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ORIGINAL RESEARCH PAPER

Sulfuric Acid Functionalized Magnetic Nanocatalyst for One-pot Green Synthesis of 2,3-Dihydroquinazolin-4 (1H) -ones

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ABSTRACT
Sulfuric acid functionalized magnetic nanocatalyst (SAMNC) has been prepared as an efficient acidic and applied in the one-pot preparation of 2,3-dihydroquinazolin-4 (1H) -one derivatives. This catalyst has been characterized by FT-IR, SEM, and VSM. According to the obtained results, including time, yield and recyclability, SAMNC could be considered as an efficient catalyst for organic transformations.

Keywords: *Sulfuric acid magnetic nanocatalyst, Solvent-free, 2,3-Dihydroquinazolin-4(1H)-ones, One-pot.*

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INTRODUCTION

Multi-component reactions (MCRs) has been greatly acknowledged due to their simplicity, user-friendly procedure, high yield of the products and one-pot synthesis. Due to the formation of multiple bonds in a continuous manner without the need for separation of intermediate adducts MCRs are gaining more attention recently [1-4]. Application of homogeneous or heterogeneous catalysts, or performing its reactions in environmental friendly solvents are new strategies for obtaining desired products [5-8].

Solvent-free organic reactions have been acted as an alternative tool for organic, synthesis particularly from the viewpoint of green chemistry. The advantages of solvent-free synthesis are Reduced pollution, lower costs, and simplicity in process and work-up [9, 10].

Application of magnetic nanocatalysts has enabled chemists a noteworthy procedure which is applicable for a wide range of reactions with easier work-up through an external magnet. Magnetic nanoparticles are modified through a coating of organic or inorganic shells which enabled the subsequent grafting and/or immobilization of homogeneous catalysts [11, 12]. Recently different acids functionalized magnetic nanoparticles have been utilized in organic synthesis [13].

Due to the diverse biological activities, synthesis of quinazolinone derivatives has attracted more

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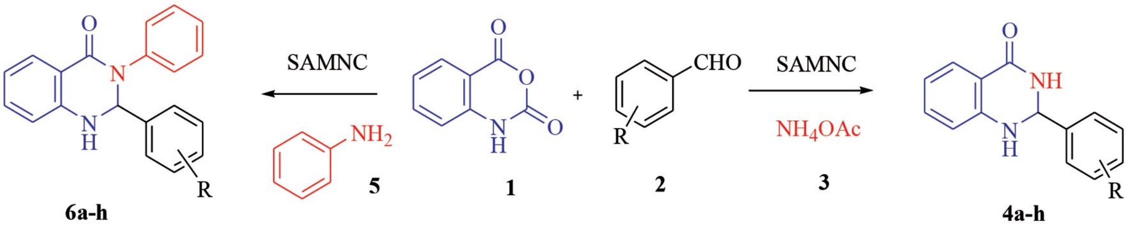
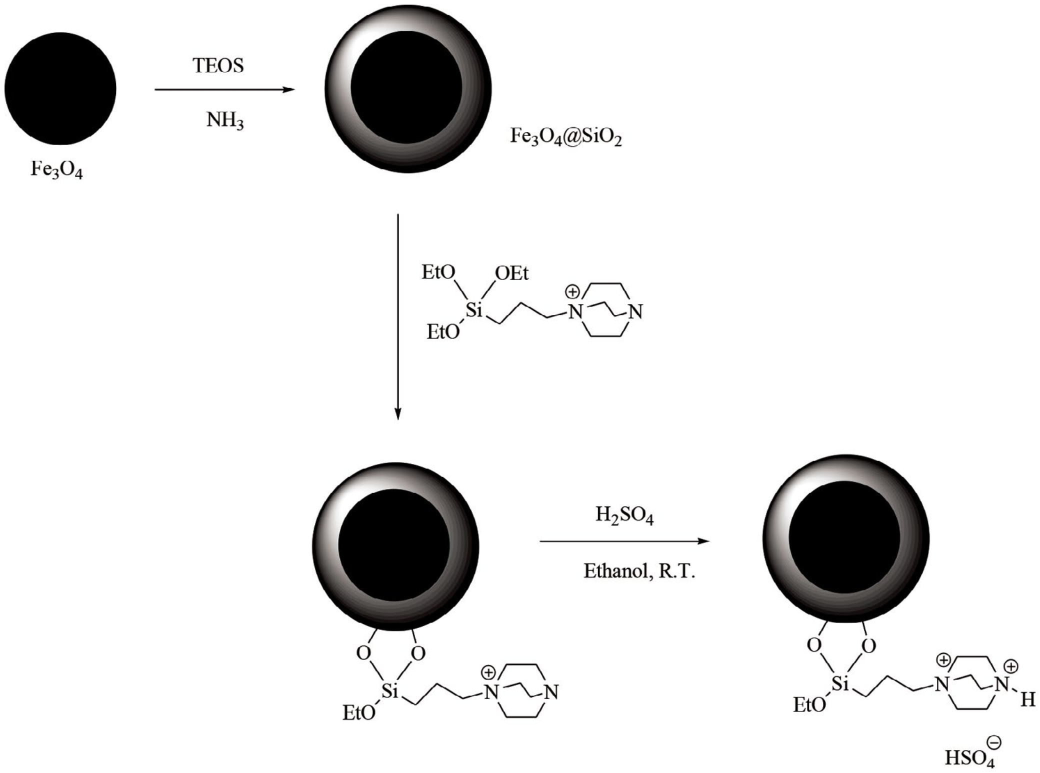
attention. Numerous synthetic methods have been developed for the synthesis of quinazolinone derivatives using silica sulfuric acid [14], gallium (III) triflate [15], molecular iodine [16], 1-butyl-3-methylimidazolium tetrafluoroborate [17], MCM-41-SO_3H [18], β-cyclodextrin [19], and metal–MWCNTs nanocomposites [20]. Most of these methods have one or more of disadvantages, such as the use of hazardous organic solvents, low yields, strongly acidic conditions, expensive moisture-sensitive catalysts, and tedious work-up procedure. Accordingly, We decided to propose a greener procedure for the preparation of 2,3-dihydroquinazolin-4(1H)-one derivatives in the presence of catalytic amounts of SAMNC under solvent-free conditions (Scheme 1).

RESULTS AND DISCUSSION

In the first step, the catalyst was prepared by grafting DABCO onto silica coated magnetite nanoparticles and subsequent acidification with sulfuric acid (Scheme 2).



Scheme. 1. Three-component reaction of isatoic anhydride (1), aromatic aldehydes (2) and ammonium acetate (3) /aniline (5) for the one-pot preparation of 2-aryl-2,3-dihydroquinazolin-4(1H)-ones (4a-h) and 2,3-disubstituted-2,3-dihydroquinazolin-4 (1H)-ones (6a-h).



Scheme. 2. Preparation of the SAMNC catalyst.

To characterize the catalyst, the IR spectrum was recorded. Accordingly the characteristic peak of Fe-O at 570 cm^{-1}, Si-O at 1080 cm^{-1} and the characteristic peak of S=O between 1100-1200 cm^{-1} is evident (Fig. 1).

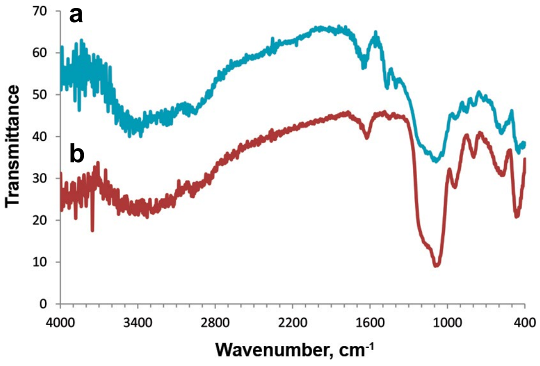


Fig. 1. IR spectrum of (a) the catalyst, (b) Fe_3O_4@SiO_2.

The SEM image of the catalyst was recorded. The average size of the nanoparticles was estimated to be 84 nm.

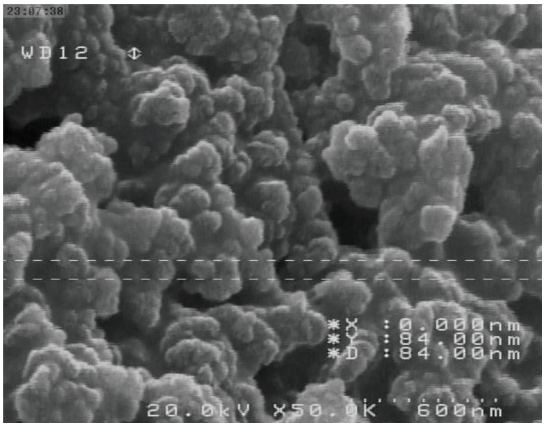


Fig. 2. The SEM image of the catalyst.

The VSM diagram of the magnetic catalyst was provided. As it is evident in Fig. 3, the magnetic saturation of about 10 emu/g was recorded for SAMNC.

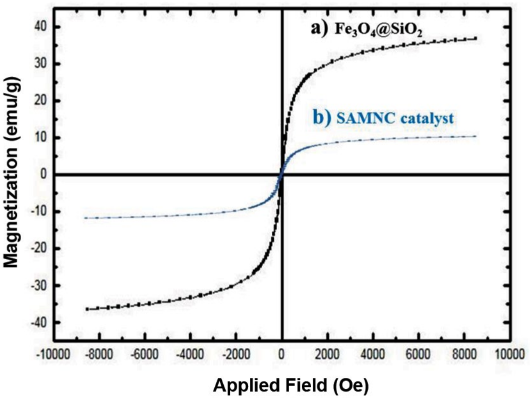


Fig. 3. The VSM diagram of (a) Fe_3O_4@SiO_2, (b) the catalyst.

After characterization of SAMNC, it was decided to evaluate its catalytic activity in the one-pot preparation of 2,3-dihydroquinazolin-4(1H)-one derivatives. To optimize the reaction conditions, isatoic anhydride (1.0 mmol), aromatic aldehyde (1.0 mmol), ammonium acetate, and SAMNC were mixed in a test tube under solvent-free conditions (Table 1).

The best results have been obtained with the molar ratio of ammonium acetate (1.5 mmol) and 3.0 mol% equal to 0.02 g of the catalyst at 100°C under solvent-free conditions. With the optimum reaction conditions in hand, it was decided to evaluate the catalytic activity of SAMNC, in the one-pot preparation of 2-aryl-2,3-dihydroquinazolin-4(1H)-ones(4a-h) (Table 2).

Table 1. Optimization of 2,3-dihydroquinazolin-4 (1H)-one derivatives in the presence of SAMNC as the catalyst, isatoic anhydride (1.0 mmol), aromatic aldehyde (1.0 mmol) and ammonium acetate

Entry	Ammonium acetate (mmol)	Catalyst (mol%)	T (°C)	Time (min)	Yield (%)
1	1.0	-	80	200	-
2	1.0	1.5	80	60	25
3	1.2	1.5	100	60	45
4	1.5	1.5	120	60	80
5	1.5	3.0	100	45	96
6	2.0	3.0	120	45	90
7	2.0	4.5	100	45	91

Table 2. One-pot preparation of 2-aryl-2,3-dihydroquinazolin-4(1H)-ones in the presence of SAMNC (3.0 mol%), isatoic anhydride (1.0 mmol), aldehyde (1.0 mmol) and ammonium acetate (1.5 mmol) at 100 °C

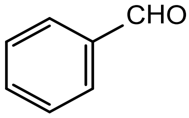
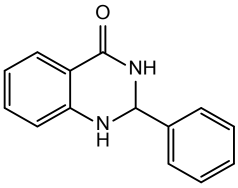
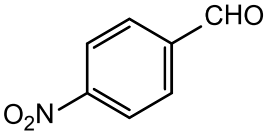
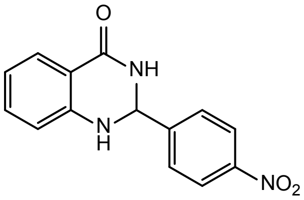
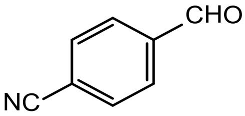
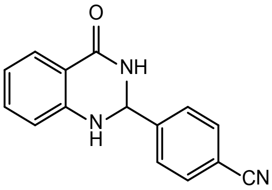
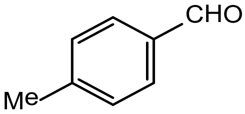
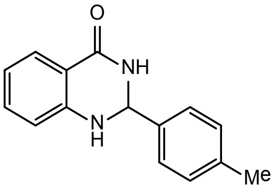
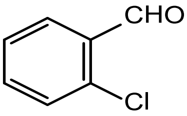
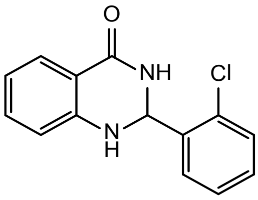
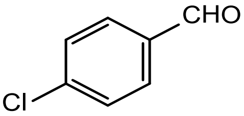
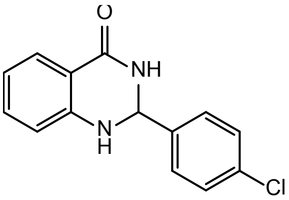
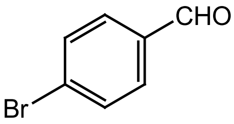
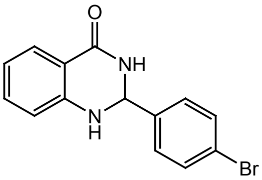
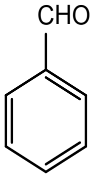
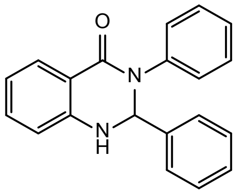
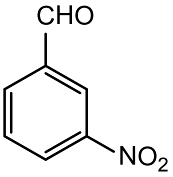
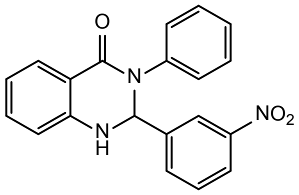
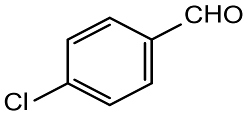
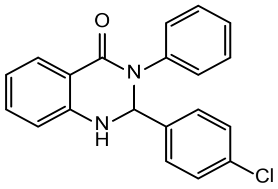
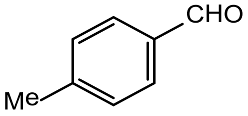
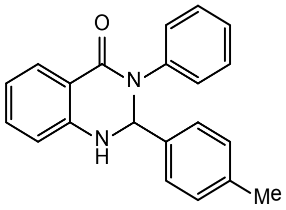
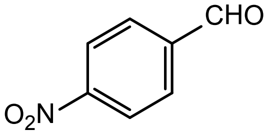
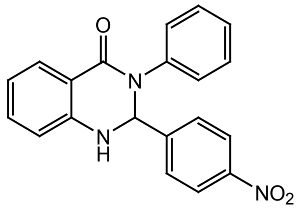
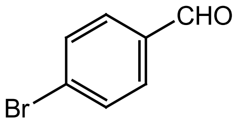
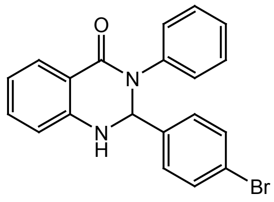
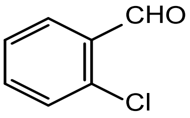
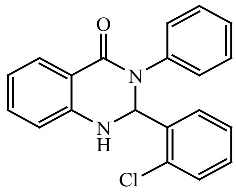
Entry	Aldehyde	Product	Time (min)	Yield (%)
1			45	96
2			50	92
3			40	94
4			55	89
5			50	87
6			45	88
7			40	91

Table 3. One-pot preparation of 2,3-disubstituted-2,3-dihydroquinazolin-4(1H)-ones (6a-h) in the presence of SAMNC (3.0 mol%), isatoic anhydride (1.0 mmol), aldehyde (1.0 mmol) and aniline (1.0 mmol) at 100 °C

Entry	Aldehyde	Product	Time (min)	Yield (%)
1			55	95
2			50	92
3			45	90
4			80	88
5			50	89
6			65	87
7			85	90

After the successful preparation of 2-aryl-2,3-dihydroquinazolin-4(1H)-ones, it was decided to evaluate the scope of the catalyst by one-pot preparation of 2,3-disubstituted-2,3-dihydroquinazolin-4(1H)-ones via the reaction of isatoic anhydride (1.0 mmol), aromatic aldehyde (1.0 mmol), aniline (1.0 mmol), and SAMNC (3.0 mol%) under solvent-free conditions. The results were summarized in Table 3.

Due to the growing interest in green chemistry, the recyclability and reusability of the catalyst were studied in the preparation of 2-aryl-2,3-dihydroquinazolin-4(1H)-ones. After completion of the reaction of isatoic anhydride (1.0 mmol), aromatic aldehyde (1.0 mmol), ammonium acetate (1.5 mmol), SAMNC (3.0 mol%, 0.02 g) was separated and washed with water, hot ethanol and dried. The catalyst was used for four subsequent cycles. Small decrease in the performance of the catalyst was observed in subsequent cycles (Fig. 4).

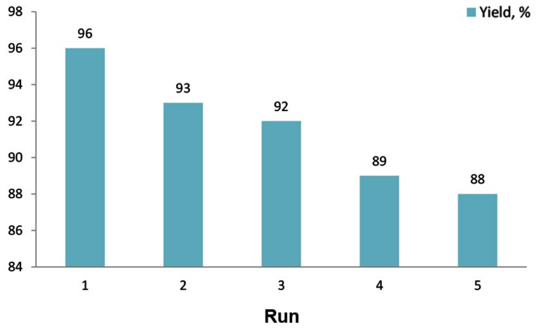


Fig. 4. The recyclability of the catalyst in the reaction of isatoic anhydride (1.0 mmol), aromatic aldehyde (1.0 mmol), and ammonium acetate (1.5 mmol) under solvent-free conditions, within 45 min.

EXPERIMENTAL

General

All commercially available chemicals were purchased from commercial sources and used without further purification. Reaction monitoring was accomplished by TLC on silica gel polygram SILG/UV 254 plates. The IR spectra were recorded on a BOMEM MB-Series 1998 FT-IR spectrophotometer using KBr pellets for the samples and the catalyst in the range of 4000–400 cm^{-1}. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ and DMSO-d_6 on a Bruker Advanced DPX 400 MHz spectrometer using TMS as internal standard. The SEM analyses were carried out using a LEO 1455VP Scanning Electron Microscope, operating at 1-30 KV. CHNS-O analysis was conducted by Costech elemental combustion system, ECS 4010. Magnetism analysis was performed on a vibrating sample magnetometer (4 in., Daghigh Meghnatis Kashan Company, Kashan, Iran) at room temperature.

General procedure for the preparation of sulfuric acid functionalized magnetic Nanocatalyst (SAMNC)

The catalyst was prepared according to the previous report [21] with further acidification of the sonicated nanoparticles with acid (98%) in ethanol at room temperature.

Determination of the acidity of the catalyst

To determine the acidity of the catalyst, SAMNC (20 mg) was added to a 25 mL aqueous solution of NaCl (1 mol/L, pH=6.51), and the resulting mixture was stirred for 2 h. The pH of the solution was reduced to 2.92, indicating the presence of 1.5 mmol/g of H^+.

General procedure for the preparation of 2,3-dihydroquinazolin-4(1H)-ones

A mixture of isatoic anhydride (1.0 mmol), aromatic aldehyde (1.0 mmol), ammonium acetate/aniline (1.2 mmol), and SAMNC (0.02 g) were thoroughly mixed and heated under solvent-free conditions at 100 °C. Completion of the reaction was indicated by TLC [ethyl acetate/n-hexane (2:5)]. After completion of the reaction (as indicated in Table 2 and Table 3) the insoluble crude product was dissolved in hot ethanol and SAMNC was removed by an external magnet. The filtrate was concentrated and the products were recrystallized from aqueous acetone or aqueous ethanol.

CONCLUSION

Sulfuric acid functionalized magnetic nanocatalyst (SAMNC) has been utilized as an efficient acidic catalyst in the one-pot preparation of 2,3-dihydroquinazolin-4(1H)-one derivatives. According to the obtained results, including time, yield and recyclability, SAMNC could be considered as an efficient catalyst for organic transformations.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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