

## Magnetic Fe<sub>3</sub>O<sub>4</sub> nanoparticles as a highly efficient catalyst for the synthesis of imidazoles under ultrasound irradiation

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### ABSTRACT

To be fairly general and catalyst is easily separated by magnetic devices and can be reused without any apparent loss of activity for the reaction. Fe<sub>3</sub>O<sub>4</sub> nanoparticles were prepared by chemical coprecipitation method and was found to be a mild and effective catalyst for the efficient, one-pot, three-component synthesis of 2,4,5-trisubstituted imidazoles at room temperature under ultrasound irradiation. The high yields of products and short reaction time were attributed to the nanosize of about 20 nm in which the catalyst could act as a nanoreactor. This methodology is found.

**Keywords:** Fe<sub>3</sub>O<sub>4</sub> nanoparticles, Imidazole, Heterogeneous catalyst, Ultrasound irradiation.

### 1. Introduction

Nanotechnology is now expanding very rapidly, as result of the unique physical and chemical properties that nanoparticles (NPs) exhibit compared to bulk materials. Magnetic iron oxide nanoparticles (MNPs) have attracted much research interest over the recent years because of their inherent properties such as large surface area and fast response under applied external magnetic field, their superparamagnety, high coercivity and low Curie temperature [1-3].

On the other hand, recent studies show that magnetic nanoparticles are excellent catalysts for organic reactions [4-6]. Additionally, the magnetic properties make the recovery of the catalyst compete by mean of an external magnetic field. These advantages even more attractive if such reactions can be conducted in aqueous media.

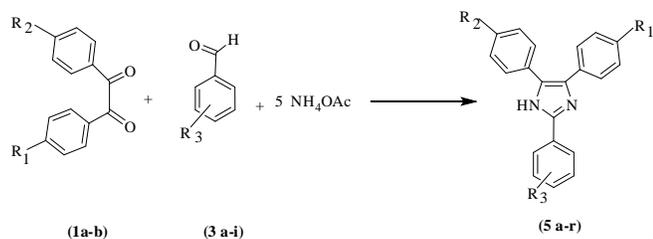
Imidazole derivatives are a very interesting class of heterocyclic compounds because they have many pharmacological properties and play important roles in biochemical processes [7, 8]. In recent years the synthesis of 2,4,5-trisubstituted imidazoles has been performed by catalysts such as Yb(OPf)<sub>3</sub> [9], ZrCl<sub>4</sub> [10], NiCl<sub>2</sub>.6H<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> [11], silica sulfuric acid (SSA) [12], polymer-supported ZnCl<sub>2</sub> [13], and phosphomolybdic acid [14]. Also some catalysts used for 1,2,4,5-tetrasubstituted

imidazoles include silica gel or zeolite InCl<sub>3</sub>-3H<sub>2</sub>O [15], silica gel/NaHSO<sub>4</sub> [16], HClO<sub>4</sub>-SiO<sub>2</sub> [17], heteropolyacids [18], BF<sub>3</sub>.SiO<sub>2</sub> [19], FeCl<sub>3</sub>.6H<sub>2</sub>O [20], and alumina [21] are applied as some common catalysts for 2,4,5-trisubstituted and 1,2,4,5-tetrasubstituted imidazoles. Despite their potential utility, some of these methods are not environmentally friendly and suffer from one or more disadvantages, for example hazardous reaction conditions, complex work-up and purification, strongly acidic conditions, high temperature, use of toxic metal catalysts, poor yields, occurrence of side reactions, and long reaction time. Therefore, the development of clean, high-yielding and environmentally friendly approach is still a challenge for organic chemists in the synthesis of highly substituted imidazoles [21].

Ultrasonic-assisted organic synthesis (UAOS) as a green synthetic approach is a powerful technique that is being used more and more to accelerate organic reactions [22-24]. UAOS can be extremely efficient and it is applicable to a broad range of practical syntheses. The notable features of the ultrasound approach are enhanced reaction rates, formation of purer products in high yields, easier manipulation and considered a processing aid in terms of energy conservation and waste minimization which compared with traditional methods, this technique is more convenient taking green chemistry concepts into account [25, 26]. However, the use of ultrasound in heterocyclic system is not fully explored [27-29].

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**Scheme 1.** One-pot synthesis of 2,4,5-trisubstituted imidazoles catalyzed by MNPs under ultrasound irradiation at ambient temperature.

In this study, we report an efficient and general method for the synthesis of trisubstituted imidazoles via one-pot condensation of 1,2-diketone **1** with aldehyde **2** and  $\text{NH}_4\text{OAc}$  using the magnetic  $\text{Fe}_3\text{O}_4$  nanoparticles, as a new heterogeneous catalyst under ultrasound irradiation (Scheme 1).

## 2. Experimental

### 2.1. Materials

Chemical reagents in high purity were purchased from the Merck Chemical Company with commercial grade.

### 2.2. Apparatus

Melting points were determined in open capillaries using an Electrothermal Mk3 apparatus and are uncorrected.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded with a Bruker DRX-400 spectrometer at 400 and 100 MHz respectively. NMR spectra were obtained in  $\text{DMSO}-d_6$  solutions and are reported as parts per million (ppm) downfield from tetramethylsilane as 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. X-ray powder diffraction (XRD) diffractometer (CuK $\alpha$  radiation,  $\lambda=0.154056\text{ nm}$ ), at a scanning speed of  $2^\circ/\text{min}$  from  $10^\circ$  to  $100^\circ$  ( $2\theta$ ). Scanning electron microscope (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. Sonication was performed in Shanghai Branson-BUG40-06 ultrasonic cleaner (with a frequency of 40 kHz and a nominal power 200 W).

### 2.3. Preparation of the magnetic $\text{Fe}_3\text{O}_4$ nanoparticles (MNPs)

$\text{Fe}_3\text{O}_4$ -MNPs were prepared using simple chemical coprecipitation described in the literature [39] 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 bottom (250 ml) under Ar atmosphere for 1 h. Thereafter, under rapid mechanical stirring, 10 ml of NaOH (10 M) was 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  $85^\circ\text{C}$  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  $60^\circ\text{C}$  in vacuum.

### 2.4. General procedure for the synthesis of 2,4,5-trisubstituted imidazoles

To a solution of 1,2-diketones derivatives (1 mmol), aldehyde (1 mmol), ammonium acetate (0.4 g, 5 mmol) in 10 ml ethanol, MNPs (5 mol%) was added and the reaction mixture was exposed to ultrasonic irradiation at room temperature. 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 3. Most of the products are known and were identified by comparison of their physical and spectral data with those of authentic samples.

#### The selected spectral data

2-(3-nitrophenyl)-4,5-bis(4-methoxyphenyl)-1H-imidazole (5o). Yellow solid. IR (KBr,  $\nu_{\text{max}}/\text{cm}^{-1}$ ): 3428 (NH), 1615 (C=C), 1523 (C=N), 1460 (N=O), 1348 (N-O), 1249 (C-O);  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ , ppm)  $\delta_{\text{H}}$ : 12.92 (s, 1H, NH), 8.92 (s, 1H, Ar-H), 8.50 (d, 1H,  $J=8.2\text{ Hz}$ , Ar-H), 8.20 (d, 1H,  $J=8.2\text{ Hz}$ , Ar-H), 7.75 (t, 1H,  $J=8.2\text{ Hz}$ , Ar-H), 7.47 (d, 2H,  $J=8.4\text{ Hz}$ , Ar-H), 7.43 (d, 2H,  $J=8.4\text{ Hz}$ , Ar-H), 7.00 (d, 2H,  $J=8.4\text{ Hz}$ , Ar-H), 6.90 (d, 2H,  $J=8.4\text{ Hz}$ , Ar-H), 3.80 (s, 3H, OMe), 3.75 (s, 3H, OMe);  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO}-d_6$ , ppm)  $\delta_{\text{C}}$ : 159.4, 158.6, 148.8, 143.1, 137.5, 132.5, 131.4, 130.8, 130.2, 128.8, 128.7, 127.9, 123.5, 122.7, 119.7, 114.6, 114.1, 55.7, 55.5; Anal. Calcd. for  $\text{C}_{23}\text{H}_{19}\text{N}_3\text{O}_4$ : C=68.82; H=4.77; N=10.47%. Found: C=68.79; H=4.75; N=10.44%.

2-(3-methoxyphenyl)-4,5-bis(4-methoxyphenyl)-1H-imidazole (5p). White solid. IR (KBr,  $\nu_{\text{max}}/\text{cm}^{-1}$ ): 3430 (N-H), 1608 (C=C), 1519 (C=N), 1246 (C-O);  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ , ppm)  $\delta_{\text{H}}$ : 12.50 (s, 1H, NH), 7.64 (d, 1H,  $J=8.0\text{ Hz}$ , Ar-H), 7.62 (s, 1H, Ar-H), 7.36-7.46 (m, 5H, Ar-H), 7.00 (d, 2H,  $J=8.4\text{ Hz}$ , Ar-H), 6.91 (dd, 1H,  $J=8.4, 2.2$

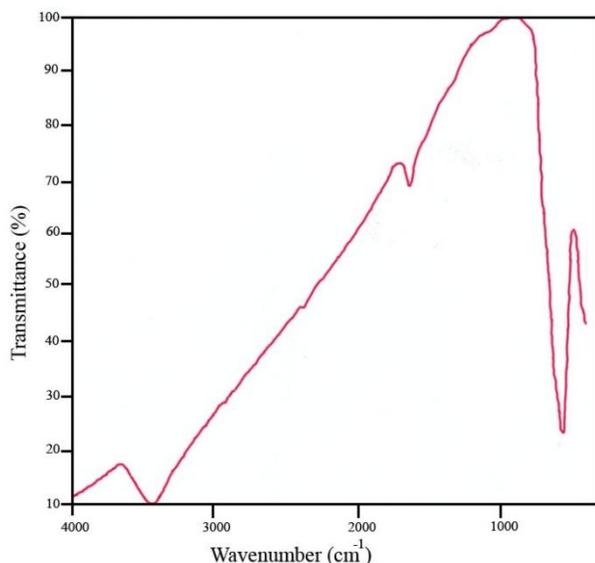


Fig. 1. FT-IR spectra of Fe<sub>3</sub>O<sub>4</sub>-MNPs.

Hz, Ar-H), 6.87 (d, 2H,  $J=8.4$  Hz, Ar-H), 3.82 (s, 3H, OMe), 3.79 (s, 3H, OMe), 3.74 (s, 3H, OMe); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>, ppm)  $\delta_C$ : 160.0, 158.9, 158.2, 145.1, 136.2, 132.3, 130.2, 130.2, 128.6, 128.2, 127.2, 124.1, 117.0, 115.5, 114.4, 114.3, 110.5, 55.6, 55.5, 55.5 ppm; Anal. Calcd. for C<sub>24</sub>H<sub>22</sub>N<sub>2</sub>O<sub>3</sub>: C=74.59; H=5.74; N=7.25%. Found: C=74.58; H=5.75; N=7.24%.

5-[4,5-bis(4-methoxyphenyl)-1H-imidazol-2-yl]-2-methoxyphenol (5q). Ash-gray solid. IR (KBr,  $\nu_{\max}/\text{cm}^{-1}$ ): 3424 (N-H), 3320 (O-H), 1615 (C=C), 1504 (C=N), 1249 (C-O); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, ppm)  $\delta_H$ : 12.26 (s, 1H, NH), 9.11 (s, 1H, OH), 7.52 (s, 1H, Ar-H), 7.37-7.46 (m, 6H, Ar-H), 6.98 (d, 2H,  $J=8.4$  Hz, Ar-H), 6.86 (d, 2H,  $J=8.4$  Hz, Ar-H), 3.80 (s, 3H, OMe), 3.78 (s, 3H, OMe), 3.73 (s, 3H, OMe); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>, ppm)  $\delta_C$ : 159.1, 158.7, 148.4, 146.9, 145.6, 129.8, 129.2, 128.4, 126.3, 126.0, 123.5, 124.1, 116.8, 114.3, 114.0, 113.2,

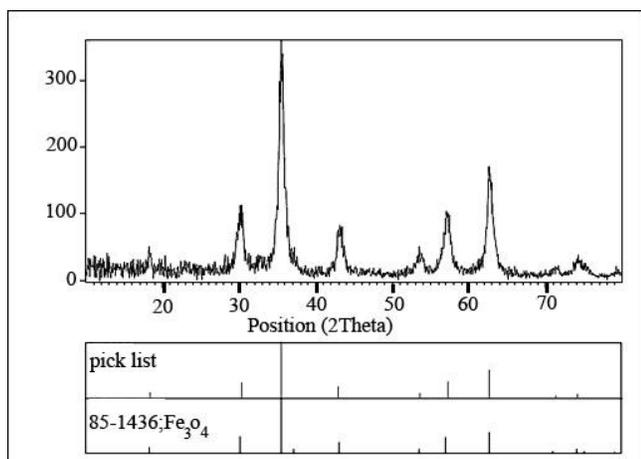


Fig. 2. XRD patterns of Fe<sub>3</sub>O<sub>4</sub>-MNPs.

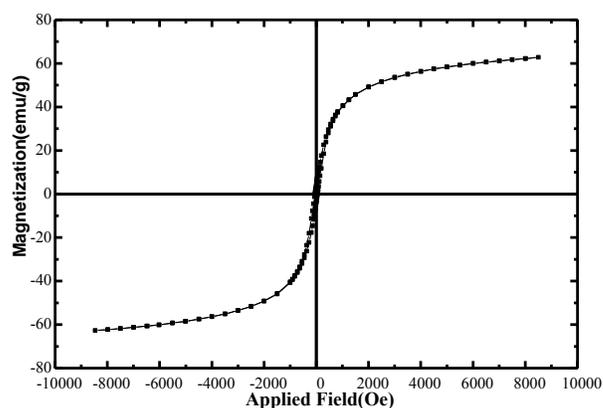


Fig. 3. Magnetization curve for Fe<sub>3</sub>O<sub>4</sub>-MNPs at room temperature.

112.5, 56.1, 55.5, 55.1; Anal. Calcd. for C<sub>24</sub>H<sub>22</sub>N<sub>2</sub>O<sub>4</sub> C=71.63; H=5.51; N=6.96%. Found: C=71.61; H=5.49; N=6.95%.

### 3. Result and Discussion

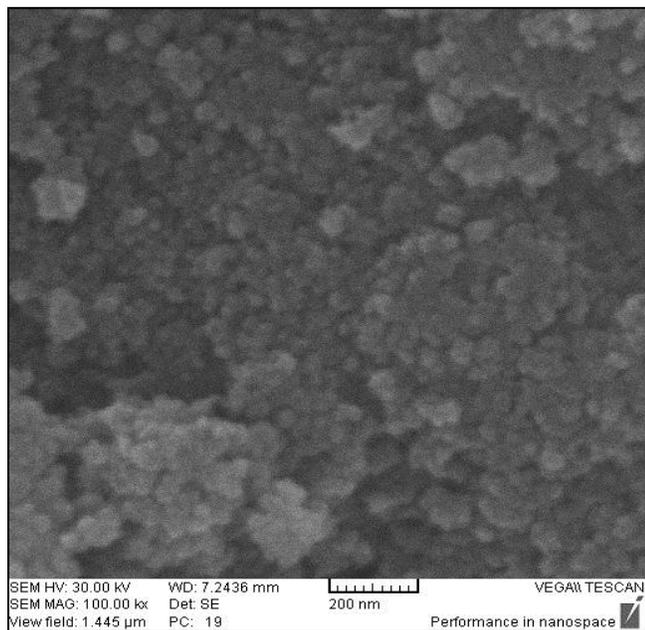
In this paper, we describe a simple and high yielding protocol for the synthesis of 2,4,5-trisubstituted imidazoles involving the three-component, one-pot condensation of aldehyde, 1,2-diketone, and NH<sub>4</sub>OAc using Fe<sub>3</sub>O<sub>4</sub> nanoparticles as a novel and eco-friendly heterogeneous catalyst.

#### 3.1. Characterization of the prepared Fe<sub>3</sub>O<sub>4</sub>-MNPs

The magnetite nanoparticles of 18-20 nm were prepared by the well-known Massart's method [30] which consists of Fe(III) and Fe(II) coprecipitation in alkaline solutions. Fig. 1 shows the Fourier transform infrared (FTIR) spectra of magnetic nanoparticles. The Fe–O stretching vibration near 580 cm<sup>-1</sup>, O–H stretching vibration near 3432 cm<sup>-1</sup> and O–H deformed vibration near 1629 cm<sup>-1</sup> were observed [31].

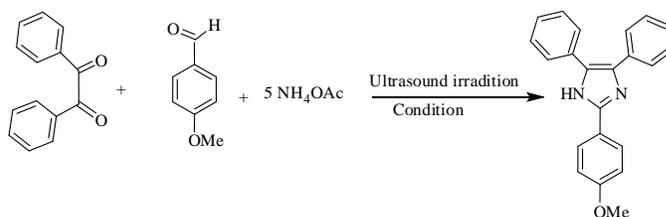
Fig. 2 presents the XRD-diffraction patterns of the prepared MNPs. The position and relative intensities of all peaks confirm well with standard XRD pattern of Fe<sub>3</sub>O<sub>4</sub> (JCPDS card No. 85-1436) indicating retention of the crystalline cubic spinel structure of MNPs. The XRD patterns of the particles show six characteristic peaks reveal a cubic iron oxide phase ( $2\theta = 18.35, 30.27, 35.53, 42.95, 53.60, 57.18, 62.69, 71.31, 74.14$ ). These are related to their corresponding indices (1 1 0), (2 2 0), (3 1 1), (4 0 0), (3 3 1), (4 2 2), (5 1 1), (4 4 0) and (5 3 1) respectively. It is implied that the resultant nanoparticles are pure Fe<sub>3</sub>O<sub>4</sub> with a spinel structure and that the grafting process did not induced any phase change of Fe<sub>3</sub>O<sub>4</sub> [32]. The crystal size of MNPs can be determined from the XRD pattern by using Debye–Scherrer's equation.

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



**Fig. 4.** SEM image of MNPs.

$D(hkl)$  is the average crystalline diameter, 0.94 is the Scherrer's constant,  $\lambda$  is the X-ray wavelength,  $\beta$  is the half width of XRD diffraction lines and  $\theta$  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. Size of MNPs were calculated to be 18 nm. The magnetization curve for  $\text{Fe}_3\text{O}_4$  nanoparticles is shown in fig. 3 Room temperature specific magnetization ( $M$ ) versus applied magnetic field ( $H$ ) curve measurements of the sample indicate a saturation magnetization value ( $M_s$ ) of  $62.76 \text{ emu g}^{-1}$ . We can also see that the magnetization curve follows a Langevin behavior over the applied magnetic field and the coercivity ( $H_c$ ) could be ignored, which can be considered as superparamagnetism [33]. SEM image is shown in Fig. 4. The SEM image shows that magnetite nanoparticles have a mean diameter of about 18 nm and a nearly spherical shape, which is consistent with



**Scheme 2.** Standard model reaction.

**Table 1.** Screening of solvent effect on model reaction.<sup>a</sup>

Entry	Solvent	Time (min)	Yield (%) <sup>b</sup>
1	Ethanol	25	88
2	Methanol	25	60
3	DCM	25	15
4	DMF	25	25
5	THF	25	30
6	Acetonitrile	25	46

<sup>a</sup>Reaction of benzil, 4-methoxybenzaldehyde and ammonium acetate (1:1:5) in presence of SA-MNPs (4 mol%) as a catalyst under ultrasonic waves (frequencies of 40 kHz).

<sup>b</sup>Isolated yield based on aldehyde.

XRD. SEM image shows the nanoparticles are well dispersed and uniform in shape and size.

### 3.2. Evaluation of the catalytic activity of MNPs through the synthesis of 2,4,5-trisubstituted imidazoles

To achieve suitable conditions for the synthesis of 2,4,5-trisubstituted imidazoles, various reaction conditions have been investigated in the reaction of 4-methoxybenzaldehyde 3b, benzil 1a, and ammonium acetate as a model reaction (Scheme 2). We examined the effect of different solvents such as EtOH, MeOH, THF, DMF,  $\text{CH}_3\text{CN}$ , and DCM on model reaction under ultrasound irradiation (frequencies of 40 kHz) at room temperature. The results were summarized in Table 1. The use of 4 mol% of MNPs in ethanol afforded

**Table 2.** Comparison of reaction time and yields with or without sonication for the synthesis of 5b product.

Entry	Catalyst (mol%)	With sonication <sup>a</sup>		Without sonication <sup>b</sup>	
		Yield (%)	Time (min)	Yield (%)	Time (min)
1	0	10	25	15	180
2	1	54	25	30	180
3	3	70	25	70	180
4	5	96	25	90	180
5	6	96	25	90	180
6	7	97	40	92	210

<sup>a</sup> Under ultrasonic waves (frequencies of 40 kHz) at room temperature.

<sup>b</sup> Reflux condition.

**Table 3.** One-pot synthesis of 2,4,5-trisubstituted imidazoles catalyzed by MNPs in EtOH under ultrasound irradiation at room temperature (method A) and reflux conditions (method B)<sup>a</sup>.

Entry	Benzil	R <sub>1</sub> ,R <sub>2</sub>	Aldehyde	R <sub>3</sub>	Product <sup>b</sup>	Method A	Method B	m.p. (°C)	
						Time (min) / Yield (%) <sup>c</sup>	Time (min) / Yield (%) <sup>c</sup>	Found	Reported [Ref]
1	1a	H	3a	H	5a	25/96	120/90	271-273	270-272 [37]
2	1a	H	3b	<i>p</i> -OMe	5b	30/94	180/87	230-231	228-231 [37]
3	1a	H	3c	<i>p</i> -Me	5c	35/88	150/83	229-232	230-233 [37]
4	1a	H	3d	<i>m</i> -Br	5d	30/94	150/90	302-304	301-303 [37]
5	1a	H	3e	<i>m</i> -OH	5e	30/90	150/85	260-261	259 [37]
6	1a	H	3f	<i>m</i> -NO <sub>2</sub>	5f	30/89	150/84	268-270	269-271 [37]
7	1a	H	3g	<i>m</i> -OMe	5g	30/90	120/90	258-260	259-262 [37]
8	1a	H	3h	<i>m</i> -OH, <i>p</i> -OMe	5h	30/96	120/93	215-216	214-216 [37]
9	1a	H	3i	<i>m</i> -OMe, <i>m</i> -OMe	5i	30/92	120/90	255-257	256-257 [37]
10	1b	OMe	3a	H	5j	35/95	130/90	202-204	201-203 [37]
11	1b	OMe	3b	<i>p</i> -OMe	5k	45/93	180/83	184-186	183-185 [37]
12	1b	OMe	3c	<i>p</i> -Me	5l	43/89	180/85	187-189	186-188 [37]
13	1b	OMe	3d	<i>m</i> -Br	5m	35/94	160/85	250-252	248-251 [37]
14	1b	OMe	3e	<i>m</i> -OH	5n	35/91	160/83	229-231	230-232 [37]
15	1b	OMe	3f	<i>m</i> -NO <sub>2</sub>	5o	35/91	160/84	242-244	240-242 [38]
16	1b	OMe	3g	<i>m</i> -OMe	5p	35/95	160/87	235-236	234-236 [37]
17	1b	OMe	3h	<i>m</i> -OH, <i>p</i> -OMe	5q	35/97	140/90	131-133	132-134 [37]
18	1b	OMe	3i	<i>m</i> -OMe, <i>m</i> -OMe	5r	35/93	140/89	194-196	195-197 [37]

<sup>a</sup> Benzil (1 mmol), Aldehyde (1 mmol), NH<sub>4</sub>OAc (5 mmol), MNPs (5 mol%).

<sup>b</sup> All products were characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, IR and MS spectra.

<sup>c</sup> Isolated yield.

a 88% yield (Table 1, entry 1) of the desired product. Therefore EtOH was chosen as solvent of reaction.

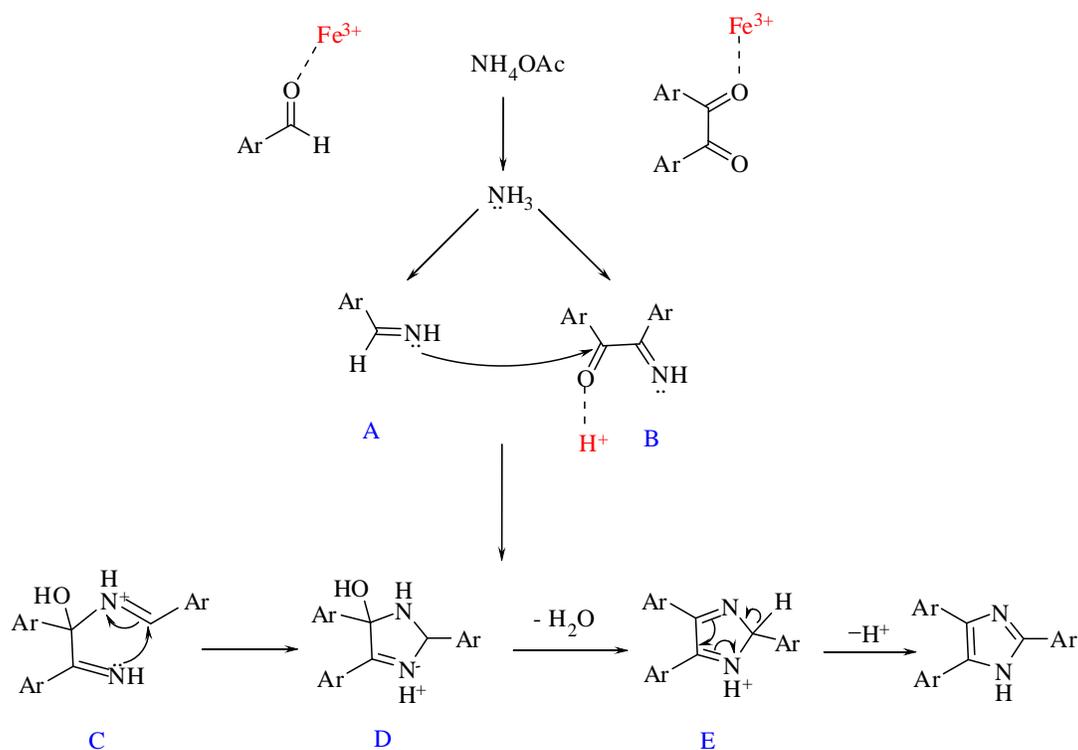
In order to verify the effect of ultrasonic irradiation, the reaction was performed in the presence of 1, 3, 5, 6 and 7 mol% of MNPs with and without ultrasonic irradiation (Table 2). In all cases, the experimental results show that the reaction times are shorter and the yields of the products are higher under sonication. The reason may be the phenomenon of cavitation produced by ultrasound.

Cavitation is the origin of sonochemistry, a physical process that creates, enlarges, and implodes gaseous and vaporous cavities in an irradiated liquid, thus enhancing the mass transfer and allowing chemical reactions to occur [34, 35].

The best results were obtained using 5 mol% of the catalyst under both conditions (Table 2, entry 4). As shown, in the absence of catalyst the yield of the product was found to be low (Table 2, entry 1).

Using the optimized reaction conditions, this process was demonstrated by the wide range of substituted and structurally divers aldehydes to synthesize the corresponding products in high to excellent yields (Table 3, method A).

Aldehydes bearing either electron-withdrawing or electron-donating groups perform equally well in the reaction and all imidazoles were obtained in high yields. For more examination of the influence of ultrasound irradiation in this transformation, comparison of the reaction under two



Scheme 3. Plausible mechanism of the reaction.

methods, ultrasound irradiation at room temperature (method A) and reflux conditions (method B) was performed. As illustrated in Table 3, method A in comparison with method B is better in both yields and especially in the reaction times (Table 3).

A plausible mechanism for the formation of trisubstituted imidazoles is envisaged in Scheme 3. Aldehyde and 1,2-diketone are first activated by MNPs ( $\text{Fe}^{+3}$ ) to afford A and B respectively. Then, imine intermediate (A), condenses further with the carbonyl carbon of 1,2 diketone imine (B) and formation of carbocation (C) followed by attack of imine nitrogen to positive center and dehydration to afford the iso-imidazole (E), which rearranges via [1,5] sigmatropic shift to the required imidazole (Scheme 3). It was suggested that ultrasound irradiation activates the reaction mixture by inducing high local temperatures and

pressure generated inside the cavitation bubble and its interfaces when it collapses and accelerates the reaction rate and shortens the reaction time [36].

The possibility of recycling the catalyst was examined using the reaction of benzil, benzaldehyde, 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 five times without any further treatment. No observation of any appreciable loss in the catalytic activity of nanocatalyst was observed (Fig. 5).

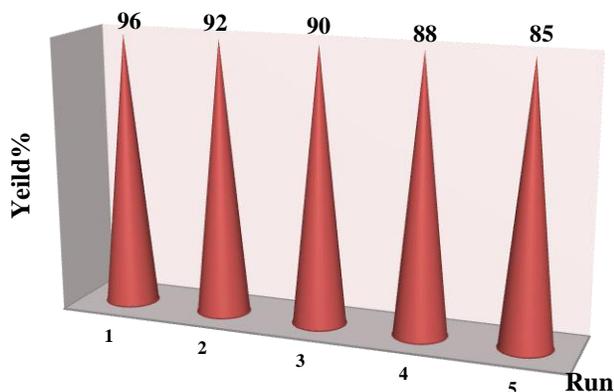
In order to show the merit of the present work in comparison with the other reported catalysts, we compared the reactions of MNPs with Ionic liquid [EMIM]OAc,

Table 4. Comparison of  $\text{Fe}_3\text{O}_4$  with other catalysts reported in the literature for the synthesis imidazoles<sup>a</sup>.

Entry	Catalyst	Amount; condition	Time	Yield <sup>b</sup> (%)	Ref.
1	Ionic liquid [EMIM]OAc	10 mol%; EtOH, u.s, r.t	1.5 h	95	40
2	Zr(acac) <sub>4</sub>	20 mol%; EtOH, u.s, r.t	45 min	88	27
3	Zinc (II) [tetra(4-methylphenyl)] Porphyrin	3 $\mu\text{mol}$ ; EtOH, u.s, r.t	70 min	94	37
4	$\text{BO}_3\text{H}_3$	5 mol; EtOH 50%, u.s, r.t	30 min	98	41
5	MNPs	5 mol; EtOH, u.s, r.t	25 min	96	This work

<sup>a</sup> Benzil (1 mmol), Aldehyde (1 mmol),  $\text{NH}_4\text{OAc}$  (5 mmol).

<sup>b</sup> Isolated yields.



**Fig. 5.** Recyclability of MNPs in the reaction of benzil (1 mmol), benzaldehyde (1 mmol) and ammonium acetate (5 mmol) under ultrasonic waves (40 KHz) at room temperature.

Zr(acac)<sub>4</sub>, Zinc (II) [tetra(4-methylphenyl)] Porphyrin, and BO<sub>3</sub>H<sub>3</sub> for the preparation of imidazole (4a) in Table 4. The results showed that MNPs is a better catalyst with respect to reaction times and yields of the products. Also magnetic Fe<sub>3</sub>O<sub>4</sub> nanoparticles not only gives high yield, purity, and short reaction time but also is a cheap, speedy, facile, and eco-friendly method throughout the course of the reaction. The superiority of Fe<sub>3</sub>O<sub>4</sub> nanocatalyst is in many different fields due to their intrinsic properties such as high surface area, low toxicity, super paramagnetic behavior, and easy separation and recovery from the reaction medium by magnetic decantation.

#### 4. Conclusion

An efficient and environmentally friendly method has been developed for the preparation of 2-aryl-4,5-diphenyl imidazoles catalyzed by MNPs under ultrasonic irradiation. This method offers several advantages including high yield, short reaction time, simple work-up procedure, ease of separation, and recyclability of the magnetic catalyst, as well as the ability to tolerate a wide variety of substitutions in the reagents.

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