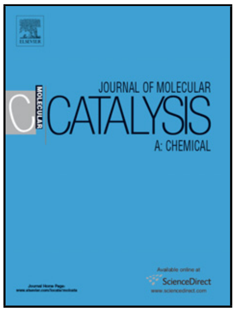

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Nitro resin supported Copper Nanoparticles: An Effective Heterogeneous Catalyst for C-N Cross Coupling and Oxidative C-C Homocoupling

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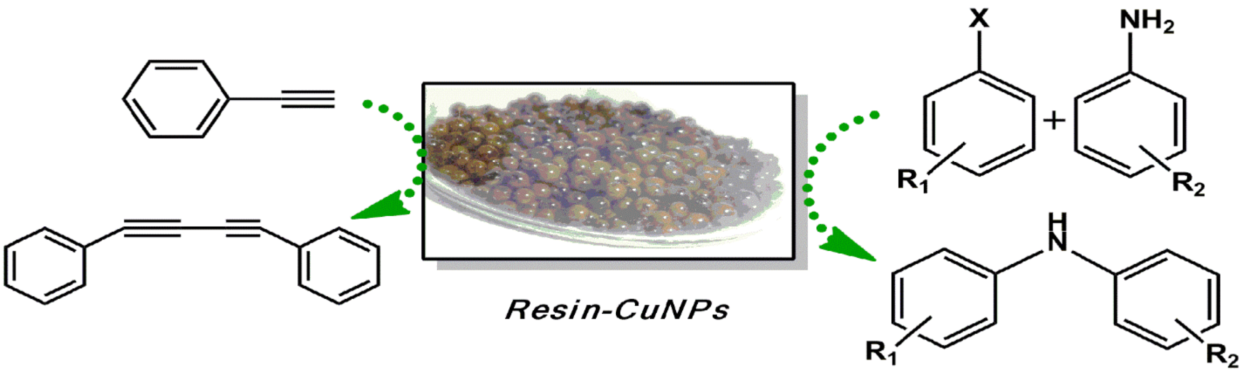
Graphical abstract



Highlights of the work

- Work presents a new nitro functionalized support for stabilizing copper nanoparticles.
- CuNPs catalyzed oxidative C-C homocoupling and C-N coupling
- C-N coupling in benign solvent.
- Catalyst regeneration and recycling.

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 phenyacetylene. 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.

KEYWORDS

Copper nanoparticles, N-arylation, oxidative homocoupling of alkynes, nitro resin supported CuNPs, Oxidative support.

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 SiO_2 [7], Al_2O_3 [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 and co-workers 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 and co-workers 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 and co-workers 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) nanoparticles. Nitrobenzene has been used as a solvent and a mild oxidant in the Skraup synthesis of quinolone [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 m^2g^{-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 to 4000 cm^{-1}. The percentage elemental composition was analyzed by C H N Elementar 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 Brucker D_2 Phaser using Cu Kα radiation (λ = 1.54184 Å) and a filter of nickel at 30 kV and 10 mA with step size 0.03 and count time 0.1s. Scanning electron microscopy (SEM) image of the bead was taken with a LEO 440i Electron Microscope after coating it with gold. UV–Visible absorption spectra were acquired on a Jasco V-570 UV–visible 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 ˚C/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. ^{1}H NMR spectra were measured in Bruker AV 400MHz 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, Mg-Kα, 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 – 15 ˚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 halides with aryl amines

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 (1mmol), 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 product was isolated after removing the solvent in a rotary evaporator. The crude after purification was identified by NMR (Scheme 2).

3. Results and discussion

3.1 Synthesis and characterization of CuNPs

Heterogenization of nanoparticles by stabilizing them on different supports and the effect of support on the catalytic reaction is an important area of research in the field of catalysis. Amberlite XAD-4 is a commercial polystyrene resin that has many physical attributes such as porosity; uniform pore size distribution, high surface area, durability and chemical stability towards acids, bases and oxidizing agents. These make it an attractive material for supporting catalysts. Functionalization of the resin can enhance their ability to stabilize metal nanocatalysis [30]. It can also impart excellent hydrophilicity to these otherwise hydrophobic resins. This enhances their metal sorption capacities as well as swelling properties. The latter enables the reactants to make better contact with the embedded catalyst [31]. Polystyrene resin was nitrated using different methods in order to obtain different degree of nitration that was measured by determining their N-content using CHN analyser. Details of resin nitration are provided in ESI. It was observed that the metal sorption capacity of resin increased with the increase in functionalization. Copper acetate was used as metal precursor and the resin beads were impregnated with nanoparticles by simple sorption reduction technique. IR spectra of the resin taken before and after impregnation showed that the chemical structure of the resin remained unchanged. The nitrated resin beads, which were pale to dark yellow in colour became brown on impregnation with copper nanoparticles. No deterioration in the colour of the resin was observed on storing the nanoparticles in dry methanol over long period of time. Nitro is not very common co-ordinating group unlike amino and carboxylic groups that are frequently used to cap and stabilize nanoparticles. However, with two oxygen atoms, there is considerable electron density on this functional group and of late, its coordinating properties with metals has been established [32]. Schematic stabilization of copper nanoparticles inside the resin pores is shown in Fig.1.

The XRD pattern of the finely powdered resin beads is shown in Fig. 2. Amorphous polymer resin showed a broad hump at 2θ value below 30. Some peaks were indicated in the 2θ region of 30° to 50° but they were unresolved. This was attributed to low loading of catalyst and nano size of the particles. The latter invariably leads to large broadening of the peaks. A catalyst with higher loading of the metal was prepared using 10 mmol solution of precursor. The peak observed near 2θ = 43.0 (Fig. 2b) was identified as (1 1 1) reflection (JCPDS No. 04-0836) corresponding to the fcc lattice of copper (0) [33]. Another scan in the range of 40° to 48° with step size 0.02 and count time of 3s was carried out (Fig. 2c) which clearly showed the peak at 43.1206. This conclusively proved the presence of Cu (0) in the catalyst. A second peak was observed at 2θ = 36.381 that corresponds to (1 1 1) reflection of oxide of copper. Thus, it can be concluded that supported copper (0) nanoparticles were covered with an oxide layer. Same was also indicated by electron diffraction obtained during TEM analysis.

The shape and size of nanoparticles was studied by HR-TEM. TEM pictures (Fig. 3.) of all the three CuNPs impregnated resins were studied and it was observed that the number of nanoparticles increased with increase in nitrogen content and hence metal sorption capacity of the resin. Mostly spherical but some irregular shaped nanoparticles were also observed. The variation in size of the nanoparticles for resin 3 with copper loading of 0.21 mmol /g was measured between 3 to 9 nm. This resin was used in all catalytic reactions.

Further studies on X-Ray Photoelectron Spectroscopy (XPS, Figure 4) confirmed the presence of both Cu^{2+} and Cu reduced species as clearly visualized in Cu2p XPS experiments. The presence of a shake-up peak (about 940–945 eV) is characteristic of Cu^{2+} species, particularly of CuO (in the absence of Cu^{2+} species, no shake-up peaks can be visualized) [34], is in good agreement with XRD results. The presence of lower Cu2p3/2 binding energy peaks (933 eV) indicates the existence of reduced copper species [35]. However, the distinction between Cu^{+} and Cu^{0} species (that appear at very similar binding energies) is only feasible through examination of the Auger spectra [36]. O1s spectra also supported the presence of Cu-O bonds with the O1s contribution (ca. 15%) centered at 529.0 eV, assigned to the presence of metal oxides [37]. The surface copper content, according to XPS, was ca. 8.1 %, with the additional confirmation of the presence of N in the materials (N1s spectra, results not shown). Nevertheless, no clear evidences of the coordination of nitro groups with copper species could be drawn from XPS data.

3.2. C-N cross coupling reaction catalyzed by Resin-CuNPs

Compounds containing aryl amines moieties are widely used as agrochemicals, pharmaceuticals, dyes, conducting polymers and as intermediates for organic synthesis [38]. The classical Ullmann reactions carried out using copper as catalyst is tricky for industrial application as it involves high temperature, stoichiometric amount of metal and high cost of waste disposal [39-41]. So, development of environmentally benign methods for N-arylation or C-N coupling is an important task. Transition metal catalyzed cross coupling reactions of aryl amines with aryl halides has been widely studied. These reactions are catalyzed by palladium or copper salts using a variety of ligands such as diamine, diimines, amino acids, β-ketoesters and 1, 10-phenanthroline derivatives, ninhydrin, diols, amino arenethiolate, phosphine ligands, hydrazones, N-hydroximides, hydroxyquinoline etc. [42, 43]. Most of these methods are homogeneous in nature which makes the recovery of catalyst difficult and the presence of stabilizing ligands further complicates the catalytic reaction. Performing these reactions under heterogeneous conditions is favorable as it facilitates work-up, recovery and reusability of the catalyst for multiple reaction cycles [44-46]. One of the highlight of nanoparticle catalysis is their ability to catalyze reactions in the absence of ligands. Our studies are especially aimed at establishing ligand less green protocols for organic synthesis in benign solvents.

The reaction between Iodobenzene and aniline was chosen as the standard reaction and reaction conditions such as optimum ratio of reactants, catalysts, solvents base etc. was established by carrying out the reaction frequently with changing parameters. A ratio of 1:1.2 between iodobenzene and aniline was found to be ideal. All the three catalyst were tried (Table 1) and best yield was observed with 200 mg of catalyst 3. This corresponded to 4.2 mmol % of copper. Presence of CuNPs was essential for the catalytic reaction as no product formed in the absence of catalyst.

The effect of other parameters on the reaction was studied and results are tabulated in Table 2. Base played an important role in this reaction and both organic as well as inorganic bases were investigated. KOH and K_2CO_3 were found to be equally effective in methanol/water system. Quantitative yield of diphenyl amine was obtained using NaO^{t}Bu in toluene. Tri ethyl amine (TEA) was ineffective as base. The reaction was studied using a variety of solvents such as acetonitrile, toluene, DMF, THF, dioxane, methanol and methanol water mixture. Good results can be obtained in both polar and non-polar type of solvents using appropriate base. However, methanol-water mixture in 4:1 ratio was considered the best choice as it was easy to remove, benign in nature and no side products were observed on the TLC of the reaction mixture.

The generality and the scope of the catalytic reaction were further explored by carrying out the reaction with different aryl halides and the results are shown in table 3. All the reported results are for the reactions carried out in MeOH - H_2O though, other solvents like DMSO and Toluene with sodium tertiary butoxide (NaO^tBu) was equally effective. N-arylation of aniline with all the three aryl halides viz. iodo, bromo and chloro were successful. However, product yield decreased as we moved from iodobenzene to chlorobenzene (table 3 entries 1, 5, 8). Effect of electron donating and electron withdrawing groups on the reactivity of aryl halides was also investigated. Especially noteworthy is the case of 4-nitro aryl halide where 4-nitroanisole was obtained as major product which indicated ring activation towards methoxylation rather than amination in the presence of strongly electron withdrawing nitro group. Replacing methanol with acetonitrile as solvent gave the corresponding amine products (table 3 entries 4, 7, 9). In case of entry 11 where an electron withdrawing nitro and electron donating methoxy group was attached, major product was the corresponding diphenyl amine.

3.3. *C-C oxidative homocoupling of phenyl acetylene catalyzed by Resin-CuNPs*

Being a versatile building block in organic chemistry, 1,3-diynes are important intermediates in the synthesis of natural products, polymers, pharmaceuticals and in material science [47, 48]. Synthesis of conjugated diynes has been reported by couplings like Elington, cadiot-chodkiewikz, sonagashira and hay-glaser etc. Lately, salts of many transition metals like Ag, Au, Ni, Pd and Cu have been used to catalyze this coupling reaction as homogeneous and heterogeneous catalysts [49-51]. However, there are only a few reports of nanoparticles as catalysts in this oxidative coupling reaction [52-54]. We have used a nitro resin for stabilization of CuNPs. Nitrobenzene has been used as a solvent and mild oxidant in the Skraup synthesis of quinoline. It has been reported as a mild oxidant in the ruthenium catalyzed oxidative coupling of alkynes [55]. These reports prompted us to explore nitro resin stabilized CuNPs for oxidative coupling of phenyl acetylene and we got excellent conversion and yield. The effect of solvent, base, catalyst concentration and temperature on the reaction was studied and the results are reported in table 4. Among the various solvents used best yield was obtained in DMSO with 96 % conversion in 8 hours. Different bases such as K_2CO_3, Na_2CO_3, KOH, NaOH, TEA etc. were studied. K_2CO_3 was selected as optimum base as it gave high conversion without any undesired products in the reaction mixture.

The generality and the scope of the catalytic reaction were further explored by carrying out reaction using different terminal alkynes and the results are shown in table 5. Homocoupling of aliphatic as well as aromatic terminal alkynes was successfully achieved. Phenyl acetylenes are activated by electron withdrawing groups. In the present case we obtained excellent yields with both strong and weak electron donating groups like $-OCH_3$, -OH, and $-CH_3$. Especially noteworthy is reaction with bromo substituted phenyl acetylene where only one product i.e. 1,4-bis(4-bromophenyl)buta-1,3-diyne was obtained.

The effect of temperature on the rate of reaction was studied by varying the temperature of oil bath from 40 to 90 °C. Quantitative conversion was obtained at 50 °C, thereafter, the yield of isolated product decreased on increasing the temperature (figure 5). The effect of catalyst concentration was studied by varying the catalyst quantity from 50 to 150 mg and the results are shown in figure 4.100 mg of catalyst was sufficient to complete the reaction. This amount of catalyst corresponds to 2.1 mol. % of the copper. The effect of time on the progress of reaction was also investigated. Reaction mixture was withdrawn at regular intervals of time and progress of reaction was monitored by GCMS. Complete conversion was observed in 8 h. Further increase in reaction temperature led to decrease in the yield of isolated product.

3.4 Recycling and reusability of the catalyst

Recycling and reusability is the most important aim of catalyst heterogenization. In this respect usage of polymer resins beads as support is highly useful as they are easy to handle and can be separated by simple filtration. Resins have tendency to sorb reagents and hence, thorough washing of beads is necessary. In the present case the catalyst was separated from the reaction mixture by filtration and washed frequently with appropriate solvents (water/methanol/acetone) to completely remove the sorbed products. The recyclability of the recovered catalyst was checked for both the reactions viz. N-arylation of iodo benzene with aniline and homocoupling of phenyl acetylene. The results are shown in figure 6. It can be seen case of N-arylaiton there is little decrease in activity. However, in case of oxidative homocoupling reaction the decrease in activity was substantial after each cycle.

Leaching is an important issue that depletes the activity of heterogeneous catalyst. A hot filtration test was performed to check leaching of the catalyst during the reactions. In both the cases reactions were stopped at half the reaction time which was 6 h for N-arylation of aniline and 4 h for homocoupling of phenyl acetylene (Figure 7). The catalyst was filtered off and the filtrate was heated further to check the progress of reaction. In both the cases no significant change in the concentration of reactants was observed. Additionally, the filtrate was analyzed for the presence of copper by Atomic absorption spectrometer (AAS) and the concentration of copper in the filtrate which was estimated to be 55 ± 10 ppb and 48 ± 10 ppb respectively.

As the leaching was very low in oxidative homocoupling, we assumed that the passivation may be due to the fact that the reaction was carried out in the presence of oxygen which can lead to the formation of oxide layer on the surface of copper nanoparticles. We passed cold 1 mmol solution of $NaBH_4$ over the catalyst and retested its activity. Quantitative results were obtained on recycling. Further, we also checked the effect of reaction parameters on the support. FTIR spectra of the used and fresh resin were taken (figure 8) and compared. It was observed that there is no change in the functional groups of the resin during N-arylation. However, after oxidative coupling the stretching frequencies of nitro group which appeared at 1526 and 1347 cm^{-1} in fresh resin changed. The band at 1526 cm^{-1} shifted to 1512 cm^{-1} and the intensity of the band at 1347 cm^{-1} decreased. This indicated the conversion of nitro group to nitroso group. This indicated that the support was acting as an oxidant in the reaction.

4. Conclusions

In summary, we report that nitro functionalized polystyrene can be used to synthesize highly stable reusable copper nanoparticles. The loading of copper metal is affected by degree of nitration This is a new robust support reported for stabilizing copper nanoparticles which is highly suitable for solution phase reactions. Copper nanoparticles were found to be stable in dry methanol over a long time and the work may throw new light on the stabilizing mediums used for nanoparticles. The catalyst was found highly active for homo coupling of phenyl acetylene. Good recycling of the catalyst, environmentally benign solvents and hardly any leaching of the metal into reaction mixture make it a promising catalyst for ligand free coupling of aryl halides with aryl amines. We are studding other applications of this catalyst.

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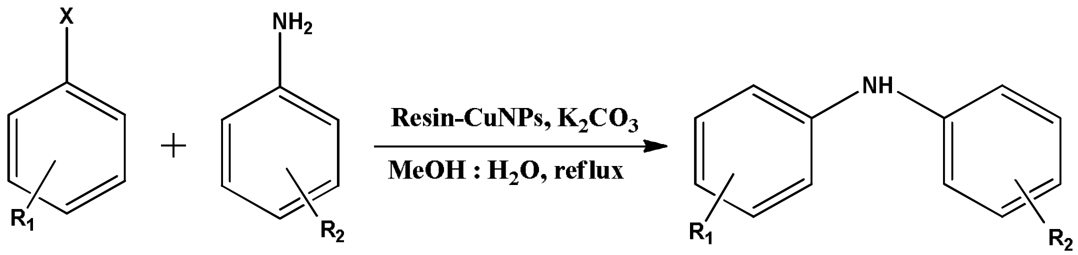
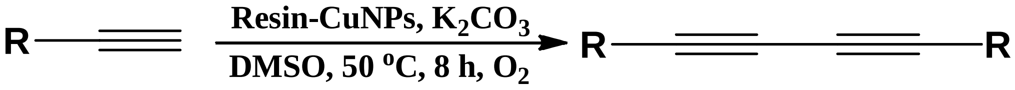


Scheme 1. C-N coupling reactions of aryl halides with aryl amines



Scheme 2. Glaser-Hay coupling of terminal alkynes

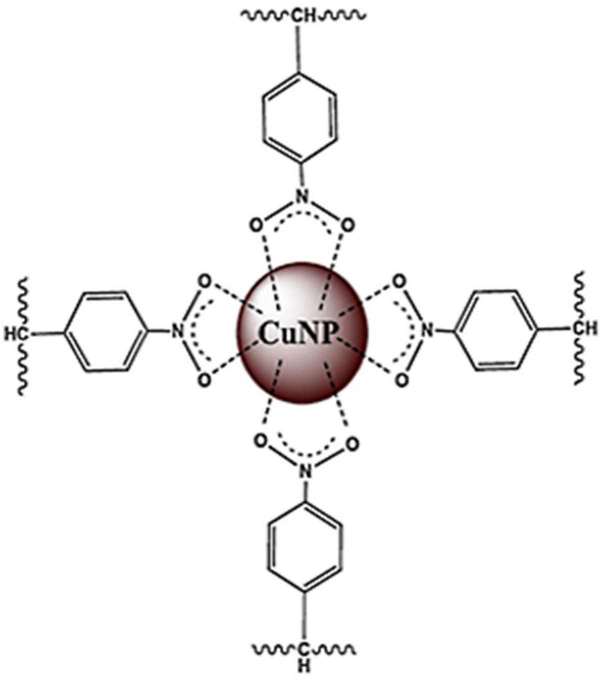


Fig. 1. Stabilization of CuNPs inside nitro functionalized resin

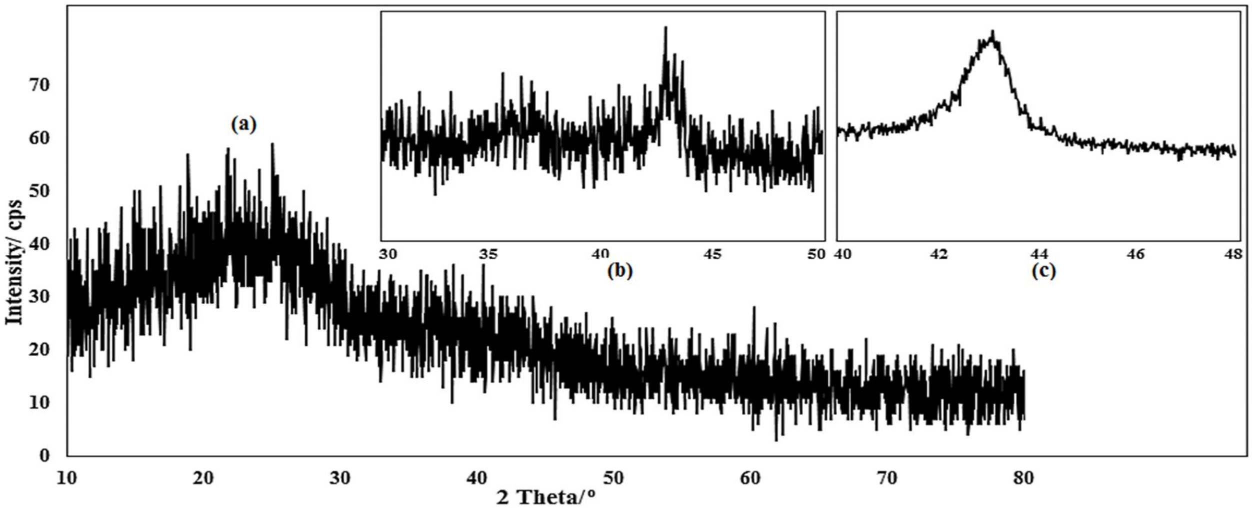


Fig. 2. XRD pattern of resin-CuNPs

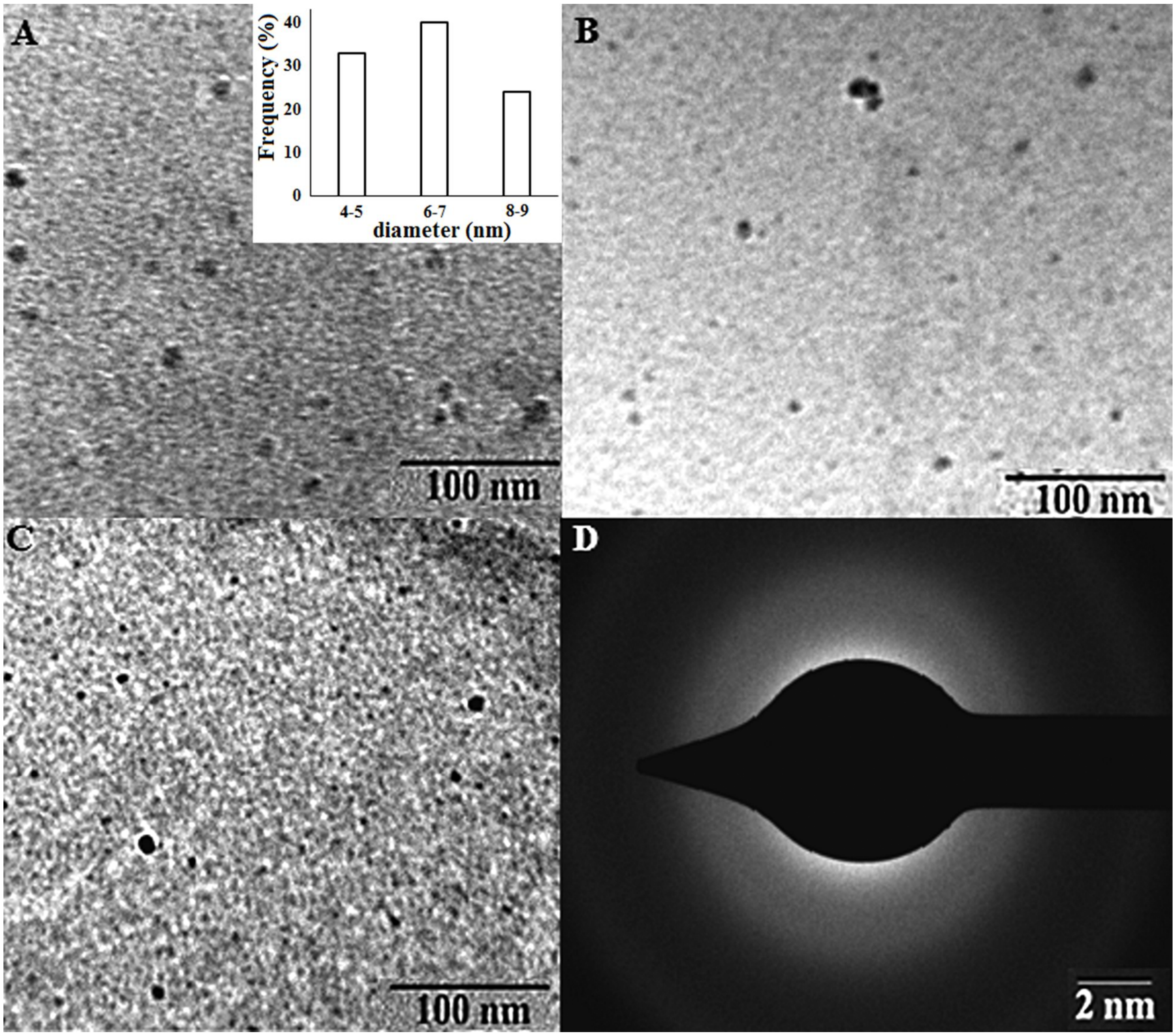


Fig. 3. TEM image of resin-CuNPs a) catalyst 3 b) Catalyst 2 c) catalyst 1 d) electron diffraction pattern

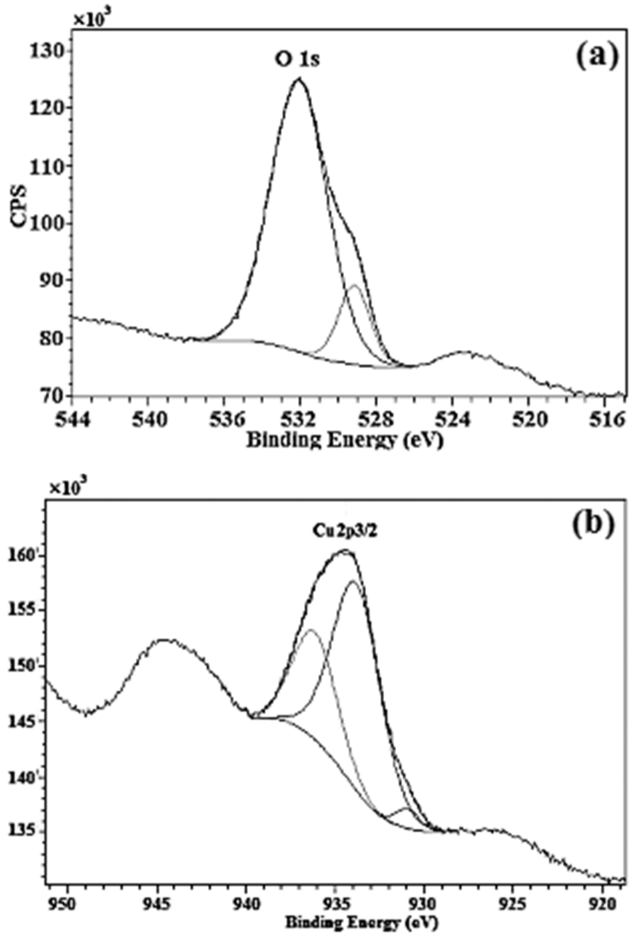


Fig. 4. a) O1s and b) Cu2p XPS spectra of Resin-CuNPs

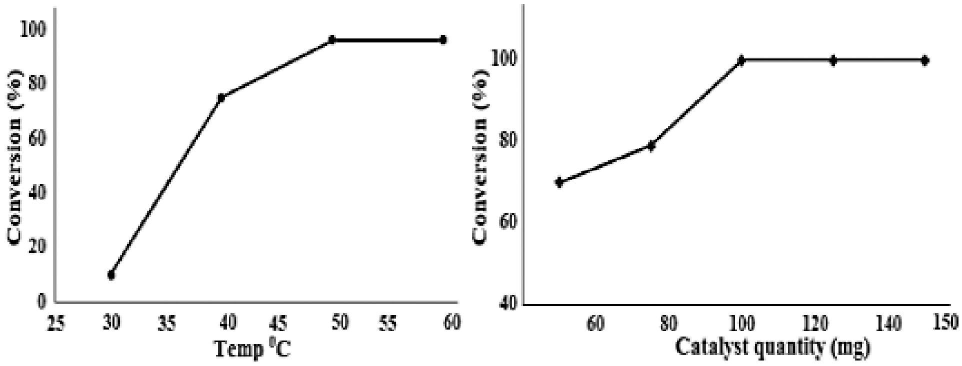


Fig. 5. Effect of Catalyst quantity and temperature on the homocoupling reaction

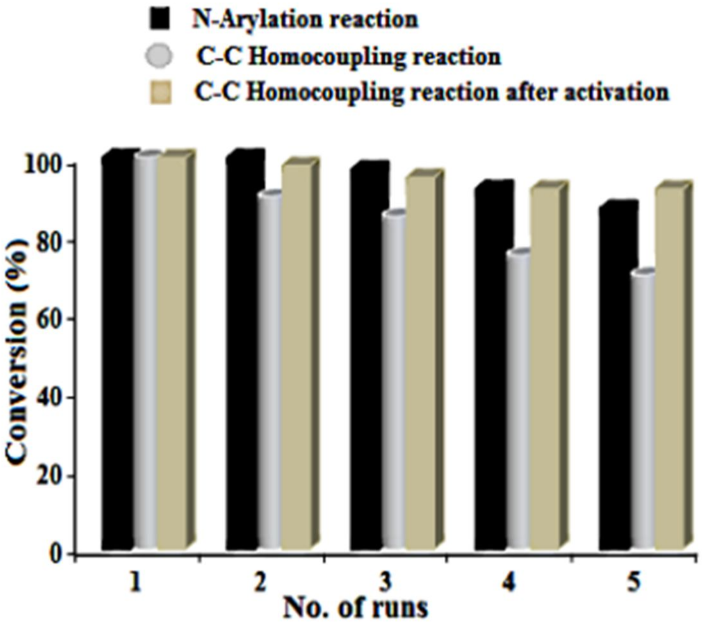


Fig.6. Recycling studies of the catalyst for N-arylation and homocoupling of phenyl acetylene

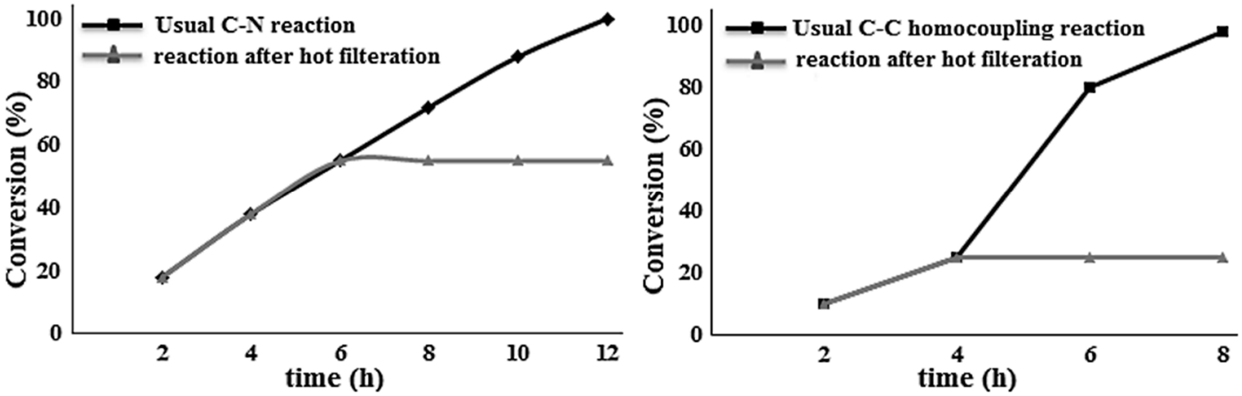


Fig. 7. Hot filteration test

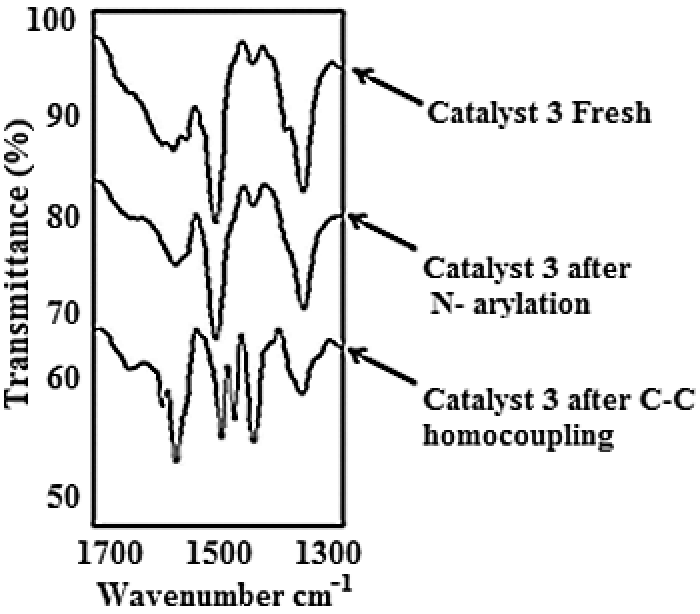


Fig. 8. FT-IR spectra of Fresh Resin-CuNPs, recycled resin after C-N coupling, recycles resin after C-C homocoupling reaction.

Table 1: N-arylation reaction catalyzed by different catalysts

Entry	Catalyst	Cu loaded mmol	Base	Yield (%)
1	Catalyst 1	0.01	K_2CO_3	56
2	Catalyst 2	0.023	K_2CO_3	70
3	Catalyst 3	0.042	K_2CO_3	99
4	Catalyst 3	0.042	-	25
5	-		K_2CO_3	trace

[a]Reaction coditions: Iodobenzene (1 mmol), aniline (1.2 mmol), 0.2 g of resin-CuNPs,K_2CO_3 (3 mmol), 5 ml (4:1) MeOH: H_2O, reflux temperature, 12 h.

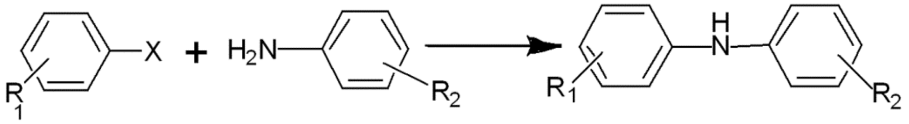
Table 2: Evaluation of the effects of the solvent, base and catalyst on the N-arylation

Entry	Base	Solvent	Yield (%)
1	K_2CO_3	1,4-dioxane	trace
2	K_2CO_3	Acetonitrile	trace

3	K_2CO_3	DMSO	92[b]
4	K_2CO_3	$MeOH:H_2O$	99[a]
5	K_2CO_3	DMF	70[b]
6	K_2CO_3	THF	trace
7	K_2CO_3	MeOH	30
8	KOH	DMSO	98[b]
9	KOH	MeOH	40
10	KOH	$MeOH:H_2O$ (4:1)	95
11	TEA	MeOH	trace
12	TEA	DMF	trace[b]
13	NaO^tBu	Toluene	95

[a]Reaction conditions: aryl halide (1 mmol), amine(1.2 mmol), K_2CO_3 (3 mmol), Catalyst 3 (200 mg), Solvent (5 ml), reflux temperature, 12 h.[b] / 120° C (for DM

Table 3. Resin-CuNPs catalyzed N-arylation of aryl halides with aryl amines and nitrogen heterocycles[a]



Entry	R_1	X	R_2	Time (h)	Yield (%)
1	H	I	H	12	99
2	$4\text{-}CH_3$	I	H	12	92
3	$4\text{-}OCH_3$	I	H	12	80
4	$4\text{-}NO_2$	I	H	12	60[b]
5	H	Br	H	12	95
6	$4\text{-}OCH_3$	Br	H	12	75
7	$4\text{-}NO_2$	Br	H	12	50[b]
8	H	Cl	H	12	85
9	$4\text{-}NO_2$	Cl	H	12	55[b]
10	H	I	4-Cl	12	96
11	$4\text{-}NO_2$, $2\text{-}OCH_3$	Cl	H	12	72
12	H	I	2-Amino pyrimidine	12	85

[a] Reaction conditions: 1 mmol aryl halide, 1.2 mmol of amine, 3 mmol of K_2CO_3, Catalyst (200 mg), $MeOH/H_2O$ (4:1) (5 ml), reflux temperature. [b]acetonitrile as solvent.

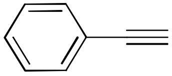
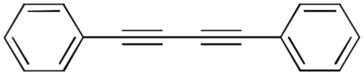
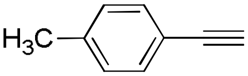
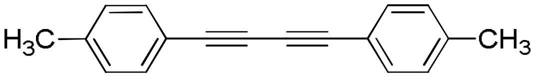
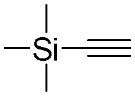
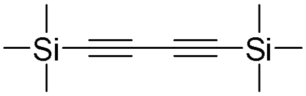
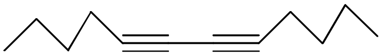
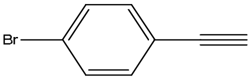
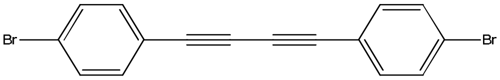
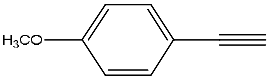
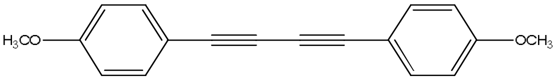
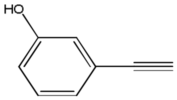
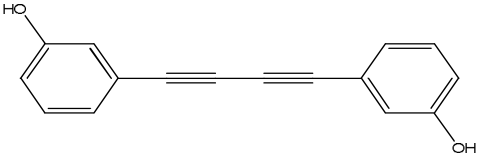
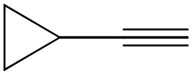
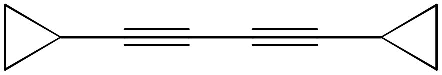
Table 4: Evaluation of the effects of the solvent and base on oxidative C-C homocoupling

Entry	Base	Solvent	Yield (%)
1	Et_3N	DMSO	Trace
2	Et_3N	MeOH	15

3	NaOH	DMSO	48
4	KOH	DMSO	58
5	Piperidine	DMSO	86
6	Na_2CO_3	DMSO	92
7	K_2CO_3	DMSO	96
8	K_2CO_3	MeOH	90
9	K_2CO_3	EtOH	88
10	K_2CO_3	Acetonitrile	80
11	K_2CO_3	THF	86
12	K_2CO_3	DMF	83
13	K_2CO_3	DMSO	Trace*

phenyl acetylene (1mmol), base (1mmol), catalyst (100 mg),solvent (3 mL), 50 °C, 8 h, O_2 gas,* in the absence of catalyst

Table 5. Resin-CuNPs catalyzed homocoupling of terminal alkynes

Entry	Substrate	Product	Yield (%)
1			95
2			95
3			92
4			90
5			94
6			92
7			95
8			trace

terminal alkyne (1mmol), base (1mmol), catalyst (100 mg), DMSO (3 mL), 50 °C, 8 h, O_2 gas