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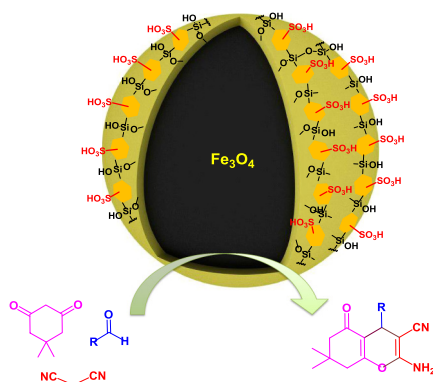
Magnetic iron oxide/phenylsulfonic acid: A novel, efficient and recoverable nanocatalyst for green synthesis of tetrahydrobenzo[b]pyrans under ultrasonic conditions

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GRAPHICAL ABSTRACT

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ABSTRACT

A novel magnetic iron oxide supported phenylsulfonic acid (Fe_3O_4@Ph-SO_3H) with core-shell structure is prepared, characterized and applied as efficient nanocatalyst for green synthesis of tetrahydrobenzo[b] pyrans. The Fe_3O_4@Ph-SO_3H was prepared *via* modification of magnetic iron oxide cores with 1,4-bis (triethoxysilyl)benzene (BTEB) followed by sulfonation of aromatic rings. The Fe_3O_4@Ph-SO_3H was characterized using FTIR, TGA, PXRD, SEM, TEM, VSM and EDX techniques. This was effectively applied for synthesis of tetrahydrobenzo[b]pyrans in water as green solvent at room temperature under ultrasonic conditions. The products were obtained in high to excellent yields at short times. The recoverability, reusability and durability of this nanocatalyst were studied under applied reaction conditions.

1. Introduction

Homogeneous Brønsted and Lewis acids are very attracted between chemists due to their widespread catalytic applications in chemical and industrial processes [1–7]. Some of well-known acid catalysts are sulfonic acid containing materials, hydrogen halides, metal complexes, metal ions, organometallic complexes and biocatalysts [6–16]. Although a lot of organic processes have been catalyzed in the presence of aforementioned homogeneous catalysts, however, these suffer from several limitations such as low thermal stability, agglomeration during reaction process, harsh reaction conditions, recovery and separation problems. Accordingly, it is very important to replace expensive dangerous

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and polluting acid catalysts with environmentally-friendly, highly stable and recoverable heterogeneous catalysts that is a significant challenge of green chemistry processes. Nanoparticles (NPs) are one of the most important and attractive support for acid catalysts, because when the size of materials decreases to nanometer scale, the surface area increases allowing excellent dispersion of the active particles as well as provides a large amount of accessible sites [17–26]. Among different kinds of NPs, magnetic nanoparticles have received interesting attention due to their unique properties such as easy separation and recovery using an external magnet, high surface area and high chemical and thermal stability [27–36]. The above-mentioned properties make magnetic NPs as powerful candidate for several applications such as drug delivery and especially as support for immobilization of metallic and organic catalysts in chemical processes. One of the most popular and strong acid that has been successfully immobilized onto magnetic NPs and widely used in different organic transformations, is sulfonic acid [37–48]. The chemical bonding of sulfonic acid groups onto magnetic NPs is achieved by various methods such as oxidation of attached thiols, hydrolysis of sulfonic acid chlorides and immobilization of perfluorosulfonic acid triethoxysilanes acid [37–50]. Some of recently developed catalysts are Fe_3O_4@MCM-48-OSO_3H [50], Fe_3O_4@Fe_2O_3-OSO_3H [44], SiMNP-SO_3H [51], SiMNP-FSO_3H [52] and Fe_3O_4@SiO_2@$PrSO_3H$ [53]. Although the latter sulfonic acid based catalytic systems have advantages of recoverability and reusability in comparison to their homogeneous counterpoints, however, the most of them were used in high loading at high temperature. Moreover, these are not lipophile in nature, therefore diffusion of organic substrates on their surfaces is low. Accordingly, design and preparation of heterogeneous magnetic hybrid organic-inorganic nanoparticles supported strong sulfonic acid groups are very important subjects between chemists.

On the other hand, in recent years multicomponent reactions (MCRs) have gained considerable attention and have become an increasingly active field of research that provides novel chemical scaffolds in a single operation and is attractive from economic as well as ecological point of view [15,54–65]. Tetrahydrobenzo[*b*]pyrans are one of the most important compounds in organic chemistry that are prepared through a MCR and have attracted much synthetic interest because of their pharmacological and biological activities such as anticancer, spasmolytic, anti-anaphylactic and anticoagulant [66–68]. Also, they have a broad range of applications as cognitive enhancers, for the treatment of neurodegenerative illness including Huntington's sickness, Parkinson's illness, amyotrophic lateral sclerosis, AIDS-associated dementia, Alzheimer's disease and Down's syndrome as well as for the treatment of myoclonus and schizophrenia [69,70]. Therefore, preparation of tetrahydrobenzo[*b*]pyrans is one of significant subject between chemists.

Accordingly, in continuous of our recent studies on the preparation of supported catalytic systems [71–80], herein for the first time a novel magnetic iron oxide nanoparticle supported phenyl sulfonic acid (Fe_3O_4@Ph-SO_3H) is prepared, characterized and applied as effective nanocatalyst in synthesis of biologically active and chemically useful tetrahydrobenzo[*b*]pyrans (Scheme 1) [81–88].

2. Experimental section

2.1. General

All chemicals including iron (II) chloride tetrahydrate (99%), iron (III) chloride hexahydrate (98%), ammonia, concentrated HCl, tetramethoxysilane (TMOS), 1,4-bis(triethoxysilyl)benzene (BTEB) and benzaldehyde derivatives were purchased from Fluka and Merck companies. The tetrahydrobenzo[*b*]pyran products were characterized *via* comparison of their physical data (FT-IR, ^{1}HNMR and ^{13}CNMR spectra) with known samples. The thermal gravimetric analysis (TGA) was measured from room temperature to 800 °C using a Rheometric Scientific model STA 1500 instrument. Fourier transform infrared (FT-IR) spectroscopy was recorded on a Brucker-Vector 22 spectrometer. To analyze the morphology and particle size of the sample, an emission scanning electron microscope (SEM, Philips, XL30) was used. Transmission electron microscopy (TEM) images were taken on a Zeiss-EM10C microscope operated at an accelerating voltage of 100 kV. X-ray diffraction (XRD) pattern was obtained with a Panalytical model X' Pert Pro focus diffractometer with Cu Ka radiation operated at 40 kV and 40 mA. The magnetic properties of the synthesized nanoparticles were investigated using vibrating sample magnetometer (VSM) of Meghnatis Daghigh Kavir Company. ^{1}HNMR and ^{13}CNMR spectra were recorded in $CDCl_3$ solvent using a Bruker Advanced DMX-400 MHz spectrometer.

2.2. Preparation of Fe_3O_4 nanoparticles

Fe_3O_4 nanoparticles were synthesized *via* improved chemical precipitation method [89]. According to this method, $FeCl_2\cdot4H_2O$ (3.1 g) and $FeCl_3\cdot6H_2O$ (7.5 g) were dissolved in 320 mL of deionized water. Then aqueous ammonia (25% wt, 30 mL) was slowly added and the obtained mixture was stirred at room temperature for 60 min at 80 °C under Ar atmosphere. The stirring was continued for another 60 min and then it was stopped and cooled to room temperature. The resulted product was collected using an external magnet and it was washed completely with distilled water and EtOH. This was dried at 70 °C for 12 h under vacuum and denoted as Fe_3O_4 nanoparticles.

2.3. Preparation of Fe_3O_4 supported phenyl groups (Fe_3O_4@Ph)

The Fe_3O_4@Ph nanoparticles were prepared as following: 0.75 g of magnetic Fe_3O_4 nanoparticles were completely dispersed in a solution of distilled water (40 mL) and EtOH (150 mL) under ultrasonic irradiations at room temperature. Then, aqueous ammonia (25% wt, 3.5 mL) was added to the reaction vessel and it was stirred at room temperature for 1 h. After that, tetramethoxysilane (TMOS, 0.7 mL) and 1,4-bis(triethoxysilyl)benzene (BTEB, 1.8 mL) were added drop-wise and the obtained mixture was stirred at the same temperature for 16 h. The resulted particles were collected and separated using an external magnet. After drying at 60 °C for 12 h, a uniform powder with core-shell structure called Fe_3O_4@Ph was obtained.

2.4. Preparation of Fe_3O_4 supported phenylsulfonic acids (Fe_3O_4@Ph-SO_3H)

For the preparation of Fe_3O_4@Ph-SO_3H, 0.4 g of Fe_3O_4@Ph was completely dispersed in distilled chloroform (20 mL) under ultrasonic conditions at room temperature. Then, a chloroform solution of chlorosulfonic acid ($ClSO_2OH$) was added slowly and the obtained mixture was stirred at room temperature for 3 h [25,27,31,39]. The resulted product was collected using an external magnet, washed several times with EtOH and water until all soluble acidic components were removed. The final particles were dried under vacuum for 20 h and denoted as Fe_3O_4@Ph-SO_3H.

2.5. Procedure for the determination of acidity of the Fe_3O_4@Ph-SO_3H

The loading of supported sulfonic acid moieties was estimated using ion-exchange pH analysis. For this, 50 mg of Fe_3O_4@Ph-SO_3H was completely dispersed in an aqueous solution of sodium