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Solvent free synthesis of ynones using magnetically recoverable Copper-ferrite nanoparticles

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ABSTRACT

A general and efficient biogenic $CuFe_2O_4$ MNP's catalyzed synthesis of ynones has been reported for the first time. The reaction occurs in solvent free conditions without the use of any harsh conditions. The average diameter of the nanoparticles was found to be 13.07 nm. The advantages of the protocol include heterogeneous catalysis, easy recyclability of the catalyst and short reaction time.

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Introduction

Ynones are the beneficial three-carbon building blocks for the synthesis of various heterocycles[1–4] and are known as Michael acceptors. They have received considerable interest because of their applications in pharmaceuticals, natural products and bioactive molecules.[5–7] They are utilized in organic and medicinal chemistry because of their bi-functional electrophilic nature. Literature has cited various synthetic methods for the synthesis of ynones. These include the cross-coupling reactions of carboxylic acid derivatives and stoichiometric metal acetylides in which the usage of various metals like magnesium,[8] silver,[9] cadmium,[10] silicon,[11] copper,[12] tin,[13] lithium,[14] gallium,[15] stibium,[16] indium,[17] zinc[18] and boron[19] reagents are applied. But using a large amount of sensitive metal acetylides made the reaction drastic and uneconomical. Therefore an alternative catalytic coupling of acyl chlorides and terminal alkynes using CuI/TMEDA,[20a] Cu NPs@MP,[20b] photoinduced synthesis of P-Perfluoroalkylated Phosphines[20c] have been reported. Using palladium as a catalyst for the formation of ynones have several disadvantages, so we have reported biogenic Copper-ferrite($CuFe_2O_4$) magnetic nanocatalyst (MNP'S) as a catalyst to couple acid chlorides and terminal alkynes for the first time. Literature have cited several methods for the formation of $CuFe_2O_4$ MNP's; Phuruangrat et al.[21] have synthesized $CuFe_2O_4$ MNP's using microwave-hydrothermal method in different pH range, Dandia et al.[22] have synthesized $CuFe_2O_4$ MNP's using ultrasonic radiation and subjected the system at 700 °C for 5 h in the furnace. These methods use harsh reaction conditions for the preparation of the nanoparticles, so we have used a natural source for the preparation of $CuFe_2O_4$ MNP's at room temperature.

In view to the context of green chemistry the use of biogenic, recyclable catalyst have always been an alternative to the hazardous synthetic catalyst. The use of biogenic $CuFe_2O_4$ MNP's have fulfilled to this agreement very efficiently. The $CuFe_2O_4$ MNP's have been synthesised using the leaves of *Lantana camara*. It is a prickly climbing aromatic shrub of the family Verbenaceae and found in around 60 tropical and sub-tropical countries worldwide.[23–26] It contains several bioactive natural products including triterpenoids, flavonoids, steroids, iridoide glycosides, oligosaccharides, phenylpropanoid glycosides, and naphthoquinones.[27–29] Day et al.,[30] Herbert et al.,[31] Sathish et al.,[32] have reported varieties of lead phytomolecules such as oleanolic acid, ursolic acid, lantanoside, linaroside, camarinic acid, verbascoside, umuhengerin and phytol in *Lantana camara*. The present study uses *Lantana camara* leaf extracts as a reducing agent in the synthesis of $CuFe_2O_4$ MNP's. The flowers of this plant also give excellent results in the synthesis of $CuFe_2O_4$ MNP's. Because of the easy availability of this plant in all regions of India as an ornamental plant, it was selected for the study, and also no study was been conducted using this plant for the synthesis of $CuFe_2O_4$ MNP's. The synthesized nanoparticles appeared to be black in colour and were characterized by SEM, SEM-EDX, TEM and VSM analysis.

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Experimental

Biogenic synthesis of $CuFe_2O_4$ MNP's

The leaves of *Lantana camara* were collected from Dibrugarh University campus, Dibrugarh Assam. They were washed thoroughly with distilled water. The plant leaf broth solution was prepared by taking 5 g of finely cut leaves and heating in a 250 mL Erlenmeyer flask with 150 mL of sterile distilled water and then boiling the mixture for 10 min before decanting it. To the decant of *Lantana camara*, 50 mg of $FeCl_3$ and 50 mg of Copper acetate were added and stirred at room temperature for 1 h. To the stirring solution 5 mL of 0.1 M NaOH was added. The resulting solution was centrifuged and washed with ethanol. It was then subjected to annealing at 300 °C for 2 h, which led to the formation of biogenic $CuFe_2O_4$ MNP's.

General Procedure for the formation of ynones at room temperature

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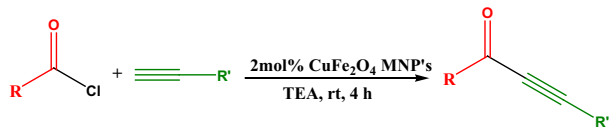

Scheme 1. Coupling of acid chlorides with terminal alkynes using $CuFe_2O_4$ MNP's.

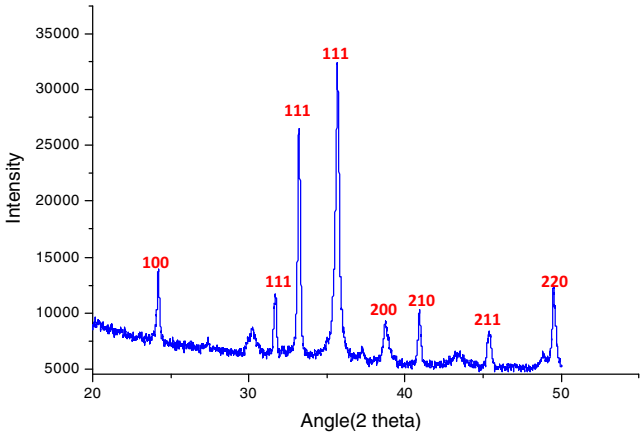

Fig. 1. Powder XRD pattern of the synthesized $CuFe_2O_4$ MNP's.

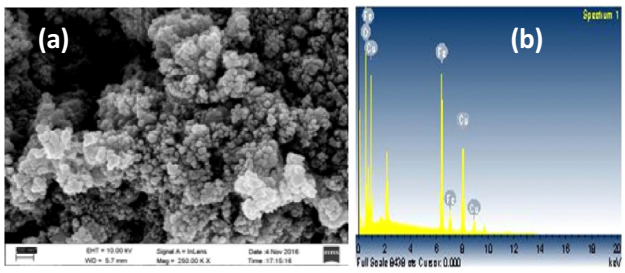

Fig. 2. (a) SEM images of the pure spherical $CuFe_2O_4$ MNP's, (b) EDX image of the nanospherical $CuFe_2O_4$ MNP'S.

Results and discussion

The biogenic $CuFe_2O_4$ MNP'S were characterized by powder XRD-diffraction method as shown in Fig. 1. The sharp diffraction peaks shows clearly the presence of highly pure crystalline $CuFe_2O_4$ nanoparticles. The diffraction peaks appeared at $2\Theta = 24.174°$, 33.196°, 34.28°, 35.65°, 38.714°, 40.876°, 44.374°, 49.482° corresponds to planes (1 0 0), (1 1 1), (1 1 1), (1 1 1), (2 0 0), (2 1 0),(2 1 1) and (2 2 0) respectively.

The SEM images show the structure and morphology of the synthesized nanoparticles (Fig. 2a). These images gives the structure of the nanoparticles to be pure spherical and also their monodispersity were observed from the SEM images. From the Energy Dispersive X-ray (EDX) spectrum (Fig. 2b) the purity of the nanoparticles was seen which clearly depicted the presence of copper, iron and oxygen element.

The TEM and HR-TEM images (Fig. 3) determined size and morphology of $CuFe_2O_4$ nanocrystals. The Selected Area Electron diffraction (SAED) pattern Fig. 3(b) shows $CuFe_2O_4$ MNP's which contain the concentric diffraction of rings due to the (1 0 0), (1 1 1) and (2 1 0) reflection of spherical Cu. From the HR-TEM image (Fig. 3c) the fringes separation was found to be 1.61 A° which is in good agreement with (1 0 0) plane and the other fringe of 2.31 A° was found to be in agreement with (1 1 1) plane of $CuFe_2O_4$ MNP's. The average diameters of the NPs were found to be 13.07 nm from the size distribution (Fig. 4).

The magnetic measurements were carried out by using VSM at room temperature. The VSM magnetization curves of biogenic $CuFe_2O_4$ showed no remanence; and coercivity is negligible, indicating the superparamagnetism of these nanomaterials (Fig. 5). The saturation magnetization value of 12.92 emu g^{-1}, from the magnetic hysteresis curve of $CuFe_2O_4$ nanoparticles revealed that it is suitable for magnetic separation. The sensitivity of the prepared catalyst is strong enough to provide an easy and effective way to separate the catalyst from the reaction system.

In the present study we first explored the influence of different organic and inorganic bases on benzoyl chloride with phenyl acetylene (Table 1). Owing to the weak nucleophilic nature of the alkynes, the use of an efficient base for enhancing the nucleophilicity power of alkynes is efficient. The use of TEA as a base, proved to be the most efficient for coupling of benzoyl chloride with phenyl acetylene (Table 1, entry 4). K_2CO_3 and Cs_2CO_3 afforded moderate yields of ynones (Table 1, entries 3, 4). Pyridine provided satisfactory results but needed longer times for the completion of the reaction. (Table 1, entry 5). The use of TEA however was preferred because of its cheapness and also abundance.

After identification of the proper base the role of different solvents was tested on the model substrate of benzoyl chloride with phenyl acetylene (Table 2). Toluene and dichloromethane were noted to be good solvents for this coupling reaction but required longer reaction time. For the diprotic solvents such as THF, DMF and acetonitrile, the results were inferior. We were surprised to find that the reaction was performed in highest yield without the use of any solvent. All further reactions were consequently carried out under neat anhydrous conditions and the results are recorded in Table 2.

By using the optimised conditions the versatility, generality and the applicability was explored for coupling 18 different structurally diverse acid chlorides with different alkynes (Table 3). With different aromatic acid chlorides and aromatic alkynes bearing electron-withdrawing or electron-donating functionalities the reaction were efficiently achieved using this method (Scheme 1).

Aliphatic acid chlorides with aliphatic or aromatic alkynes were also coupled efficiently, but needed longer reaction time (Table 3).

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