



Design of chitosan-dithiocarbamate magnetically separable catalytic nanocomposites for greener aqueous oxidations at room temperature

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ABSTRACT

A Fe₃O₄-chitosan (Fe₃O₄-CS) nanocomposite was prepared using an *in situ* approach via co-precipitation of Fe²⁺ and Fe³⁺ under basic conditions, followed by carbon disulfide post-modification and subsequent functionalisation with NH₂-Fe³⁺ functionalities. The multifunctional magnetically separable nanomaterial was employed as catalyst in the room temperature aqueous oxidation of benzylic alcohols in the presence of H₂O₂. Excellent yields to oxidation products (>90%) could be obtained under mild reaction conditions at short times of reaction (typically 2–3 h), with the catalyst successfully recovered by a simple magnet and reused at least for 8 runs without a significant decrease in product yields.

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Introduction

The field of heterogeneous catalysis experienced a number of developments in recent years motivated by their possibilities in industrial applications due to their easy recovery, reusing and potential in the synthesis of important chemical and pharmaceutical compounds [1–3]. Magnetic-based catalysts attracted a great deal of attention featuring magnetic separation and the possibility to retrieve them from reaction media using a simple magnet [4–67]. In this regard, magnetic separation has been incorporated to a variety of catalytically active bio- and synthetic polymers [7] and supramolecules (SP) [8] to design magnetic@polymer/SP [9,10]. Chitosan (CS) is a widely abundant and most versatile biopolymer, ubiquitous in crustaceans [11], which has been employed in a wide range of applications including water treatment, biomedical systems and catalysis [12–16]. CS contains both amine and hydroxyl groups which additionally have the potential to serve for a number of chemical functionalisations with various types of reactants (e.g. aldehydes, acetylacetonate, anhydride, and carbon disulfide) [17,18] to generate a target biomaterial to coordinate

with a metal, load a drug, toxic compounds removal and related others [18–21].

The combination of Fe₃O₄ and CS to generate magnetic chitosan nanocomposites as organocatalysts [22], chelating agents for catalytically active transition metals in catalyst preparation as well as non-catalytic applications including metal ion removal [23] and medical applications (i.e. bio-conjugating agent for drug delivery systems [24–26]), clearly illustrates the potential of such nanomaterials. Particularly related to catalytic applications, Fe₃O₄-CS has been utilised for Pd coordination [27] as well as *in situ* production of catalytically active Pd nanoparticles supported on Fe₃O₄-CS [10]. The proposed concept could provide a greener protocol featuring simplicity in catalyst recycling as well as easy work-up and fast processing.

Various types of additional modifications have also been attempted using chitosan as support [28] to provide tunable mechanochemical properties with even new functionalities. However, further post-modification strategies have been rarely investigated for Fe₃O₄-CS [29].

In the present contribution, we have aimed to design a multi-functional magnetic chitosan nanocomposite material using carbon disulfide and dithiocarbamate (DTC) for the functionalization of Fe₃O₄-CS (Mag-CSDTC), followed by Fe³⁺ coordination, to generate a highly active and selective oxidation ferbam-like nanocatalyst (ferbam = ferric dimethyl-dithiocarbamate) [30] for aqueous room temperature oxidations (Fig. 1). CSDTC was first synthesized by

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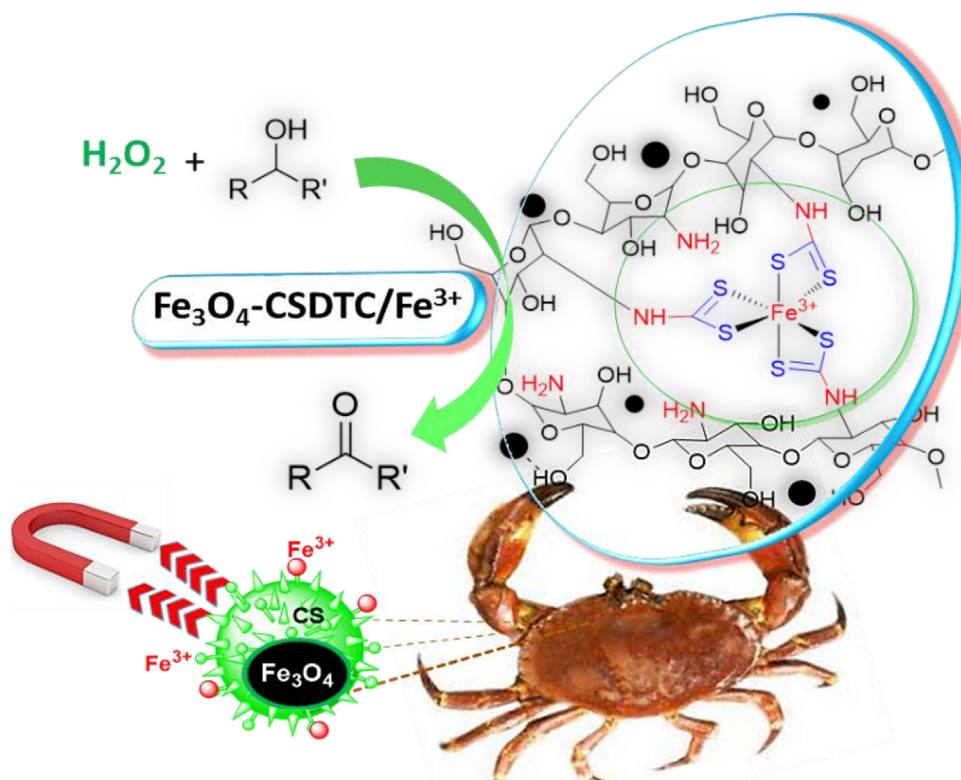


Fig. 1. Design of Ferbam-type nanocatalysts for aqueous room temperature benzylic alcohol oxidations.

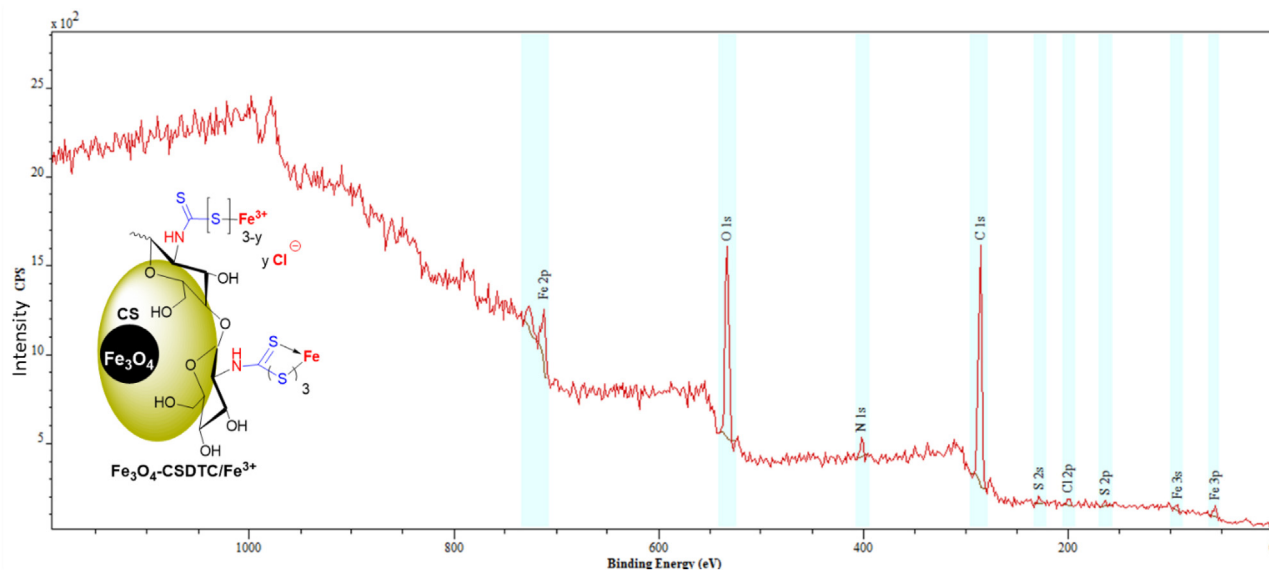


Fig. 2. XPS survey spectra of $\text{Fe}_3\text{O}_4\text{-CSDTC/Fe}^{3+}$.

Muzzarelli and Tanfani [17] finding many applications in drug delivery and water treatment [31–33]. However, there is no evidence for catalytic applications of CSDTC or its modified materials (Fig. 2).

Experimental

Material and instruments

All reagents were purchased from Merck (Germany) and Sigma-Aldrich and used without further purification. IR spectra were recorded on a Shimadzu IR-460 spectrometer. The progress of reactions was monitored by thin layer chromatography (TLC). SEM

images of the samples were recorded with a Zeiss-DSM 960A microscope. TEM images were obtained by using a Zeiss EM 900 electron microscope. The crystalline phases of the nanoparticles were recognized by XRD measurements (Philips-PW1800 diffractometer). X-ray photoelectron spectroscopy (XPS) analysis was performed by Gamma data-scientia ESCA 200 hemispherical analyzer equipped with an Al $K\alpha$ (1486.6 eV) X-ray source.

Preparation of magnetic $\text{Fe}_3\text{O}_4\text{-CS}$ nanocomposites

Synthesis of $\text{Fe}_3\text{O}_4\text{-CS}$ was performed according to a literature protocol [34] with a slight modification. Accordingly, 2 g of CS were dissolved in 100 mL distilled water containing 3 mL glacial acetic

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