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Immobilized tungstate on magnetic poly(2-ammonium ethyl acrylamide): A high loaded heterogeneous catalyst for selective oxidation of sulfides using H₂O₂

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ABSTRACT

A heterogeneous tungstate-based catalyst has been prepared for selective oxidation of sulfides to sulfoxides in the presence of 30% H₂O₂. The catalyst was prepared via immobilization of high amounts of WO₄²⁻ onto the cross-linked poly(ammonium ethyl acrylamide) coated magnetic nanoparticles (MNP). FT-IR, TEM, TGA, VSM, XRD, EDX, and CHN analysis were used for characterization of catalyst. Variety of sulfides successfully converted to the related sulfoxides using 1 mol% of catalyst at room temperature in high yields. The catalyst was easily recovered and reused up to 6 times without loss of activity.

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Introduction

Oxidation reactions continue to play an important role in organic chemistry, and the increasing demand for catalytic oxidation methods in modern organic synthesis has led to a range of selective and mild oxidation processes. These reactions can be based on metal catalysis, organocatalysis, or biocatalysis [1]. Among these, catalytic oxidation processes based on transition metals have the broadest and most diverse applications both in laboratory and industry and to date numerous metal-catalytic systems have been reported for various oxidation reactions [1–3].

Application of tungsten species as catalyst was since Nyoyri et al. who used sodium tungstate (Na₂WO₄) to convert cyclohexene to adipic acid [4–6]. After that, various types of homogeneous W-base systems have been broadly examined due to the fact that they have high activity and selectivity in the most applicable oxidation processes including epoxidation of alkenes [7], oxidation of alcohols to aldehydes [8], oxidation of sulfides to sulfoxide [9,10], oxidative cleavage or halogenation of olefins [11], oxidative desulfurization [12], and metathesis and isomerization of alkenes

[13]. Importantly, they are activated with H₂O₂ as terminal oxidant which is an environmental oxidant due to the co-production of water and owing a large amount of active oxygen [4–14]. Although homogeneous W-based catalysts have high activity and selectivity, but they suffer from some important drawbacks like catalyst recovery/reusability and the essential use of phase transfer catalyst has also made them impractical, especially for industrial production processes [15–18]. Recently, immobilization (heterogenization) of W-spices onto the solid support including silica [19–21], ordered mesoporous silica [22–24], magnetic nanoparticles [25–27], TiO₂ [28], and layered double hydroxide [29] has been growing up to overcome these problems.

However, in this regard, considerable effort has been exerted to improve the loading of tungsten species on the support surface and its ability of transferring to organic phase. It seems that functionalization of solid support by polymeric multilayer shell (grafting methods) provides a large number of active catalytic sites containing W-spices with increasing solubility in different organic solvents because of the carbon skeleton [25,30–32].

Continuing our works on polymeric supported catalysts [33,34], in this work, we report a novel Na₂WO₄/H₂O₂ based catalytic system in which tungstate is immobilized into the network of the cross-linked poly (ammonium ethyl acrylamide) coated on magnetic nanoparticles (MNP). The applicability of ensuing

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catalyst was probed through selective oxidation of sulfides to sulfoxides. To the best of our knowledge, only a few polymeric/magnetic/W-based catalysts are reported for oxidation of sulfide to sulfoxide [17,25,35–37]. Sulfoxides are broadly applicable intermediates in organic synthesis for C–C bond formation, molecular rearrangement or as chiral auxiliaries [38,39]. In addition, they are substructures of many pharmaceuticals products, such as drugs, and agrochemicals [40,41]. The traditional procedures for this transformation usually suffer from some drawbacks importantly overoxidation of sulfoxides to sulfones. Using toxic, expensive, and equimolar amount of oxidants, difficult separation of product and deoxygenated waste from the reaction mixture are other disadvantages of most of the reported protocols [42–45]. In the context of the reported supported heterogeneous catalysts, low loading of oxidant is notable [46–48]. Thus, presentation of effective, selective, and green catalysts can be useful in both laboratory and industry.

Experimental

Reagents and analysis

Azobisisobutyronitrile (AIBN, Kanto, 97%) was recrystallized from ethanol. Methyl acrylate (Sigma–Aldrich) was distilled before use. All other chemical compounds were obtained from Merck and were used without further purification.

The chemical structures of samples were characterized by Fourier transform infrared (FTIR) spectroscopy using an ABB Bomem MB-100 spectrometer. Thermal gravimetric analysis (TGA) was performed using a TGA Q 50 thermogravimetric analyzer with a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ under a nitrogen atmosphere. A Philips CM30 transmission electron microscope (TEM) was utilized to investigate the morphology of nanoparticles. Magnetizations of samples were measured by vibrating sample magnetometer (Meghnatis Daghigh Kavir Co., Kashan, Iran). Tungstate ions were measured by atomic absorption spectrometer (AAS, Shimadzu 680 A) or inductively coupled plasma–optical emission spectrometry (ICP-OES, Perkin-Elmer DV 4300). The XRD pattern was recorded on a RigakuD/Max-3c X-ray diffractometer.

Synthesis of vinyl functionalized magnetic nanoparticles (MNP@MPS)

Silica coated Fe_3O_4 nanoparticles (MNPs) were synthesized based on our previously reported method [49]. 1.0 g of MNP was dispersed in 40 mL dry ethanol followed by addition of 2 mL of ammonium solution. 3 mL of 3-(trimethoxysilyl)propylmethacrylate (MPS) was added and the mixture was stirred at $65\text{ }^{\circ}\text{C}$ for 48 h. The MPS coated magnetic nanoparticles (MNP@MPS) were magnetically separated and washed several times with methanol ($4 \times 40\text{ mL}$) and dried under vacuum at $50\text{ }^{\circ}\text{C}$.

Synthesis of catalyst (MNP@CP(AEAM))/W

To a suspension of fully dispersed MNP@MPS (0.50 g in 200 mL methanol) in a 500 mL single-necked flask, 2 g methyl acrylate, 0.5 g of MBA, and 70 mg of AIBN were added. The flask was completely deoxygenated by bubbling purified argon for 30 min and then equipped with fractionating column, Liebig condenser, and a receiver. The polymerization process initiate when heating the flask from ambient temperature to the boiling state to in an oil bath. The reaction was ended after about 130 mL of methanol was distilled from the reaction mixture within 5 h. The obtained cross-linked poly(methylacrylate) coated MNP (MNP@CP(MA)) were magnetically separated and washed two times with water and three times with methanol (1.40 g product).

MNP@CP(MA) nanoparticles (1.0 g) were dispersed by ultrasonic in 60 mL methanol in a 100 mL single-necked flask. Then, 25 mL ethylenediamine was added and the mixture was stirred at $60\text{ }^{\circ}\text{C}$ for 72 h. Cross-linked poly(aminoethyl acrylamide) coated MNP (denoted as MNP@CP(AEAM)) was magnetically separated and washed three times with 50 mL methanol and then dried at $60\text{ }^{\circ}\text{C}$ for 12 h (0.92 g product).

0.50 g of MNP@CP(AEAM) was dispersed in a 10 mL deionized H_2O and then 2.5 mL HCl (37%) was added and the mixture stirred for 3 h. Finally, the resulting nanoparticles (MNP@CP(AEAM))/Cl were magnetically separated and washed with H_2O ($3 \times 50\text{ mL}$) and ethanol ($2 \times 50\text{ mL}$) and dried at r.t.

The resulting powdered materials were subjected to anion exchange reaction. The resulting MNP@CP(AEAM)/Cl was added to 50 mL saturated of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (1.0 g). The mixture was stirred for 2 days at room temperature. The solid products (MNP@CP(AEAM))/W were then magnetically separated, washed with water ($5 \times 100\text{ mL}$) and methanol ($2 \times 20\text{ mL}$) and dried under vacuum at $50\text{ }^{\circ}\text{C}$ (0.43 g product).

General procedure for oxidation of sulfide to sulfoxide catalyzed by MNP@CP(AEAM))/W

In a round-bottomed flask, 1.5 mmol H_2O_2 , 1 mmol sulfide, 4 mL solvent MeCN: H_2O (1:1) and 1 mol% MNP@CP(AEAM))/W (11 mg) were mixed and stirred at room temperature for a defined time. After the completion of the reaction, the catalyst was separated by an external magnet and washed with methanol, dried at $50\text{ }^{\circ}\text{C}$ and stored for another run. The product mixture was extracted by ethyl acetate and analyzed by gas chromatography (GC).

Results and discussion

Preparation and characterization of catalyst

The catalyst (MNP@CP(AEAM))/W was constructed in a few steps showed in Scheme 1. Fe_3O_4 magnetic nanoparticle was selected as catalyst core with the aim of facilitating the catalyst separation using external magnet. Coating of Fe_3O_4 by SiO_2 causes thermal and chemical stabilities and easier functionalization. Then, silica coated Fe_3O_4 (MNP) was functionalized by MPS to allow the covalent grafting of polymer onto the surface of MNP in the next step. The coating of cross-linked poly(methyl acrylate) shell onto the MNP core was performed by copolymerization of methyl acrylate and MBA as cross-linker through the distillation–precipitation–polymerization method [50]. This multi-layered core–shell structure efficiently increases the surface to volume ratio and provides enormous active sites onto the catalyst surface. Afterward, amidation of MNP@CP(MA) by ethylenediamine followed by neutralization of terminal NH_2 with HCl provides MNP@CP(AEAM)/Cl. The resulting powdered materials were then subjected to anion exchange reaction with WO_4^{2-} as oxidant spice to produce final catalyst MNP@CP(AEAM))/W.

The surface modifications of all catalyst synthetic intermediates were screened using FT–IR analysis (Fig. 1). As indicated in Fig. 1, the characteristic bands within 640, 1035, and $3200\text{--}3500\text{ cm}^{-1}$ in all samples (except Na_2WO_4) can be indexed to the typical stretching vibration of Fe–O, Si–O–Si, and O–H, respectively. The IR spectrum of MNP@MPS showed absorption peaks at 1461 and 1713 cm^{-1} attributed to C=C and C=O of MPS and confirmed the grafting of MPS. In the IR spectrum of MNP@CP(MA) characteristic peak of cross-linked poly(methyl acrylate) can be seen at 1735 cm^{-1} attributed to ester groups. This also was confirmed by increasing the intensity of absorption peak at 2929 related to stretching C–H of alkyl groups. Amidation of CO_2Me functional

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