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Original 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

Eshagh Rezaee Nezhad* , Reza Tahmasebi

National Iranian Drilling Company (NIDC), Ahwaz Khuzestan Iran P.O. Box 61635901

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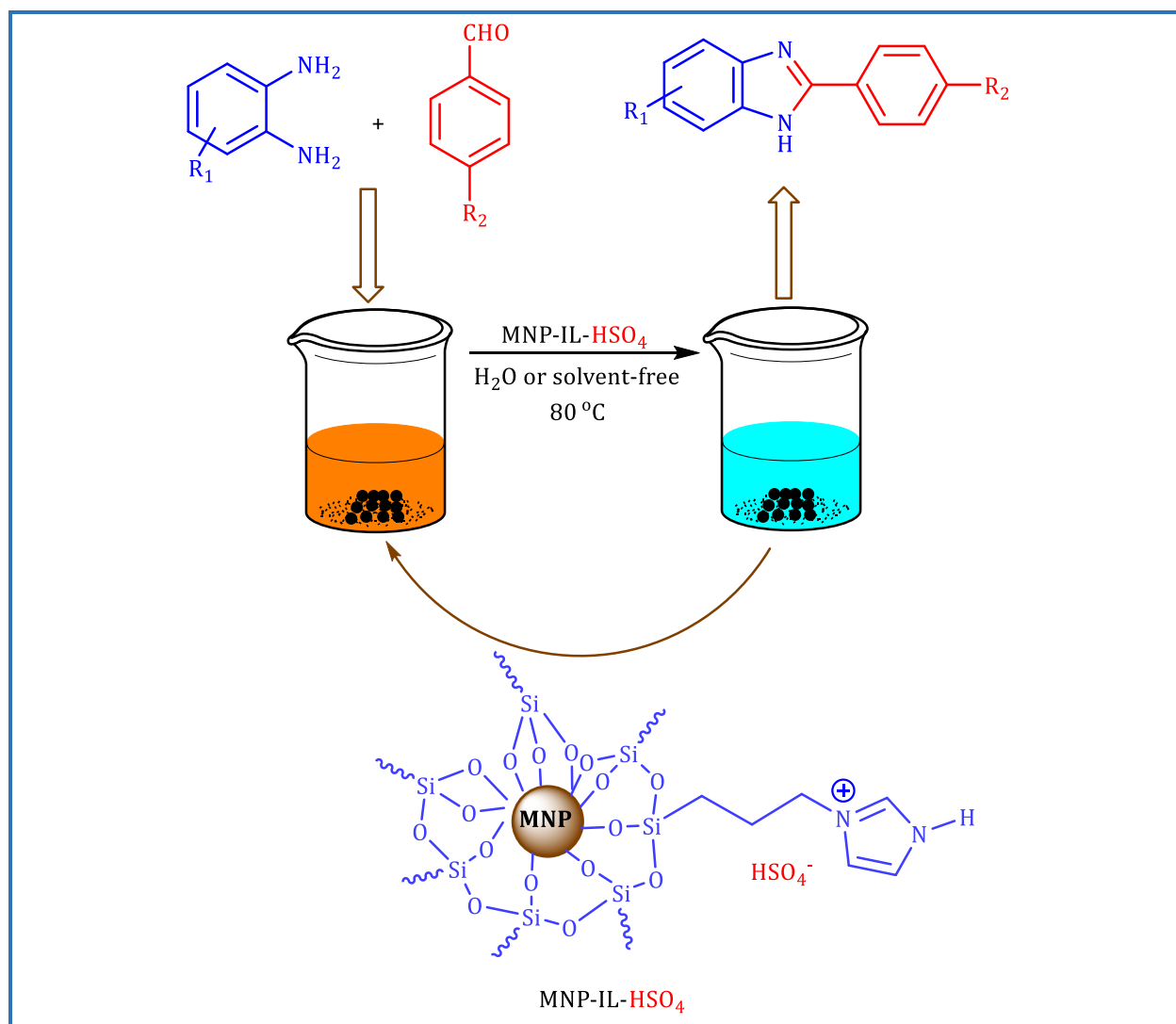
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ABSTRACT

The Fe_3O_4 nanoparticles and the supported ionic liquid ($\text{Fe}_3\text{O}_4\text{-IL}$) were produced and, then, 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, showed an insignificant loss in activity. The catalyst can be readily isolated by using an external magnet in such a way that no obvious loss of activity was observed specifically when the catalyst was reused in seven consecutive runs.

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 been recently 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 other products by an external magnet, which helps us to achieve simple separation of the catalysts without filtration [12–14].

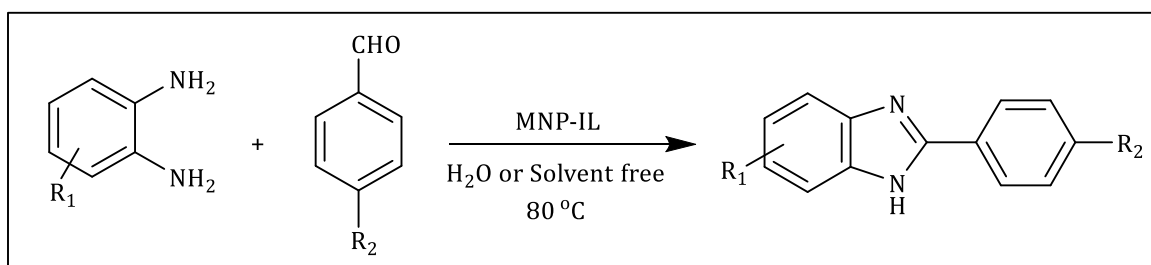
Ionic liquids (ILs), which have been widely promoted as green solvents, have attracted a great amount of interest and attention because of their applicability in industry and many fields of chemistry. This is more likely due to their chemical and thermal stability, low vapor pressure, and high ionic conductivity. Over the last few years, ILs have been generally 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], CO₂ cycloaddition reactions [24], Suzuki coupling reactions [25], and three-component condensations [26].

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

Experimental

Materials and methods

FeCl₂.4H₂O (99%), FeCl₃.6H₂O (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 ¹³C NMR spectra with the 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 N₂ 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-HSO₄ was added to the mixture. After mechanical agitation under N₂ atmosphere at 50 °C for 4 h, it (NMPs) was separated by magnetic decantation, washed with acetonitrile and dichloromethane, and, finally, 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, the mixture was added drop wise with vigorous stirring into a H₂O (15 mL). In cases where the product precipitated as a free flowing solid, it was collected by filtration, washed with H₂O and, then, 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-HSO₄ functionalized MNPs combines the advantages of ionic liquids with those of heterogeneous catalysts. The Si-Im-HSO₄ MNPs catalyst was synthesized by a multi-step procedure, as shown in [Scheme 2](#), and characterized by various techniques.

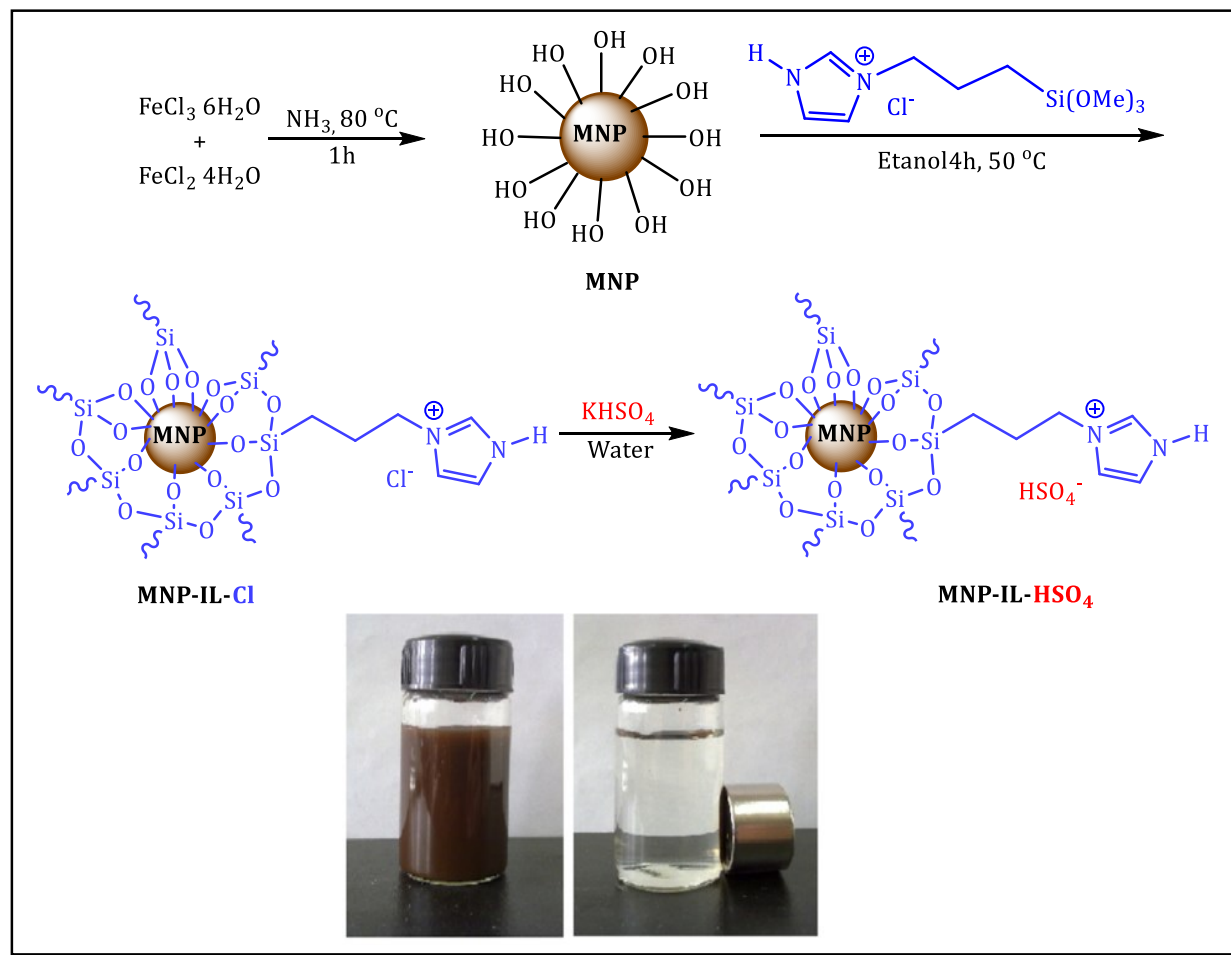
An infrared spectrum was obtained in the 400–4000 cm⁻¹ range by a Perkin Elmer FT-IR spectrometer. KBr pellets were used for solid samples. The infrared spectroscopy presents a useful tool to initially detect the success of the immobilization process. The magnetic nanoparticles (MNPs) which have been considered as attractive and interesting materials have 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. Besides, different reaction conditions were studied for the optimization. First condensation of o-phenylenediamine and benzaldehyde was performed with different mg MNP-IL and temperatures in order 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 the optimized MNP-IL (Table 3). The conversion was 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 to 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

^aYield 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 ₂ Cl 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
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^aYield 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 were studied using o-phenylenediamine and benzaldehyde as the 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	94	91	90	88	85
Yield (%)					
Solvent-free	92	90	88	86	84
Yield (%)					

Conclusion

In this study, Fe₃O₄ magnetic nanoparticles were synthesized and functionalized with Si-Im-HSO₄ ionic liquid. We described a simple and highly efficient protocol for the 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 to 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.

Orcid

Eshagh Rezaee Nezhad  0000-0002-5136-5347

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