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SiO_2-functionalized melamine-pyridine group–supported $Cu(OAc)_2$ as an efficient heterogeneous and recyclable nanocatalyst for the *N*-arylation of amines through Ullmann coupling reactions

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ABSTRACT

This study reports a convenient approach to prepare SiO_2/CCPy/$Cu(OAc)_2$ as a novel nanocatalyst, in which melamine-bearing pyridine groups have functionalized SiO_2 and can act as a capping agent to stabilize Cu(II) species. The catalyst is characterized through Fourier transform infrared, transmission electron microscopy, field emission scanning electron microscopy (FESEM), Brunauer–Emmett–Teller (BET), thermogravimetric analysis, inductivity coupled plasma (ICP), and energy dispersive X-ray (EDX) techniques. Furthermore, its catalytic behavior is evaluated in the *N*-arylation of indole, imidazole, and aniline during Ullmann-type C–N coupling reactions. Moreover, it has been proved that the heterogeneous nanocatalyst can be feasibly recovered by filtration and reused in five consecutive reaction cycles without any noticeable loss of its catalytic activity. The results clarified that the devised method is advantageous from several perspectives, that is, low catalyst loading, high product yield, experimental simplicity, broad substrate scope, and short reaction time.

1. Introduction

Transition metal–based catalysis of C–N bond formation through cross-coupling reactions is a powerful method for preparing important compounds that are highly demanded in pharmaceutical, material, and chemical industries [1–4]. For this reason the development of convenient and effective catalyst synthesis methods has attracted much attention. Some studies have reported successful C–N coupling of nucleophilic aromatic groups with aryl halides by using catalysts based on palladium [2,4], nickel [3], and copper [5]. Lower cost of Cu-based catalysts has motivated their large-scale industrial applications. Therefore, synthetic chemists have attempted to focus on Cu-based catalysts and introduce milder methods for the synthesis of Cu-containing catalysts. One of the simplest and cheapest solutions of producing *N*-aryl nitrogen heterocycles is using the Ullmann-type coupling of aryl halides with nitrogen heterocycles [6–8]. Cu-based catalysts can catalyze Ullmann reactions, meantime their efficiencies can be promoted if their copper sources, ligands, bases, and other additives be selected, correctly.

Recently, several mild and efficient methods have been adopted for *N*-arylation of heterocyclic amines, for example, Refs. [9–11]. Although these reported methods of Cu-catalyzed *N*-arylation of amines are highly efficient, they rely on homogeneous catalysis and restrict separation of the catalysts from the reaction mixture. This issue can be overcome by developing recyclable and efficient heterogeneous catalysts through immobilization of catalytically

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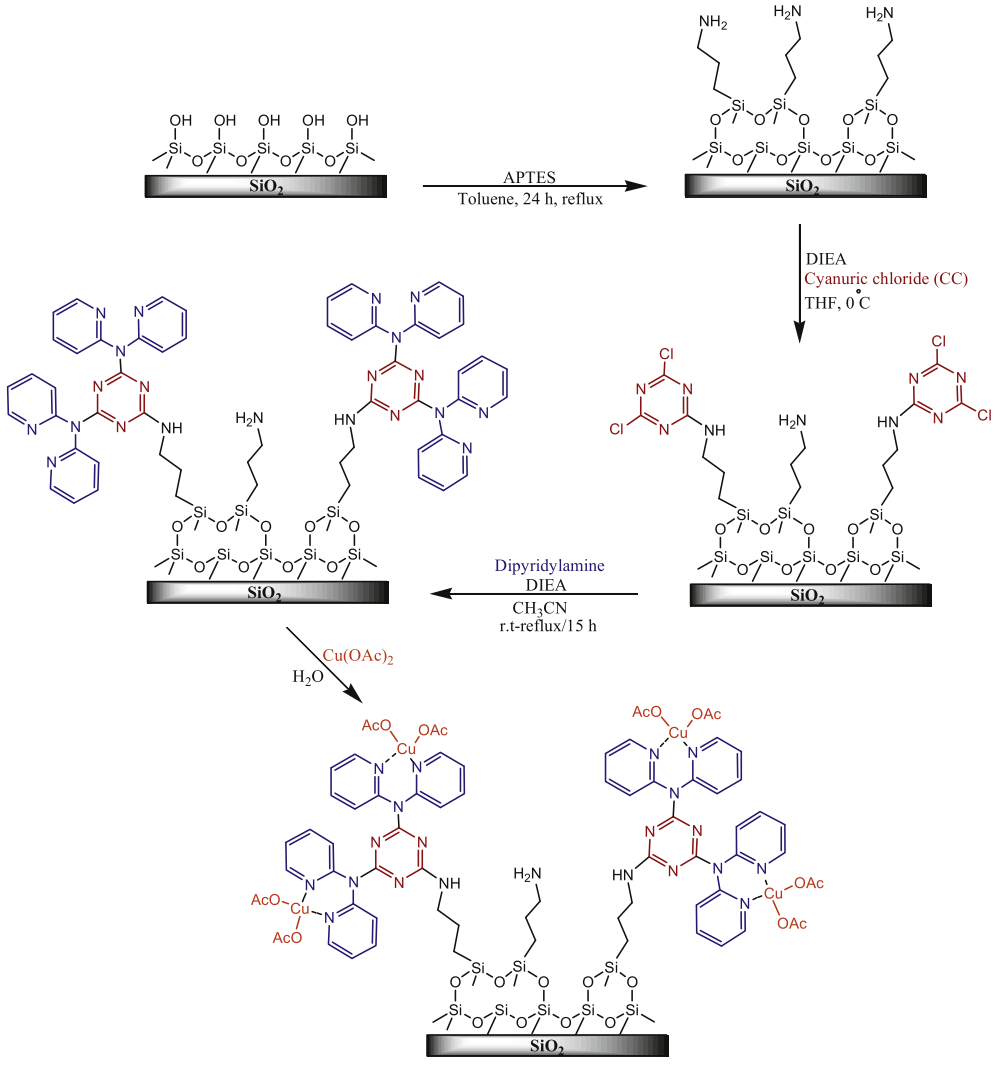
active species, for example, organometallic complexes, on a solid support [12]. In this respect, many heterogeneous Cu-based catalytic systems have been proposed to perform cross-coupling reactions. Some notable examples include Merrifield resin–supported phenanthroline copper(I) complex [13], Cu immobilized on organic–inorganic hybrid materials [14], Cu immobilized on MCM-41 [15], Cu ferrite nanoparticles (NPs) [16], $[Cu_{30}I_{16}(mtpmt)_{12}(\mu_{10}\text{-}S_4)]$ [17], Al_2O_3–supported Cu(II) catalyst [18], glycerol ingrained Cu [19], CuO nanocatalyst [20], and polymer-supported Cu(II) catalyst [21].

This study aims to prepare a silica-supported Cu catalyst. The major concern is that making silica-based hybrid materials with a high portion of organic functional groups is difficult because of the heterogenous distribution of active sites on silica particles. To achieve a homogeneous distribution of organic functional groups on silica-hybrid materials, several approaches, such as surface patterning, surface functionalization with dendrimers, and molecular/ion imprinting, have been reported [22–29]. As an alternative approach, our research group reported the design and preparation of an SBA-15/CCPy/Pd(II) nanocatalyst by grafting melamine-bearing pyridine groups on SBA-15 and depositing Pd NPs for stable catalysis of Suzuki–Miyaura reactions and *N*-arylation of indoles [[30], 4h]. Because the results of our previous works on synthetic application of nanocatalysts [31] were encouraging, herein we report a novel heterogeneous catalytic system based on $Cu(OAc)_2$ immobilization on melamine-bearing pyridine-modified SiO_2 particles (Scheme 1). This novel catalyst is air stable, can be reused, and shows excellent catalytic performance for C–N coupling in Ullmann reactions.

2. Experimental section

2.1. Preparation of SiO_2/CCPy

Thirty milliliters of anhydrous toluene, 1.0 g of SiO_2, and 0.36 g (3.0 mmol) of 3-aminoropropyl trimethoxysilane were added to a 100-mL round-bottom flask. The solution was refluxed under an inert atmosphere for 24 h, filtered, washed subsequently with toluene, dichloromethane, and methanol,



Scheme 1. Schematic diagram of SiO_2/CCPy/$Cu(OAc)_2$ fabrications.

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