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A reusable polymer supported copper(I) complex for the C–N bond cross-coupling reaction

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ABSTRACT

The Ullmann coupling of amines with aryl iodide as well as arylboronic acids and N(H)-heterocycles with arylboronic acids has been carried out efficiently using PS-LCu(I) catalyst. The copper complex has been prepared and characterized by using scanning electron microscope (SEM), elemental analysis, atomic absorption spectroscopy (AAS), Thermo gravimetric analysis and spectrometric methods like Fourier transform infrared spectroscopy (FTIR). The effects of various parameters such as temperature, solvent and base on the reaction system were studied. The reusability experiments show that the catalyst can be used five times without much loss in the catalytic activity.

The synthesis of N-aryl amines and N-aryl heterocycles is an active area in organic synthesis due to their occurrence in biologically important natural products, pharmaceuticals and their applications in materials research [1,2]. Among the various strategies developed to date, the copper-catalyzed Ullmann reaction has proven to be the most convenient synthetic route for installing an N-aryl functionality [3,4]. In addition, Buchwald [5] and Hartwig [6,7] have reported on Pd mediated C–N bond formation. However, the cost of reagents and removal trace palladium from late stage synthetic intermediate are the major drawbacks of this method. Copper mediated amination and N-arylation is another choice of reaction for the production of these compounds due to cheap price and environmental friendly nature. However, copper-mediated couplings are still the reaction of choice for large and industrial scale formation of C–N bonds. The reaction system mostly employs an in situ generated catalyst from a copper source and highly efficient N/P-containing ligands such as amino acids, [8] diamines, [9] diimines, [10] pyridine, [11] oximephosphine oxides [12] and phosphoramidite [13]. In spite of the significant advances in this area, very few reports employing a structurally well defined and stable copper complex as a catalyst have been reported [14–16]. Chan and Lam established an efficient approach to *N*-arylimidazoles via $Cu(OAc)_2$-mediated coupling of imidazoles with readily available arylboronic acids [17]. Later, Collman and coworkers reported using Cu(II) complexes with nitrogen-chelating bidentate ligands in the coupling of imidazoles at room temperature [18]. Very recently, Xie and coworkers have shown the simple copper salt catalyzed coupling of imidazoles with arylboronic acids in protic solvent without any base [19]. Recently, calcium hydroxyapatite has been used as a heterogeneous support for transition metals, and the supported hydroxyapatite is used for organic transformations [20].

Nowadays solid-phase technique has gained much importance in this cross-coupling reaction. Homogeneous catalysts have some disadvantages, such as they may easily be destroyed during the course of the reaction and they cannot be easily recovered after the reaction for reuse. These disadvantages can be overcome by anchoring metal on suitable supports. There are many examples of heterogeneous catalysts for C–N coupling reactions and they are prepared by different approaches like encapsulation or immobilization of a catalytically active metal complex on solid supports [21].

In this present work, *N*-arylation reactions of various N(H)-heterocycles with arylboronic acids were carried out in methanol with PS-LCu(I) catalyst, without the need of any organic co-solvent, base or additives such as phase transfer catalysts. This catalyst was also effective in amination reactions of primary amines with various aryl halides as well as arylboronic acids. The experimental results reveal that the anchoring of the complex on a solid support not only exhibits improved catalyst activity, stability and selectivity of the product but also enables easy recovery and reuse of the catalyst.

The synthesis of the immobilized PS-LCu(I) catalyst illustrated in Scheme 1. It was readily prepared through a two-step procedure. Firstly the 0.2 g of chloromethylated polystyrene copolymer (2) treated with 0.979 g of β-alanine (1) to produce the corresponding polymer supported ligand (PS-L) in the presence of sodium carbonate (0.490 g) in *N,N*-dimethylformamide (DMF) to obtained a light brown polymer. The polymer was washed thoroughly with DMF to remove excess β-alanine and then with 1 M HCl to remove excess base. Finally, it

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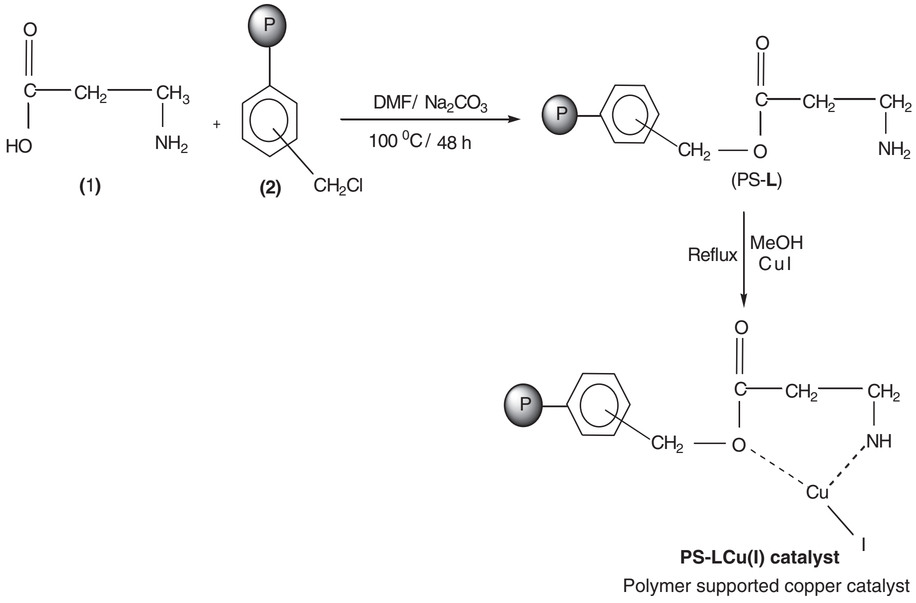

Scheme 1. Synthesis of the PS-LCu(I) catalyst.

was washed with double distilled water, dried and stored at room temperature for further use. Then the polymer anchored β-alanine ligand (1 g) in methanol (20 mL) was treated with 5 mL 1% (w/v) methanolic solution of copper iodide over a period of nearly 30 min under constant stirring. Then the reaction mixture was refluxed for 24 h. The green color copper complex thus formed was filtered and washed thoroughly with ethanol and dried in room temperature under vacuum.

The outline for the preparation of PS-LCu(I) catalyst is given in Scheme 1.

Table 1
Chemical composition of various compounds and PS-LCu(I) catalyst.

Compound	Color	C %	H %	Cl %	N %	Cu %
(1)	White	40.45	7.87	–	15.73	–
(2)	White	70.82	5.90	23.28	–	–
(PS-L)	White	70.24	7.32	–	6.83	–
PS-LCu(I)	Green	47.29	4.60	–	4.60	0.83 0.82[a]

[a] Used catalyst.

Due to insolubilities of the PS-LCu(I) catalyst in all common organic solvents, its structural investigation was limited to its physicochemical properties, chemical analysis, SEM, TGA and IR spectroscopic data. Table 1 provides the data of elemental analysis of different functionalized polymer and the complexes. Copper content in the catalysts determined by AAS suggests 0.83 wt.% Cu in the catalyst. The band at 676 cm^{-1} for –C–Cl stretching had disappeared in the polymer anchored ligand. A few new bands appeared, e.g. those at 3422 cm^{-1} along with bands at 1641 cm^{-1} showed the presence of free –NH_2 groups in the ligand. On complexation with copper, the frequency of free –NH_2 groups is reduced in intensity. In addition, the bands at 528 cm^{-1} may be assigned to the Cu–N [22] stretching vibration. The scanning electron micrographs of the PS-L and PS-LCu(I) catalyst clearly show the morphological change which occurred on the surface of polystyrene after loading of metal on it (Fig. 1A and B). Energy dispersive spectroscopy analysis of X-rays (EDAX) data for the PS-L and PS-LCu(I) catalyst is given in Fig. 2A and B. The EDX data also inform that the attachment of copper metal on the surface of the polymer matrix. Thermal stability of the complex was investigated using TGA-DTA at a heating rate of 10 °C /min in air over a temperature range of 30–600 °C.

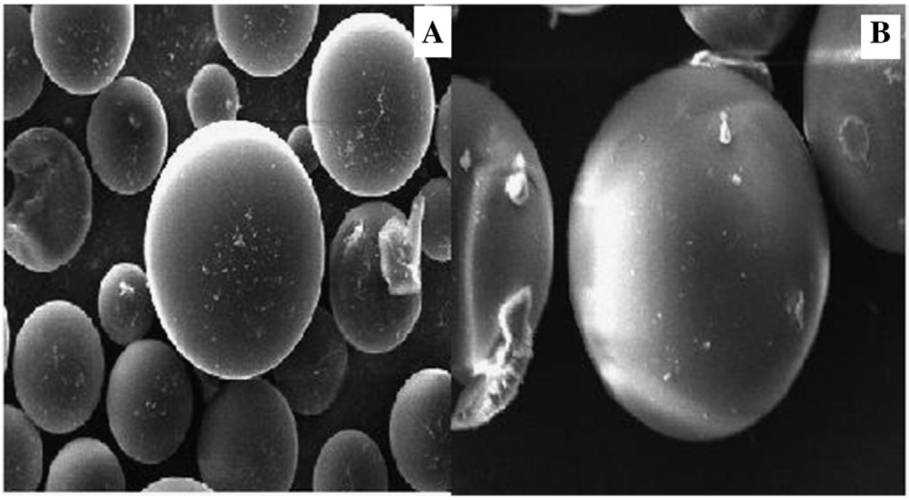

Fig. 1. FE SEM image of PS-L (1A) and PS-LCu(I) catalyst (1B).