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Sulfamic acid-functionalized silica-coated magnetite nanoparticles as a recyclable catalyst for the facial synthesis of benzimidazole derivatives

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Sulfamic acid-functionalized silica-coated magnetic nanoparticles (SO_3H-Fe_3O_4@SiO_2 MNPs) were synthesized and applied as an effective catalyst for the synthesis of benzimidazole derivatives through the reaction between aldehydes and *o*-phenylenediamine or 4-methylbenzene-1,2-diamine under ultrasound-promoted conditions. The reactions were optimized in the terms of solvent, time, temperature, and amount of catalyst. The reactions proceed smoothly under mild conditions to yield the respective products in excellent yields and in short reaction times (45 minutes). The identified catalyst can be easily separated by an external magnetic field and reused for five fresh runs without significant loss of catalytic activity.

Keywords: Heterocycles, Benzimidazoles, Sulfonated magnetic nanoparticles, Nanocatalyst, Green chemistry, Ultrasound-promoted

INTRODUCTION

It is an unquestionable fact that environmental issues are some of the important concerns during past few decades. The major portion of environmental pollution is related to growth of industrialization (*e.g.,* chemical technologies). Therefore, many approaches have been developed for the preparation and use of efficient and recoverable heterogeneous catalysts in the case of chemical products. These catalysts have emerged as useful for making organic transformations academically and industrially eco-friendly and economically viable [1]. In this context, nanoparticles have received a great deal of attention as heterogeneous catalysts, in part due to their interesting structural properties and high catalytic activities [2-5]. In recent years, a growing number of approaches have been developed for preparation of supported heterogeneous nanocatalysts by immobilizing different homogeneous precursors on a solid support. These immobilized nanocatalysts offer many advantages over their non-supported counterparts in being low- or non-toxic, air- and moisture-compatible, easily separable and recyclable [6-8]. Despite the above mentioned advantages, these nanocatalysts often suffer from the tedious task of recycling *via* expensive ultra-centrifugation, which limits their utility as catalysts. However, the issues of separation and reusability of these nanocatalysts have been solved using magnetic nanoparticles (MNPs) as excellent supports amenable to simple magnetic separation [9-12].

Magnetic nanoparticles (MNPs) have been extensively used in biomedical and pharmaceutical areas [13, 14], and have found potential applications for cell [15] and protein separation [16], drug delivery systems [17], magnetic resonance imaging (MRI) [18], and hyperthermia cancer treatment [19]. Moreover, MNPs are good supports for immobilization of homogeneous catalysts [20], and can be effectively functionalized through appropriate surface modifications [21-37]. Therefore, MNPs-supported catalytic systems can be considered as powerful candidates due to their high surface area, magnetic properties, facile separation, and low cost [38, 39]. Based on these attractive properties, many MNPs-supported catalysts have been successfully utilized for catalyzing a broad series of chemical reactions such as oxidation [40], polymerization [41], and even enzymatic reactions [42]. In recent years, a variety of magnetic nano-oxides functionalized using different acidic groups such as phosphotungstic acid ($H_3PW_{12}O_{40}$), Preyssler-type heteropolyacids, sulfamic, and sulfonic acids have been prepared and successfully applied for selectively catalyzing various chemical reactions [43,44].

These NPs have superior properties including high magnetic strength, easy construction, eco-friendliness, and diverse potential applications in different fields [45-47].

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Nitrogen-containing heterocyclic compounds are well-documented and many of them widely occur naturally. Many of these compounds constitute the largest portion of chemical entities which provide useful scaffolds for many natural products, fine chemicals and biologically active pharmaceuticals that have vital importance to life [48-51]. Among these heterocyclic compounds, benzimidazole derivatives are of particular interest due to their applications in medicinal chemistry and modern drug industry, based on their significant biological and pharmaceutical properties such as anticancer, anti-HIV, anti-tumor, antibacterial, antiviral, antifungal and antihistamine activities [52-61].

There are several previously reported methods for the synthesis of benzimidazole derivatives using various catalytic reagents such as sulfamic acid [62], silica sulfuric acid [63], *p*-TSA [64], Lewis acid [65], $FeCl_3{\cdot}6H_2O$ [66], nano-$TiCl_4.SiO_2$ [67], poly(*N*, *N*-dibromo-*N*-ethyl-benzene-1, 3-disulfonamide) (PBBS) and *N*, *N*, *N*, *N*-tetrabromobenzene-1,3-disulfonamide (TBBDA) [68], sulfonic acid-functionalized imidazolium salts/$FeCl_3$ [69], nano indium oxide [70], nano-solid acid catalysts [71], *P*-TsOH [72] and Shirasagi KL [73]. Most of the mentioned synthesis methods suffer from some disadvantages, such as large amount of catalysts, tedious work up procedures, difficult isolation of the catalyst, and also the applied catalysts cannot be recovered and reused.

In continuation of our interest for developing more benign, eco-friendly, and efficient heterogeneous nanocatalysts and their application for the synthesis of various heterocyclic compounds including benzimidazoles [74, 75], herein, we are encouraged to examine for the first time the catalytic capability of our previously synthesized sulfamic acid-functionalized silica-coated magnetic nanoparticles (SO_3H-Fe_3O_4@SiO_2 MNPs) [76], as an efficient and magnetically recoverable heterogeneous catalyst for the synthesis of benzimidazole derivatives. The reactions were optimized in the terms of solvent, time, temperature, and amount of catalyst.

EXPERIMENTAL

Materials and methods

Chemicals used in this work were purchased from Fluka (Switzerland) or Merck (Darmstadt, Germany) chemical companies and were used without purification. Fourier Transform Infrared (FTIR) spectra were recorded in KBr pellets on a Shimadzu 435-U-04 FTIR spectrometer (Kyoto, Japan). Proton nuclear magnetic resonance (^{1}H NMR) spectra were obtained on a 400 MHz Bruker instrument (Bruker, Ettlingen, Germany) in DSMO-d_6 or $CDCl_3$ as solvents and tetramethylsilane (TMS) as internal standard. Ultrasonication was performed in a Sonica- 2200 ETH series ultrasound cleaner with a frequency of 45 kHz. Melting points were measured on a SMPI apparatus (UK).

Synthesis of the catalyst (SO_3H-Fe_3O_4@SiO_2)

The catalyst has been previously synthesized and fully characterized by our research group as reported [76]. In brief, the Fe_3O_4 NPs were synthesized according to the method reported by Rafiee *et al*. [77], and then a silica layer was coated on the surface of the Fe_3O_4 NPs in order to protect the MNPs from possible oxidation or aggregation [78, 79]. The synthesized Fe_3O_4@SiO_2 NPs were functionalized using 3-chloropropyltrimethoxysilane (Fe_3O_4@SiO_2-Cl) [80]. Then, the Fe_3O_4@SiO_2-Cl NPs were reacted with ethylene diamine through a substitution nucleophilic reaction to afford diamine-functionalized MNPs (Fe_3O_4@SiO_2@NH-NH_2). Ultimately, the Fe_3O_4@SiO_2@NH-NH_2 MNPs were reacted with chlorosulfonic acid, which resulted in the sulfonation of both amino groups to produce SOH-Fe_3O_4@SiO_2 MNPs. The successful synthesis of the catalyst was established by performing different analytical techniques in our previous work [76].

General procedure for the SO_3H-Fe_3O_4@SiO_2-catalyzed synthesis of benzimidazole derivatives (3a-i)

A mixture of *o*-phenylenediamine or 4-methylbenzene-1,2-diamine (**1**; 1 mmol), aldehyde (**2**; 1 or 2 mmol), and 0.02 g of the catalyst (SO_3H-Fe_3O_4@SiO_2) in ethanol (5 mL) was sonicated at 50 °C. After completion of the reaction (during 45 min monitored by TLC) the reaction mixture was diluted with hot ethanol (5 mL) and stirred until the solid materials dissolved completely. The catalyst was recovered magnetically using an external magnetic bar. Afterward, distilled water (20 mL) was added to the reaction mixture and the solid products were collected by filtration and dried in air. Finally, the crude products were washed in diethyl ether for purification. All synthesized products are known compounds (**3a-i**) which were characterized by their melting points, as well as spectral (FTIR and ^{1}HNMR) analyses and compared with their corresponding data reported in the literature.

Some selected data

1-benzyl-6-methyl-2-phenyl-1H-benzoimidazole (3a): mp: 160-163 °C; FTIR (KBr, ν_{max} /cm^{-1}):

3051, 2926, 2855, 1612, 1594, 1502, 1448, 1413, 1371, 1223; ^{1}H NMR (400 MHz, DMSO-d_6): 2.40 (s, 3H, CH_3), 5.55 (s, 2H, CH_2), 6.98-7.71 (m, 13H, H-Ar), 9.33 ppm.

1-(2-chlorophenylmethyl)-2-(2-chlorophenyl)-1H-benzoimidazole (3b): mp: 157-159 °C; FTIR (KBr, ν_{max} /cm^{-1}): 3059, 2950, 1612, 1572, 1522, 1441, 1396, 1355, 1280; ^{1}H NMR (90 MHz, DMSO-d_6): 5.33 (s, 2H, CH_2), 6.54-7.83 (m, 12H, H-Ar), 9.33 ppm.

1-(4-hydroxyphenylmethyl)-2-(4-hydroxyphenyl)-1H-benzoimidazol (3c): mp: 252-254 °C; FTIR (KBr, ν_{max} /cm^{-1}):3448, 3026, 2925, 2854, 1612, 1597, 1515, 1444, 1395, 1266; ^{1}H NMR (90 MHz, DMSO-d_6): 5.33 (s, 2H, CH_2), 6.79-7.16 (m, 12H, H-Ar), 9.33, 9.89 (s, 2H, OH) ppm.

2-(4-fluorophenyl)-6-methyl-1H-benzoimidazole (3f): mp: 183-186 °C; FTIR (KBr, ν_{max}/cm^{-1}): 3452, 3068, 2924, 2854, 1630,1609, 1506, 1472, 1447, 1431, 1383, 1227; ^{1}H NMR (400 MHz, DMSO-d_6): 2.50 (s, 3H, Me), 7.03-8.20 (m, 7H, H-Ar), 12.75 (s, 1H, NH) ppm.

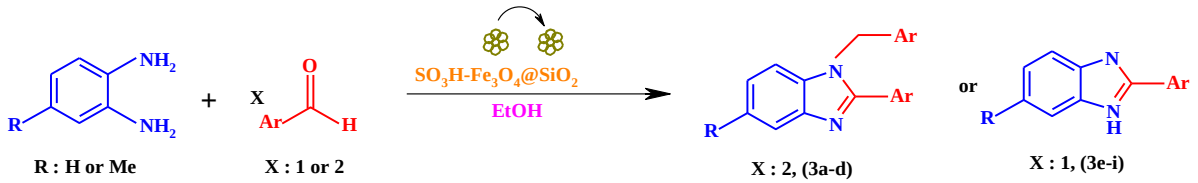
2-(4-hydroxyphenyl)-6-methyl-1H-benzoimidazole (3g): mp: 252-257 °C; FTIR (KBr, ν_{max} /cm^{-1}): 3398, 3064, 2923, 2854, 1631,1610, 1595, 1513, 1447, 1395, 1255; ^{1}H NMR (400 MHz, DMSO-d_6): 1.08 (s, 3H, Me), 6.91-7.41 (m, 7H, H-Ar), 7.99 (s, 1H, NH), 9.98 (s, 1H, OH) ppm.

RESULTS AND DISCUSSION

In this research, following our previously reported procedure [76], for the first time we have chosen and employed the SO_3H-Fe_3O_4@SiO_2 MNPs as an efficient and recyclable catalyst in the facial and green synthesis of benzimidazole derivatives (Scheme 1). The applied catalyst in the present investigation involves the organo sulfamic acid moiety which has been supported covalently on the surface of silica-coated MNPs.

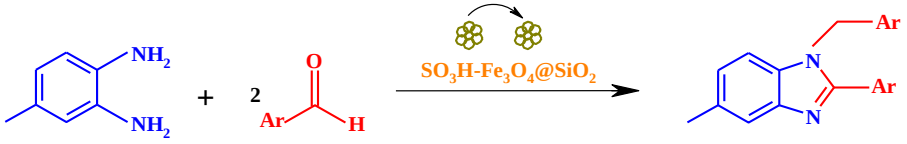
Optimization of the reactions

The catalytic capability of the SO_3H-Fe_3O_4@SiO_2 MNPs was investigated in the synthesis of benzimidazole derivatives by the reaction of aldehydes and *o*-phenylenediamine or 4-methylbenzene-1,2-diamine under ultra-sonicate conditions. In order to optimize the reaction conditions, the reaction of benzaldehyde (**1**) and 4-methylbenzene-1,2-diamine (**2**) was chosen as model reaction and the effects of different reaction parameters were studied. The results obtained are summarized in Table 1. The effects of temperature, different solvents, and various amounts of the catalyst were screened under different reaction conditions (reflux, ultrasonic, solvent-free, and room temperature). The most appropriate reaction condition was obtained using ethanol as the solvent, 0.02 g of the catalyst per mmol of aldehyde at 50 °C for 45 min under ultra-sonicate conditions (entry15). Upon increasing of the catalyst amount no improvement in the reaction yield and rate was observed (entry 16). The reaction was also examined in absence of the catalyst under the same conditions which resulted in low rate and trace yield (entry 17). This achievement interested us to extend the scope of the explained methodology to a diverse series of substituted aromatic aldehydes (**1a-i**) in the reaction with *o*-phenylenediamine or 4-methylbenzene-1,2-diamine (**2**) under the optimized conditions (Scheme 1). In general, all reactions proceeded smoothly to furnish the respective products in relatively short reaction times with excellent and comparable yields irrespective of the nature of the substituent groups bonded to the aromatic ring. All the products (**3a-i**) obtained were known compounds which were characterized on the basis of their physical and spectral (FTIR and ^{1}HNMR) analysis and compared with the corresponding data reported in the literature (Table 2).



Scheme 1. Synthesis of 2-arylmethyl-1-*H*-1,3-benzimidazoles (3**a-d**), and 2-aryl-benzimidazoles (3**e-i**) catalyzed by SO_3H-Fe_3O_4@SiO_2 MNPs.

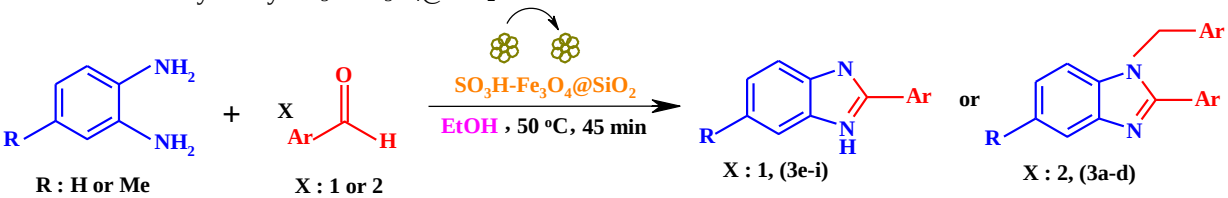
Table 1. Screening the reaction parameters for the model synthesis of 1-benzyl-6-methyl-2-phenyl-1*H*-benzoimidazole.[a]



Entry	Catalyst (g)	Solvent	Temperature (ºC)	Reaction conditions	Time (h)	Yield (%)[b]
1	0.01	H_2O	r.t.	Thermal	4.5	trace
2	0.01	EtOH	r.t.	Thermal	4.5	38
3	0.01	H_2O /EtOH 1:1	r.t.	Thermal	4.5	23
4	0.01	CH_3CN	r.t.	Thermal	4.5	31
5	0.01	EtOH	45	Thermal	4	45
6	0.01	EtOH	60	Thermal	4	52
7	0.01	EtOH	80	Thermal	3.5	59
8	0.01	EtOH	80	Reflux	3	75
9	0.01	EtOH	40	Ultra-sonicate	2	62
10	0.01	EtOH	50	Ultra-sonicate	1	90
11	0.01	EtOH	60	Ultra-sonicate	1.5	70
12	0.01	no solvent	60	Thermal	3	68
13	0.01	no solvent	80	Thermal	2	73
14	0.01	no solvent	100	Thermal	2.5	59
15	0.02	EtOH	50	Ultra-sonicate	0.75	91
16	0.03	EtOH	50	Ultra-sonicate	1.5	72
17	no catalyst	EtOH	50	Ultra-sonicate	4	10

[a]Conditions: benzaldehyde (2 mmol), 4-methylbenzene-1,2-diamine (1 mmol), solvent (5 mL).
[b] Isolated pure yield.

Table 2. Synthesis of 2-aryl-1-arylmethyl-1*H*-1,3-benzimidazoles (**3a-d**) and 2-aryl-benzimidazoles (**3e-i)** catalyzed by SO_3H-Fe_3O_4@SiO_2 MNPs under ultra-sonicate conditions at 50 ºC.[a]



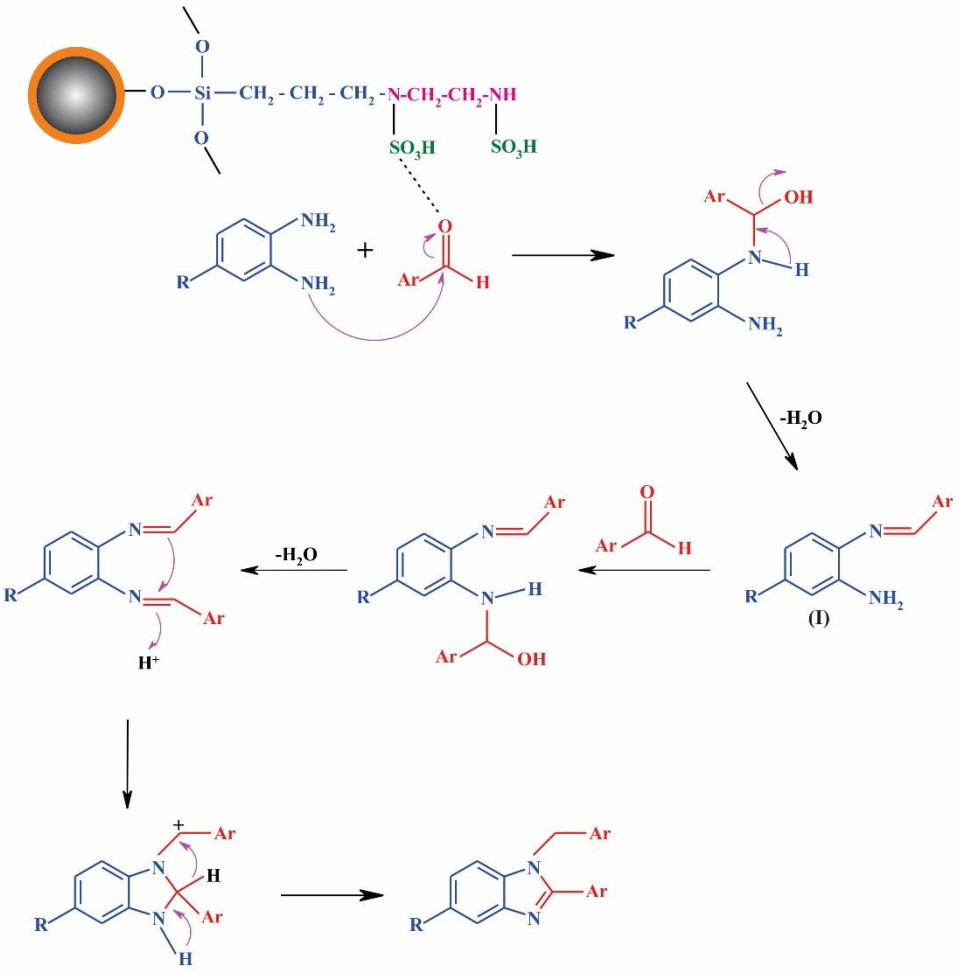
Entry	Ar	Product	Yield (%)[b]	Mp (˚C)	
				Found	Reported
1	C_6H_5	**3a**	91	160-163	159-161[63]
2	2-ClC_6H_4	**3b**	83	157-159	158-159[74]
3	4-OHC_6H_4	**3c**	78	252-254	254-256[74]
4	3-$NO_2C_6H_4$	**3d**	88	165-168	167-168[74]
5	3-$NO_2C_6H_4$	**3e**	93	196-198	186-188 [83]
6	4-FC_6H_4	**3f**	83	183-186	182-183[81]
7	4-OHC_6H_4	**3g**	80	252-257	244-246[82]
8	4-ClC_6H_4	**3h**	87	281-282	281-283[83]
9	4-MeC_6H_4	**3i**	79	273-276	268-270[83]

[a] Conditions: aldehyde (**1**; x mmol), *o*-phenylenediamine or 4-methylbenzene-1,2-diamine (**2**; 1 mmol), catalyst (0.02 g), ethanol (5 mL), ultra-sonicate conditions, 50 ºC, 45 min.
[b] Isolated pure yield.

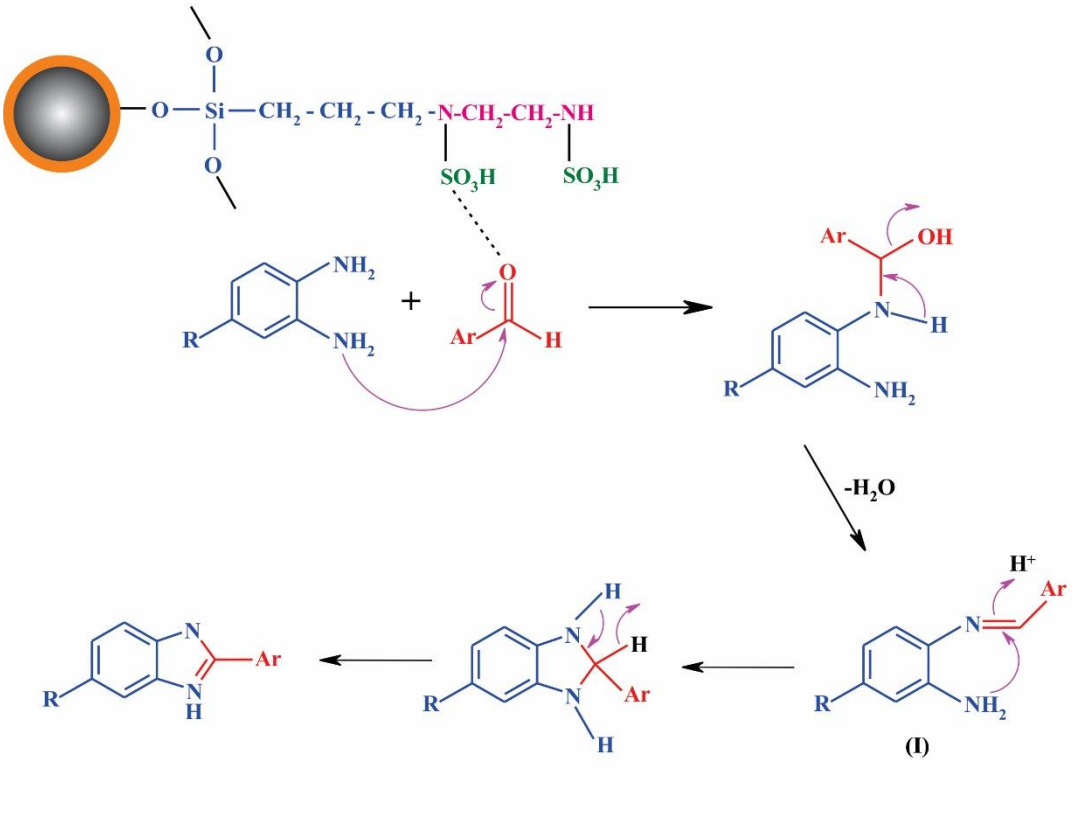
Proposed catalytic reaction mechanisms in the synthesis of benzimidazole derivatives

The proposed mechanism for describing the formation of 2-aryl-1-arylmethyl-1*H*-1,3-benzimidazoles (**3a-d**) is depicted in Scheme 2. First, nucleophilic addition of the amine group of *o*-phenylenediamine or 4-methylbenzene-1,2-diamine (**2**) was carried out on the catalyst-activated aldehyde (**1**) to form the Knoevenagel type intermediate **I.** The amine group of this intermediate reacts with the second molecule of catalyst-activated aldehyde followed by intramolecular nucleophilic cyclization, as well as dehydration to afford the expected products (**3a-d**). The suggested mechanism for the synthesis of 2-aryl-benzimidazoles (**3e-i**) is similar, as shown in Scheme 3. First, the nucleophilic addition of the amine group of *o*-phenylenediamine or 4-methylbenzene-1,2-diamine (**2**) on the catalyst-activated aldehyde (**1**) leads to formation of Knoevenagel type intermediate **I.** In the following step, the intermediate **I** undergoes intramolecular nucleophilic cyclization followed by dehydration to furnish the expected products (**3e-i**).

On the other hand, the suggested mechanism for the synthesis of 2-aryl-benzimidazoles (**3e-i**) is similar, as shown in Scheme 3. First, the nucleophilic addition of the amine group of *o*-phenylenediamine or 4-methylbenzene-1,2-diamine (**2**) on the catalyst-activated aldehyde (**1**) leads to formation of Knoevenagel type intermediate **I.** In the following step, the intermediate **I** undergoes intramolecular nucleophilic cyclization followed by dehydration to furnish the expected products (**3e-i**).



Scheme 2. Proposed mechanism for the SO_3H-Fe_3O_4@SiO_2 MNPs-catalyzed synthesis of 2-aryl-1-arylmethyl-1*H*-1,3-benzimidazoles.



Scheme 3. Proposed mechanism for the SO_3H-Fe_3O_4@SiO_2 MNPs-catalyzed synthesis of 2-aryl-benzimidazoles.

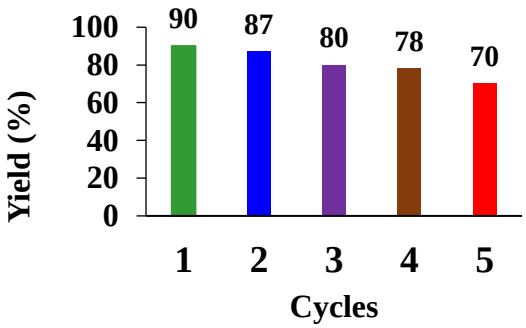


Figure 1. Catalytic reusability of SO_3H-Fe_3O_4@SiO_2 MNPs in the synthesis of 1-benzyl-5-methyl-2-phenyl-1*H*-benzoimidazole.

Reusability of the catalyst

The reusability of the catalyst SO_3H-Fe_3O_4@SiO_2 was examined for the model reaction of benzaldehyde and 4-methylbenzene-1,2-diamine. The recycling process involves the isolation of the catalyst after the end of reaction using an external magnet bar. The recovered catalyst was washed with ethanol followed by drying in an oven overnight. As shown in Figure 1, the recovered catalyst can be used for five consecutive fresh runs without any significant loss of the catalytic activity.

CONCLUSIONS

We have developed a facial and green procedure for the synthesis of benzimidazole derivatives through the reaction of aromatic aldehydes with *o*-phenylenediamine or 4-methylbenzene-1,2-diamine under ultrasonic conditions in the presence of SO_3H-Fe_3O_4@SiO_2 MNPs as an effective and magnetically recyclable nanocatalyst. The reactions were optimized in terms of solvent, time, temperature, and amount of catalyst. The reactions proceed smoothly under mild conditions to yield the respective products in excellent yields and in short reaction times. It was demonstrated that the

developed SO_3H-Fe_3O_4@SiO_2 MNPs can be reused for five fresh runs without significant loss of catalytic activity.

Supporting Information: *Supplementary data associated with this manuscript can be found in the online version at DOI: 10.34049/bcc.51.4.4829.*

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