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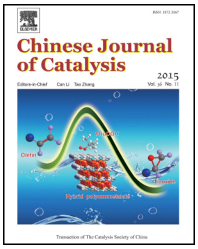

Article

Catalytic role of Cu(I) species in Cu_2O/CuI supported on MWCNTs in the oxidative amidation of aryl aldehydes with 2-aminopyridines

H. N. Hareesh [a], K. U. Minchitha [a], N. Nagaraju [b], N. Kathyayini [a,*]

[a] Department of Nanobiosciences, Centre for Emerging Technologies, Jain Global Campus, Jain University, Jakkasandra Post, Kanakapura Taluk, Ramanagara District–562112, Karnataka, India

[b] Catalysis Research Laboratory, Department of Chemistry, St. Joseph's College and Research Centre, 46 Langford Road, Shanthinagar Bengaluru–560027, Karnataka, India

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ABSTRACT

Cu_2O and CuI were supported on multiwalled carbon nanotubes (MWCNTs) using a wet impregnation method, and the resulting materials were fully characterized by powder X-ray diffraction, Fourier transform infrared spectroscopy, scanning electron microscopy with energy dispersive X-ray spectroscopy, transmission electron microscopy, and temperature-programmed desorption with ammonia analysis. The results of these experiments revealed that Cu_2O and CuI were deposited on the MWCNTs in the cubic and γ phases, respectively. These results also showed that the Cu-containing MWCNTs exhibited weak to strong electron-accepting (Lewis acidic) properties. The catalytic activities of these materials were studied for the synthesis of biologically significant *N*-(pyridin-2-yl)benzamides *via* the oxidative amidation of aryl aldehydes with 2-aminopyridines. The yields of the products were in the range 50%–95% with 100% selectivity. Notably, the CuI/MWCNT catalyst was much more effective than the Cu_2O/MWCNT catalyst with respect to the isolated yield of the product, although the latter of these two catalysts exhibited much better recyclability. A preferential interaction was observed between the polar nature of the acid-activated MWCNTs and the ionic Cu_2O compared with covalent CuI. The differences in these interactions had a significant impact on the rate of the nucleophilic attack of the amino group of 2-aminopyridine substrate on the carbonyl group of the aryl aldehyde.

1. Introduction

Research towards the development of solid, acid-base and redox catalysts for organic transformations under environmentally benign conditions is a particularly active area in heterogeneous catalysis [1,2]. There are several important advantages associated with heterogeneous catalysis, including simple experimental procedures, mild reaction conditions, and the generation of minimal chemical waste. Heterogeneous catalysts can be solid catalysts or catalysts supported on an inert or active material. In general, materials with a porous texture are preferred as solid supports for heterogeneous catalysts because their high surface area. In these cases, the catalytically active species are uniformly dispersed on the surface of the porous support. In several instances, supported materials have been shown to exhibit improved catalytic performance compared with the free catalysts, as well as offering significant reductions in the effective cost of the active catalyst [3–6].

Multiwalled carbon nanotubes (MWCNTs) are currently recognized as potential supports for catalytically active transi-

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* Corresponding author. Tel: +91-98-86506387; Fax: +91-80-27577211; E-mail: nkathyayini45@gmail.com

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tion metals/metal oxides, and the catalytic activities of these systems have been explored in a variety of different organic transformations for the synthesis of fine chemicals [7–10]. MWCNTs have high surface area because of their small size and cage-like mesoporous structures. Although pristine MWCNTs are chemically inert, they can be oxidized by an acid treatment process, which makes them chemically reactive through the formation of surface defects and oxofunctionalities [11]. These structural features of functionalized MWCNTs make them suitable for the uniform distribution of catalytically active species on their surface. Furthermore, the mesoporous structure of MWCNTs facilitates intraparticle mass transfer processes in the reaction medium, which promote chemical interactions between the reactant molecules [12,13]. Based on their unique properties, MWCNTs are considered to be good materials for the development of novel supported transition-metal oxide catalysts.

The amide bond is a key functionality in a wide range of important chemicals, including peptides, polymers, and pharmaceutical agents. Considerable research efforts have been directed towards the development of efficient and economically viable methods for the synthesis of amide bonds using different organic transformations [14,15]. Amides are traditionally synthesized by the reaction of activated carboxylic acid derivatives with an amine using an suitable coupling reagent, e.g., propylphosphonic anhydride (T3P), *N*,*N*,*N*′,*N*′-tetramethyl-O-(benzotriazol-1-yl)uronium tetrafluoroborate (TBTU), 1-bis (dimethylamino)methylene-1H-1,2,3-triazolo[4,5-*b*]pyridinium 3-oxide hexafluorophosphate (HATU) and dicyclohexylcarbodiimide (DCC). Surasani et al. [16] reported the synthesis of amides via a C–N coupling reactions using a palladium catalyst under homogeneous conditions. Kathiravan et al. [17] reported the synthesis of a series of amides from esters and amines using a Ru-complex. In a separate study, Porco and co-workers [18] reported the use of Zr(O-*t*-Bu)$_4$ in combination with an activator (e.g., 1-hydroy-7-azabenzotriazole (HOAt) or 1-hydroxybenzotriozole (HOBt)) for the formation of amides from esters and amines.

Cu-based catalysts are used extensively in organic transformations [19]. In recent years, considerable progress has been made towards the development of copper-catalyzed oxidative amidation reactions to provide access to a wide range of amide derivatives. For example, Li et al. [20] reported the oxidative amidation of aldehydes with amine hydrochlorides in the presence of a CuI-AgIO$_3$ catalyst using aqueous *tert*-butyl hydroperoxide as an oxidant. In a later study, Kathiravan et al. [17] described the Cu-catalyzed reactions of amides derived from 8-aminoquinoline with a variety of aryl halides for the synthesis of substituted amides. Primary, secondary, and tertiary amides can also be synthesized using copper sulfate or copper(I) oxide as a catalyst with *tert*-butyl hydroperoxide as an oxidant [21]. For example, Yang et al. [22] described the synthesis of *N*-(pyridin-2-yl)benzamides *via* the oxidative amidation of aryl aldehydes with 2-amino pyridines in the presence of CuI, while Diwakar et al. [23] reported the synthesis of the same derivatives from benzoyl chloride and 2-amino 5-bromopyridine in the presence of pyridine.

It is understood from the literature that the catalytic activity of Cu-based catalysts can be significantly influenced by the physical and chemical properties of the Cu species. Furthermore, consideration of the reported protocols reveals that the reagents and catalysts commonly used in the processes are generally expensive, toxic and non-recyclable and usually require tedious work up procedures for the separation of the product. Therefore, there is an urgent need to develop improved catalytic processes to overcome these issues and provide facile access to a wide range of *N*-(pyridin-2-yl)benzamides and their derivatives that could be used to support structure-activity relationship studies.

In this study, we have developed a series of catalysts for the oxidative amidation of benzaldehydes with 2-aminopyridines. These catalysts were prepared by depositing Cu$_2$O and CuI on MWCNTs using a wet impregnation method. This research was conducted based on the following considerations: (1) the importance of developing new and efficient heterogeneous catalysts for the synthesis of fine chemicals; (2) the application of copper-based catalysts in organic transformations, especially oxidative amidation reactions; (3) the biological application of *N*-(pyridin-2-yl)benzamides [23,24]; and (4) the significance of understanding the synergetic effect of the mesoporous structure of MWCNTs and the catalytically active transition-metal ion species deposited on their surfaces. The resulting binary composites of MWCNTs with Cu$_2$O and CuI were evaluated in terms of their surface properties and their catalytic activities towards the synthesis of *N*-(pyridin-2-yl)benzamides from aryl aldehydes and 2-amino pyridines *via* an oxidative amidation reaction.

2. Experimental

2.1. Materials

MWCNTs were purchased from Reinste Nano Ventures Private Ltd. and used as received. Concentrated H$_2$SO$_4$, concentrated HNO$_3$, Cu(OAc)$_2$, CuI, Cu$_2$O, and Na$_2$SO$_3$ were obtained from Merck. All of the chemicals used in the current study were purchased as the analytical grade and used without further purification.

2.2. Preparation of the catalysts

2.2.1. Acid activation of the MWCNTs

A portion of the MWCNTs (0.5 g) was immersed in a 1:3 (*v*/*v*) mixture of concentrated HNO$_3$ and concentrated H$_2$SO$_4$ (100 mL), and the resulting mixture was heated on a mantle at 80 °C for 6 h. The mixture was then cooled to room temperature before being carefully diluted with 2 L of deionized water. The resulting mixture was stirred overnight with a magnetic stirrer before being filtered to give a solid, which was washed with deionized water until the pH of the filtrate was neutral. The solid was then dried in air at 80 °C overnight to give the activated MWCNTs, which were stored in a desiccator prior to being used. This material will be referred here after as F/MWCNT (functionalized multiwalled carbon nanotubes).