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Synthesis and characterization of copper nanoparticles supported on reduced graphene oxide as a highly active and recyclable catalyst for the synthesis of formamides and primary amines

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ABSTRACT

We report here the synthesis of reduced graphene oxide supported copper nanoparticles (rGO/Cu NPs) from copper (II) sulfate pentahydrate and graphite precursors using a simple protocol. The catalyst was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), brunauer-emmett-teller (BET) and energy dispersive X-ray spectroscopy (EDS). The rGO/Cu NPs is proved to be a useful heterogeneous catalyst in Cu-catalyzed formamidation and amination of arylboronic acids. The catalyst can be recovered by simple filtration from the reaction mixture and reused several times without significant loss of catalytic activity.

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1. Introduction

Formamides are valuable intermediates in the synthesis of pharmaceutically important compounds [1,2]. In addition, the formamides moiety is used to protect the nitrogen in amines and in the synthesis of formamidines and isocyanides [3,4]. Furthermore, formamides can be acted as a Lewis base catalyst in reactions such as allylation, synthesis of acid chlorides from carboxylic acids and hydrosilylation of carbonyl compounds [5,6].

Formylation of amines is a known reaction in synthetic formamides [7-16]. A number of synthetic methods have been reported in the literature about the *N*-formylation of amines and various reagents are available for these reactions such as acetic formic anhydride, chloral, triethyl orthoformate, activated formic acid using DCC or EDCI, activated formic esters, ammonium formate, 2,2,2-trifluoroethyl formate and Natrolite zeolite [7-16].

Earlier reported methods for the *N*-formylation of amines suffer from certain disadvantages such as the use of expensive, moisture sensitive, toxic reagents and homogeneous catalysts, low yields, long reaction times, tedious work-up, waste control and formation of side products [7-16]. Therefore, the development

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of a catalytic synthetic method for formamides still remains as an active research area.

Among various catalysts for the carbon-carbon and carbon-heteroatom coupling reactions, homogeneous copper catalysts have been widely investigated [17], while less expensive heterogeneous copper catalysts received scanter attention. Thus, the use of ligand-free heterogeneous Cu catalysts is often desirable from the perspective of process development due to their easy handling, simple recovery, and recycling.

Graphene, a single hexagonally flat layer graphite sheet that consists of sp^2 carbon atoms covalently bonded in a honeycomb crystal lattice [18], has been intensively studied due to its unique structural and electronic properties and applications. The combination of highest electron mobility, high chemical, mechanical and thermal stability with the large specific surface area (theoretically calculated value, 2630 m^2/g), potential low manufacturing cost and metal immobilization capacity offer many interesting applications in a wide range of fields including catalysts, field-effect transistors, chemical sensors, field emitters and hydrogen storage media [18]. The dispersion of metal or metal oxides nanoparticles onto the surface of graphene or between the graphene layers potentially provides a new way to develop catalytic materials. However, only a few studies have involved the application of graphene oxide and other chemically modified graphene-based materials (CMGs) as

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heterogeneous catalysts for facilitating synthetically useful transformations [19-24]. Graphene oxide, a delaminated layer of graphite oxide (GO), is typically prepared by the exhaustive oxidation of graphite to graphite oxide using strongly acidic and oxidizing conditions, followed by the subsequent mechanical/chemical or thermal exfoliation of graphite oxide to graphene oxide sheets (Fig. 1). Recently, many studies have been reported on the preparation of graphene sheets through the chemical reduction of exfoliated graphite oxide which can be readily used as a catalyst support. Metal salts or nanoparticles easily approach the surface of GO because of the presence of carboxyl, hydroxyl, and epoxide functional groups on the edge, top, and bottom surface of each sheet [25-27].
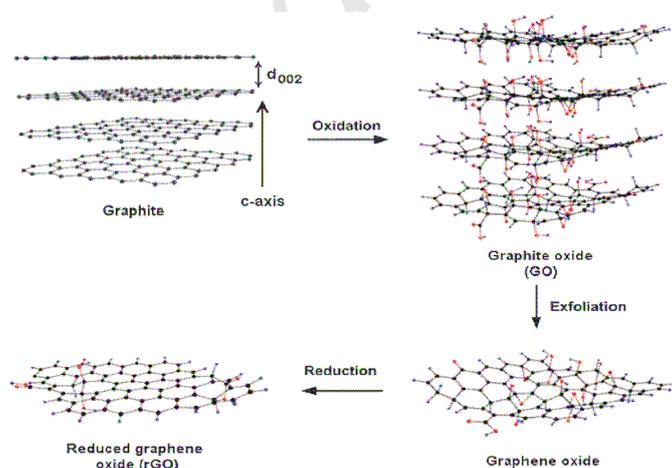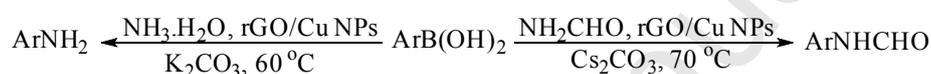

Fig. 1. Illustration on the preparation of reduced graphene oxide (adapted from ref. 28).

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In continuation of our recent studies on application of heterogeneous catalysts [29,30], we hereby report a new protocol for the formamidation and amination of arylboronic acids using copper nanoparticles supported on reduced graphene oxide (rGO/Cu NPs) as a stable heterogeneous catalyst under ligand-free conditions (Scheme 1). This catalyst is safe, environmentally benign with fewer disposals problems.

$$ArNH_2 \xleftarrow[\text{K}_2\text{CO}_3,\ 60\ ^\circ\text{C}]{\text{NH}_3.\text{H}_2\text{O},\ \text{rGO/Cu NPs}} ArB(OH)_2 \xrightarrow[\text{Cs}_2\text{CO}_3,\ 70\ ^\circ\text{C}]{\text{NH}_2\text{CHO},\ \text{rGO/Cu NPs}} ArNHCHO$$

Scheme 1. Synthesis of formamides and primary amines using rGO/Cu NPs as a heterogeneous catalyst.

The combination of metal nanoparticles with a reduced graphene oxide offers the possibility to obtain nanostructured systems with thermal stability, solubility and recovery possibilities. Reduced graphene oxide/copper nanoparticles (rGO/Cu NPs) composite was prepared by using GO and $CuSO_4.5H_2O$ as the raw materials (see Supporting Information). Graphite oxide used in this work was prepared by the oxidation of graphite powder with $H_2SO_4/KMnO_4$ according to a modified Hummers method [31,32]. GO prepared by this way is widely used as the precursor of graphene to synthesize the reduced graphene oxide (rGO). Cu NPs have been obtained by reduction of $CuSO_4.5H_2O$ with $NaBH_4$.

2. Experimental

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2.1. Instruments and reagents

All reagents were purchased from the Merck and Aldrich chemical companies and used without further purification. Products were characterized by different spectroscopic methods, elemental analysis (CHN) and melting points. The NMR (Nuclear Magnetic Resonance) spectra were recorded in acetone and DMSO. ^{1}H NMR spectra were recorded on a Bruker Avance DRX 90, 300 and 500 MHz instrument. The chemical shifts (δ) are reported in ppm relative to the TMS as internal standard. *J* values are given in Hz. FT-IR (Fourier transform infrared) spectra were recorded on a Perkin-Elmer 781 spectrophotometer. Melting points were taken in open capillary tubes with a BUCHI 510 melting point apparatus and were uncorrected. The elemental analysis was performed using Heraeus CHN-O-Rapid analyzer. TLC was performed on silica gel polygram SIL G/UV 254 plates. X-ray diffraction measurements were performed with a Philips powder diffractometer type PW 1373 goniometer. It was equipped with a graphite monochromator crystal. The X-ray wavelength was 1.5405 A° and the diffraction patterns were recorded in the 2θ range (10-60) with scanning speed of 2º/min. Morphology and particle dispersion was investigated by scanning electron microscopy (SEM) (Cam scan MV2300). The chemical composition of the prepared nanostructures was measured by EDS (Energy Dispersive X-ray Spectroscopy) performed in SEM.

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The Brunauer-Emmett-Teller (BET) specific surface areas (SBET) and the porosity of the samples were evaluated on the basis of nitrogen adsorption isotherms measured at 77 K using a BELSORP-max nitrogen adsorption apparatus (Japan Inc.). All the samples were degassed at 150 ºC before nitrogen adsorption measurements. The BET surface area was determined using the adsorption data in the relative pressure (P/P0) range of 0.05-0.35. The desorption isotherm was used to determine the pore size distribution using the Barret-Joyner-Halender (BJH) method.

2.2. Preparation of graphene oxide

Graphene oxide was synthesized from commercial graphite by modified Hummers method [31,32]. The commercial graphite powder (10 g) was put into 230 mL concentrated H_2SO_4 that had been cooled to bellow of 20 °C with a circulator. 300 G potassium permanganate ($KMnO_4$) was added with stirring, so that the temperature of the mixture was fixed at bellow of 20 °C. Then, the temperature of the reaction was changed and brought to 40 °C and mixture was stirred at 40 °C for 1h. 500 mL de-ionized water was added to the mixture, causing an increase in temperature to 100 °C. After that, 2.5 mL H_2O_2 (30 wt. %) was slowly added to the mixture supplementary this solution was diluted by addition lit de-ionized water. For purification, the suspension was washed with 1:10 HCl solution (200 mL) in order to remove metal ions by filter paper and

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funnel. The suspension was washed with much de-ionized water at several times, until the filtrate became neutral to remove remaining salt impurities. The graphene oxide was characterized by XRD and FT-IR spectroscopy [33].

2.3. Preparation of reduced graphene oxide (rGO)

Chemical reduction of graphene oxide to reduced graphene oxide was done according to a new procedure. Suspension aqueous colloids of GO were prepared from the dried graphene oxide (GO) by mechanical stirring and heat treatment with a circulator. In the experiment, 10 g of graphene oxide was stirred into 1 L of distilled water. This dispersion was stirring using a Fisher mechanical stirring until it became a clear solution with no visible particulate material. After that, the pH of the solution was increased to 10 by adding NaOH solution and 20 mL of hydrazine monohydrate was added, to the solution at 95 ^{o}C and stirred for 4 h, subsequently the reaction was completed, the reduced graphene oxide was collected by filtration as a black powder. The obtained powder was washed with distilled water several times to until the pH is nearly 7 and until to remove the excess hydrazine. The final product was dried in a vacuum oven at 100 ^{o}C for 24 h.

2.4. Preparation of Cu NPs

Cu NPs are synthesized by the chemical reduction method reaction of copper (II) sulfate pentahydrate ($CuSO_4.5H_2O$) with sodium borohydride via wet method. Briefly, in the first stage, 200 mL of sodium hydroxide solution

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(NaOH) with a concentration of 2 M is added slowly with stirring to 100 mL copper sulphate solution with a concentration of 2 M. The solution temperature was raised to 80 ºC with vigorous stirring. Copper hydroxide $(Cu(OH)_x)$ and copper oxide (CuO_x) are formed and deposited as sediments. Then, the sediments are filtered and recovered. Distilled water and glucose are added to obtained precipitate and agitated until the color of the solution changed into dark red. Glycine (NH_2-CH_2-COOH) is added to the aqueous solution and this solution was placed into an ultrasonic bath. Then 100 ml of sodium borohydride solution (24 M), as a reducing agent, is added to solution drop by drop. The mixture is filtered, washed with distilled water and dried at 110 ºC in an inert atmosphere (N_2). The molar ratio of the mixture Cu^{+2}:NaOH:Glycine:$NaBH_4$ are 1:2:1:12 respectively [34,35].

2.5. Preparation of rGO/Cu NPs

The rGO powder was suspended in di-ionized water by sonication for 45 minutes to make rGO dispersed equably. Then, Cu nanoparticle was added to the suspended solution and was heated at 110 °C with stirring for 12 h. Afterward, the mixture is filtered by buchner funnel and washed with doubly distilled water three times. The resulting products were dried in an oven at 100 °C for 12 h. The flowcharts for rGO/Cu NPs preparation were presented in Figure 2.
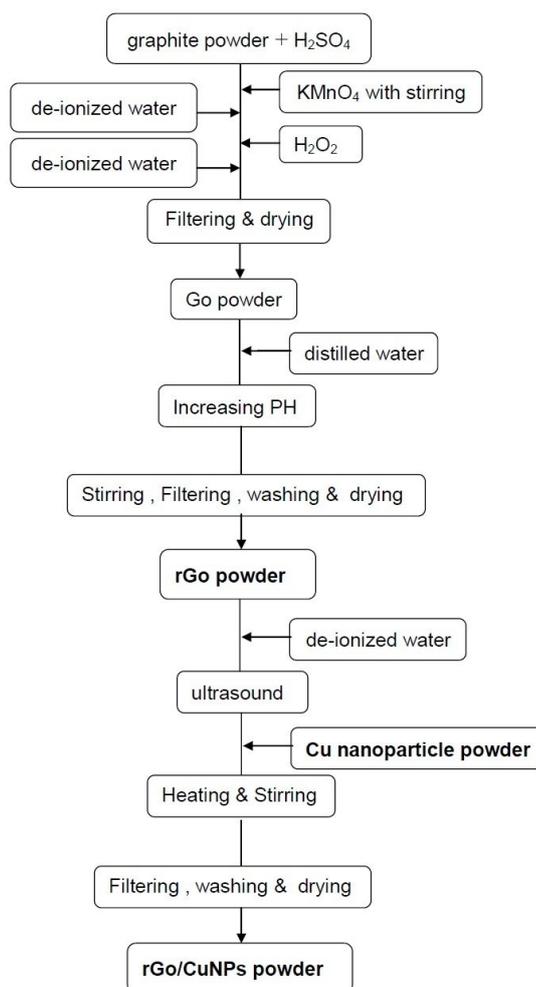
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Figure 2. Flowchart of rGO/Cu NPs preparation.

2.6. General procedure for the synthesis of formamides

A mixture of the appropriate arylboronic acid (1.0 mmol), NH_2CHO (2.5 mmol), base (1.3 mmol) and rGO/Cu NPs (25 mg) was stirred at 70 °C for the appropriate time. After completion of reaction (as monitored by TLC), ethyl acetate and water was added and organic layer was separated. Then, aqueous layer was extracted with ethyl acetate, washed with water, dried over $MgSO_4$, filtered and evaporated under reduced pressure. The residue was purified by column chromatography to give the desired pure products. All products are

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known in the literature and were characterized by IR, NMR and melting points and their spectroscopic data identical to that reported in the literature [15,16].

2.7. General procedure for the synthesis of primary amines:

RGO/Cu NPs (25 mg), arylboronic acid (1.0 mmol), K_2CO_3 (1.3 mmol), 25-28% aqueous ammonia (5 mmol) and methanol (4 mL) were added to a 50 mL round-bottomed flask. The reaction mixture was stirred under reflux conditions for the appropriate time. After completion of the reaction as monitored by TLC, the mixture was filtered, and the solvent of the filtrate was removed under vacuum with the aid of a rotary evaporator. The residue was purified by column chromatography on silica gel to afford the product. All products are known in the literature and the physical data (mp, IR, NMR) of the products were found to be identical with those reported in the literature [36,37].

3. Results and discussion

3.1. Characterization of catalyst

The crystalline structure of catalyst was confirmed with powder XRD (X-ray Powder Diffraction) measurements. The X-ray diffraction pattern revealed that Cu nanoparticles are very air-sensitive and easily oxidized to Cu_2O and CuO. X-Ray diffraction pattern of rGO/Cu NPs was shown in Figure 3. RGO exhibits a broad peak (002) at about of $2\theta = 25°$ [38]. The diffraction peak at 43.5° is

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correspond to (111) plane of fcc structure of copper. These results indicate that Cu nanoparticles have been combined with rGO. Peaks at 36.2° and 73.7[0] and peaks at 42.6° and 62.6° are respectively attributed to Cu_2O and CuO and appears because of oxidation of Cu nanoparticles [39].
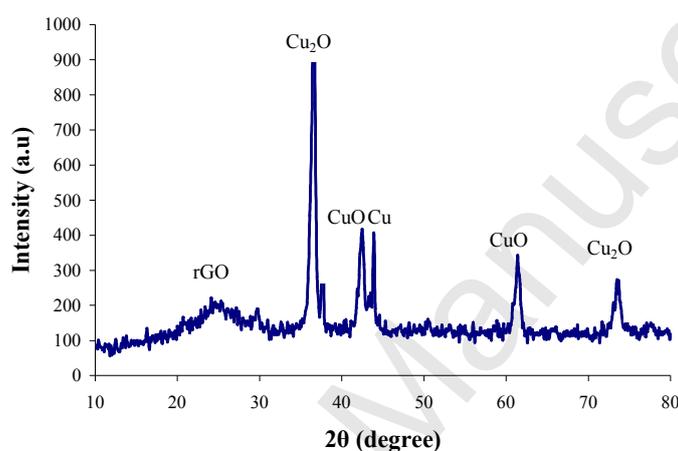

Figure 3. XRD pattern of rGO/Cu NPs.

A Scanning electron microscopic (SEM) image showed that uniform 90 nm sized copper nanoparticles were produced. SEM image of rGO/Cu NPs is shown in Figure 4. It is clearly observed that the Cu grain pervaded between rGO sheets, which displays a good combination between rGO sheet and CuNPs.

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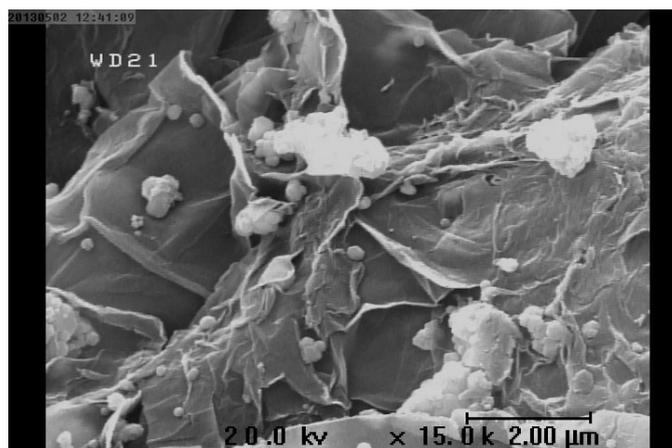
Figure 4. SEM image of rGO/Cu NPs.

We used Energy Dispersive X-ray Spectroscopy (EDS) to determine chemical composition of catalyst. In the EDS spectrum of catalyst, peaks related to C, O and Cu were observed. The atomic and weight ratios are listed in Table 1.

Table 1.

Atomic and weight ratios of catalyst.

Element	Series	Norm. C [wt %]	Atom. C [at %]
Carbon	K series	48.48	69.05
Oxygen	K series	21.35	22.83
Copper	K series	30.16	8.12

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The surface area of catalyst was determined by BET. The N_2 adsorption-desorption isotherm and Barrett-Joyner-Halenda (BJH) pore size distribution plot of rGO/Cu NPs showed in Figure 5. The BET (Brunauer-Emmett-Teller) surface area and single point total pore volume are 29.96 m^2 g^{-1} and 5.2×10^{-2} cc g^{-1}, respectively.
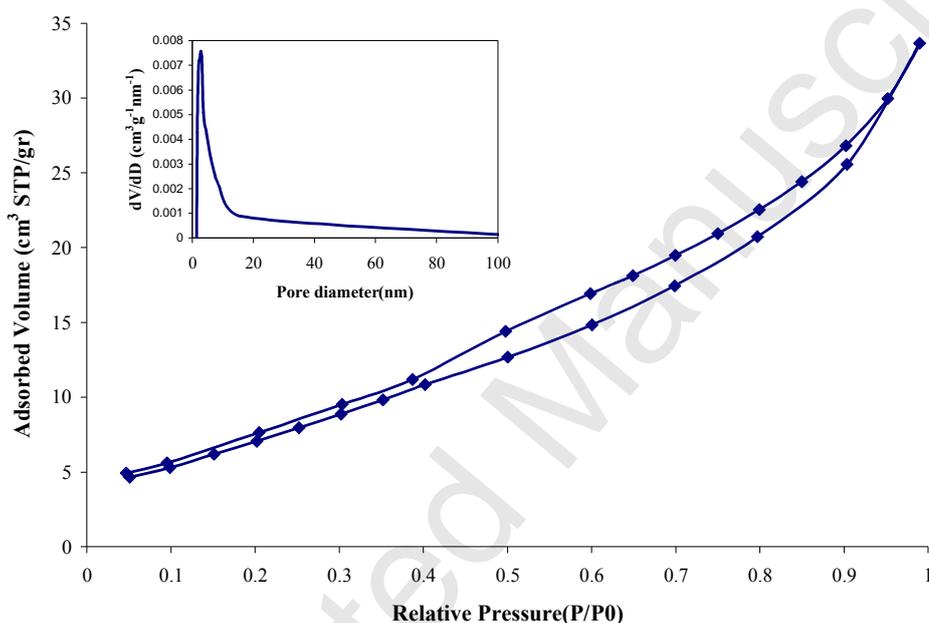

Figure 5. The N_2 adsorption-desorption isotherm and Barrett-Joyner-Halenda (BJH) pore size distribution plot of catalyst.

3.2. Activity of rGO/Cu NPs catalyst for the preparation of formamide products

The catalytic behavior of the rGO/Cu NPs was studied for the synthesis of formamides and amines from arylboronic acids. Reaction conditions were optimized for the formamidation reaction using phenylboronic acid as a substrate, NH_2CHO and rGO/Cu NPs as catalyst in the presence of various

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solvents and bases under various temperature conditions (Table 2). In the absence of catalyst, the reactions did not proceed after a long reaction time. However, addition of rGO/Cu NPs to the mixture caused rapid enhancement of the formamidation of arylboronic acids with high yields. Interestingly, when the reaction was carried out in the absence of solvent and only in the presence NH_2CHO (as both solvent & formylating agent), good conversion was achieved (Table 2, entry 5). The results indicated that base had a demonstrative effect on the yield of product (Table 2, entry 9). Among the various bases tested, Cs_2CO_3 is an effective base (Table 2, entry 5). The best result was obtained with phenylboronic acid (1.0 mmol), NH_2CHO (2.5 mmol), rGO/Cu NPs (25 mg) and Cs_2CO_3 (1.3 mmol) at 70 ºC, which resulted the product in a good yield (88%).

Table 2.

The formylation reaction phenylboronic acid with NH_2CHO under different reaction conditions.[a]

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Entry	Base	Solvent	Temperature (°C)	Yield (%)[b]
1	Cs_2CO_3	H_2O	100	21
2	Cs_2CO_3	MeOH	64	56
3	Cs_2CO_3	MeCN	81	61
4	Cs_2CO_3	Toluene	110	62
5	Cs_2CO_3	NH_2CHO[c]	70	88
6	KOAc	NH_2CHO[c]	70	40
7	Na_2CO_3	NH_2CHO[c]	70	79
8	Et_3N	NH_2CHO[c]	70	75
9	None[d]	NH_2CHO[c]	70	31

[a] Reaction conditions: $PhB(OH)_2$ (1.0 mmol), NH_2CHO (2.5 mmol), base (1.3 mmol), rGO/Cu NPs (25 mg), 70 °C, 9 h.

[b] Isolated Yield.

[c] As both solvent and formylating agent.
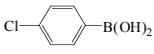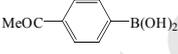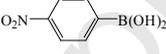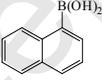
[d] No base.

Next we examined the utility of the rGO/Cu NPs catalyst with other arylboronic acids (Table 3). Arylboronic acids contain both electron-releasing and electron-withdrawing groups underwent the conversion in good to excellent

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yields. The formation of formamides was confirmed by melting point and IR spectra, which showed two characteristic peaks, one between 3300 and 3400 cm^{-1} (secondary NH) and the other between 1640 and 1680 cm^{-1} (*N*-formyl, C=O) [4i-j]. The relevant ^{1}H NMR spectrum shows two distinctive pro-ton signals; one is related to NH of the *N*-formamides and another belongs to the aldehyde [4i-j].

Table 3.
Formylation of different arylboronic acids by the rGO/Cu NPs.

$$ArB(OH)_2 + NH_2CHO \xrightarrow[\text{Cs}_2\text{CO}_3,\ 70\ ^\circ\text{C}]{\text{rGO/Cu NPs}} ArNHCHO$$

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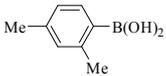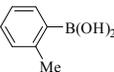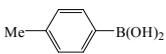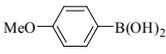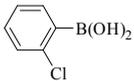
Entry	Product	Time (h)	Yield%[a]
1	C₆H₅—B(OH)₂	9	88
2	Me—C₆H₃(Me)—B(OH)₂	9	91
3	C₆H₄(Me)—B(OH)₂	9	93 (92,92,90)[b]
4	Me—C₆H₄—B(OH)₂	9	89
5	MeO—C₆H₄—B(OH)₂	9	92
6	C₆H₄(Cl)—B(OH)₂	15	86
7	Br—C₆H₄—B(OH)₂	14	88
8	Cl—C₆H₄—B(OH)₂	14	89
9	MeOC—C₆H₄—B(OH)₂	15	80
10	O₂N—C₆H₄—B(OH)₂	15	77
11	naphthyl—B(OH)₂	9	91

[a] Yields are after work-up.

[b] Yield after the fourth cycle.

3.3. Activity of rGO/Cu NPs catalyst for the preparation of primary amines

Due to the importance of primary aromatic amines in synthetic organic chemistry and in industry for the manufacture of pharmaceuticals, polymers and

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medicinal compounds [4i-j,40-43], we next turned our attention to applying rGO/Cu NPs to the synthesis of primary aromatic amines via the amination reaction of arylboronic acids with aqueous ammonia. In our experiment, aqueous ammonia is used as nitrogen source, which can significantly reduce the cost of the production.

We initially selected phenylboronic acid as a model substrate for optimization of the reaction conditions in the presence of various solvents and bases (Table 4). As expected, no target product could be detected in the absence of a copper catalyst (Table 4, entry 8). As shown in Table 4, among the various solvents tested in the presence of rGO/Cu NPs as catalyst, methanol led to significant conversion. When methanol was used as solvent, it could form hydrogen bonds with ammonia and thereby prevent the release of ammonia from solution. The reactivity of the catalyst in methanol in the presence of different bases was also investigated. Among the tested bases, K_2CO_3 was found to be superior for the highest yield of *N*-phenylformamide. The best result was obtained with phenylboronic acid (1.0 mmol), rGO/Cu NPs (25 mg), K_2CO_3 (1.3 mmol), $NH_3.H_2O$ (5.0 mmol), and MeOH (5 mL) at reflux, which obtained the product in a good yield (89%).

Table 4.

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Copper catalyzed amination of phenylboronic acid with $NH_3.H_2O$ using various bases and solvents.[a]

Entry	Base	Solvent	Temperature (^{o}C)	Yield ($\%$)[b]
1	Cs_2CO_3	H_2O	100	22
2	Cs_2CO_3	DMF	80	58
3	Cs_2CO_3	MeCN	81	64
4	Cs_2CO_3	MeOH	Reflux	87
5	K_3PO_4	MeOH	Reflux	72
6	KOAc	MeOH	Reflux	62
7	K_2CO_3	MeOH	Reflux	89
8	K_2CO_3	MeOH	Reflux	0^{c}

[a] Reaction conditions: $PhB(OH)_2$ (1.0 mmol), $NH_3.H_2O$ (5.0 mmol), base (1.3 mmol), rGO/Cu NPs (25 mg), solvent (5 mL), 15 h.

[b] Isolated Yield.

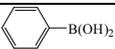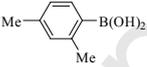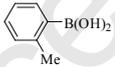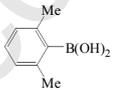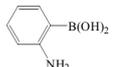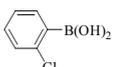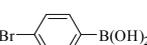[c] In the absence of catalyst under reflux conditions, no reaction occurred.

To demonstrate the scope of the application of rGO/Cu NPs, a wide range of functionalized arylboronic acids were coupled with aqueous ammonia under the optimized conditions. As expected, both arylboronic acids with electron-rich or
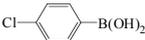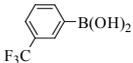
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electron-poor substituents and neutral arylboronic acids afforded good to excellent yields (Table 5) when reacted with aqueous ammonia. Significantly, the reactions between 2-aminophenylboronic acid and aqueous ammonia afforded corresponding 1,2-diaminobenzene product in good yield (Table 5, entry 5). The products were characterized by IR spectroscopy and melting points.

Table 5.

Amination of different arylboronic acids by the rGO/Cu NPs.

$$ArB(OH)_2 + NH_3.H_2O \xrightarrow[K_2CO_3, 60\ ^oC]{rGO/Cu\ NPs} ArNH_2$$
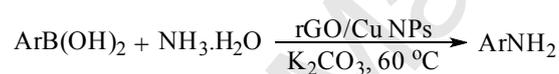
Entry	Product	Time (h)	Yield%[a]
1		15	89
2		14	92 (92,91,89)[b]
3		14	92
4		13	87
5		13	89
6		16	91
7		21	90

21
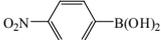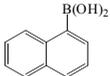
8	Cl—⟨benzene⟩—B(OH)₂	21	92
9	F₃C—⟨benzene⟩—B(OH)₂	21	84
10	O₂N—⟨benzene⟩—B(OH)₂	22	74
11	⟨naphthalene⟩—B(OH)₂	17	90

^a Yields are after work-up.

^b Yield after the fourth cycle.

To the best of our knowledge, catalyst rGO/Cu NPs is one of the most general and active catalysts reported so far for the synthesis of formamides and primary amines. These results represent a significant advancement in the C-N coupling reaction. Although the mechanism of Cu-catalyzed coupling is not obvious and further studies to elucidate the detailed reaction mechanism are ongoing in our laboratory.

3.4. Catalyst recyclability

Finally, the reusability of the catalyst was checked in the reaction of 2-methylphenylboronic acid with NH_2CHO under the present reaction conditions (Table 3, entry 3). After the completion of the reaction, ethyl acetate was added and the insoluble catalyst was separated from the reaction mixture by filtration. The catalyst was washed with water and ethyl acetate several times, dried and

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employed for the next reaction. The activity of the four consecutive runs (93%, 92%, 92% and 90%) revealed the practical recyclability of the applied catalyst. This reusability demonstrates the high stability and turnover of catalyst under operating condition. The reusability of the catalyst was also studied for the amination reaction of 2,4-dimethylphenylboronic acid with $NH_3.H_2O$ under the present reaction conditions (Table 5, entry 2). The catalytic activity did not decrease considerably after four catalytic cycles. The reusability of the catalysts is one of the most important benefits and makes them useful for commercial applications.

4. Conclusions

In conclusion we have developed an efficient copper catalyzed protocol for the preparation of formamides and primary amines form arylboronic acids. An efficient, easily recoverable and reusable rGO/Cu NPs catalyst was prepared and characterized by SEM, XRD, BET and EDS spectroscopy. This method has the advantages of high yields, elimination of homogeneous catalysts, simple methodology and easy work up. The rGO/Cu NPs is eco-friendly catalyst because it produces little waste, and can be recovered by simple filtration and successively reused without the significant loss of activity.

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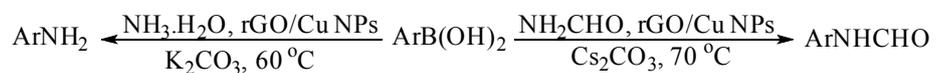[13] P. G. Reddy, G. D. K. Kumar, S. Baskaran, Tetrahedron Lett. 41 (2000) 9149.

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Synthesis and characterization of copper nanoparticles supported on reduced graphene oxide as a highly active and recyclable catalyst for the synthesis of formamides and primary amines

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$$ArNH_2 \xleftarrow[K_2CO_3,\ 60\ ^oC]{NH_3.H_2O,\ rGO/Cu\,NPs} ArB(OH)_2 \xrightarrow[Cs_2CO_3,\ 70\ ^oC]{NH_2CHO,\ rGO/Cu\,NPs} ArNHCHO$$

Graphical Abstract

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Highlights:

- ➢ Formamidation and amination of different arylboronic acids using rGO/Cu NPs.

- ➢ The catalyst was characterized using the powder XRD, SEM, BET and EDS spectroscopy.

- ➢ Catalyst can be easily recovered and reused.

- ➢ Operational simplicity, short reaction times and high yields.

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