Short Communication

Synthesis, characterization and heterogeneous catalytic activity of diamine-modified silica-coated magnetite-polyoxometalate nanoparticles as a novel magnetically-recoverable nanocatalyst

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ABSTRACT

Magnetite-polyoxometalate hybrid nanomaterials, $Fe_3O_4@SiO_2@NH-NH_2-PW$, was prepared by grafting of $H_3PW_{12}O_{40}$ on the diamine-functionalized Fe_3O_4 magnetite nanoparticles. This new heterogeneous nanocatalyst demonstrated a catalytic performance in the synthesis of tetrahydrobenzo[b]pyrans and Knoevenagel condensation in aqueous media. The nanocatalyst could easily be separated from the reaction solution by using an external magnet and recycled several times. The recovered catalyst was reused for at least seven runs without significant loss in catalytic activity. The resulting nanomaterials were characterized with different physicochemical techniques, such as Fourier transform infrared (FT-IR), transmission electron microscopy (TEM), scanning electron microscopy (SEM), powder X-ray diffraction (XRD), energy dispersive X-ray analysis (EDAX), thermogravimetric analyze (TGA) and alternating gradient force magnetometer (AGFM). SEM and TEM analyses indicated that nanoparticles had relatively uniform spherical nanoparticles and the average size of $Fe_3O_4@SiO_2@NH-NH_2-PW$ was approximately 60 nm.

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1. Introduction

Heteropoly acids (HPAs), especially the Keggin-type, as multi-electron oxidants or strong acids have attracted much attention in the last three decades [1,2]. Their acid strength is mostly higher than many mineral or conventional solid acids [3]. The major disadvantages of HPAs as catalysts are low surface areas ($<10 m^2/g$) and solubility in polar media. The maximum surface area of their monovalent salts is about $180 m^2/g$. Increasing the surface area can be achieved by dispersing the HPAs on solid supports with a high surface area [2].

Supported HPA catalysts are important since they can easily be recovered from reaction mixtures and reused. Therefore, much work has been focused on immobilizing HPAs onto different acidic or neutral supports, like SiO_2, TiO_2, zeolites, acidic ion-exchange resins, clays, active carbons, polymers and polyaniline–graphene composite [1–7]. However, SiO_2, which is relatively inert towards HPAs, is the one most often used. Despite the high surface areas of silica supported HPAs, filtration or centrifugation is needed and the separation process is still a difficult and time consuming process.

On the other hand, the demand for environmental friendly and efficient technologies has attracted considerable attention in the use and development of porous solids as catalyst. The use of nanoparticles

(NPs) offers many advantages due to their unique size and physical properties. In the past decade, the synthesis and the use of magnetic nanoparticles (MNPs) have been studied and applied in different research fields, such as industrial applications, biological applications, magnetic resonance imaging (MRI), drug delivery, bioseparation, hyperthermia, and catalytic applications [8–11].

Nanoparticles have also come into view as high surface area heterogeneous catalysts and catalyst supports; however, they are frequently difficult to be removed from the product mixture. Recent studies show that magnetic nanoparticles are excellent supports for various catalysts [8–18] and can easily be separated and recycled from the products by an external magnet. Surface functionalized magnetic iron oxide nanoparticles are a kind of novel functional material which have been widely used in biotechnology and catalysis. Moreover, the surface of iron oxide NPs could be modified by organic or inorganic materials, such as polymers, biomolecules, silica, metals, etc. and have been used in a wide range of catalytic reactions including oxidation, epoxidation, esterification, hydration, hydrogenation, enantioselective acylation, nitroaldol condensation, Mitra Baylis–Hillman reaction, coupling reaction, cycloaddition, photocatalysis and so forth. [11–16]. More recently, polyoxometalate-functionalized magnetic nanoparticles have attracted much attention and been widely used as active species in organic reactions catalysis [17–24]. $H_3PW_{12}O_{40}$ have been immobilized on amine-functionalized Fe_3O_4 magnetite nanoparticles, [21–23] and successfully applied to the oxidation of dibenzothiophene and photocatalytic dyes degradation under UV irradiation.

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In this article, we report the synthesis and characterization of di-amine modified silica coated magnetite-polyoxometalate nanoparticles as a novel nanomagnetically-recoverable catalyst and evaluate its catalytic activity in the synthesis of tetrahydrobenzo[b]pyran derivatives and Knoevenagel condensation in aqueous media. To the best of our knowledge, this is the first time that $H_3PW_{12}O_{40}$ supported on diamine-functionalized Fe_3O_4 magnetite nanoparticles is reported.

2. Materials and methods

2.1. Materials

All chemicals were purchased from Merck chemical company, with no further purification applied to them. Fourier transform infrared spectra were recorded using FT-IR Nicolet 6700 spectrometer using KBr plates. Scanning electron micrographs (SEMs) of the samples were taken with Hitachi S-4160. Transmission electron microscopy (TEM) was performed with a Philips microscope (EM 208, Tokyo, Japan) operating at 100 kV. The X-ray diffraction (XRD) was recorded on a Philips X'Pert MPD diffractometer equipped with Cu K$_\alpha$ radiation ($\lambda = 1.54056$ Å) operated at 40 kV and 30 mA. EDAX analysis was carried out by NEW XL30 144-2.5 by an active area of 10 mm^2 instrument. Thermogravimetric analyses (TGA) were performed using a TGA Q50 V6.3 Build 189 instrument. The magnetic properties were investigated by a home-made alternative gradient force magnetometer (AGFM) in the magnetic field range of −5000 to 5000 Oe at room temperature. Melting points were measured with an Electrothermal 9100 apparatus. NMR spectra were recorded with a Bruker DRX-250 AVANCE instrument (250.1 MHz for ^{1}H and 62.5 MHz for ^{13}C) with DMSO as solvent. Chemical shifts are given in ppm (δ) relative to internal TMS. All yields refer to isolated products after purification. Products were characterized by comparison to authentic samples and by spectroscopy data (FT-IR, ^{1}H NMR and ^{13}C NMR spectra). The spectra and some of the figures are given in *Supporting Information*.

2.2. Methods

2.2.1. Synthesis of the magnetic Fe_3O_4 nanoparticles

Fe_3O_4 nanoparticles were prepared by chemical co-precipitation of Fe^{3+} and Fe^{2+} ions with a molar ratio of 2:1 [24]. $FeCl_3 \cdot 6H_2O$ (21.6 mmol, 5.838 g) and $FeCl_2 \cdot 4H_2O$ (10.8 mmol, 2.147 g) were dissolved in 100 mL deionized water at 80–85 °C under N_2 atmosphere. Then, 10 mL of 25% NH_4OH was immediately injected into the reaction mixture. The reaction mixture was stirred for another 30 min and then cooled to room temperature. The black precipitate was washed twice with distilled water and twice with 0.02 M solution of NaCl. Magnetic Fe_3O_4 nanoparticles were magnetically separated. The average diameter of obtained magnetic Fe_3O_4 nanoparticles was estimated at approximately 20 nm by SEM (Fig. 3a).

2.2.2. Synthesis of silica-coated magnetite nanoparticles ($Fe_3O_4@SiO_2$)

Silica-coated magnetite nanoparticles were prepared with Stöber method, according to the reported method [25]. 0.7 g of magnetic Fe_3O_4 was dispersed in a mixture of 32 mL ethanol, 8 mL deionized water, and 0.6 mL concentrated ammonia aqueous solution by ultrasonication for 30 min. Subsequently, 0.4 mL of tetraethyl orthosilicate (TEOS) was added dropwise. After being stirred for 24 h at room temperature, the resulted solid was magnetically separated, washed twice with water and twice with ethanol, and then dried at 60 °C. The average diameter of obtained magnetic nanoparticles was estimated at approximately 30 nm by SEM (Fig. 3b).

2.2.3. Synthesis of chloropropyl-modified silica-coated magnetite nanoparticles ($Fe_3O_4@SiO_2$-Cl)

0.7 g of $Fe_3O_4@SiO_2$ was dispersed in 100 mL of toluene and ultrasonicated for 30 min. Then, 1 mL of 3-chloropropyltrimethoxysilane was added dropwise into the dispersion and ultrasonicated for 30 min. Subsequently, the mixture was refluxed at 110 °C under constant stirring for 24 h. The products were magnetically separated and washed two times with toluene and two times with ethanol and then dried at 60 °C.

2.2.4. Synthesis of diamine-functionalized modified silica coated magnetite nanoparticles ($Fe_3O_4@SiO_2@NH-NH_2$)

0.7 g of $Fe_3O_4@SiO_2$-Cl was dispersed in 70 mL of CH_3CN and ultrasonicated for 20 min. Then, KI (7 mmol, 1.162 g) and K_2CO_3 (7 mmol, 0.967 g) were added into the dispersion and ultrasonicated for 15 min. Subsequently, 20 mmol ethylenediamine (1.34 mL) was added to a solution and the mixture was stirred under reflux condition for 24 h. The obtained solid was then magnetically collected from the solution and washed abundantly with water/ethanol and dried at 60 °C.

2.2.5. Synthesis of diamine modified silica coated magnetite-polyoxometalate nanoparticles ($Fe_3O_4@SiO_2@NH-NH_2PW$)

0.3 g of $Fe_3O_4@SiO_2@NH-NH_2$ was dispersed in 50 mL of deionized water and ultrasonicated for 30 min. Then, a solution of $H_3PW_{12}O_{40}.6H_2O$ (0.42 mmol, 1.254 g) in 20 mL deionized water was added dropwise into the solution and ultrasonicated for 30 min and the mixture was stirred for 24 h at room temperature. Finally, the formed $Fe_3O_4@SiO_2@NH-NH_2$-PW was magnetically separated and washed twice with water and dried at 60 °C. $H_3PW_{12}O_{40}$ supported on diamine-functionalized Fe_3O_4 magnetite nanoparticles was synthesized as a novel nanomagnetically-recoverable catalyst. SEM (Fig. 3c) and TEM (Fig. 3d) analyses indicated that the average size of $Fe_3O_4@SiO_2@NH-NH_2$-PW was approximately 60 nm.

2.3. Catalytic reactions

2.3.1. General procedure for the synthesis of tetrahydrobenzo[b]pyrans

A mixture containing an aromatic aldehyde (1 mmol), malononitrile (1.2 mmol, 0.079 g), 5,5-dimethyl-1,3-cyclohexanedione (1 mmol, 0.140 g) and $Fe_3O_4@SiO_2@NH-NH_2$-PW (0.030 g) in water (4 mL) was stirred at reflux for an adequate amount (Table 2). The progress of the reaction was monitored by TLC (eluent: n-hexane/EtOAc, 10:7). After completion of the reaction, 5 mL EtOAc was added and the catalyst was separated by an external magnet. Then, the product was extracted with EtOAc (3 × 5 mL) and dried with anhydrous Na_2SO_4. After evaporation of EtOAc, the crude product was recrystallized from EtOH to afford the solid product in excellent yield.

2.3.2. General procedure for the Knoevenagel condensation

A mixture containing an aromatic aldehyde (1 mmol), malononitrile or ethylcyanoacetate (1.2 mmol), and $Fe_3O_4@SiO_2@NH-NH_2PW$ (0.030 g) in water (4 mL) was stirred at reflux for an adequate amount of time (Table 4). The progress of the reaction was monitored by TLC (eluent: n-hexane/EtOAc, 2:1). After completion of the reaction, 5 mL EtOAc was added and catalyst was separated by an external magnet. Then, the product was extracted with EtOAc (3 × 5 mL) and dried with anhydrous Na_2SO_4. After evaporation of EtOAc, the crude product was recrystallized from EtOH to afford the solid product in excellent yield.

3. Results and discussion

3.1. Catalyst preparation and characterization

First, the chemical co-precipitation of $Fe2^+$ and Fe^{3+} ions in the basic solution led to the formation of Fe_3O_4 magnetite nanoparticles [24]. Then, in order to avoid possible oxidation or aggregation of the iron oxide nanoparticles, a layer of SiO_2 was coated on the nanoparticles. This was achieved using the modified Stöber method [25]. Treatment of