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Short Communication

Copper nanoparticle decorated organically modified montmorillonite (OMMT): An efficient catalyst for the *N*-arylation of indoles and similar heterocycles

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ABSTRACT

A highly active ligand-free and efficient copper nanoparticle decorated OMMT catalyzed *N*-arylation of NH-heterocycles, i.e. indole, imidazole, benzimidazole, pyrrole, carbazole has been demonstrated.

1. Introduction

N-arylated heterocycles are important building blocks in organic synthesis as well as in pharmaceutical and agrochemical industries [1–3]. Often, transition metal catalysts have been employed for this purpose via C–N bond formation [4–7]. Over the past decades, Pd and Cu complexes have been introduced effectively for C–N coupling reactions [8–10]. Generally, Cu catalysts are preferred over the noble metal (often Pd) catalysts from the industrial, environmental and economic points of view [11–14]. Sometimes, traditional Cu catalysts require ligands such as 2-oxocyclohexanecarboxylate 2-amino-pyrimidine-4, 6-diol, and amino acids, which on scale up lead to the problem of waste disposal [15–17]. A number of copper catalysts have been reported over the last decades [18–23]. Both Cu(I) and Cu(II) nanoparticles (NPs) have been reported as catalysts for C–N coupling reactions [24,25]. Buchwald et al. reported bulky Cu_2O/4,7-dimethoxy-1,10-phenanthroline catalyst for coupling of imidazoles with arylbromide [13]. The process demands the use of harmful solvents (PrCN and NMP) and also the 4,7-dimethoxy-1,10-phenanthroline is a very expensive one. Nano-CuO has been found to be a highly active catalyst for *N*-arylation reaction; however the reaction is limited to activated aryliodide only [26]. Li et al. has reported a general and efficient method for the *N*-arylation of heterocycles using Cu_2O/1,10-phenanthroline catalyst system under solvent free condition [27]. Although there are several reports for *N*-arylation, still there are scopes for further development in terms of superior catalyst, simple and greener reaction conditions, versatility of the reaction, etc. Inspired by the activity of both Cu(I) and Cu(II) NPs in C–N coupling reaction, we have developed a Cu decorated nanoclay catalyst system for the C–N coupling of indole with arylbromide (Scheme 1). The developed catalyst has various advantages over the bare Cu(I) and Cu(II) NPs or the other Cu reagents like good recoverability, reusability, high activity, and short reaction time. Furthermore, imidazole, benzimidazole, pyrrole, carbazoles etc. can also be effectively *N*-arylated under the standard reaction condition.

2. Experimental

2.1. Materials and methods

Organically modified montmorillonite (OMMT) (octadecylamine modified, 25–30%), was purchased from Aldrich. All other chemicals were purchased from Merck and were used as received without further purification. X-ray diffraction (XRD) data were collected with a Rigaku X-ray diffractometer (Miniflex) using Cu Kα radiation. The morphology of the catalyst was analyzed by scanning electron microscopy (JSM-639LV, JEOL) and transmission electron microscopy (JEOL 2100×, 200 kV). NMR spectra were obtained from a JEOL JNM ECS 400 MHz spectrophotometer in $CDCl_3$ with TMS as the internal standard. A Nicolet (Impact 410) FT-IR spectrophotometer was used to record the

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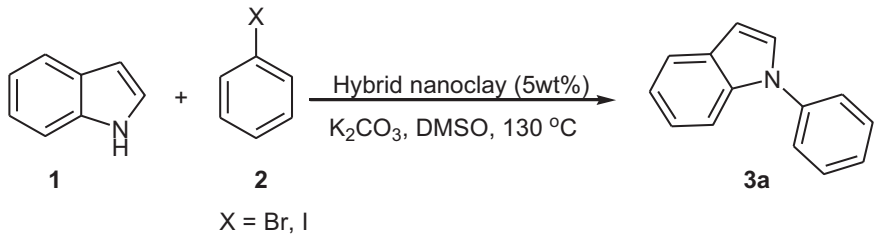
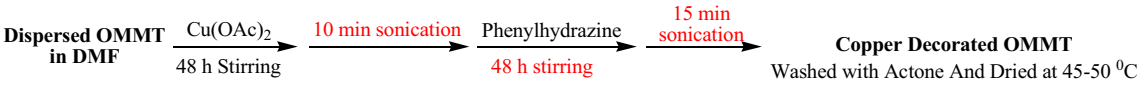


Scheme 1. *N*-arylation of indoles catalyzed by copper clay nanohybrid.



Scheme 2. Preparation of copper decorated OMMT.

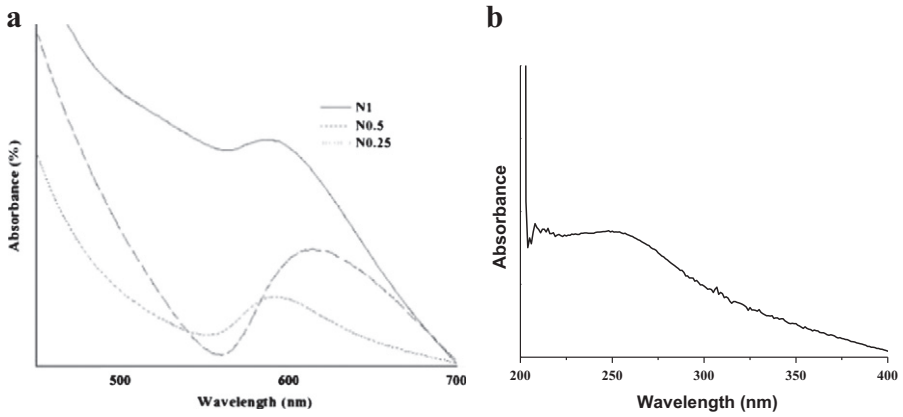


Fig. 1. UV–visible spectra of (a) N1, N0.5 and N0.25 nanohybrids and (b) OMMT + $Cu(OAc)_2$ without adding a reducing agent.

IR spectra of the samples in KBr pallets. Thermal stability of the catalyst was determined using TGA (SHIMADZU-TGA50 thermal analyzer). GC–MS was carried out on a gas chromatograph (Perkin Elmer, Claurus 600) equipped with thermal conductivity detector (TCD), and Elite wax column (30 mm in length and 0.25 mm in diameter). UV–visible spectroscopic analysis was done in a SHIMADZU UV-2550 spectrophotometer.

2.2. Preparation of the catalyst

1 g of OMMT was dispersed in 50 mL DMF and then sonicated for 20 min. To achieve theoretical copper loading in the clay/copper weight ratio of 1:1, 1:0.5 and 1:0.25 (coded as N1, N0.5 and N0.25, respectively), 3.16 g, 1.58 g and 0.792 g of $Cu(OAc)_2$ were dissolved in 30 mL, 15 mL and 8 mL DMF respectively. The $Cu(OAc)_2$ solutions were then added to the clay suspension and stirred for 24 h under ambient condition, followed by sonication for 10 min. The Cu precursor was then reduced in the presence of montmorillonite by adding $PhNHNH_2$ in the optimized mole ratio of 1:3 ($Cu(OAc)_2$/$PhNHNH_2$). The solution was stirred at room temperature for 48 h followed by sonication for 15 min. The suspension so obtained consisting of Cu NPs embedded in montmorillonite was centrifuged and washed repeatedly with acetone. The resulting solid phase was dried at 45–50 °C under vacuum (Scheme 2).

2.3. Typical procedure for the N-arylation of heterocycles

Cu-clay nanohybrid (N1, 5 wt.%) was added to a mixture of bromobenzene (1.2 mmol), imidazole (1 mmol) and K_2CO_3 (2 mmol) in DMSO and stirred at 130 °C. The reaction was monitored by thin layer

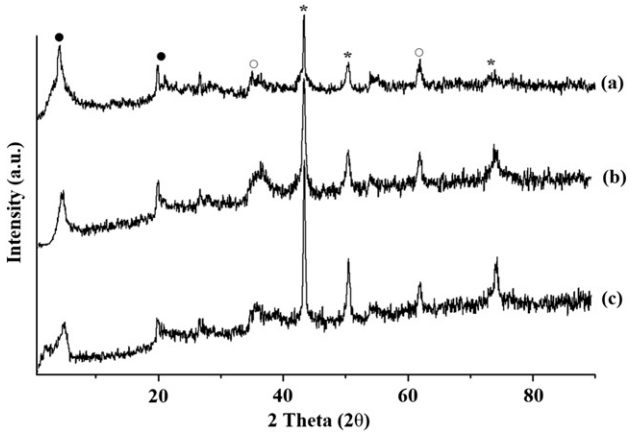


Fig. 2. XRD of the catalysts (a) N0.25, (b) N0.5 and (c) N1.