



Nitro resin supported copper nanoparticles: An effective heterogeneous catalyst for C–N cross coupling and oxidative C–C homocoupling

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ABSTRACT

In the present study, we investigate the synthesis and catalytic activity of copper nanoparticles (CuNPs) stabilized onto a novel nitro functionalized polystyrene resin. The deposited nanoparticles were characterized by various analytical techniques and TEM images, revealed uniformly distributed copper nanoparticles of sizes 3–9 nm. We effectively used the resin impregnated CuNPs for C–N coupling of various aromatic amines with aryl halides and for the oxidative C–C homocoupling of phenylacetylene. Further, recycling of the catalyst, leaching of metal ions and post reaction changes in the support were studied and it was concluded that the support acts as oxidant during the homocoupling of phenyl acetylene which is oxidative by nature.

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1. Introduction

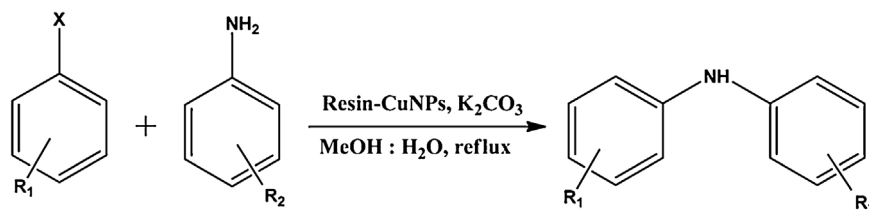
The catalysis of carbon–carbon and carbon–nitrogen bond formation is central to synthetic chemistry especially synthesis of pharmaceuticals and functional materials. Burgeoning literature on nanocatalysis indicates the interest of researchers in metals other than routinely used and expensive palladium, platinum etc. [1,2]. Copper(0) at nanoscale, is being widely explored for such coupling reactions [3–5] as it is not only cheaper but also less toxic compared to palladium. But due to its reactive nature, stabilization of copper in nanoform and its reuse is difficult. Copper nanoparticles not only need protection against aggregation but also from atmospheric oxidation or surface hydroxylation [6]. A good support can fulfil both these aims. Many supports such as SiO₂ [7], Al₂O₃ [8,9], MgO [10], Y-Zeolite [11], graphene [12], graphene oxide [13], perlite [14], ionic liquids [15,16], PVC [17], have been reported for stabilization of copper nanoparticles. Polymer supports are generally more attractive for liquid phase reactions. Recently, John Mondal et al. have developed two new heterogeneous Cu(0) nanocatalysts, where CuNPs were deposited on carbonaceous matrix and nanoporous polymer DVAC-1, and studied their catalytic performance for the coupling reactions of aryl iodides and bromides with

primary and secondary aliphatic amines in aqueous solution [18]. Borah et al. have stabilized copper onto montmorillonite while Islam et al. have stabilized copper on polyaniline to carry out “click” reaction between azide and terminal alkynes [19,20]. Gholinejad have stabilized copper nanoparticles on Agarose, a bio-organic and degradable polymer, to carry out “click” reaction between azide and terminal alkynes [21]. Reddy et al. synthesized copper nanoparticles on cellulose support and successfully catalyzed N-arylation of nitrogen heterocycles with aryl halides and aryl boronic acids [22].

Supporting of nanocatalysts on cross-linked resins is not new and recent development have shown that synthesis of nanoparticles on resin is easy as the polymer matrix can effectively control the size of nanoparticles [23,24]. Polystyrene resins functionalized with acidic or basic groups have been reported to stabilize nanoparticles of Ag, Au, Pd, Ni etc. and successfully used in organic synthesis [25]. But there are hardly any example of copper nanoparticles being supported on such resins though, a few cases of bimetallic nanoparticles are there [26]. In our lab, we have earlier synthesized palladium and gold nanoparticles supported on a commercially available nonfunctional Amberlite XAD-4 resin where, the formation of stable and recyclable catalyst with excellent activity towards C–C coupling reactions was achieved [27,28]. However, we observed that copper nanoparticles synthesized in this inert resin were not stable and brown coloured CuNPs impregnated resin beads quickly changed colour to bluish green on keeping. This was attributed to surface hydroxylation of copper(0) nanoparti-

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Scheme 1. C–N coupling reactions of aryl halides with aryl amines.

cles. Nitrobenzene has been used as a solvent and a mild oxidant in the Skraup synthesis of quinoline [29]. It is a polar group and can enhance the hydrophilicity of extremely hydrophobic polystyrene. To the best of our knowledge nitro functionalized resin has never been explored for the synthesis of nanoparticles. Prompted by this information, we functionalized Amberlite XAD-4 resin with nitro group with an assumption that negatively charged oxygen atoms may co-ordinate with surface atoms of copper nanoparticles aiding their stabilization. Copper nanoparticles synthesized in this modified resin were found to be stable and were characterized by various analytical techniques. We studied C–N coupling of aryl amines aryl halides and oxidative C–C homocoupling of phenyl acetylene. All the reaction parameters were studied and conditions were optimized for the best reaction yield.

2. Experimental

2.1. Materials and instruments

All chemicals used were of analytical grade or of the highest purity available. Amberlite XAD-4 (surface area $725 \text{ m}^2 \text{ g}^{-1}$ mesh sizes 20–40) and copper acetate were purchased from Aldrich. Aryl halides, and acetylene derivatives were purchased from Aldrich. Ethyl acetate, methanol, K_2CO_3 and NaBH_4 were purchased from Finar Chemicals. Water used in all experiments was purified by Millipore-Q system. All glassware was thoroughly cleaned with freshly prepared 3:1 HCl/HNO_3 (aqua regia) prior to use. Nitration was carried out by using three different procedures to prepare nitro functionalized resin with different N-content (see Supplementary information).

IR spectra were recorded on Bruker FT-IR spectrophotometer as pellets after mixing with KBr. The pellet containing 1 mg of sample was scanned within a range of $600\text{--}4000 \text{ cm}^{-1}$. The percentage elemental composition was analyzed by C H N Elemental Vario Micro Cube analyzer. High resolution transmission electron microscopy (HR-TEM) pictures were taken using a Hitachi (H-7500) instrument. The swollen resin beads were milled and a drop of alcoholic suspension was placed into a 200 mesh carbon coated copper grid. It was then dried to evaporate the solvent and used for microscopy. The powder XRD of the catalyst was recorded on Bruker D₂ Phaser using $\text{Cu K}\alpha$ radiation ($\lambda = 1.54184 \text{ \AA}$) and a filter of nickel at 30 kV and 10 mA with step size 0.03 and count time 0.1 s. Scanning electron microscopy (SEM) image of the bead was taken with a LEO 440i Electron Microscope after coating it with gold. UV–vis absorption spectra were acquired on a Jasco V-570 UV–vis spectrophotometer. GC–MS measurements were carried on Shimadzu-QP 5000/QP 5050 A with DB – 5 MS column, detector temperature 300°C , column heating rate $15^\circ\text{C}/\text{min}$ upto 300°C , He gas flow rate of 1 ml/min. Atomic absorption spectroscopy (AAS) measurements were carried out on an Atomic absorption spectrophotometer SL-243 Elico instrument: Voltage 619 V, nebulizer flow 7 ml/min, wavelength 324.8 nm, slit width 0.5 nm, current 5.0 mA and air-acetylene flame. ^1H NMR spectra were measured in Bruker AV 400 MHz using CDCl_3 as solvent and TMS as internal standard. Mass spectra were recorded by injecting the samples in ESI

ionizer of Shimadzu LCMS 2010 with the single quadruple analyzer. XPS measurements were conducted at an ultrahigh vacuum (UHV) multipurpose surface analysis system (Specs™ model, Germany) at the SCAI in Universidad de Cordoba (Spain), operating at pressures $<10^{-14}$ MPa using a conventional X-Ray source (XR-50, Specs, $\text{Mg-K}\alpha$, 1253.6 eV) in a “stop-and-go” mode to reduce potential damage due to sample irradiation. The survey and detailed high-resolution spectra (pass energy 25 and 10 eV, step size 1 and 0.1 eV, respectively) were recorded at room temperature using a Phoibos 150-MCD energy analyser. Powdered samples were deposited on a sample holder using double sided adhesive tape and subsequently evacuated under vacuum ($<10^{-6}$ Torr) overnight. Eventually, the sample holder containing the degassed sample was transferred to the analysis chamber for XPS studies. Binding energies were referenced to the C1s line at 284.6 eV from adventitious carbon.

2.2. Preparation of resin supported copper nanoparticles (Resin-CuNPs)

The resin supported copper nanoparticles were synthesized by a simple sorption-reduction method. Initially, the nitro functionalized Amberlite XAD-4 beads (5.0 g) were washed repeatedly with water to remove reagents, swollen in methanol and then equilibrated with 100 ml of 5 mmol solution of copper acetate in methanol. After 24 h, the excess solution was drained off and the metal was reduced by passing cold aqueous NaBH_4 (0.1 mol dm^{-3} $10\text{--}15^\circ\text{C}$) solution. Excess reagent was removed by washing the beads with water and the CuNPs impregnated beads were stored in dry methanol.

2.3. General procedure for the N-arylation of aryl amines with aryl halides

In a 25 ml round bottom flask a mixture of 4:1 methanol/water, aryl halide (1 mmol), Resin-CuNPs (0.2 g), K_2CO_3 (3 mmol) and aryl amine (1.2 mmol) were taken and heated at reflux temperature for 12–24 h in an oil bath under inert conditions. Resin beads were filtered off at the end of reaction while the solution was still hot. After a work up with dichloromethane and water, the organic layer was separated, dried over anhydrous Na_2SO_4 . The crude products obtained after removal of solvent (Scheme 1) were purified by column chromatography (ethyl acetate: hexane) and identified by mass or ^1H NMR spectroscopy (see ESI).

2.4. Synthesis of 1,4-diphenylbuta-1,3-diyne by homocoupling of phenyl acetylene

In a 25 ml two necked round bottom flask containing phenyl acetylene (1 mmol), base (1 mmol), catalyst (100 mg) and DMSO (3 ml), O_2 gas was purged with the help of a balloon. The flask was heated at 50°C for 8 h and the progress of the reaction was monitored by TLC. After the completion of the reaction, the catalyst was separated while the solution was still hot and the reaction quenched by pouring the filtrate in chilled water. The reaction mixture was extracted with ethyl acetate and a light yellow crude

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