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Effective preparation of amine-functionalized nano magnetite as a precursor of novel solid acid catalyst for one-pot synthesis of xanthenes under solvent-free conditions

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ABSTRACT

In this work, a facile route was developed for the preparation of amine-functionalized magnetite nanoparticles by co-precipitation method. These amine-functionalized magnetite nanoparticles were sulfonated and then used as novel heterogeneous acid catalyst and their catalytic activities were investigated in the green synthesis of 14-aryl-14H-dibenzo[a,j]xanthenes under thermal and solvent free conditions. The catalyst was characterized by FT-IR, SEM, EDX, XRD, TGA and VSM. Also, the catalyst could be recovered easily and reused several times without any significant loss of its catalytic activity.

1. Introduction

Sulfuric acid is a required catalyst for the production of industrial chemicals. Nevertheless, it suffers from several problems and difficulties, such as device corrosion, neutralization of waste acids and the difficulty of its separation from the product. The principles of green chemistry have incited the use of recyclable strong solid acids as replacements for such unrecyclable homogeneous acid catalysts. Unlike a homogeneous acid catalyst, the hiring of a heterogeneous acid catalyst does not require neutralization of the remaining acid and can be separated more easily from reaction products by filtration. Solid-supported catalysts are a significant and growing field in heterogeneous catalysis [1]. Among solid-supported catalysts, nano supports have attracted much attention because of their physical and chemical properties and possess a great potential as heterogeneous catalysts [2,3]. Fe_3O_4 nanoparticles are outstanding catalyst supports due to their superparamagnetism and high surface area, easy to provide, ease of surface modification, and low toxicity [4–6]. Different synthetic methods for preparing magnetite nanoparticles have been reported in the literature such as micro-emulsions [7], solvothermal processing [8], thermal decomposition [9] and co-precipitation [10]. Between the different techniques for magnetite preparation, the coprecipitation technique is a comfortable way to synthesize magnetite nanoparticles. In this method, Fe^{2+} and Fe^{3+} ions are commonly precipitated in alkaline solutions such as NH_4OH, KOH or NaOH [11]. There are now several information on the preparation of amine-functionalized Fe_3O_4 nanoparticles that are intersected into one step synthesis and two-steps synthesis. In the majority of works, a two-step synthesis procedure has been employed for the synthesis of amine-functionalized magnetite nanoparticles. In the first step, nanoparticles are synthesized by corresponding chemical methods. In the second step, appropriate coupling factors such as (3-aminopropyl) trimethoxysilane (APTMS), 3-aminopropyltriethoxysilane (APTES), 3-(2-aminoethylamino propyl)-triethoxysilane (AEAPTES) and 3-(2-aminoethylaminopropyl)-trimethoxysilane (AEAPTMES) [12,13], have been used to functionalize magnetite nanoparticles. These methods also suffer from some disadvantages such as a long reaction time [14] and the use of toxic solvent such as toluene and methanol [13–15].

In recent years, several researches have been made to one-step synthesis of amine-functionalized magnetite nanoparticles. In these reports, amine-functionalized Fe_3O_4 have been prepared using methods such as thermal decomposition [16] and solvothermal [17–20] which require high temperatures (~200 °C) and long reaction times (~6–8 h).

Xanthenes are biologically important compounds and possess various biological factors such as antibacterial, antiviral,

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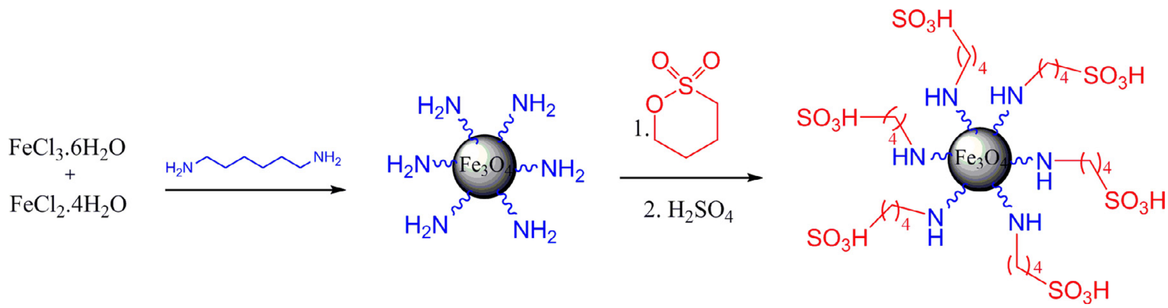

Scheme 1. Preparation of Fe_3O_4-HDA-SO_3H nanocatalyst.

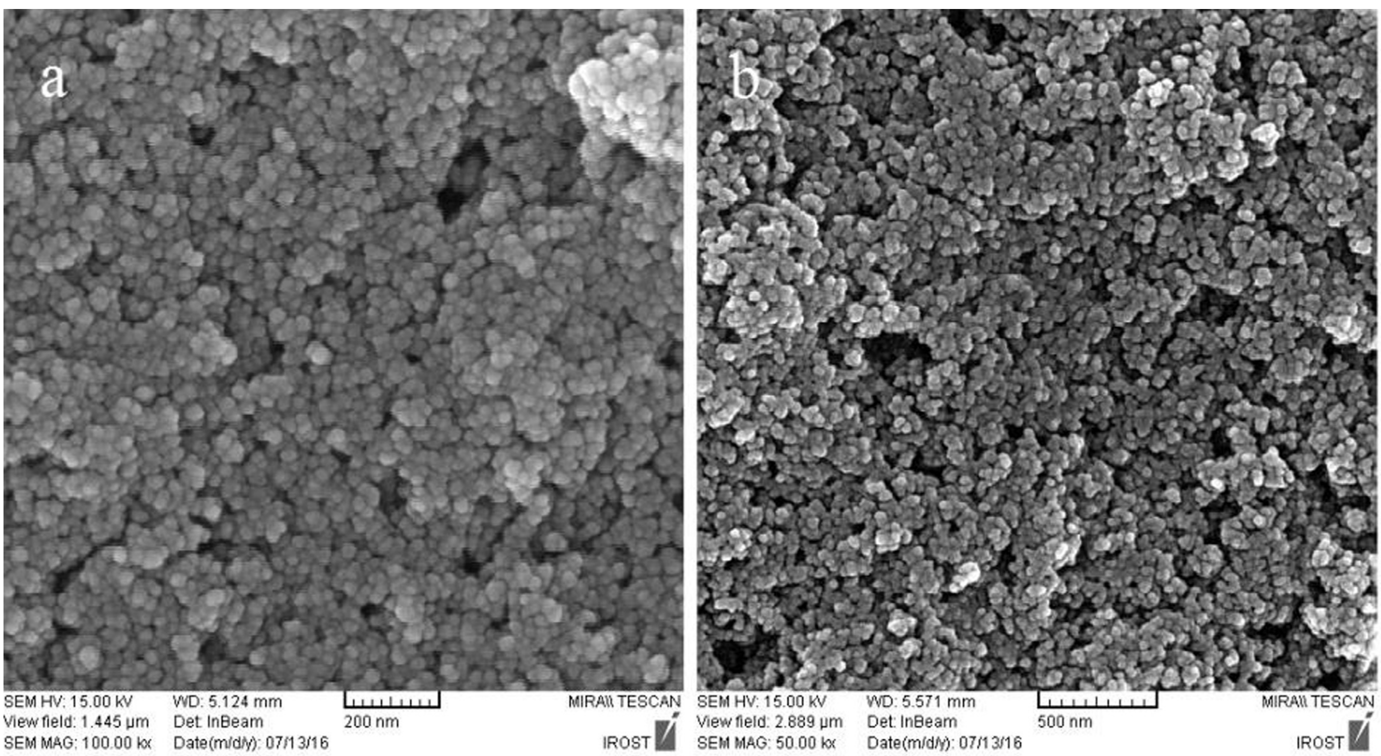

Fig. 1. SEM image of (a) Fe_3O_4-HDA NPs, (b) Fe_3O_4-HDA-SO_3H NPs.

anti-inflammatory and uses in photodynamic behavior. They can also be used as dyes, laser technologies and fluorescent materials. A number of xanthenes based compounds have been isolated from a plant species. Many methods for the synthesis of xanthene derivatives have been reported in the literature [21–26], containing trapping of benzynes by phenols [27], cyclodehydrations [28], cyclic 1,3-dicarbonyl compounds and aldehydes [29], cyclocondensation between 2-hydroxy aromatic aldehydes and 2-tetralone [30].

As part of our interest toward methodologies and nanocatalyst, we report a novel and facile one-pot synthesis of amine functionalized Fe_3O_4 nanoparticles *via* co-precipitation method using ferric chloride and ferrous chloride as iron sources and 1,6-hexanediamine as both precipitator and coupling agent in aqueous solution. Co-precipitation technique does not produce or use any toxic intermediates or solvents, does not require precursor complexes, and carries out at 100 °C. Also we report a procedure for the synthesis of sulfonic acid functionalized magnetic nanoparticles as recyclable strong solid acid catalyst for the synthesis of xanthenes under solvent-free conditions.

2. Experimental

2.1. Materials and apparatus

The chemicals used in this work were purchased from Fluka and Merck Chemical Companies and used without purification. IR spectra were obtained as KBr pellets on a Perkin-Elmer 781 spectrophotometer and on an impact 400 Nicolet FT-IR spectrophotometer. ^{1}H NMR and ^{13}C NMR were recorded in $CDCl_3$ solvent on a Bruker DRX-400 MHz spectrometer with tetramethylsilane as internal reference. XRD patterns were recorded by an X'PertPro (Philips) instrument with 1.54 °A wavelengths of X-ray beam and Cu anode material, at a scanning speed of 2°/min from 10° to 80° (2Θ). The SEM images of prepared catalysts were taken on a FE-SEM Hitachi S4160 instrument. The magnetic properties of nanoparticles have been measured with a vibrating sample magnetometer (VSM, PPMS-9T) at 300 K in Iran (University of Kashan, Iran). A Bandelin ultrasonic HD 3200 with 6 mm diameter model KE 76 probe was used to generate ultrasonic irradiation.

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