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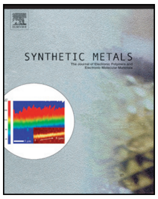

Synthesis, characterization and morphology of new magnetic fluorochromate hybrid nanomaterials with triethylamine surface modified iron oxide nanoparticles

Ali Maleki*, Rahmatollah Rahimi, Saied Maleki

Department of Chemistry, Iran University of Science and Technology, Tehran 16846-13114, Iran

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ABSTRACT

Magnetic fluorochromate Fe_3O_4@SiO_2@TEA@[CrO_3F] was synthesized by ethylene glycol route. The structures, morphologies and properties of the catalyst were characterized by using X-ray diffraction (XRD), Fourier transform infrared (FT-IR), elemental analysis, X-ray fluorescence (XRF), solid state UV–vis, transmission electron microscopy (TEM), scanning electron microscope (SEM), N_2 adsorption–desorption (BET and BJH) and vibrating sample magnetometer (VSM). The quantity of chromium is approximately 0.32%, which confirms the immobilization amount of $[CrO_3F]^-$ which is equal with 0.006 mol/100 g.

1. Introduction

The selective oxidation of alcohols to the related aldehydes is a commonly used conversion in organic synthesis and therefore types of methods have been developed. A good number of Cr(VI) complexes are being used in the oxidation of organic compounds. Halochromates have been used as mild and selective oxidizing reagents in synthetic organic chemistry. The search for new oxidizing agents is of interest to synthetic organic chemists. Many such reagents have been developed in recent years with some success. In recent years, important improvements were achieved by the use of new oxidizing agents such as benzimidazolium fluorochromate, N-methyl benzylammonium fluorochromate, tributylammonium chlorochromate, pyridinium fluorochromate, imidazolium dichromate and isoquinolinium bromochromate [1–5].

Homogeneous catalysts usually activate at relatively mild states and show high activities and selectivities but have difficult separation and regeneration of the catalyst from the reaction mixture. Covalent grafting of a homogeneous catalyst on solid supports may reduce the active surface area and reactivity of immobilized catalysts.

Immobilized homogeneous catalysis has achieved a new impulse with the advent of nanotechnology. Due to the large surface area of nanoparticles, high loadings of catalytically active sites are guaranteed and thus nanoparticles-supported homogeneous catalysts display high catalytic activity and selectivity. In spite of this, nanometer-sized particles are difficult to separate by traditional filtration techniques and expensive ultracentrifugation is often needed to have a good separation of the catalyst from the reaction mixture. This inadequacy could be prevented using magnetic nanoparticle (MNPs) supports. An external magnet could easily separate the immobilized catalysts from the reaction mixture, which results in more successful separation than usual methods [6].

We have focused on using magnetic nanoparticles Fe_3O_4 (MNPs) for immobilization of fluorochromate as separable oxidant catalyst. In this paper, the magnetically nanoparticles Fe_3O_4 (MNPs) were synthesized. The external surface of Fe_3O_4 was coated with silica shell to obtain Fe_3O_4@SiO_2 (SCMNPs). Then, Fe_3O_4@SiO_2 nanoparticles were functionalized by 3-chloropropyltrimethoxysilane and triethylamine to create cationic part as a support (TEASCMNPs). Lastly, anionic fluorochromate was immobilized on TEASCMNPs through ionic interaction and Fe_3O_4@SiO_2@TEA@$[CrO_3F]^-$ (FC-TEASCMNPs) was formed. Because of the presence of magnetite core, the prepared hybrid

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* Corresponding author. Tel.: +98 21 77240540 50; fax: +98 21 73021584.
E-mail addresses: maleki@iust.ac.ir, alimaleki_2003@yahoo.com (A. Maleki).

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nanomaterials have magnetic properties which make them easily separable in potential applications in various fields such as catalytic oxidation of olefins, alcohols and multicomponent reactions where they can act as magnetically recoverable catalyst.

2. Experimental

2.1. Materials and instrumentation

All chemicals were purchased from Merck, Fluka and Aldrich chemical companies and were used without further purification.

X-ray powder diffraction (XRD) analysis was conducted on Philips-PW1800 diffractometer in the 2θ range of 4–90°. Fourier transform infrared (FT-IR) spectra were recorded in transmission mode with a Perkin–Elmer Spectrum RXI FT-IR spectrometer. The powder samples were ground with KBr and compressed into a pellet. FT-IR spectra in the range 4000–400 cm^{-1} were recorded in order to investigate the nature of the chemical bonds formed. Chemical analyses of the samples were carried out with Philips-PW1480 X-ray fluorescence (XRF). Solid state UV–vis was registered by Jasco spectrometer. Scanning electron microscopy (SEM) images of the samples were taken with Zeiss-DSM 960A microscope. Transmission electron microscopy (TEM) analysis was performed using a Zeiss EM 900 electron microscope operating at 80 kV. VSM measurements were performed by using a Vibrating sample magnetometer (BHV-55, Riken, Japan) in the magnetic field range of −10,000–10,000 Oe at room temperature. The specific surface area (BET method), the total pore volume and the mean pore diameter (BJH method) were measured using a N_2 adsorption–desorption isotherm by using an ASAP^{TM} micromeritics 2020 instrument.

2.2. Preparation of Fe_3O_4 magnetite nanoparticles (MNPs)

Fe_3O_4 nanoparticles were prepared by ethylene glycol method. 100 ml mixed salt solution of anhydrous $FeCl_3$ and (0.3 M) and $FeCl_2{\cdot}4H_2O$ (0.15 M) was taken in three necked round bottom flask fixed with air condenser. 16 g of urea and 400 ml of ethylene glycol was added. The reaction mixture was mixed well and then refluxed at 160 °C with constant magnetic stirring for 6 h. After one and half-hour the color of solution turned to black and then the precipitate formed. The reaction mixture was cooled to room temperature and the colloidal black precipitate was centrifuged at 2000 rpm. Precipitate was washed with methanol and acetone and then dried at 60 °C for 6 h under vacuum [7].

2.3. Encapsulation of Fe_3O_4 nanoparticles with SiO_2 (Fe_3O_4@SiO_2) (SCMNPs)

Fe_3O_4 nanoparticles were encapsulated by SiO_2 through sol–gel process. First, 1 g Fe_3O_4 nanoparticles, 2 mL tetraethylorthosilicate (TEOS) and 0.4 g alkylphenols polyoxyethylene (OP-10) were added into 80 mL deionized water, and the mixture was ultrasonicated to become a stable emulsion. After 1 h, the emulsion was added into a mixture of 100 mL ethanol and 12 mL $NH_3{\cdot}H_2O$. The reaction solution was stirred at a rate of 400 rpm at room temperature for 4 h. The obtained products were magnetically separated, washed by ethanol for times and dried at 80 °C [8].

2.4. Functionalizing of silica coated magnetite nanoparticles Fe_3O_4@SiO_2 (SCMNPs) with triethylamine (TEASCMNPs)

The synthesis of the TEA-functionalized MNPs was like to that expressed in formerly with some changes. First, 1.0 g dried Fe_3O_4@SiO_2 were suspended in 25 mL toluene. Then 3-chloropropyltrimethoxysilane (5 g) was added. The suspension was stirred mechanically and refluxed at 90 °C for 24 h. After cooling to room temperature, the consequential product was collected by an external magnetic field and washed with 30 mL toluene, 50 mL ethanol–water mixture (1:1 v/v) and 50 mL deionized water in turn. After drying in vacuum at 60 °C for 8 h, the as ready chloropropyl-modified magnetic silica nanoparticles were placed in a flask containing 50 mL toluene and triethylamine (TEA) (3.1 g). The mixture was refluxed at 87 °C with stirring for 24 h. The solid product was then separated by a magnet, washed with methanol (50 mL), petroleum ether (50 mL), absolute ethyl alcohol (50 mL), and water (50 mL) sequentially and dried in vacuum [9].

2.5. Synthesis of fluorochromate(VI) $[CrO_3F]^-$

Chromium(VI) oxide (2 g, 0.02 mol) was dissolved in water in a polyethylene beaker and 40% hydrofluoric acid (1.5 mL, 0.03 mol) was added under continuous magnetic stirring with 1000 rpm at 0 °C until an orange solution was formed [10].

2.6. Synthesis of Fe_3O_4@SiO_2@TEA@$[CrO_3F]$ (FC-TEASCMNPs)

Fe_3O_4@SiO_2@TEA (1 g) was dispersed into 100 mL of distilled water, and $[CrO_3F]^-$ (0.1 mmol) was added. The resulting mixture was left for stirring for 24 h at room temperature. Then, the resulting Fe_3O_4@SiO_2@TEA@$[CrO_3F]$ was washed with water and diethyl ether thoroughly and dried under vacuum at 60 °C [11].

3. Results and discussion

3.1. Synthesis of magnetite fluorochromate nanomaterials

The order of stages in the immobilization of magnetite nanoparticles with fluorochromate has been shown in Fig. 1. In the first stage, Fe_3O_4 magnetic nanoparticles were synthesized by ethylene glycol method. In our work, $FeCl_3$, $FeCl_2{\cdot}4H_2O$ and urea were dissolved in ethylene glycol, and then $Fe(OH)_3$ and $Fe(OH)_2$ precipitated. $CO(NH_2)_2$ plays a key role in the synthesis of Fe_3O_4. $CO(NH_2)_2$ is easily hydrolyzed at a high temperature in solution, and amounts of water were present in our system originating from the ethylene glycol