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Orginal Research Article

Ionic liquid supported on magnetic nanoparticles as an efficient and reusable green catalyst for synthesis of benzimidazole derivatives under solvent and solvent-free conditions

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ABSTRACT

The Fe_3O_4 nanoparticles and the supported ionic liquid (Fe_3O_4-IL) were produced and used as efficient magnetic catalysts to synthesize the benzimidazole derivatives under solvent and solvent-free conditions. Quantitative conversion of the reactants was achieved under solvent-free conditions; catalyst reusability, through convenient magnetic decantation, showing an insignificant loss in activity. The catalyst can be readily isolated by using an external magnet and no obvious loss of activity was observed when the catalyst was reused in seven consecutive runs.

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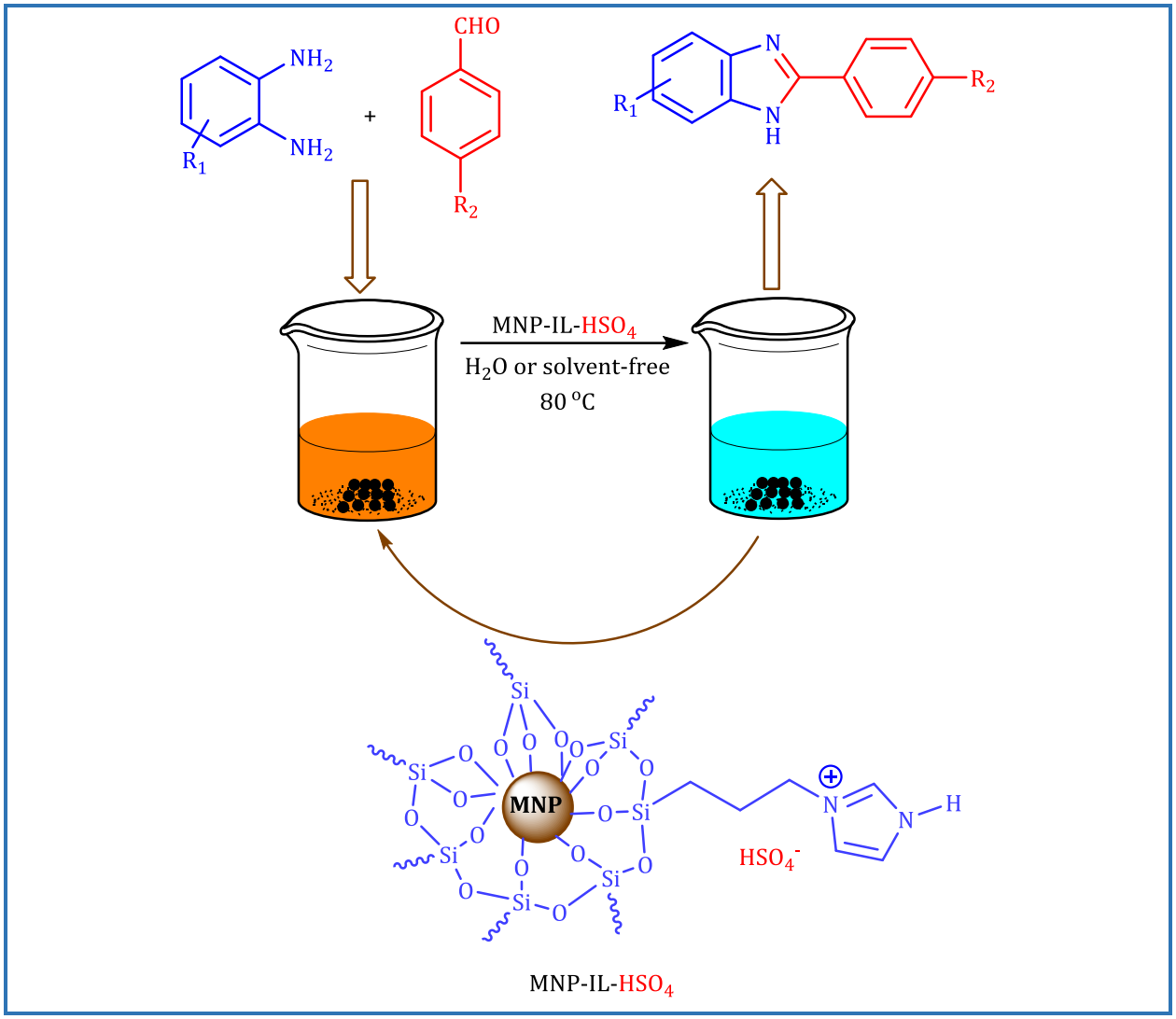
Graphical Abstract



Introduction

Magnetic nanoparticles (MNPs) have been considered as attractive and interesting materials due to their high surface area and unique magnetic properties. Moreover, they have a wide range of novel applications in various fields such as, magnetic fluids [1], catalysis [2, 3], biology and medical applications [4], magnetic resonance imaging (MRI) [5, 6], data storage [7], and environmental remediation [8, 9]. MNPs have recently been viewed as attractive materials either as catalysts or as supporters for immobilization of homogeneous and heterogeneous catalysts [10, 11]. Their well-adapted biocompatible and biodegradable characteristics as well as their basic magnetic characteristics could be denoted for functional organic materials grafted to MNPs. Magnetic

nanocatalysts can easily be separated and recycled from the other products by an external magnet, which achieves simple separation of the catalysts without filtration [12–14].

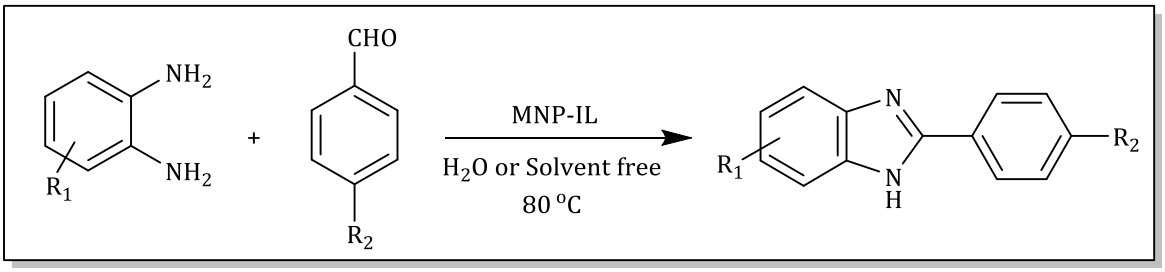
Ionic liquids (ILs), which have been widely promoted as green solvents, have attracted a great amount of interest and attention because of their applicability in industry and many fields of chemistry. This is more likely due to their chemical and thermal stability, low vapor pressure, and high ionic conductivity. Over the last few years, ILs have generally been used as solvents for organic synthesis, catalysis, and also have been used as media for extraction processes [15, 16]. Therefore, catalytic systems developed on MNPs aids have been successfully used in catalyzing a wide range of organic reactions including knoevenagel reaction [17, 18], nucleophilic substitution reactions of benzyl halides [19], epoxidation of alkenes [20], synthesis of α-amino nitriles [21], hydrogenation of alkynes [22], esterifications [23], CO_2 cycloaddition reactions [24], Suzuki coupling reactions [25], and three-component condensations [26].

In this research study, magnetic nanoparticles which can support ionic liquids were tested and analyzed as a new heterogeneous catalyst to synthesize the benzimidazole derivatives under solvent and solvent-free condition at 80 °C (Scheme 1).

Experimental

Materials and methods

$FeCl_2.4H_2O$ (99%), $FeCl_3.6H_2O$ (98%), aromatic aldehyde, and other chemical materials were purchased from Fluka and Merck and were used without further purification. Products were characterized by comparing the physical data, IR and ^1H NMR, and ^{13}C NMR spectra with known samples. NMR spectra were recorded in DMSO on a Bruker Advance DPX 400 MHz instrument spectrometer using TMS as an internal standard. The purity determination of the products and reaction monitoring were accomplished by TLC on silica gel polygram SILG/UV 254 plates. IR spectra of the compounds were obtained on a Perkin Elmer spectrometer version 10.03.06 using a KBr disk. The particle morphology was examined using SEM and TEM.



Scheme 1. Synthesis of benzimidazoles by using MNP-IL

Synthesis of magnetic nanoparticles supported ionic liquid (MNP-IL)

The magnetite nanoparticles were prepared by the conventional co-precipitation method [27]. A schematic representation of the synthesis of magnetic nanoparticles supporting ionic liquids is shown in Scheme 1. In the first step, a mixture of 3-chloromethoxypropylsilane (4.4 mL, 24 mmol) and 1-Methylimidazole (1.97 g, 24 mmol) was heated at 120 °C for 8 h with continuous stirring under N_2 atmosphere. Then, the sulfuric acid 96% (2.35 g, 24 mmol) was added dropwise over a period of 10 min at room temperature. The reaction mixture was stirred for 2 h under the pressure of nitrogen to remove the produced HCl. The obtained MNPs powder (0.75 g) was dispersed in 100 mL ethanol/water (Volume ratio, 1:1) solution by sonication for 30 min, and then Si-Im-HSO_4 was added to the mixture. After mechanical agitation under N_2 atmosphere at 50 °C for 4 h, it (NMPs) was separated by magnetic decantation, washed with acetonitrile and dichloromethane, and left to dry in a desiccator.

Typical procedure for the synthesis of benzimidazoles under solvent or solvent-free condition

A mixture of o-phenylenediamine (1 mmol) and aromatic aldehyde (1.1 mmol) was well stirred with catalyst (20 mg) in 10 mL of water in a round bottomed flask, or under solvent-free conditions at 80 °C (Scheme 1). The progress of the reaction was followed by TLC. After completion of the reaction, mixture was added drop wise with vigorous stirring into a H_2O (15 mL). In cases where the product precipitated as a free flowing solid, it was collected by filtration, washed with H_2O and dried. Since the catalyst can be separated from the reaction mixture using an external magnetic field, it was recovered with a simple magnet after the dilution of the reaction mixture with water.

Results and discussion

Immobilization of Si-Im-HSO_4 functionalized MNPs combines the advantages of ionic liquids with those of heterogeneous catalysts. The Si-Im-HSO_4 MNPs catalyst was synthesized by a multi-step procedure, as shown in Scheme 2, and characterized by various techniques.

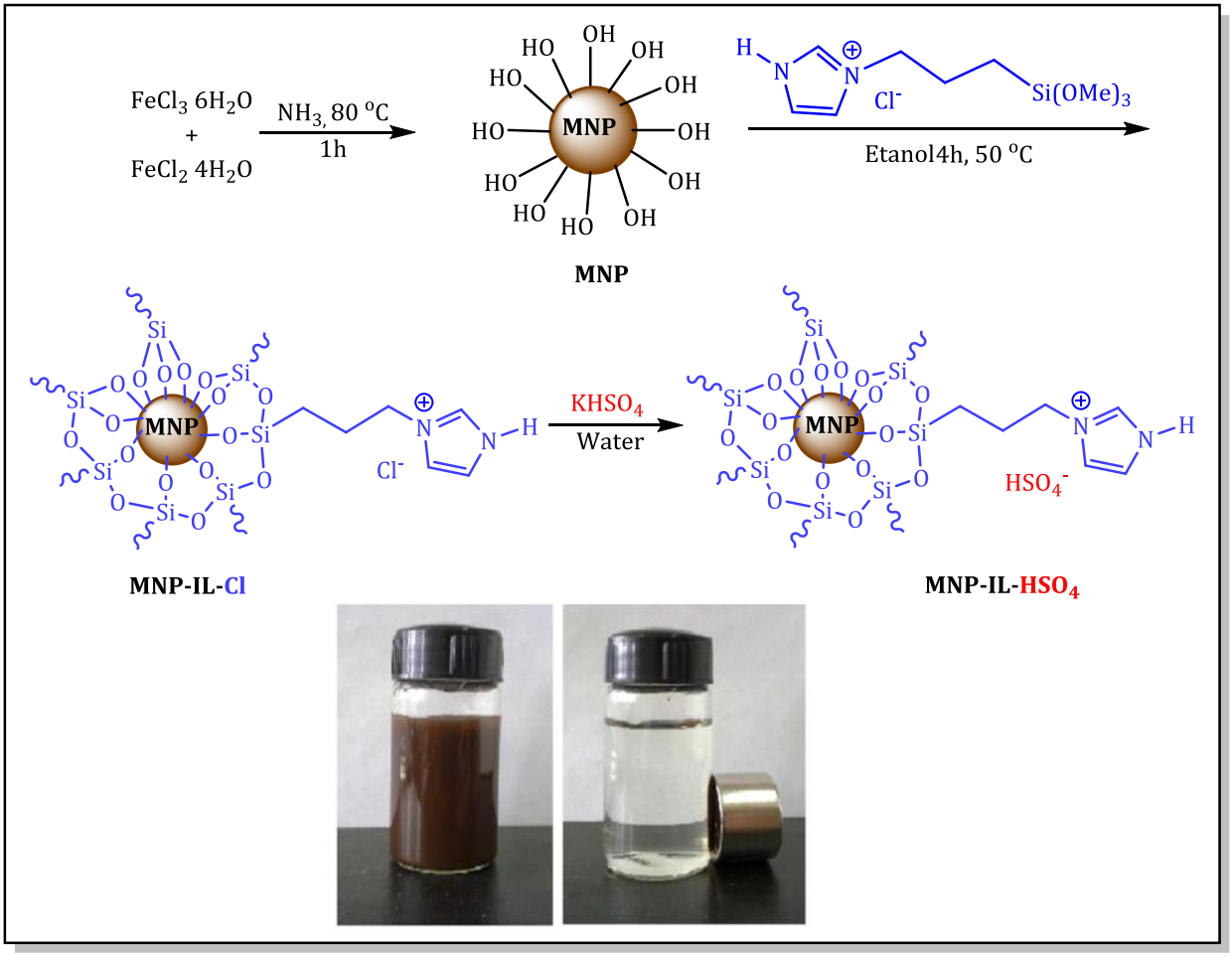
An infrared spectrum was obtained in the 400–4000 cm^{-1} range by a Perkin Elmer FT-IR spectrometer. KBr pellets were used for solid samples. The infrared spectroscopy presents a useful tool to initially detect the success of the immobilization process. The magnetic nanoparticles (MNPs) were considered as attractive and interesting materials has been more and more increased, because of their high surface area and unique magnetic properties.

The catalyst concentration varied over a range of 5–25 mg MNP-IL on the basis of the total volume of the reaction mixture. As mentioned before, we carried out the reaction of o-phenylenediamine and aromatic aldehyde. Different reaction conditions were studied for

optimization. First condensation of o-phenylenediamine and benzaldehyde was performed with different mg MNP-IL and temperatures to optimize the reaction conditions in water and solvent free condition (Table 1).

After optimizing the conditions, we examined the generality of these conditions to other reactions of o-phenylenediamine and various aromatic aldehydes in the presence of optimized MNP-IL (Table 3). The conversion completed during 20–75 min.

Aromatic aldehydes, with strong electron withdrawing substituents, including the nitro group, required a relatively longer reaction time with lower yields (Table 2, entries 6-9), whereas aryl aldehydes, carrying electron donating groups, gave excellent yields of the products (Table 2, entries 10 and 11) in a shorter reaction time. As can be seen in Table 3, MNP-IL as a catalyst afforded good results in comparison to the other catalysts. In order to evaluate the efficiency of our method, more recently developed methods were compared with our present method on the basis of the yields and reaction times parameters. The results of this comparison are given in Table 4.



Scheme 2. Synthesis of magnetic nanoparticles supported ionic liquid (MNP-IL)

Table 1. Optimization of experimental conditions for synthesis of benzimidazole by using MNP-IL

Entry	MNP-IL (mg)	Temperature (°C)	In solvent		Solvent-free	
			Time (min)	Yield (%)[a]	Time (min)	Yield (%)[a]
1	5	r.t.	75	38	75	32
2	5	60	40	52	40	45
3	10	60	30	63	30	58
4	20	80	20	94	20	92
5	25	80	20	93	20	86
6	20	60	25	90	25	81

[a] Yield after Purification

Table 2. Optimization of solvent

Entry	Solvent	Time (min)	Yield (%)
1	Water	20	94
2	EtOH	30	82
3	Water:EtOH(50:50)	25	86
4	CH_2Cl_2	55	38
5	$CHCl_3$	60	30

Table 3. Synthesis of benzimidazoles catalyzed by MNP-IL

Entry	R1	R2	In solvent		Solvent-free	
			Time (min)	Yield (%)[a]	Time (min)	Yield (%)[a]
1	H	H	20	94	20	92
2	4-Me	H	25	94	30	87
3	H	4-Cl	25	90	30	88
4	H	2-Cl	25	88	35	86
5	4-Me	4-Cl	20	92	30	91
6	H	2-NO_2	60	86	60	84
7	4-Me	2-NO_2	55	83	55	85
8	H	4-NO_2	60	84	75	87
9	4-Me	4-NO_2	50	86	60	84
10	H	4-$N(Me)_2$	20	92	20	90
11	4-Me	4-OH	20	92	20	91

[a] Yield after Purification

Table 4. Compare of catalytic ability with other catalysts

Entry	Catalyst/solvent/temperature	Time (min)	Yield (%)	Ref.
1	SBSA/Water/r.t.	30	93	28
2	$Zn(OAc)_2$/Solvent Free/r.t.	10	92	29
3	$Yb(OPf)_3$/ Toluene/90 °C	6 h	98	30
4	$ZrCl_4$/ EtOH/r.t.	60	93	31
5	MNP-IL Solvent Free /80 °C	20	92	This work
6	MNP-IL / Water /80 °C	20	94	This work

Catalyst reusability is of major importance in heterogeneous catalysis. The recovery and reusability of the catalyst was studied using o-phenylenediamine and benzaldehyde as model reaction. Since the catalyst can be separated from the reaction mixture using an external magnetic field, it was recovered with a simple magnet after the dilution of the reaction mixture with water. The catalyst was consecutively reused seven times without any noticeable loss of its catalytic activity (Table 5).

Table 5. The catalyst reusability of MNP-IL in 5 cycles

Run	1	2	3	4	5
In solvent Yield (%)	94	91	90	88	85
Solvent-free Yield (%)	92	90	88	86	84

Conclusion

In this study, Fe_3O_4 magnetic nanoparticles were synthesized and functionalized with Si-Im-HSO_4 ionic liquid. We described a simple and highly efficient protocol for preparation of the dihydropyrimidinones using MNP-IL as catalyst. The advantages of this procedure are its simplicity of operation, very short reaction times in comparison with the other procedures, and the high yields of products. Also, the catalyst can be easily recovered by simple magnetic decantation and reused several times with no loss of activity.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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