Catalysis Communications 80 (2016) 44–48

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short communication

# Synthesis of Cu@CF@SBA15: A Versatile catalysts for (i) reduction of dyes, trifluralin, Synthesis of (ii) DHPMs by Biginelli reaction and (iii) 1,2,3-triazole derivatives by 'Click reaction'

Barun Kumar Ghosh, Subhenjit Hazra, Narendra Nath Ghosh *

*Nano-Materials Lab, Department of Chemistry, Birla Institute of Technology and Science, Pilani, K. K. Birla Goa Campus, Zuarinagar, Goa 403726, India*

ARTICLE INFO

*Article history:*
Received 14 January 2016
Received in revised form 9 March 2016
Accepted 24 March 2016
Available online 4 April 2016

*Keywords:*
Magnetically separable catalyst
Cu nanoparticle
Dyes
Trifluralin
Biginelli reaction
Click reaction

ABSTRACT

Herein, we are reporting a facile route to synthesize magnetically separable Cu nanoparticle loaded $CoFe_2O_4$@SBA15 catalysts, which exhibits high catalytic activity towards (i) reduction of various synthetic dyes, trifluralin, (ii) synthesis of DHPMs via Biginelli reaction pathway in solventless condition and (iii) 1,2,3-triazole derivatives by 'Click reaction' in aqueous medium. To the best of our knowledge, this is the first time one single catalyst is reported which shows its high activity for these three important reactions.



## 1. Introduction

In this paper we are reporting a versatile magnetically separable catalyst which acted as catalyst in (i) decolorization/ reduction of various dyes and trifluralin, (ii) Biginelli reaction to synthesize 3,4 dihydropyrimidin 2(1*H*)-ones (or thiones) (DHPMs) in solvent free condition and (iii) synthesis of 1,4-disubstituted 1,2,3-triazoles in aqueous medium using 'click reaction'. We have synthesized a catalyst for these three types of reactions because these reactions are very important in various perspectives. (i) Synthetic dye containing colored effluents, discharged from various dye based industries, cause water pollution and pose severe threat to human life. Strong color of dyes causes serious aesthetic and ecological problems to the receiving aquatic ecosystems, such as inhibition of benthic photosynthesis. Moreover, some of the dyes are carcinogenic and mutagenic in nature [1–4]. (ii) Synthesis of DPHMs and derivatives are important because of their wide range pharmaceutical and therapeutic applications such as calcium channel blockers, anti-inflammatory agents, antihypertensive, anti-tumor, adrenergic and neuropeptide antagonists etc [5–9]. Biginelli multicomponent reaction pathway is the most direct and elegant methodology for synthesis of DHPMs. To overcome some of the limitations such as harsh reaction conditions, usage of reagent excess, high temperature, toxic solvent, purification issues, low yields, low sensitivity, long reaction times etc [7] associated with commonly used synthetic routes development of a novel catalyst for Biginelli reaction is much required. (iii) Synthesis of 1,4-disubstituted 1,2,3-triazoles by 'click reaction' has gained immense interest because it acts as scaffold for large number of biological active chemicals, pharmaceuticals, agrochemicals, drug molecules with significant anti-HIV activity, anti microbial activity against Gram positive bacteria etc [10–12]. Though various synthetic routes have been reported for synthesis of 1,4-disubstituted 1,2,3-triazoles, but most of the methods suffer from insignificant reactivity, use of volatile organic solvents, requirement of additives, high reaction temperature, low yields, formation of undesired side products, usage of homogeneous catalysts which are difficult to separate from reaction mixture etc [10]. Therefore, to address these issues we have designed a heterogeneous catalyst which can exhibit excellent catalytic activity towards decolorization of various synthetic dyes via reduction reaction, Biginelli reaction to synthesize DHPMs in solvent less condition and synthesis of 1,4-disubstituted 1,2,3-triazoles based compounds in aqueous medium. Moreover, easy magnetic separation of these catalysts from reaction mixture is an important feature of this catalyst.

## 2. Experimental

### 2.1. Synthesis of Catalysts

Synthesized catalyst consists of $CoFe_2O_4$ nanoparticles (CF) as magnetic core and a coating of porous silica (SBA15) on the surface of

* Corresponding author.
*E-mail address:* naren70@yahoo.com (N.N. Ghosh).

http://dx.doi.org/10.1016/j.catcom.2016.03.016
1566-7367/

CF. Catalytically active Cu nanoparticles have been immobilized on the surface of porous matrix provided by SBA15. Here CF nanoparticles (average particle size ~25 nm) have been synthesized by using a novel EDTA precursor based method, developed by us [13]. CF nanoparticles were then dispersed in an aqueous mixture of Pluronic P123, which acted as liquid crystal template. In this mixture calculated amount of TEOS was added and the reaction mixture was allowed to age for 24h at 90°C. The gel thus formed was separated magnetically and calcined at 550°C for 3h in air atmosphere to remove the pore structure directing agent, Pluronic P123. This porous silica coated CF nanoparticles will be referred as CF@SBA15. Cu nanoparticles were immobilized on the porous surface of CF@SBA15 by soaking it in an aqueous solution of $CuCl_2$ followed by dropwise addition of $NaBH_4$ solution. $NaBH_4$ reduced $Cu^{2+}$ ions to Cu nanoparticles. This material now onwards will be referred as Cu@CF@SBA15.

(Details of the materials used and synthesis procedure have been provided in Electronic supplementary information).

### 2.2. Characterization

Details of characterization techniques used are provided in electronic supplementary information.

### 2.3. Catalytic Activity Test

The catalytic activities of Cu@CF@SBA15 have been tested for (i) Reduction of various dyes (4 Nitrophenol (4-NP), Methyl Orange (MO), Methylene Blue (MB) Congo red (CR), Rhodamine B (RhB)) and a herbicide (trifluralin) in presence of excess $NaBH_4$, (ii) Synthesis of 5-Ethoxycarbonyl-4-phenyl-6 methyl-3,4-digydropyridin-2(1*H*)-one and 5-Ethoxycarbonyl-4-phenyl-6-methyl-3,4-dihydropyrimidin-2(1*H*)-thione using Biginelli reaction in solventless condition and (iii) Synthesis of 2-phenyl-2-(4-phenyl-1*H*-1,2,3-triazole-1-yl) ethanol and 2-(4-Phenyl-1*H*-1,2,3-triazol-1-yl) cyclohexanol using 'click reaction' in aqueous medium. (Details of experimental procedures are provided in electronic supplementary information).

## 3. Results and discussions

### 3.1. Characterization of materials

XRD spectra (Fig. 1) of CF@SBA15 showed a broad peak in 2θ range of 10- 30°, indicating the presence of amorphous $SiO_2$ along with sharp peaks at 2θ = 18.2°, 30.1°, 35.5°, 37.1°, 43.1°, 53.4°, 56.9° and 62.6° corresponding to (111), (220), (311), (222), (400), (422), (511), and (440) diffraction planes of $CoFe_2O_4$ [JCPDS Card no 22-1086].

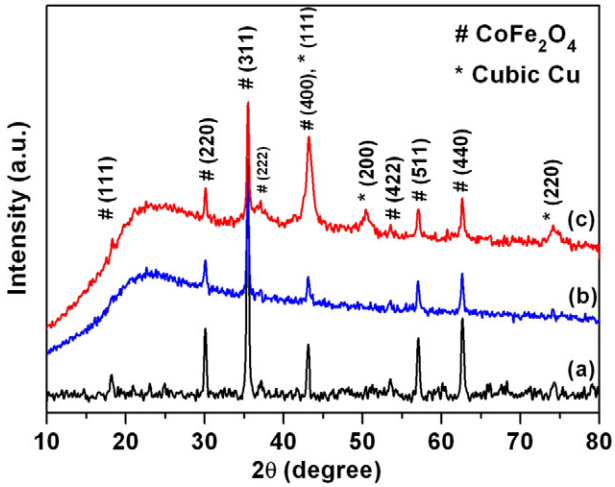


**Fig. 1.** Powder XRD patterns of (a) CF nanoparticle, (b) CF@SBA15 and (c) Cu@CF@SBA15.

For Cu@CF@SBA15, presence of all these peaks and additional peaks at 2θ = 43.2°, 50.29°, 74.2° corresponding to (111), (200) and (220) planes of cubic Cu [JCPDS No. 04-0836] confirmed the presence of Cu nanoparticle, SBA15 and $CoFe_2O_4$ in the synthesized catalyst. It is important to note that no impurity phase was detected by XRD. Crystallite size of CF and Cu (calculated by Scherrer formula) were found to 26 nm and 8 nm.

HRTEM micrographs (Fig. 2) of Cu@CF@SBA15 also revealed the formation of a uniform 60- 80 nm thick coating of porous SBA15 on the surface of CF nanoparticle and presence of Cu nanoparticles on the surface of porous matrix provided by SBA15. It was also observed that regular porous structure with long range ordering of pore channels were remained preserved in SBA15 coating after impregnation of Cu nanoparticle.

Multiple point BET surface area and average pore size of Cu@CF@SBA15 were determined from $N_2$ adsorption-desorption analysis (Fig. S1, supplementary information). Presence of type-IV isotherm with H1 hysteresis loop indicated the mesoporous nature of SBA15 coating. Surface area and average pore size of this SBA15 coating after Cu impregnation were found to be 205.86 $m^2/g$ and 3.71 nm (Table S1, supplementary information). This porous structure, which hosted the catalytically active site, i.e., Cu nanoparticles, might help to adsorb the reactant molecules and facilitates the reactions.

### 3.2. Catalytic activity of Cu@CF@SBA15

To investigate the catalytic property of the synthesized catalyst, Cu@CF@SBA15, the reduction reactions of various dyes such as 4-NP, MO, MB, CR and RhB were performed in presence of excess $NaBH_4$. The reactions were monitored by UV-Vis spectroscopy. It has been observed that, times required to complete the reduction reactions at room temperature were 4, 6, 4, 6 and 4 min for 4-NP, MO, MB, CR, and RhB respectively (Fig. 3) (Table S2, supplementary information). Due to the reduction reactions the colors of the dye solutions were disappeared. No reaction occurred when the reactions were tested in presence of (i) only catalyst Cu@CF@SBA15 (no $NaBH_4$) and (ii) only $NaBH_4$ (no catalyst). This catalytic reduction reaction (in presence of both $NaBH_4$ and catalyst) proceeded via relaying of electrons from $BH_4^-$ donor to the acceptor (dye molecules). [4,14] Hydrogen atom, which was formed from $BH_4^-$, after Electron Transfer (ET) to the catalytically active site (i.e., Cu nanoparticle) attacked the dye molecule to reduce it. This ET induced hydrogenation of functional groups to reduce dye molecules occurred spontaneously. Here, Cu nanoparticles play a role of storing electrons after ET from $BH_4^-$. Negatively charged Cu nanoparticles acted as nanoelectrode with negative potential [4]. As the initial concentration of $NaBH_4$ was very high and it remained constant throughout the reaction, this catalytic reaction was considered to follow pseudo first order kinetics [4,14]. The apparent rate constants ($k_{app}$) were 1.10 $min^{-1}$ (4-NP), 0.64 $min^{-1}$ (MO), 0.86 $min^{-1}$ (MB), 0.77 $min^{-1}$ (CR) and 0.85 $min^{-1}$ (RhB) (Fig. S2, supplementary information). These $k_{app}$ values were comparable and in some cases higher than the values reported in the literature where various catalysts were used for the reduction of dyes (Table S3, supplementary information) [3,4,14–24].

Reduction reaction of 4-nitrophenol to 4-aminophenol is important because 4-NP not only presents in effluents of dye based industries and causes water pollution but also 4-aminophenol is an active precursor and intermediate of various drugs such as paracetamol, phenacelin, etc. [14] Moreover, as Cu@CF@SBA15 exhibited its high catalytic efficiency towards reduction of -$NO_2$ group of 4-NP, it provoked us to investigate the decolorization of trifluralin via reduction of its -$NO_2$ groups. Trifluralin is an herbicide, which is used in various countries to control variety of annual grass and broadleaf weed species. But, it remains in water as pesticide residue. As it is highly toxic in nature it caused severe water pollution. Fig. 3(F) illustrates that, Cu@CF@SBA15