmosphere at a heating rate of 5 °C min^{-1}. X ray photoelectron spectroscopy (XPS) was investigated using a PHI Quantera II XPS Scanning Microprobe. Melting points were determined for solid products in open capillaries using an Electro thermal 9100 without further correction. For oils, the ^1H and ^{13}C NMR spectra matched those reported in the literature and were submitted for review.

2.2. Catalyst preparation

2.2.1. General procedure for the synthesis of Fe_3O_4 nanoparticles and Fe_3O_4@SiO_2

At first magnetic nanoparticles Fe_3O_4 and Fe_3O_4@SiO_2 were prepared in accordance to our earlier report [49]. Fe_3O_4 MNPs were

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