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Oxo-vanadium immobilized on polydopamine coated-magnetic nanoparticles (Fe_3O_4): A heterogeneous nanocatalyst for selective oxidation of sulfides and benzylic alcohols with H_2O_2

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ABSTRACT

Polydopamine (PDA)-coated Fe_3O_4 nanoparticles (Fe_3O_4@PDA) were synthesized through a simple and green procedure. In this study, for the first time, successful immobilization of oxo-vanadium (V=O) on surface of Fe_3O_4@PDA as a magnetic adsorbent and stabilizing agent. The structure, morphology and physicochemical properties of the synthesized nanocatalyst [VO(PDA)@Fe_3O_4] were characterized by different analytical techniques such as high resolution transmission electron microscopy (HRTEM), field emission scanning electron microscope (FESEM), energy-dispersive X-ray spectroscopy (EDS), vibrating sample magnetometer (VSM), X-ray photoelectron spectroscopy (XPS), inductively coupled plasma (ICP) and FT–IR spectroscopy. VO(PDA)@Fe_3O_4 nanoparticles illustrated high catalytic activity as a recyclable nanocatalyst in the chemoselective oxidation of sulfides to sulfoxides and benzylic alcohols to aldehydes using green oxidant of hydrogen peroxide in high-yield. The synthesized catalyst can be used several times with no considerable leaching and change in its activity. Both improvement of catalytic performance and easy separation for the reaction procedure were obtained because of the presence of oxo-vanadium and the magnetic core.

1. Introduction

The selective oxidation of sulfides to sulfoxides or sulfones has been an endeavor for a long time and is a valuable conversion used in organic chemistry [1,2]. The outcomes resulted in scientists attempting to validate the chance of formulating an innovative method for the oxidation of sulfides. After the earliest recorded procurement of sulfoxides by Maercker in 1865, a large portion of procedures have been advanced for this transformation of sulfides to sulfoxides [3], and a number of other oxidants, including high-valence metal salts, concentrated HNO_3 [4], *m*-chloroperoxybenzoic acid, sodium metaperiodate [5], halogens, and nitrogen pentoxide, have been vastly applied for the oxidation of sulfides [6–10]. Regrettably, a large portion of the procedures utilize hazardous, toxic reagents [11] or complex reaction methods [12] are convoyed by overoxidation of sulfoxides to the expected sulfones or other undesired by-products [13,14]. To deal with these restrictions and accounting the eco-sustainability, green chemistry, and especially atom economy, a great amount of research has been focused on enhancing innovative and effective catalytic systems, based on the employment of aqueous 30% H_2O_2 as a final ecological oxidant due to its extraordinary advantages such as its low cost, eco-friendliness, efficient-oxygen content, and the formation of water as a side product [15].

Using a homogeneous catalyst in such a process will require the expensive catalyst to be removed from the reaction vessel and a chromatographic method for this retrieval is unavoidable [16]. We are therefore reliant on manufacturing catalytic arrangements that are based on organic material and metal as well as supported catalysts for the activation of hydrogen peroxide in this procedure [17], which can simply be retrieved from the reaction vessel and reemployed. Despite the advancements made over the years, most of the methods mentioned in academic literature describe fruitless efforts at controlling the reaction for selective and excellent yielding procurement of sulfoxide or sulfone. All the while, a selection of vanadium (V) Schiff base complexes have received noticeable praise for their great functional compatibilities and selectivity in the oxidation of sulfides [18].

Nano science enables us to scale down the size of particles and make nanoparticles with unique properties [19]. Many types of nanoparticles have been synthesized for use as catalysts in reactions [20]. The synthesis of magnetic nanoparticles that show high activity in addition to being easily recovered, separated, and reused in reactions are the ideal catalyst from a “green chemist’s” point of

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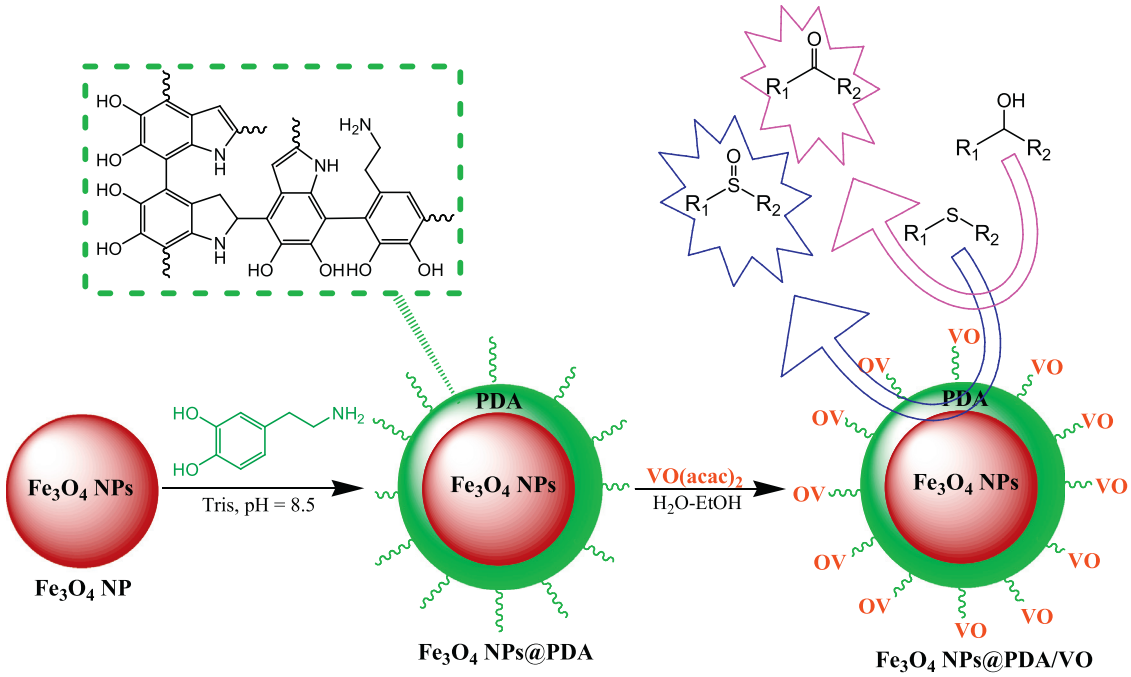

Scheme 1. Synthesis of VO(PDA)@Fe_3O_4 and its application for oxidizing sulfides to sulfoxides chemo-selectively using H_2O_2.

view [21]. Especially Fe_3O_4 nanoparticles have attracted many attentions because of their unique properties [22].

The nm-sized metal oxides are not target selective and are unsuitable for samples with complex matrices [23a]. Therefore, a suitable coating is essential to overcome such limitations. Also, surface modification stabilizes the NPs and also prevents their oxidation. However, MNPs can efficiently be functionalized based on the formation of relatively stable linker between hydroxyl groups on the NPs surface and suitable anchoring agents such as phosphonic acid and dopamine derivatives [23b]. So, PDA as a humic-like substance having a lot of phenolic hydroxyl and amine functional groups on the framework can be used in the modification of MNP. Moreover, the feasibility of complexation of polyphenols or catechol with polyvalent cations in simple aqueous solutions can improve the surface properties and capacity of the PDA@Fe_3O_4 NPs for to adsorption and stabilization of metal ions [23c]. Therefore, the nano-adsorbent (PDA@Fe_3O_4 NPs) has potential ability as stabilizing agent for immobilization of vanadium ions to make a novel magnetically separable and reusable nanocatalyst (Scheme 1). So, in the context of developing the effective and eco-friendly heterogeneous catalysts [24], we conducted synthesis of oxo-vanadium immobilized on polydopamine coated-MNPs (VO(PDA)@Fe_3O_4) as a new catalyst for oxidizing the sulfides to sulfoxides and benzylic alcohols to aldehydes chemo-selectively using hydrogen peroxide as a green oxidant (Scheme 1).

2. Experimental section

2.1. Materials and apparatus

All the reagents were purchased from Aldrich and Merck and were used without any purification. The pure Tris (hydroxy methyl) amino methane hydrochloride ($H_2NC(CH_2OH)_3$.HCl), dopamine hydrochloride, ferricchloridehexahydrate ($FeCl_3$•$6H_2O$), ferrouschloridetetrahydrate ($FeCl_2$•$4H_2O$), sodium hydroxide, deionized water, acetonitrile, vanadyl acetylacetonate, NaCl, ethanol, sulfides were obtained from Sigma Aldrich and Merck. All reagents were of analytical grade and used without further purification. Tris–HCl (pH 8.5, 0.1 M) buffer solution was prepared by dissolving appropriate amount of $H_2NC(CH_2OH)_3$ HCl in DDW and pH was adjusted by adding appropriate amounts of 0.1 M NaOH solution. The crystalline structures of the samples were evaluated by X-ray diffraction (XRD) analysis on a Bruker D8 Advance diffractometer with CuKα radiation at 40 kV and 20 mA. Fourier transform infrared (FT-IR) spectra were recorded with a Perkin Elmer 65 spectrometer in the range of 400–4000 cm^{-1}. Transmission electron microscopy (TEM) analysis was performed on a Phillips CM10 microscope at an accelerating voltage of 200 kV. Magnetization measurements were carried out on a BHV-55 vibrating sample magnetometer (VSM). Thermal stability of the catalyst was investigated by thermogravimetric analysis (TGA, TSTA Type 503) at a heating rate of 10 °C/min under nitrogen atmosphere.

2.2. Preparation of Fe_3O_4, PDA@Fe_3O_4 and VO(PDA)@Fe_3O_4 magnetic nanoparticles

The magnetic Fe_3O_4 nanoparticles were prepared by the chemical coprecipitation method [24a], and the detailed procedure is described below. $FeCl_2$•$4H_2O$ (2 g) and $FeCl_3$•$6H_2O$ (5.2 g) were dissolved into 25 mL deoxygenated water followed by adding 0.85 mL of concentrated hydrochloric acid. The resulting solution was dropped into 250 mL of 1.5 M NaOH solution under vigorous stirring and N_2 protection at 353 K. The obtained magnetic nanoparticles were separated from solution by a powerful magnet and rinsed with 200 mL deionized water three times. Finally, the products were dried at 40 °C to give Fe_3O_4 nanoparticles.

Fe_3O_4 nanoparticles (1 g) were dispersed in 500 mL Tris buffer (10 mM, pH 8.5), then dopamine (1 g) was added, and the mixture solution was mechanically stirred for 24 h at room temperature. After reaction, the PDA@Fe_3O_4 nanoparticles were isolated with a magnet and washed with deionized water and anhydrous ethanol and dried at 40 °C to give PDA@Fe_3O_4.

In the next step, 500 mg of synthesized PDA@Fe_3O_4 was sonically dispersed in EtOH–H_2O (1:1, 100 mL) for 20 min. Then, 0.265 g of vanadyl acetylacetonate (0.001 mol) was dissolved in 20 mL water and added to the obtained mixture. The resulted mixture

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