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ARTICLE

Copper Nanoparticles Supported on Starch Micro Particles as a Degradable Heterogeneous Catalyst for Three-Component Coupling Synthesis of Propargylamines

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

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Novel copper nanoparticles supported on starch micro particles (CuNPs@MS) was prepared successfully and characterized by SEM, EDX, TEM, SAED, TGA, XPS, and XRD analyses. The easy synthesized and thermally stable CuNPs@MS has been applied as green, degradable, and eco-friendly catalyst in three component reaction of amines, aldehydes and alkynes for preparation of diverse propargylamines. Reactions were performed under heterogeneous conditions and catalyst were successfully recycled for five consecutive runs with small decrease in activity.

Introduction

Transition metal catalyzed reaction of an aldehyde, an alkyne, and an amine (A3 coupling)¹ is important and easy method to access propargylamines compared to the traditional methods such as reaction of less commercially available propargyl halides with amines² or using stoichiometric amounts of lithium or magnesium acetylides with imines.³ The obtained propargylamines are important synthetic intermediates for the synthesis of divers nitrogen- containing biologically active compounds and potential therapeutic agents.⁴ In recent years application of different transition metals such as gold,⁵ indium,⁶ iron,⁷ zinc,⁸ Cu/Ru,⁹ iridium,¹⁰ silver,¹¹ and nickel¹² through C-H bond activation of terminal alkynes have been reported. However, since copper catalysts precursors are cheap, available, and highly reactive, many A3 coupling reactions have been reported using copper as a source of heterogeneous or homogeneous catalysts.¹³ As a mentioned, since propargylamines have extensive application in pharmaceutically active compounds, contamination of product with toxic metal is not desirable and using heterogeneous catalysts with high turnover number and recyclable ability is highly attractive for A3 coupling reaction.

Along this line different heterogeneous copper catalysts supported on different solid supports such as Fe₃O₄,¹⁴ MCM-41,¹⁵ SiO₂,¹⁶ montmorillonite,¹⁷ zeolites,¹⁸ mesoporous Cu/Al¹⁹

have been reported for A3 coupling reactions under heterogeneous condition. Recently, we have also reported periodic mesoporous organosilica (PMO) supported gold²⁰ and copper²¹ nanoparticles as efficient catalysts in A3 coupling reactions.

In recent years, using ecofriendly and biodegradable materials as supports for stabilization of metal nanoparticles has attracted great attention.²² Along this line, we have reported agarose as naturally abandon and cheap biopolymer for stabilization of palladium and copper nanoparticles and their applications in Pd catalyzed carbon-carbon²³ and Huisgen 1,3-dipolar cycloaddition reactions.²⁴ Among the different natural polymers, starch is most common carbohydrate consisting of a large number of glucose units linked by glycosidic bonds with complete biodegradability,²⁵ low cost and renewability²⁶ and can be regenerated from carbon dioxide and water by photosynthesis in plants.²⁴ In continuation with our interest on heterogeneous copper catalysts and A3 coupling reaction, herein, we wish to report copper nanoparticles supported on starch micro particles as green and sustainable catalyst in three component coupling of amines, aldehydes and alkynes.

Results and discussion

Prepared starch micro particles was dissolved and sonicated in deionized water and after addition of aqueous solution of

$\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$, final starch supported copper nanoparticles was obtained by addition of NaBH_4 as a reducing agent at 30 °C. The obtained material is referred as CuNPs@MS throughout the text of this article. Copper loading on the CuNPs@MS was determined using ICP analysis to be 0.25 mmol g^{-1} . Thermogravimetric analysis of prepared CuNPs@MS showed three main weight losses between 25–700 °C. First weight loss (25–120) is related to physisorbed water and organic solvents and second and third ones are related to decomposition of starch polysaccharide structure. This diagram confirms thermal stability and negligible structure leaching of CuNPs@MS up to 300 °C (Figure 1).

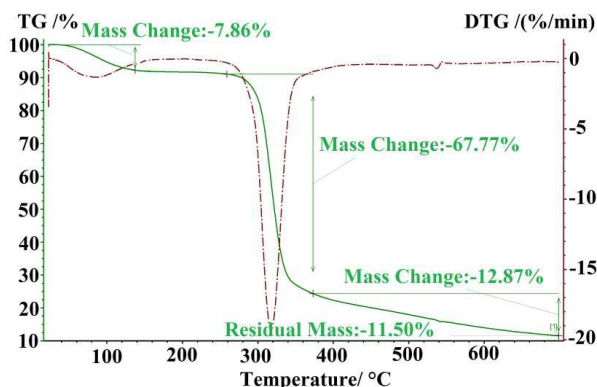


Fig 1. Thermogravimetric diagram of the CuNPs@MS

Scanning electron microscope (SEM) image of CuNPs@MS showed presence of highly uniform and micro sized starch particles (Figure 2a). Also, the presence of copper and carbon in the structure of CuNPs@MS was confirmed by energy-dispersive X-ray spectroscopy (EDX) (Figure 3) obtained from SEM analysis.

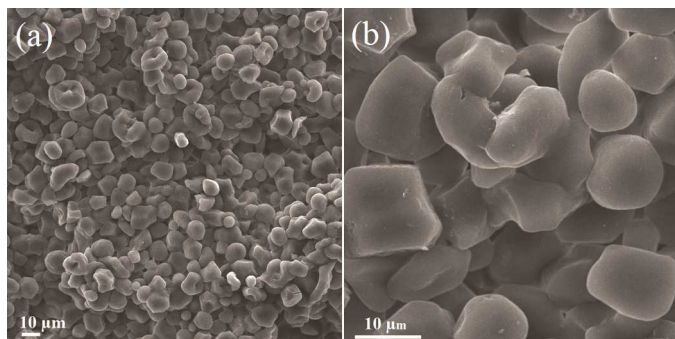


Fig. 2 (a) SEM image of the catalyst; (b) SEM image of reused catalyst after 3rd run.

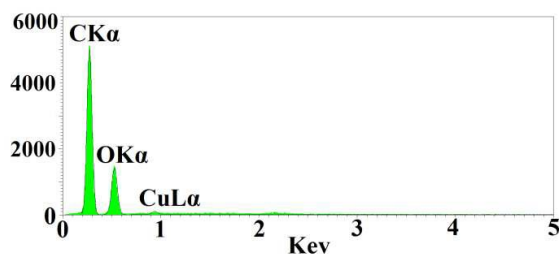


Fig. 3 EDX spectrum of CuNPs@MS

TEM image of CuNPs@MS confirmed presence of copper nanoparticles in average size of 15–20 nm supported on starch micro particles (Figure 4a and 4b). Figure 4c shows the selected area diffraction pattern (SAED) analysis with prominent ring pattern corresponding to Cu. The diffraction pattern shows prominent rings with interplanar spacing values of 0.20, 0.18, 0.12 and 0.109 nm corresponding to (111), (200), (220) and (311) planes respectively for Cu with fcc structure (JCPDS no. 04-0836). Thus the diffraction analysis shows the presence of Cu in the cubic structures.

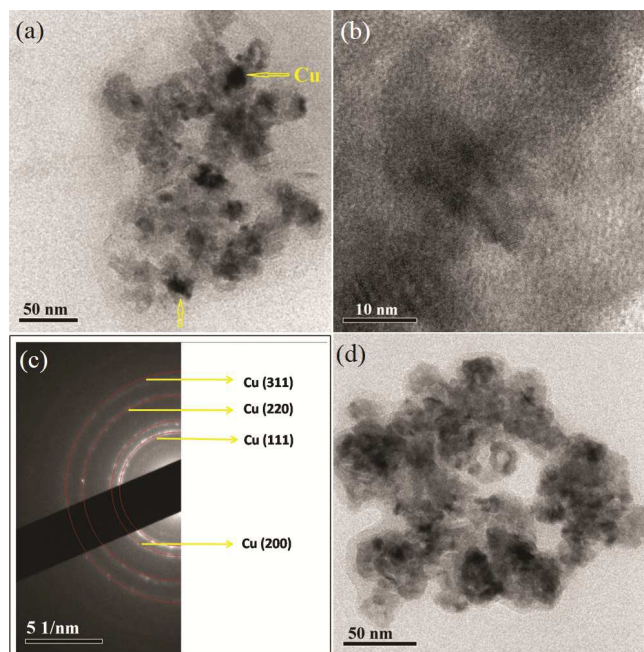


Fig.4 (a) and (b) TEM images of CuNPs@MS in different magnifications; (c) SAED analysis of the CuNPs@MS; (d) TEM images of reused catalyst after 3rd run.

X-ray crystallography of prepared material (Figure 5a) showed both (111) phases for Cu_2O (JCPDS no. 05-0667) and Cu (JCPDS no. 04-0836) at 2θ values of 36.3 and 43.2 respectively confirming presence of both Cu(0) and Cu(I) species in catalyst structure.²⁴

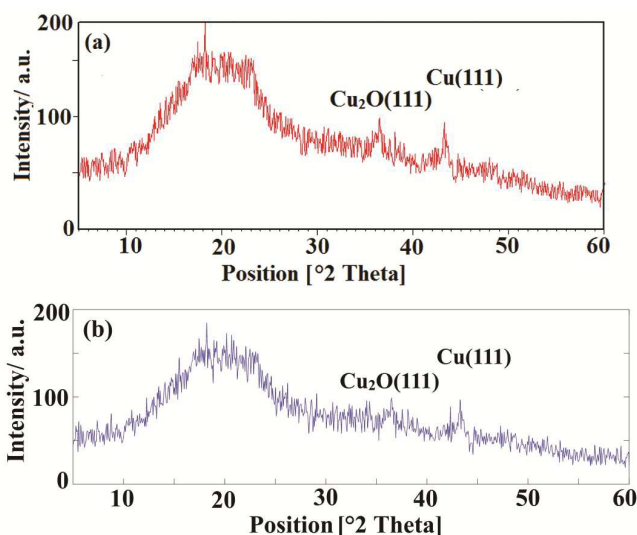


Fig. 5 (a) XRD pattern of the catalyst; (b) XRD pattern of reused catalyst after 3rd run.

Furthermore, the X-ray photoelectron spectrum (XPS) spectra, for Cu 2p_{3/2} of the prepared material showed two main peak at 933.5 and 935.6 eV related to metallic Cu and Cu₂O species respectively (Figure 6).²⁷

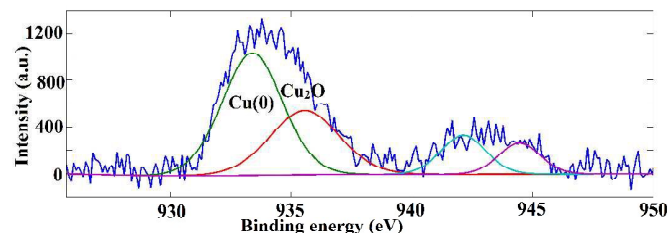


Fig 6. XPS spectrum of the CuNPs@MS

The Brunauer Emmett Teller (BET) surface area of the CuNPs@MS was determined by physisorption of nitrogen (N₂) to be 68 m²g⁻¹.

The catalytic activity of prepared CuNPs@MS was tested in three component coupling reaction of amine, aldehyde and alkyne for the preparation of propargylamines. In order to find optimized reaction conditions, reaction of benzaldehyde, piperidine and phenylacetylene in the presence of 0.3 mol% catalyst was selected as the model reaction and effect of solvent and reaction temperature were studied. Study of reaction in different solvents such as H₂O, CH₃CN, EtOH, 1,4-dioxane, DMSO, DMF, and THF at room temperature afford low yields with highest yield using THF (Table 1, entries 1-7). Increasing reaction temperature to 60 °C improved reaction yields (Table 1, entries 8-13). However, best isolated yield was obtained using THF as a solvent within 20 h (Table 1, entry 13). Results of Table 1 indicated that decreasing reaction time caused drops in reaction yields (Table 1, entries 14-16). Also, it was found that using low amounts of copper catalyst, desired products were obtained in lower isolated yields (Table 1, entries 17-19), therefore; 0.3 mol% of catalyst was selected as suitable amount for this reaction. It was worth mentioning that according to the thermal stability of the catalyst which was 300 °C, catalyst can easily tolerate finding optimized reaction conditions.

Table 1. Screening of different solvents and temperatures for the reaction of benzaldehyde, phenylacetylene and piperidine.^a

Entry	Solvent	Temp. (°C)	Time (h)	Yield(%)
1	H ₂ O	30	20	30

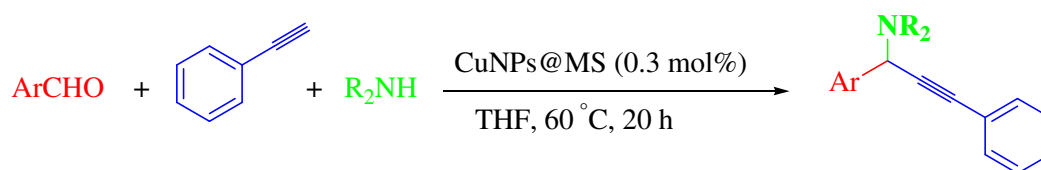
Table 2. Reactions of structurally different aldehydes with amines and phenylacetylene.^a

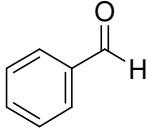
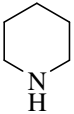
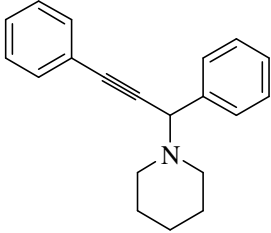
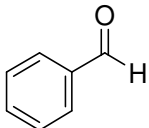
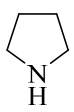
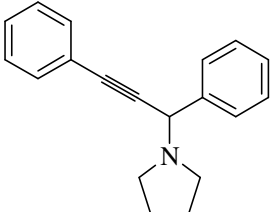
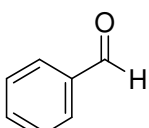
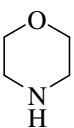
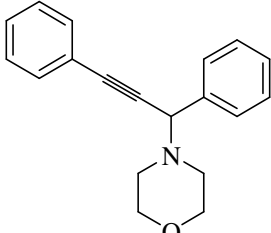
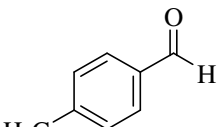
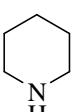
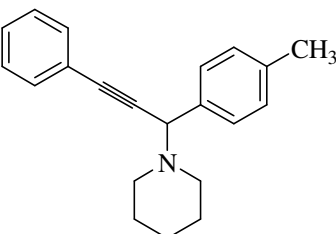
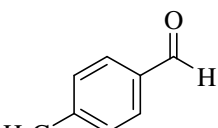
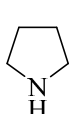
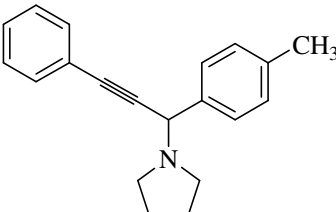
2	CH ₃ CN	30	20	20
3	EtOH	30	20	12
4	1,4-dioxane	30	20	6
5	DMSO	30	20	0
6	THF	30	20	41
7	DMF	30	20	11
8	CH ₃ CN	60	20	65
9	EtOH	60	20	45
10	H ₂ O	60	20	55
11	DMSO	60	20	10
12	1,4-dioxane	60	20	30
13	THF	60	20	96
14	THF	60	18	90
15	THF	60	14	76
16	THF	60	8	50
17	THF	60	20	84 ^b
18	THF	60	20	71 ^c
19	THF	60	20	64 ^d

^aReaction conditions: benzaldehyde (1 mmol), piperidine (1.5 mmol) phenylacetylene (1.2 mmol), catalyst (0.3 mol %) and solvent 1.5 mL.

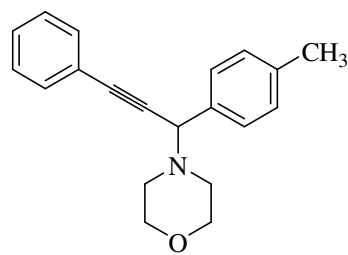
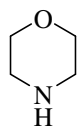
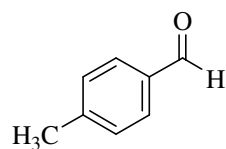
^bUsing 0.18 mol% catalyst. ^cUsing 0.12 mol% catalyst. ^dUsing 0.06 mol% catalyst

With the optimized reaction conditions in hand, various aldehydes including either electron releasing or withdrawing groups such as Me, OMe, Br and Cl as well as benzaldehyde and 1-naphthaldehyde were reacted efficiently with phenylacetylene and different amines such as piperidine, morpholine, and pyrrolidine (Table 2). Also, reaction of furfural as a heterocyclic aldehyde with piperidine and phenylacetylene were proceeded efficiently and desired product was obtained in excellent yield (Table 2, entry 12). Furthermore reaction of butanal and heptanal as the aliphatic aldehydes with morpholine and phenylacetylene were performed well and afford desired products in excellent yields (Table 2, entries 17,18). We have also studied reactivity of diphenylamine with benzaldehyde and phenylacetylene under optimized reaction conditions. However, result indicated that reaction did not proceed and starting material were intact.



Entry	ArX	Michael acceptor	Product	Isolated Yield (%) ^a
1			 1a	96
2			 1b	95
3			 1c	95
4			 1d	95
5			 1e	94

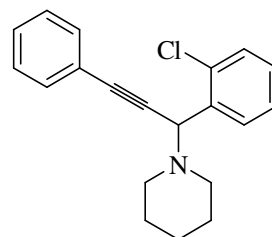
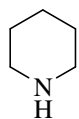
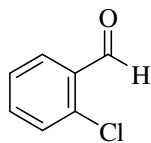
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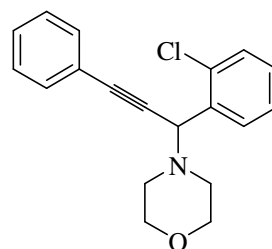
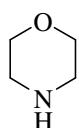
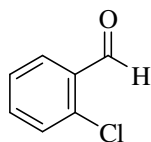
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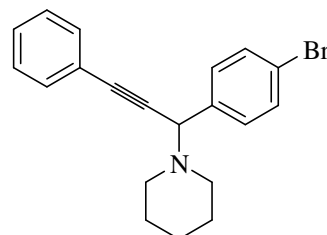
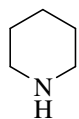
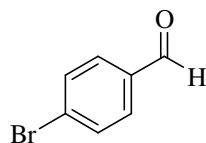
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90

1h

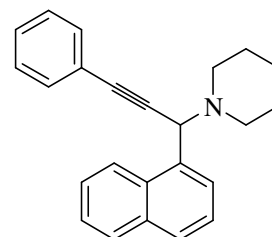
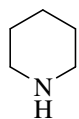
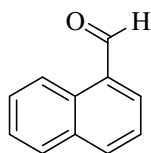
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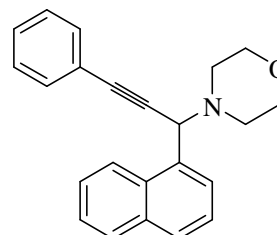
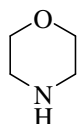
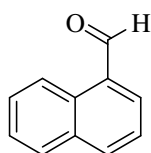
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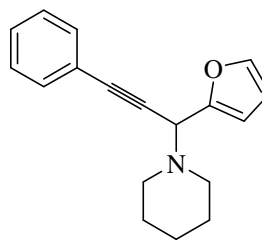
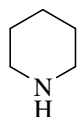
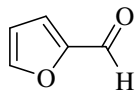
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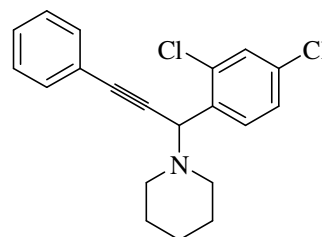
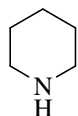
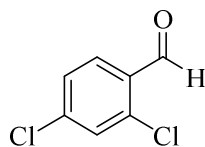
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**1l**

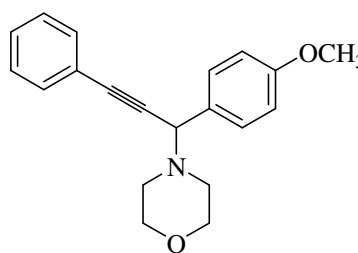
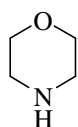
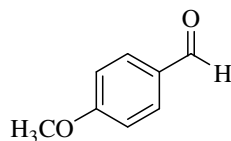
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**1m**

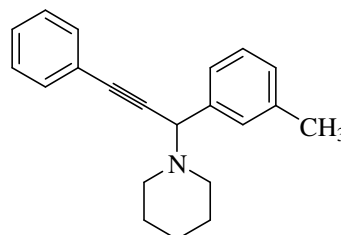
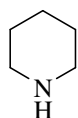
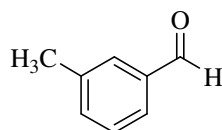
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**1n**

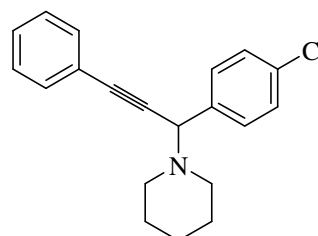
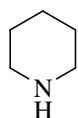
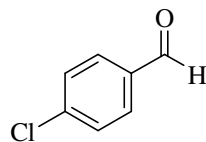
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**1o**

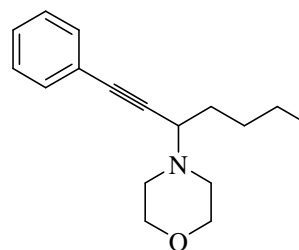
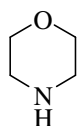
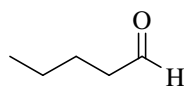
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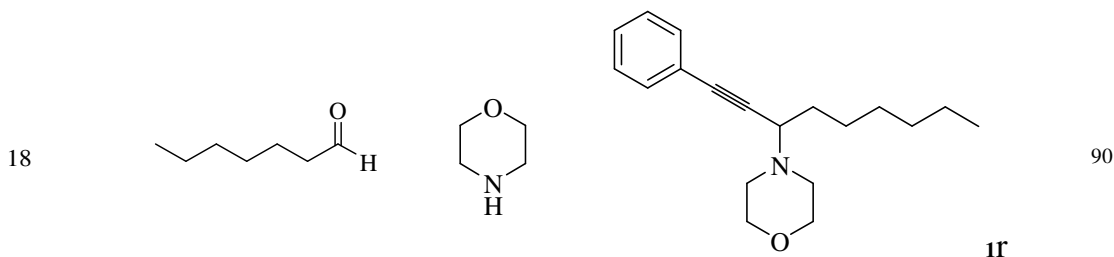
**1p**

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17

**1q**

94



^a Reaction conditions: Aldehyde (1 mmol), amine (1.5 mmol), phenylacetylene (1.2 mmol), catalyst (0.3 mol %) and THF 1.5 mL.

Proposed mechanism for the reaction is the same with well-known mechanism for A3 coupling reaction (Figure 7).^{21, 28} Reaction proceed *via* the activation of the C_{sp}-H bond of the terminal alkyne by the CuNPs@MS. Then, alkynyl-Cu intermediate react with the immonium ion generated in situ from the reaction of aldehyde and secondary amine to produce the corresponding propargylic amine product, and regenerate the active CuNPs@MS species for further reactions.

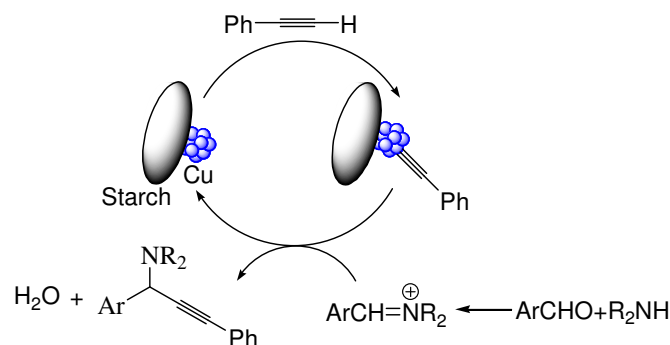


Fig. 7 Proposed reaction mechanism using CuNPs@MS

Recyclability of heterogeneous catalysts is important factor from the economical and sustainable chemistry stand points. Along this line we have studied recyclability of catalyst for the reaction of benzaldehyde, piperidine and phenylacetylene under optimized reaction conditions. After completion of the reaction in each run catalyst was separated by centrifugation and reused in another reaction batch. Result of this study indicated that the catalyst is recyclable for five consecutive runs with small drops in catalytic activity (Figure 8). The slow decrease in reaction yields during recycling process is may reslut of strong intraction between Cu NPs and available free hydroxy groups of starch particles. This result was confirmed by ICP analysis of reaction solution after five reaction cycle which showed small leaching of copper species (1.4%) to reaction medium.

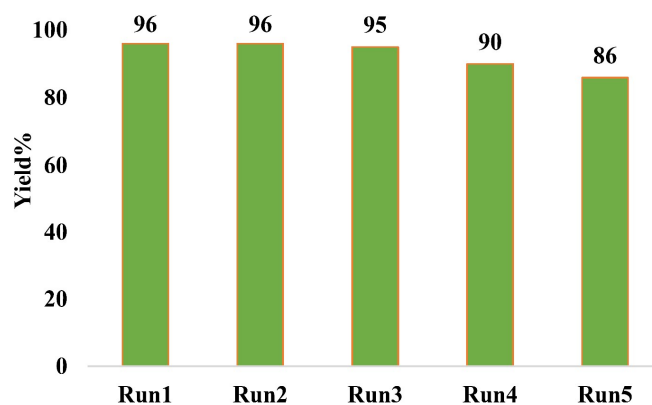


Fig. 8 Recycling of catalyst for the reaction of benzaldehyde, piperidine and phenylacetylene

SEM (Figure 2b) and TEM (Figure 4d) images of the catalyst after 3rd run showed preserve of catalyst structure during the reaction. Furthermore, XRD analysis of reused catalyst after 3rd run showed copper nanoparticle states were intact within the reaction (Figure 5b).

Conclusions

In conclusion, in this study we have used micro starch particles as a cheap, abandon, green support for stabilization of copper nanoparticles. The new material was characterized using different technics and applied as an efficient catalyst in three component coupling reaction of amines, aldehydes and alkynes. Using this catalyst, various aldehydes reacted with different amines and phenylacetylene under heterogeneous conditions. The catalyst was recyclable and recycled for five consecutive runs with small decrease in reactivity.

Experimental:

All chemicals were purchased from Sigma-Aldrich, Acros and Merck Chemical Companies and were used without further purification. Column chromatography was carried out on silica gel 60 Merck (230-240 mesh) in glass columns (2 or 3 cm diameter) using 15-30 grams of silica gel per one gram of the crude mixture. ¹H NMR was recorded at 250 MHz and ¹³C NMR was recorded at 62.5 MHz in CDCl₃ using TMS as internal standard. X-ray diffraction (XRD) was recorded on Philips X'PertPro. The size of the particles of the catalyst was determined by transmission electron microscopy using Philips CM-120 instrument.

Preparation of starch micro particles:²⁹ 1.25 gr corn starch was dissolved in 25 mL distilled water at room temperature and 25 mL acetone was added. The high molecular weight starch separated and then dissolved in 25 mL distilled water with a stirring rate of 750 rpm and pH of the new solution was adjusted at 2.5. Starch particles were obtained by addition of 75 mL acetone. For stabilization of particles a cross-linking agent glutaraldehyde (0.25 ml) was added and system stirred at 750 rpm for 12 h. Then, the acetone was evaporated and material was dried over oven at 50 °C.

Preparation of CuNPs@MS: Mixture of starch micro particles (0.5 gr) in 15 mL H₂O was sonicated for 60 min. Then, Cu(OAc)₂·H₂O (0.025gr, 0.1mmol) which already dissolved in 4 mL H₂O gradually added to suspension and stirred for 2h at room temperature. Then, NaBH₄ (0.4 mmol, 0.015 gr) which already dissolved in 6 mL H₂O was added drop wise under argon atmosphere and reaction mixture stirred at 750 rpm for 48 h at 30 °C. The catalyst was collected after filtration, washed with water (3×10 ml), and dried in oven at 60°C.

General procedure for A3 coupling reaction: The catalyst (12 mg, 0.3 mol%) was added to a mixture of aldehyde (1 mmol), phenylacetylene (1.2 mmol) and amine (1.5 mmol) in THF (1.5 mL) and the mixture was stirred at 60 °C for 20 h under argon atmosphere. After the complication of reaction, the solvent evaporated under reduced pressure. The crude product was obtained by column chromatography (EtOAc, hexane) to afford propargylamines in high to excellent yields. All products were known and confirmed by ¹H NMR, ¹³C NMR.

Acknowledgements

The authors are grateful to Institute for Advanced Studies in Basic Sciences (IASBS) Research Council and Zanjan University for support of this work. The authors are also thankful to Mrs. Sara Nayeri, Mr. Mehran Razeghi and Mohammad Seyedhamzeh for technical helps.

Notes and references

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Graphical abstract

Starch supported Cu NPs as a degradable heterogeneous catalyst for A3 coupling reaction

