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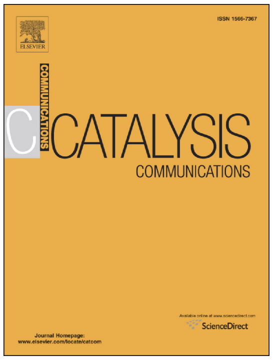

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Cu-doped $CoFe_2O_4$ nanoparticles as magnetically recoverable catalyst for C-N cross-coupling reaction

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ABSTRACT: A new hybrid catalyst has been developed by immobilizing copper acetate onto surface of cobalt ferrite magnetic nanoparticles bearing N-O chelating ligand. The magnetic core of the catalyst was synthesized via ultrasound assisted co-precipitation method and characterized by FT-IR, XRD, EDX, SEM, TEM, TGA and VSM analysis. The catalyst was found to be very active for C-N bond forming reaction. Coupling of amines and aryl boronic acid could be achieved in high yield in methanol in presence of triethylamine at room temperature. After completion of the reaction the catalyst could be recovered using an external magnet and reused for consecutive catalytic cycles without significant decrease in the catalytic activity.

Keywords: Magnetic nanoparticles,N-arylation, boronic acid, aniline,imidazole

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1. Introduction

In organic synthesis, carbon – heteroatom bonds are very important, as they are present in wide range of compound starting from biologically active compounds to natural products and from pharmaceuticals to industrially important compounds [1,2,3].In 1998, Chan, Evans and Lam developed a mild protocol with Cu-catalyst for oxidative amination of aryl boronic acids[4,5,6,7]. After this report, a number of modifications have been made in this field to improve the efficiency of the process by using different copper compounds such as $Cu(OAc)_2$[8],CuCl[9],$Cu(OTf)_2$[10],CuF_2[11] and Cu-β-cyclodextrin complex[12], $Cu[(DMAP)_4I]I$ [13] etc. With time, this method became a popular N-arylation process; due to easy availability of different copper salts and boronic acids. Besides these, there are several reports of C-N bond formation reaction using various metals such as Cu, Pd, Ni and Fe [9] [14-18]. Although homogeneous catalysts provide huge potential for carrying out organic transformations, catalyst recovery becomes a major problem for practical and industrial applications [13]. Several attempts were made to develop efficient homogenous catalyst for Chan-Lam process of C-N bond forming reaction. However, limited efforts have been made to develop heterogeneous catalytic processes for this particular transformation, with only a few methods outlined[19-21]. Examples of heterogeneous catalytic approach include the use of polymer immobilized copper complex [19], copper(I)-exchanged zeolites [20] and copper (II) oxide nanoparticles [21].These heterogeneous catalyst suffers from some drawbacks such as longer reaction time (8-24h), high catalyst loading and high reaction temperature [19, 20] which limits its use. To the best of our knowledge there is no report on the use of magnetic nanoparticles for carrying out Chan–Lam reaction. Magnetic nanoparticles (MNPs) have several

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advantages over other catalysts because of their unique physical and chemical properties which include its high surface area to volume ratio, ordered pore arrangement, superparamagnetic behavior and easy separation from reaction mixture using an external magnet.

We intend to report herein, a new type of hybrid catalyst prepared by immobilizing copper acetate onto the surface of cobalt ferrite magnetic nanoparticles bearing N-O chelating ligand. The as synthesized Cu-magnetic catalyst exhibit excellent catalytic activity for Chan-Lam coupling reaction of both primary and secondary amines with aryl boronic acids.

2. Experimental

General Comment:

Chemicals used are of analytical grade and procured from commercial sources. Column chromatography was performed with silica gel (230-400 mesh).^{1}H and ^{13}C NMR spectra were obtained from Bruker 300 MHz spectrometer with $CDCl_3$ as the solvent usingTMS internal standard.

The synthesized catalyst was characterized by using various characterization techniques such as FT-IR, XRD, EDX, SEM, TEM, TGA and VSM analysis. X-ray powder diffraction (XRD) patterns obtained were used for the identification of silica coating and metal incorporation over $CoFe_2O_4$ i.e. $CoFe_2O_4$@SiO_2-NH_2-Furfural-Cu(OAc)$_2$ samples using a Bruker D-8 Advance X-ray diffractometer with Cu-Kα radiation at wavelength 1.5418 Å operated at voltage 40 kV and current 30 mA. The XRD data were collected in the 2θ range of 5-80°. An Affinity-1 SHIMADZU, FT-IR spectrophotometer was used for recording the FT-IR spectra of $CoFe_2O_4$@SiO_2-NH_2-Furfural-Cu (OAc)$_2$ samples in the form of KBr pallets in mid IR-region of 4000-500 cm^{-1}. Morphology of the magnetic nanoparticles was investigated by transmission

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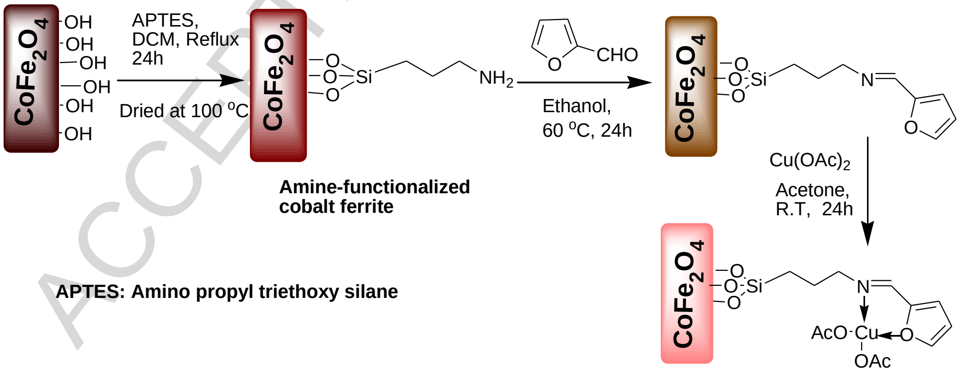
electron microscopy (200 KV TEM, JEOLJEM 2100). Chemical composition and morphology of synthesized $CoFe_2O_4@SiO_2$-NH_2-Furfural-$Cu(OAc)_2$ were evaluated by JEOL JSM-6360 scanning electron microscope equipped with an energy dispersive X-ray spectrometer (EDX). The thermo gravimetric analysis (TGA) of copper incorporated samples was recorded on Mettler Toledo TGA/DSC 1, STAR system analyzer in the temperature range 300K-1023K with heating rate of 10 K min^{-1} in nitrogen gas atmosphere. The magnetic properties of the synthesized $CoFe_2O_4@SiO_2$-NH_2-Furfural-$Cu(OAc)_2$ nanoparticles were determined by vibrating sample magnetometer (Lakeshore 7410). ^1H and ^{13}C-NMR Spectra were obtained in $CDCl_3$ using Bruker 300 MHz instrument.

2.1.Procedure for the synthesis of $CoFe_2O_4@SiO_2$-NH_2-Furfural-$Cu(OAc)_2$ nano magnetic catalyst

The catalyst was synthesized in four steps (Scheme 1).Initially, the cobalt ferrite magnetic core was synthesized by following previously reported procedure via an ultrasound assisted co-precipitation method [22, 23].



Scheme 1: Synthetic route for the synthesis of $CoFe_2O_4@SiO_2$-NH_2-Furfural-$Cu(OAc)_2$.

2.1.1. Synthesis of the $CoFe_2O_4@SiO_2$ –NH_2nanocomposite

The as prepared hydrophilic $CoFe_2O_4$ nanoparticles 200 mg were dispersed in 20 mL of deionized water under continuous ultra-sonication. In the meantime,8 mL of aqueous ammonia

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solution (25 wt.%) and 80 mL of ethanol was added to it. Next, 3 mL of TEOS was added drop wise into the above solution, and it was placed under vigorous stirring condition at room temperature for 24h. The products were separated using an external magnet and washed several times with water and dried at 50 °C for 6h.

Amine functionalized cobalt ferrite silica composite was prepared by refluxing 500 mg of $CoFe_2O_4@SiO_2$nanoparticles with 2 mmol of 3-aminopropyl-trimethoxysilane (M. Wt.: 221.37 $gmol^{-1}$, Density: 0.946 g/mL) in dry dichloromethane (50 mL) for 24h. The solid was separated with the help of a magnet, washed with methanol and then with dichloromethane, and, finally dried at 100°C under vacuum for 6h to yield the desired nanoparticles [24].

2.1.2. Synthesis of $CoFe_2O_4@SiO_2$–NH_2–furfural–nanocomposite

The oven dried amino propyl silica composite(500mg) was taken in absolute ethanol (50 mL) in a 100 round bottomed flask and treated with furfural (5 mmol) at 60 °C for 24h. The ligand-grafted magnetic-silica composite was separated using an external magnet, washed with ethanol thoroughly to remove unreacted furfural. It was then dried in air at 95 °C overnight to get the corresponding Schiff base product.

2.1.3. Synthesis of $CoFe_2O_4@SiO_2$–NH_2–furfural–$Cu(OAc)_2$ catalyst

The catalyst was prepared by stirring a mixture of furfural-grafted amine functionalized cobalt ferrite (200mg) and copper acetate (90 mg, 0.5 mmol) in acetone (30 mL) at room temperature for 24h. Initially the copper acetate was sonicated for 30 minutes to get a solution of copper acetate. Then the pre-synthesized MNPs were added to it and left for stirring. After stirring for 24h, the catalyst was separated using external magnet, washed with acetone till washings were free from excess copper. It was then dried in air at 95 °C overnight [24]. The catalyst was dried

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at 70 °C in a vacuum oven for 4h before using for Chan- Lam reaction. The probable structures of catalysts were shown in the Scheme 1.

2.2. General procedure for the Chan-Lam C-N cross-coupling reaction

In a typical reaction, arylboronic acid (1 mmol), amino-compound (1 mmol), catalyst (5 wt.%), Et_3N (2 mmol) were mixed in methanol (5 mL) in a 25 mL round bottomed flask. The reaction mixture was subjected under continuous stirring at room temperature for 5h. Reaction was monitored from time to time using TLC. After completion of the reaction, catalyst was separated with the aid of an external magnet and reaction mixture was taken in ethyl acetate. The organic layer was washed using brine solution, dried over sodium sulfate. After evaporating the solvent, the crude product was purified by column chromatography using 230-400 silica mesh. The recovered catalyst was washed with methanol and ethyl acetate, dried in oven and kept in desiccator for further use

3. Results and Discussion

3.1 Characterization

The presence of the acetate in the synthesized composite was confirmed from the IR spectra as shown in Fig. 1. Absorption at 1510 cm^{-1} is due to the stretching vibrations of the COO^- group of the acetate ion of the copper acetate. Other absorptions bands at 1630 cm^{-1}, 2860 cm^{-1} and3400 cm^{-1} are due to the–C=N of Schiff base, =CH group of propyl group of APTES and –OH stretching respectively [25].

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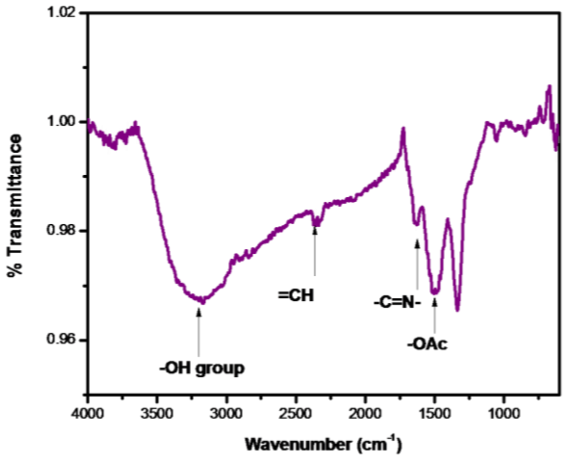

Fig. 1. IR Spectra of $CoFe_2O_4@SiO_2$-NH_2-furfural-$Cu(OAc)_2$

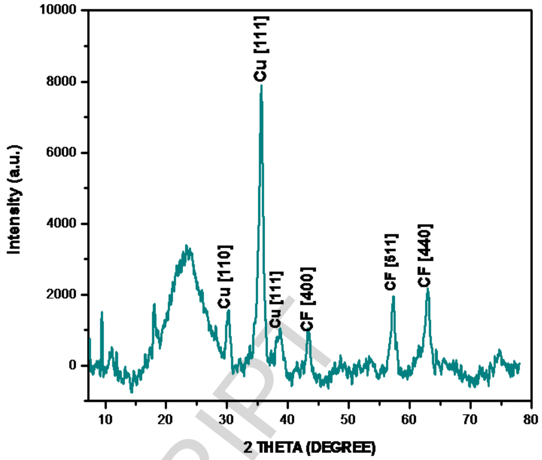

Fig. 2. XRD pattern of $CoFe_2O_4@SiO_2$-NH_2-furfural-$Cu(OAc)_2$

PXRD pattern of the $CoFe_2O_4@SiO_2$-NH_2-Furfural-$Cu(OAc)_2$ nanoparticles are shown in Fig. 2. XRD Pattern reveals the nanocrystalline nature of the sample. Diffraction peaks at 2θ values of 30, 35, 39, 43, 59 and 64 were observed which resembles to the (110), (111), (111), (400), (511) and (440) diffraction planes respectively. Broad peak from 2θ value between 20-30° resembles the characteristic peak for amorphous SiO_2 in the core shell structure [26]. All the diffraction peaks match with the JCPDS (International Center for Diffraction Data) of standard $CoFe_2O_4$ and copper nanoparticles. Morphology of the synthesized magnetic nanoparticles and the elemental analysis was determined using SEM and EDX analysis as shown in SI (Fig.S1, Fig.S2). From the EDX analysis, the amount of Cu doped was found to be 4.74 wt %. Fig.3 shows the TEM image of the synthesized $CoFe_2O_4@SiO_2$-NH_2-Furfural-$Cu(OAc)_2$ composite. TEM image showed that the particles were nearly spherical. Various concentric rings in the SAED pattern resemble the crystalline nature of the synthesized composite. Particle size as obtained from the image shows that most particles are in the range of 5 nm that is better explained from the particle size

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distribution plot (Fig. S3 in SI). Thus, from the above explanation we can infer that the synthesized composite is in the nano range.

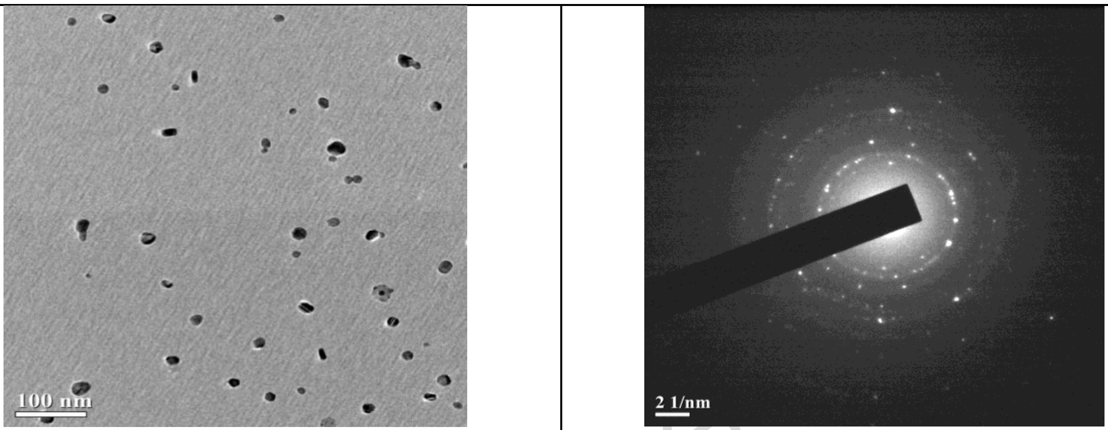

Fig.3. TEM image of (a) $CoFe_2O_4@SiO_2$-NH_2-Furfural-$Cu(OAc)_2$ (b) SAED pattern of $CoFe_2O_4@SiO_2$-NH_2-Furfural-$Cu(OAc)_2$

The magnetic behavior of the synthesize nanocomposite was assessed by studying the M-H curve(Fig. S4 in SI).Figure S5 in SI represents the thermogravimetric analysis of the synthesized $CoFe_2O_4@SiO_2$-NH_2-Furfural-$Cu(OAc)_2$ composite. Initial weight loss of ~2.28 % takes place within 100-150 °C, which may be due to desorption of the water from the surface of the composite [27]. Thereafter weight loss of ~19.5 % takes place within the range of 300-600 °C which may be due to the decomposition of organic moiety attached to the surface of cobalt ferrite nanocatalyst.

3.2. Evaluation of catalytic activity

After successful synthesis of thermally stable, copper acetate incorporated cobalt ferrite functionalized MNP, we intended to examine its catalytic activity for the Chan–Lam type C-N cross coupling reactions [20, 28-32].For optimizing the reaction condition, we initially carried out the reaction of aniline with phenyl boronic acid as model substrates

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using 5wt% of catalyst in the presence of most commonly used base triethylamine and pyridine. The reaction was carried out in 1 mmol scale using 2 mmol of base in ethanol (5 mL) as solvent at room temperature for 3h (Table 1, entry 1). The progress of the reaction was monitored by using TLC. We could isolate only 66% of the desired product via column chromatography using a mixture of petroleum ether and ethyl acetate as eluent. After the initial survey, the reaction was screened with three more solvents such as methanol, acetonitrile and DMF. The use of methanol produced the best result with 94% yield. Our study revealed that an increase in reaction time from 3h to 5h proved more efficient in terms of yield of the final product (Table 1, entry 2 and 3). We have also investigated the effect of concentration of catalyst on the reaction keeping all other parameters same. On decreasing the amount of catalyst to 2 wt.%, the reaction yield was found to decrease significantly to 65% (Table 1, entry 4) and the use of 10 wt.% of catalyst led to marginal increase in yield to 96%(Table 1, entry 5). Another study was carried out by changing the nature of the organic base by replacing Et_3N with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and pyridine and keeping all other condition of the reaction unchanged. This particular variation rather produced poorer results (Table 1, entry 8 and 9).We have also carried out the reaction in absence of the Cu catalyst as well as in presence of $CoFe_2O_4$, $CoFe_2O_4$-SiO_2, $CoFe_2O_4$-SiO_2-NH_2instead of $CoFe_2O_4$@SiO_2-NH_2-Furfural-Cu$(OAc)_2$ as catalyst. However, none of these experiments could produce any fruitful result even after continuing the reaction for 12h (Table 1, entry 10-13). So, the optimum yield was found by using equimolar amount (1:1) of the substrates in methanol using 5 wt.% of catalyst at room temperature(Table 1, entry 3). The turnover frequency (TOF) for this reaction was found to be 41.6 h^{-1}.

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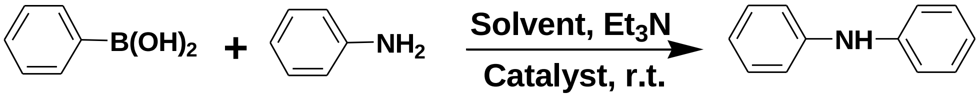
Table 1. Optimization of reaction condition using $CoFe_2O_4@SiO_2$-NH_2-Furfural-$Cu(OAc)_2$ catalyst



Entry	Solvent	Base	Catalyst Conc.(wt.%)	Time (h)	Yield (%)[b]
1	Ethanol	Et_3N	5	3	66
2	CH_3OH	Et_3N	5	3	82
3	**CH_3OH**	**Et_3N**	**5**	**5**	**94**
4	CH_3OH	Et_3N	2	5	65
5	CH_3OH	Et_3N	10	5	96
6	CH_3CN	Et_3N	5	5	40
7	DMF	Et_3N	5	5	35
8	CH_3OH	DBU	5	5	20
9	CH_3OH	Pyridine	5	5	32
10	CH_3OH	Et_3N	--	12	n.r.
11	CH_3OH	Et_3N	10 [c]	12	n.r.
12	CH_3OH	Et_3N	10 [d]	12	n.r.
13	CH_3OH	Et_3N	10 [e]	12	n.r.

[a]Reaction condition: Phenyl boronic acid (1 mmol), Aniline (1 mmol), Base (2 mmol), Solvent (5 mL), r.t.[b]Isolated yield after chromatographic purification, [c] $CoFe_2O_4$ as catalyst;[d] $CoFe_2O_4$-SiO_2 as catalyst;[e] $CoFe_2O_4$-SiO_2-NH_2 as catalyst; n.r.: no reaction.

After getting the optimized reaction condition in hand, we extended the scope of the reaction for a variety of boronic acid and amino compounds. Accordingly, numbers of substrates that are structurally and electronically diverse have been employed for this particular C-N cross coupling reactions. Results are summarized in Table 2. The reaction was found successful for a variety of primary and secondary amines and heterocycles such as imidazole with different boronic acids. Optimum amount of 5 wt% (based on the boronic acid) of catalyst was found to be sufficient for

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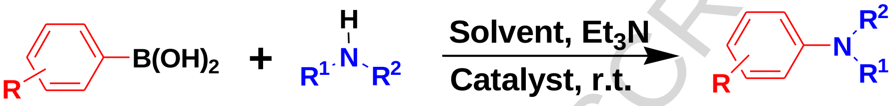
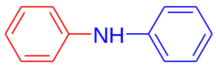
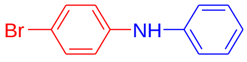
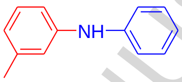
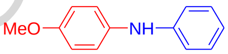
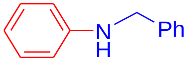
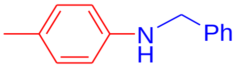
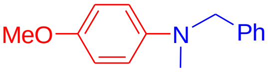
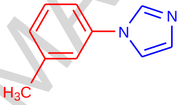
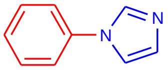
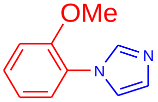
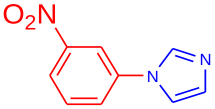
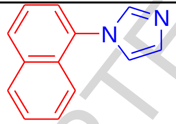
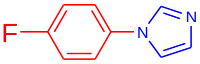
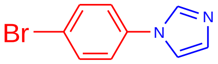
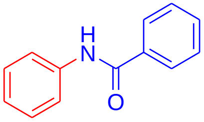
all the cases in this study at room temperature. Coupling of benzamide with boronic acid could also be very successfully carried out under the catalytic influence of the new magnetic material (Table 2, entry 15). This method is applicable to a large variety of substituted boronic acid with a negligible effect on its yield.

Table 2. Substrate scope of Chan-Lam reaction catalysed by $CoFe_2O_4$@SiO_2-NH_2-Furfural-Cu $(OAc)_2$ catalyst.



 1a, 94%	 1b, 80%	 1c, 84%	 1d, 82 %	 1e, 87%
 1f, 78%	 1g, 83%	 1h, 81%	 1i, 92%	 1j, 75%
 1k, 78%	 1l, 85%	 1m, 72%	 1n, 81%	 1o, 83%

Reaction condition: aryl boronic acid (1mmol), Amine (1 mmol), catalyst (5 wt. %), CH_3OH (5 mL), r.t., 5h, Yields reported are isolated yield after chromatographic purification

3.3. Reusability Test:

To test the reusability of the catalyst, the catalyst was separated from the reaction mixture by using an external magnet. It was then washed with ethyl acetate and methanol, dried in oven, kept in desiccator for further use. We have examined the reusability of this heterogeneous catalyst for the N-arylation reaction of aniline and phenyl boronic acid under the optimized reaction conditions. It was observed that the catalyst could be reused

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for at least seven catalytic cycles without loss in activity (Fig. S6 in SI). To check the characteristic of spent catalyst, we have carried out Powder XRD analysis of the catalyst after each cycle. From the analysis, no significant changes in catalyst characteristic were found even after seven catalytic cycles (Fig. S7 (a) of SI). We have also compared the surface area of the catalyst, before the reaction and after 7th catalytic cycle of use. The BET-surface area of the catalyst before carrying out the reaction is 9.2262 m^2/g (Fig. S7 (b) of SI), and the surface area of the catalyst after seventh catalytic cycles is 8.8802 m^2/g (Fig. S7 (c) of SI). Thus, there is a slight decrease in its surface area after reusing the catalyst for seven consecutive times.

4. Conclusions

In conclusion, we have synthesized a copper incorporated cobalt ferrite magnetic nanocatalyst via ultrasound assisted co-precipitation method. The catalyst was synthesized by attaching a $Cu(OAc)_2$-Schiff base complex onto the surface of $CoFe_2O_4$magnetic nanoparticle. The catalytically active $CoFe_2O_4$@SiO_2-NH_2-Furfural-$Cu(OAc)_2$ material was successfully applied as a reusable catalyst for the Chan-Lam type cross coupling reaction of aryl boronic acids with aryl amines and heterocycles. The catalyst offers several advantages over other catalyst such as high stability, easy separation of catalyst with the aid of an external magnet and its reusability for successive reactions without significant loss in its catalytic activity.

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References:

1. G. Evano, N. Blanchard, M. Toumi, Chem. Rev.108 (2008)3054–3131.
2. F. Monnier, M. Taillefer, Angew. Chem. Int. Ed. 47(2008) 3096–3099.
3. L. Liang, Z. Li, X. Zhou, Org. Lett., 11(15) (2009)3294-3297.
4. D. M. T. Chan, K. L. Monaco, R-P. Wang, M. P. Winters, Tetrahedron Lett. 39 (1998) 2933.
5. J. J. Li, Name Reaction, 4th ed.; Springer: Berlin, (2009) 101-104.
6. P. Y. S. Lam, C. G. Clark, S. Saubern, J. Adams, M. P. Winters, D. M. T. Chan, A. Combs, Tetrahedron Lett. 39(1998) 2941-2944.
7. D. A. Evans, J. L. Katz, T. R. West, Tetrahedron Lett. 39(1998) 2937-2940.
8. I. Gonza´lez, J. Mosquera, C. Guerrero, R. Rodrı´guez, J. Cruces, Org. Lett. 11 (8) (2009) 1677-1680.
9. S-Y. Moon, J. Nam, K. Rathwell, W-S. Kim, Org. Lett.16(2014) 338-341.
10. Z-G. Zheng, J. Wen, N. Wang, B. Wu, X-Q. Yu, Beilstein J. Org. Chem. 4 (2008) 1-6.
11. J-T. Yu, H. Guo, Y. Yi, H. Fei, Y. Jiang, Adv. Synth. Catal. 356(2014) 749-752.
12. B. Kaboudin, Y. Abedi, T. Yokomatsu, Eur. J. Org. Chem. (2011) 6656-6662.
13. S. Roy, M. J. Sarma, B. Kashyap, P. Phukan, Chem. Commun. 52(2016) 1170-1173.
14. D. S. Raghuvanshi, A. K. Gupta, K. N. Singh, Org. Lett. 14(17)(2012)4326-4329.
15. Y. Hirai, Y. Uozumi, Chem. Commun. 46 (2010) 1103-1105.
16. S. Sa, M. B. Gawande, A. Velhinho, J. P. Veiga, N. Bundaleski, J. Trigueiro, A. Tolstogouzov, O. M. ND. Teodoro, R. Zboril, R. S. Verma, P. S. Branco, Green Chem. 16(2014) 3494-3500.
17. P. Ruiz-Castillo, S. L. Buchwald, Chem. Rev. 116 (2016) 12564-12649.
18. J. Bariwal, E.V. Eycken, Chem. Soc. Rev. 42 (2013) 9283-9303.

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19. M. Islam, S. Mondal, P. Mondal, A. S. Roy, K. Tuhina, N. Salam, S. Paul, D. Hossain, M. Mobarok, Transition Met Chem. 36 (2011) 447–458.
20. T. Garnier, R. Sakly, M. Danel, S. Chassaing, P. Pale, Synthesis. 49 (2017) 1223-1230.
21. R. K. Borah, P. K. Raul, A. Mahanta, A. Shchukarev, J-P. Mikkola, A. J. Thakur, Synlett. 28 (2017) 1177-1182.
22. C. Borgohain, K. K. Senapati, D. Mishra, K. C. Sarma, P. Phukan, Nanoscale. 2(2010)2250–2256.
23. K. K. Senapati, S. Roy, C. Borgohain, P. Phukan, J. Mol. Catal. A: Chem. 352(2012) 128–134.
24. P. R. Likhar, S. Roy, M. Roy, M. L. Kantama, R. L. De, J. Mol. Catal. A: Chem. 271 (2007) 57–62.
25. G. V. Manohara, RSC Adv. 4(2014) 46126-46132.
26. C. S. Gill, B. A. Price, C. W. Jones, J. Catal. 251(2007) 145–152.
27. R. Hosseinzadeh, N. Aghili, M. Tajbakhsh, Catal. Lett. 146 (2016) 193–203.
28. J. P. Collman, M. Zhong, Org. Lett. 2(2000)1233-1236.
29. J. P. Collman, M. Zhong, L. Zeng, S.Costanzo, J. Org. Chem. 66(2001)1528-1531.
30. N. Debreczeni, A. Fodor, Z. Hell, Catal. Lett. 144(2014)1547–1551.
31. K. S. Rao, T-S. Wu, Tetrahedron. 68(2012)7735-7754.

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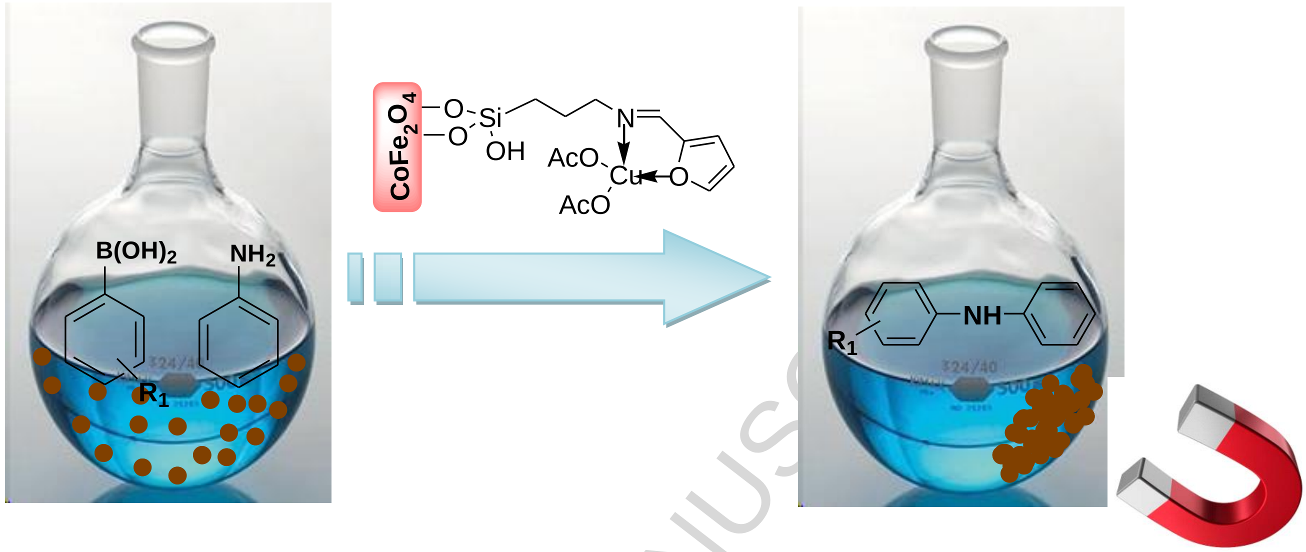
GRAPHICAL ABSTRACT:



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HIGHLIGHTS

- Cu-doped $CoFe_2O_4$ magnetic nanoparticles for the C-N coupling
- Recovery of catalyst using an external magnet and reusability.
- Excellent yield.
- Low catalyst loading.
- Useful for wide range of aryl boronic acids.

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