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Immobilized ionic liquid on superparamagnetic nanoparticles as an effective catalyst for the synthesis of tetrasubstituted imidazoles under solvent-free conditions and microwave irradiation

Javad Safari*, Zohre Zarnegar

Laboratory of Organic Compound Research, Department of Organic Chemistry, College of Chemistry, University of Kashan, PO Box: 87317-51167, Kashan, Islamic Republic of Iran

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ABSTRACT

The ionic liquid 1-methyl-3-(3-trimethoxysilylpropyl) imidazolium chloride was immobilized on superparamagnetic Fe₃O₄ nanoparticles (IL-MNPs) and used as an efficient heterogeneous catalyst for the one-pot synthesis of 1,2,4,5-tetrasubstituted imidazoles under solvent-free conditions using microwave irradiation. The reactions in conventional heating conditions were compared with the microwave-assisted reactions. The combined merits of microwave irradiation and immobilized ionic liquid on superparamagnetic nanoparticles make the four-component condensation with safe operation, low pollution, and rapid access to products and simple work-up.

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1. Introduction

The developing of new multicomponent reactions (MCRs) and improving the known MCRs are an area of considerable current interest [1–3]. As opposed to the classical way to synthesize complex molecules by sequential synthesis, MCRs allow the assembly of complex molecules in one-pot and show a facile execution, high atom-economy and high selectivity [4–7]. As a one-pot reaction, MCRs generally afford good yields and are fundamentally different from two-component and step-wise reactions in several aspects [4] and permit a rapid access to combinatorial libraries of complex organic molecules for an efficient lead structure identification and optimization in drug discovery.

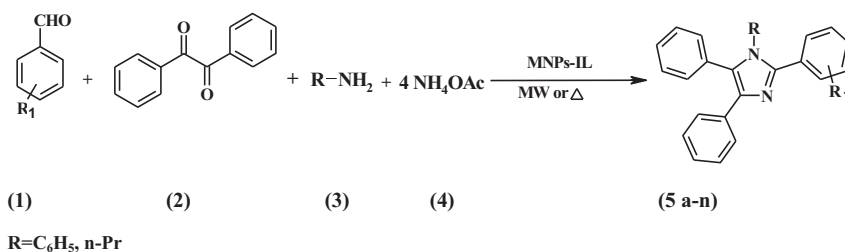
Multi-substituted imidazoles are a very interesting class of heterocyclic compounds because they have many pharmacological properties and play important roles in

biochemical processes [8,9]. In recent years, the synthesis of 2,4,5-trisubstituted imidazoles has been performed by catalysts such as Yb(OPf)₃ [10], ZrCl₄ [11], NiCl₂·6H₂O/Al₂O₃ [12], silica sulfuric acid (SSA) [13], polymer-supported ZnCl₂ [14], and phosphomolybdic acid [15]. Also some catalysts used for 1,2,4,5-tetrasubstituted imidazoles, including silica gel or zeolite InCl₃·3H₂O [16], silica gel/NaHSO₄ [17], HClO₄–SiO₂ [18], heteropolyacids [19], BF₃·SiO₂ [20], and FeCl₃·6H₂O [21], are applied as some common catalysts for 2,4,5-trisubstituted and 1,2,4,5-tetrasubstituted imidazoles.

Despite the many methods available for the synthesis of imidazoles, some of these synthetic methods are not environmentally friendly and suffer from one or more drawbacks, such as harsh reaction conditions, complex work-up and purification, strongly acidic conditions, high temperature, the use of toxic metal catalysts, unsatisfactory yields, occurrence of side reactions, and long reaction time. Therefore, the development of clean, high-yielding, mild, and green approach is still a challenge for the synthesis of substituted imidazole derivatives [9].

* Corresponding author.

E-mail address: Safari@kashanu.ac.ir (J. Safari).



Scheme 1. One-pot synthesis of 1,2,4,5-tetrasubstituted imidazoles catalyzed by IL-MNPs conventional heating conditions or using microwave irradiation.

Ionic liquid (IL) technology is a new environmentally benign approach toward modern synthetic chemistry [22–25]. ILs have attractive properties, including undetectable vapour pressure, reasonable thermal stability, reusability, and talent to dissolve many organic and inorganic substrates [23–25]. Additionally, IL as catalyst has been exploited in controlling organic reactions [26,27]. ILs have been used as an efficient catalyst for an improved and rapid synthesis of imidazoles [28–30]. Zang et al. synthesized 2-aryl-4,5-diphenyl imidazoles, using IL 1-ethyl-3-methylimidazole acetate as an efficient catalyst at room temperature under ultrasound irradiation [31]. IL, *N*-methyl-2-pyrrolidonium hydrogen sulfate has been used as a reusable catalyst for the one-pot synthesis of highly substituted imidazoles under thermal solvent-free conditions in excellent yields of products [32].

Though ILs possessed such promising advantages, their widespread practical application was still hampered by several disadvantages:

- high viscosity, which resulted in only a minor part of ILs taking part in the catalyzed reaction for chemical production;
- homogeneous reaction, which was difficult for separation and reuse procedures;
- consequently high cost for the use of relatively large amounts of ILs as opposed to economic criteria [33,34].

Thus, in order to solve these problems mentioned earlier, immobilized IL catalyst as a novel solid catalyst combining the advantageous characteristics of ILs, inorganic acids and solid acids had been designed for catalysed reactions [35,36].

During the past decades, advances in nanoscience and nanotechnology have pushed forward the synthesis of functional magnetic nanoparticles (MNPs), which is one of the most active research areas in advanced materials. MNPs that have unique magnetic properties and other functionalities have enabled a wide spectrum of applications [37]. Iron oxide magnetic nanoparticles (Fe₃O₄-MNPs) are approximately 20–30 nm in size containing a single magnetic domain with a single magnetic moment and exhibit superparamagnetism [38]. Additionally, recent studies show that MNPs are excellent supports for catalysts [39]. The supported catalysts proved to be effective and easily separated from the reaction media by applying an external magnetic field.

Since the introduction of a controlled and precise microwave reactor, microwave-assisted organic synthesis (MAOS) has had a significant impact on synthetic chemistry, especially those reactions under solvent-free circumstances, with the remarkable merits of reduced reaction time, improved yields, suppressed side reactions, decreased environmental pollutions and safe operations. Therefore, a large and continuing survey has been made throughout nearly all classes of thermal reactions for improvements upon microwave heating. The polar nature of ILs makes them ideal for use in solvent-free microwave irradiation [40].

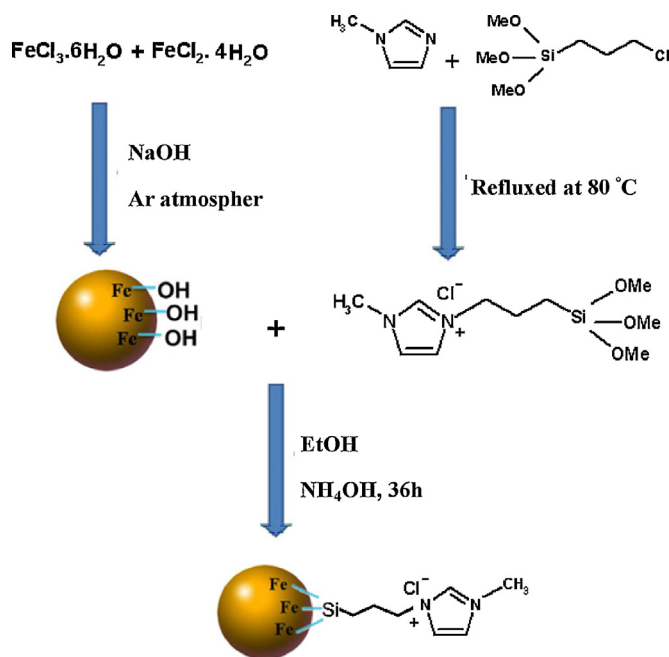
One of the aims we have in mind is to introduce an efficient catalyst for synthesis of 1,2,4,5-tetrasubstituted imidazoles with cost effectiveness and mild conditions in high yields. In this work, our objective is to functionalize magnetite nanoparticles with 1-methyl-3-(3-trimethoxysilylpropyl) imidazolium chloride to obtain a heterogeneous catalyst for the synthesis of 1,2,4,5-tetrasubstituted imidazoles under solvent-free conditions and microwave irradiation. To the best of our knowledge, there is no report about the synthesis of highly substituted imidazoles by such a magnetically recoverable nanocatalyst. The heterogeneous catalyst could be recovered easily by an external magnet and reused many times without significant loss of its catalytic activity (Scheme 1).

2. Results and discussion

2.1. Characterization of the prepared IL-MNPs

Scheme 2 shows the sequence of events in the functionalization of MNPs with 1-methyl-3-(3-trimethoxysilylpropyl)-1*H*-imidazol-3-ium chloride. In the first step, the magnetite nanoparticles of 18–20 nm were prepared by coprecipitation of iron(II) and iron(III) ions in basic solution at 85 °C, using the method described by Massart [41,42]. Then, 1-methyl-3-(3-trimethoxysilylpropyl) imidazolium chloride (IL), was prepared from the reaction of *N*-methyl imidazole with (3-chloropropyl)trimethoxysilane at 80 °C [43]. In the second step, the external surface of MNPs was coated with IL to obtain IL-MNPs.

Fig. 1 shows the Fourier transform infrared (FT-IR) spectra of both the unfunctionalized and functionalized MNPs. The Fe–O stretching vibration near 580 cm⁻¹, the O–H stretching vibration near 3432 cm⁻¹ and the O–H deformed vibration near 1625 cm⁻¹ were observed for



Scheme 2. Preparation steps for fabricating 1-methyl-3-(3-(trimethoxysilyl)propyl)-1H-imidazol-3-ium chloride-functionalized magnetic Fe_3O_4 nanoparticles.

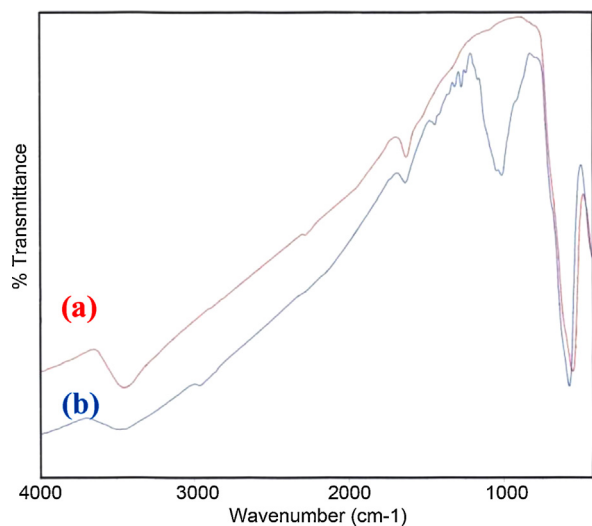


Fig. 1. The comparative FT-IR spectra for (a) magnetic nanoparticles, (b) IL-MNPs.

both in Fig. 2 a and b. The significant features observed for Fig. 2(b) are the appearance of the peaks at 1007 cm^{-1} (Si–O stretching) and at 2800 cm^{-1} ($-\text{CH}_2$ stretching). These results provided the evidences that IL-methyl were successfully attached to the surface of Fe_3O_4 nanoparticles.

Fig. 2 presents the X-ray powder diffraction (XRD) patterns of the prepared MNPs and IL-MNPs. The position and relative intensities of all peaks confirm well with standard XRD pattern of Fe_3O_4 (JCPDS card No. 79-0417),

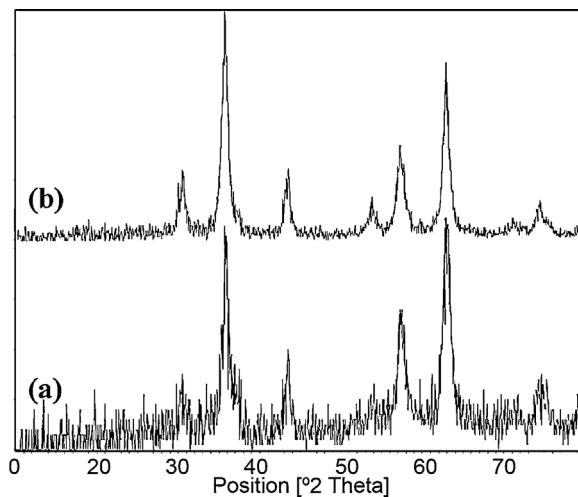


Fig. 2. X-ray powder diffraction patterns of (a) magnetic nanoparticles, (b) IL-MNPs.

indicating retention of the crystalline cubic spinel structure during functionalization of MNPs. The XRD patterns of the particles show six characteristic peaks, revealing a cubic iron oxide phase ($2\theta = 30.35, 35.95, 43.45, 53.70, 57.25, 62.88, 71.37, 74.46$). These are related to their corresponding indices (2 2 0), (3 1 1), (4 0 0), (3 3 1), (4 2 2), (3 3 3), (4 4 0) and (5 3 1), respectively [35]. It is implied that the resultant nanoparticles are pure Fe_3O_4 with a spinel structure and that the grafting process did not induce any phase change of Fe_3O_4 .

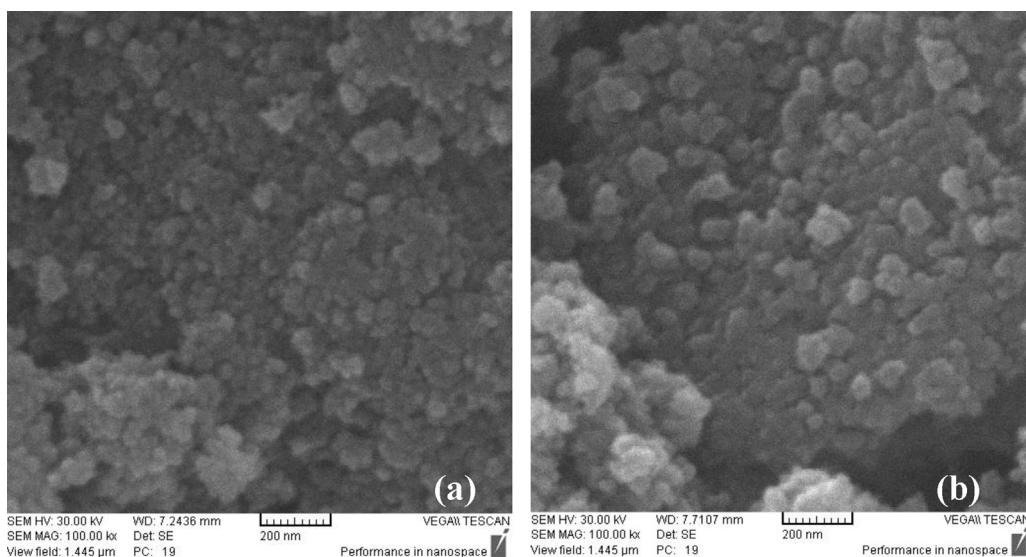


Fig. 3. The Scanning electron microscope image of (a) magnetic nanoparticles, (b) IL-MNPs.

The crystal size of MNPs and IL-MNPs nanoparticles can be determined from the XRD pattern by using Debye–Scherrer's equation:

$$D(hkl) = \frac{0.94\lambda}{\beta \cos\theta}$$

where $D(hkl)$ is the average crystalline diameter, 0.94 is the Scherrer's constant, λ is the X-ray wavelength, β is the half width of XRD diffraction lines and θ is the Bragg's angle in degree. Here, the (3 1 1) peak of the highest intensity was picked out to evaluate the particle diameter of the nanoparticles. MNPs and IL-MNPs were calculated to be 12 nm and 30 nm, respectively.

The IL-functionalized magnetic Fe_3O_4 nanoparticles could be separated to the sidewall of the container after 30 s, using a magnet of 2000 Gs, suggesting that the

obtained MNPs had an excellent magnetic responsiveness, which prevents composite nanoparticles from aggregation and enables them to redisperse rapidly when the magnetic field is removed.

The scanning electron microscope (SEM) image shows that magnetite (Fe_3O_4) particles have a mean diameter of about 18 nm and a nearly spherical shape as shown in Fig. 3. Fig. 3 a and b shows that IL-MNPs particles still keep the morphological properties of Fe_3O_4 , except for a slightly larger particle size and smoother surface (more than 20 nm in size), where silica are uniformly coated on the Fe_3O_4 particles to form silica shell.

The magnetization curve for Fe_3O_4 nanoparticles and IL-MNPs is shown in Figure 4. Room temperature specific magnetization (M) versus applied magnetic field (H) curve measurements of the sample indicate a saturation magnetization value (M_s) of 40.5 emu/g, lower than that

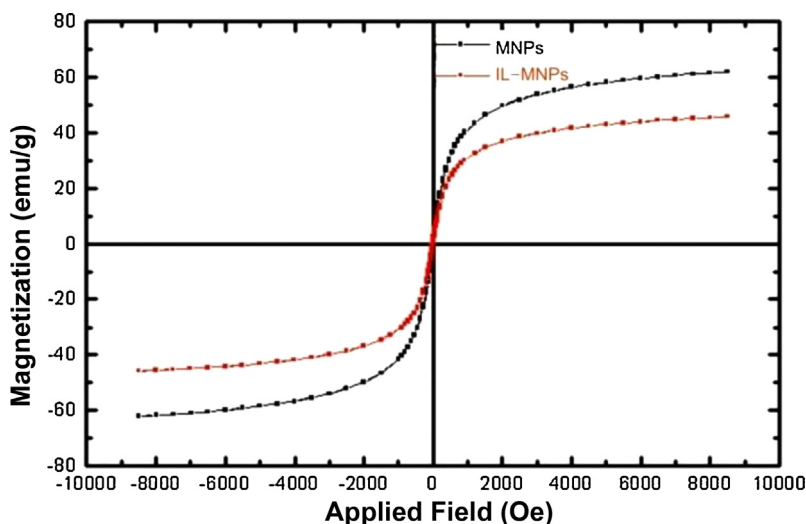


Fig. 4. Magnetization curves for the prepared magnetic nanoparticles and IL-MNPs at room temperature.

Table 1
Optimization one-pot synthesis of tetrasubstituted imidazoles under classical heating conditions^a.

Experimental number	Catalyst (g)	Time (min)	Temperature (°C.)	Yield (%)
1	0.0	60	90	10
2	0.08	35	90	40
3	0.1	35	90	50
4	0.12	35	90	50
5	0.0	45	110	15
6	0.08	30	110	60
7	0.1	30	110	70
8	0.12	30	110	70
9	0.0	40	120	25
10	0.08	25	120	79
11	0.1	25	120	90
12	0.12	25	120	90
13	0.0	35	130	30
14	0.08	20	130	63
15	0.1	20	130	90
16	0.12	20	130	90

^a Benzil (1 mmol), benzaldehyde (1 mmol), aniline (1 mmol) and ammonium acetate (5 mmol).

of bare MNPs (60.1 emu g) due to the coated shell. In Figure 4, we can also see that the two magnetization curves both follow a Langevin behavior over the applied magnetic field and the coercivity (H_C) could be ignored, which can be considered as superparamagnetism [44].

2.2. Evaluation of the catalytic activity of IL-MNPs through the synthesis of 1,2,4,5-tetrasubstitutedimidazols

Efficiency of the reaction is mainly affected by the amount of catalyst and temperature. As indicated in Table 1, the best results have been obtained at 120 °C with an amount of 0.1 g IL-MNPs (Table 1, entry 11) and the yield of reaction with increasing the amount of IL-MNPs or temperature is not considerably increased. It is important to note that in the absence of catalyst, the yield of the product was found to be low.

The successful results of IL-MNPs catalyzed synthesis of tetrasubstituted imidazoles under solvent-free classical heating conditions or using microwave irradiation in the absence of solvent are given in Table 2. In a typical experiment, a mixture of aldehyde (1 mmol), benzil (1 mmol), aniline (1 mmol), ammonium acetate (5 mmol) and IL-MNPs (0.1 g) was stirred for 35–70 min in a tube under conventional heating conditions at 120 °C or using microwave irradiation at 100 W for 5–25 min. After the reaction was completed, the reaction mixture was dissolved in acetone and the catalyst was separated by an external magnet and the reaction mixture was filtrated. The filtrate was concentrated on a rotary evaporator under reduced pressure and the solid product obtained was washed with water and recrystallized from acetone–water.

Results from IL-MNPs-catalyzed condensation reaction of benzil, ammonium acetate with different aromatic

Table 2
One-pot synthesis of tetrasubstituted imidazoles in the presence of IL-MNPs as a heterogeneous catalyst under solvent-free classical heating conditions or using microwave irradiation.

Entry	R ₁	(R) amine	Product ^a	Yield (%) ^a	Time (min)	M.p.(°C.) Found/Reported
				Δ^b	MW ^c	
1	H	C ₆ H ₅	5a	88(45)	95(15)	216–218 ^d
2	3-Me	C ₆ H ₅	5b	87(60)	92(18)	184–186 ^e
3	4-Me	C ₆ H ₅	5c	82(60)	90(18)	186–188 ^f
4	4-Cl	C ₆ H ₅	5d	92(35)	98(10)	160–163 ^f
5	3-NO ₂	C ₆ H ₅	5e	80(35)	95(15)	243–246 ^g
6	2-OH	C ₆ H ₅	5f	80(70)	86(20)	252–254 ^f
7	4-OH	C ₆ H ₅	5g	73(70)	80(25)	282–285 ^g
8	4-OMe	C ₆ H ₅	5h	80(60)	90(20)	177–180 ^f
9	2-OMe	C ₆ H ₅	5i	85(50)	94(20)	207–211 ^f
10	3,4-(OMe) ₂	C ₆ H ₅	5j	77(70)	90(20)	178–180
11	H	n-Pr	5k	90(40)	95(10)	87–89
12	4-Cl	n-Pr	5l	93(35)	98(5)	85–87
13	4-Me	n-Pr	5m	85(50)	93(15)	78–83
14	4-OMe	n-Pr	5n	82(55)	91(15)	76–80

^a Isolated yield based on aldehyde.

^b Under classical heating conditions at 120 °C.

^c Using microwave irradiation.

^d Reference [42].

^e Reference [44].

^f Reference [45].

^g Reference [46].

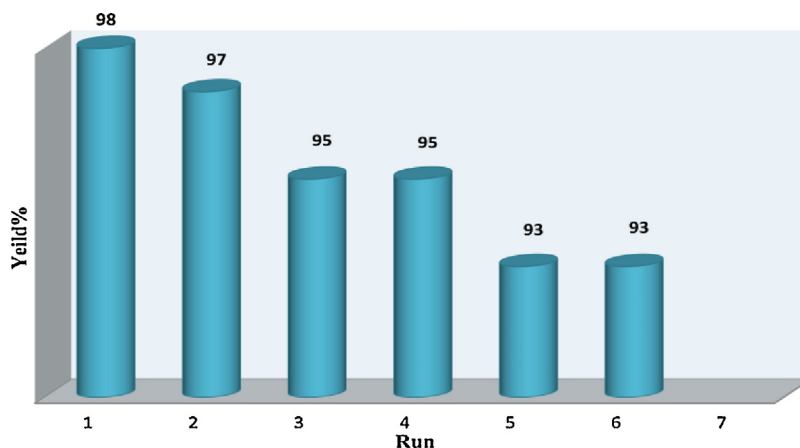


Fig. 5. Recyclability of IL-MNPs in the reaction of benzil (1 mmol), benzaldehyde (1 mmol), aniline (1 mmol) and ammonium acetate (5 mmol) under microwave irradiation.

aldehydes and primary aliphatic and aromatic amine under solvent-free classical heating conditions and using microwave irradiation are given in Table 2. As shown, the presence of electron-withdrawing groups on the aromatic aldehydes and primary amines produced high yields of 1,2,4,5-tetrasubstituted imidazoles. Also, microwave irradiation has shown better yields and especially reaction times.

Most of the products are known and were identified by comparison of their physical and spectral data with those of authentic samples. All melting points were compared satisfactorily with those reported in the literature.

The possibility of recycling the catalyst was examined using the reaction of benzil, benzaldehyde, aniline and ammonium acetate under optimized conditions. Upon completion, the catalyst was separated by an external magnet and was washed with acetone, and the recycled catalyst was saved for the next reaction. The recycled

catalyst could be reused six times without any further treatment. No observation of any appreciable loss in the catalytic activity of nanocatalyst was observed (Fig. 5). As observed in Fig. 6, the XRD of the recovered nanocatalyst was indexed according to the magnetite phase (JCPDS card No. 79-0417), and so there is no considerable change in its magnetic phase. Thus, the magnetite nanocatalyst is stable during the synthesis of tetrasubstituted imidazoles.

In summary, we have been able to introduce an efficient and environmentally friendly approach for the synthesis of biologically active tetrasubstituted imidazoles by one-pot four-component condensation of benzil, aldehydes, amines and ammonium acetate using IL-MNPs as a recyclable catalyst under solvent-free conditions and microwave irradiation. This method offers several advantages, including high yield, short reaction time, simple work-up procedure, and ease of separation by an external magnet.

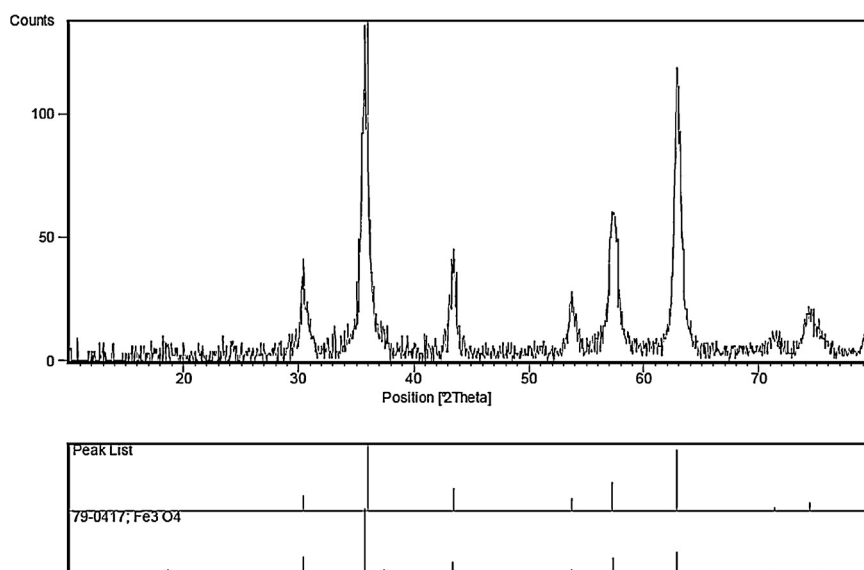


Fig. 6. X-ray powder diffraction patterns of recovered IL-MNPs after four recovery.

3. Conclusions

An efficient and environmentally friendly method has been developed for the synthesis of 1,2,4,5-tetrasubstituted imidazoles catalyzed by IL-MNPs under solvent-free conditions and microwave irradiation. This method offers several advantages, including high yield, short reaction time, simple work-up procedure, easiness of separation, and recyclability of the magnetic catalyst, as well as the ability to tolerate a wide variety of substitutions in the reagents.

4. Experimental method

High-purity chemical reagents were purchased from the Merck Chemical Company. All materials were of commercial reagent grade. Melting points were determined in open capillaries using an Electrothermal Mk3 apparatus and are uncorrected. ^1H NMR and ^{13}C NMR spectra were recorded with a Bruker DRX-400 spectrometer at 400 and 100 MHz, respectively. NMR spectra were obtained in DMSO- d_6 and CDCl_3 solutions and are reported as parts per million (ppm) downfield from tetramethylsilane as an internal standard. The abbreviations used are: singlet (s), doublet (d), triplet (t) and multiplet (m). FT-IR spectra were obtained with potassium bromide pellets in the range $400\text{--}4000\text{ cm}^{-1}$ with a Perkin-Elmer 550 spectrometer. A mass spectrum was recorded by a QP-1100EX Shimadzu spectrometer. The element analyses (C, H, N) were obtained from a Carlo ERBA Model EA 1108 analyzer carried out on Perkin-Elmer 240c analyzer. The UV-vis measurements were obtained with a GBC cintra 6 UV-vis spectrophotometer. Nanostructures were characterized using a Holland Philips Xpert XRD diffractometer (CuK α , radiation, $\lambda = 0.154056\text{ nm}$), at a scanning speed of $2^\circ/\text{min}$ from 10° to 100° (2θ). SEM was performed on a FEI Quanta 200 SEM operated at a 20 kV accelerating voltage. The samples for SEM were prepared by spreading a small drop containing nanoparticles onto a silicon wafer and being dried almost completely in air at room temperature for 2 h, and then were transferred onto SEM conductive tapes. The transferred sample was coated with a thin layer of gold before measurement. Microwave synthesis was carried out on a Sanle SPII-2 singlemode microwave reactor (made in Nanjing, China) with infrared temperature probe and successively adjustable 0–700 W output power.

4.1. Preparation of the magnetic Fe_3O_4 nanoparticles

Fe_3O_4 -MNPs were prepared using simple chemical coprecipitation as described in the literature [41] with little modification. Typically, 20 mmol of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 10 mmol of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ were dissolved in 75 ml of distilled water in a three-necked round-bottom flask (250 mL) under Ar atmosphere for 1 h. Thereafter, under rapid mechanical stirring, 10 ml of NaOH (10 M) were added into the solution within 30 min with vigorous mechanical stirring and ultrasound treatment under continuous Ar atmosphere bubbling. After being rapidly stirred for 1 h, the resultant black dispersion was heated to 85°C for 1 h.

The black precipitate formed was isolated by magnetic decantation, exhaustively washed with double-distilled water until neutrality, and further washed twice with ethanol and dried at 60°C under vacuum.

4.2. Synthesis of 1-methyl-3-(3-trimethoxysilylpropyl)-1H-imidazol-3-ium chloride (IL)

1-Methylimidazole (13.6 mL, 0.17 mol) and (3-chloropropyl) trimethoxysilane (31 mL, 0.17 mol) were refluxed at 80°C for three days in the absence of any catalyst and solvent under Ar atmosphere. The unreacted materials were washed with diethyl ether ($3 \times 8\text{ mL}$). The diethyl ether was removed under reduced pressure at room temperature, followed by heating under high vacuum, to yield a yellowish viscous liquid. Isolated yield was 98% [43].

FT-IR (KBr, cm^{-1}): 1656, 1612, 1584. ^1H NMR (400 MHz, CDCl_3): δ_{H} (ppm): 10.22 (broad, 1H, Are-H), 7.59 (1H, dd, $J = 7.89$ and 2.86 Hz , Are-H), 7.26 (1H, dd, $J = 7.89$ and 2.79 Hz , Are-H), 4.06 (2H, t, $J = 7.25\text{ Hz}$, $-\text{NCH}_2$), 3.86 (3H, s, $-\text{NCH}_3$), 3.30 (9H, s, OCH_3), 1.74 (2H, tt, $J = 7.14\text{ Hz}$, $-\text{CH}_2$), 0.37 (2H, t, $J = 7.09\text{ Hz}$, SiCH_2). ^{13}C NMR (100 MHz, CDCl_3 , TMS): $\delta_{\text{C}} = 138.13$, 123.34, 121.58, 58.53, 51.66, 36.51, 24.32, 18.2, 7.03. Anal. Calcd.: C, 48.45; H, 8.39; N, 8.69. Found: C, 48.35; H, 8.32; N, 8.79.

4.3. Modification of magnetic nanoparticles with ionic liquid to obtain IL-MNPs.

IL-MNPs were prepared using the method described in the literature [47] with little modification. Typically, freshly prepared magnetite nanoparticles (2 g) were suspended in ethanol (95%, 250 mL), and sonicated for 60 min. The resulted suspension was mechanically stirred, followed by addition of a solution of ethanol (95%, 100 mL) containing IL (6 g, 18.5 mmol) and concentrated ammonia (28%, 1 mL). The stirring under Ar was continued for 36 h. The modified magnetite nanoparticles were magnetically separated and washed three times with ethanol (95%, 50 mL) and then dissolved in methanol (200 mL) and stirred mechanically for 30 min. Ether (50 mL) was added and the modified nanoparticles were magnetically separated, washed with ether (50 mL) and dried under vacuum for 24 h. Typically, 3–3.5 g of brownish-black powder could be obtained.

4.4. General procedure for the synthesis of 1,2,4,5-tetrasubstituted imidazoles

A mixture of benzil (1 mmol), ammonium acetate (5 mmol), aldehyde (1 mmol), primary aliphatic and aromatic amine (1 mmol) and IL-MNPs (0.1 g) was stirred with a glass bar at 120°C or irradiated in a microwave oven at 100 W for the appropriate time. The progress of reaction was followed by TLC. After the reaction was completed, the catalyst was separated by an external magnet and reused as such for the next experiment. The reaction mixture was dissolved in acetone and filtered. The filtrate was concentrated on a rotary evaporator under reduced pressure and the solid product obtained was washed with

water and recrystallized from acetone–water 9:1 (v/v). Pure products were obtained in excellent yields, as summarized in Table 2.

4.5. Spectral data for new derivatives of 1,2,4,5-tetrasubstituted imidazoles 5j–n

4.5.1. 2-(3,4-dimethoxyphenyl)-1,4,5-triphenyl-1H-imidazole ($C_{29}H_{24}N_2O_2$, 5j)

M.p = 178–180 °C, UV-Vis (EtOH) λ_{\max} : 311 nm; IR (KBr) ν : 3045, 1617, 1578 cm^{-1} ; 1H NMR (400 MHz, DMSO- d_6): δ_H 3.61 (s, J = 8.4 Hz, 6H), 6.85 (d, J = 8.8 Hz, 2H), 7.15–7.33 (m, 16H) ppm; ^{13}C NMR (100 MHz, DMSO- d_6): δ_C 55.9, 112.7, 115.6, 121.2, 122, 122.3, 123.8, 126.9, 128.7, 130.1, 130.5, 132.5, 132.8, 150.4, 152.8, 153.3 ppm; M.S. (70 eV) m/z (%): 432 (M^+ , 55), 417 (50), 402 (44), 77 (32); Anal. Calcd. for $C_{29}H_{24}N_2O_2$: C 87.80, H 5.60, N 6.60%; Found: C 87.82, H 5.58, N 6.61%.

4.5.2. 2,4,5-triphenyl-1-propyl-1H-imidazole ($C_{24}H_{22}N_2$, 5k)

M.p = 87–89 °C, UV-Vis (EtOH) λ_{\max} : 284 nm; IR (KBr) ν : 3025, 1597, 1479 cm^{-1} ; 1H NMR (400 MHz, DMSO- d_6) δ_H 0.51 (t, J = 6.8 Hz, 3H), 1.32 (m, J = 6.8 Hz, 2H), 3.81 (t, J = 7.2 Hz, 2H), 7.10–7.55 (m, 13H), 7.7 (d, J = 6.8 Hz, 2H) ppm; ^{13}C NMR (100 MHz, DMSO- d_6): δ_C 11.5, 24, 53.6, 121.5, 122.8, 124, 125.2, 126.2, 126.9, 128.4, 128.8, 130.1, 132.8, 156.7 ppm; M.S. (70 eV) m/z (%): 338 (M^+ , 68), 323 (65), 309 (57), 295 (43), 15 (40); Anal. Calcd. for $C_{24}H_{22}N_2$: C 85.17, H 6.55, N 8.28%; found: C 85.14, H 6.56, N 8.30%.

4.5.3. 2-(4-chlorophenyl)-4,5-diphenyl-1-propyl-1H-imidazole ($C_{24}H_{21}N_2Cl$, 5l)

M.p = 85–87 °C, UV-Vis (EtOH) λ_{\max} : 294 nm; IR (KBr) ν : 3025, 1645, 1489 cm^{-1} ; 1H NMR (400 MHz, DMSO- d_6): δ_H 0.51 (t, J = 6.8 Hz, 3H), 1.34 (m, J = 6.8 Hz, 2H), 3.81 (t, J = 7.2 Hz, 2H), 7.15–7.30 (m, 12H), 7.34 (d, J = 7.2 Hz, 2H) ppm; ^{13}C NMR (100 MHz, DMSO- d_6): δ_C 11.5, 24.2, 53.5, 121.5, 122.7, 124.3, 125.8, 126.2, 127, 128.4, 129.1, 130.4, 132.8, 135.6, 156.6 ppm; MS (70 eV) m/z (%): 435 (M^+ , 55), 432 (53), 417 (50), 402 (44), 77 (32); Anal. Calcd. for $C_{24}H_{22}N_2Cl$: C 77.30, H 5.68, N 7.51%; found: C 77.32, H 5.69, N 7.48%.

4.5.4. 2-(4-methylphenyl)-4,5-diphenyl-1-propyl-1H-imidazole ($C_{25}H_{24}N_2$, 5m)

M.p = 78–83 °C, UV-Vis (EtOH) λ_{\max} : 294 nm; 1H NMR (400 MHz, DMSO- d_6): δ_H 0.52 (t, J = 6.8 Hz, 3H), 1.30 (m, J = 6.8 Hz, 2H), 2.50 (s, 3H), 3.80 (t, J = 7.2 Hz, 2H), 7.12–7.35 (m, 12H), 7.50 (d, J = 8 Hz, 2H); IR (KBr): ν 3028, 1620, 1497 cm^{-1} ; ^{13}C NMR (100 MHz, DMSO- d_6): δ_C 11.3, 22, 24.2, 53.4, 121.1, 122.9, 124, 125.3, 126.2, 127, 127.9, 128.8, 130.2, 130.9, 133, 142.4, 156.2 ppm; MS (70 eV) m/z (%): 352 (M^+ , 70), 323 (52), 309 (59), 295 (46), 15 (37); Anal. Calcd. for $C_{25}H_{24}N_2$: C 85.19, H 6.86, N 7.95%; found: C 85.17, H 9.21, N 7.55%.

4.5.5. 2-(4-methoxyphenyl)-4,5-diphenyl-1-propyl-1H-imidazole ($C_{25}H_{24}N_2O$, 5n)

M.p = 76–80 °C, UV-Vis (EtOH) λ_{\max} : 305 nm; IR (KBr) ν : 3016, 1628, 1510 cm^{-1} ; 1H NMR (400 MHz, DMSO- d_6): δ_H 0.50 (t, J = 6.8 Hz, 3H), 1.33 (m, J = 6.8 Hz, 2H), 3.05 (s, 3H),

3.81 (t, J = 7.2 Hz, 2H), 7.10–7.30 (m, 12H), 7.46 (d, J = 8 Hz, 2H) ppm; ^{13}C NMR (100 MHz, DMSO- d_6): δ_C 11.5, 24.3, 53.4, 55.9, 117.1, 121.2, 122.8, 123.8, 125.3, 126.2, 126.8, 128.7, 130.1, 132, 132.6, 156.7, 160.8 ppm; MS (70 eV) m/z (%): 368 (M^+ , 59), 337 (52), 323 (59), 309 (48), 234 (46), 31 (30); Anal. Calcd. for $C_{25}H_{24}N_2O$: C 81.49, H 6.56, N 7.60%; found: C 51.46, H 6.58, N 7.61%.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.crci.2013.01.019>.

References

- [1] A. Domling, I. Ugi, *Angew. Chem. Int. Ed.* 39 (2000) 3168.
- [2] J. Zhu, H. Bienayme, *Multi Component Reactions*, Wiley-VCH, Weinheim, 2005.
- [3] A. Domling, *Chem. Rev.* 106 (2006) 17.
- [4] J. Safari, S.H. Banitaba, S.D. Khalili, *J. Mol. Catal. A Chem.* 335 (2011) 46.
- [5] R.R. Nagawade, D.B. Shinde, *Acta Chim. Slov.* 54 (2007) 642.
- [6] D.M. D'Souza, T.J. Mueller, *Chem. Soc. Rev.* 36 (2007) 3169.
- [7] C.C.A. Cariou, G.J. Clarkson, M. Shipman, *J. Org. Chem.* 73 (2008) 9762.
- [8] A. Puratchikody, M. Doble, *Bioorg. Med. Chem. Lett.* 15 (2007) 1083–.
- [9] J. Safari, S.D. Khalili, M. Rezaei, S.H. Banitaba, F. Meshkani, *Monatsh Chem.* 141 (2010) 1339.
- [10] M. Shen, C. Cai, W. Yi, J. Fluorine Chem. 129 (2008) 541.
- [11] G.V.M. Sharma, Y. Jyothi, P. Sree Lakshmi, *Synth. Commun.* 36 (2006) 2991.
- [12] M.M. Heravi, K. Bakhtiari, H.A. Oskooie, S. Taheri, *J. Mol. Catal. A: Chem.* 263 (2007) 279.
- [13] A. Shaabani, A. Rahmati, E. Farhangi, Z. Badri, *Catal Commun.* 8 (2007) 1149.
- [14] L. Wang, C. Cai, *Monatsh Chem.* 140 (2009) 541.
- [15] S.D. Jadhve, N.D. Kokare, S.D. Jadhve, *J. Heterocycl. Chem.* 45 (2009) 1461.
- [16] S.D. Sharma, P. Hazarika, D. Konwar, *Tetrahedron Lett.* 49 (2008) 2216.
- [17] A.R. Karimi, Z. Alimohammadi, J. Azizian, A.A. Mohammadi, M.R. Mohammadzadehi, *Catal. Commun.* 7 (2006) 728.
- [18] S. Kantevari, S.V.N. Vuppapapati, D.O. Biradar, L. Nagarapu, *J. Mol. Catal. A: Chem.* 266 (2007) 109.
- [19] M.M. Heravi, F. Derikvand, F.F. Bamoharram, *J. Mol. Catal. A: Chem.* 263 (2007) 112.
- [20] B. Sadeghi, B.B.F. Mirjalili, M.M. Hashemi, *Tetrahedron Lett.* 49 (2008) 2575.
- [21] M.M. Heravi, F. Derikv, M. Haghighi, *Monatsh. Chem.* 139 (2008) 31.
- [22] A.K. Burrell, R.E.D. Sesto, S.N. Baker, T.M. McCleskey, G.A. Baker, *Green Chem.* 5 (2007) 449.
- [23] J.P. Hallett, T. Welton, *Room-temperature ionic liquids: solvents for synthesis and catalysis 2*, *Chem. Rev.* 111 (2011) 3508.
- [24] P. Wasserscheid, T. Welton (Eds.), *Ionic Liquids in Synthesis*, Weinheim, Wiley-VCH, 2007.
- [25] D.A. Kotadia, S.S. Soni, *J. Mol. Catal. A: Chem.* 353–354 (2012) 44.
- [26] H. Zang, M. Wang, B.W.J. Cheng, *Ultrason. Sonochem.* 16 (2009) 301.
- [27] S.P. Borikar, T. Daniel, *Ultrason. Sonochem.* 18 (2011) 928.
- [28] S.A. Siddiqui, U.C. Narkhede, S.S. Palimkar, T. Daniel, R.J. Lahoti, K.V. Srinivasan, *Tetrahedron* 61 (2005) 3539.
- [29] M.V. Chary, N.C. Keerthysri, S. Vupallapati, N. Lingaiah, S. Kantevari, *Catal. Commun.* 9 (2008) 2013.
- [30] M. Xia, Y. Lu, *J. Mol. Catal. A: Chem.* 265 (2007) 205.
- [31] H. Zang, Q. Su, Y. Mo, B.W. Cheng, S. Jun, *Ultrason. Sonochem.* 17 (2010) 749.
- [32] H.R. Shaterian, M. Ranjbar, *J. Mol. Liq.* 160 (2011) 40.

- [33] S. Sahoo, P. Kumar, F. Lefebvre, S.B. Halligudi, *Appl. Catal. A* 354 (2009) 17.
- [34] L.L. Zhu, Y.H. Liu, J. Chen, *Ind. Eng. Chem. Res.* 48 (2009) 3261.
- [35] W. Chen, Y.Y. Zhang, L.B. Zhu, J.B. Lan, R.G. Xie, J.S. You, *J. Am. Chem. Soc.* 129 (2007) 13879.
- [36] J. Miao, H. Wan, G. Guan, *Catal. Commun.* 12 (2011) 353.
- [37] A. Kong, P. Wang, H. Zhang, F. Yang, S.P. Huang, Y. Shan, *Appl. Catal. A: Gen.* 417–418 (2012) 183.
- [38] J. Zhu, J. He, X. Du, R. Lu, L. Huang, X. Ge, *Appl. Surf. Sci.* 257 (2011) 9056.
- [39] A. Hu, G.T. Yee, W. Lin, *J. Am. Chem. Soc.* 127 (2005) 12486.
- [40] M. Xia, Y. Lu, *J. Mol. Catal. A: Chem.* 265 (2007) 205.
- [41] D. Yang, Ji. Hu, S. Fu, *J. Phys. Chem. C* 113 (2009) 7646.
- [42] M. Kidwai, P. Mothsra, V. Bansal, R.K. Somvanshi, A.S. Ethayathulla, S. Dey, T.P. Singh, *J. Mol. Catal. A: Chem.* 265 (2007) 177.
- [43] A. Chrobok, S. Baj, W. Pudło, Andrzej Jarzebski, *Appl. Catal. A: Gen.* 366 (2009) 22.
- [44] A.R. Khosropour, *Ultrason. Sonochem.* 15 (2008) 659.
- [45] S.N. Murthy, B. Madhav, Y.V.D. Nageswar, *Tetrahedron Lett.* 51 (2010) 5252.
- [46] K.F. Shelke, S.B. Sapkal, S.S. Sonar, B.R. Madje, B.B. Shingate, M.S. Shingare, *Bull. Korean Chem. Soc.* 30 (2009) 1057.
- [47] A. Taher, J.B. Kim, J.Y. Jung, W.S. Ahn, M.J. Jin, *Synlett* (2009) 2477.