



Original article

Synthesis and characterization of a new magnetic bromochromate hybrid nanomaterial with triethylamine surface modified iron oxide nanoparticles



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ABSTRACT

We describe a novel method for the synthesis a new magnetic bromochromate hybrid nanomaterial, Fe₃O₄@SiO₂@TEA@[CrO₃Br], as a catalyst. The physical properties, morphology and magnetic investigations of magnetic bromochromate hybrid nanomaterials are identified by transmission electron microscopy (TEM), scanning electron microscopy (SEM) and vibrating sample magnetometer (VSM) techniques. Fourier transform infrared (FT-IR), elemental analysis, X-ray fluorescence (XRF), X-ray diffraction (XRD) were also used for structural identification. The quantity of chromium is approximately 0.38%, which confirms to the immobilization amount of [CrO₃Br]⁻ and is equal to 0.007 mol/100 g.

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1. Introduction

A series of compounds containing chromium (VI) has been examined as versatile reagents capable of oxidizing almost every oxidizable functional group. New chromium (VI) reagents were also tested for the effective and selective oxidation of organic substrates, specifically alcohols, under mild conditions. In recent years, considerable progress was achieved by the application of these new oxidizing agents. Quaternary ions, such as ammonium and phosphonium, are often used as phase transfer catalysts. This could make triphenylpropylphosphonium bromochromate (VI) a more useful and strong oxidizing agent. This compound was used for quantitative oxidation of many organic substrates [1,2].

Over the last decade, magnetic organic–inorganic nanocomposites have become of considerable interest as magnetic catalysts in both academic and industrial fields. The use of these magnetic nanoparticle catalysts can address the isolation and recycling problem encountered in many heterogeneous and homogeneous catalytic reactions, since they can also be recovered with an external magnetic field and their catalytic efficiency remains after many repeated reaction cycles [3]. Most importantly, the magnetic-supported catalysts show not only high catalytic activity, but also high degree of chemical stability and they do not swell in organic solvents.

The Fe₃O₄ nanoparticles are easily prepared and surface functionalized and can be isolated and recycled from the solution by an external magnetic field. Thus, the catalyst supported on Fe₃O₄ nanoparticles can be easily separated from the reaction system and reused. At present, much attention is focused on the synthesis of magnetic core–shell structures by coating a SiO₂ shell around a preformed nanoparticle. Silica coatings can not only keep the magnetic cores from erosion in acidic solutions, but also effectively screen from intersystem dipolar interactions, and provide a platform for easy surface modification by silanol groups that are useful for practical applications. As a result, the silica-coated, magnetic nanoparticles have received more and more attention as promising candidates for wide applications.

Homogeneous catalysts show higher catalytic activities than their heterogeneous counterparts because of their solubility in reaction media, which increases catalytic site accessibility for the substrate. But, the recycling of homogeneous catalysts is often tedious and time consuming and there is also product contamination observed when these catalysts are reused. Transition metals have been considerably studied because of their ability for use as catalysts in a wide range of reactions. However, homogeneous metal catalysts are easily deactivated through the formation of dimeric peroxo and m-oxo species. To overcome the aforementioned drawbacks, the recent applications of complex of metal ions supported on superparamagnetic Fe₃O₄@SiO₂ nanoparticles were reported as an efficient, selective and recyclable catalyst for reactions [4–8].

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We report in this paper on the preparation and chemical–physical properties, morphology, and magnetic investigations of new bromochromate immobilized Fe_3O_4 magnetic nanoparticles, $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{TEA}@\text{[CrO}_3\text{Br]}$, as a catalyst. The resulting $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{TEA}@\text{[CrO}_3\text{Br]}$ showed a superparamagnetic property with a high magnetic saturation (M_s) value of 37 emu/g at room temperature, allowing the bromochromate, as the magnetic component of the support, to be rapidly and efficiently collected with the help of a magnet.

2. Experimental

2.1. Materials and instrumentation

All chemicals were purchased from Merck, Fluka and Aldrich chemical companies and were used without further purification. Fourier transform infrared (FT-IR) spectra were recorded with Perkin-Elmer Spectrum RXI FT-IR spectrometer; using pellets of the nanomaterials diluted in KBr. The crystalline phase of the nanoparticles were recognized by means of X-ray diffraction (XRD) measurements using $\text{Cu K}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$) on a Philips-PW1800 diffractometer in the 2θ range of $4\text{--}90^\circ$. Chemical analyzes of the samples were completed with Philips-PW1480 X-ray fluorescence (XRF). Scanning electron micrograph (SEM) images of the samples were taken with Zeiss-DSM 960A microscope with attached camera. Transmission electron microscopy (TEM) images were obtained through Zeiss EM 900 electron microscope operating at 80 kV. Magnetic susceptibility measurements were performed using a vibrating sample magnetometer (BHV-55, Riken, Japan) in the magnetic field range of $-10,000$ Oe to $+10,000$ Oe at room temperature.

2.2. Synthesis of magnetite nanoparticles (Fe_3O_4 MNPs)

In general, FeCl_3 (4.8 g) and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (2.0 g) were dissolved in distilled water (40 mL) which was deaerated by bubbling with nitrogen for 30 min to remove any dissolved oxygen. The solution was then stirred for 15 min for complete mixing under nitrogen gas. An aqueous NaOH (8.75 g in 50 mL) was added to the iron salts solution rapidly and solution changes color from orange to black immediately. The resulting solution was then stirred at room temperature for 30 min. The particles were collected with a handheld magnet and centrifuged two times after washing with water. The final precipitate was then dried overnight in a vacuum oven at 60°C [9].

2.3. Preparation of silica coated magnetite nanoparticles ($\text{Fe}_3\text{O}_4@\text{SiO}_2$) (SCMNPs)

Firstly, Fe_3O_4 nanoparticles (2.0 g) were dispersed in a solvent mixture of ethanol (70 mL) and H_2O (10 mL) by sonication for 15 min. Then $\text{NH}_3 \cdot \text{H}_2\text{O}$ (5 mL) and tetraethyl orthosilicate (TEOS) (5.0 mL) were added sequentially. The mixture was stirred for 24 h under vigorous mechanical stirring. Then, the $\text{Fe}_3\text{O}_4@\text{SiO}_2$ precipitate was collected by a permanent magnet, and rinsed repetitively with deionized water until the filtrate was neutral. Then $\text{Fe}_3\text{O}_4@\text{SiO}_2$ was washed three times with ethanol and dried in vacuum [10–12].

2.4. Functionalizing of silica coated magnetite nanoparticles $\text{Fe}_3\text{O}_4@\text{SiO}_2$ (SCMNPs) with triethylamine (TEASCMNPs)

The synthesis of the TEA-functionalized MNPs was like to that described in previously with some modifications. Firstly, 1.0 g of dried $\text{Fe}_3\text{O}_4@\text{SiO}_2$ was 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 resulting 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 prepared chloropropyl-modified magnetic silica nanoparticles were placed in a flask containing 50 mL toluene and triethylamine (TEA) (3.1 g) and 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) consecutively and dried in vacuum [13].

2.5. Synthesis of bromochromate (VI), $[\text{CrO}_3\text{Br}]$

Hydrogen bromide (HBr 47%, 1 mL) was added to a solution of CrO_3 (0.01 mol/100 mL) in H_2O under stirring at room temperature until an orange solution was formed [2].

2.6. Synthesis of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{TEA}@\text{[CrO}_3\text{Br]}$ (BCr-TEASCMNPs)

The $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{TEA}$ (1 g) was dispersed into 100 mL of distilled water and $[\text{CrO}_3\text{Br}]$ – (0.1 mmol) was added and the resulting mixture was stirred for 24 h at room temperature. After that, the resulting $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{TEA}@\text{[CrO}_3\text{Br]}$ was separated easily from the solution with the help of an external magnetic force, thoroughly washed with water and diethyl ether and dried under vacuum at 60°C [14].

3. Results and discussion

In continuation of efforts in the progress of green synthetic methods, herein we report a novel strategy for the synthesis a new catalyst of a magnetic bromochromate hybrid nanomaterial, $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{TEA}@\text{[CrO}_3\text{Br]}$. Initially, magnetite (Fe_3O_4) nanoparticles were prepared by coprecipitation of iron(II) and iron(III) ions from a basic solution at room temperature using the method described. Then, the $\text{Fe}_3\text{O}_4@\text{SiO}_2$ core–shell was created by TEOS and $\text{NH}_3 \cdot \text{H}_2\text{O}$. In the next stage, the $\text{Fe}_3\text{O}_4@\text{SiO}_2$ core–shell was functionalized using chloropropyltrimethoxysilane plus triethylamine in separate reactions. Finally, bromochromate was immobilized on the $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{TEA}$ and magnetic bromochromate hybrid nanomaterials were formed.

The catalyst has been characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM) and vibrating sample magnetometer (VSM), Fourier transform infrared (FT-IR), elemental analysis, X-ray fluorescence (XRF) and X-ray diffraction (XRD).

3.1. Characterization of the prepared magnetite–bromochromate nanomaterials

Fig. 1 shows the results of the X-ray diffraction patterns analysis of the magnetite bromochromate nanoparticles. The results are in

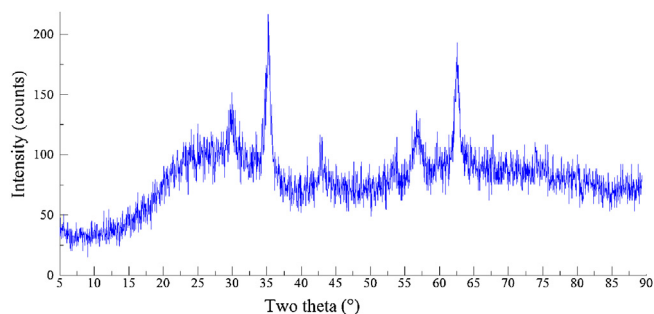


Fig. 1. XRD pattern of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{TEA}@\text{[CrO}_3\text{Br]}$.

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