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Carbon nitride supported copper nanoparticles: A heterogeneous catalyst for the *N*-arylation of hetero-aromatic compounds

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Abstract: Graphitic carbon nitride supported copper nanoparticle composite (Cu-gCN) has been found to be an active catalyst for *N*-arylation of hetero-aromatic system (pyrrole, pyrazole and substituted indole) and benzamide molecule, with high product selectivity and from good to excellent yields, using substituted aryl bromide as a coupling partner. The intercalated structure and the amine functional group of carbon nitride preventing the aggregation of the catalytically active copper species during the reaction and the recyclability study shows the stable performance of the catalyst without the significant loss of catalytic activity.

Keywords: N-arylation; carbon nitride; copper nanoparticles.

1. Introduction

Substituted heteroarene molecules have enormous applicability to a variety of research areas, ranging from biology to the materials sciences.¹⁻⁵ The *N*-arylation has been recognized as one of the most important transformations of $-N\underline{H}$ containing hetero-aromatic compounds, such as, pyrrole, pyrazole and indole etc. Copper mediated aromatic nucleophilic substitution reactions were reported by Fritz Ullmann and Irma Goldberg.⁶ Stoichiometric amounts of copper salts together with higher reaction temperature were major limitations of this methodology in spite of its numerous industrial applications.^{7, 8}

With time researchers have made significant progress to minimize these problems by applying the catalytic amount of copper salt with ligands or by preformed catalysts and have achieved the moderate optimal reaction conditions. Copper catalyzed *N*-arylation for imidazole⁹ and other nitrogen containing heterocycles¹⁰ using milder reaction condition have appeared in recent

literatures. Some strategies have also been reported for mild reaction conditions for the title reaction using aryl lead¹¹ or aryl bismuth¹² as the coupling partner. Utilization copper salts with several ligands, such as, racemic L-proline,¹³ 1, 10-phenanthroline¹⁴ and di-imine ligands¹⁵ have also remain effective. Successful efforts have been also made for the photocatalytic *N*-arylation for imidazole and phenylboronic acid using copper-graphene system as a catalyst under irradiation of visible light recently.¹⁶

Again, palladium also proved as an effective catalyst for such kind of title reaction. Palladium catalyzed intramolecular *N*-arylation of sulfonamides has been described by Buchwald¹⁷ and since then significant progress for palladium catalyzed *N*-arylation of using various type of ligands have also been reported.¹⁸ Recent literature shows that palladium catalyst, in presence of various biaryl ligands, has the excellent performance for the *N*-arylation of cyclopropylamines using aryl bromide as coupling partner.¹⁹ Despite of these certain successes, in general, ligand synthesis, moisture sensitivity, toxicity, cost effectiveness of the catalyst and the limitation of substrate scope are still remaining the challenge and which need more modification of this methodology.

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During last few decade, with the advent of nanotechnology, nanomaterials replace the classical strategies of several conventional research areas like catalysis, sensing, medicine and electronics. Among them, catalysis has been emerged as the most successful branch where nanomaterials are frequently used. Dispersed metal nanoparticles, on solid support or stabilizer, such as carbon based materials,²⁰ metal oxides,²¹ zeolites²² and clays materials,²³ have high exposed surface area, so that the reactant molecules have more exposure towards the catalyst surface, rather than the soft stabilizers, like ligands,²⁴ polymers,²⁵⁻²⁷ dendrimers²⁸ and surfactants,²⁹ where the catalyst species are within the stabilizer and that limits the accessibility for the reactant molecule toward the catalyst surfaces and there by the catalytic performances.³⁰ Solid supported catalyst, for heterogeneous liquid-phase organic transformation reactions, are easy to handle during the recycling process and which is important for industrial, environmental and economical point of view. In this current manuscript we like to report the *N*-arylation reaction for both the hetero-aromatic and aromatic systems using various substituted aryl bromide molecules as the coupling partner in the presence of carbon nitride supported copper nanoparticle composite catalyst.

2. Experimental Section

2.1. Materials and instrumentation

Ultra-pure water was used to prepare the solution of $CuSO_4$, $5H_2O$ (10^{-2} mol dm⁻³). All the chemicals as well as the solvents were purchased for this study were 'used as received' without further purification.

The JEOL (JEM-2100), 200keV, transmission electron microscope (TEM) with LaB₆ electron source was used for the microscopic analysis of the sample. An ultra-thin windowed energy dispersive X-ray spectrometer (EDS) attached to the TEM was used to determine the chemical composition of the samples. TEM specimens were onto a carbon coated nickel TEM grids. Infrared spectra were collected utilizing a Shimadzu IRAffinity-1 with a spectral resolution of 0.5 cm⁻¹. The XRD patterns were recorded on a Shimadzu XD-3A X-ray diffractometer operating at 20 kV using Cu-K α radiation (k = 0.1542 nm). The measurements were performed over a diffraction angle range of 2 θ = 20° to 80°. The XPS spectra were collected in an ultra-high vacuum chamber attached to a Physical Electronics PHI 560 ESCA/SAM system. ¹H NMR and ¹³C NMR spectra were recorded on Bruker Ultrashield 400 (400 MHz for ¹H and 100 MHz for ¹³C {¹H} in CDCl₃).

2.2. Synthesis:

2.2.1. General procedure for the preparation of Cu-gCN:

In a typical experiment, 15 g of urea was kept in a covered crucible at 80 $^{\circ}$ C under ambient pressure for 12h. After that the dried urea was put in a Muffle Furnace for 4h at 550 $^{\circ}$ C. The lemon yellow colored product was washed several time with distilled water to remove the residual alkaline species (e.g. ammonia) on the sample surface and again dried at 80 $^{\circ}$ C for 24 hours under vacuum. In the second stage of the synthesis, each 0.5 g of the resultant product was dispersed in 10 mL of water 2 separate 25 mL of round bottom flux. A 0.1 M of CuSO₄.5H₂O (3.95 mL and 7.9 mL) was added drop wise (5 wt% and 10 wt% loading of Cu) to each flux. After that, 5 mL of 1×10⁻³ M NaBH₄ solution was added to each flux drop wise for the resultant material, Cu(0)-gCN, was characterized using different techniques and applied as catalyst for the *N*-arylation reaction.

2.2.2. General procedure for the Ullmann reaction:

To a 25 mL round bottom flask fitted with magnetic stirrer were added -*N*H containing heteroaromatics **1** (1.0 mmol), arylhalide **2** (1.2 mmol), Cs_2CO_3 (650 mg, 2.0 mmol) and 5mg of CugCN catalyst (5 wt% or 10 wt% loaded Cu) in dry toluene (4 mL). The reaction mixture was stirred under reflux at 100 °C for 12h. After completion (monitored by TLC), the reaction mixture was allowed to cool at room temperature and diluted with 20 mL of distilled water; the solution was extracted with ethyl acetate (3 × 20 mL). The organic layer was separated and dried over anhydrous MgSO₄. Removal of the solvent resulted in a residual mass which was subjected to column chromatography over silica gel using hexane and an increasing proportion of ethyl acetate as eluent to provide the corresponding products.

3. Results and Discussion

3.1. Characterization of material

The TEM image (Figure 1A) of the Cu-*g*CN composite, where nanoparticles are seen, with wide range of size distribution ranging from 5 to 20 nm, on the carbon nitride support material.

The EDS spectra (Figure 1B) derived from placing the electron beam directly on a nanoparticle in the carbon nitride support. The EDS analyses confirmed that copper was only found associated with the nanoparticles, the nickel peak in the spectra are from the nickel grid used for the microscopic study.

The XRD pattern (Figure 2A) of the of the Cu-gCN sample show an intense peak at 27.33°, which indexed as the (002) stacking peak of the conjugated aromatic ring of the support material.³² Other three peaks at 43.18°, 50.20° and 74.06° are assigned for the (111), (200) and (220) crystal face of metallic copper. The low intensity peak at about 35.80° can be assigned for (111) crystal face of the Cu₂O, possible due to the surface oxidation of the copper nanoparticles particles.



Figure 1: (A) The TEM image shows the distribution of the copper nanoparticles (dark spots) on the carbon nitride support, where the sizes of the nanoparticles are within range between 5-20 nm. (B) The EDS spectra shows the presence of copper (derived by placing the electron beam directly on a dark spots on the carbon nitride support) and the nickel peak in the spectra are from the nickel grid.

To identify the chemical state of the copper, X-ray photoelectron spectroscopy (XPS) measurements were performed. The Cu 2p region of the XPS spectrum of the Cu-*g*CN composite sample is illustrated in Figure 2B, which reveals the presence of $2p_{3/2}$ and $2p_{1/2}$ peaks at binding energies of 932.75 and 953.4 eV, respectively. It is not clear whether the peak at 932.75 eV is due to metallic copper or Cu₂O because the Cu $2p_{3/2}$ binding energies and peak widths of these two species are similar³¹ but the symmetric nature of the Cu $2p_{3/2}$ spectrum indicates the presence of only metallic copper in the Cu-*g*CN sample. The evidence of formation of Cu(I) species, from Cu₂O as indicated in the XRD pattern, is not visible in the XPS signal probably due to the X-ray-induced reduction of Cu(I) species.³² In the IR spectra (Figure 2C), the vibrational bands

attributed for C=N and C-N stretching modes and falls within the range from 1240 to 1700 cm⁻¹ for both *g*CN and Cu-*g*CN samples. The out-of-plane bending vibration has been observed at 810 and 872 cm⁻¹, due to the presence of typical heptazine rings, for *g*CN (a) and Cu-*g*CN (b) samples, respectively. The broad band, between 3000-3500 cm⁻¹, appear for uncondensed terminal amino groups ($-NH_2$ or =NH groups) for both the samples. The shifting of peak positions for all the vibrational bands have been observed towards the higher wavelength region for the sample Cu-*g*CN, as compared with gCN sample, indicates the functionalization of the copper nanoparticle with the nitrogen from the support material.



Figure 2: (A) The XRD pattern of the of the copper-carbon nitride composite system, where the peak at 27.33° represent the (002) stacking peak of the conjugated aromatic ring of the carbon nitride. The peaks at 43.18°, 50.20° and 74.06° are assigned for the (111), (200) and (220) crystal face of metallic copper, whereas, the (111) crystal face of the Cu₂O has been represented by the low intensity peak at 35.80°. (B) The X-ray photoelectron spectroscopy shows the presence of $2p_{3/2}$ and $2p_{1/2}$ peaks at binding energies of 932.75 and 953.4 eV, respectively, with the symmetric nature of the Cu $2p_{3/2}$ spectrum. (C) The FTIR spectra of the *g*CN (a) and Cu-*g*CN (b) samples.

3.2. Optimization of reaction condition

The reaction between pyrrole (1a) and 4-bromobenzonitrile (2d) was taken as model reaction system to yield the N-arylated product, 4-(1H-pyrrol-1-yl)benzonitrile (3ad) for the optimization of reaction conditions (Table S1, supporting information). Carbonate, acetate, alkoxide and phosphate type of bases have been screened for the reaction. Among them, Cs₂CO₃ appeared to be the most suitable base for the reaction (entries 3 and 5). Various high boiling point solvents, such as, xylene, toluene, N,N-dimethylacetamide (DMAc), N,N-dimethylformamide (DMF), Nmethyl-2-pyrrolidine (NMP) and tetrahydrofuran (THF) have been tested for the solvent optimization study and toluene was chosen for the current methodology by considering all the entries listed in table S1. Again, by comparing the different entries in table S1, we found 5 wt% of loading of copper nanoparticles on the support, Cu-gCN (5 mg), was the best choice since further increase of copper loading has not shown any improvement in terms of yield of **3ad** for the present methodology (entries 3 and 5). It is also important to mention that 100 °C was found to be optimum temperature for the current reaction since at 80 °C no desired product has been formed (entry 8), as monitored by thin layer chromatography (TLC) technique. We also have observed that further increase of the temperature at 120 °C does not have any positive effect on the yield of the product. In the absence of any base molecule the homocoupling product of aryl halide has been formed (entry 4).

3.3. Substrate scope

Based on the above optimized reaction conditions, entry 5, we have explored the versatility of the Cu-gCN catalyst for the *N*-arylation of various hetero-aromatic system using different substituted aryl bromide molecules as a coupling partner and the results are summarized in Tables 1. All the substrates produced the expected *N*-arylated product with very good to excellent yields and selectivity.

When pyrrole (1a) was used as a substrate, the aryl bromide molecules, such as, bromobenzene (2a), electron withdrawing group substituted 4-bromonitorbenzene (2b), 4-bromobenzonitrile (2d) and electron donating group substituted 4-bromoanisole (2c) and 4-bromotoluene (2e), formed the desired *N*-arylated products of 1-phenyl-1*H*-pyrrole (3aa), 1-(4-nitrophenyl)-1*H*-pyrrole (3ab), 1-(4-methoxyphenyl)-1*H*-pyrrole (3ac), 4-(1*H*-pyrrol-1-yl)benzonitrile (3ad) and 1-*p*-tolyl-1*H*-pyrrole (3ae) with the yield of 78%, 88%, 82%, 92% and 85%, respectively, table 1. The other $-N\underline{H}$ containing 5 member hetero-aromatic compound pyrazole (1b) was also coupled with -NO₂ (2b), -OMe (2C), -CN (2d) and -COMe (2g) substituted bromobenzene molecules with the formation of desired *N*-arylated products 1-(4-nitrophenyl)-1*H*-pyrazole (3bb), 1-(4-methoxyphenyl)-1*H*-pyrazole (3bc), 4-(1*H*-pyrazol-1-yl)benzonitrile (3bd), (4-(1H-pyrazol-1-yl)phenyl)ethanone (3bg) with the yield of 85%, 93%, 95% and 90%, respectively, table 1.

Motivated by the above observations, we have shifted our attention towards the indole (1c) and substituted indole moieties (aldehyde, 1d, and acetyl, 1e), one of the privileged hetero aromatic structures in the realm of organic chemistry, to imply the present methodology to get access of their corresponding *N*-arylated coupling products. It was observed that all the moieties have reacted with the substituted aryl bromide molecules to produce the expected compounds from good to excellent yield ranging from 75% to 92% of the isolated products (Table 1). In the presence of Cu-gCN catalyst, indole (1c) was reacted with bromobenzene (2a), 4-bromonitorbenzene (2b), 4-bromobenzonitrile (2d), 4-bromoanisole (2c) and 4-bromotoluene (2e) and form the corresponding products **3ac**, **3cb**, **3cc**, **3cd** and **3ce** with 80%, 85%, 80%, 92% and 86% of isolated yield, respectively. It is important to mention that *o*-bromotoluene (2f) was also participated in title reaction with indole and formed 1-*o*-tolyl-1*H*-indole (3ef), successfully, with 78% of isolated yield.

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(a) Reaction conditions: Hetero-aromatics 1(1.0 mmol), arylbromide 2 (1.2 mmol), Cs₂CO₃ (650 mg, 2.0 mmol), Cu-*g*CN catalyst (5 mg, 5 wt% of Cu) and Toluene (4mL). (b) Isolated yield.

In a similar way, indole-3-carboxaldehyde (1d) have also performed the *N*-arylation reaction with a set of aryl bromide molecules, namely, bromobenzene (2a), 4-bromobenzonitrile (2d), 4-bromoanisole (2c) and 4-bromotoluene (2e) and resulted the arylated products 1-phenyl-1*H*-

indole-3-carbaldehyde (**3da**), 1-(4-methoxyphenyl)-1*H*-indole-3-carbaldehyde (**3dc**), 4-(3formyl-1H-indol-1-yl)benzonitrile (**3dd**) and 1-*p*-tolyl-1*H*-indole-3-carbaldehyde (**3de**) with the isolated yield ranging from 82% to 89%. In contrary, when 4-bromoacetophenone (**2g**) was reacted with indole-3carboxaldehyde (**1d**), an aldol condensation product, (*E*)-1-(4bromophenyl)-3-(1H-indol-3-yl)prop-2-en-1-one (**3dg**), with 90% isolated yield has been achieved as the main product and a trace amount of the corresponding *N*-arylated compound was noticed.

As expected, 3-acetylindole (1e) also underwent the title reaction with bromobenzene (2a), 4bromonitorbenzene (2b), 4-bromoanisole (2c) and 4-bromobenzonitrile (2d) to produce the corresponding *N*-arylated products, 1-(1-phenyl-1*H*-indol-3-yl)ethanone (3ea), 1-(1-(4nitrophenyl)-1*H*-indol-3-yl)ethanone (3eb), 1-(1-(4-methoxyphenyl)-1H-indol-3-yl)ethanone (3ec) and 4-(3-acetyl-1H-indol-1-yl)benzonitrile (3ed), with the yields of 79%, 83%, 75% and 85%, respectively (Table 1).

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With the success of the *N*-arylation of the hetero-aromatic system, we were interested to widen the substrate scope, by maintaining the current optimized reaction condition, for mono arylation at $-N\underline{H}_2$ group present in the aromatic system. We have chosen benzamide molecule (4) as the source of $-N\underline{H}_2$ group and bromobenzene (2a) and various electron withdrawing and donating group substituted aryl bromide molecules, such as, 4-bromonitorbenzene (2b), 4bromobenzonitrile (2d), 4-bromoanisole (2c), 4-bromotoluene (2e) and *o*-bromotoluene (2f), as the coupling partner for this reaction. The mono-arylated products of *N*-phenylbenzamide (5a), *N*-(4-nitrophenyl)benzamide (5b), N-(4-methoxyphenyl)benzamide (5c), N-(4cyanophenyl)benzamide (5d), *N-p*-tolylbenzamide (5e) and *N-o*-tolylbenzamide has been formed with 85%, 94%, 89%, 93%, 90% and 84% of yield, respectively (Table 2).

Table 2: Substrates scope for C-N cross coupling reaction between benzamide and substituted aryl bromides. ^{a, b}



(a) Reaction conditions: Benzamide **4** (121 mg, 1.0 mmol), arylbromide **2** (1.2 mmol), Cs_2CO_3 (650 mg, 2.0 mmol), Cu-gCN catalyst (5 mg, 5 wt% of Cu) and Toluene (4mL). (b) Isolated yield.

3.4. Scaling up, durability and the kinetic study of the catalyst

The demand of heterogeneous catalysis lies in its durability and recyclability study that could allow the catalyst to serve the purpose of repetitive use. The reaction between pyrrole (1a) and 4-bromobenzonitrile (2d) was chosen as the substrates for *N*-arylation reaction to obtain the product 4-(1*H*-pyrrol-1-yl)benzonitrile (3ad) using carbon nitride supported copper catalyst by maintaining the reaction condition as mentioned in table S1 (entry 5, supporting information).

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Figure 3: (A) The histogram from the recyclability study of the copper-carbon nitride catalytic system. The figure shows that the used material is also active as a catalyst without a significant loss of catalytic performance. (B) The TEM image of the used catalyst at the end of the sixth cycle reveals the enlargement of the copper nanoparticles. (C) The kinetic study shows the formation of the product, 4-(1*H*-pyrrol-1-yl) benzonitrile, as a function of time.

To perform this study for the purpose of convenience, we have increased the amount of all the reagents, including the catalyst, by a factor of ten. After completion of the first cycle, a yield of 92% of targeted the product **3ad** was achieved whereas at the end of the sixth cycle a moderate deactivation of the reaction has been noticed with the yield of 80% of the *N*-arylated product. At the end of each cycle, the catalyst was recovered by filtration technique then washed with ethyl acetate followed by drying in air and was reused for the next cycle. The graphical representation (Figure 3A) shows a relation between the yield percentage of product (**3ad**) and the number of cycles and the result demonstrates that the used material was also active as a catalyst without a significant loss of catalytic performance. At the end of last cycle, the recovered catalyst was characterized by TEM and a significant amount of particles enlargement has been noticed (Figure 3B), which is possibly due to the Ostwald ripening process.³³ The gradual decrease of the product yield (%) per cycle could be accounted mainly due to two reasons, firstly, loss of composite catalyst during the filtration and washing process and, secondly, the particle

New Journal of Chemistry

agglomeration, which causes the decrease of the effective surface area or the active sites of the catalyst. To find the possibility of metal leaching from the carbon nitride support, we have performed the inductively coupled plasma mass spectrometry (ICP-MS) analysis of the filtrate, collected during the recyclability study, and we found that instrument did not able to record any copper species within the range of its detection limit.

The stronger metal-support (Cu-N) interaction, as evidenced by FTIR spectra (Figure 2C), could be responsible to prevent the metal leaching phenomenon in this current study.

For the kinetic study (Figure 3C), we have followed the first cycle of the above reaction where there was no intended product, 4-(1*H*-pyrrol-1-yl)benzonitrile (**3ad**), has been formed for the first two hours, which is due to the required induction time for the reaction. From the kinetic graph it is evident that initially, for 2-4h, the rate of the reaction was slow and after that a steady conversion has been achieved. A slower rate again observed during the later stage of the reaction probably due to the solid product formed during the reaction block the active site or the surface of the copper nanoparticles causes the deactivation of the reaction.

3.5. Proposed mechanism

The mechanism of the title reaction has been represented in Scheme 1. In the presence of CugCN (A) the oxidative addition of aryl bromide produce the Cu(II)-gCN intermediate **B** which under goes base mediated (Cs₂CO₃) transmetallation to generate the intermediate **C**. Reductive elimination occurs in the intermediate **C** to regenerate the active metallic copper species and the *N*-arylated product to complete the catalytic cycle.

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Scheme 1: A proposed catalytic cycle for the N-arylation reaction.

It is also important to mention some, previously reported, similar type of *N*-arylation reactions using copper as a catalytic.

Previous report	Reagent and condition	Entry	Yield (%) in the previous report	Yield (%) in the present report	Reference
[a]	CuO hollow spheres, KO ^t Bu, Toluene, 180 ⁰ C, 18h	3aa 3ac	80 34	78 82	34
[b]	Copper and Porous Zinc- Based MOF, Cs_2CO_3 , DMSO, 90^0C , hydrogen atmosphere	3bb 3bc 3bd 3bg	99 82 91 95	85 93 95 90	35
[c]	CuI- binaphthyl amine complex, Aryl iodide, Toluene, Cs ₂ CO ₃ , 82 ^o C	3ca 3cc 3ce	80 76 76	99 80 86	36

Table 3: Comparative literature survey of the N-arylation reaction using copper catalyst

4. Conclusion

In summary, a simple and straight forward procedure for synthesis of carbon nitride supported copper nanoparticles (Cu-gCN) has been reported where the synthesized material was successfully implied as catalyst towards *N*-arylation reaction. Number of hetero aromatic compounds, such as, pyrrole, pyrazole and substituted indoles and aromatic compounds, like benzamide molecule, show *N*-arylation coupling with various types of aryl bromide molecules. We also note that the reaction between 4-bromoacetophenone and indole-3 carboxaldehyde forms only the aldol condensation product. We showed the recycling competence of the synthesized material as a catalysts and the efficiency can be retained for at least six consecutive cycles.

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