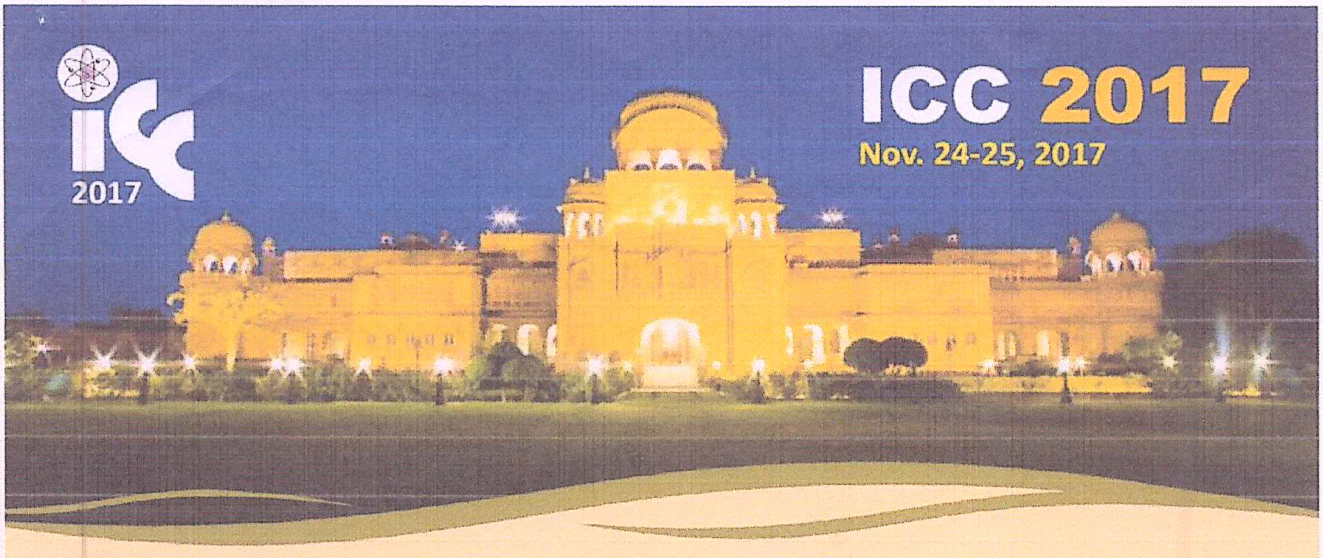

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» **Acceptance of Paper : October 20, 2017**
» **Registration up to : November 04, 2017**
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Preparation, characterization and catalytic application of $CoFe_2O_4$ nanoparticles in the synthesis of benzimidazoles

Ravikumar M. Borade, Pavan R. Shinde, Swati B. Kale, and Rajendra P. Pawar

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Preparation, Characterization and Catalytic Application of $CoFe_2O_4$ Nanoparticles in the Synthesis of Benzimidazoles

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Abstract. A highly efficient magnetically recoverable cobalt ferrite nano-catalyst was prepared by sol-gel autocombustion method using glycine as green fuel. The prepared material has been characterized by X-ray powder diffraction and scanning. An investigation of its catalytic activity showed it to be a heterogeneous Lewis acid catalyst for the synthesis of substituted benzimidazoles. The aqueous ethanol used as green solvent for the reaction. The nm size range of these particles facilitates the catalysis process, as an increased surface area available for the reaction. The easy separation of the catalyst by an external magnet and their recovery and reuse in next cycle reaction are additional benefits.

INTRODUCTION

Magnetic nanoparticles have gained considerable interest in various disciplines such as ferrofluids, magnetic drug delivery, separations, magnetic high-density information storage, magnetic resonance imaging (MRI), and cancer hyperthermia treatment [1, 2]. Magnetic nanoparticles are attractive catalysts since they can be separated from the reaction medium after magnetization by an external magnet. Magnetic separation is an intriguing alternative to filtration or centrifugation as it prevents the loss of catalyst and enhances reusability [3]. Clearly, the development of magnetic nanoparticles with tunable catalytic activity is of great significance for both academia and industry. The cubic spinel ferrites represent an important class of magnetic transition metal oxide materials. Among ferrites, nano cobalt ferrite is very important for its potential use in high-density recording media, adsorption, sensors and magnetic technologies. A literature survey revealed that few attempts have been made to prepare nano cobalt ferrite and to study its potential application in organic synthesis.

In the past few years, highly efficient couplings catalyzed by various nano magnetic catalysts have been described. Hu reported that such a coupling can also be catalyzed by Fe_3O_4 [4]. Unfortunately, Fe_3O_4 nanoparticles are usually unstable and the coagulation of the nanoparticles during the reaction is frequently unavoidable. We report herein the synthesis of $CoFe_2O_4$ magnetic nanospheres with tunable diameters in the range of 20–30 nm and their application in organic synthesis as highly efficient recyclable catalysts in synthesis of benzimidazole derivatives.

The benzimidazole nucleus has a significant biological activity and present in several bioactive molecules and is considered to be the privileged substructures for drug design. Variety of benzimidazole derivatives has been found to possess anticancer, antiviral, antihypertension and some other properties. Benzimidazoles structures are important building blocks in organic synthesis and found in several classes of drugs, based on the possible substitution at different positions of the benzimidazole nucleus. Introduction of a small substituent into the 2- and 5-position is characteristic for benzimidazole anti-helmentics; alternatively, bulky 2-substituents characterizing drug used in the treatment of peptic ulcer and are sometimes referred as proton pump inhibitors; bulky 1- and 2-substituents are found in H1-anti-histamines. In the past few decades, a lot of significant methods to construct benzimidazoles have been subsequently developed [5]. Among these methods, Aldehydes are desirable starting materials in benzimidazole synthesis due to their ready availability and non-toxic nature. Using o-phenylenediamine and aldehyde as the starting

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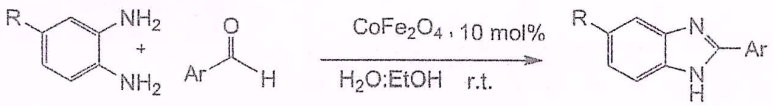
materials to construct benzimidazoles have considerable attention, the direct condensation of o-aryldiamines and aldehydes is the most convenient method. In this context several methods and catalysts have been reported for benzimidazole synthesis including the condensation of o-aryldiamines and aldehydes[6, 7]. Unfortunately, many of these processes suffer some limitations, such as drastic reaction conditions, long reaction time, use of moisture sensitive, expensive, hazardous, non-reusable catalysts, low yields, tedious work-up procedure and co-occurrence of several side reactions. In view of these, the search for finding a cost effective, mild and simple protocol from both an economical and environmental point of view, we wish to present our results on the synthesis of Benzimidazoles using cobalt ferrite nano-catalyst (Scheme-1).



R = H, -CH_3

Scheme-1

EXPERIMENTAL

Materials and Methods: All chemicals were purchased from Merck, s. d. fine-chem limited Mumbai and Rankem Chemical Companies and used without purification. Purity of compounds were checked by thin layer chromatography (TLC) on Aluchrosep Silica Gel 60/UV254 pre-coated sheets, melting points of synthesized compounds were determined in open glass capillaries on TANCO® melting point apparatus. All compounds were known, and obtained physical and spectroscopic data were compared with literatures data.

Synthesis of $CoFe_2O_4$ nanoparticles: The nanostructured cobalt ferrite sample was synthesized by sol-gel auto combustion method using glycine as a fuel. AR grade chemicals such as cobalt nitrate ($Co(NO_3)_2\,6H_2O$), ferric nitrate ($Fe(NO_3)_3\,9H_2O$) and glycine ($C_2H_5NO_2$) were used for the synthesis. The metal nitrates to fuel ratio was taken as 1:3. Ammonia solution was added to maintain the pH of the solution at 7. The as-synthesized powder is sintered at 500 °C for 4 h and then used for further investigations. The prepared sample was characterized by X-ray diffraction (XRD) technique by Regaku model. The XRD patterns were recorded at room temperature in the 2θ range of 20° to 80° using Cu-Kα radiation (λ = 1.54056 Å). Morphology of the prepared sample was studied using scanning electron microscope (SEM) JEOL-JSM 840 model at operating voltage of 20 kV.

Synthesis of Benzimidazoles: o-Phenylenediamine (1mmole), aromatic aldehyde (1mmole), water: ethanol (2:8 ml) and $CoFe_2O_4$ (10 mmol%) were mixed in single necked 50 ml round bottom flask. The mixture was stirred at room temperature for appropriate time (Table-1). The progress of the reaction was monitored by TLC (AcOEt / hexane; 1:4). After completion of reaction, the mixture was dissolve in ethyl acetate and separated the catalyst by external magnet. Filtrate was evaporated under reduced pressure to obtain pure crystals of compound. The catalyst was washed with diethyl ether, dried and without charged in furnace reused in another reaction.

RESULTS AND DISCUSSION

Structural analysis

Fig 1 illustrates X-ray Diffraction pattern of cobalt ferrite nanoparticles. A close examination of XRD pattern reveals the presence of (220), (311), (222), (400), (422), (511) and (440) planes belonging to cubic spinel structure. The analysis of XRD pattern confirms the formation of single phase cubic structure. Using XRD data lattice constant, X-ray density, Unit cell volume and particle size were obtained using standard relations reported in the literature [8, 9]. These values of structural parameters are presented in table 1. It is observed from table 1 that the lattice constant of the cobalt ferrite nanoparticles is in good agreement with that of reported in literature [10]. The particle size (22.7 nm) reflects the nanocrystalline nature of the prepared cobalt ferrite.

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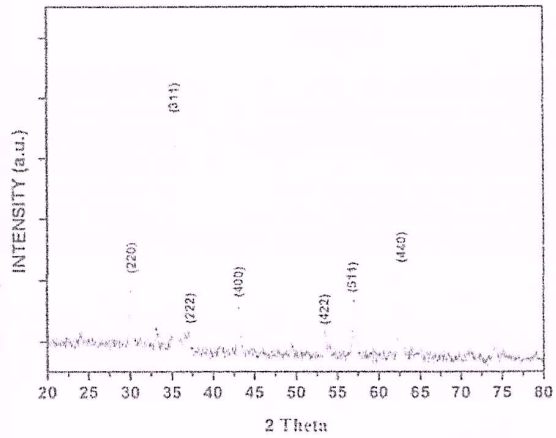


FIGURE 1. To X-ray diffraction pattern of $CoFe_2O_4$ nanoparticles

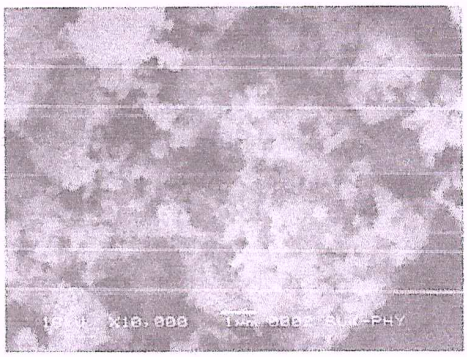


FIGURE 2. SEM image of $CoFe_2O_4$ nanoparticles

TABLE 1. Lattice parameter (a), X-ray density (d_x) bulk density (d_B), percentage porosity (% P), average crystallite size (D), average grain size (G), specific surface area (S), surface to volume ratio (S/V) of cobalt ferrite nanoparticles

a (Å)	dx (gm/cm^3)	d_B (gm/cm^3)	V (Å^3)	% P	D (nm)	G (nm)	S (cm^2/gm)	S/V
8.36	5.34	4.18	584.27	21.72	22.7	76.32	14.47	0.025

Morphological analysis

The surface morphology of the prepared cobalt ferrite nanoparticles investigated through scanning electron microscopy technique (Fig 2) shows spherical morphology and uniform grain growth. The grain size obtained by SEM analysis is of the order of 76.32 nm confirming the nanocrystalline nature of the prepared cobalt ferrite. The specific surface area was also calculated from the SEM analysis. The values of grain size, specific surface area and surface to volume ratio are given in table 1.

Thus, the cobalt ferrite nanoparticles synthesized by sol-gel auto combustion technique were well characterized by X-ray diffraction and Scanning electron microscopy. The structural parameters show that the prepared cobalt ferrite nanoparticles can be successfully used as a catalyst for the synthesis of benzimidazole on account of their nano size and large specific surface area.

Catalytic study

In addition to synthesis of cobalt ferrite nanoparticles, we also report an efficient practical protocol for the synthesis of 2-substituted benzimidazole derivatives in good yields using eco-friendly reusable heterogeneous cobalt ferrite nanocatalyst. In order to show the generality of this method the optimized system was used for the synthesis of other derivatives summarized in table 2, (10 mol %) of catalyst was sufficient to catalyze the reaction. Aldehyde containing electron withdrawing substituent shows fast reaction in minimum time, due to increased electrophilic character of aromatic aldehydes.

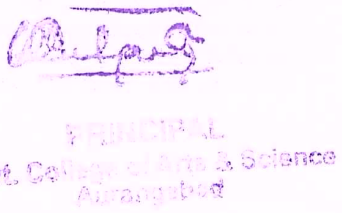
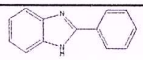
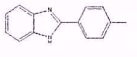
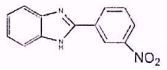
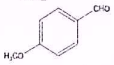
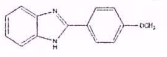
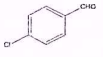
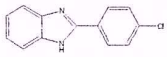
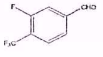
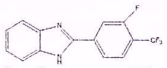
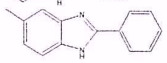
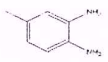
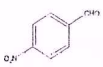
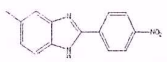
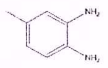
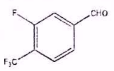
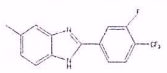
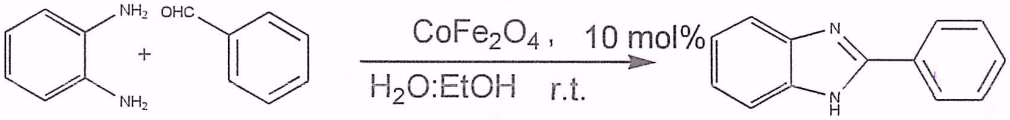


TABLE 2. Synthesis of 2-phenyl-1H-benzimidazole using Cobalt ferrite nanocatalyst

Entry	Diamines	Aldehydes	Products	Yield (%)a	Time (min)	MP (°C) Observed (MP Lit.)
1				97	10	293-295 (295)
2				94	10	274-276 (275-276)
3				96	10	279-282 (280-282)
4				92	11	222-225 (223-226)
5				90	09	290-291 (292-294)
6				90	08	174-176 (174)
7				95	10	235-236 (235-236)
8				97	08	240-242 (240-241)
9				96	07	174-176 (174)

The effect of reusability / recyclability of catalyst were also examined, for this reaction we prepared 2-phenyl-1H-benzimidazole (1c) by use of o-phenylenediamine (1a) and bazaldehyde (1b) as starting material. At the end of reaction, the catalyst was separated by filtration, washed with ethyl acetate and reused under similar conditions; there was no remarkable loss in the activity in reuse of this catalyst as shown in Scheme 3, Table 3.



1a 1b 1c

Scheme -2

TABLE 3. Recyclability of the Cobalt ferrite nanocatalyst for synthesis of 2-phenyl-1H-benzimidazole (b-Isolated yield)

Entry	1	2	3	4	5	6	7
Number or run	Fresh	1	2	3	4	5	6
Yields[b] (%)	97	94	91	88	87	86	86

CONCLUSIONS

In conclusion, we developed one pot synthesis practical procedure for preparation of 2-substituted benzimidazoles catalyzed by cobalt ferrite nanocatalyst as a heterogeneous catalyst using aqueous ethanol as green solvents. This method offers some advantages in terms of simplicity, mild reaction condition, simple workup procedure and reusability of inexpensive, eco-friendly catalyst without side product. The catalyst is separated by external magnet and reused for next reaction cycle without calcinations.

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