

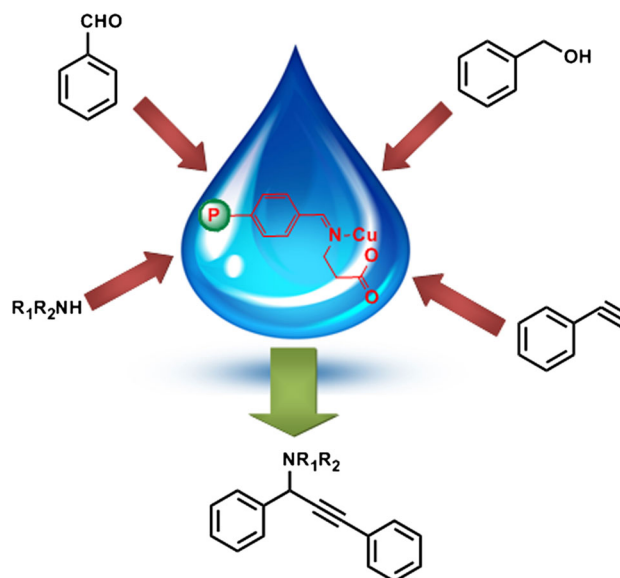
Functionalized Polystyrene Supported Copper(I) Complex as an Effective and Reusable Catalyst for Propargylamines Synthesis in Aqueous Medium

Md. Mominul Islam¹ · Anupam Singha Roy^{1,2} · Sk. Manirul Islam¹

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Abstract An efficient procedure for the one-pot synthesis of propargylamines is A^3 coupling in which an alkyne, an aldehyde, and an amine are coupled together. Here, we report that polystyrene supported Cu(I) catalyst is excellent for A^3 coupling in water without using any additives or hazardous organic solvents. The polystyrene supported Cu(I) catalyst was synthesized and its catalytic activity was also evaluated in the synthesis of propargylamines in oxidative A^3 -coupling reaction with benzyl alcohols instead of their aldehydes in water. This protocol offers several advantages such as high yields of the desired product, reaction in aqueous medium and recyclability of the catalyst. It gives well to excellent yields for a variety of substrates. As it acts as heterogeneous catalyst, it can be easily separated from the reaction mixture and reused without appreciable loss of activity.

Graphical Abstract Polymer supported copper catalyst, Cu-PS-ala, acts as a heterogeneous catalyst for the one pot synthesis of propargylamines via A^3 coupling reaction in water using aldehydes or alcohols, amines and alkynes.



Keywords Polymer supported Cu(I) catalyst · One-pot synthesis · Propargylamines · A^3 coupling · C–H activation

Md. Mominul Islam and Anupam Singha Roy have contributed equally to this manuscript.

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1 Introduction

The efforts from the last century have resulted in the development of a number of synthetic pathways. However, the exceedingly high cost of chemicals and the increasing awareness on their potential environment hazards have persuaded a fresh look at devising more efficient and eco-friendly alternate ways for chemical synthesis [1, 2]. The one-pot multi-component reaction (MCR) is one of the best useful synthetic routes to generate complex structures with greater structural and skeletal diversity [3, 4]. Generally, these MCRs take place in one-pot and show a higher economy of atom and

steps and also the selectivity. Besides, they are easy to perform and also lower the cost, time and energy. A three component coupling of carbonyl compounds-amines-alkynes is one of the best reported processes for C–C bond formation [5–7] and has received much more attention in recent years. The resultant propargylamines, obtained from the above coupling reaction, are synthetically versatile key intermediates [8, 9] for the preparation of natural products and a large number of nitrogen containing biologically active compounds such as conformationally restricted peptide isosteres, oxotremorine analogues, and β -lactams. The conventional methods for the preparation of the propargylamine moiety have usually followed direct amination of propargyl halides [10], phosphates, triflates [11] or acetates [12] or utilized the high acidity of terminal alkynic C–H bond to form alkynyl-metal reagents by reaction with strong bases [13–15]. But unfortunately, the reagents, used in these processes, have to take in stoichiometric ratios, and are highly sensitive to moisture and also require strictly controlled reaction conditions. So an easy and efficient synthetic route is required, which is applicable for the synthesis of the wide range of propargylamines [16–18]. In recent years, a huge progress on an alternative atom-economical nucleophilic addition of in situ generated metal-acetylides to imines and enamines has been made by C–H activation, where water is the only by-product [19]. The alkynic C–H bond can be activated by using various homogeneous or heterogeneous catalysts containing transition metal ions such as gold [20], zinc [21], iron [22], silver [23], indium [24], iridium [25, 26], mercury [27], ruthenium [28] and copper [29–33] etc. Among these transition metals, we turned our attention to the use of copper because it is an efficient, cheap and non-toxic element and can be used for the synthesis of many organic compounds [34]. Commonly, the reported copper catalysts are homogeneous and the main drawbacks of these complexes are the chance of metal contamination with the final product and the difficulty to recover and reuse these catalysts for subsequent reactions. To overcome these drawbacks, copper was immobilised on various supports to form the corresponding heterogeneous catalysts which have received considerable attention in recent years [35–39]. Several methods for the preparation of propargylamines in water were reported [40–42], some of them required highly expensive Au [41] or Ag [42]. These information's prompted us to present our results for the preparation of propargylamines using polymer supported copper(I) catalyst in water.

To the best of our knowledge, there is currently no report of employing polystyrene supported Cu(I) catalyst in A^3 -coupling reactions. Herein, we report that polymer supported Cu(I) catalyst is an efficient catalyst in the A^3 coupling reactions of aldehydes, amines and alkynes under aerobic conditions in aqueous medium. Moreover, the effects of solvent and temperature, and the recycling potential of the

catalyst have been studied. This catalyst could be easily separated from the reaction mixture by filtration and reused several times without significant degradation in activity.

2 Experimental

2.1 Materials and Instruments

Chloromethylated polystyrene (5.5 mmol Cl/gm of resin) was purchased from Sigma-Aldrich. All other chemicals used for this investigation purposes were purchased from commercial sources and were used without purification. Before use, all solvents were distilled and dried following the standard process.

A PerkinElmer 2400 C elemental analyzer was used to collect micro-analytical data (C, H and N). The FT-IR spectra of the samples were recorded from 400 to 4000 cm^{-1} on a PerkinElmer FT-IR 783 spectrophotometer. A Mettler Toledo TGA/SDTA 851 instrument was used for TGA. The morphology of the functionalized polystyrene and complex was analyzed using a scanning electron microscope (Zeiss EVO40, UK) equipped with EDX facility. The copper content in the catalyst was determined using a Varian AA240 atomic absorption spectrophotometer. NMR spectra were monitored on a Bruker AMX-400 NMR spectrophotometer (400 MHz for ^1H NMR) using tetramethylsilane as internal standard.

2.2 Synthesis of Polymer Supported Ligand

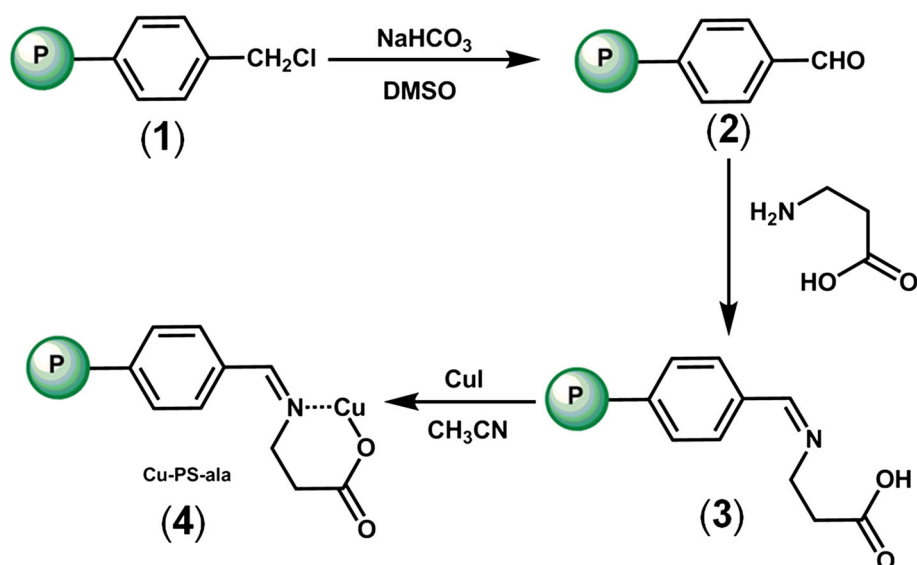
Chloromethylated polystyrene beads (**1**) were functionalized with aldehyde group according to a literature procedure [43]. Then β -alanine (0.4 gm) was added to the stirred aldehyde-bearing polymer beads (**2**) (1 gm) in methanol (25 mL) and refluxed for next 20 h. After filtration and washing with absolute methanol, the polymeric ligand (**3**) was obtained.

2.3 Loading of Metal on to the Polymeric Ligand

Polymeric ligand (**3**) (1 gm) was stirred for 20 h with CuI (0.07 gm) in acetonitrile (20 mL) under refluxing condition. At the end of the reaction, the resulting metal-loaded polymer (**4**) was filtered, washed with acetonitrile, methanol and finally dried under vacuum for 6 h at 90 $^\circ\text{C}$.

2.4 General Procedure for the A^3 -Coupling Reaction in Water-Medium

A mixture of polymer supported Cu(I) catalyst, Cu-PS-ala (0.010 g), aldehyde (1 mmol), phenylacetylene (1 mmol) and amine (1.2 mmol) in 5 mL water was placed in a 10 mL round



Scheme 1 Outline for the synthesis of polymer supported copper(I) catalyst

bottom flask and stirred at reflux condition. The reaction was monitored by TLC. After the given reaction time the catalyst was removed by simple filtration. The filtrate was concentrated under reduced pressure and extracted with ethyl acetate from water. The desired product was isolated from the extracted organic part by column chromatography. The known products were characterized by comparison of their ^1H NMR data with the data already described in the literature.

3 Results and Discussion

3.1 Characterization of Polymer Supported Copper(I) Complex

The first step in the accomplishment of this goal was the preparation of polymer supported Cu(I) catalyst (Scheme 1). The catalyst was prepared by stirring polymer supported ligand (3) in acetonitrile solution of CuI for 20 h. The catalyst was separated by simple filtration and dried under vacuum at 90°C for 6 h.

Elemental analysis data for polymer supported ligand and copper catalyst are given in Table 1. Amount of copper metal was determined by using atomic absorption spectrophotometer. Copper content in the catalyst is 3.98 wt%. Copper content remained almost unchanged even after recycling the catalyst for six cycles.

3.1.1 IR Spectral Study

In the FT-IR spectrum (Fig. 1a) a new peak appeared at 1703 cm^{-1} which was assigned to carbonyl C=O bond

Table 1 Chemical composition of polymer supported ligand (3) and Cu-PS-ala catalyst (4)

Compound	C %	H %	N %	Cu %
3	74.96	6.36	4.61	
Cu-PS-ala (4)	72.01	6.03	4.45	3.98 (3.96) ^a

^a Copper content of recycled catalyst after 6th cycles

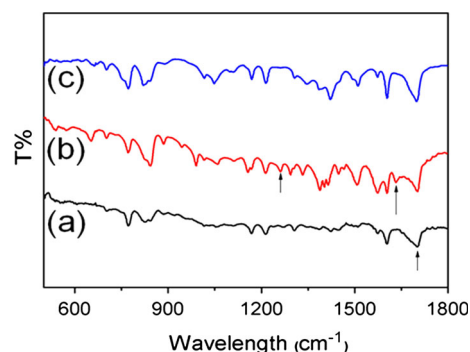


Fig. 1 FT-IR spectra of a aldehyde functionalized polymer, b polymer supported Schiff base ligand and c polymer supported Cu(I) catalyst Cu-PS-ala

stretching vibration of the $-\text{CHO}$ group. In the aldehyde functionalized polymer (2) the C-Cl peak due to $-\text{CH}_2\text{Cl}$ group at 1264 cm^{-1} was absent [44]. In the polymeric support (3) a new peak at 1633 cm^{-1} is observed which indicated the formation of C=N bond (Fig. 1b). This band shifted to lower wave numbers after complexation with copper. It suggested the coordination of the Schiff base to

the copper through the azomethine nitrogen. The phenolic (C–O) stretching frequency was observed in the region of 1262 cm^{-1} in ligand (**3**), which shifted to lower frequency in the complex, indicating coordination of metal through the phenolic oxygen (Fig. 1c).

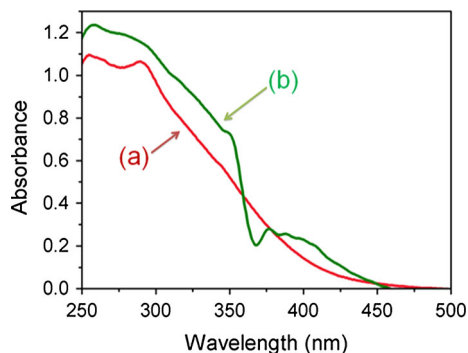


Fig. 2 DRS-UV-Vis spectra of polymer supported Schiff base ligand (**3**) (a) and Cu-PS-ala catalyst (b)

3.1.2 DRS-UV Spectroscopy

The electronic spectra of the polymer supported Schiff base ligand and copper catalyst (Cu-PS-ala) have been recorded in the diffuse reflectance spectrum mode and given in Fig. 2. Both in the Schiff base ligand and copper catalyst, broad bands around 260–350 nm are observed. This absorption bands may be attributed to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition in phenyl moiety. The bands at 370 nm in Cu-PS-ala arise due to LMCT.

3.1.3 Scanning Electron Micrographs (SEM) and Energy Dispersive X-ray Analyses (EDX)

The scanning electron micrographs of the polymer supported β -alanine ligand and copper(I) catalyst are presented in Fig. 3a and b, respectively. The morphological changes in the polymer supported ligand and polymer supported catalyst are quite evident from these images. Quite uniform and negligible variation in size is observed throughout the

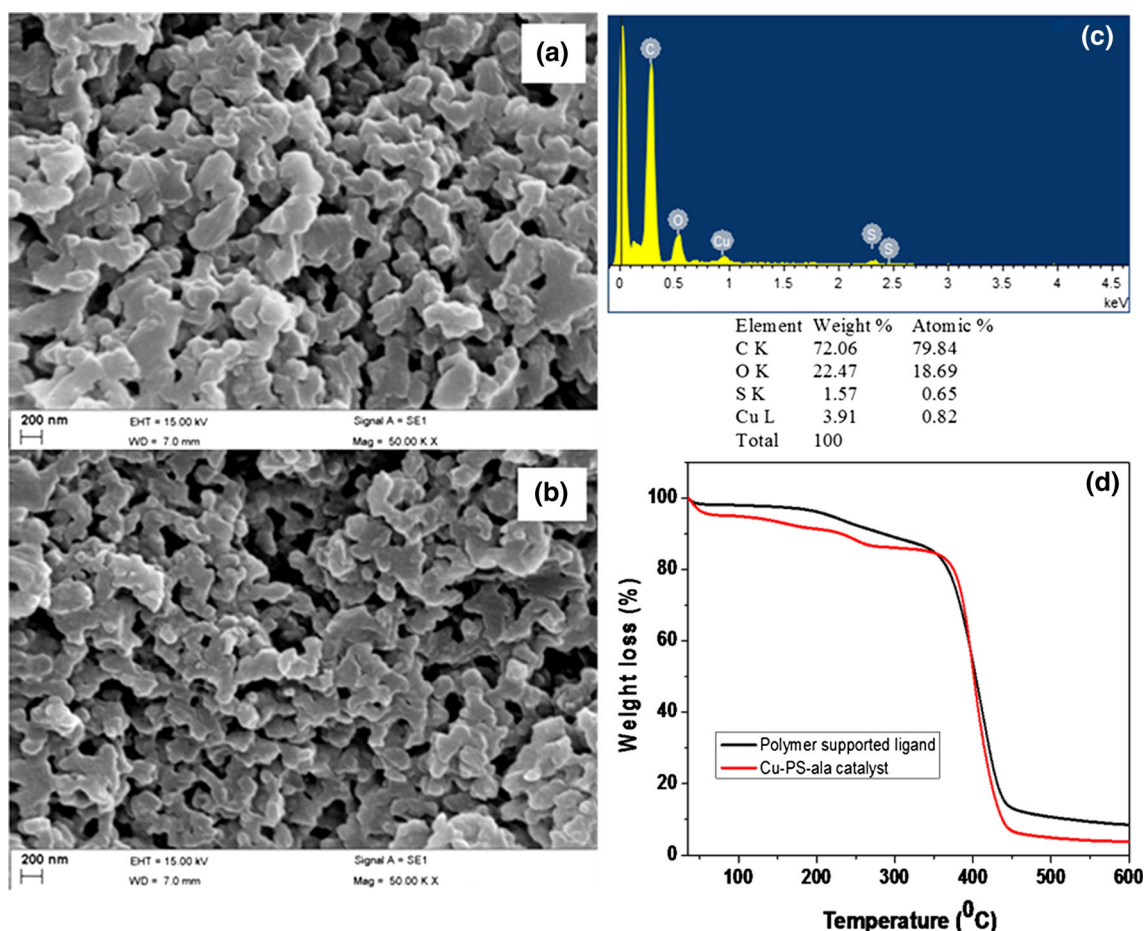


Fig. 3 SEM images of **a** polymer supported Schiff base ligand and **b** polymer supported Cu(I) catalyst Cu-PS-ala, **c** EDAX data of polymer supported Cu(I) catalyst, Cu-PS-ala, **d** TGA plots for polymer supported ligand and Cu-PS-ala catalyst

specimens. Energy dispersive spectroscopy analysis of X-rays (EDAX) data for the polymer supported copper complex is given in Fig. 3c. The EDX data also confirm the presence of copper on the surface of the polymer matrix.

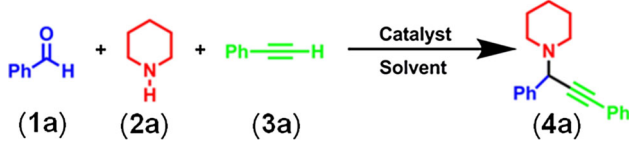
3.1.4 TGA Studies

TGA curves of both the polymer supported ligand (**3**) and catalyst are given in Fig. 3d. The ligand and copper catalyst were stable up to 350–370 °C and above this temperature they decomposed. So, thermogravimetric analysis suggests that the polymer supported copper complex degrades at higher temperature.

3.2 Catalytic Activity

After the successful preparation and characterization of the polymer supported copper catalyst, we studied its activity in the coupling of aldehydes, amines, and alkynes. In order to find the optimum reaction conditions, the activity of the heterogeneous copper catalyst was examined in a model reaction using benzaldehyde (**1a**), piperidine (**2a**) and phenylacetylene (**3a**) under refluxing conditions (Table 2). A controlled reaction under refluxing conditions in absence of the catalyst gave no expected product even after 3 days, irrespective of the solvent used (Table 2, entries 1 and 2). The desired product was generated in 80 % yield when CuI was used (Table 2, entry 3). In comparison, polymer supported copper catalyst, Cu-PS-ala, gave slightly better yield than CuI. When 0.005 g of Cu-PS-ala was used, the yield of the product was low even after long reaction time (Table 2, entry 5) but 0.010 g of Cu-PS-ala was found to be optimal (Table 2, entry 4). However, using 0.015 and 0.020 g of Cu-PS-ala catalyst no improvement of yield was observed (Table 2, entries 6 and 7). To check the effect of solvent, the above reaction was performed in various solvents like toluene, acetonitrile, THF, DCM and water. From Table 2, it is evident that water is the best solvent (Table 2, entry 4). Moderate yields were obtained when the reaction was performed in toluene, acetonitrile and THF (Table 2, entries 9, 10 and 11) and a poor result was observed when the reactions were carried out in DCM (Table 2, entry 8). Next we examined the effect of the temperature. The reaction was carried out at 50, 70 °C and reflux conditions (entries 4, 12 and 13). Also, we have checked the A³ coupling reaction between benzaldehyde, piperidine and phenylacetylene under refluxing conditions using CuI and Schiff base derived from β -alanine and benzaldehyde (entry 14). This system generated slightly lower (86 %) desired product compared to Cu-PS-ala catalyst. Finally, from Table 2 it can be seen

Table 2 The optimization of amount of catalyst, solvents and temperature in the three-component coupling of benzaldehyde, piperidine and phenylacetylene



Entry	Catalyst (g)	Solvent	t/h	Yield 4a (%) ^a
1	–	THF	36	0
2	–	H ₂ O	48	0
3	CuI	H ₂ O	6	80
4	0.01	H ₂ O	6	95
5	0.005	H ₂ O	12	78
6	0.015	H ₂ O	6	95
7	0.02	H ₂ O	6	96
8	0.005	DCM	12	15
9	0.005	PhMe	12	58
10	0.005	THF	12	68
11	0.005	CH ₃ CN	12	62
12 ^b	0.01	H ₂ O	6	46
13 ^c	0.01	H ₂ O	6	74
14 ^d	CuI	H ₂ O	6	86

Benzaldehyde (1 mmol), piperidine (1.2 mmol), phenylacetylene (1 mmol), solvent (5 mL) Reflux conditions

^a Based on isolated yields. CuI = 6.26×10^{-3} mmol (entries 3 and 14)

^b Reaction carried out at 50 °C

^c Reaction carried out at 70 °C

^d Reaction carried in presence of CuI and Schiff base ligand derived from β -alanine and benzaldehyde

that the best result was achieved with Cu-PS-ala (0.010 g) under reflux conditions in water.

We have chosen a variety of aldehydes and amines to expand the scope and simplicity of the polymer supported Cu(I) catalyst, Cu-PS-ala promoted three component coupling reaction under the optimized reaction conditions. Structurally diverse aldehydes and amines possessing a wide range of functional groups were employed as reaction substrates. The results are given in Table 3. Aromatic aldehydes with electron-donating groups reacted rapidly, while in case of aldehydes with electron-withdrawing groups reactivity decreased and required longer reaction times. In addition, heteroaromatic aldehydes also gave products (Table 3, entries 9 and 10). To extend the scope of the reaction, various cyclic and acyclic secondary amines such as piperidine, morpholine, pyrrolidine, and diethylamine were used and tolerated well (Table 3, entries 11, 12 and 13). To broaden the utility of our catalyst we tested this three-component coupling with a more challenging substrate aniline. After a prolonged reaction time, a

Table 3 One-pot synthesis of propargylamine derivatives from aldehydes, amines, and alkyne, by using Cu-PS-ala as the catalyst



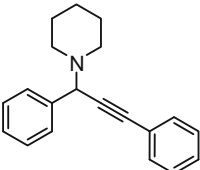


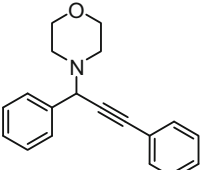
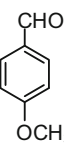

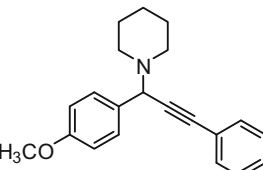
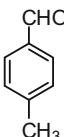

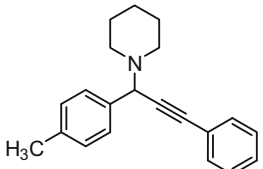
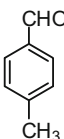

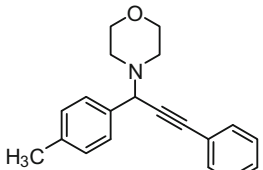
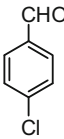

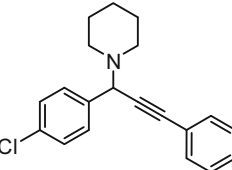
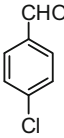

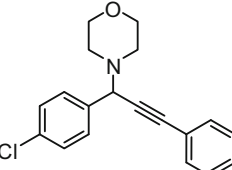
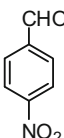

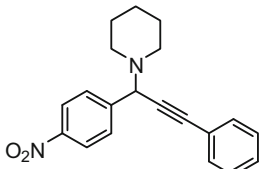
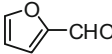

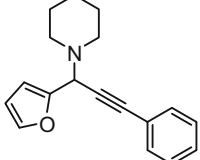
Entry	Aldehyde	Amine	Product	Time (h)	Yield (%) ^b
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2				6	91
3				6	94
4				6	92
5				6	89
6				6	88
7				6	85
8				16	-
9				6	87

Table 3 continued

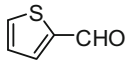

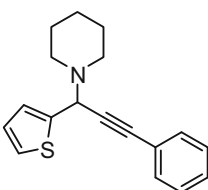
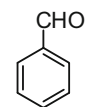

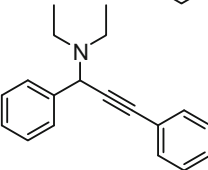
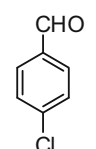

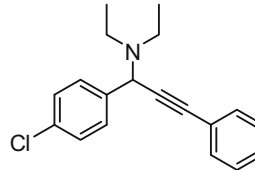
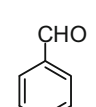

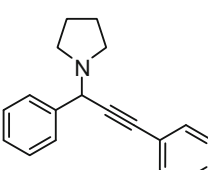
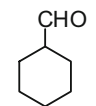

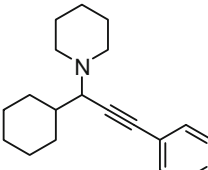
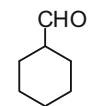

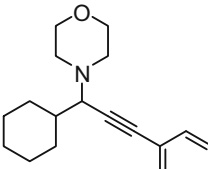

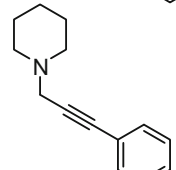

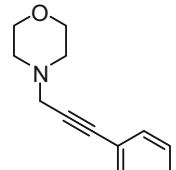

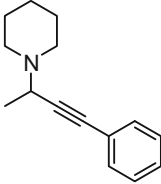
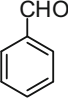
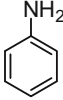
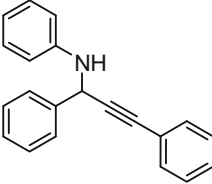
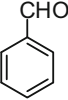

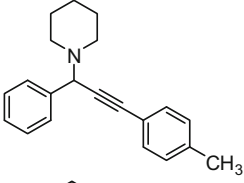
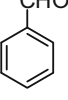

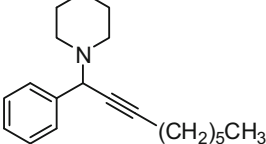
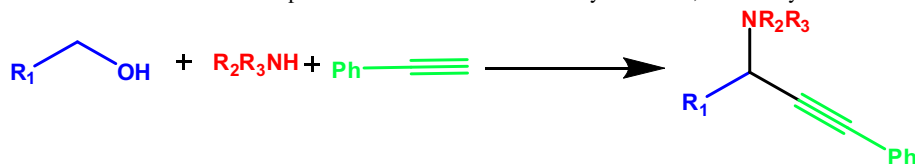
Entry	Aldehyde	Amine	Product	Time (h)	Yield (%) ^b
10				6	84
11				6	84
12				6	80
13				6	89
14				6	94
15				6	92
16	HCHO			6	93
17	HCHO			6	90

Table 3 continued

Entry	Aldehyde	Amine	Product	Time (h)	Yield (%) ^b
18	CH ₃ -CHO			6	90
19				16	49
20				6	94
21				16	67

Aldehyde (1 mmol), Amine (1.2 mmol), alkyne (1 mmol), catalyst (0.01 g), water (5 mL) under reflux conditions

^a Based on isolated yields

Table 4 Oxidative three-component reaction of various benzyl alcohols, secondary amines and phenylacetylene catalyzed by Cu(I)-PS-ala

Entry	R ₁	R ₂ R ₃ NH	Yield (%) ^a
1	Ph	Morpholine	76
2	4-MeC ₆ H ₄	Morpholine	55
3	4-ClC ₆ H ₄	Morpholine	79
4	4-MeC ₆ H ₄	Piperidine	58
5	4-ClC ₆ H ₄	Piperidine	80
6	4-ClC ₆ H ₄	Pyrolidine	66

Alcohols (1 mmol), amine (1.2 mmol), phenylacetylene (1.3 mmol), H₂O (5 mL), Cu-PS-ala (0.01 g), 6 h, reflux conditions, air

^a Isolated yield

moderate yield of the desired product was obtained (Table 3, entry 18). Under the same reaction conditions several alkynes such as tolyl-substituted ethyne and 1-octyne can be used to give the corresponding propargylamines. Toly-substituted ethyne gave good yields but in

case of aliphatic alkyne, moderate yield of the corresponding propargylamine was obtained after longer reaction time. The results indicated that both aromatic and aliphatic aldehydes were transformed to the corresponding propargylamines in excellent yields.

To the best of our knowledge, there is currently limited report of employing alcohols instead aldehyde in A^3 -coupling reactions. We have studied the catalytic activity of the polymer supported copper catalyst in the oxidative A^3 -coupling reactions of benzyl alcohols, phenylacetylene and secondary amines under aerobic conditions in aqueous media. The scope of various benzyl alcohols, amines and phenylacetylene was examined in the oxidative A^3 reaction (Table 4). The benzyl alcohol with an electron-withdrawing group gave a higher yield as compared to that with an electron donating group (Table 4, entries 2, 3 and 4). In addition, piperidine or pyrrolidine can also be applied in this A^3 -coupling (Table 4, entries 4, 5, and 6).

Probable reaction mechanism for the one-pot, three components synthesis of propargylamines catalyzed by polymer supported Cu(I)-PS-ala under heterogeneous conditions follow the well established earlier mechanism [45–47].

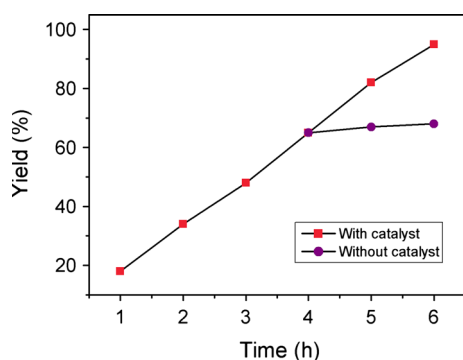


Fig. 4 Heterogeneity test in the A^3 coupling of benzaldehyde, phenylacetylene and piperidine

4 Test for Heterogeneity

To verify the heterogeneity of the catalyst 1 mmol benzaldehyde, 1 mmol phenylacetylene 1.2 mmol piperidine and 0.01 g catalyst were allowed to stir in 5 mL water under reflux conditions. This reaction was stopped at 4 h, and the yield was found to be 65 %. At this time, the catalyst was separated and the reaction was continued with the filtrate for next 2 h. After total 6 h the extent of yield was found to remain almost unchanged (Fig. 4). This information indicates that the reaction followed a heterogeneous pathway.

Further, the leaching of copper from the catalyst was analyzed from EDX and IR spectra of the used catalyst. FT-IR spectrum of the reused catalyst was quite similar to that of the fresh catalyst which indicates the heterogeneous nature of the catalyst (Fig. 5b). The amount of copper in the recycled catalyst was determined from AAS and found that it was remained almost unchanged.

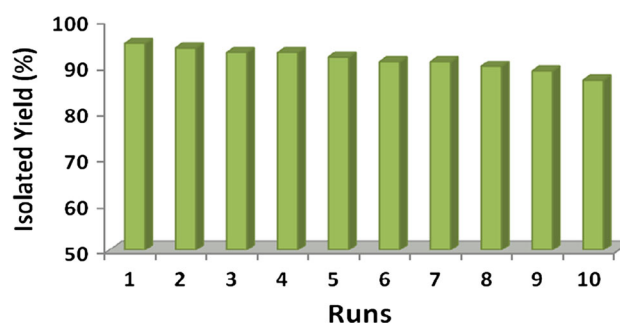


Fig. 6 Recycling experiment of Cu-PS-ala

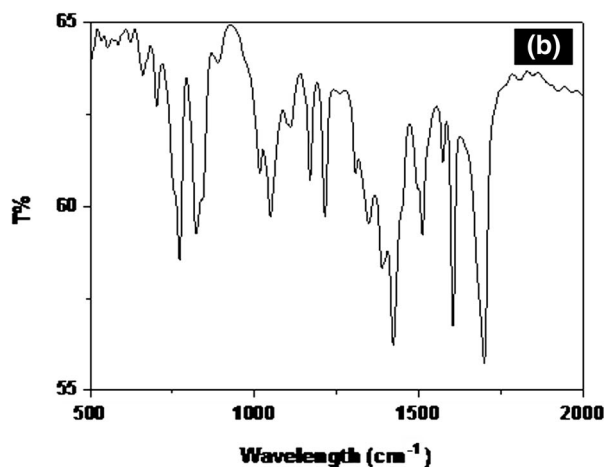
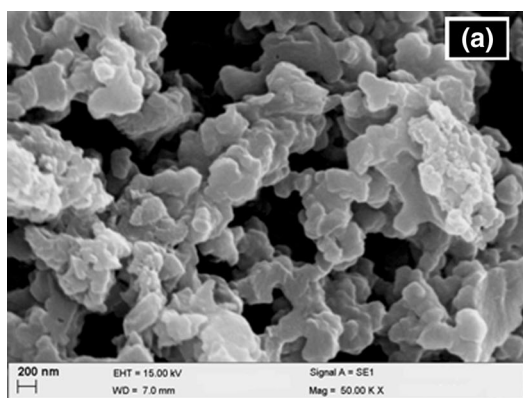


Fig. 5 SEM image (a) and FT-IR spectra (b) of recycled catalyst

Table 5 Comparison of catalytic activity of Cu-PS-ala with other literature reported methods

A ³ coupling	Catalyst	Reaction conditions	Time (h)/yield (%) [Ref.]
Benzaldehyde + phenylacetylene + piperidine	SiO ₂ -NH-Cu (2 mol%)	Solvent free, r.t	24/79 [48]
	Cu Zeolites (20 mg)	CH ₃ CN, 60 °C	25/35 [49]
	Zn dust (15 mol%)	CH ₃ CN, reflux	9/90 [21]
	Au nanoparticles, 10 mol%	CH ₃ CN, 75–80 °C	5/94 [20]
	Nanocrystalline CuO	Toluene, 90 °C	6/82 [50]
	NiCl ₂ (5 mol%)	Toluene, 111 °C	4/95 [51]
	Cu-PS-ala	Water, Reflux	6/95*
Benzyl alcohol + phenylacetylene + morpholine (oxidative A ³ -coupling)	Au@GO-IL	Water, 100 °C, air	18/90 [52]
	Cu-PS-ala	Water, Reflux, air	6/76*

* Present study

5 Recycling of Catalyst

After each reaction, the catalyst was separated from the reaction mixture by filtration. The recovered catalyst was thoroughly washed with methanol and diethyl ether to remove organic materials. Then the catalyst was dried at 55 °C for 4 h under vacuum to activate and to use in a new reaction. It was found that the recovery can be successfully achieved more than ten successive reaction runs (Fig. 6).

6 Comparative Study

In order to show the importance of this study, we compared the obtained result with the recently reported results. For this purpose, reaction between benzaldehyde, phenylacetylene and piperidine were chosen for comparison on the basis of reaction conditions and yields of the product (Table 5). It is worth mentioning that this method is simple, eco-friendly and more efficient compared to the other reported methods.

7 Conclusions

We have synthesized and characterized polystyrene supported Cu(I) catalyst and its catalytic activity was tested in A³-coupling reaction. We optimized the reaction in water under refluxing condition. Use of water as solvent implies that the reaction is eco-friendly. The reaction scope was broad when secondary aliphatic amines were used and some unprecedented propargylamines have been prepared. Besides the reported substrates, some explorative experiments indicated that the new catalyst worked with more challenging reactions such as aromatic amines, though the results in this case are only modest. This catalyst system shows excellent activity and good yields for a variety of propargylamine through aerobic oxidation of benzyl

alcohols followed by A³-coupling using different combinations of secondary amines and terminal alkynes. The simple protocol, broad scope of the substrates and recycling of the catalyst permitted us to look forward to a good future of this process in academic as well as in industry.

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