Chinese Chemical Letters 24 (2013) 211–214

Contents lists available at SciVerse ScienceDirect

Chinese Chemical Letters

journal homepage: www.elsevier.com/locate/cclet

Original article

Supported *N*-propylsulfamic acid on magnetic nanoparticles used as recoverable and recyclable catalyst for the synthesis of 2,3-dihydroquinazolin-4(1*H*)-ones in water

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ARTICLE INFO

Article history:
Received 7 September 2012
Received in revised form 5 December 2012
Accepted 10 December 2012

Keywords:
Magnetic nanoparticles
N-Propylsulfamic acid
Nanocatalyst
2,3-Dihydroquinazolin-4(1*H*)-ones
Cyclocondensation
Anthranilamide

ABSTRACT

An efficient and eco-friendly method is reported for the synthesis of 2-substituted-2,3-dihydroquinazolin-4(1*H*)-ones from direct cyclocondensation of anthranilamide with aldehydes and ketones using *N*-propylsulfamic acid supported onto magnetic Fe_3O_4 nanoparticles (MNPs-PSA) as a recoverable and recyclable nanocatalyst in good to excellent yields in water at 70 °C. The catalyst was readily separated using an external magnet and reusable without significant loss of their catalytic efficiency.

1. Introduction

Magnetic nanoparticles are efficient, readily available, high-surface-area resulting in high catalyst loading capacity and outstanding stability heterogeneous supports for catalysts [1]. More importantly, magnetic separation of the magnetic nanoparticles is more effective than filtration or centrifugation [2], simple, economical and promising for industrial applications [3]. Among the various magnetic nanoparticles used as the core magnetic support, Fe_3O_4 nanoparticles are arguably the most extensively studied [4] because of their simple synthesis, low cost, and relatively large magnetic susceptibility [5]. Recently, preparation and application of several supported catalysts on magnetic Fe_3O_4 nanoparticles have been reported [6–11].

2,3-Dihydroquinazolin-4(1*H*)-ones are an important class of fused heterocycles with a wide range of pharmaceutical and biological activities [12]. These compounds can easily be oxidized to their quinazolin-4(3*H*)-one analogues [13], which also include important pharmacologically active compounds [14]. Various methods have already been proposed for the synthesis of these compounds [15]. A general procedure for the synthesis of 2,3-dihydroquinazolin-4(1*H*)-ones involves the condensation reaction of anthranilamide with aldehyde or ketone in the presence of various promoting agents [16–23]. Although reported methods produce good results in many instances, the development of efficient, simple, easy work-up and environmentally benign protocols using recyclable catalysts and green solvents for the synthesis of these important compounds is still desirable and in demand.

Sulfamic acid (H_2NSO_3H, SA), a common inorganic acid, is nonvolatile, noncorrosive, stable, water resistance and incapable of forming complexes, making it an outstanding alternative to metal catalysts in different areas of organic synthesis as an efficient and green reagent [24,25]. The main drawback of SA just like any heterogeneous or homogeneous catalyst is its separation from the reaction mixture by filtration or liquid–liquid techniques which cause the loss of catalyst in many reactions. To overcome this drawback, SA can be immobilized on magnetic nanoparticles. In recent years, organic reactions in aqueous media have received high priority in view of green methodology [26].

2. Experimental

General procedure for the synthesis of 2,3-dihydroquinazolin-4(1*H*)-ones: The MNPs-PSA (10 mg) was added to a mixture of anthranilamide (1 mmol, 0.136 g) and aldehyde or ketone

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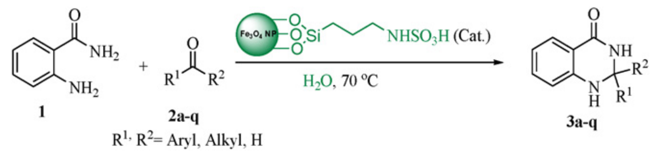
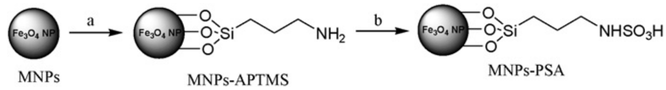
1001-8417/$ – see front matter
http://dx.doi.org/10.1016/j.cclet.2013.01.032



Scheme 1. MNPs-PSA catalyzes the synthesis of 2,3-dihydroquinazolin-4(1*H*)-ones in water.



Scheme 2. Synthesis of MNPs-PSA: (a) 3-aminopropyltriethoxysilane, ethanol/water, rt, 8 h and (b) chlorosulfuric acid, dichloromethane, rt, 2 h.

(1 mmol) in water (2 mL). Then the mixture was stirred for the appropriate time at 70 °C. The progress was monitored by TLC. After completion of the reaction, the reaction mixture was cooled to room temperature. CH_2Cl_2 (2 × 5 mL) was added and the catalyst was separated by an external magnet. The resulting mixture was washed with brine (10 mL) and dried over anhydrous Na_2SO_4. CH_2Cl_2 was evaporated under reduced pressure to afford the essentially pure products. In some cases, the product was recrystalized from ethanol for further purification.

3. Results and discussion

In continuation of our efforts in the development of green synthetic methodologies [27–30], herein we report catalytic application of MNPs-PSA as magnetically heterogeneous nanocatalysts for the synthesis of 2-substituted-2,3-dihydroquinazolin-4(1*H*)-ones from direct cyclocondensation of anthranilamide with aldehydes or ketones in water at 70 °C (Scheme 1).

Initially, the MNPs-PSA was synthesized according to the method reported recently with some modifications as shown in Scheme 2 [31]. Magnetite (Fe_3O_4) nanoparticles were prepared by coprecipitation of iron (II) and iron (III) ions in basic solution at 85 °C using the method described [32].

The catalyst has been characterized by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD) and by comparisons with authentic sample. A SEM image of MNPs-PSA is shown in Fig. 1A. It was confirmed that the catalyst was made up of nanometer-sized particles. The IR spectrum of MNPs-PSA shows peaks that are characteristic of a functionalized SA group, which clearly

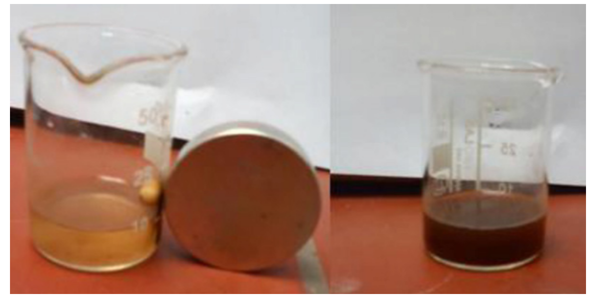


Fig. 2. Image showing MNPs-PSA can be separated by applied magnetic field. A reaction mixture in the absence (right) or presence of a magnetic field (left).

differentiates from that of the unfunctionalized Fe_3O_4 nanomagnets and aminopropyl-functionalized magnetic nanoparticles (Fig. 1B). XRD pattern of MNPs-PSA is shown in Fig. 1C, the position and relative intensities of all peaks confirm well. To determine the acid amount on the surface, the prepared catalyst (100 mg) was added to an aqueous NaCl solution (1 mol/L, 10 mL) with an initial pH 5.93. The mixture was stirred for 0.5 h after which the pH of solution decreased to 1.72, indicating an ion exchange between sulfamic acid protons and sodium ions, this is equal to a loading of 1.9 mmol/g of sulfamic acid group. This result confirmed by back-titration of the catalyst.

Subsequently, in order to optimize the reaction conditions, we evaluated the influence of different amounts of catalyst on the model cyclocondensation reaction of anthranilamide (1 mmol) and 4-methoxybenzaldehyde (1 mmol) in water at 70 °C on reaction time and yield of product (Table 1). When adding catalyst, the reaction times were reduced, however 10 mg of MNPs-PSA was chosen as the desired condition.

In order to extend the scope of this cyclocondensation reaction, the various benzaldehyde derivatives, including electron-donating and electron-withdrawing groups on aromatic ring, terephthaldehyde and aliphatic ketones were investigated in the presence of the catalytic amount of MNPs-PSA in water at 70 °C, the results are summarized in Table 2.

As shown in Table 2, aromatic aldehydes electron-donating group yielded corresponding 2-substituted-2,3-dihydroquinazolin-4(1*H*)-ones in shorter reaction time and higher yield, whereas aromatic aldehydes with electron-withdrawing groups gave longer reaction times. For aliphatic ketones such as acetone and cyclohexanone, relatively slower reactions were observed (Table 2, entries 15 and 16). We have developed this synthetic method for the preparation of bis-2,3-dihydroquinazolin-4(1*H*)-one in a 2:1

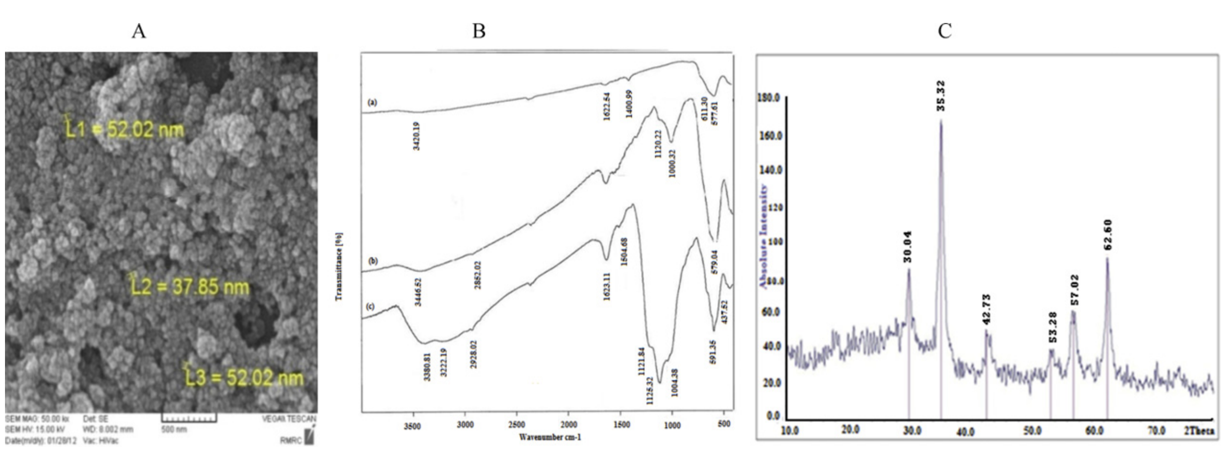


Fig. 1. (A) SEM images of MNPs-PSA, (B) the comparative FT-IR spectra for (a) MNPs, (b) MNPs–APTMs and (c) MNPs-PSA, and (C) the XRD pattern of MNPs-PSA.