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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.

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 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, $2630\,m^2\,g^{-1}$), 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 heterogeneous catalysts for facilitating synthetically useful transformations [19–24]. Graphene oxide, a delaminated layer of graphite oxide (GO), is typically prepared by the exhaustive

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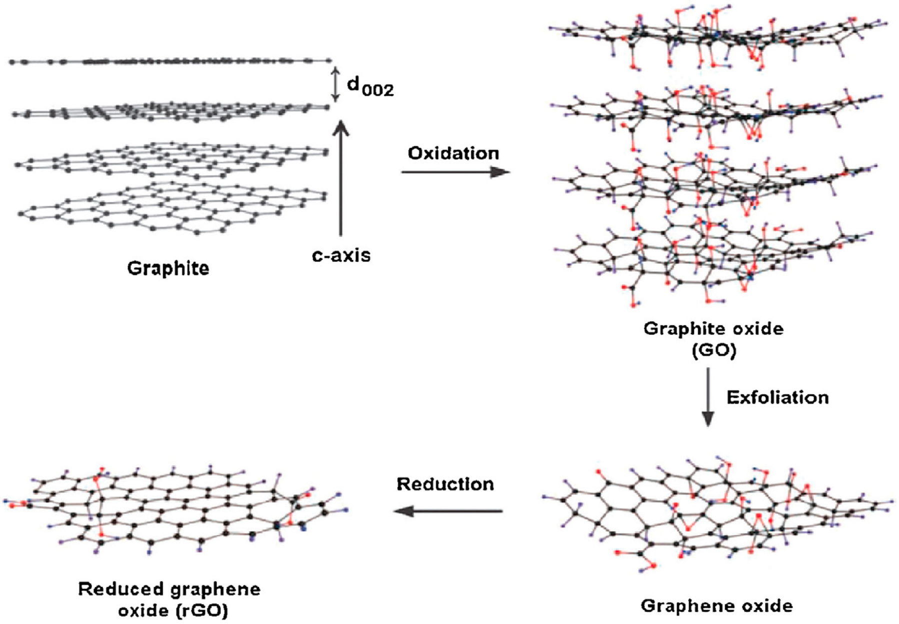
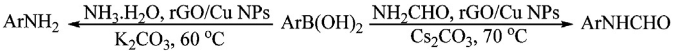


Fig. 1. Illustration on the preparation of reduced graphene oxide.

Source: Adapted from Ref. [28]



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

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

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].

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.

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. 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 $CuSO_4{\cdot}5H_2O$ with $NaBH_4$.

2. Experimental

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 Å and the diffraction patterns were recorded in the 2θ range (10–60) with scanning speed of 2°/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. 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 °C 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 1 h. 500 mL de-ionized water was added