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Ultrasonic-assisted environmentally-friendly synergetic synthesis of nitroaromatic compounds in core/shell nanoreactor: A green protocol

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ABSTRACT

An efficient sonochemical protocol for the nitration of aromatic compounds was described in the presence of a catalytic amount of sulfuric acid-functionalized silica-based core/shell magnetic nanocomposite at room temperature in an eco-friendly and recyclable media, deep eutectic solvent (DES), based on choline chloride and urea. The particle size, morphology and elemental analysis of the core/shell nanocatalyst were carried out by TEM, SEM, EDX and XRD analyses. The nanocatalyst and DES were easily recovered from the reaction mixture quantitatively and reused several times.

1. Introduction

Ultrasonic irradiation (USI), as a safe technique and green energy source, has attracted many attentions of scientific and industrial researchers for several applications in chemical processes. In comparison with traditional methods, the procedure is more convenient, fast, simple and easily controlled. A large number of organic reactions can be carried out in higher yields, shorter reaction times or milder conditions under USI. An explanation to understanding to the acceleration of reactions under sonic condition can be explained by the phenomenon of acoustic cavitation and cage effects that perform high temperatures and pressures within few seconds and lead to acceleration of rate of the reactions, when compared to the traditional methods which generally require longer reaction time, high temperatures and expensive reagents. Therefore, this powerful technique can be regarded as an efficient reaction media for green, economical and environmentally-friendly approach in organic functional group productions/transformations such as nitration of aromatic compounds [1].

Recently, due to some drawbacks of ionic liquids such as toxicity, poor biodegradability, high cost, and difficulty in preparation methods, DESs, a new class of green reaction media, has been emerged as an interesting alternatives. DESs are generally composed of two or three safe and readily available and inexpensive components that are capable of associating with each other through hydrogen bonds. DESs naturally have a very high depression in freezing point and form liquids at temperatures between room temperature and 70 °C. Moreover, since the purity of DESs only depends on the purity of their components, therefore, requires neither purification nor complex synthesis. They can be obtained via simple preparation procedure, high purity and relatively cheap cost. Due to these advantages, DESs are going to be favorable candidate in many field of technology e.g. catalysis, synthesis, reaction media, extraction processes, electrochemistry and material chemistry [2].

The process of nitration of aromatic compounds, as a very valuable organic reaction, could be achieved with many nitrating reagents. The NO_2-substitued aromatics are extensively applied for the preparation of various chemically and pharmaceutically important products such as dyes, perfumes, plastics, explosives and so on. The traditional nitrations of aromatic compounds are routinely carried out under strongly acidic conditions such as concentrated H_2SO_4 and HNO_3 [3]. They usually produce a lot of acid waste that is not eco-friendly, is difficult and time-consuming for treatment and also causes damage of the equipment e.g. corrosion. These problems have generated many efforts for finding alternative methods for the nitration reaction. Therefore, there are various reports in the literature claiming agents and conditions for the nitration [3–17]. A few solid acid catalysts have been tested so far such as MoO_3/SiO_2 [4], SO_4^{2-}/SiO_2 [5], $WO_3–TiO_2/SiO_2$ [6], $WO_3–SO_4^{2-}/SnO_2$ [7], zeolite-based solid acid catalysts [8], melamine–$(H_2SO_4)_3$ [9] and polyvinylpyrrolidone–$(H_2SO_4)_n$ [10]. Also, various NO_2^+ sources such as nitronium salts in organic media [11], $Zn(NO_3)_2{\cdot}6H_2O$ [12], guanidinium or alkyl nitrates [13], N_2O_4 or N_2O_5 [14], acetyl nitrates [15] and other acids which are alternatives to sulfuric acid, have been used [16]. It has been claimed that those catalytic methods usually led to minimum byproducts and could produce the most important *para* isomer as the major product.

In recent decade, magnetic organic–inorganic nanocomposites have become of considerable interest because the magnetic catalysts in both academic and industrial fields have significant advantages. Core/shell

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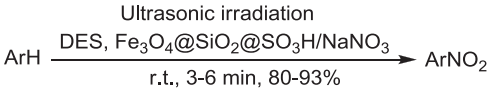

Scheme 1. Sonochemical SMNCS-catalysed nitration of aromatic compounds in DES.

nanomaterials and supported magnetic metal nanoparticles have emerged as a new class of nanocatalysts. Due to high surface area, nanocatalysts generally exhibit higher catalytic activity than classic heterogeneous acid catalysts. The SO_3H-immobilized silica-coated superparamagnetic Fe_3O_4 nanoparticles are a fantastic class of recoverable, supported and heterogeneous strong acidic catalysts for diverse chemical transformations. Other organic and inorganic compounds could be placed on magnetic nanoparticles coated with silica which could be used as a heterogeneous magnetic catalyst in chemical reactions [17–22].

In connection with our previous research focused on design, preparation and performance of nanocatalysts in the organic chemical reactions and functional group transformations [17–30], the aim of the present protocol is nitration of aromatic and heteroaromatic compounds by using of sulfuric acid-functionalized silica-based magnetic nanocomposite (Fe_3O_4@SiO_2@SO_3H) along with sodium nitrate ($NaNO_3$) (SMNCS) in DES by USI at room temperature (Scheme 1). This research can be classified as a green approach for the efficient and rapid nitration of aromatic compounds by using of a recyclable nanocatalyst under mild reaction conditions.

2. Results and discussion

Fe_3O_4@SiO_2@SO_3H (SMNC) as an efficient superparamagnetic heterogeneous nanocomposite catalyst was produced based on the literature described procedures [28–32]. To this purpose, a solution of concentrated aqueous ammonia was loaded to a as-prepared solution of $FeCl_3{\cdot}6H_2O$ and $FeCl_2{\cdot}4H_2O$ in distilled H_2O to yield Fe_3O_4 nanoparticles. Then, these nanoparticles were diluted via a solution of water, ethanol and concentrated aqueous ammonia. A solution of tetraethylorthosilicate (TEOS) in ethanol was then loaded to the mixture and Fe_3O_4@SiO_2 nanoparticles were obtained. Chlorosulfonic acid was added to a solution of Fe_3O_4@SiO_2 in *n*-hexane. Then, HCl was removed from the reaction pot. The resulted Fe_3O_4@SiO_2@SO_3H was separated using an external magnet.

The sizes of the prepared nanoparticles were studied via scanning electron microscopy (SEM) images. The analysis of SEM image of Fe_3O_4@SiO_2–SO_3H clearly showed a monodispersed spherical shape of Fe_3O_4@SiO_2@SO_3H nanoparticles (Fig. 1). As can be seen in the chart, the distribution of the particles sizes was approximately narrow and the range of the sizes of the nanoparticles was about 15–25 nm and average particles size of Fe_3O_4@SiO_2 was approximately 30 nm for 100 particles size distribution analysis.

Energy-dispersive X-ray (EDX) spectroscopy analysis approved the presence of O, Si, S and Fe elements in the structure of the nanocomposite catalyst and the approximate amount of Fe loading in Fe_3O_4@SiO_2@SO_3H catalyst was nearly 30% (Fig. S1 in Supporting Information file).

The structure of Fe_3O_4@SiO_2 and Fe_3O_4@SiO_2@SO_3H have been analyzed by X-ray diffraction (XRD) patterns (Fig. 2). Similar peaks obtained in both of the Fe_3O_4@SiO_2 and Fe_3O_4@SiO_2@SO_3H XRD patterns indicates that the core crystalline structures of the spinel ferrite during the silica-coating process was suitably maintained. The mean crystallite size was around 30 nm calculated by using Debye-Scherrer formula's formula: $D = 0.9\lambda/\beta\cos\theta$; where D is the particle size, λ is the X-ray wavelength (nm), θ is Bragg's angle, and β is the full-width at half maximum (FWHM) of plane (3 1 1) [28–33].

As shown in Fig. 3, the transmission electron microscopy (TEM) image revealed that the Fe_3O_4@SiO_2@SO_3H nanocomposite made as supports of the catalyst had good spherical morphologies and arranged core/shell structures. During the seeded sol–gel method, the thickness of silica shell of the Fe_3O_4@SiO_2 particles can be appropriately adapted by controlling the addition amount of TEOS as silica source. In comparison with large size supported solid catalysts, those involving small size nanoparticles have higher specific surface area and may disperse homogenously in solvents that will have strong effects on the catalysis applications. By providing various magnified images in relatively good to high contrast and resolution, useful clues was obtained about the inner layers information of the core/shell to confirm the formation of the Fe_3O_4@SiO_2@SO_3H nanocatalyst.

To study the catalytic activity of the nanocomposite system, the pilot test was carried out for the nitration of toluene by using of SMNCS. After several experiments, it was found that the best reaction condition was using 0.04 g of Fe_3O_4@SiO_2@SO_3H in 2 g of DES at room temperature under USI. In addition, sonication instrument was optimized by working in 20–60 kHz under 150–300 W conditions. The best acoustic pressures during cavitation and microject formation conditions for efficient nitration of aromatic compounds were observed in 40 kHz and 250 W frequency and power, respectively. The optimized reaction conditions gave the product in a very short reaction time (3 min) and high yield (93%) at low frequency and power of ultrasonic irradiation (Table 1, entry 3).

To compare the efficiency of SMNCS with some other reports in nitration of toluene, we have investigated other works that are listed in Table 2. $Ph_2PCl/I_2/AgNO_3$ carries out the reaction at room temperature in 60 min in 66% yield for *para*-substituted derivative (entry 1). HNO_3/P_2O_5/silica gel gives the product at room temperature in 7 min in 56% yield (entry 2). HNO_3/ZBS-15 gives the product at 100 °C in 240 min in 55% yield (entry 3). Another reagent is HNO_3/Lanthanide(III) nosylates that carries out the reaction in 1,2-dichloroethane at room temperature

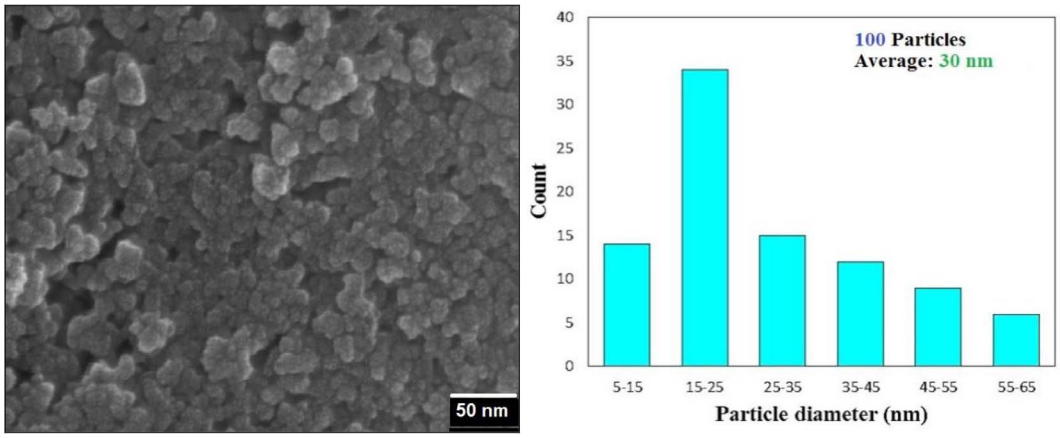

Fig. 1. SEM image and particle size distribution diagram of Fe_3O_4@SiO_2@SO_3H.