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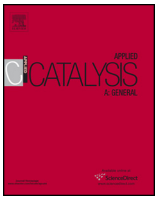

A reusable polystyrene-supported copper(II) catalytic system for *N*-arylation of indoles and Sonogashira coupling reactions in water

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ABSTRACT

A polymer–anchored Cu(II) *N*,*N*-dimethylethylenediamine complex was prepared and characterized by various techniques, including Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), atomic absorption spectroscopy (AAS), and thermogravimetric analysis (TGA). This heterogeneous Cu(II) catalyst, efficiently works for the *N*-arylation of indoles and Sonogashira coupling of terminal alkynes with aryl halides in aqueous medium. The effect of solvent, and base for the C—N, and C—C coupling reactions were reported. Further, the catalyst can be easily recovered quantitatively by simple filtration and reused up to four times without significant loss of its catalytic activity.

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1. Introduction

Transition metal-catalyzed aryl–nitrogen and aryl–carbon bond forming via cross-coupling reactions represent a powerful means for the preparation of various compounds, which have high utilities in biological, pharmaceutical, and material science [1–4]. Various strategies were developed for the *N*-arylation of heterocycles. The Ullmann-type coupling of aryl halides with nitrogen heterocycles represents a straightforward and inexpensive approach to *N*-aryl nitrogen heterocycles [5–7]. The efficiency of copper-catalyzed Ullmann reactions was improved by the correct choice of copper sources, bases, ligands, and other additives in the past few years; several mild and efficient methods were reported for the *N*-arylation of indoles [8–10]. Although this copper-catalyzed *N*-arylation of indoles or other heterocycles are highly efficient, the problem with homogeneous catalysis is the difficulty to separate catalyst from the reaction mixture. To overcome this, the development of a highly efficient and recyclable heterogeneous catalyst, by immobilization of catalytically active species, i.e., organometallic complexes, onto a solid support is essential [11]. Till date, many heterogeneous copper catalytic systems were developed for the cross-coupling reactions, such as Merrifield resin supported phenanthroline copper(I) complex [12], immobilized copper in organic–inorganic hybrid material [13], immobilized copper in MCM-41 [14], copper ferrite nanoparticles [15], $[Cu_{30}I_{16}(mtpmt)_{12}(\mu_{10}\text{-}S_4)]$ [16], Al_2O_3-supported Cu(II) catalyst [17], glycerol ingrained copper [18], nano copper oxide catalyst [19], and polymer supported copper(II) catalyst [20].

The Sonogashira-type coupling between terminal alkynes with aryl halides is commonly employed for the synthesis of molecules containing acetylenic moiety. Homogeneous copper catalysis has been reported for cross-coupling reactions [21,22]. Generally, various ligands are applied for effective coupling reactions. Recently, Bolm and co-workers have demonstrated that the coupling of aryl iodides and terminal alkynes could readily be performed by using a sub-loaded amount of $[Cu(DMEDA)_2]Cl_2{\cdot}H_2O$ [23,24]. Thus, compared to palladium-copper, the lone copper catalyst is more attractive and considered to be a better choice for the coupling of aryl halides and terminal alkynes [25–27]. The copper catalyst together with bis-nitrogen compounds such as 1,10-phenanthroline [28,29], and ethylenediamine [30] are effective catalytic systems for alkynylation of aryl halides. Recently, we have reported homogeneous thiopseudourea Pd(II) complex as catalyst for the cross-coupling reactions [31,32].

Polystyrene is also one of the most popular polymeric supports used in synthetic organic chemistry because of its low cost, ready availability, chemical inertness, and facile functionalization. In recent years, a variety of aqueous catalytic systems and polymer-supported metal catalysts for the C—C coupling reactions were reported [33–35]. From the standpoint of environmentally benign organic synthesis, the development of highly active and easily

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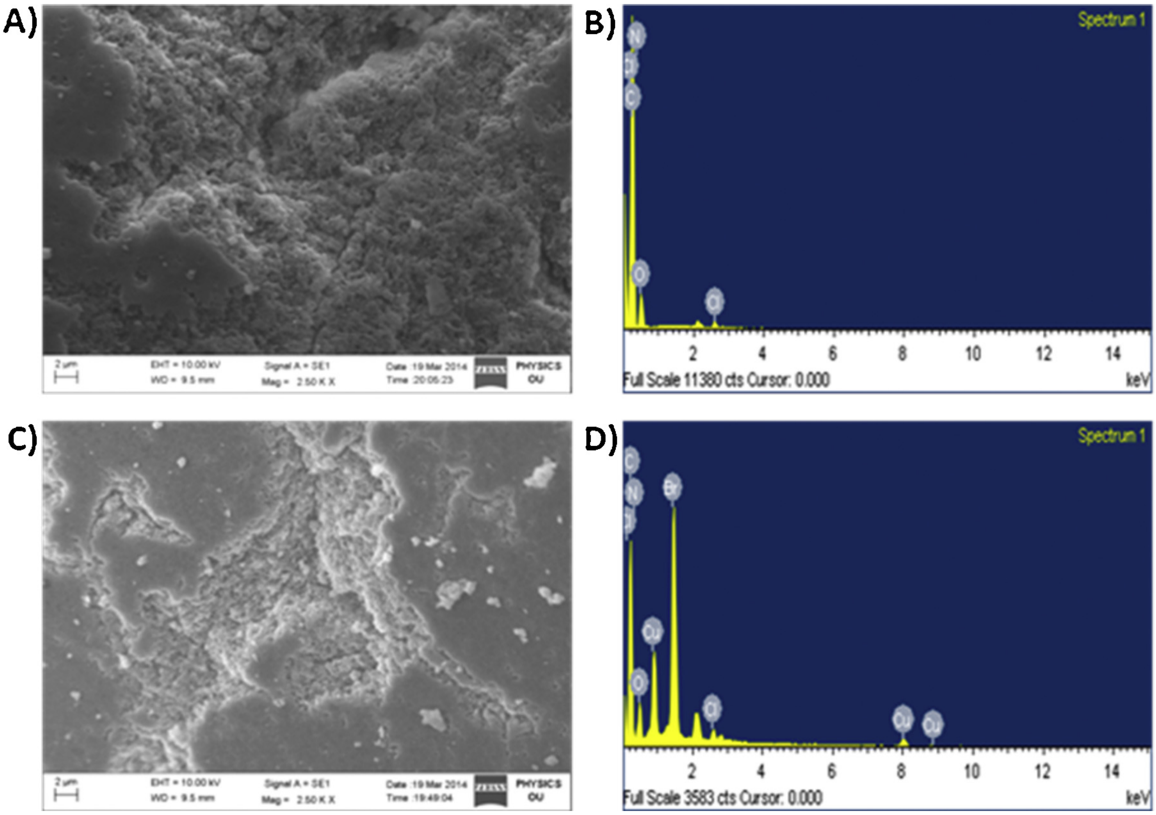

Fig. 1. SEM–EDX of polystyrene-supported *N*,*N*-dimethylethylenediamine ligand ((A) and (B)) and polystyrene-supported Cu(II) complex **3** ((C) and (D)).

reusable immobilized catalysts in aqueous media is of great interest to chemists.

However, to the best of our knowledge, no reports are available on *N*-arylation of indoles and Sonogashira coupling reactions catalyzed by polystyrene-supported Cu(II) complex. Herein, we report the synthesis and characterization of new polystyrene-supported copper complex catalyst and its application to cross-coupling reactions in water.

2. Experimental

All reagents and substrates were purchased from Aldrich. Chloromethylated polystyrene (5.5 mmol/g Cl loading, crosslinked with 5.5% DVB (divinylbenzene), particle size 16–50 mesh) was purchased from Aldrich Chemical Company. $CuBr_2$ was procured from Merck and used without further purification.

*2.1. Preparation of polymer-bound N,N-dimethylethylenediamine **2***

A polymeric ligand was prepared by the following procedure reported in the literature [36]. A 250 mL round-bottom flask equipped with a magnetic stirrer was charged with CH_3CN (100 mL). To this chloromethylated polystyrene (0.5 g, 2.25 mmol/Cl), *N*,*N*-dimethylethylenediamine (2.3 mL, 22.5 mmol) **1**, and NaI (14.9 mg, 0.1 mmol) were added and the mixture was refluxed for 48 h. The mixture was filtered and the residue was washed sequentially with CH_3CN (3 × 20 mL), 1:1 CH_3OH–1 M aq K_2CO_3 (3 × 20 mL), 1:1 CH_3OH–H_2O (3 × 20 mL), and Et_2O (3 × 10 mL), and then dried in an oven.

*2.2. Preparation of polystyrene-supported Cu(II) complex **3***

To the polystyrene-supported ligand EtOH (100 mL) was added and kept for 30 min. A solution of $CuBr_2$ (0.5 g) in EtOH (10 mL) was then added, and the mixture was kept at 50 °C for 6 h. The brown colored complex, impregnated with the metal, was filtered, washed thoroughly with EtOH (3 × 30 mL), and finally dried in vacuum at 70 °C for 24 h.

2.3. General experimental procedure for N-arylation reaction

The catalyst **3** (30 mg, 0.03 mmol of Cu), indole (1.0 mmol), aryl halides (1.2 mmol), K_2CO_3 (276 mg, 2 mmol), cetyltrimethylammonium bromide (36 mg, 0.1 mmol), and water (3 mL) were added to a reaction vessel. The mixture was stirred at 110 °C for 10 h, then cooled to room temperature and catalyst was filtered, the filtrate was extracted with ethyl acetate (3 × 10 mL). The combined organic layers were extracted with water, saturated brine solution, and dried over anhydrous Na_2SO_4. The organic layers were evaporated under reduced pressure and the resulting crude product was purified by column chromatography by using ethyl acetate/hexane (1:4) as eluent to give the corresponding N-substituted indoles.

2.4. General experimental procedure for Sonogashira cross-coupling reaction

In a typical reaction, a mixture of aryl halides (1.2 mmol), phenylacetylene (1.5 mmol), K_2CO_3 (276 mg, 2 mmol), cetyltrimethylammonium bromide (36 mg, 0.1 mmol), H_2O (3 mL) and catalyst **3** (30 mg, 0.03 mmol of Cu) was stirred at 110 °C for 10 h, then cooled to room temperature, filtered and washed with ethyl acetate (3 × 10 mL). The combined organic layers were extracted with water, saturated brine solution, and dried over anhydrous Na_2SO_4.

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