



Research Article

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Ho³⁺ doped CoFe₂O₄ nanoparticles: A highly efficient, magnetically recoverable and reusable catalyst for one-pot three-component synthesis of 2,4,5 -triaryl-1H-imidazoles

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ABSTRACT

An efficient Ho³⁺ doped CoFe₂O₄ nanoparticles catalyzed one-pot synthesis of 2,4,5-triaryl-1H-imidazoles has been developed via three-component condensation of benzil or benzoin, aromatic aldehydes, and ammonium acetate in ethanol. The catalyst can be easily separable using magnet and reused with almost the same catalytic activity. The proposed method is advantageous due to its little catalyst loading, short reaction time, catalyst reusability, and excellent yields.

Keywords: Ho³⁺ doped CoFe₂O₄ nanoparticles; One-pot three-component reaction; Benzil; Benzoin; Aromatic aldehydes; Ammonium acetate

INTRODUCTION

Multicomponent reactions (MCR) [1-3] have become important tools for the rapid generation of molecular complexity and diversity with predefined functionality in chemical biology and drug discovery [4-6]. These reactions are often discovered by serendipity, but rational design strategies are now playing an increasing role because of their convergent nature, superior atom economy, and straightforward experimental procedures in the construction of target compounds by the introduction of several diversity elements in a single operation, resulting in substantial minimizations of waste, labor, time, and cost. MCRs, a powerful and virtually reliable target-guided synthetic approach, has extensively been used and applied for the rapid construction of molecular-level complex architectures, and interest from different branches of science is expanding exponentially [7].

Interest in imidazole-containing structures stems from their widespread biological activities and their use in synthetic chemistry. The imidazole ring system is one of the most important substructures found in a large number of natural products and pharmacologically active compounds [8-12]. In recent years, substituted imidazoles are substantially used in ionic liquids [13] that have been given a new approach to 'Green Chemistry'. Triarylimidazole derivatives have many biological activities, for example, herbicidal [14], fungicidal [15], anti-inflammatory [16], and antithrombotic activities [17]. In addition, they are used in photography as photosensitive compound [18]. Literature survey reveals that there are several methods for synthesizing them, mainly using nitriles and esters [19-21] as the starting materials. The first synthesis of the imidazole core 2,4,5-triphenylimidazoles using 1,2-dicarbonyl compounds aldehydes and ammonia, was proposed by Japp and Radziszewski [22, 23]. Subsequently, many other methods for synthesis of this important heterocycle have been published [24, 25]. Recently some methods for synthesis of tetra-substituted imidazoles are reported [26]. However, some of these previous methods have suffered from one or more drawbacks like high temperature requirement, highly acidic conditions, and the use of metal

cyanides for preparation of the nitrile compounds that limit their utility [27, 28]. Some of methods have resorted to harsh conditions (e.g. the formamide synthesis, which requires excess reagents, H₂SO₄ as a condensing agent, 150-200 °C, 4-6 h, 40-90% [29-31]). Due to these reasons, the development of mild, efficient and versatile method is still important.

In recent times, several transition metal oxides in the form of nanoparticles were employed as recyclable catalysts for one-pot multicomponent reactions [32]. In general, nanomaterials with natural morphologies containing higher surface area as reactive sites allow them to act as effective catalysts for organic synthesis [33]. These nanoparticles have provided a simplified isolation procedure for the product, with small amounts of catalyst, affording easy recovery and recyclability of the catalyst. In some cases, recovery of the nanoparticles from the reaction mixtures is so difficult that conventional techniques such as filtration or centrifugation are not enough for an efficient recovery. To overcome this issue, the use of magnetic nanoparticles has emerged as a viable solution; their insoluble and paramagnetic nature enables easy and efficient separation of the catalysts from the reaction mixture with an external magnet. Inspired by the utilization of Ho³⁺ doped CoFe₂O₄ nanoparticles as magnetically recoverable and reusable catalyst for the synthesis of 2,4,5-triaryl-1*H*-imidazoles and as a part of our continuous interest in the field of multicomponent reactions [34, 35], herein we wish to report an efficient synthesis of 2,4,5-triaryl-1*H*-imidazoles via one-pot three-component condensation reaction of benzil or benzoin, aromatic aldehydes and ammonium acetate in high yields and short reaction times by using Ho³⁺ doped CoFe₂O₄ nanoparticles as a green, robust and easily recoverable catalyst (Scheme 1 and 2).

EXPERIMENTAL SECTION

All reagents and solvents used were obtained from the Sigma and Avra synthesis. The purity of the synthesized compounds was checked by TLC. Melting points were determined in open capillary tubes. ¹H NMR spectra were recorded on a 400 MHz Varian-Gemini spectrometer and are reported as parts per million (ppm) downfield from a tetramethylsilane internal standard. The following abbreviations are used; singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m) and broad (br). Mass spectra were taken with Micromass-QUATTRO-II of WATER mass spectrometer.

General procedure for the synthesis of 2,4,5-triaryl-1*H*-imidazoles 4(a-n)

A mixture of benzil or benzoin (1.0 mmol), aromatic aldehydes (1.0 mmol), ammonium acetate (4.0 mmol), and Ho_xCoFe_{2-x}O₄ (x = 0.05) nanoparticles (5 mol %) in ethanol (25 mL) was refluxed (80 °C). The completion of the reaction was checked with TLC (n-hexane: ethyl acetate 4:1). After completion of reaction, the catalyst was magnetically removed from the reaction mixture. The solution was cooled to room temperature and poured on ice-water (50 ml) to get the precipitated solid. It was collected by filtration, washed with water and dried to give the corresponding 2,4,5-triaryl-1*H*-imidazoles. All synthesized compounds were characterized with ¹H NMR and mass. Also the melting points recorded and compared with the corresponding literature melting points and found to be matching with those.

2,4,5-triphenyl-1*H*-imidazole (4a)

Off-white solid; mp 272-274 °C; ¹H NMR (400 MHz, DMSO): δ = 7.52-7.60 (m, 6H), 7.69-7.75 (m, 3H), 7.88-7.95 (m, 6H), 8.92 (br, 1H); MS (EI, 70 eV): *m/z* = 296 [M+H]⁺.

2-(4-chlorophenyl)-4,5-diphenyl-1*H*-imidazole (4f)

Off-white solid; mp 180-182 °C; ¹H NMR (400 MHz, CDCl₃): δ = 7.35-7.65 (m, 6H), 7.70 -7.76 (m, 2H), 7.93-8.15 (m, 6H), 8.75 (br, 1H); MS (EI, 70 eV): *m/z* = 330 [M+H]⁺.

RESULTS AND DISCUSSION

Ho³⁺ doped CoFe₂O₄ nanoparticles were prepared by our research group [36] through sol-gel auto-combustion route to achieve homogeneous mixing of the chemical constituents on the atomic scale and better sinterability. Analytical grade cobalt nitrate (Co(NO₃)₂·3H₂O), holmium nitrate (Ho(NO₃)₃·5H₂O), iron nitrate (Fe(NO₃)₃·9H₂O) and citric acid (C₆H₈O₇·H₂O) were used to prepare the Ho_xCoFe_{2-x}O₄ (x = 0.0, 0.05, and 0.1) ferrite compositions. Reaction procedure was carried out in air atmosphere without protection of inert gases. The prepared powder then annealed at 600 °C for 4 h. The particle size was studied by scanning electron microscope (SEM) and the identification of nanoparticles was based on the analysis of SEM images. The SEM micrographs are shown in Fig. 1(a-c) and showed good spherical shaped particles in the material. The SEM pictures also indicate nearly uniform distribution of particles.

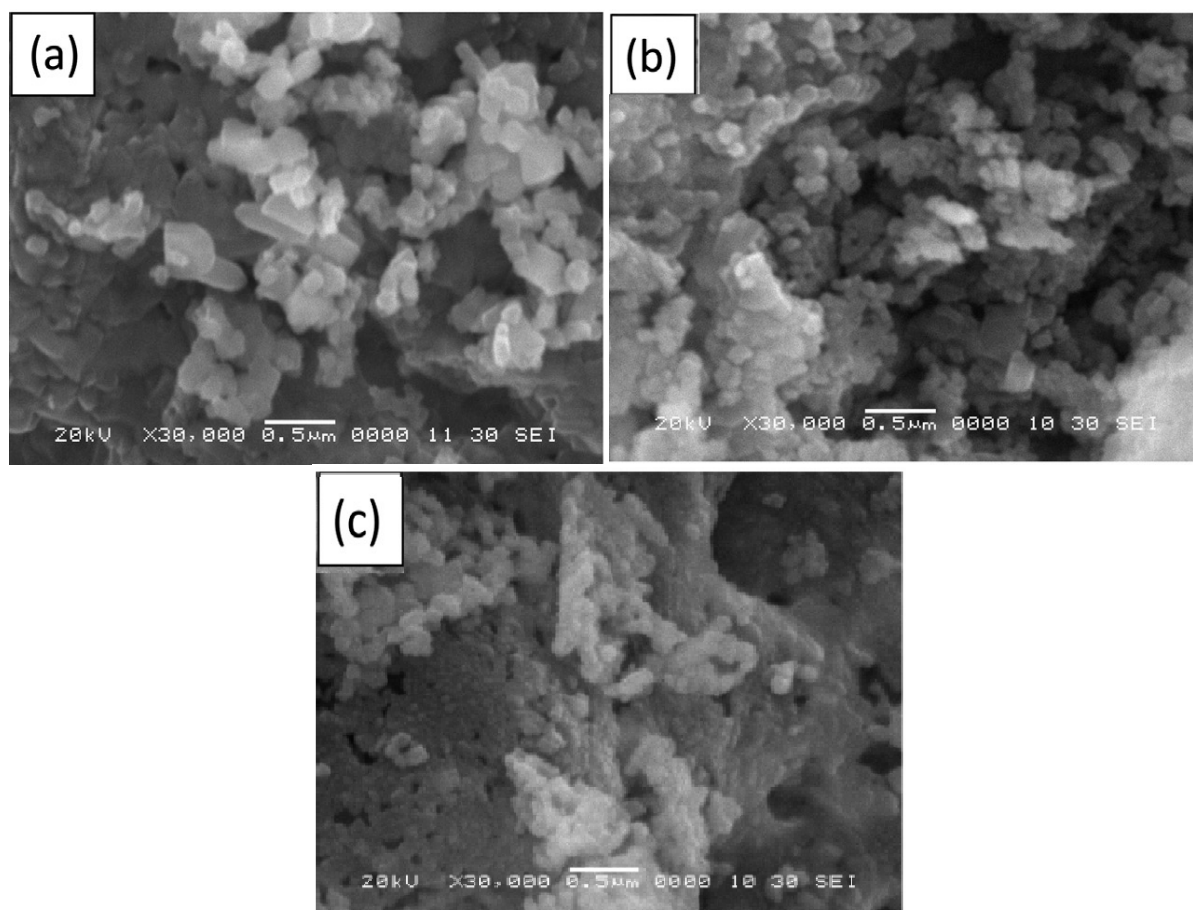


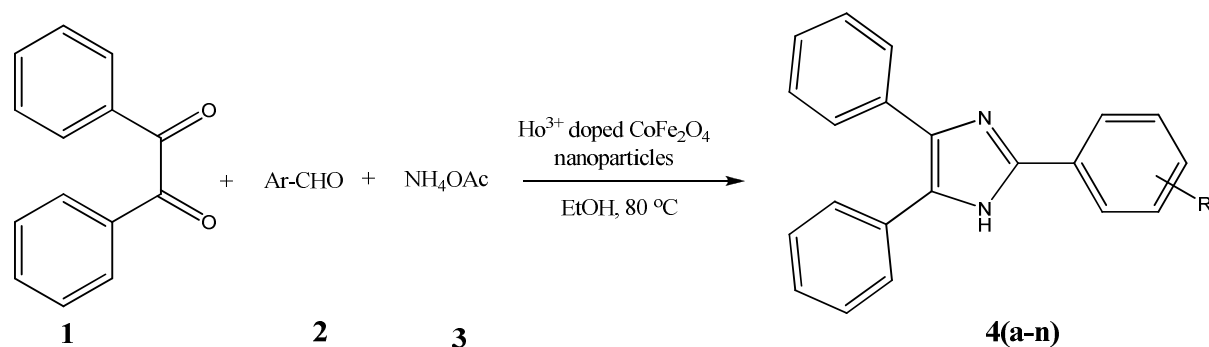
Figure 1- SEM images of $\text{Ho}_x\text{CoFe}_{2-x}\text{O}_4$ where (a) $x = 0.0$, (b) $x = 0.05$, and (c) $x = 0.1$

Initially, to study the catalytic efficiency of Ho^{3+} doped CoFe_2O_4 nanoparticles, all the three $\text{Ho}_x\text{CoFe}_{2-x}\text{O}_4$ ($x = 0.0$, 0.05 , and 0.1) nanoparticles were screened to find out best ferrite composition of Ho^{3+} doped CoFe_2O_4 nanoparticles using synthesis of 2,4,5-triphenyl-1*H*-imidazole (**4a**) as model reaction. The reaction was carried out using benzil (**1**) (1.0 mmol), benzaldehyde (**2**) (1.0 mmol) and ammonium acetate (**3**) (4.0 mmol) in ethanol (25 mL) as solvent using Ho^{3+} doped CoFe_2O_4 nanoparticles (20 mol %) as catalyst (Table 1). The title compound **4a** was isolated with 98% yield in the presence of $\text{Ho}_x\text{CoFe}_{2-x}\text{O}_4$ ($x = 0.05$) nanoparticles in shorter reaction time (10 min) than with other nanoparticles $\text{Ho}_x\text{CoFe}_{2-x}\text{O}_4$ ($x = 0.0$ and 0.1). After deciding the nanoparticles, the amount of nanoparticles (catalyst load) was optimized for model reaction (**4a**). The catalyst was added in amounts of 30, 20, 15, 10, 5, and 0 mol %. The results indicate that increase in amount of catalyst from 20 mol % to 30 mol % did not show any change in yield and time of reaction (Table 1, Entry 4). Also, when catalyst load was decreased sequentially from 20 mol % to 5 mol %, the results indicate, there were no change in yield and time of the reaction. When no catalyst was added (0 mol %) for model reaction, there was only small amount (Yield 25 %) of product obtained after 180 min. Therefore, 5 mol % of the catalyst $\text{Ho}_x\text{CoFe}_{2-x}\text{O}_4$ ($x = 0.05$) nanoparticles was assumed to ensure the best yield (98 %) in short reaction time (10 min). Thus, our results make the process under study more attractive and interesting from the viewpoint of economy and simplicity.

Table 1- Optimization of reaction conditions and catalyst load (mol %) of Ho^{3+} doped CoFe_2O_4 nanoparticles for the synthesis of 2,4,5-triphenyl-1*H*-imidazole (**4a**)

Entry	Catalyst (nanoparticles)	Catalyst loading (mol %)	Time (min)	Yield of 4a , % ^a
1	$\text{Ho}_x\text{CoFe}_{2-x}\text{O}_4$ ($x = 0.0$)	20	30	78
2	$\text{Ho}_x\text{CoFe}_{2-x}\text{O}_4$ ($x = 0.05$)	20	10	98
3	$\text{Ho}_x\text{CoFe}_{2-x}\text{O}_4$ ($x = 0.1$)	20	45	85
4	$\text{Ho}_x\text{CoFe}_{2-x}\text{O}_4$ ($x = 0.05$)	30	10	98
5	$\text{Ho}_x\text{CoFe}_{2-x}\text{O}_4$ ($x = 0.05$)	15	10	97
6	$\text{Ho}_x\text{CoFe}_{2-x}\text{O}_4$ ($x = 0.05$)	10	10	98
7	$\text{Ho}_x\text{CoFe}_{2-x}\text{O}_4$ ($x = 0.05$)	5	10	98
8	$\text{Ho}_x\text{CoFe}_{2-x}\text{O}_4$ ($x = 0.05$)	0 (No catalyst)	180	25

^a Hereinafter, isolated yield of pure product.



Scheme 1- Synthesis of 2,4,5-triarylimidazoles using benzil (1), aromatic aldehydes (2), and ammonium acetate (3) using 5 mol % $\text{Ho}_x\text{CoFe}_{2-x}\text{O}_4$ ($x = 0.05$) nanoparticles as catalyst

Table 2- Synthesis 2,4,5-triaryl-1H-imidazoles 4(a-n) using benzil or benzoin, aromatic aldehydes and ammonium acetate using 5 mol % $\text{Ho}_x\text{CoFe}_{2-x}\text{O}_4$ ($x = 0.05$) nanoparticles in ethanol

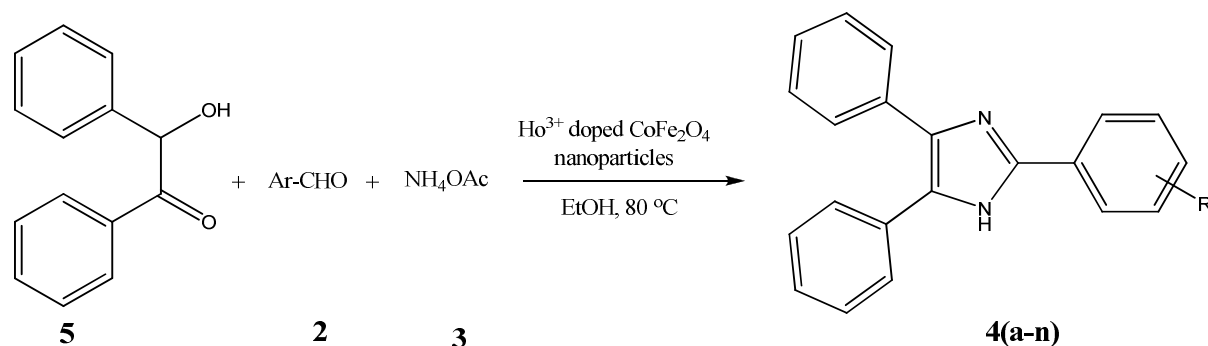
Entry	Aromatic aldehydes	Melting point ($^\circ\text{C}$)		Time (min)		^a % Yield	
		Observed	Literature	Benzil	Benzoin	Benzil	Benzoin
4a		272-274	274-275 [38]	10	15	98	93
4b		228-230	227-229 [38]	15	20	95	90
4c		230-232	230-231 [38]	10	15	98	92
4d		266-268	265-267 [38]	10	20	96	90
4e		254-256	256-258 [39]	15	15	98	95
4f		180-182	186 [38]	20	25	92	85
4g		256-258	260-262 [38]	20	25	90	88
4h		246-248	248-250 [40]	25	25	88	84
4i		198-200	200-202 [39]	20	25	98	92
4j		258-260	260-262 [39]	20	20	95	90
4k		244-246	245-247 [41]	20	25	95	92

^a Hereinafter, isolated yield of pure product.

To assess the generality of this approach, various aromatic aldehydes were reacted with benzil and ammonium acetate under optimized conditions to obtain 2,4,5-triaryl-1H-imidazoles **4(a-n)** (Scheme 1). As shown in Table 2,

aldehydes containing either electron-withdrawing or electron-releasing groups gave the corresponding 2,4,5-triaryl-1*H*-imidazoles (**3a-3h**) in high yields. In addition, it was specifically considerable that aryl aldehydes bearing electron-releasing groups such as $-\text{CH}_3$, $-\text{OCH}_3$, $-\text{OH}$, and $-\text{N}(\text{CH}_3)_2$ reacted very smoothly in short reaction times and higher yields (Table 2, **4b-4e**) while electron-withdrawing substitutions such as $-\text{Cl}$ and $-\text{CN}$ (Table 2, **4f-4h**) showed less reactivity in this condensation reaction. As shown in Table 2, these condensation reactions also proceed suitably when different heteryl-aromatic aldehydes were used in the synthesis of 2,4,5-triaryl-1*H*-imidazoles derivatives (**4i-4n**) in short reaction times and high yields.

1,2-diketones (like benzil) are usually prepared from the α -hydroxy ketones (like benzoin) catalyzed by various oxidants. Some of these catalysts are toxic, costly and also required the tedious experimental procedures [37]. To avoid the preparation of starting material 1,2-diketones like benzil, the synthesis of 2,4,5-triphenyl-1*H*-imidazole **4a** was studied using benzoin (**5**) (1.0 mmol), benzaldehyde (**2**) (1.0 mmol) and ammonium acetate (**3**) (4.0 mmol). Surprisingly, using the similar reaction conditions, 2,4,5-triphenyl-1*H*-imidazoles **4a** was isolated in 93 % yield within short reaction time (15 min). Encouraged by this result, we extended the methodology for synthesis of various 2,4,5-triaryl-1*H*-imidazoles **4(a-n)** using benzoin, various aromatic aldehydes and ammonium acetate (Scheme 2). The yields obtained were in the range of 84 % to 95 % (Table 2). Similar trends were also observed for Scheme 2, that is, aryl aldehydes bearing electron-releasing groups gave the corresponding 2,4,5-triaryl-1*H*-imidazoles in higher yield as compared with aryl aldehydes bearing electron-withdrawing substitutions.



Scheme 2- Synthesis of 2,4,5-triaryl-imidazoles using benzoin (**5**), aromatic aldehydes (**2**) and ammonium acetate (**3**) using 5 mol % $\text{Ho}_x\text{CoFe}_{2-x}\text{O}_4$ ($x = 0.05$) nanoparticles as catalyst

Catalyst reusability is of major concern in heterogeneous catalysis. The recovery and reusability of the catalyst was investigated in this reaction for model reaction (**4a**). The reaction was carried out using benzoin (**1**) (1.0 mmol), benzaldehyde (**2**) (1.0 mmol) and ammonium acetate (**3**) (4.0 mmol) in ethanol (25 mL) as solvent using 5 mol % of $\text{Ho}_x\text{CoFe}_{2-x}\text{O}_4$ ($x = 0.05$) nanoparticles as catalyst. After completion of reaction (monitored by TLC), catalyst recycling was achieved by fixing the catalyst magnetically at the bottom of the flask with a strong magnet, after which the solution was taken off with a pipette, the solid washed twice with acetone and the fresh substrate dissolved in the same solvent was introduced into the flask, allowing the reaction to proceed for the next run. The catalyst was consecutively reused five times without any noticeable loss of its catalytic activity (Cycle number and yield of **4a**: 1, 98 %; 2, 98 %; 3, 97 %; 4, 97 %; 5, 96 %). These catalysts are highly magnetic and their saturation magnetization values are found to be 67.05 and 68.55 emu/g, which are much higher than other reported magnetic catalysts [36]. Therefore, they could be easily and almost completely separated by an external magnet which is of a great advantage for $\text{Ho}_x\text{CoFe}_{2-x}\text{O}_4$ ($x = 0.05$) nanoparticles as heterogeneous catalyst.

The work-up of these reactions was very clean and required only pouring of the reaction mixture over ice-water after removing the catalyst with the help of magnet, and the desired products were thus isolated with high purity. To the best of our knowledge, the synthesis of 2,4,5-triaryl-1*H*-imidazoles derivatives using Ho^{3+} doped CoFe_2O_4 nanoparticles as catalyst has not been reported previously. The catalyst is not only efficient but also mild and easy to handle.

CONCLUSION

In conclusion, we have developed a highly efficient one-pot three-component method for the synthesis of 2,4,5-triaryl-1*H*-imidazole derivatives from benzoin or benzil, aromatic aldehydes and ammonium acetate in ethanol using Ho^{3+} doped CoFe_2O_4 nanoparticles. Advantages of the proposed procedure include simplicity, high yield, short reaction time, ease of separation and reusability of the magnetic catalyst. The method overcomes the earlier disadvantages and therefore will be of general use and interest to synthetic chemists.

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