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Cu-grafted mesoporous organic polymer: A new recyclable nanocatalyst for multi-component, N-arylation and S-arylation reactions

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Abstract

A new mesoporous Cu-MPTA-1 nanocatalyst has been synthesized via simple and facile in-situ radical polymerization of triallylamine in the presence of organic–organic self-assembly of anionic surfactant SDS, followed by grafting of Cu(II) at room temperature under inert atmosphere. This nanomaterial has been characterized by elemental analysis, powder X-ray diffraction (XRD), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FT-IR), UV-vis diffuse reflectance spectroscopy (DRS), thermogravimetric analysis (TGA), N_2 adsorption–desorption studies, X-ray photoelectron spectroscopy (XPS) and EPR spectroscopy. The Cu-MPTA-1 act as an efficient heterogeneous nanocatalyst exhibiting high catalytic activity for the N-arylation and S-arylation reactions using water as green solvent and also exhibited excellent catalytic activity for the one-pot synthesis of propargylamines via a three component coupling of an alkyne, an amine and an aldehyde at room temperature. Moreover, the catalyst is easily recoverable and can be reused for six times without appreciable loss of catalytic activity in the three component coupling reaction. So, the highly dispersed Cu(II) sites in the Cu-grafted mesoporous polymer could be responsible for the observed high activities of the Cu-MPTA-1 catalyst in the coupling reactions. No

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evidence of leached Cu from the catalyst during the course of reaction has been observed, suggesting true heterogeneity in the catalytic process.

Keywords: Mesoporous material, poly-triallylamine, Cu-grafting, N-arylation, S-arylation, propargylamines.

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Introduction

Catalyst plays a significant role for the efficient synthesis of several value added fine chemicals. In this context it is pertinent to mention that nanomaterials have huge potential to be employed as catalyst for improving efficiency, selectivity and yield of the catalytic processes. Over a decade of extensive research, nanomaterials have emerged as one of the most promising catalysts because of their unique surface properties, which are largely different from their corresponding bulk materials.[1-2] Due to their huge difference with bulk, nanomaterials have found extensive utility in numerous frontline areas such as electronic, optical, catalytic, coating, medical, sensor applications, etc.[3] The higher surface to volume ratio in the nanocatalyst signifies large number of active sites participating in the reaction. Further, different types of organic transformations catalyzed

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by self-assembled nanoparticles are gaining increasing importance in recent times.[4] Currently Cu-nanoparticles have attracted a considerable awareness in the field of catalysis[5-6] and as well as in the energy conversions.[7] From the past one decade it is believed that copper, in the nanoform provides fascinating catalytic activity in various organic transformations. Due to the low cost of Cu compared to Au, Ag, Pd, Pt, Ru and Rh, it has attracted particular attention as catalyst for various organic reactions.[8-9] In this context, mesoporous organic polymers carrying the reactive functional groups at the surface of the mesopores[10-14] can provide an ideal tethering agent for the active metals to bind at its surface strongly. Due to extensive cross-linking, polymeric materials are highly desirable material for long term stabilization of the entrapped metal centres, which reduces the possibility of leaching of the metal under reaction conditions.[15] Furthermore, Cu-grafted functionalized heterogeneous catalysts provide the advantages of simplified isolation of the product, easy recovery, enhanced stability and recyclability of the catalysts, which is highly desirable to address the industrial and environmental concerns over their respective homogeneous counterpart.

Multi-component reactions in one-pot syntheses play a significant role in modern synthetic chemistry. Three-component coupling of an aldehyde, amine and alkyne (A^3-coupling) is one of the best examples and has received much attention in recent years. There are several reports on highly efficient three-component couplings of aldehyde, alkyne, and amine (A^3-coupling) in organic media, ionic liquid, or under solvent-free condition catalyzed by metallic copper, silver, gold, iron, nickel, iridium and other catalysts via catalytic C–H activation to afford various propargylamines.[16] The resultant propargylamines are versatile intermediates for organic synthesis[17] and important structural elements of natural products, making agrochemicals and potential drug molecules.[18]

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In this context it is also pertinent to mention that the transition metal/metal complex catalyzed formation of carbon–carbon and carbon-heteroatom bonds has emerged as a versatile and powerful tool in chemical synthesis. In particular, the N-arylation of nitrogen nucleophiles with aryl halides and the S-arylation of thiols with aryl halides have witnessed considerable importance due to the versatility of the products, which are prevalent in compounds of biological, pharmaceutical, chemical and materials interest. Since its discovery, the copper-mediated Ullmann coupling reaction[19] is still the straight forward method to prepare the requisite carbon–heteroatom bonds. Ullmann condensations have proven to be a convenient efficient and recyclable catalytic method for the syntheses of N- and S- arylated compounds. Heterogeneous Cu-catalysts that have been used for N-arylation and S- arylation in different organic solvents would be environmentally acceptable if the reaction can be carried out in water. Today a considerable effort has been devoted to perform organic reactions in aqueous medium replacing the hazardous organic solvents, because of its environmental acceptability, abundance and low cost.[20–21]

Very recently we have reported the synthesis of a mesoporous poly-triallylamine (MPTA-1) using an anionic surfactant sodium lauryl sulfate as template.[22] Surface of this mesoporous polymer contains N-donor sites, which can tether with Cu-sites strongly. Herein we report, the strategy for the synthesis of a new Cu-grafted nanomaterial Cu–MPTA-1 and its excellent catalytic activity in three-component couplings of aldehyde, alkyne and amine (A^3 coupling), N-arylation reaction of aryl halides with imidazole and also S-arylation reaction of aryl halides with aryl thiols in aqueous medium.

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Experimental Section

Materials

Triallylamine (TAA) was obtained from Sigma Aldrich. *N,N,N',N'*-tetramethylenediamine (TEMED) and ammonium persulfate (APS) were obtained from Loba Chemie, India. Sodium lauryl sulfate (SDS) was purchased from Loba Chemie and used as structure-directing agent. Cupric sulphate pentahydrate ($CuSO_4.5H_2O$), NaOH and hydrazine hydrate ($N_2H_4.H_2O$) was purchased from Merck, India. All other reagents and substrates were also purchased from Merck, India.

Physical measurements

Powder X-ray diffraction (XRD) patterns of different samples were analyzed with a Bruker D8 Advance X-ray diffractometer using Ni–filtered Cu Kα (λ=0.15406 nm) radiation. Transmission electron microscopy (TEM) images of the mesoporous polymer were obtained using a JEOL JEM 2010 transmission electron microscope operating at 200 kV. Thermogravimetric analysis (TGA) was carried out using a Mettler Toledo TGA/DTA 851e. UV-Vis spectra were taken using a Shimadzu UV-2401PC doubled beam spectrophotometer having an integrating sphere attachment for solid samples. Nitrogen adsorption–desorption experiments were carried out using a Bel Japan Inc. Belsorp-HP surface area analyzer at 77 K. Prior to gas adsorption, the sample was degassed for 4 h at 393 K under high vacuum conditions. X−ray photoluminescence spectroscopy (XPS) measurements were performed on a Omicron nanotech operated at 15 kV and 20 mA current using monochromatic Al Kα X−ray source. EPR measurement was performed on a Bruker EMX EPR spectrometer at X-band frequency (9.46 GHz) at liquid nitrogen temperature (77 K). The reaction products were quantified by using a Varian 3400 gas chromatographic instrument equipped with a

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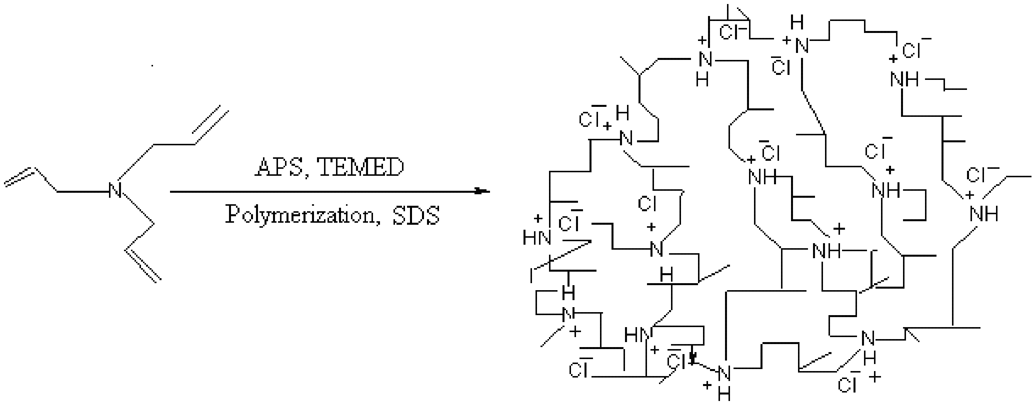
30m CP-SIL8CB capillary column and a flame ionization detector and identified by Trace DSQ II GC-MS equipped with a 60m TR-50MS capillary column.

Preparation of the catalyst

Synthesis of mesoporous polytriallylamine MPTA-1

MPTA-1 was synthesized through the aqueous-phase polymerization of triallylamine under hydrothermal condition by using APS as initiator (Scheme 1).[22] In a typical synthesis 2.35 g (0.00814 mol) of SDS was dissolved in 40 ml of water with constant stirring followed by the addition of 2.23 g (0.01628 mol) of TAA. Then 0.94 g (0.00814 mol) of TEMED was added in this mixture and conc. HCl (12N) was also added dropwise to obtain a clear solution. This helps the protonation of the N-atoms of the triallylamine molecules, which facilitates the ionic interaction with the sulfonate group of the SDS molecules. The pH of the gel was maintained at *ca* 7.0. Finally, 7.42 g (0.03256 mol) of APS dissolved in 10 ml of water was added quickly into the solution with vigorous stirring and a white precipitated appeared immediately. The resultant slurry was stirred for another 1 h and then autoclaved at 348 K for 3 days without stirring. Final pH of the synthesis gel was *ca* 4.0-5.0. The resultant precipitate was filtered and washed with deionized water, yielding mesoporous polymer MPTA-1.



Scheme 1. Schematic diagram showing the formation of mesoporous polymer MPTA-1

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Synthesis of Cu-MPTA-1 nanocatalyst

In typical synthesis, 250 mg mesoporous polytriallylamine MPTA-1 was dissolved 10 ml double distilled water with stirred for 2 h in 100 ml RB flask. In aqueous solution of MPTA-1 0.2 mmol $CuSO_4$ was added and again stirred for 2 h. It was followed by the drop-wise addition of NaOH solution (1.0 M, 1.0 ml) with constant stirring till the solution attained the desired pH. A deep blue solution appeared. One interesting observation to note here is that as the pH was increased, the colour of the solution changed from greenish blue to dark blue. Then, 4 mmol $N_2H_4.H_2O$ in 6 ml H_2O was added drop-wise with constant stirring under the nitrogen atmosphere. In the presence of nitrogen atmosphere, the resulting solution was allowed to stir for overnight at room temperature and then heated at 80 ^{0}C for 3 h and formed brick red colour solution which indicated the grafting Cu-species at the surface of the porous polymer. Then the precipitates were collected by centrifugation and washed with double distilled water for several times, yielding mesoporous Cu-MPTA-1 nanocatalyst.

One-pot synthesis of propargylamines catalyzed by Cu-MPTA-1 nanocatalyst

In a 50 ml RB flask, cyclohexanecarboxaldehyde (0.112 g, 1.0 mmol), phenyl acetylene (0.112 g, 1.1 mmol), piperidine (0.094 g, 1.1 mmol) was taken in CH_2Cl_2 (10 ml) was added. In this mixture 0.05 g Cu-MPTA-1 catalyst was added under stirring. Then the reaction was continued under stirring at room temperature for 24 h. The reaction mixtures were collected at different time intervals and identified by GC-MS and quantified by GC. After the completion of the reaction, the catalyst was filtered off and washed with water followed by acetone and dried in oven. The filtrate was extracted three times with ethyl acetate (3 x 20 ml) and the combined organic layers were dried with anhydrous Na_2SO_4 by vacuum. The filtrate was concentrated and the resulting residue was purified by column chromatography on silica gel to provide the desired product

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General Procedure for N-arylation of N–H heterocycles with aryl halides catalyzed by Cu-MPTA-1 nanocatalyst

In an oven dried 50 ml RB flask, Cu-MPTA-1 catalyst (0.05 g), aryl halide (1 mmol), imidazole (1.2 mmol), KOH (2 mmol), and 10 ml water were stirred under nitrogen atmosphere at 120 ^{0}C. The reaction mixtures were collected at different time interval and identified by GC-MS and quantified by GC analysis. After the completion of the reaction, the catalyst was filtered off and washed with water followed by acetone and dried in oven. The filtrate was extracted three times with ethyl acetate (3 x 20 ml) and the combined organic layers were dried with anhydrous Na_2SO_4 by vacuum. The filtrate was concentrated and the resulting residue was purified by column chromatography on silica gel to provide the desired product

General procedure for aryl-sulfur coupling reaction of thiophenol with aryl halides catalyzed by Cu-MPTA-1 nanocatalyst

Cu-grafted mesoporous polymer Cu-MPTA-1 was used as a catalyst for the aryl-sulfur coupling of thiophenol with aryl halides. To a solution of halides (1 mmol) and thiophenol (121 mg, 1.1 mmol) in 3 ml of H_2O, K_2CO_3 (276 mg, 2 mmol) and Cu-grafted catalyst (0.05 g) were added. At the end of specified time, the reaction mixture was filtered and the filtrate was analyzed by using a Varian 3400 gas chromatograph equipped with a 30 m CP-SIL8CB capillary column and a flame ionization detector. Identification of the products was also confirmed using GC-MS. After the completion of the reaction, the catalyst was filtered off and washed with water followed by acetone and dried in oven. The filtrate was extracted three times with ethyl acetate (3 x 20 ml) and the combined organic layers were dried with anhydrous Na_2SO_4 by vacuum. The filtrate was concentrated and the resulting residue was purified by column chromatography on silica gel to provide the desired product

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Results and discussion

Characterization of Cu-MPTA-1 material

X-ray diffraction: Small angle powder XRD pattern of the sample Cu-MPTA-1 is shown in Figure 1. For the sample a single and broad diffraction peak is obtained in the small angle 2θ value of 2.5 degree, corresponding to the presence of a disordered mesostructure in the material and absence of long range ordering in the material. This result agrees well with the small angle powder XRD pattern of the parent MPTA-1.[22] The *d* spacing for the Cu-MPTA-1 sample was 3.53 nm, moderately decreased from parent MPTA-1 due to Cu-grafting.

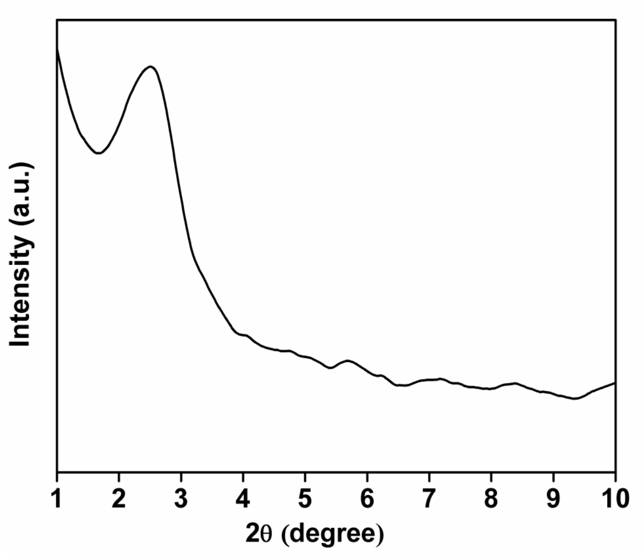

Figure 1. Small angle Powder XRD patterns of Cu-MPTA-1 material

Electron microscopy analysis: In Figure 2 TEM images of the Cu-MPTA-1 samples are shown. In this Figure dark spots could be attributed to the presence of grafted Cu^{+2} sites and from these images it is clear that these Cu-nanoclusters are uniformly distributed throughout the specimen grid. The FFT diffractogram of a selected area of the grid is shown in the inset of the Figure 2C. Diffraction spots in this FFT pattern suggested crystalline feature of the copper species[23] bound at the surface of Cu-MPTA-1.

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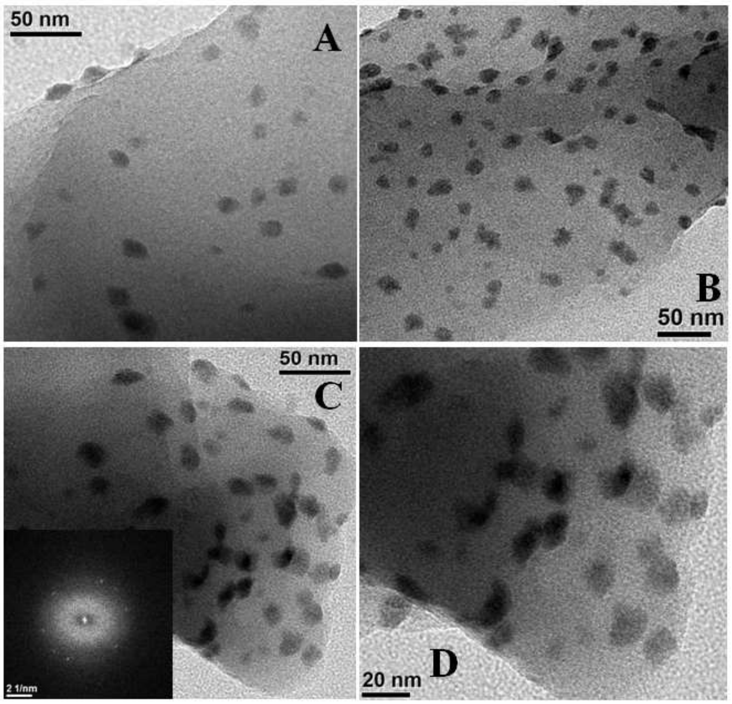

Figure 2. TEM images of the Cu-MPTA-1 material

UV-visible spectroscopic study: The UV-Vis absorption spectrum of the Cu-MPTA-1 displayed absorption peak maxima at 236 nm and a shoulder at *ca*. 700 nm (Figure 3). Former peak could be attributed due to the chromophoric organic functionality of the polymer matrix whereas, weak absorption at 700 nm could be assigned to the *d-d* transition, which is a characteristic absorption band of Cu(II) in metal complexes.[24-25]

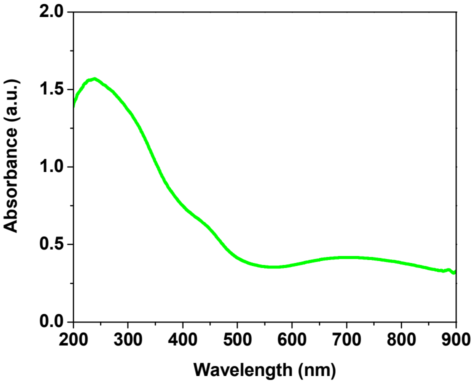

Figure 3. DRS-UV-visible absorption spectra of Cu-MPTA-1 material.

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Thermal analysis: The quantitative determination of the organic content and the framework stability of the Cu-MPTA-1 samples are obtained from the thermogravimetric (TG) and differential thermal analysis (DTA) under N_2 flow. TGA-DTA curve of Cu-MPTA-1 materials are shown in Figure 4. The TGA of this material showed the first weight loss below 100 ^{0}C due to desorption of physisorbed water. This was followed by a gradual decrease in the weight after 200 ^{0}C. Thus this thermal analysis data suggested that Cu-MPTA-1 sample is stable up to 200 ^{0}C.

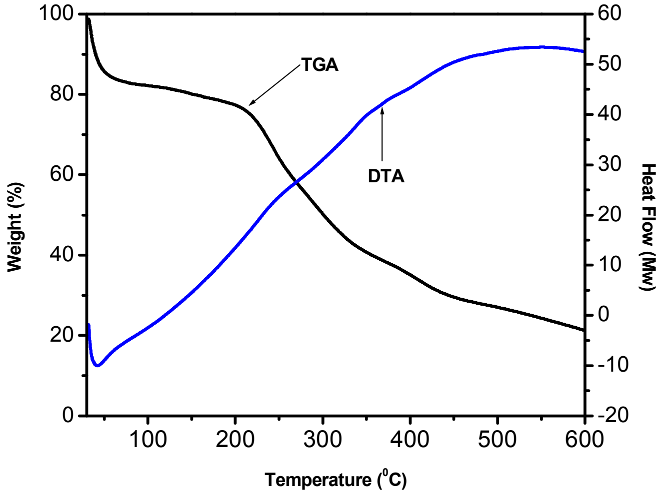

Figure 4. TGA plot and (b) DTA plot of Cu-MPTA-1 material.

N_2 adsorption/desorption: The surface area and porosity of Cu-MPTA-1 material is determined by N_2 adsorption/desorption at 77 K. N_2 adsorption/desorption isotherm is shown in Figure 5. This isotherm shows the type IV adsorption isotherm having hysteresis characteristics of mesoporous materials.[26] The BET surface areas of template-free MPTA-1 and Cu-MPTA-1 are 134 m^2g^{-1} and 35 m^2g^{-1}. The total pore volume of Cu-MPTA-1 material is 0.0427 ccg^{-1}. The pore size distribution of the sample has been estimated from these isotherms by using the non-local density functional theory (NLDFT) and this is shown in the

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inset of the Figure 5. As seen from the plot that the maximum in the pore widths are centred at 1.43 nm and 4.16 nm. Peak at 4.16 nm could be attributed to interparticle pores, whereas considerable decrease in the mesopore size to 1.43 nm and surface area to 35 m^2g^{-1} in Cu-MPTA-1 vis-à-vis MPTA-1 suggests that Cu-sites are anchored in the inner surface of the pores.

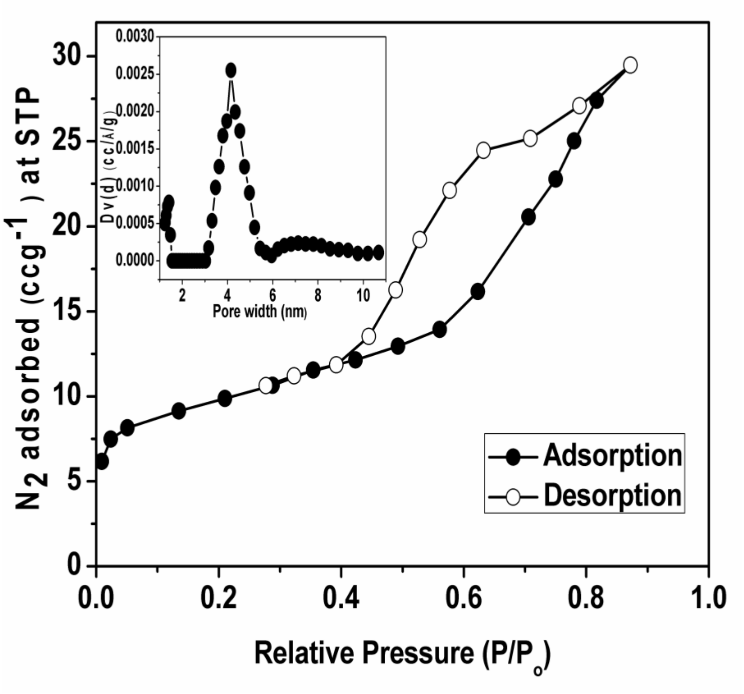

Figure 5. N_2 adsorption/desorption isotherm of Cu-MPTA-1 and pore size distribution curve is shown in the inset.

XPS analysis: In Figure 6 the XPS profile of Cu-MPTA-1 material is shown. The XPS data shows peak centred at 937.6, 530.0 and 287.0 eV. These binding energies correspond to Cu2$p_{3/2}$, O1s and C1s, respectively.[27] In Figure 2, there is only one peak for O1s. The peak at 529.7 eV has been assigned in the literature for the O^{2-} bonded to metal in the oxide frameworks.[27a] Further, the single peak confirms that there are no free surface hydroxyl groups on the catalyst. Figure shows the XPS spectrum of the Cu2*p* region for the resultant Cu-nanocatalyst. The binding energy of the Cu2$p_{3/2}$ peak at 937.6 eV and indicates that

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copper species are only present as Cu(II) state in the form of Cu-nanoclusters in mesoporous Cu-MPTAT-1.[27b-27d]

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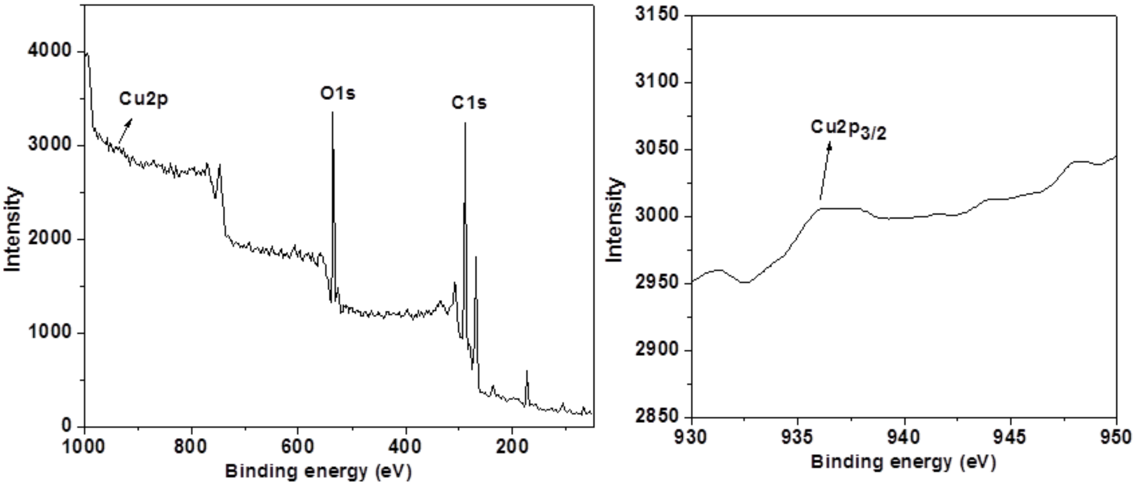

Figure 6. XPS data of Cu-MPTA-1

Electron paramagnetic resonance study: In Figure 7 the EPR spectrum of the Cu-MPTA-1 in solid state at room temperature (300 K) is shown. It provides information on the nature of the metal ion environment in the Cu-grafted mesoporous polymer. It shows strong axially symmetric signal,[28] which could be attributed to the highly dispersed or isolated Cu(II) species interacting with the porous polymeric support. In the low field region parallel component due to hyperfine interaction between unpaired electron and nuclear spin of copper (I= 3/2) is observed, whereas in high field region perpendicular component ($g_{\perp} = 1.99$) remains unresolved. Further, the EPR spectrum of Cu-MPTA-1 reveals the following parameters: $g_{\|} = 2.24$ and $A_{\|} = 0.018$ cm^{-1}

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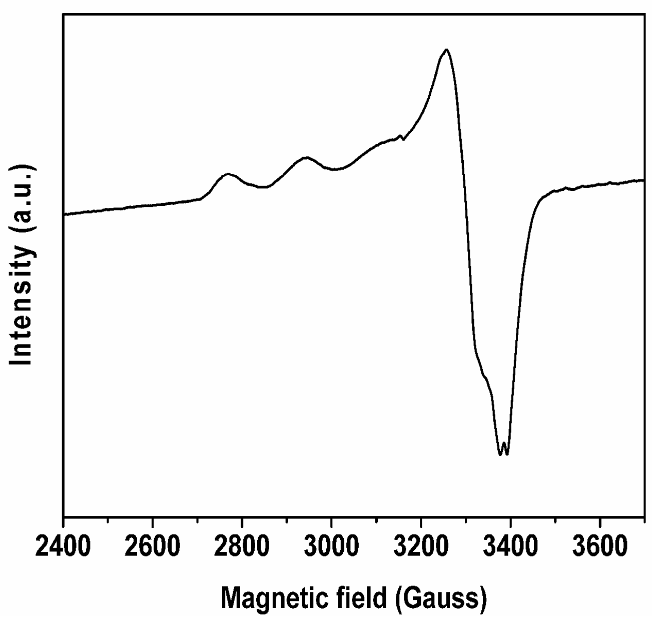

Figure 7. EPR spectrum of Cu-MPTA-1 material.

Catalytic activity

Since metal ions supported over mesoporous systems exhibit high catalytic activity in a wide range of the industrially important catalytic reactions and these are extensively studied, we decided to investigate the catalytic activity of the mesoporous polymer Cu-MPTA-1 in the C-N and C-S coupling reaction in water as solvent and A^3 coupling reaction at room temperature.

N-arylation reaction of imidazole with aryl halides catalyzed by Cu-MPTA-1

The N -arylation reaction is a convenient method for the C–N bond formation between N–H heterocycles with aryl halides. To test the applicability of the copper catalyst, we examined the N-arylation reaction between N–H heterocycles with various aryl halides and imidazole in water as solvent using KOH at 120^0 C as model reaction (Scheme 2).

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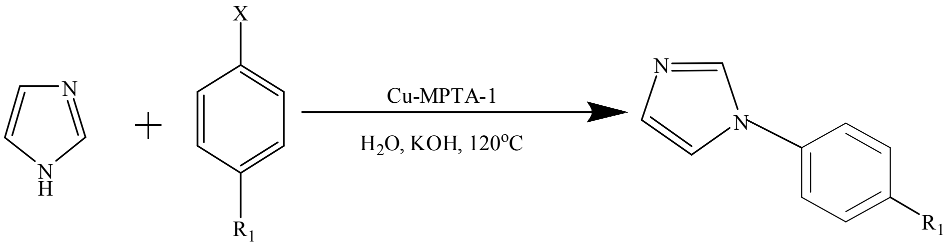

X=I, Br; R_1 = H, Me, OMe, COMe, NO_2

Scheme 2. N-Arylation of imidazoles with different aryl halides.

Several bases were screened using the copper catalyst for the N-arylation of imidazole with iodobenzene in water as solvent at 120 ^{0}C, and the results are summarized in Table 1. A variety of bases (i.e., K_2CO_3, K_3PO_4, Cs_2CO_3, LiOH, NaOH, and KOH) was screened. As seen in Table 1, we noticed that the base was necessary in this coupling reaction, and no product was obtained in the absence of the base (Table 1, entry 7). Among the various bases, obviously, strong bases exhibited higher catalytic ability than carbonate (Table 1, entries 1–6). The organic base like Et_3N was almost inactive (entry 6). Longer reaction time would bring some by-products. Nevertheless, we have got little product when the coupling reaction was performed at 80 ^{0}C for 12 h (Table 1, entry 8). From the above discussions, it can be seen that the best yield was obtained in the N-arylation reaction of imidazole with iodobenzene by using KOH in water at 120 ^{0}C for 12 h.

Table 1. N-arylation reaction using mesoporous Cu-MPTA-1 nanocatalyst at various bases [a]

Entry	Base	Solvent	Yield (%)[b]
1	**KOH**	**H_2O**	**91**
2	K_2CO_3	H_2O	50
3	K_2PO_4	H_2O	58

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4	NaOH	H_2O	80
5	Cs_2CO_3	H_2O	42
6	Et_3N	H_2O	12
7	-	H_2O	0
8[c]	KOH	H_2O	trace

[a] Reaction conditions: Cu-catalyst (0.05 g), 1 mmol of iodobenzene, 1.2 mmol of imidazole, 2 mmol base, water (10 ml), N_2 atm. [b] Yield determined by GC and GCMS analysis. [c] At 80 ^{0}C for 12 h.

With optimized conditions now in hand, we explored the scope of this process with respect to aryl iodide structure, and the results are summarized in Table 2. To our delight, the N-arylation of imidazole is smoothly performed with the extensive pool of aryl iodides to afford the corresponding products in good to excellent yields. It was observed that iodoarenes with electron-withdrawing groups (Table 2, entries 4, 5) reacted at a faster rate than iodo-arenes with electron-donating groups (Table 2, entries 2, 3). Sterically hindered 2-iodotoluene took longer duration to afford a good yield (Table 2, entry 6). Extension of this arylation process with aryl bromides yielded interesting results. The use of bromobenzene in place of iodobenzene afforded lower conversion with 70% yield (entry 7) with longer reaction time. Bromobenzene with an electron-donating group gave lower yield (entry 8), whereas bromobenzene with an electron-withdrawing group gave excellent yield of product (entry 9).

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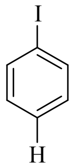
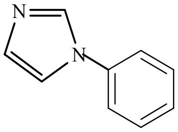
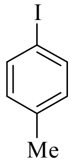
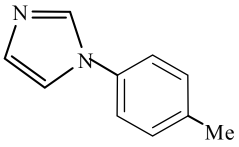
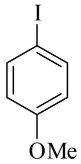
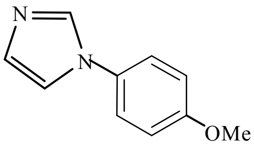
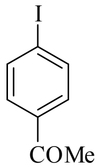
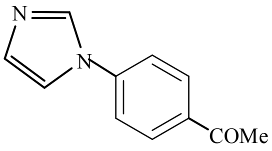
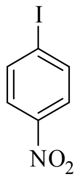
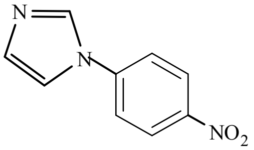
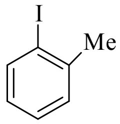
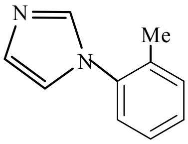
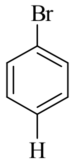
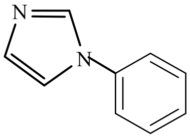
Table 2: N-Arylation of imidazoles with different aryl halides using mesoporous Cu-MPTA-1 nanocatalyst[a]

Entry	Aryl halides	Products[b]	Time (h)	Yield (%)[c]
1			12	91
2			15	80
3			18	78
4			12	92
5			12	93
6			15	60
7			18	70

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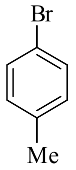
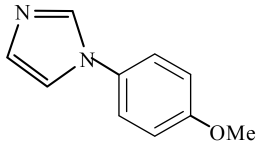
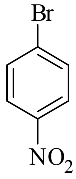
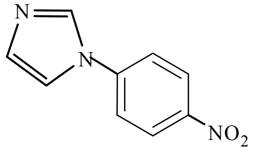
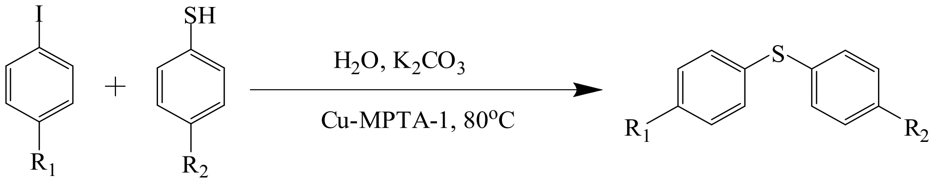
8			20	30
9			18	73

[a]Reaction conditions: Cu-MPTA-1 nanocatalyst (0.05 g), aryl halide (1 mmol), imidazole (1.2 mmol), KOH (2 mmol), H_2O (10 ml), 120 ^{0}C, N_2 atm. [b]Products were identified by comparison of their ^{1}H-NMR spectral data those reported in the literature. [c]Isolated yield

Aryl-sulfur coupling reaction of Thiophenol with Aryl iodide catalyzed by Cu-MPTA-1

Diaryl sulfides formed via C–S cross-coupling reaction from aryl halides bearing different nucleophilic phenyl rings have significant roles in biological, pharmaceutical, and material research. Here, we have explored the catalytic efficiency of the Cu-MPTA-1 nanocatalyst in C–S cross-coupling reactions of thiophenol with aryl iodide in green solvent water using K_2CO_3 as a mild base at 80 ^{0}C (Scheme 3).



R_1= H, CH_3, OCH_3, NO_2, Br, Cl

R_2= H, OMe, Cl

Scheme 3. General procedure for aryl-sulfur coupling reaction of Thiophenol with Aryl iodide

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To optimize the reaction conditions, a series of bases K_2CO_3, Cs_2CO_3, KOH, Et_3N and pyridine were screened on the C–S cross-coupling reaction (Table 3). In a comparison of the efficiency of a variety of inorganic (Table 3, entries 1–3) and organic bases (entries 4 and 5) were used to afford aryl sulfides. Potassium hydroxide was found to act as an poor base, whereas Cs_2CO_3 was effective to some extent and other bases were not at all effective. Despite that the respective sulfide could be detected employing the related bases screened, K_2CO_3 showed the best performance, furnishing the desired product in quantitative yield (entry 1). Noteworthy is that in the absence of a base no formation of product was observed (Table 3, entry 7). In view of the extreme moisture-sensitivity and expense of Cs_2CO_3, cheap and stable K_2CO_3 was the preferred base for use in the Cu-MPTA-1 catalyzed coupling reaction. As a result, K_2CO_3 was selected as the optimum base.

Table 3. The effect of base on the mesoporous Cu-MPTA-1 catalyzed C–S coupling reactions.[a]

Entry	Base	Yield (%)[b]
1	**K_2CO_3**	**95**
2	Cs_2CO_3	76
3	KOH	52
4	Et_3N	40
5	Pyridine	10
6	None	0

[a]Reaction conditions: iodobenzene (1 mmol), thiophenol (1.1 mmol) , water (3 ml), base (2 mmol), Cu- MPTA-1 (0.05g), temperature (80^0C), Time (12h). [b]Yields were determined by GC and GCMS analysis.

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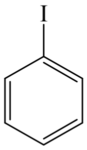
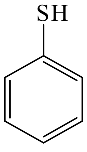
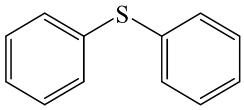
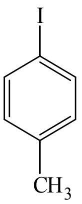
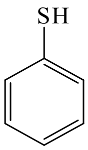
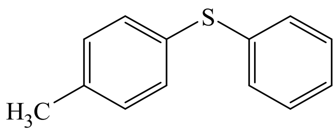
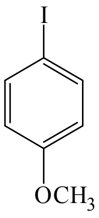
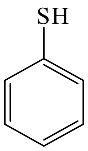
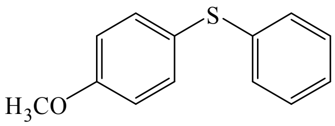
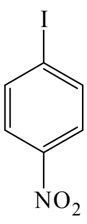
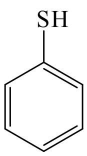
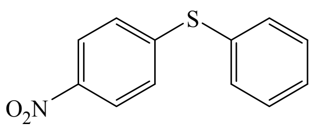
Using the optimized conditions, the present reaction was further expanded to a broader range of aryl thiols and aryl iodides in order to evaluate the scope and limitations of the method, as outlined in Table 4. In general, the reactions are very clean and high yielding. Aryl iodides with an electron withdrawing group were more reactive in comparison to those with an electron donating group. Thus, the reaction of aryl iodides with methyl and methoxy substituents gave the corresponding C–S cross-coupled products in 72-80% yield, while the reaction of aryl iodides with nitro substituent completed in 87% yield. The effect of different halogen substituents in the coupling of thiophenol is also shown in the Table 4.The order of reactivity of different halobenzenes are iodobenzene > bromobenzene > chlorobenzene, which is observed in our case.

Table 4. **C–S coupling reactions catalyzed by mesoporous Cu-MPTA-1 nanocatalyst[a].**

Entry	ArI	ArSH	Products[b]	Yield (%)[c]
1				95
2				80
3				72
4				87

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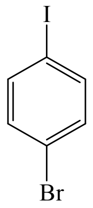
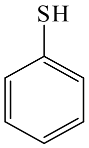
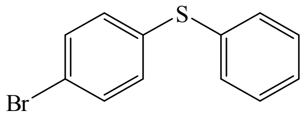
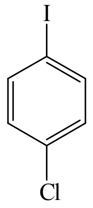
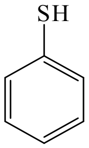
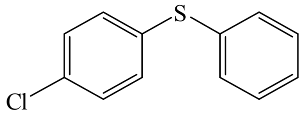
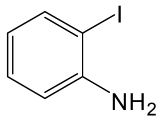
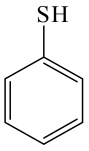
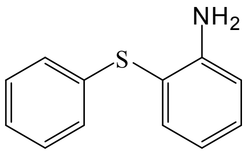
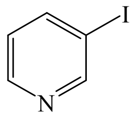
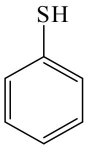
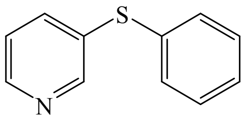
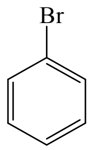
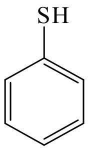
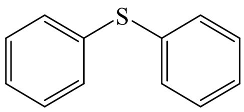
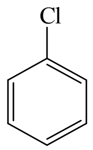
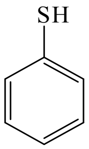
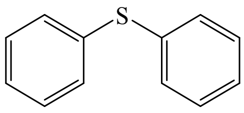
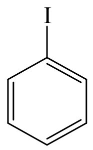
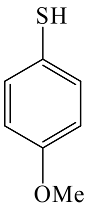
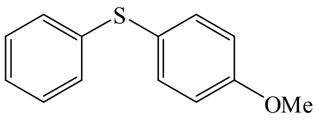
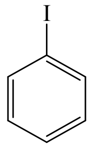
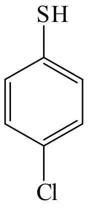
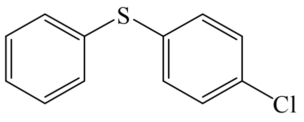
5				90
6				43
7				85
8				71
9				56
11				23
12				69
13				55

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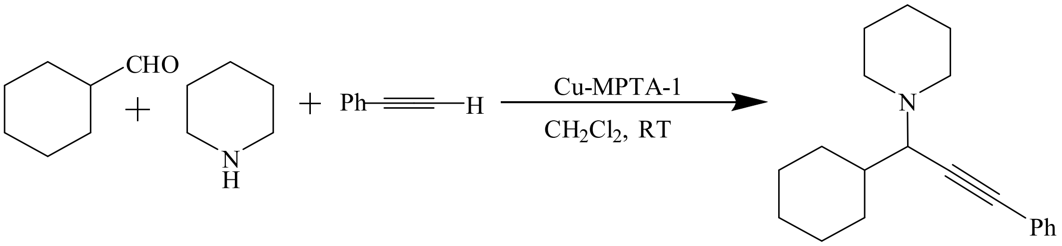
[a]Reaction conditions: aryl iodides (1 mmol), thiophenol (1.1 mmol) , water (3 ml), K_2CO_3 (2 mmol) and Cu- nanocatalyst (0.05g), temperature (80 ^{0}C), Time (12 h). [b]Products were identified by comparison of their ^{1}H-NMR spectral data those reported in the literature. [c]Isolated yield

Catalytic activity of mesoporous Cu-MPTA-1 nanocatalyst for 'one-pot' A^3 coupling reaction

Herein, we have explored the catalytic efficiency of the Cu-MPTA-1 nanocatalyst in the synthesis of propargylamines by the one-pot three-component coupling reaction of aldehydes, amines and alkynes (A^3-coupling) at room temperature. Propargylicamines, products of the A^3-coupling, are important synthetic intermediates for potential therapeutic agents and natural products. As a comparison, we used Cu-MPTA-1 as a nanocatalyst to test the catalytic performance of this nanomaterial for A^3-coupling reaction. The effect of mesoporous Cu-MPTA-1 nanocatalyst on their catalytic activity for the A^3-coupling reaction was investigated using cyclohexanecarboxaldehyde, phenylacetylene and piperidine as a model reaction (Scheme 4).



Scheme 4. Synthesis of A^3-coupling reaction

In order to optimize the conditions of the A^3 reaction, the effect of solvent was surveyed (Table 5, entries 4 – 10). Among the solvents tested in Table 5, CH_2Cl_2, CH_3CN, DMF, THF and solvent-free conditions all gave excellent yields of 75 – 93% (Table 5, entries 1-4 and 9). However, solvents such as CH_3OH, toluene, H_2O and AcOEt were not suitable for the

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reaction and no satisfactory yields were obtained (Table 5, entries 5 – 8). When the amount of the catalyst loading was increased to 0.5 mol%, there was no obvious increase in the yield of the reaction (Table 5, entry 10), and the reaction did not occur under catalyst-free conditions (Table 5, entry 11). Thus, the optimized conditions for the A^3 reaction are 0.1 mo l% catalyst and CH_2Cl_2 as solvent at room temperature. It noteworthy that the high yields of the A^3 reaction obtained only with a catalyst loading of 0.1 mo l% are very competitive to other catalyst systems.

Table 5. The effects of various variables in the three-component coupling of cyclohexane carbaldehyde, piperidine and phenylacetylene catalyzed by the mesoporous Cu-MPTA-1 nanocatalyst[a]

Entry	Catalyst loading (%)	Solvent	Yield (%)[b]
1	**0.1**	**CH_2Cl_2**	**93**
2	0.1	CH_3CN	85
3	0.1	DMF	80
4	0.1	THF	81
5	0.1	CH_3OH	10
6	0.1	Toluene	58
7	0.1	H_2O	50
8	0.1	AcOEt	60
9	0.1	Neat	75
10	0.5	CH_2Cl_2	93
11	-	CH_2Cl_2	-

[a] Reaction conditions : cyclohexanecarboxaldehyde (1.0 mmol), phenylacetylene (1.1 mmol), piperidine (1.1 mmol), nanocatalyst, CH_2Cl_2(1 mL), room temperature for 24 h. [b] GC yield based on cyclohexanecarboxaldehyde.

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To expand the scope of this A^3-coupling, various aldehydes, alkynes and amines were used as substrates under the optimized reaction conditions. The results are summarized in Table 6. From these results we found that the conditions were equally applicable to the coupling a variety of aromatic aldehydes including heterocyclic aldehydes with either piperidine, morpholine or pyrrolidine utilizing phenylacetylene, giving the corresponding propargylamines in high yields in room temperature.

Under the optimized conditions, aliphatic aldehydes such as cyclohexanecarboxaldehyde, iso-butyraldehyde, 2-ethylbutanal, formaldehyde and heptanal all give both higher conversions and greater yields at room temperature within 12-24 h (Table 6, entries 1-6). However, aromatic aldehydes were less reactive than aliphatic aldehydes, and the reaction could proceed at 60 ^{0}C in yields of 59 – 65% (Table 6, entries 7-9). We also found that a variety of terminal aromatic alkynes with substituted groups in *para* - and *meta* - positions could be effectively reacted with cyclohexanecarboxaldehyde and piperidine under the present reaction conditions (Table 6, entries 12-15). Note that the reactions proceeded smoothly to give the corresponding propargylamines in a good yield. The presence of electron-rich groups on the benzene ring (entries 12-14) increased the reactivities of the alkynes whereas electron-withdrawing groups (Table 6, entry 15) on the benzene decreased the yield.

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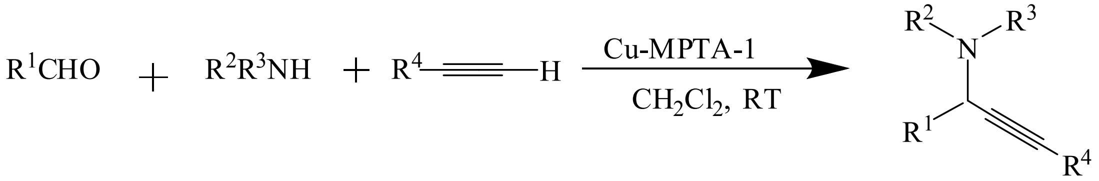
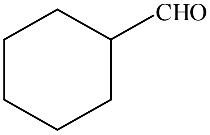
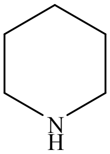
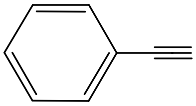
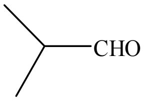
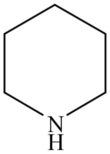
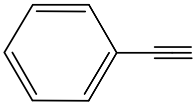
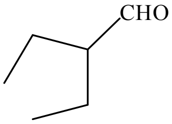
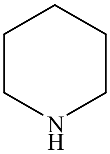
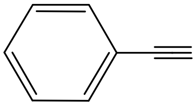
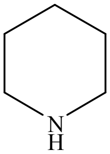
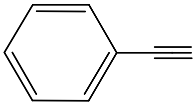
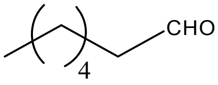
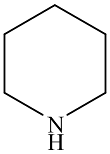
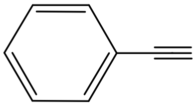
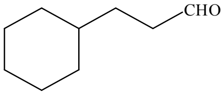
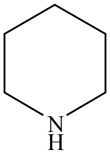
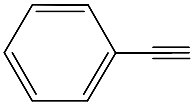
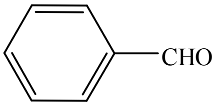
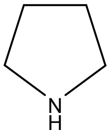
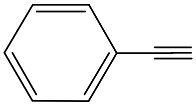
Table 6. The three-component (A^3) coupling reaction catalyzed by the mesoporous Cu-MPTA-1nanocatalyst[a]



Entry	Aldehyde	Amine	Alkyne	Temperature (°C)	Time (h)	Yield (%)[b]
1				RT	24	93
2				RT	12	85
3				RT	12	70
4	HCHO			RT	12	91
5				RT	12	71
6				RT	24	79
7				60	24	65

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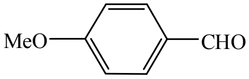
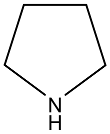
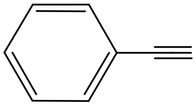
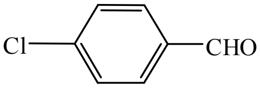
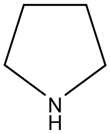
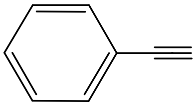
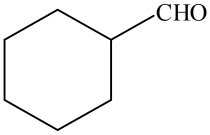
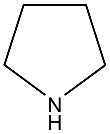
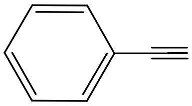
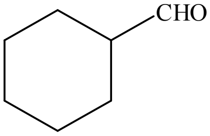
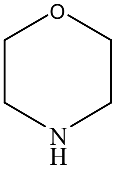
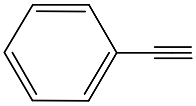
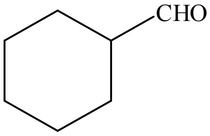
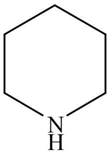
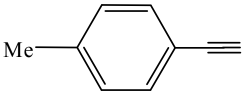
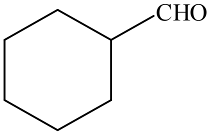
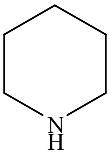
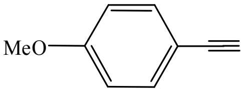
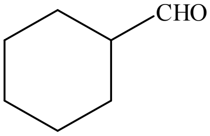
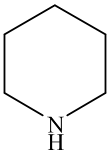
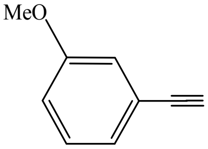
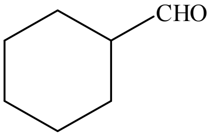
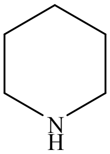
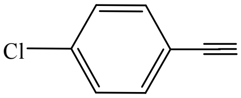
8				60	24	54
9				60	24	61
10				RT	12	91
11				RT	24	78
12				RT	24	92
13				RT	24	88
14				RT	24	82
15				RT	24	65

[a]Reaction conditions: aldehyde (1.0 mmol), alkyne (1.1 mmol), amine (1.1 mmol), nanocatalyst (0.1 mol%), CH_2Cl_2(1 mL), room temperature. [b]Isolated yield. Products were identified by comparison of their ^{1}H-NMR spectral data those reported in the literature.

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Comparison with other reported system

One-pot A^3-coupling reactions via various aldehydes, alkynes and amines and also N-arylation of iodobenzene with imidazole, S-arylation of iodobenzene with thiophenol under heterogeneous conditions over a variety of catalysts has been studied (Table 7). Table 7 provides a comparison of the results obtained for our present catalytic system with those reported in the literature.[29-31] From Table 7, it is seen that present catalyst exhibited higher yields compared to the other reported system.[29-31] Reactions conducted at room temperature or at moderately low temperature for shorter reaction time. Most importantly most of the coupling reactions occurred in water over our Cu-nanocatalyst.

Table 7 Comparison of catalytic activity of the present catalyst in the N-arylation, S-arylation and A^3 coupling reactions with other reported systems

Entry	Copper Source	N-arylation reaction	S-arylation reaction	Synthesis of propargylamines	Ref.
		Yield (%)	Yield (%)	Yield (%)	
1	Cat2 (Mesoporous Silica Supported Copper catalyst)	89	-	-	29
2	Cu(II)-DA-30-A	-	99	-	30
3	Cu/NCNTs	-	-	85	31
4	Cu-MPTA-1	91	95	93	This study

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Recycling of Catalyst

For a heterogeneous catalyst, it is important to examine its ease of separation, recoverability and reusability. The reusability of the mesoporous Cu-MPTA-1 nanocatalyst was investigated in N-arylation, S-arylation and A^3-coupling reactions (cyclohexanecarboxaldehyde, phenyl acetylene and piperidine). After each run, ethyl acetate was added to dilute the reaction mixture and the organic layer was dried with anhydrous Na_2SO_4 by vacuum. The filtrate was concentrated and the resulting residue was purified. After a simple wash using ethyl acetate and dried, the catalyst was reused for the next run and almost consistent activity was observed for next six consecutive cycles (Figure 8). As seen from the figure that the catalyst can be efficiently recycled and reused for repeating cycles without appreciable decrease in product yield. TEM image (Figure S1 in the supporting information) of the reused catalyst did not show any substantial change compared with the fresh catalyst.

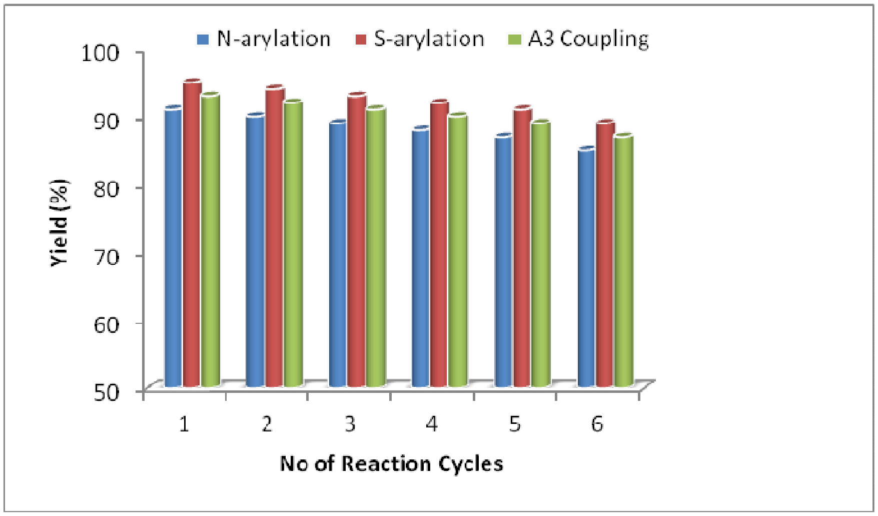

Figure 8. Recycling efficiency for the N-arylation, S-arylation and A^3 Coupling reactions.

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Heterogeneity Test

Hot Filtration Test

To examine whether copper was being leached out from the solid support to the solution, experiment has been carried out in the C-S coupling reaction with our supported Cu-MPTA-1 nanocatalyst. A typical hot filtration test was performed in the S-arylation to investigate whether the reaction proceeded in a heterogeneous or a homogeneous fashion. For the rigorous proof of heterogeneity, a test was carried out by filtering catalyst from the reaction mixture at 80 ^{0}C after 4 h and the filtrate was allowed to react up to the completion of the reaction (6 h). In this case no change in conversion was observed, which suggests that the catalyst is heterogeneous in nature. No evidence for leaching of copper or decomposition of the complex catalyst was observed during the catalytic reaction. It was noticed that after filtration of the catalyst from the reactor at the reaction temperature, coupling reactions do not proceed further. Atomic absorption spectrometric analysis of the supernatant solution of the reaction mixture thus collected by filtration also confirmed the absence of copper ions in the liquid phase. Thus, results of the hot filtration test suggested that Cu was not being leached out from the solid catalyst during the cross-coupling reactions.

Conclusions

From our experimental observations we can conclude that a new Cu-nanocatalyst has been developed by grafting of Cu(II) at the surface of mesoporous polymer MPTA-1. This Cu-nanocatalyst has been successfully used as a heterogeneous catalyst for the N-arylation reaction of imidazole with aryl halides and S-arylation reaction of thiophenol with aryl halides in water as green solvent and one pot A^3 coupling reaction at room temperature with excellent yields. Thus the catalytic process is green and it offers a number of advantages, such as easy work-up and separation of the catalyst from the reaction mixture by filtration,

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reusability for several times with often minimal loss of activity. These key findings of this nanotechnology based recyclable heterogeneous catalysis provided herein is inherently advanced, economical and environmentally sustainable for the one pot synthesis of propargylamines, S-arylation and N-arylation reactions.

Acknowledgements

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