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Application of surface modified nano ferrite nickel in catalytic reaction (epoxidation of alkenes) and investigation on its antibacterial and antifungal activities

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ABSTRACT

Newly, magnetic nanoparticles have extensively been used as alternative catalyst supports, in the view of their high surface area which results in high catalyst loading capacity, high dispersion, low toxicity, environmental preservation, distinguished stability, and suitable catalyst reusing. In the present study, the magnetite nanoparticles, $NiFe_2O_4$@Ag and $NiFe_2O_4$@Mo, were synthesized and characterized. The antimicrobial activities and catalytic properties of synthesized nanoparticles were tested afterwards. For synthetizing the nanoparticle $NiFe_2O_4$@Ag, silver ions were loaded onto the surface of the modified $NiFe_2O_4$ and reduced to silver crystal by adding $NaBH_4$. The antibacterial effects of $NiFe_2O_4$@Ag were examined against two species of soil and plant related bacteria named *Bacillus subtilis* (gram positive) and *Pseudomonas syringae* (gram negative), respectively. The antifungal activity of this nanoparticle was evaluated against two species of plant pathogenic fungi called *Alternaria solani* and *Fusarium oxysporum*. Biological results indicated that the synthesized material has shown an excellent antibacterial and antifungal activity against all examined bacteria and fungi so that, their growth were completely inhibited 24 h after treatment with $NiFe_2O_4$@Ag. For the synthesis of a heterogeneous catalyst $NiFe_2O_4$@Mo, complex $Mo(CO)_6$ was loaded onto the surface of the modified $NiFe_2O_4$ nanoparticle. This catalyst was found as an efficient catalyst for epoxidation of cis-cyclooctene and a wide variety of alkenes, including aromatic and aliphatic terminal ones using tert-butyl hydroperoxide as oxidant. This new heterogenized catalyst could easily be recovered by using a magnetic separator and reused four consecutive and loss only 13% of its catalytic activity.

1. Introduction

The nanosized MFe_2O_4 (magnetite), has been recognized as a significant member of spinel type ferrite, which comprises remarkable utilization potentials in tissue imaging [1], purposed drug transfer [2], environmental area [3], memory storage systems, the sensors, catalysis, magnetic resonance imaging (MRI) and magnetically managed drug transfer [4–5]. So far, among different explored materials, the spinel ferrites MFe_2O_4 that M could be Co, Mn or/and Ni, are appearing as promising materials, particularly for biomedical applications. The nanoparticles (NPs) are generally synthesized by physical and chemical procedures, for example laser ablation, chemical or physical vapor deposition, coprecipitation [6], microemulsion [7], sol-gel [8] and ultrasound irradiation [9]. Recently, thermal parsing technique was reported as an opportunity for making mono-dispersed magnetic nanoparticles. The utilization of nanoparticles in organic reactions has been engrossed superb interest due to their action as highly effective catalysts. Nanocatalysts may act as a bridge to fill the gap between homogeneous and heterogeneous catalysis because of their well dispersion attributes, great catalytic activity and selectivity.

The nanoparticles can also possess antimicrobial activity for example silver nanoparticles are appearing as an innovative generation of antibacterial factor [10]; which are utilized in hygiene [11], medical applications [12], and antibacterial water filter [13]. Antimicrobial specifications of silver ions and silver based compounds have been offered for a diversity of applications. Many studies have demonstrated that silver nanoparticles are extremely stable and toxic to bacteria, fungus, and viruses for instance *Escherichia coli*, *Staphylococcus aureus*, *Bacillus subtilis*, *Klebsiella mobilis*, *Mycobacterium tuberculosis*, *Candida albicans*, *hepatitis B*, human immunodeficiency virus-1, and syncytial virus [14–15]. Silver nanoparticles do not only have a strong antibacterial activity but also can inhibit a broad spectrum of bacteria and fungi [16]. In this study, we have synthesized $NiFe_2O_4$ nanoparticle by hydrothermal manner with extremely hydrophilic uniform spherical nano-assemblies of ultra-small amine functionalized $NiFe_2O_4$ nanoparticle. The synthesis

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method was included heating metal chloride precursors in ethylene glycol in attendance of sodium acetate and ethanolamine. Ethanolamine was utilized as a stabilizer and also for the surface functionalization with $-NH_2$ groups. In the other step, molybdenum hexacarbonyl was stabilized on the $NiFe_2O_4$ spinel, the catalyst of $NiFe_2O_4$@Mo was formed and its catalytic activity was checked. The activity and reusability of catalyst were investigated in alkenes epoxidation with TBHP. To assay the nanoparticle antibacterial activity, Ag^+ ions were stabilized on the $NiFe_2O_4$ spinel, and its antibacterial effect was evaluated against two species of soil and plant related bacteria named *Bacillus subtilis* (gram positive) and *Pseudomonas syringae* (gram negative), respectively. The antifungal activity of $NiFe_2O_4$@Ag was assessed against two species of plant pathogenic fungi called *Alternaria solani* and *Fusarium oxysporum*.

2. Experimental

2.1. Materials and methods

Ferrite chloride hexahydrate ($FeCl_3.6H_2O$), Nickel chloride ($NiCl_2$), Ethylene glycol(EG), Ethanolamine (EA), Sodium acetate (NaAc), Silver nitrate ($AgNO_3$), Sodium borohydride ($NaBH_4$), Tetrahydrofuran (THF), Hexa carbonyl Molybdenum ($Mo(CO)_6$), Potato Dextrose Agar (PDA) and Nutrient Agar (NA) were in analytical grade and used as received without further purification. All metal chlorides, PDA and NA were bought from the Merck, Germany. Ethylene glycol and ethanolamine have been purchased from Sigma-Aldrich. Bacteria and fungi were provided by Department of Plant Protection, Faculty of Agriculture, Ferdowsi University of Mashhad, Iran.

2.2. Preparation of $NiFe_2O_4$ nanoparticle

Amine functionalized super-paramagnetic $NiFe_2O_4$ nanoparticle was synthesized by the thermal decomposition of $NiCl_2$ and $FeCl_3$ in ethylene glycol in attendance of sodium acetate and ethanolamine. In summary, $FeCl_3.6H_2O$ (1.13 g, 4.2 mmol) and anhydrous $NiCl_2$ (0.499 g, 2.1 mmol) were taken in 30 ml ethylene glycol and 0.5 g of sodium acetate was added to the obtained solution. The solution was stirred for 30 min at 80 °C pursued by addition of 15 ml of ethanolamine. Total solution was heated at 150 °C for 12 h under the hydrothermal condition until the black colloidal particles emerged in the reaction mixture. Then it was cooled down till room temperature. Particles were recovered using a magnetic separator, washed with distilled water for several times and dried in hot air oven at 80 °C for 2 h.

2.3. Synthesis of $NiFe_2O_4$ @ Ag

For the synthesis of $NiFe_2O_4$@Ag nanoparticle, $NiFe_2O_4$ (1 g) was dispersed in 3 ml distilled water in a 50 ml flask. 1 ml of 0.1 M $AgNO_3$ was added to the solution and stirring was continued for 4 h. Then, $NiFe_2O_4$ was removed and the free Ag + ions attached to the outer surface of $NiFe_2O_4$ was washed with distilled water. $NiFe_2O_4$ was again dispersed in 3 ml distilled water and pursued by dropping 4–5 ml of 0.05 M $NaBH_4$ solution. When the reaction was completed, the sample was filtered and washed with distilled water. Finally, $NiFe_2O_4$@Ag was dried at 100 °C for 3 h.

2.4. Synthesis of $NiFe_2O_4$ @ Mo

In a beaker of 50 ml, 0.1 g of $Mo(CO)_6$ with 15 ml of Tetrahydrofuran (THF) as a solvent were stirred for 30 min under the UV light. The contents were transferred into a 50 ml flask and 0.3 g $NiFe_2O_4$ was added to the solution and refluxed at 80 °C for 6 h. The obtained precipitate was washed with tetrahydrofuran. Lastly, $NiFe_2O_4$@Mo was dried at 80 °C for 2 h.

2.5. Antibacterial activity test

The antibacterial activity of $NiFe_2O_4$@Ag nanoparticles, was evaluated using agar diffusion method, relatively quickly and easily. *Bacillus subtilis* (as a gram positive) and *Pseudomonas syringae* (as a gram negative) bacteria were selected for this experiment. The standard strains of bacteria were cultured on Nutrient Agar medium and incubated at 37 °C for 24 h. After a period of incubation, bacterial suspensions were prepared from the bacterial colonies culture [17]. Bacterial suspensions were prepared with 10^6 CFU/ml concentration using a hemocytometer, then streaked over the surface of nutrient agar plates containing different concentrations of silver nanoparticle (0.066, 0.66 and 6.66 $mg \cdot ml^{-1}$) to obtain uniform growth. The number of grown colonies were counted 24 and 48 h after incubation at 37 °C. Each treatment had three replications. The silver-free NA plates were cultured under the same condition and used as controls.

2.6. Antifungal activity test

The antifungal activity of $NiFe_2O_4$@Ag nanoparticles were tested on two plant pathogenic fungi called *Alternaria solani* and *Fusarium oxysporum*, in the plates containing PDA (Potato Dextrose Agar). The media was completed with 0, 0.05, 0.5 and 5 $mg \cdot ml^{-1}$ of silver nanoparticle ($NiFe_2O_4$@Ag), independently. An agar plug of 8 mm diameter containing grown fungi was simultaneously inoculated at the center of each plates and incubated at 35 °C. Silver-free PDA plates, cultured under the same condition and used as controls. Growth diameter was measured after 2, 4 and 6 days of incubation. Each treatment had three replications.

2.7. General procedure for epoxidation of alkenes

The $NiFe_2O_4$@Mo catalyst was tested for its catalytic activity. To a 10 ml round bottom flask equipped with a magnetic stirring bar, alkene (0.5 mmol), oxidant, $NiFe_2O_4$ @Mo catalyst and solvent were mixed and refluxed. After the reaction, the catalyst was removed by a magnetic separator and the reaction products were analyzed by gas chromatography cum-mass spectrometry. The analysis time for each sample was approximately 20 min. The reaction was also performed in the absence of catalyst at the same experimental condition. The details of the reaction condition are summarized in the Tables 2 and 3.

2.8. Catalyst reusability

In a typical experiment, after regaining the catalyst from the reaction mixture, it was washed with CCl_4 several times, dried in oven at 80 °C and reused under the same condition. The precise procedures of the recycling test are summarized in the Table 3. The nature of the regained catalyst was investigated by FT-IR spectra, in which the CO bands have been disappeared in the FT-IR spectra (Fig. 1).

2.9. Characterization studies

High resolution X-ray diffraction (XRD) patterns were collected using Bruker D8 discover diffractometer with Cu Kα radiation ($\lambda = 0.15406$ nm) in the 2θ range from 20° to 80°. Fourier transform infrared spectra (FTIR) were recorded in the range 4000–400 cm^{-1} on a Rayleigh WQF-520 spectrum one using the KBr pellet technique. The samples morphology were investigated using field emission scanning electron microscopy (FE-SEM, Mira 3-XMU) with an accelerating voltage of 15 kV. The thermo-gravimetric experiments were conducted on a TG-DTA 503 STA thermo-analyzer under air atmosphere with a heating rate of 10 °C/min from the room temperature till 600 °C. The surface composition of $NiFe_2O_4$@Mo catalyst was investigated through the X-ray photoelectron spectroscopy (XPS) in an ESCA-2000 (VG microtech) apparatus. Chemical analysis was performed by inductive