

Article

Catalytic role of Cu(I) species in Cu₂O/CuI supported on MWCNTs in the oxidative amidation of aryl aldehydes with 2-aminopyridines

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ABSTRACT

Cu₂O 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 Cu2O 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 Cu₂O 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.

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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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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-AgIO₃ 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 Cu₂O 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 Cu₂O 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 H₂SO₄, concentrated HNO₃, Cu(OAc)₂, CuI, Cu₂O, and Na₂SO₃ 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 HNO₃ and concentrated H₂SO₄ (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).

2.2.2. Preparation of Cu₂O/MWCNT and CuI/MWCNT catalysts

MWCNTs containing 1, 5, 10, 15, 20, and 25 wt% Cu₂O or CuI were prepared using a wet impregnation method. Cu₂O was deposited on the MWCNTs by reducing Cu(OAc)₂ in the presence of Na₂SO₃, while CuI was impregnated on the MWCNTs using CuI. A typical procedure for the preparation of Cu₂O/MWCNT containing 20 wt% Cu₂O is as follows. A mixture of F/MWCNT (0.11 g), Cu(OAc)2 (0.084 g), and Na2SO3 (0.05 g) in deionized water (20 mL) was mixed for 2 h in a mortar and pestle to give a homogeneous mixture. The resulting catalyst was initially dried at 100 °C overnight and then heated at 200 °C for 3 h in a hot air oven. The catalyst was washed with a small volume (ca. 100 mL) of deionized water to remove any of the unwanted water soluble products formed during the chemical reaction between Cu(OAc)2 and Na2SO3, which can be represented as $2Cu(00CCH_3)_2 + Na_2SO_3 + 2H_2O \rightarrow Cu_2O + Na_2SO_4 +$ 4CH₃COOH.

The washed catalyst was then heated at 200 °C to remove any physically adsorbed water molecules. CuI/MWCNT containing 20 wt% CuI was prepared in a similar manner using by mixing F/MWCNT (0.16 g) and CuI (0.040 g) with deionized water (20 mL) in a mortar and pestle until a homogeneous mixture was obtained. The resulting paste was then subjected to the sequential drying, washing, and drying steps described above for the preparation of Cu₂O/MWCNT to give the desired CuI/MWCNT. MWCNTs containing different weight percentages of Cu₂O and CuI were prepared using the wet impregnation method and have been represented as 1%-25% Cu₂O/MWCNT and 1%-25% CuI/MWCNT, respectively.

2.3. Characterization of the catalysts

The F/MWCNT, 20% Cu₂O/MWCNT, and 20% CuI/MWCNT catalysts were characterized using a variety of different analytical techniques, including powder X-ray diffraction (PXRD), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS), transmission electron microscopy (TEM), and temperature-programmed desorption with ammonia (NH₃-TPD). These analyses were conducted to develop a better understanding of the physico-chemical properties of these catalysts because they showed a high level of catalytic activity towards the synthesis of N-(pyridin-2-yl)benzamides via the oxidative amidation of aryl aldehydes with 2-aminopyridines. PXRD patterns were recorded on a Panalytical X'Pert pro X-ray diffractometer using monochromated Cu K_{α} radiation ($\lambda = 0.154$ nm) in the 2θ range of 2°–70° with a scanning rate of 2°/min. The morphological characteristics and elemental compositions of the catalyst particles were investigated by SEM-EDS on a Model system. TEM images of the catalysts were recorded using a Tecnai transmission electron microscope at 200 kV. Samples of the catalyst were dispersed in ethanol under ultrasonic irradiation at a frequency of 43 kHz for 2 h at room temperature. A drop of the resulting suspension was placed on a carbon-coated copper grid to record the TEM images. NH₃-TPD experiments were measured using a Mayura Analytical instrument to determine the strength and concentration of the acidic sites on

the surfaces of the catalysts. For the NH₃-TPD measurements, a small sample (0.1 g) of the catalyst was initially degassed at 100 °C for 45 min under a stream of He. The material was then cooled to 50 °C and held at this temperature for 45 min under a steady stream of NH₃. During this time, the NH₃ molecules were adsorbed onto the acidic sites on the surface of the solid catalyst. Desorption studies were conducted by increasing the temperature from 50 to 550 °C in the presence of He.

2.4. Catalytic activity studies

The catalytic activities of the F/MWCNT, 1%–25% Cu₂O/MWCNT, and 1%–25% Cu_I/MWCNT catalysts were studied using the amidation reaction of benzaldehyde with 2-aminopyridine as a model reaction. It was noteworthy that only 20% Cu₂O/MWCNT and 20% Cu_I/MWCNT exhibited a good catalytic activity, hence only these two catalysts were checked for their catalytic activity in the amidation of substituted benzaldehydes with 2-aminopyridines. For this reason, these two catalysts were selected for further evaluation to assess the scope and limitation of the amidation reaction using a series of substituted benzaldehydes and 2-aminopyridines (Scheme 1).

In a typical procedure, a mixture of substituted benzaldehyde (5 mmol) (I), substituted 2-aminopyridine (4.5 mmol) (II), and catalyst (0.1 g) in THF (10 mL) was heated at 80 °C for 6 h in a round-bottom flask fitted with a water cooled condenser in the presence of air. The progress of the reaction was monitored by thin layer chromatography (TLC). Upon completion of the reaction, the mixture was cooled to room temperature and diluted with ethyl acetate (10 mL). The resulting suspension was then filtered to allow for the recovery of the solid catalyst. The filtrate was evaporated to dryness under vacuum to give a residue, which was purified by column chromatography over silica gel eluting with a 7:3 (ν/ν) mixture of *n*-hexane and ethyl acetate to give *N*-(pyridin-2-yl)benzamide (III).

All the products were fully characterized by melting point (M.P.), FT-IR, ¹H NMR, and LC-MS analysis. FT-IR spectra were recorded as KBr pellets on a Nicolet Model Impact 400D FT-IR spectrometer with 4 cm⁻¹ resolution. ¹H NMR spectra were recorded at 400 MHz on a Bruker Advance NMR spectrometer using CDCl₃ as solvent. TMS ($\delta = 0$) was used as an internal reference for the ¹H NMR analysis. Melting points were recorded in open capillary tubes and have been reported as the uncorrected values. LC-MS analysis was conducted on a Shimadzu QP 5000 LC-MS instrument.





3. Results and discussion

3.1. Characterization of catalysts

3.1.1. PXRD results

PXRD patterns of the F/MWCNT, 20% Cu₂O/MWCNT, and 20% Cu₁/MWCNT catalysts are shown in Fig. 1. The diffraction peaks at 25.96° and 43.49° were attributed to the (002) and (100) *hkl* planes of the graphite structure of the MWCNTs. The diffraction peaks at $2\theta = 28.41^{\circ}$, 36.28°, 42.06°, and 61.38° for the 20% Cu₂O/MWCNT were attributed to the (110), (111), (200), and (220) crystal planes of the cubic phase of Cu₂O (JCPDS 78-2076) [25–27]. The 20% Cu₁/MWCNT catalyst contained diffraction peaks at $2\theta = 25.60^{\circ}$, 29.48°, 42.30°, 49.96°, 61.23°, and 67.43°, which were attributed to the (111), (200), (220), (311), (400), and (331) planes of crystalline γ -CuI, respectively (JCPDS 00-083-115) [28,29].

3.1.2. FT-IR analysis

The FT-IR spectra of the F/MWCNT, 20% Cu₂O/MWCNT, and 20% CuI/MWCNT catalysts are shown in Fig. 2. The absorption bands at 3500 and 1628 cm-1 were assigned to hydroxyl (-OH) and C=C bonds, respectively, while the absorption band at 1733 cm⁻¹ was assigned to the carbonyl group (C=O) of the F/MWCNT. Functionalization is an important step for the chemical activation of carbon nanotubes because the resulting functional groups provide a platform for the formation of strong binding interactions between the surface of the support and the active metal species [30]. However, the absorption bands observed for the 20% CuI/MWCNT and 20% Cu2O/ MWCNT catalysts were more intense than those observed for the F/MWCNT. For example, the 20% Cu₂O/MWCNT catalyst exhibited IR bands around 622 cm⁻¹, which is the characteristic of the lattice vibrations of the Cu₂O [31] present on the surface of the carbon nanotubes. Furthermore, the FT-IR spectrum of the 20% CuI/MWCNT catalyst contained absorption bands at 611 and 495 cm⁻¹, which are the two characteristic vibrations of γ -CuI [32]. The results of these FT-IR studies therefore confirm that the Cu species have been successfully deposited on the MWCNTs.



Fig. 1. PXRD patterns of the F/MWCNT (1), 20% Cu₂O/MWCNT (2), and 20% Cul/MWCNT (3) catalysts.



Fig. 2. FT-IR spectra of the F/MWCNT (1), 20% Cu₂O/MWCNT (2), and 20% Cul/MWCNT (3) catalysts.

3.1.3. SEM-EDS results

The SEM images and EDS profiles of the F/MWCNT, 20% Cu₂O/MWCNT, and 20% CuI/MWCNT catalysts are shown in Fig. 3. These SEM images revealed that there were significant changes in the morphological characteristics of the F/MWCNT following the deposition of copper oxide/iodide. In these catalytic materials, the surfaces of the tubular structures of the F/MWCNT were associated with different sized particles, which could be attributed to the copper oxide/iodide particles. Taken together with their EDS profiles, the SEM images of these materials allowed for the determination of the atomic percentages of carbon, oxygen/iodide, and copper.



Fig. 3. SEM-EDS images of the F/MWCNT (a), 20% $\rm Cu_2O/MWCNT$ (b), and 20% CuI/MWCNT (c) catalysts.

3.1.4. TEM analysis

TEM images of the 20% Cu₂O/MWCNT and 20% Cu₁/ MWCNT catalysts are shown in Fig. 4. The TEM image of the 20% Cu₂O/MWCNT catalyst in Fig. 4(a) clearly shows that Cu₂O nanoparticles were deposited on the inner and outer walls of the MWCNTs. The high resolution TEM image of the 20% Cu₂O/MWCNT catalyst in Fig. 4(b) clearly indicates that the Cu₂O nanoparticles were also present within the tubular structure of the MWCNTs. In the case of 20% Cu₁/MWCNT, agglomerated Cu₁ particles were observed together with the tubular structure of the MWCNTs (Fig. 4(c)).

3.1.5. NH3-TPD

NH₃ can interact with the surface of a material by physisorption or chemisorption processes through the lone pair of electrons on its nitrogen atom. The strength of this interaction depends on the electron accepting properties (i.e., Lewis acidity) of the interacting species with strongly electron accepting species forming stronger interaction with ammonia molecules. It has been reported that NH₃ desorption peaks in the range of 50–250 °C correspond to weakly acidic sites on the surface of the catalyst, while those in the range of 250–350 °C are indicative of moderately/strongly acidic sites. Furthermore, NH₃ desorption peaks above 350 °C correspond to strongly acidic sites on the surface of the catalyst [33]. The NH₃ desorption peak area can therefore be used to represent the concentration of the acidic sites on the surface of a catalyst.

The NH₃-TPD profiles of the F/MWCNT, 20% Cu₂O/MWCNT, and 20% CuI/MWCNT catalysts are shown in Fig. 5. The F/MWCNT catalyst contained two desorption peaks in the ranges of 100–300 and 300–550 °C, which indicated the presence of weakly acidic sites, as well as a low concentration of moderately/strongly acidic sites. In contrast, the 20% Cu₂O/ MWCNT catalyst contained desorption peaks in the ranges of 150–300 and 300–450 °C, which indicated the presence of high concentrations of both weakly and moderately strong acidic sites. In the case of 20% CuI/MWCNT, the NH₃-TPD profile contained a strong desorption peak in the range of 100–200 °C, which indicated a high concentration of weakly acidic sites. The 20% CuI/MWCNT catalyst also contained a broad desorption peak in the range of 350–500 °C, which indicated a low con-



Fig. 5. TPD-NH $_3$ profiles of the F/MWCNT (1), 20% Cu $_2$ O/MWCNT (2), and 20% CuI/MWCNT (3) catalysts.

centration of strongly acids sites. The differences in the NH_3 -TPD profiles of the three different catalysts therefore indicated that there were significant differences in their electron pair accepting properties.

Thus, the data provided above clearly demonstrate that the Cu(I) species had been successfully deposited on the surface of the carbon nanotube support as the cubic phases of Cu₂O and γ -CuI. Notably, these results clearly show that these materials exhibit different electron accepting properties.

3.2. Catalytic activity studies

The catalytic activities of the F/MWCNT, 20% Cu₂O/ MWCNT, and 20% CuI/MWCNT catalysts were investigated towards the reaction of benzaldehyde with 2-aminopyridine in tetrahydrofuran (THF) at 80 °C over 6 h. The activities of Cu₂O and CuI were also investigated for the same reaction under the same conditions (Table 1). The results of these screening experiments revealed that F/MWCNT did not exhibit any catalytic activity towards this reaction (Table 1, entry 5). In contrast, the Cu₂O/MWCNT and CuI/MWCNT materials both exhibited catalytic activity towards the reaction, with the isolated yield increasing as the weight percentage of Cu₂O and CuI deposited on the MWCNTs increased. The isolated yield of the desired prod-



Fig. 4. TEM images of 20% Cu₂O/MWCNT (a, b) and 20% CuI/MWCNT (c) catalysts.

Table 1

Isolated percentage yield of N-(pyridin-2-yl)benzamide with different catalysts used.

Entry	Catalyst	Quantity of catalyst (g)	Yield (%)		
1	Cu ₂ O	0.02	20		
2	CuI	0.02	43		
3	Cu ₂ O	0.10	45		
4	CuI	0.10	85		
5	F/MWCNT	0.10	NC		
6	1% Cu ₂ O/MWCNT	0.10	NC		
7	5% Cu ₂ O/MWCNT	0.10	8		
8	10% Cu ₂ O/MWCNT	0.10	25		
9	15% Cu ₂ O/MWCNT	0.10	40		
10	20% Cu ₂ O/MWCNT	0.10	85		
11	25% Cu ₂ O/MWCNT	0.10	85		
12	1% CuI/MWCNT	0.10	10		
13	5% CuI /MWCNT	0.10	28		
14	10% CuI/MWCNT	0.10	42		
15	15% CuI/MWCNT	0.10	65		
16	20% CuI/MWCNT	0.10	93		
17	25% CuI/MWCNT	0.10	93		

Reaction conditions: benzaldehyde 5 mmol, 2-aminopyridine 4.5 mmol, THF 10 mL, 80 °C, 6 h.

NC: No conversion.

uct reached a plateau in both cases at 20% loading (Table1, entries 10 and 16). Notably, the Cu₂O and CuI catalysts exhibited 100% selectivity for the expected N-(pyridin-2-yl)benzamide products, with low isolated yields (Table 1, entries 1-4). The 20% Cu₂O/MWCNT and 20% CuI/MWCNT catalysts afforded isolated yields that were significantly higher than those achieved with pure Cu2O and CuI respectively (85% versus 45% and 93% versus 85%, respectively). These observations indicated that the support was playing an important role in enhancing the catalytic activities of Cu₂O and CuI. The recyclability of these catalysts was also investigated and the results revealed that the 20% Cu₂O/MWCNT catalyst could be recycled up to four times without any discernible decrease in its catalytic activity. In contrast, the 20% CuI/MWCNT catalyst showed a significant reduction in its catalytic activity after each cycle. For example, the 20% CuI/MWCNT catalyst gave an isolated yield of only 25% after its fourth cycle. From these experimental analysis, it may be inferred that copper compounds exhibit catalytic activity towards the oxidative amidation of benzaldehydes with 2-aminopyridines and that their catalytic activities can be enhanced by depositing these materials on an MWCNT support. A review of recent reports from the literature revealed several studies pertaining to the use of copper compounds as homogenous catalysts in oxidative amidation reactions [20,22,34]. For example, CuI, CuBr, CuCl, and Cu(OAc)₂ have been used as catalysts in the presence of air as an oxidizing agent under homogeneous conditions to obtain amidation products with yields in the range of 5%-45% [22]. Furthermore, the use of CuBr2 and Cu(OTf)2 in the presence of a surfactant with I2 as an oxidizing agent has been used to synthesize amides with yields in the range of 80%-93% [34]. However, to the best of our knowledge, there have been no reports in the literature concerning the use of heterogeneous catalysts for

the oxidative amidation of aryl aldehydes with 2-amino pyridines. In this study, we have investigated the amidation of a series of benzaldehydes with 2-amino pyridines under heterogeneous conditions using air as an oxidizing agent and obtained the corresponding products in isolated yields of 85%–93%. There are several important advantages to our newly developed process, including the use of an environmentally benign oxidizing agent, a clean protocol for the isolation of the product, and the reusability of the catalyst.

It is well known that the catalytic yield in heterogeneous catalytic process depends on the relative adsorption and desorption of the reactants and products from the catalyst, respectively. With this in mind, we have conducted several experiments and made an attempt to understand the electron accepting properties of Cu₂O and CuI supported on MWCNTs on the outcome of this oxidative amidation reaction.

The higher activity of the 20% CuI/MWCNT catalyst compared with the 20% Cu₂O/MWCNT catalyst can be explained as follows. CuI is more covalent in character than Cu₂O. This difference in the covalent properties of these materials can be attributed to the higher polarizability of the large iodide ion (206 pm) compared with the oxide ion (126 pm). Furthermore, Cu₂O can interact more effectively with the polar groups present on the functionalized carbon nanotubes than CuI because it can form polar-polar interactions much more readily than non-polar-polar interactions. The formation of strong interactions between Cu₂O and the MWCNT support would lead to the deposition of Cu₂O not only on the surface of the support but also throughout the bulk of the support. In contrast, most of the CuI would be deposited on the surface of the support because of its relatively weak interaction with the polar groups present on the functionalized carbon nanotubes. Most of this material would therefore be available for the reactants, leading to the observed higher level of catalytic activity. Furthermore, the CuI catalyst would leach much more readily from the support into the reaction because of its weak interactions with the functional groups on the surface of the support owing to its non-polar nature. This would explain the observed decrease in the catalytic activity of this material when it was recycled and reused in subsequent runs.

3.3. Generality of the catalytic activity of the Cu₂O/MWCNT

In light of the reusability of the 20% Cu₂O/MWCNT catalyst, we conducted a series of additional experiments to assess the scope of this catalyst using a variety of substituted benzaldehydes and 2-aminopyridines. The aromatic ring of the benzaldehyde was decorated with a variety of different functional groups, including 2-C₂H₅, 4-C₃H₇, 4-OC₂H₅, 4-F, 4-Cl, 4-CN, or 4-N(CH₃)₂, while the 2-aminopyridine was substituted with a 4-CH₃ or 4,6-(CH₃)₂ group.

The nature of the substituent on the aromatic ring of the benzaldehyde had a significant effect on the yield of the amidation reaction. For example, the presence of an electron-donating substituent (i.e., $4-C_2H_5$, $4-C_3H_7$, or $4-OC_2H_5$) on the aromatic ring of benzaldehyde gave much higher yields of the product than the presence of an electron-withdrawing substit-

uent (i.e., 4-F, 4-Cl, and 4-CN) (Table 2).

A plausible reaction mechanism for the oxidative amidation of the aryl aldehydes with 2-aminopyridines in the presence of a copper-based catalyst is shown in Scheme 2. According to this mechanism, the lone pair of electrons on the nitrogen atom of the 2-amino pyridine substrate would coordinate to a Cu atom on the MWCNTs to form intermediate **A**. The subsequent combination of an aryl aldehyde with **A** would lead to the formation of the complex intermediate **B** *via* the nucleophilic attack of the amino group of the 2-aminopyridine on the carbonyl group of the aryl aldehyde. This step would be followed by a proton transfer to produce hemiaminal **C**, which would undergo an oxidation reaction to give the desired *N*-(pyridin-2-yl)benzamide product **D** with the regeneration of the catalyst. The mechanism proposed above is consistent with the electron-accepting properties of the Cu species and the observed NH₃-TPD results. This mechanism is also consistent with the observed variations in the reactivity of the benzaldehyde substrate depending on the electron-withdrawing/donating properties of the substituent on the aromatic nucleus. The precise nature of the substituent would have a significant influence on the rate of the nucleophilic attack of the 2-aminopyridine on the carbonyl carbon of the aldehyde. Similarly, given that the copper in CuI is less electropositive than the Cu in Cu₂O, it would interact to a much lesser extent with the lone pair of electrons on the N atom of the pyridine ring. The lone pair of electrons on the N atom of the amino group (–NH₂) would therefore be more available for the nucleophilic attack of the

Table 2

Catalytic activities of the 20% Cu₂O/MWCNT and 20% CuI/MWCNT catalysts towards the oxidative amidation reactions of a series of different aryl aldehydes with substituted 2-amino pyridines.

Entry	R ₁	R ₂	Product	Yield (%)		Entwr	D	D	Droduct	Yield (%)	
				Cu ₂ O	CuI	Епиу	K 1	K 2	Product	Cu ₂ O	CuI
1	Н	Н		85	93	10	2-(C ₂ H ₅)	4-CH ₃	O N N	85	95
2	2-(C ₂ H ₅)	Н	C H N	81	91	11	4-C(CH ₃) ₂	4-CH ₃	O H H H	80	86
3	4-C(CH ₃) ₂	Н	O M M M N	80	85	12	4-0C ₂ H ₅	4-CH ₃	N N N	79	85
4	4-F	Н	F N N	64	58	13	4-F	4-CH ₃	F H H	63	70
5	4-Cl	Н	CI N H N	70	75	14	4-Cl	4-CH3		65	72
6	4-0C ₂ H ₅	Н	N N	82	86	15	4-CN	4-CH ₃	NC NC N	50	63
7	4-N(CH ₃)2	Н	N N N N N N N N N N N N N N N N N	65	72	16	4-N(CH ₃) ₂	4-CH ₃		60	69
8	4-CN	Н	NC	52	58	17	4-N(CH ₃) ₂	4,6-CH ₃	O H H H	58	66
9	Н	4-CH ₃		84	92						



Scheme 2. Plausible reaction mechanism for synthesis of *N*-(pyridin-2-yl)benzamides in the presence of the Cu(1)/MWCNT catalyst.

carbonyl carbon atom of the aldehyde, which would explain the higher product yield observed for the 20% CuI/MWCNT catalyst versus the 20% Cu₂O/MWCNT catalyst.

3.4. Spectroscopic data of N-(pyridin-2-yl)benzamides

N-(Pyridin-2-yl)benzamide* (Table 2, entry 1): Yellow solid. M.P.: 80–82 °C; IR (cm⁻¹): 3640, 3346, 1655, 1599, 1534, 1440, 1322, 1260, 750, 714; ¹H NMR (400 MHz, DMSO-*d*₆): δ 8.98 (br s, 1H), 8.42 (d, *J* = 8.4 Hz, 1H), 8.24 (d, *J* = 3.2 Hz, 1H), 7.95 (d, *J* = 7.2 Hz, 2H), 7.79–7.75 (m, 1H), 7.58 (d, *J* = 1.7 Hz, 1H), 7.54–7.47 (m, 2H), 7.08–7.05 (m, 1H); MS (EI) *m/z*: 199 [M+H]⁺.

2-Ethyl-*N*-(pyridin-2-yl)benzamide* (Table 2, entry 2): Pale yellow solid. M.P.: 116–118 °C; IR (cm⁻¹): 3438, 3188, 2762, 2715, 2490, 1603, 1542, 1465, 1394, 1370, 1285, 1139, 997, 806; ¹H NMR (400 MHz, DMSO-*d*₆): δ 9.50 (br s, 1H), 8.16–8.14 (m, 1H), 7.91 (s, 1H), 7.51 (d, *J* = 1.64 Hz, 1H), 7.40–7.41 (m, 1H), 7.39 (d, *J* = 2.4 Hz, 2H), 7.35(m, 2H), 3.10 (q, *J* = 6.9 Hz, 2H), 1.35 (t, *J* = 6.98 Hz, 3H); MS (EI) *m/z*: 227.1 [M+H]⁺.

4-Isopropyl-*N*-(pyridin-2-yl)benzamide** (Table 2, entry 3): Yellow solid. M.P.: 124–126 °C; IR (cm⁻¹): 3746, 3166, 1905, 1666, 1599, 1518, 1454, 1387, 1289, 1158, 1112, 859; ¹H NMR (400 MHz, DMSO-*d*₆): δ 9.11 (br s, 1H), 8.5 (d, *J* = 2.2 Hz, 1H), 8.35–8.29 (m, 2H), 8.21 (d, *J* = 3.2 Hz, 1H), 7.82 (d, *J* = 6.8 Hz, 1H), 7.77–7.72 (m, 2H), 7.68–7.63 (m, 1H), 3.12 (s, 1H), 1.53 (s, 6H); MS (EI) *m/z*: 241 [M+H]⁺.

4-Fluoro-*N*-(pyridin-2-yl)benzamide* (Table 2, entry 4): Yellow solid. M.P.: 106–109 °C; IR (cm⁻¹): 3343, 3052, 2923, 1655, 1599, 1532, 1438, 1320, 1075, 1027, 750; ¹H NMR (400 MHz, DMSO-*d*₆): δ 9.17 (br s, 1H), 8.29–8.25 (m, 2H), 8.16 (d, *J* = 8.2 Hz, 1H), 7.95 (d, *J* = 7.8 Hz, 1H), 7.89–7.85 (m, 2H), 7.63–7.58 (m, 1H), 7.68–7.63 (m, 1H); MS (EI) *m/z*: 217 [M+H]⁺.

4-Chloro-*N*-(pyridin-2-yl)benzamide* (Table 2, entry 5): Off-white solid. M.P.: 115–118 °C; IR (cm⁻¹): 3340, 3004, 2839, 1666, 1599, 1532, 1461, 1416, 1289, 1253, 1211, 1024, 849, 806; ¹H NMR (400 MHz, DMSO-*d*₆): δ 8.90 (br s, 1H), 8.35 (d, *J* = 6.2 Hz, 1H), 8.33–8.31 (m, 2H), 8.21 (d, *J* = 5.4 Hz, 1H), 7.92–7.88 (m, 2H), 7.78–7.72 (m, 1H), 7.23–7.19 (m, 1H). MS (EI) *m/z*: 233 [M+H]⁺.

4-Ethoxy-*N*-(pyridin-2-yl)benzamide* (Table 2, entry 6): Yellow solid. M.P.: 130–132 °C; IR (cm⁻¹): 3438, 3180, 2966, 2930, 2874, 1680, 1613, 1573, 1532, 1412, 1278, 1166, 1094, 997, 884, 816; ¹H NMR (400 MHz, DMSO-*d*₆): δ 8.90 (br s, 1H), 8.33–8.21 (m, 2H), 8.30 (d, *J* = 4.4 Hz, 1H) 8.14–8.10 (m, 1H), 7.96–7.95 (m, 2H), 7.84 (d, *J* = 5.6 Hz, 1H), 7.69–7.64 (m, 1H), 2.92 (q, *J* = 7.2 Hz, 2H), 1.31 (t, *J* = 7.0 Hz, 3H); MS (EI) *m/z*: 243 [M+H]⁺.

4-(Dimethylamino)-*N*-(pyridin-2-yl)benzamide** (Table 2, entry 7): Yellow solid. M.P.: 128–130 °C; IR (cm⁻¹): 3191, 2959, 1681, 1638, 1630, 1610, 1574, 1528, 1413, 1296, 1278, 1166, 842, 756; ¹H NMR (400 MHz, DMSO-*d*₆): δ 9.68 (br s, 1H), 8.68–8.62 (m, 2H), 8.56 (d, *J* = 6.8 Hz, 1H), 8.48 (d, *J* = 5.2 Hz, 1H), 6.82–6.76 (m, 2H), 6.56 (d, *J* = 4.8 Hz, 1H), 6.46–6.42 (m, 1H), 3.98 (s, 3H), 3.86 (s, 3H); MS (EI) *m/z*: 242 [M+H]⁺.

4-Cyano-*N*-(pyridin-2-yl)benzamide* (Table 2, entry 8): Reddish brown solid. M.P.: 117–119 °C; IR (cm⁻¹): 3438, 3205, 2997, 2230, 1680, 1606, 1571, 1506, 1303, 1222, 1162, 1099, 997, 853; ¹H NMR (400 MHz, DMSO- d_6): δ 9.20 (br s, 1H), 8.98–8.95 (m, 2H), 8.88 (d, *J* = 7.2 Hz, 1H), 8.68 (d, *J* = 5.6 Hz, 1H), 8.52–8.46 (m, 2H), 7.89 (d, *J* = 6.2 Hz, 1H), 7.26–7.23 (m, 1H); MS (EI) *m/z*: 224 [M+H]⁺.

N-(4-Methylpyridin-2-yl)benzamide* (Table 2, entry 9): Yellow solid. M.P.: 109–111 °C; IR (cm⁻¹): 3442, 2922, 2856, 1690, 1662, 1595, 1420, 1293, 1091, 1010, 891, 841, 759; ¹H NMR (400Hz, DMSO- d_6): δ 9.85 (br s, 1H), 8.24 (s, 1H), 8.02–8.02 (m, 2H), 7.98–7.93 (m, 2H), 7.49–7.34 (m, 3H), 2.37 (s, 3H); MS (EI) *m/z*: 213 [M+H]⁺.

2-Ethyl-*N*-(4-methylpyridin-2-yl)benzamide* (Table 2, entry 10): Yellow solid. M.P.: 123–125 °C; IR (cm⁻¹): 3441, 3240, 2923, 2803, 1655, 1606, 1570, 1521, 1413, 1373, 1293, 1199, 943, 887, 689; ¹H NMR (400 MHz, DMSO-*d*₆): δ 9.16 (br s, 1H), 8.33 (s, 1H), 7.77–7.71 (m, 1H), 7.51(d, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 7.2 Hz, 1H), 7.32 (d, *J* = 7.8 Hz, 1H), 7.26–7.23 (m, 1H), 6.88 (s, 1H), 2.90 (q, *J* = 7.2 Hz, 2H), 2.38 (s, 3H), 1.28 (t, *J* = 7.2 Hz, 3H); MS (EI) *m/z*: 241 [M+H]⁺.

4-Isopropyl-*N*-(4-methylpyridin-2-yl)benzamide** (Table 2, entry 11): Yellow solid. M.P.: 122–124 °C; IR (cm⁻¹): 3434, 3191, 2920, 1676, 1616, 1567, 1446, 1419, 1281, 1222, 1158, 845, 704; ¹H NMR (400 MHz, DMSO-*d*₆): δ 8.90 (br s, 1H), 8.29 (s, 2H), 2.88 (s, 2H), 7.34 (d, *J* = 7.2 Hz, 2H), 6.90 (s, 1H), 2.98 (s, 1H), 2.41 (s, 3H), 1.28 (s, 6H); MS (EI) *m/z*: 255 [M+H]⁺.

4-Ethoxy-*N*-(4-methylpyridin-2-yl)benzamide* (Table 2, entry 12): Yellow solid. M.P.: 130–133 °C; IR (cm⁻¹): 3423, 3096, 2850, 1689, 1602, 1530, 1485, 1409, 1258, 1229, 1019, 1009, 889; ¹H NMR (400 MHz, DMSO-*d*₆): δ 9.19 (br s, 1H), 8.32 (s, 1H), 8.13 (d, *J* = 4.8 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 6.93 (d, *J* = 4.8 Hz, 1H), 2.75 (q, *J* = 7.6 Hz, 2H), 2.4 (s, 3H); MS (EI) *m/z*: 257 [M+H]⁺.

4-Fluoro-*N*-(4-methylpyridin-2-yl)benzamide* (Table 2, entry 13): Yellow solid. M.P.: 108–111 °C; IR (cm⁻¹): 3456, 3200, 2977, 2878, 1673, 1624, 1578, 1510, 1438, 1399, 1226, 1015, 885, 758. ¹H NMR (400 MHz, DMSO-*d*₆): *δ* 9.17 (br s, 1H),

8.29 (s, 1H), 8.10 (d, *J* = 4.2 Hz, 1H), 7.99 (d, *J* = 5.2 Hz, 2H), 7.19–7.15 (m, 2H), 6.94 (d, *J* = 4.0 Hz, 1H), 2.43 (s, 3H); MS (EI) *m/z*: 231 [M+H]⁺.

4-Chloro-*N*-(4-methylpyridin-2-yl)benzamide* (Table 2, entry 14): Off-white solid. M.P.: 119–121 °C; IR (cm⁻¹): 3389, 3118, 2988, 1647, 1628, 1550, 1498, 1428, 1258, 1226, 1001, 856, 740, 738; ¹H NMR (400 MHz, DMSO-*d*₆): δ 9.10 (br s, 1H), 8.23 (s, 1H), 8.18 (d, *J* = 4.8 Hz, 1H), 7.97–7.94 (m, 2H), 7.50–7.47 (m, 2H), 6.86 (d, *J* = 5.2 Hz, 1H), 2.53 (s, 3H); MS (EI) *m/z*: 247 [M+H]⁺.

4-Cyano-*N*-(4-methylpyridin-2-yl)benzamide* (Table 2, entry 15): Brown solid. M.P.: 121–124 °C; IR (cm⁻¹): 3197, 3110, 2950, 2248, 1670, 1610, 1465, 1423, 1340, 1258, 1219, 1020, 877, 745; ¹H NMR (400 MHz, DMSO-*d*₆): δ 9.21 (br s, 1H), 8.21 (s, 1H), 8.18–8.10 (m, 2H), 7.96 (d, *J* = 5.6 Hz, 1H), 7.46–7.41 (m, 2H), 6.91 (d, *J* = 5.6 Hz, 1H), 2.41 (s, 3H); MS (EI) *m/z*: 238 [M+H]⁺.

4-(Dimethylamino)-*N*-(4-methylpyridin-2-yl)benzamide** (Table 2, entry 16): Yellow solid. M.P.: 119–122 °C; IR (cm⁻¹): 3451, 3078, 2950, 2899, 2850, 1638, 1620, 1558, 1298, 1226, 874, 789; ¹H NMR (400 MHz, DMSO-*d*₆): δ 10.2 (br s, 1H), 8.29 (s, 1H), 8.23 (d, *J* = 8.8 Hz, 1H), 8.15 (d, *J* = 5.2 Hz, 1H), 6.85 (d, *J* = 3.6 Hz, 1H), 6.64 (d, *J* = 8.8 Hz, 1H), 6.52 (m, 2H), 4.04 (s, 6H), 2.38 (s, 3H), 2.37 (s, 3H); MS (EI) *m/z*: 256 [M+H]⁺.

4-(Dimethylamino)-*N*-(4,6-dimethylpyridin-2-yl)benzamide ** (Table 2, entry 17): Yellow solid. M.P.: 140–142 °C; IR (cm⁻¹): 3367, 3310, 2922, 2850, 1676, 1640, 1618, 1589, 1523, 1420, 1408, 1356, 1245, 996, 856; ¹H NMR (400 MHz, DMSO-*d*₆): *δ* 8.93 (br s, 1H), 8.19 (s, 1H), 8.01 (d, *J* = 4.4 Hz, 1H), 7.80 (d, *J* = 8.8 Hz, 2H), 6.79 (d, *J* = 5.2 Hz, 1H), 6.63 (d, *J* = 9.2 Hz, 2H), 2.96 (s, 3H), 2.91 (s, 3H), 2.30 (s, 3H); MS (EI) *m/z*: 270 [M+H]⁺.

* Reported compounds; **New compounds.

3.5. Reusability of the catalysts

The recyclability properties of the 20% Cu₂O/MWCNT and 20% CuI/MWCNT catalysts were evaluated against the oxidative amidation reaction of benzaldehyde with 2-aminopyridine for the synthesis of N-(pyridin-2-yl)benzamide using THF as a solvent. Upon completion of the reaction, catalyst was removed



Fig. 6. Recyclability of the 20% Cu₂O/MWCNT and 20% CuI/MWCNT catalysts based on the yield of *N*-(pyridin-2-yl)benzamide following the reaction of benzaldehyde with 2-aminopyridine at 80 °C for 6 h in THF.

from the reaction mixture by filtration and washed sequentially with ethyl acetate and acetone before being dried at 200 °C in a hot air oven for 12 h and reused in a fresh reaction. The 20% Cu₂O/MWCNT catalyst showed good recyclability with no discernible decrease in its catalytic activity after four cycles, as indicated by a consistently high yield of the desired *N*-(pyridin-2-yl)benzamide product. In contrast, the activity of the 20% CuI/MWCNT catalyst decreased significantly with every run, as exemplified by a significant decrease in the yield of the desired *N*-(pyridin-2-yl)benzamide product with each cycle (Fig. 6).

Upon completion of the fourth cycle, the two catalysts were separated from their reaction mixtures and dried at 200 °C. The FT-IR spectra and PXRD patterns of the catalysts were subsequently recorded and the results are shown in Figs. 7 and 8, respectively. It is noteworthy that the FT-IR spectrum of the 20% Cu₂O/MWCNT catalyst contained a lattice vibration for Cu₂O at 622 cm⁻¹. Furthermore, the PXRD pattern of this catalyst contained diffraction peaks at $2\theta = 28.41^\circ$, 36.28°, 42.06°, and 61.38°, which correspond to the (110), (111), (200), and (220) crystal planes of Cu₂O, respectively. However, the FT-IR spectrum of 20% CuI/MWCNT contained two characteristic absorption bands at 611 and 495 cm⁻¹. Furthermore, the absence of any diffraction peaks for CuI confirmed that this material was not present on the MWCNTs. Further experiments to



Fig. 7. FT-IR spectra of the 20% $Cu_2O/MWCNT$ (1) and 20% Cul/MWCNT (2) catalysts after four reaction cycles.



Fig. 8. PXRD patterns of the 20% $Cu_2O/MWCNT$ (1) and 20% Cul/MWCNT (2) catalysts after four reaction cycles.

compare the amounts of copper in the fresh and recycled catalysts using a colorimetric method indicated that there had been no significant leaching of copper from the 20% Cu₂O/MWCNT catalyst. However, in the case of 20% Cu₁/MWCNT, these experiments revealed that 34% of the copper had leached from the catalyst after four cycles. These experiments therefore revealed that 20% Cu₂O/MWCNT is much better than 20% Cu₁/MWCNT with respect to its reusability.

3.6. Effect of the catalyst amount, solvent, temperature, and duration on the yield over 20% Cu₂O/MWCNT

Further experiments were conducted to assess the catalytic activity of the 20% $Cu_2O/MWCNT$ catalyst for the synthesis of *N*-(pyridin-2-yl)benzamide by varying the amount of catalyst, as well as investigating different solvents, temperatures, and reaction times. The results of these experiments are presented in Figs. 9–11.

The catalytic activity of the 20% Cu₂O/MWCNT catalyst was measured by varying the amount of catalyst added to the reaction from 0.01 to 0.2 g (Fig. 9). The results showed that the catalytic activity increased as the catalyst amount increased up to 0.1 g of catalyst, where the yield of the desired product reached a plateau. Based on these results, a catalyst charge of 0.1 g was selected as the optimum amount of catalyst for the reaction.

The oxidative amidation reaction was conducted in the presence of several different solvents, including THF, DMF, EtOAc, chloroform, DCM, and ethanol, to determine the effects of these different solvents on the yield of the product, and the results are shown in Fig. 10. It is noteworthy that THF and DMF provided good yields of *N*-(pyridin-2-yl)benzamide, although the use of DMF complicated the isolation of the desired product. The use of polar aprotic solvents (e.g., THF and DMF) gave high yields of the desired product, while polar protic solvents such as ethanol gave much lower yields. This difference in the yield could be attributed to the presence or absence of hydrogen bonding interactions between the amino groups of the 2-aminopyridine substrate and the solvent, which could have a significant impact on the availability of the amino group for the



Fig. 9. Effect of different amounts of the 20% Cu₂O/MWCNT catalyst on the isolated yield of the product. Reaction conditions: benzaldehyde 5 mmol, 2-aminopyridine 4.5 mmol, THF, 80 °C, 6 h.



Fig. 10. Effect of different solvents on the synthesis of *N*-(pyridin-2-yl)benzamide in the presence of the 20% $Cu_2O/MWCNT$ catalyst at 80 °C for 6 h.

amidation reaction. Based on these results, THF was identified as the most efficient solvent for the synthesis of *N*-(pyridin-2yl)benzamides. It is noteworthy that these observations are consistent with the proposed mechanism.

The effect of the temperature and reaction time on the yield of the oxidative amidation of benzaldehyde with 2-aminopyride in the presence of the 20% Cu₂O/MWCNT catalyst were also studied. The temperature was varied in the range of 40–120 °C at intervals of 20 °C, with the respective reactions being conducted over 2, 4, 6, 12, and 24 h (Fig. 11). It is noteworthy that the reaction did not proceed at room temperature even after 24 h. The results revealed that the highest isolated yield of the product was obtained at 80 °C after a reaction time of 6 h. Increasing the reaction time to 8, 12, or 24 h at 80 °C did not lead to an increase in the isolated yield of the product. Furthermore, increasing the reaction temperature above 80 °C did not lead to an increase in the yield of the product.

4. Conclusions

Cu₂O and CuI supported on acid activated MWCNTs were



Fig. 11. Effect of the reaction temperature and reaction time on the activity of the 20% Cu₂O/MWCNT catalyst towards the oxidative amidation of benzaldehyde with 2-aminopyridine.

found to be an efficient heterogeneous catalysts for the synthesis of N-(pyridin-2-yl)benzamides under mild reaction conditions with 100% selectivity and good yields. Notably, the 20% Cu₂O/MWCNT catalyst could be recycled up to four times without any discernible decrease in its catalytic activity or leaching of the catalytically active component into the reaction mixture. This catalyst also demonstrated a broad substrate scope and provided access to a wide range of substituted N-(pyridin-2-yl)benzamides in good yields with high selectivity. The characterization of these catalysts revealed that the copper species on the surfaces of the carbon nanotubes were cubic phase of Cu_2O and γ -CuI and they possessed different electron-accepting properties, which had a significant impact on their catalytic activities. In terms of the oxidative amidation reaction, the results revealed that an electron-donating group on the aromatic ring of the benzaldehyde led to an increase in the rate of nucleophilic attack of the amino group of the 2-aminopyridine substrate on the carbonyl carbon of the aldehyde. Thus, these results shows that the 20% Cu₂O/MWCNT catalyst is much more recyclable than the 20% CuI/MWCNT for

the synthesis of N-(pyridin-2-yl)benzamides.

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Graphical Abstract

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

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Several composite Cu(I) species supported on MWCNTs have been synthesized using a wet impregnation method. Characterization revealed the formation of cubic phase Cu₂O and γ -phase CuI on the MWCNTs. The 20% Cu₂O/MWCNT and 20% CuI/MWCNT catalysts were efficient for the synthesis of *N*-(pyridin-2-yl)benzamides under mild reaction conditions with 100% selectivity and good yields.

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