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Fe_3O_4@SiO_2/collagen: An efficient magnetic nanocatalyst for the synthesis of benzimidazole and benzothiazole derivatives

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ABSTRACT

In this project, Fe_3O_4@SiO_2 was synthesized and combined with collagen for the preparation of Fe_3O_4@SiO_2/collagen. It was characterized by FT-IR, ^{1}H NMR, VSM, XRD, EDX, SEM and TEM. This nanocatalyst has some interesting advantages such as facile synthetic procedure, high catalytic activity, easy separation and acceptable reusability. It was applied as an efficient nanocatalyst in the synthesis of benzimidazole and benzothiazole derivatives. This method offers several advantages including high yields, short reaction times, easy workup process and environmentally benign reaction conditions.

1. Introduction

Benzimidazole and benzothiazole derivatives possess a variety of biotic activities. These heterocyclic compounds have shown different pharmacological activities such as antibacterial, antiulcer, antihypertensive, antiviral, antifungal, anticancer, and antihistamine activities [2–7].

Benzimidazole derivatives exhibit significant activity against several viruses such as HIV [3,8], influenza and human cytomegalovirus (HCMV) [8]; they also act as topoisomerase inhibitors [3], selective neuropeptide YY1 receptor antagonists [11], angiotensin II inhibitors [13], and smooth muscle cell proliferation inhibitors [14] and have much more importance in organic synthesis.

Collagen is the most common protein family in the body of living creatures [17]. Collagen has an important role in the formation of tissues and organs and is involved in various functional expressions of cells. Skin, bone, tendon, teeth and blood vessels are some of the living organs where collagen can be found. The main sources of commercial collagen are limited to those of land-based creatures, such as bovine or porcine skins and bones [19].

Collagen has usefulness in a wide variety of biomedical biological applications. As the primary reason, collagen has superior biocompatibility compared with other natural polymers, such as albumin and gelatine. In addition, it can form fibres with extra strength and stability. These features are derived from its enriched functional groups, cross-linkage of its fibres and its supramolecular structure [21].

Until now, a number of methods have been developed for the synthesis of benzimidazoles [22–25]. Generally, 2-substituted benzimidazoles are synthesized using 1,2-phenylendiamine with aldehydes and/or acyl chlorides, carboxylic acids, and orthoesters. However, some synthesis conditions comprise the use microwave irradiation in an acidic medium [26] and/or refluxing in the presence of homo/heterogeneous catalysts such as acetic acid [27], silica supported sulfuric acid [28], Zinc-proline [29], $Yb(OTf)_3$ [30], etc.

In addition, a lot of methods have been reported for the synthesis of benzothiazoles by condensation of benzene,

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2-aminothiophenol with acyl chlorides or aldehydes. In this case, synthesis procedures include the use of ionic liquid [31] and/or microwave irradiation with a SiO_2 catalyst [32] and/or refluxing in the presence of homo/heterogeneous catalysts such as acetic acid [33], active carbon in toxic solvents [34] and Chitosan-supported Fe_3O_4 [35].

To the best of our knowledge, most of the methods for the synthesis of benzimidazoles and benzothiazoles suffer from one or some disadvantages such as low yields, harsh reaction conditions, time consuming process, use of expensive catalysts and tedious workups. Thus presently, the development of environmentally benign, high-yielding and fast synthesis of benzimidazole and benzothiazole derivatives remains a desired goal in organic synthesis. In this work, we report a highly efficient procedure for the preparation of benzimidazole and benzothiazole derivatives in ethanol (EtOH) media using Fe_3O_4@SiO_2/collagen as an efficient magnetic reusable nanocatalyst.

2. Experimental

2.1. Materials and methods

Hydrolysed collagen was of industrial grade (Parvar Novin-e Tehran Co., Mw ¼ 2000–20,000 Da), which is available in the market, and it has approximately 20% insoluble inorganic salts [36,37]. All chemicals were purchased from Merck, Fluka and Sigma–Aldrich companies and were used without further purification.

All reactions and the purity of benzimidazole and benzothiazole derivatives were monitored by thin-layer chromatography (TLC) using aluminium plates coated with silica gel F254 plates (Merck) using ethyl acetate, *n*-hexane and methanol as eluents. Melting points were determined in open capillaries using an Electrothermal 9100 instrument.

Fourier transform infrared (FT-IR) spectra were recorded on a Shimadzu FT-IR 8400s using KBr plates of samples. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Bruker 400 ultrashield and DMSO-d_6 was used as the solvent. A transmission electron microscope (TEM) from day-petronic company of Iran was used. Scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis were performed on a VEGA II TESCAN using 30 KV in high vacuum and Au spin coating for SEM sample preparation. Wide-angle powder X-ray diffraction (XRD) patterns of the solids were obtained in a JEOL with a Cu Kα (λ = 0.15420 nm) X-ray irradiation source in a 2θ range between 5° and 80°. Magnetic properties were recorded by the vibrational sampling magnetometry (VSM) technique in 1.5 T external magnetic fields at room temperature, by using a MDK-6 instrument.

2.2. Preparation of Fe_3O_4 magnetic nanoparticles

Fe_3O_4 nanoparticles were synthesised via a coprecipitation method by using ferric chloride ($FeCl_3 \cdot 6H_2O$) and ferrous chloride ($FeCl_2 \cdot 4H_2O$) that was introduced in our previous paper [38]. Briefly, Ferric chloride and ferrous chloride dissolved in degassed water and ammonia solution were added to this mixture under vigorous stirring. When pH increases, black colloids of Fe_3O_4 nanoparticles were formed. Fe_3O_4 nanoparticles were separated by using an external magnet in isoelectric point (pH ~ 8). Then, the collected precipitate was poured in EtOH 50% and separated by using a magnet (rinsed using magnet separation) three times. Finally, Fe_3O_4 nanoparticles were dried in a vacuum oven.

2.3. Preparation of the Fe_3O_4@SiO_2/collagen nanocatalyst

First, 2 g of Fe_3O_4 nanoparticles and 5 mL of tetraethyl orthosilicate (TEOS) were added in a 500-mL round bottom flask that contains 150 mL EtOH 50%. In the second vessel, 10 g of collagen was dissolved in 100 mL of a dilute acetic acid solution (5%) under vigorous stirring. A homogeneous supernatant of the second mixture was added to the Fe_3O_4 mixture. The flask was poured in an ultrasonic bath for 30 min. Then, NH_4OH (10%) was added dropwise to the mixture until the pH reached about eight. In the next step, the residue was collected by using an external magnet; it was poured in a Teflon autoclave that contains EtOH (50%) and heated at 90 °C for 6 h. The resulting product was separated by external magnetic fields, dispersed in EtOH 50% and rinsed three times. Finally, it was dried in a vacuum oven at 60 °C for 12 h.

2.4. Synthesis of the non-magnetic nanocatalyst (SiO_2/collagen)

The nonmagnetic nanocatalyst (SiO_2/collagen) was synthesised by the same procedure (mentioned in 2.3.) without using Fe_3O_4 and tripling the amount of TEOS.

2.5. Synthesis of the non-silicate magnetic nanocatalyst (Fe_3O_4@collagen)

The non-silicate magnetic nanocatalyst (Fe_3O_4@collagen) was synthesised by the same procedure (mentioned in 2.3) without using TEOS in the synthesis procedure.

Table 1
Optimization of the catalysts and solvents for synthesis of benzimidazole.[a]

Entry	Type & amount of catalyst[b]	Solvent	Time (min)	Yield (%)
1	Non-additive	EtOH	1080	25
2	50 (Collagen)	H_2O[c]	_	_
3	50 (Collagen)	EtOH[d]	50	85
4	50 (Fe_3O_4)	EtOH	240	30
5	50 (Fe_3O_4@collagen)	EtOH	20	96
6	50 (SiO_2@collagen)	EtOH	25	95
7	50 (Fe_3O_4@SiO_2)	EtOH	150	53
8	10 (Fe_3O_4@SiO_2/collagen)	EtOH	20	68
9	50 (Fe_3O_4@SiO_2/collagen)	EtOH	20	97
10	80 (Fe_3O_4@SiO_2/collagen)	EtOH	20	56
11	160 (Fe_3O_4@SiO_2/collagen)	EtOH	20	30
12	50 (Fe_3O_4@SiO_2/collagen)	EtOH	15	97
13	50 (Fe_3O_4@SiO_2/collagen)	H_2O	15	Trace
14	50 (Fe_3O_4@SiO_2/collagen)	CH_2Cl_2	15	80
15	50 (Fe_3O_4@SiO_2/collagen)	$CHCl_3$	15	49
16	50 (Fe_3O_4@SiO_2/collagen)	CH_3CN	15	_
17	50 (Fe_3O_4@SiO_2/collagen)	Solvent free	15	_

[a] Benzimidazoles synthesis conditions: 1 mmol 1,2 phenylendiamine, 1 mmol 3-nitrobenzaldehyde, 4 mL solvent at rt.
[b] Catalyst (mg).