



A novel cooperative Lewis acid/Brønsted base catalyst $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-APTMS-Fe(OH)}_2$: An efficient catalyst for the Biginelli reaction



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ARTICLE INFO

Article history:

Received 11 January 2017

Received in revised form 17 March 2017

Accepted 31 March 2017

Available online 12 April 2017

Dedicated in memory of Shohadaye Gom-nam.

Keywords:

Cooperative catalysis

Lewis acid

Brønsted base

Biginelli reaction

ABSTRACT

A complex of ferrous- and hydroxide ions was generated within a core-shell magnetic nanocatalyst of 24 ± 3 nm. The catalytic activity of material was explored in the synthesis of 3,4-dihydropyrimidine-2-(1*H*)-one/thione (DHPM) derivatives in neat condition. The products are synthesized in high yields (85–98%) in 15–20 min. Neither Fe- nor hydroxide leaching in the reaction medium was detected by AAS and pH analysis, respectively. The catalyst has a convenient reusability after seven consecutive reaction cycles giving a cumulative turnover frequency $>5600 \text{ h}^{-1}$.

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1. Introduction

The synthesis of DHPMs has been of considerable interests because of their diverse range of biological properties [1–6]. Traditionally, the first choice in the preparation of DHPMs involves the Biginelli reaction [7,8]. Diverse kinds of improvements were reported for this reaction [9–37]. Nevertheless, there still are some lacks such as using expensive reagents, expensive/non-recoverable catalysts, long reaction times, requirement for strong acids as catalysts, tiresome workup, laborious separation and use of organic solvents.

Many studies have progressed on preparation and application of immobilized catalysts on diverse solid supports [38–45]. Since common heterogeneous catalysts suffer from the requirement for diffusion of reagents into their bodies [46], their activities decrease sharply. Reducing the size of particles to the nano-scale, enhances the availability of the catalytic sites [47], thus nanocatalysts have the aptitude to connect homogenous and heterogeneous catalysts together [48]. Despite the appropriate effect on reactivity, reducing the size of particles undoubtedly makes the isolation of the catalyst difficult [49–51,4]. To overcome this problem, over the

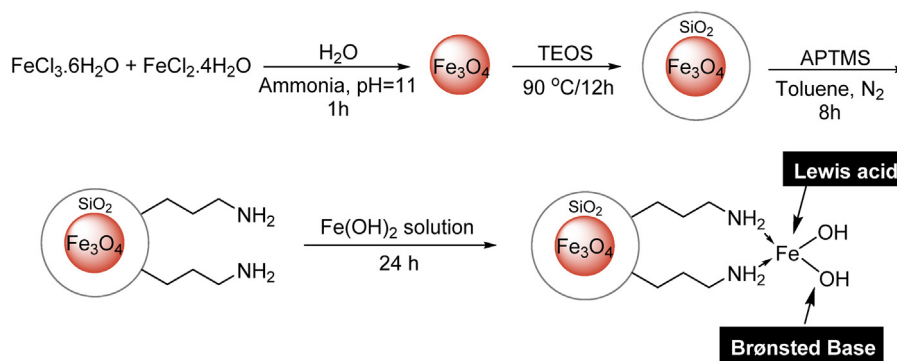
last decade, magnetic nanoparticles have presented as an effective troubleshooting way [52–70].

Cooperative catalysts can activate the reaction substrates in a dual mode by exhibiting two different catalytic functions simultaneously. Hence, in recent years they have prevailed as the most elegant class of artificial catalysts [71–77]. To date, there are some examples of their applications in organic syntheses. Chae et al. introduced a tetrametallic ruthenium- μ -oxo- μ -hydroxo catalyst for the alcohol oxidation [78]. Lewis acid/Brønsted acid salicylato titanocene in the Mannich reaction [79], cooperative effect of Pt-Rh/Ba/Al and CuZSM-5 catalysts for NO_x reduction [80], effect of Ce and Mn in $\text{MnCe/Al}_2\text{O}_3$ by [81], Co(II) complex incorporated into amino-functionalized MIL-101(Cr) for cyclohexane selective oxidation [82], Ni nanoparticles on basic hydrotalcite support [83], combination of Co and W catalysis in dehydrogenation of unactivated alkanes [84] as well as alloy nanocrystals on MOFs [85] are some examples of this type of catalysts.

In continuation of our research area in the design and synthesis of novel catalysts [86–92], we decide to explore a novel cooperative ferrous ion (Lewis acid)- and hydroxide (Brønsted base) functionalized magnetic interphase catalyst and its application in the Biginelli reaction.

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Scheme 1. Preparation of the catalyst.

2. Experimental

2.1. The preparation of catalyst

Ferric chloride (5.0 mmol) and ferrous chloride (2.5 mmol) were successively dissolved in de-ionized water (20 mL). The resulting solution was then added slowly into aqueous ammonia (25%, 40 mL) under vigorous stirring. After addition of tetraethyl orthosilicate at 90 °C, stirring was continued overnight. The resulting silica supported magnetite colloid was separated and washed repeatedly with de-ionized water and EtOH. Then, the final dark-brown product was dried at 200 °C (led to 88% yield). 3-Aminopropyl trimethoxysilane (4.5 mL) was added to a suspension of silica supported magnetite (1 g) in dry toluene and heated to 110 °C for 10 h. Afterwards, the solid was collected by magnetic separation, washed with water and DCM several times, and dried at 60 °C overnight (in 92% yield). The resulting material was denoted as Fe₃O₄@SiO₂-APTMS. Ferrous chloride (0.5 mmol) and potassium carbonate (2 Equiv.) was mixed in water led to the generation of Fe(OH)₂ which was added to 1 g of the prepared material in water and refluxed overnight. After drying at 100 °C, Fe₃O₄@SiO₂-APTMS-Fe(OH)₂ was obtained in about 89% yield.

2.2. Ion-exchange pH analysis of Fe₃O₄@SiO₂-APTMS-Fe(OH)₂

50 mg of the Fe₃O₄@SiO₂-APTMS-Fe(OH)₂ was added to a solution of NaCl (1 M, 25 mL) with an initial pH = 6.45 and the mixture stirred for 3 h at r.t. The pH of solution increased to 6.67. The result confirmed that no notable leaching of hydroxide ions occurred in reaction conditions (<10⁻⁴ mmol per gram of the Fe₃O₄@SiO₂-APTMS-Fe(OH)₂).

2.3. Elemental analysis of Fe₃O₄@SiO₂-APTMS-Fe(OH)₂

The elemental analysis of Fe₃O₄@SiO₂-APTMS-Fe(OH)₂ was done using a Perkin Elmer CHN elemental analyzer. Characterization showed 3.78% C, 1.12% N and 1.18% H (=0.43 mmol Fe(OH)₂ g⁻¹). Results confirmed other data.

2.4. Typical procedure for the synthesis of DHPMs catalyzed by Fe₃O₄@SiO₂-APTMS-Fe(OH)₂

In a reaction vessel 10 mg of Fe₃O₄@SiO₂-APTMS-Fe(OH)₂ (equal to 0.0043 mmol surface Fe) was added to a mixture of ethyl acetoacetate (1 mmol), an aryl aldehyde (1 Equiv.) and urea/thiourea (1.2 Equiv.). The reaction was progressed at 80 Equiv. -C until the completion. At the end, Fe₃O₄@SiO₂-APTMS-Fe(OH)₂ was magnetically recovered after addition of cold EtOH. The product was purified by re-crystallization from EtOH. The puri-

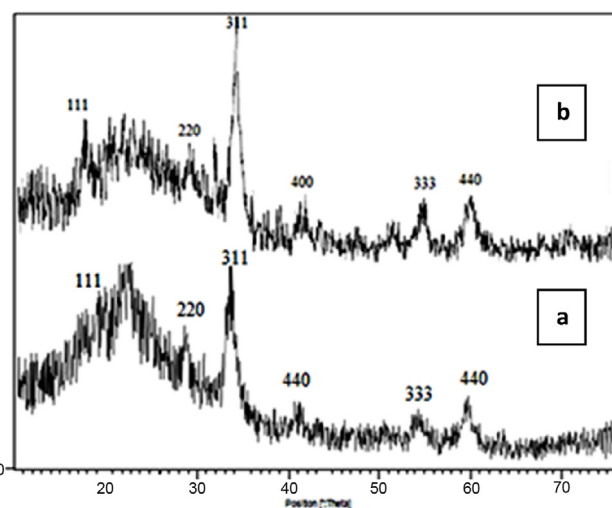


Fig. 1. X-ray diffraction patterns of Fe₃O₄@SiO₂ (a) and Fe₃O₄@SiO₂-APTMS-Fe(OH)₂ (b).

ties of prepared DHPMs were confirmed by comparison of their spectroscopic data by the literatures.

3. Results and discussions

The general procedure for synthesis of Fe₃O₄@SiO₂-APTMS-Fe(OH)₂ is represented in Scheme 1. Fe₃O₄@SiO₂ nanoparticles were synthesized according to the literature [93]. Then, the surfaces of the synthesized nanoparticles were modified by the covalently grafting of organic linker 3-aminopropyltrimethoxysilane to generate Fe₃O₄@SiO₂-APTMS. In the final step, the synthesized interphase material was again modified via a Fe(OH)₂ resulted in the generation of Fe₃O₄@SiO₂-APTMS-Fe(OH)₂. The synthesized materials were characterized by different techniques including XRD, FT-IR, SEM, EDX and elemental analysis (CHN).

The crystalline structures of the as-synthesized Fe₃O₄@SiO₂ and Fe₃O₄@SiO₂-APTMS-Fe(OH)₂ were confirmed by XRD and the results are shown in Fig. 1(a) and (b). In Fig. 1a, diffraction peaks at 2θ = 18.5°, 30.3°, 35.5°, 43.0°, 57.2°, 63.0° corresponded to the highly crystalline cubic spinel structure of Fe₃O₄. The generation of SiO₂ was proved by the band at 2θ = 22°. These results proved that the surface of magnetite was successfully coated with the silica shell. The XRD patterns of the Fe₃O₄@SiO₂-APTMS-Fe(OH)₂ (Fig. 1b) was similar to that of Fe₃O₄@SiO₂ in line shape demonstrating that no change in the crystal structure happened during the introduction of organic functional groups.

The surface modification of the prepared materials was also characterized by FT-IR spectroscopy. The FTIR spectra

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