



Short communication

Cobalt ferrite magnetic nanoparticles as highly efficient catalyst for the mechanochemical synthesis of 2-aryl benzimidazoles

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ABSTRACT

A highly efficient magnetically separable nano cobalt ferrite catalyst was synthesized via the sol-gel auto combustion method, characterized by powder XRD, SEM, TEM, UV-Visible, FT-IR, magnetic study, and BET isotherm analysis. The synthesized material was found to be an efficient heterogeneous Lewis acid catalyst for the synthesis of 2-aryl benzimidazole derivatives via solvent-free mechanochemical synthesis. The notable features of this new protocol include solvent-free reaction, cost-effectiveness, good yields, and environmental friendliness to afford the products within a short reaction time along with easy recovery and reuse of the nano catalyst.

1. Introduction

Magnetic nanoparticles are well recognized for stringent properties leading to a plenty of applications and have acquired a considerable interest in various fields, including magnetic drug delivery, magnetic resonance imaging, magnetic high-density information storage, and cancer hyperthermia treatment [1]. Furthermore, the magnetic nanoparticles constitute effective catalysts in synthetic chemistry due to ease of separation by an external magnet. Magnetic separation is an intriguing and distinguishing characteristic of these materials that makes magnetically separable catalysts more popular over their non-magnetic catalytic materials. Their magnetic property prevents the loss of material and enhances reusability, leading to cost-effectiveness and promising alternatives for industrial applications [2]. Thus, the development of magnetic nanoparticles with tunable catalytic activity has become an area of academic and industrial research. The cubic spinel ferrites constitute an important class of magnetic transition metal oxide materials. Among the spinel ferrites, cobalt ferrite nanoparticles are of great interest due to their potential applications in adsorption, sensors, recording media, memory chips, magnetic technologies, and catalysis [3]. Cobalt ferrite possesses a moderate saturation magnetization, high electrical resistivity, moderate photo-catalytic properties, and reproducible characteristics [4]. Mixed metal oxide nanoparticles

(MMONs) are widely studied, and are actively pursued in the development of greener reaction protocols in synthetic organic chemistry [5]. Catalytic processes developed by using magnetically separable MMONs are quite simple, economically efficient, and more environmentally benign, thus constituting effective tools of “green chemistry” [6]. The MMONs are sustainable alternatives to conventional materials due to their high surface area, robustness, cheapness, and economical nature. The MMONs particles possess enhanced surface area that assists to increase the contact between reactants dramatically, thus mimicking the homogeneous counterparts. The insolubility of this material in common organic solvents renders their ease of separation from the reaction mixture, making easy product isolation without much efforts. Thus, MMONs represent the most important and widely employed materials in the field of catalysis [7].

An eco-friendly sustainable protocol focuses on the reduction of wastes, minimum or no use of solvents, and the development of methods with easy product separation, isolation, and purification. Mechanochemical processes follow the features of sustainable chemistry and thus have emerged as an attractive alternative to the traditional methods [8]. These involve the reactions induced by the mechanical energy of grinding or ball-milling. Mechanochemical synthesis by “ball-milling” is successful for typical organic reactions [9]. Thus, in the recent era, these methods have become popular for the development of synthetic routes

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for heteroaromatic compounds of biological interest [10]. Among the benzo-fused heteroaromatics, benzimidazoles are the common structural scaffolds of biological interest [11]. Benzimidazoles are well recognized for a wide range of pharmacological activities, including: antibacterial, antifungal, antiviral, antihypertensive, anticancer, anti-ulcer, and antihistaminic potential [12]. The scaffolds are the parts of commercially marketed drugs such as esomeprazole that is an anti-ulcerative drug [13]. Besides, imidazoles constitute the key intermediates in various organic reactions [14] and present in the skeletons of several functional materials [15]. Thus, the development of new strategies for the synthesis of these heterocyclic compounds becomes inevitable. Traditionally, benzimidazoles are synthesized by the condensation of *o*-phenylenediamine with aldehyde / carboxylic acid or its derivatives by using various catalysts and reagents such as clay supported titanium catalyst [16], sulfonic acid functionalized graphene oxide [17], lanthanum chloride [18], NaY zeolite [19], Fe₃O₄@-SiO₂@polyionene/Br₃-core-shell magnetic nanoparticles [20], magnetic core-shell nanoparticles containing I₃⁻ [21], *p*-toluene sulfonic acid [22], ceric ammonium nitrate / polyethylene glycol [23], silver carbonate on celite [24], aluminum nitride / aluminum [25], 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone DDQ [26], and so on.

In continuation of our research on the development of magnetic nanocatalysts for organic transformations [27], we herein report a green synthesis of cobalt ferrite nanocatalyst by sol-gel auto combustion and the development of an efficient mechanochemical protocol for the synthesis of 2-aryl benzimidazoles by using cobalt ferrite NPs as a magnetically separable heterogeneous catalyst (Scheme 1). The synthesis of benzimidazoles was studied by grinding a mixture of *o*-phenylenediamine and aldehydes in the presence of a catalytic amount of cobalt ferrite nanocatalyst in an agate mortar-pestle to afford the products in high yields. The protocol is solvent-free and environmentally benign involving easy separation of the catalyst in a short reaction time.

2. Experimental

2.1. Materials and methods

All the required chemicals were Merck or SD Fine made and used without further purification. The reaction progress was monitored by Thin Layer Chromatography (TLC) on Aluchrosep Silica Gel 60 TLC plates under UV- 254 nm light. Melting points of the products were determined in capillaries open at one end on a Tanco® melting point apparatus. The synthesized products were characterized by ¹H and ¹³C NMR after using a Bruker Avance II 400 NMR spectrometer at 400 MHz in CDCl₃ solvent and using TMS as an internal standard. The mass

spectra were obtained on a Shimadzu-GCMS-QP2010 spectrometer operating at 70 eV.

2.2. Sol-gel auto combustion method for the preparation of cobalt ferrite magnetic nanoparticles

Cobalt ferrite magnetic nanoparticles were synthesized by the sol-gel auto combustion method after using glycine as a green fuel. AR grade chemicals such as cobalt nitrate Co(NO₃)₂·6H₂O, ferric nitrate (Fe(NO₃)₃·9H₂O), and glycine (C₂H₅NO₂) were used for the synthesis. The metal nitrates to fuel ratio was taken as 1:4.4. Ammonia solution was added to maintain the pH of solution at 7. The resulting powder was sintered at 600 °C for 5 h, characterized, and then used for further investigations.

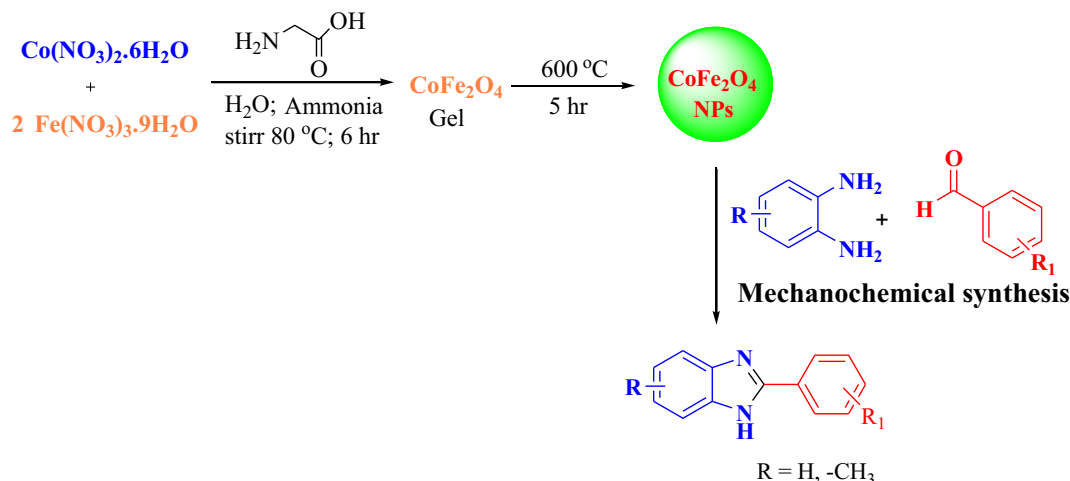
2.3. Characterization of nano cobalt ferrite

The synthesized nano cobalt ferrite was characterized for its surface, morphology, optical, magnetic, and electrical properties. The material was characterized by powder X-ray diffraction (XRD) (Regaku model). The X-ray diffractograms of the sample were recorded at ambient temperature in the 2θ range from 20° to 80° by using Cu-Kα radiation (λ = 1.54056 Å). Scanning Electron Microscope (SEM) images of the sample were obtained on JEOL-JSM 840 SEM analyzer at an operating voltage of 20 kV attached with EDX equipment.

The optical investigations of the nanomaterial were studied after using PerkinElmer UV WinLab Lambda 900 UV/VIS/NIR, in the wavelength range of 200–800 nm. Magnetic properties of the films were studied by a vibrating sample magnetometer (Lakeshore VSM 7410) at room temperature. Transmission electron microscopy (TEM, Philips CM200) was used for microstructural analysis and surface morphology.

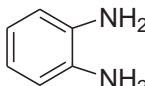
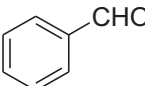
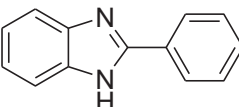
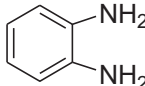
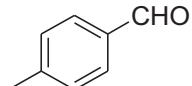
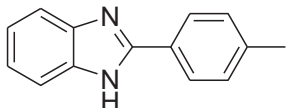
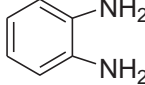
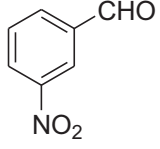
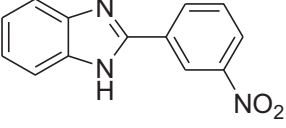
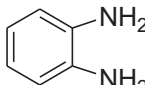
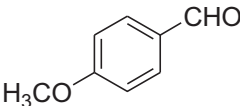
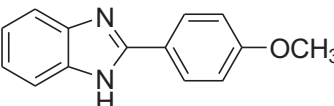
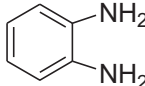
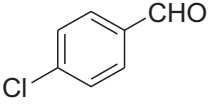
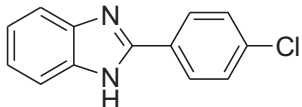
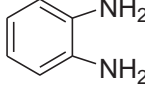
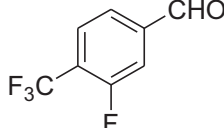
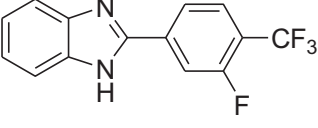
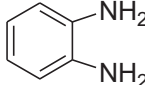
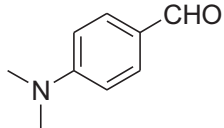
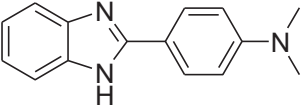
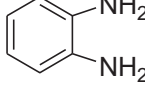

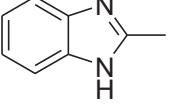
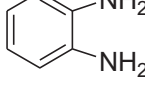
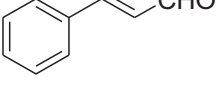
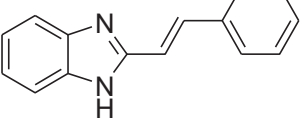
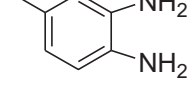
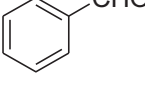
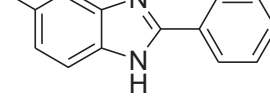
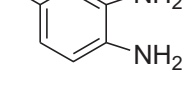
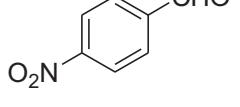
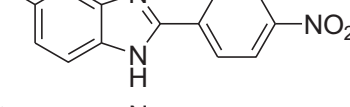
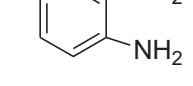
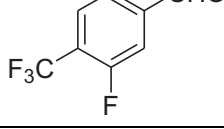
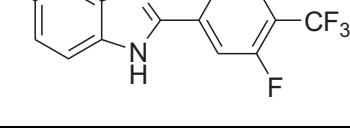
2.4. General procedure for the synthesis of 2-aryl benzimidazole derivatives using CoFe₂O₄ nanocatalyst

A mixture of aldehyde (0.5 mmol), *o*-phenylenediamine (1 mmol), and CoFe₂O₄ nanoparticles (5 mol%) was ground in an agate mortar and pestle. The contents were turned into a pasty mass after 5 to 10 min of grinding. After this, the remaining half quantity of the aldehyde (0.5 mmol) was added, and the grinding was continued for a further time as specified in Table 1. The reaction progress was monitored on TLC by using AcOEt: n-hexane (1:4) as the mobile phase. After completion of the reaction as indicated by TLC, the reaction mixture was diluted with ethyl acetate (10 mL) and the catalyst was separated by an external magnet. The filtrate was evaporated under reduced pressure to obtain pure



Scheme 1. Synthesis of CoFe₂O₄ NPs and their catalytic activity for the mechanochemical synthesis of benzimidazoles.

Table 1
 . Synthesis of 2-phenyl-1*H*-benzimidazoles using cobalt ferrite nanocatalyst under mechanochemical grinding.^a

Entry	Diamines	Aldehydes	Products	Yield (%) ^b	Time (min)	MP (°C) Observed [MP Lit.][Ref]
1				97	10	293–295 [292] [30]
2				94	10	274–276 [275–276] [18]
3				95	08	205–207 [202–205] [31]
4				92	10	222–225 [226] [30]
5				90	08	290–291 [294] [32]
6				90	08	175–176 [174] [35]
7				96	08	287–289 [288–290] [18]
8				92	07	173–174 [173–175] [34]
9				88	10	195–197 [200] [34]
10				93	08	235–236 [236] [34]
11				96	08	240–242 [240] [35]
12				94	07	174–175 [174] [36]

^a Reaction condition: Phenylene diamine (1.0 mmol), aldehyde (1.0 mmol), catalyst (5 mol%)

^b Isolated yield of product.

crystals of the 2-aryl benzimidazole. The catalyst was washed with diethyl ether, dried in the furnace at 110 °C and reused for subsequent runs.

2.4.1. Spectral data of the representative compounds:

2-(3-Nitro Phenyl)-1H-Benzimidazole (Table 1, Entry 3): $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ ppm 8.76 (s, 1H), 8.66 (s, 1H), 8.28–8.30 (d, 1H), 8.24–8.22 (d, 1H), 7.66–7.60 (m, 1H), 7.14–7.11 (m, H), 6.82–6.77 (m, 2H); IR (cm^{-1}): 3375, 2883, 1615, 1519, 1347; Mass (m/z): 240.0 (M).

2-(4-N,N-Dimethylaniline)-1H-Benzimidazole (Table 1, Entry 7): $^1\text{H NMR}$ (400 MHz, CDCl_3) δ ppm: 12.49 (s, 1H), 7.98–8.01 (m, 2H), 7.48 (s, 2H), 7.11–7.14 (m, 2H), 6.78–6.86 (m, 2H), 2.9 (s, 6H); MS (ESI) m/z : 238 [$\text{M} + \text{H}$] $^+$; IR (cm^{-1}): 3387, 3047, 1607.

3. Results and discussion

In the present study, glycine was used as a green fuel for the synthesis of cobalt ferrite nanoparticles by the sol-gel auto combustion method. Glycine, the first amino acid is abundantly available and has a negative heat of combustion. It is a non-hazardous and eco-friendly material compared to oxalic acid and citric acid fuels used in the traditional sol-gel method. Because of the negative heat of combustion, glycine provides a sufficient temperature required for the combustion to form pure spinel ferrite nanoparticles of CoFe_2O_4 .

3.1. X-ray diffraction (XRD) analysis

The cobalt ferrite nanoparticles were characterized for phase purity by using the XRD technique. The XRD pattern recorded at room temperature is shown in Fig. 1, which reveals reflections belonging to the cubic spinel structure of cobalt ferrite nanocatalyst before (CF-0) and after the seventh reuse (CF-7). It can be observed that all the reflections are identical. The absence of any extra peak indicates high purity of the material. From XRD data, the single-phase cubic spinel structure of the material was confirmed, and there was no alteration observed in the structure of cobalt ferrite catalyst before and after catalytic applications. It indicates high stability of the catalyst towards solvents and chemical environments. The XRD data, crystallite size, the lattice constant, and unit cell volume were found as 12 nm, 8.378 Å, and 588.05 Å³, respectively. These values are in good agreement with those reported in the literature.

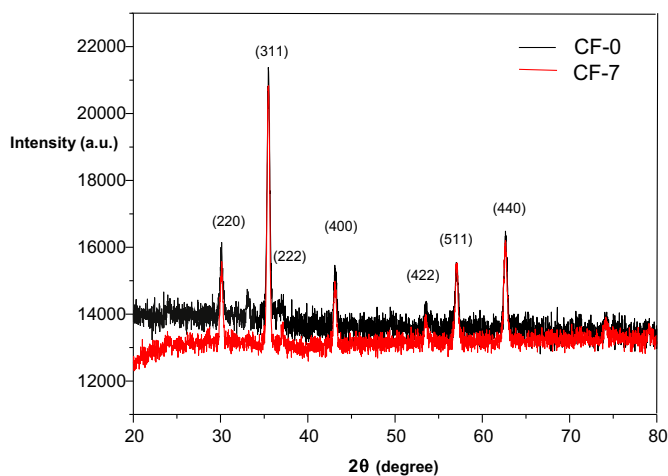


Fig. 1. XRD pattern of CoFe_2O_4 nanoparticles fresh (CF-0) and after seventh reuse (CF-7).

3.2. Morphology study

The surface morphology of cobalt ferrite nanoparticles was investigated by Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) analyses. Fig. S1 shows the SEM micrographs of the cobalt ferrite nanoparticles (Supplementary Information, SI). Morphology of the material indicated the presence of spherical grains. Agglomeration of the grains could be possibly due to synthetic procedure and experimental conditions. TEM analysis conducted to understand the crystalline size and morphology (Fig. 2) of cobalt ferrite nanoparticles before use as catalytic material (CF-0) indicated the presence of spherical nanoparticles. Some particles were agglomerated, and some separated as can be observed in Fig. 2. Particle size of the nanoparticles was found to be in the range of 10 to 15 nm, which is in good agreement with the fine conformity and crystallite size calculated on the basis of XRD.

3.3. FT-IR analysis

FTIR analysis of the fresh (CF-0) and seventh times reused (CF-7) catalyst is depicted in the Supporting Information (SI). The comparison of the spectra shows no change in the IR absorption frequency, indicating no change in the catalyst structure (Fig. S2, SI). In the FT-IR spectrum of CF-0, two absorption IR bands appeared at 420 cm^{-1} (μ_2) and 551 cm^{-1} (μ_1), while in the FT-IR spectrum of reused CF-7 cobalt ferrite nanocatalyst absorption bands appeared at 412 cm^{-1} (μ_2) and 547 cm^{-1} (μ_1), which correspond to intrinsic vibrations of the octahedral complex and intrinsic vibrations of the tetrahedral complex, respectively. The presence of these two absorption bands in the FT-IR spectrum reveals the formation of a cubic spinel structure. From the FT-IR analysis of the fresh (CF-0) and seventh times reused (CF-7) catalyst, only a minute deviation from 420 cm^{-1} to 412 cm^{-1} and from 551 cm^{-1} to 547 cm^{-1} was observed. The FTIR spectra of CoFe_2O_4 spinel were compared with the standard [28]. Absence of major change in the IR absorption frequency in the CF-0 and CF-07 samples indicates no remarkable change in the structure of the catalyst, thus high stability of the material.

3.4. Magnetic properties study

The M-H plot of the synthesized cobalt ferrite nanoparticles was recorded at room temperature and the nature of the curve is depicted in Fig. 3.

Using the M-H plot, the values of the magnetic parameters such as

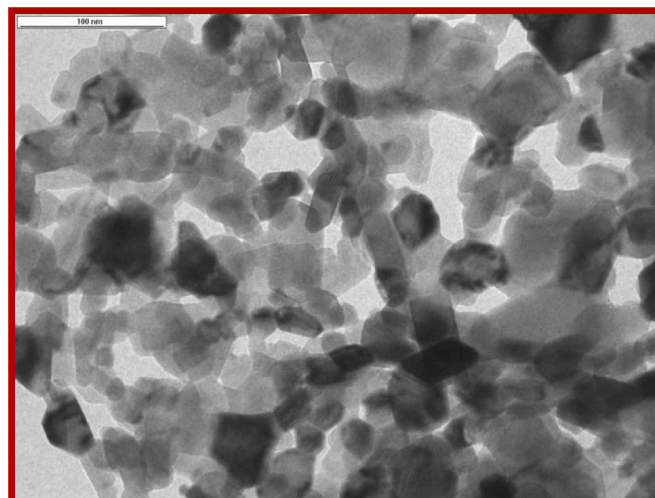


Fig. 2. TEM image of CoFe_2O_4 nanoparticles.

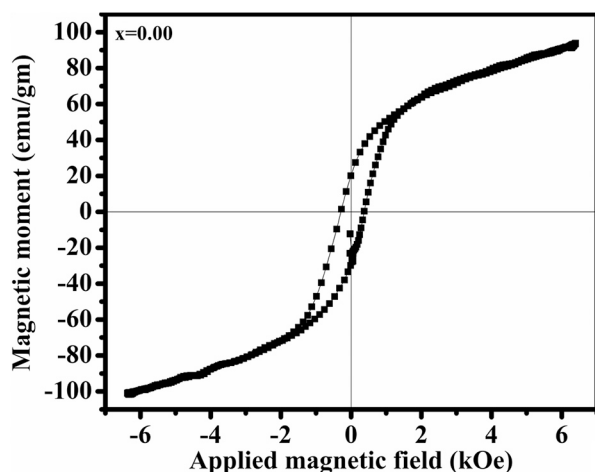


Fig. 3. M-H plot of CoFe_2O_4 nanoparticles.

saturation magnetization (M_S), remanence magnetization (M_r), and coercivity (HC) were deduced. The values of the M_S , M_r , and HC were found to be 83.89 emu/g, 20.13 emu/g, and 287.62 Oe, respectively. These values match well with reported values [29]. Thus, the cobalt ferrite nanoparticles showed good magnetic properties.

3.5. BET surface area measurements

Fig. 4 depicts the N_2 -adsorption-desorption isotherm of CoFe_2O_4 nanoparticles measured by the Autosorb iQ Station 2 instrument. The analysis revealed the formation of porous nanoparticles having average pore width of 3.95 Å and a surface area of 8.1 m^2/g . The isotherm displays a typical H_2 -type hysteresis for CoFe_2O_4 nanoparticles, which is usually attributed to the predominance of mesopores.

3.6. UV-visible studies

The optical properties of the cobalt ferrite fresh nanocatalyst (CF-0) were investigated by UV-Vis spectroscopy in the wavelength range 400–1000 nm (Fig. S3, SI). The energy band gap was anticipated by plotting a Tauc plot of $h\nu$ versus $(ah\nu)^2$ for direct intercept method. The optical absorption coefficient was calculated by the following Eq. (1):

$$ah\nu = A(h\nu - E_g)^{\frac{1}{2}} \quad (1)$$

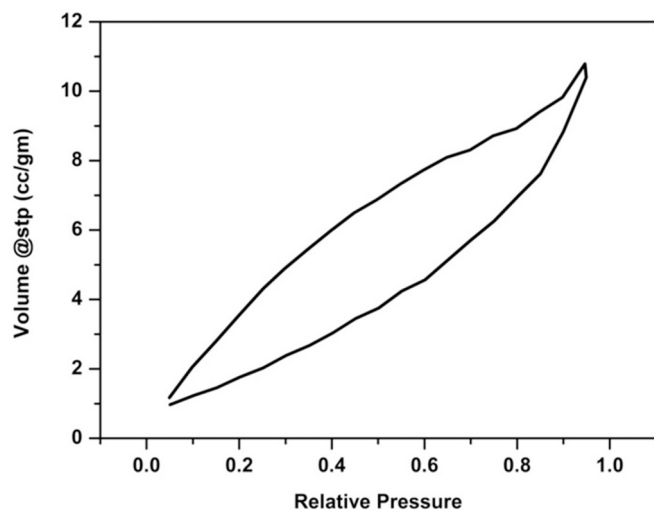


Fig. 4. N_2 -adsorption-desorption isotherm of CoFe_2O_4 nanoparticles.

where, a , h , ν , A , and E_g are the light frequency, Planck constant, absorption coefficient, proportionality constant and band gap, respectively. Cobalt ferrite catalyst (CF-0) has a band gap energy of 2.784 eV.

3.7. Catalytic activity and recyclability

Catalytic activity and reusability of cobalt ferrite nanoparticles synthesized by the green route were studied for the synthesis of 2-substituted benzimidazole derivatives via eco-friendly mechano-chemical synthesis. To show the generality of this method, several aldehydes were screened for the synthesis of corresponding benzimidazoles as summarized in Table 1. The catalyst optimization conditions are shown in Table S1 (SI). 5 mol% of the catalyst was sufficient to catalyze the reaction. In general, aldehydes bearing electron-withdrawing substituents show a fast reaction in minimum time due to the increased electrophilic character of aromatic aldehydes. The synthesis of benzimidazoles was achieved in high yields by simply grinding a mixture of *o*-phenylenediamine and the corresponding aldehydes with cobalt ferrite nanocatalyst in an agate mortar pestle. As envisaged, the CoFe_2O_4 catalyst was effectively separated from the reaction mixture by an external magnetic field after the completion of the reaction. We used the same catalyst for subsequent runs from fresh to seventh catalytic run. The decreasing yields for the subsequent runs can be accounted for minor losses of the catalytic material during its recovery at each run.

The utility of catalyst for scalable synthesis was also attempted for the reaction of OPD with cinnamaldehyde (5 mmol) using the mortar and pestle. The reaction required 16 min for completion when carried out on 5 mmol of cinnamaldehyde. The more time required for the completion of the reaction can be possibly accounted for the limitation of mechanochemical synthesis for scale-up processes.

A plausible mechanism for the green and practical method to construct benzimidazoles is illustrated in Scheme 2. *o*-phenylenediamine (**1a**) and benzaldehyde (**1b**) initially dehydrate to form imine (**1c**). The intermediate **1d** was generated through the intramolecular 1, 2-addition of intermediate **1c**. Finally, the intermediate **1d** was easily oxidized by air to produce the desired product **1e** with the loss of water molecule.

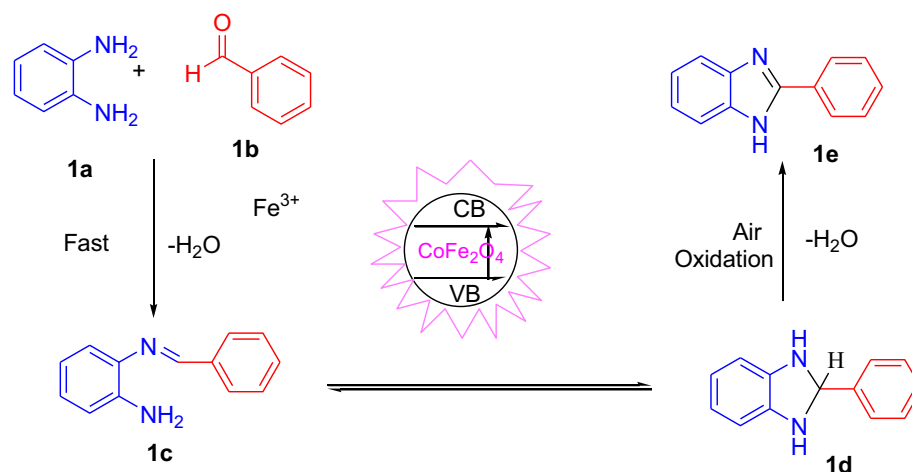
The reusability of the catalyst was also examined. We prepared 2-phenyl-1*H*-benzimidazole (**1e**) by using *o*-phenylenediamine (**1a**) and benzaldehyde (**1b**) as the starting materials. At the end of the reaction, the catalyst was separated by an external magnet, washed with ethyl acetate, and reused under similar conditions. The catalyst worked without remarkable loss of activity (Table S2, SI).

The comparison of present protocol with some of the literature methods is summarized in Table 2. It is noted that the method described herein constitutes a valuable addition to the existing methods for the synthesis of benzimidazoles by the reaction of aldehydes with OPD. Thus, in summary, in the present work, we have developed a green and practical method to construct benzimidazoles, which are ubiquitous structural units in several biologically active compounds. In addition, oxidant-free conditions, and the use of air as the oxidant make this transformation green, practical, and environment friendly.

4. Conclusions

In conclusion, we have developed an efficient and cost-effective synthesis of spinel cobalt ferrite magnetic nanocatalyst by sol-gel auto combustion method using water as solvent and glycine as a green fuel. The cobalt ferrite nanocatalyst was thoroughly characterized by different spectroscopic techniques. Cobalt ferrite magnetic nanomaterial has been demonstrated to be a highly efficient catalytic material as a unique heterogeneous Lewis acid catalyst for the synthesis.

of 2-aryl benzimidazole derivatives via solvent-free mechanochemical synthesis. The catalyst could be easily separated from the reaction mixture by using an external magnet which was reused several times



Scheme 2. A plausible mechanism for the synthesis of 2-arylbenzimidazoles.

Table 2

Comparison of the present protocol with some literature methods for the synthesis of benzimidazoles.

Sr. No.	Conditions	Yield (%)	Reference
1.	Lanthanum chloride (10 mol%), Acetonitrile, r. t., 2–4 h	85–95	[18]
2.	NaY Zeolite (100 mg for 0.0025 mol of OPD), EtOH, r.t., 48 h	26–93	[19]
3.	Fe ₃ O ₄ @SiO ₂ @polyionene/Br ₃ - MNPs (0.05 g / mmol of OPD), solvent free, 110 °C, 12–90 min	67–97	[20]
4.	Fe ₃ O ₄ @SiO ₂ @(CH ₂) ₃ N ⁺ Me ₃ I ₃ ⁻ (0.007 g / mmol of OPD), 100 °C, 13–20 min	88–94	[21]
5.	CAN (5 mol%), PEG, 50 °C, 1.5–3 h	90–98	[23]
6.	Ag ₂ CO ₃ /Celite (25 mol%), EtOH, 70 °C, 3 h	88–99	[24]
7.	AlN/Al (20 wt%), ethanol, reflux 30–90 min	87–93	[25]
8.	CoFe ₂ O ₄ (5 mol%), grinding, 7–11 min	88–97	Present work

without appreciable loss of its initial catalytic activity. Operational simplicity, solvent-free condition, cleaner reaction profile, easy workup, higher yields, and short reaction times make this protocol more valuable.

Declaration of Competing Interest

The authors declare no conflict of interest.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.catcom.2021.106349>.

References

- [1] S. Singamaneni, V.N. Bliznyuk, C. Binek, E.Y. Tsybal, Magnetic nanoparticles: recent advances in synthesis, self-assembly and applications, *J. Mater. Chem. 21* (2011) 16819–16845, <https://doi.org/10.1039/C1JM11845E>.
- [2] Y. Zheng, P.D. Stevens, Y. Gao, Magnetic nanoparticles as an orthogonal support of polymer resins: applications to solid-phase Suzuki cross-coupling reactions, *J. Organomet. Chem.* 71 (2006) 537–542, <https://doi.org/10.1021/jo051861z>.
- [3] A. Pradeep, P. Priyadharsini, G. Chandrasekaran, Sol-gel route of synthesis of nanoparticles of MgFe₂O₄ and XRD, FTIR and VSM study, *J. Magn. Mater.* 320 (2008) 2774–2779, <https://doi.org/10.1016/j.jmmm.2008.06.012>.
- [4] S. Jauhar, J. Kaur, A. Goyal, S. Singhal, Tuning the properties of cobalt ferrite: a road towards diverse applications, *RSC Adv.* 6 (2016) 97694–97719, <https://doi.org/10.1039/C6RA21224G>.
- [5] M.B. Gawande, V.D.B. Bonifácio, R.S. Varma, I.D. Nogueira, N. Bundaleski, C.A. A. Ghumman, O.M.N.D. Teodorod, P.S. Branco, Magnetically recyclable magnetite-ceria (Nanocat-Fe-Ce) nanocatalyst—applications in multicomponent reactions under benign conditions, *Green Chem.* 15 (2013) 1226–1231, <https://doi.org/10.1039/C3GC40375K>.
- [6] A. Dandia, V. Parewa, A.K. Jain, K.S. Rathore, ZnS nanoparticle-catalyzed synthesis of spiroindole derivatives in aqueous medium via Knoevenagel condensation followed by Michael addition, *Green Chem.* 13 (2011) 2135–2145, <https://doi.org/10.1039/C1GC15244K>.
- [7] J.C. Védrine, ID Heterogeneous catalysis on metal oxides, *Catalysts* 7 (2017) 341, <https://doi.org/10.3390/catal7110341>.
- [8] G.W. Wang, Mechanochemical organic synthesis, *Chem. Soc. Rev.* 42 (2013) 7668–7700, <https://doi.org/10.1039/C3CS35526H>.
- [9] T. Szuppa, A. Stolle, S.E.S. Leonhardt, B. Ondruschka, Ball milling in organic synthesis: solutions and challenges, *Chem. Soc. Rev.* 40 (2011) 2317–2329, <https://doi.org/10.1039/C0CS00195C>.
- [10] G. Brahmachari, S. Das, L-Proline catalyzed multicomponent one-pot synthesis of gem-diheteroarylmethane derivatives using facile grinding operation under solvent-free conditions at room temperature, *RSC Adv.* 4 (2014) 7380–7388, <https://doi.org/10.1039/C3RA44568B>.
- [11] G. Yadav, S. Ganguly, Structure activity relationship (SAR) study of benzimidazole scaffold for different biological activities: a mini-review, *Eur. J. Med. Chem.* 97 (2015) 419–443, <https://doi.org/10.1016/j.ejmech.2014.11.053>.
- [12] M. Boiani, M. González, Imidazole and benzimidazole derivatives as chemotherapeutic agents, *Mini-Rev. Med. Chem.* 5 (2005) 409–424, <https://doi.org/10.2174/1389557053544047>.
- [13] L.J. Scott, C.J. Dunn, G. Mallarkey, M. Sharpe, Esomeprazole: a review of its use in the management of acid-related disorders, *Drugs* 62 (2002), <https://doi.org/10.2165/00003495-200262100-00006>, 1503–1338.
- [14] R.S. Keri, A. Hiremathad, S. Budagumpi, B.M. Nagaraja, Comprehensive review in current developments of benzimidazole-based medicinal chemistry, *Chem. Bio. & Drug Design* 86 (2015) 19–65, <https://doi.org/10.1111/cbdd.12462>.
- [15] Z. Song, W. Zhang, M. Jiang, H.H. Sung, R.T. Kwok, H. Nie, I.D. Williams, B. Liu, B. Z. Tang, Synthesis of imidazole-based aiegens with wide color tunability and exploration of their biological applications, *Adv. Funct. Mater.* 26 (2016) 824–832, <https://doi.org/10.1002/adfm.201503788>.
- [16] V. Kannan, K. Sreekumar, Clay supported titanium catalyst for the solvent free synthesis of tetrasubstitutedimidazoles and benzimidazoles, *J. Mol. Cat. A: Chem.* 376 (2013) 34–39.
- [17] M.B. Swami, A.H. Jadhav, S.R. Mathpati, H.G. Ghuge, S.G. Patil, Eco-friendly highly efficient solvent free synthesis of benzimidazole derivatives over sulfonic acid functionalized graphene oxide in ambient condition, *Res. Chem. Intermed.* (2013), <https://doi.org/10.1007/s11164-016-2745-y>.
- [18] Y. Venkateswarlu, S.R. Kumar, P. Leelavathi, Facile and efficient one-pot synthesis of benzimidazoles using lanthanum chloride, *Org. & Med. Chem. Lett* 3 (2013), <http://www.orgmedchemlett.com/content/3/1/7>.
- [19] A. Mobinikhaedi, N. Forughifar, M. Zendeheidi, M. Jabbarpour, Conversion of aldehydes to benzimidazoles using NaY zeolite, *Synth. Reactivity Inorg. Metal-Org. Nano-Metal Chem* 38 (2008) 390–393, <https://doi.org/10.1080/15533170802132261>.

- [20] E. Dezfoolnezhad, K. Ghodrati, R. Badri, $\text{Fe}_3\text{O}_4@/\text{SiO}_2@/\text{polylonene}/\text{Br}_3\text{-core-shell}$ magnetic nanoparticles: a novel catalyst for the synthesis of imidazole derivatives in solvent-free conditions, *NJC* 40 (2016) 4575–4587, <https://doi.org/10.1039/C5NJ02680F>.
- [21] E. Korani, K. Ghodrati, M. Asnaashari, Magnetic Core-shell nanoparticles containing I-3 as a novel catalyst for the facile synthesis of imidazole, thiazole and pyrimidine derivatives in solvent-free conditions, *Silicon* 10 (2018) 1433–1441, <https://doi.org/10.1007/s12633-017-9623-0>.
- [22] A.J. Kadhim, A.C. Kazim, Synthesis and characterization of benzimidazole by using *o*-phenylenediamine with different aldehydes and carboxylic acids in the presence of *p*-TsOH as a catalyst, *Orient. J. Chem.* 34 (2018) 2131–2136.
- [23] M. Kidwai, A. Jahan, D. Bhatnagar, Polyethylene glycol: a recyclable solvent system for the synthesis of benzimidazole derivatives using CAN as catalyst, *J. Chem. Sci.* 122 (2010) 607–612.
- [24] E. Soleimani, M.M. Khodaei, H. Yazdani, P. Saei, J.Z. Reza, Synthesis of 2-substituted benzimidazoles and benzothiazoles using Ag_2CO_3 / celite as an efficient solid catalyst, *J. Iran. Chem. Soc.* (2013), <https://doi.org/10.1007/s13738-015-0592-1>.
- [25] N.S. Kanhe, S.U. Tekale, N.V. Kulkarni, A.B. Nawale, A.K. Das, S.V. Bhoraskar, R. D. Ingle, R.P. Pawar, Micron-particulate crystalline hexagonal aluminium nitride: a novel, efficient and versatile heterogeneous catalyst for the synthesis of some heterocyclic compounds, *J. Iran. Chem. Soc.* 10 (2013) 243–249, <https://doi.org/10.1007/s13738-012-0152-x>.
- [26] H. Naeimi, Z. Babaei, Microwave-assisted practical and simple method for heterocyclization of *o*-phenylenediamine and aldehydes using DDQ as oxidant agent, *Green Chem. Lett. Rev* 10 (2017) 129–133, <https://doi.org/10.1080/17518253.2017.1314555>.
- [27] R.M. Borade, S.B. Somvanshi, S.B. Kale, R.P. Pawar, K.M. Jadhav, Spinel zinc ferrite nanoparticles: an active nanocatalyst for microwave irradiated solvent free synthesis of chalcones, *Mater. Res. Express* 7 (2020), 016116.
- [28] P. Motavallian, B. Abash, H. Abdollah-Pour, Zr doping dependence of structural and magnetic properties of cobalt ferrite synthesized by sol-gel based Pechini method, *J. Magn. Magn. Mater.* 451 (2018) 577–586, <https://doi.org/10.1016/j.jmmm.2017.11.112>.
- [29] S.B. Kale, S.B. Somvanshi, M.N. Sarnaik, S.D. More, S.J. Shukla, K.M. Jadhav, Enhancement in Surface Area and Magnetization of CoFe_2O_4 Nanoparticles for Targeted Drug Delivery Application, *AIP Conference Proceedings*, AIP Publishing, 2018, p. 030193.
- [30] B.A. Abdelkrim, K. Bougrin, M. Soufiaoui, Synthèse chimiosélective des benzimidazoles sur silice traitée par le chlorure du thionyle, *Tetrahedron Lett.* 44 (2003) 5935–5937, [https://doi.org/10.1016/S0040-4039\(03\)01387-X](https://doi.org/10.1016/S0040-4039(03)01387-X).
- [31] M. Maphupha, W.P. Juma, C.B. de Koning, D. Brady, A modern and practical laccase-catalysed route suitable for the synthesis of 2-arylbenzimidazoles and 2-arylbenzothiazoles, *RSC Adv.* 8 (2018) 39496–39510.
- [32] B.A. Abdelkrim, S. Bakkas, M. Soufiaoui, Benzimidazoles: oxydation hétérocyclisante par le nitrobenzène ou le diméthylsulfoxyde Sur silice et sous irradiation micro-ondes ou ultra-violet, *Tetrahedron Lett.* 39 (1998) 4481–4484, [https://doi.org/10.1016/S0040-4039\(98\)00868-5](https://doi.org/10.1016/S0040-4039(98)00868-5).
- [34] K. Bahrami, M.M. Khodaei, A. Nejati, Synthesis of 1,2-disubstituted benzimidazoles, 2-substituted benzimidazoles and 2-substituted benzothiazoles in SDS micelles, *Green Chem.* 12 (2010) 1237–1241.
- [35] P.A. Shaikh, Synthesis of some Novel Heterocyclic Compounds like, Flavanones, Pyrimidines and Imidazoles by Using Environment Friendly Catalysts, Ph. D. Thesis, Swami Ramanand Teerth Marathwada University, Nanded, India, 2010, pp. 225–226.
- [36] R.N. Nadaf, S.A. Siddiqui, T. Daniel, R.J. Lahoti, K.V. Srinivasan, Room temperature ionic liquid promoted regioselective synthesis of 2-aryl benzimidazoles, benzoxazoles and benzthiazoles under ambient conditions, *J. Mol. Catal. A Chem.* 214 (2004) 155.