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Synthesis of copper nanoparticles supported on a microporous covalent triazine polymer: an efficient and reusable catalyst for *O*-arylation reaction

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Abstract

Copper nanoparticles were supported on a microporous covalent triazine polymer prepared by the Friedel-Crafts reaction (Cu@MCTP-1). The resulting material was characterized by powder X-ray diffraction, thermogravimetric analysis, N_2-adsorption-desorption isotherms at 77 K, transmission electron microscopy, X-ray photoelectron spectroscopy, and inductively coupled plasma optical emission spectroscopy, and Cu particles with an average size of 3.0 nm and a BET total surface area of *ca.* 1002 m^2g^{-1} were obtained. Cu@MCTP-1 was evaluated as a heterogeneous catalyst for the Ullmann coupling of *O*-arylation over a series of aryl halides and phenols without employing expensive ligands or inert atmosphere, which produced an excellent yield of the corresponding diaryl ethers. The catalyst could be recovered by simple centrifugation and was reusable at least five times with only a slight decrease in catalytic activity.

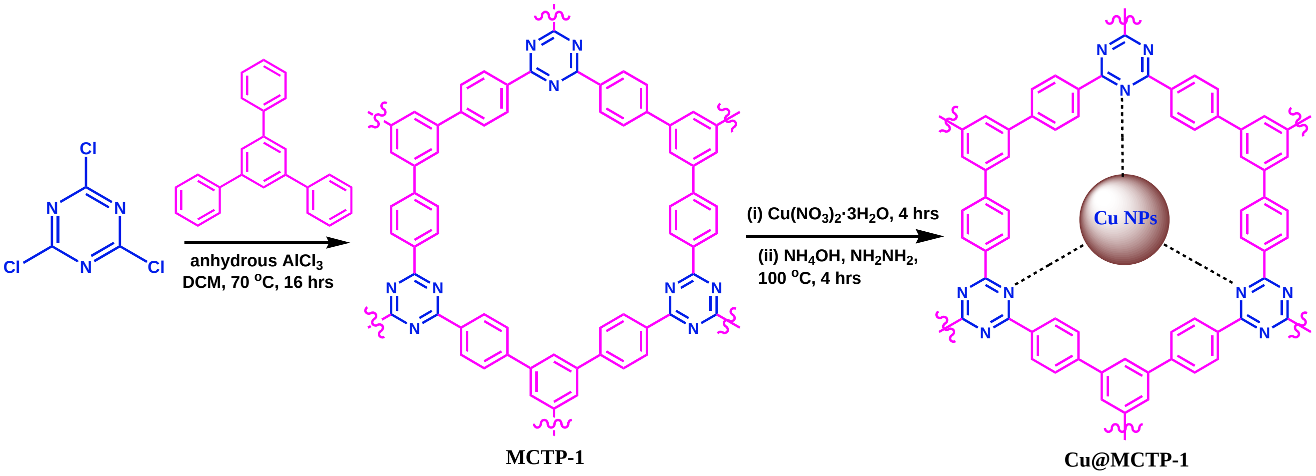
Keywords: copper nanoparticles, covalent triazine polymer, Ullmann coupling, *O*-arylation, heterogeneous catalyst.

Introduction

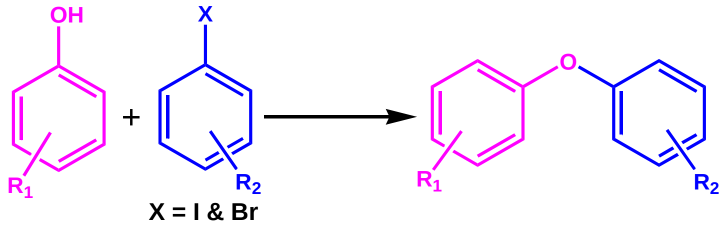
Aryl-O bond (diaryl ether linkage) formation is an important and challenging task in both synthetic and industrial chemistry. The reaction produces important chemical intermediates of the biological, pharmaceutical, life science, and materials interest.[1] Traditionally, diaryl ethers are prepared *via* nucleophilic substitution of phenols with aryl halides. This method, however, suffers from drawbacks such as high reaction temperature (>200 °C), necessity for a stoichiometric amount of catalyst, and low to moderate product yield with a long reaction time.[2] To overcome these problems, palladium catalysts with different ligand groups have been tested for the formation of C-O bond. However, these Pd catalyst-based homogeneous coupling methods have limitations, such as the use of air and moisture-sensitive phosphine ligands, high cost of Pd salts, contamination of the products, and tedious multistep protocols necessary for the ligand synthesis and work-up process.[3] Concurrently, researchers have also been examining the use of Cu-catalyzed Ullmann coupling using *N*-donors, *N*- and *O*- donors and *P*-based ligands, such as neocuproinem,[4] 1,10-phenanthroline,[5] *N*,*N*-dimethylglycine,[6] tripod ligands,[7] pyrrolidine-2-phosphonic acid phenyl monoester,[8] β-keto esters,[9] di-imine derivatives,[10] nicotinic acid,[11] β-diamide-based hybrid silica,[12] metformin,[13] and 2-carbomethoxy-3-hydroxyquinoxaline-di-*N*-oxide.[14] These protocols proceeded homogeneously, and again the high cost of ligands, product contamination and need for catalyst recovery are problems to overcome. Thus the development of active, ligand-free, inexpensive, moisture-stable, and recyclable heterogeneous catalytic systems for the clean synthesis of C-O bonds is highly desirable.

In recent years, synthesis of metallic nanoparticles (NPs) supported on a porous material and their applications in catalytic reactions have attracted considerable attention owing to the high surface-to-volume ratio in NPs that can enhance the interaction between the reactants and catalyst, which can lead to increase the product yields compared to homogeneous catalysts.[15] In addition, catalysis by metal NPs has advantages such as easy catalyst separation from the reaction mixture, fast catalytic reaction rates, and reuse with better retention of the catalytic activity than their bulk counterparts. Supported Cu NPs are currently attracting more interest than other transition metal NPs of Au, Ag and Pd, because of their broad applications and lower cost.[16] Catalysts based on Cu_2O, CuO and Cu NPs have also been considered for the synthesis of diaryl ethers. Benyahya *et al.* developed a sol-gel immobilized CuI-catalyst for the arylation of phenols with aryl iodides/bromides.[17] Park *et al.* developed the Cu_2O nanocube catalytic system for the diaryl ethers synthesis from aryl halides and phenols at 150 °C.[18] Sun *et al.* used magnetic $CuFe_2O_4$ NPs for the Ullmann coupling synthesis of diaryl ethers at 135 °C.[19] Wang *et al.* reported the CuO/γ-Al_2O_3 catalyzed C-O coupling reaction of iodobenzene with *m*-cresol at 150 °C.[20] Heydari *et al.* reported the α-Fe_2O_3@CuO nanocomposite catalyzed the same coupling reactions with an external diketone ligand in an argon atmosphere.[21] Recently, Nagarkar *et al.* prepared Cu NPs on nafion-graphene nano-ribbons by an electrochemical method and used them as a catalyst for Ullmann coupling synthesis of ethers.[22] Li *et al.* showed that carbon nanofiber-supported Cu NPs catalyzed the Ullmann coupling of *O*-arylation at 140 °C.[23] However, almost all the methods attempted thus far involved high cost catalytic systems and had a limited scope of applications. The development of simple, active and low-cost heterogeneous catalysts for the Ullmann coupling of *O*-arylation reactions are still highly desirable.

Porous covalent triazine polymers (CTPs) have emerged as a novel platform for heterogeneous catalysts and support material. They have excellent textural properties with high surface area and pore volume, tunable composition, and exhibit high thermal and chemical stability to most organic solvents, and can be prepared *via* easy synthesis protocols at low cost.[24] They have been considered for gas storage and separation, drug delivery, super capacitors, photo-degradation of organic compounds and catalysis.[25] CTPs with high nitrogen contents in the framework enable the effective immobilization of metallic NPs, which leads to a uniform particle size distribution, because the particles are immobilized permanently inside their cavities.[26] Bhaumik *et al.* reported that Pd NPs were immobilized by the triazine units in mesoporous polymers and the covalent imine networks catalyzed the C-C coupling reactions.[27] Liu *et al.* reported the preparation of Pd NPs supported on the triazine moiety in covalent organic polymers, and used them for CO oxidation reactions.[28] Edwards *et al.* developed porous melamine-formaldehyde polymers to stabilize Pd, which served as a catalyst for Suzuki coupling reactions.[29] Recently, Pitchumani *et al.* reported that Pd and Cu(II) ions immobilized on the triazine units in porous materials as efficient catalysts for the Sonogashira, Heck and Chan-Lam coupling reactions.[30] Chen *et al.* developed Pd NPs supported on a similar porous organic material CTF-1 for the catalytic hydrogenation of *N*-heterocycles, and Ru NPs for NH_3 decomposition.[31] To the best of the authors' knowledge, however, there are no reports on the utilization of a nitrogen-rich CTPs for stabilizing Cu NPs and their applications in catalysis. Recently, we reported an inexpensive Friedel-Crafts synthesis of microporous CTPs (MCTPs) based on readily available cyanuric chloride with tri-/dual site-reactive 1,3,5-triphenylbenzene (MCTP-1) / *trans*-stilbene (MCTP-2).[32] In a continuation of that work, MCTP-1 was applied as a solid support to immobilize the Cu NPs (Scheme 1), which was tested as a catalyst towards environmentally benign and efficient Ullmann cross coupling of *O*-arylation reaction (Scheme 2).



Scheme 1. Synthesis of the Cu NPs supported on MCTP-1 (Cu@MCTP-1)



Scheme 2. Ullmann cross coupling of *O*-arylation

Experimental section

Synthesis of Cu NPs supported on MCTP-1 (Cu@MCTP-1)

Unless specified otherwise, all chemicals were purchased from commercial suppliers and used as received. $Cu(NO_3)_2·3H_2O$ (70 mg) was dissolved in 4 mL of methanol and then MCTP-1 material (500 mg) was added with stirring at room temperature over a 2 h period. The solid was then filtered, and washed with methanol to remove the unreacted $Cu(NO_3)_2·3H_2O$. The freshly prepared Cu^{2+} incorporated MCTP-1 was added to 5 mL of water, and NH_4OH (2 mL; 28%) and hydrazine hydrate (2 mL) were then added with vigorous stirring. Finally, the mixture was transferred to a 15 mL capacity Teflon-lined stainless steel autoclave and heated to 100 ^oC for 4 h in an oven. After heating, the autoclave was cooled to room temperature and the solid

Cu@MCTP-1 was collected by filtration, washed with methanol, and kept under a nitrogen atmosphere. MCTP-1 was prepared using the procedure reported elsewhere.[32]

Characterization

The powder X-ray diffraction (PXRD, Rigaku) patterns of the catalysts were recorded using CuKα (λ=1.54 Å) with 0.5^{o} min^{-1} over the scanning range of 4-80^{o}. The N_2 adsorption-desorption isotherms were measured in a BELsorp-Max (BEL, Japan) at 77K. The specific surface areas and pore sizes of the samples were calculated using the Brunauer–Emmett–Teller (BET) and nonlocal density functional theory (NL-DFT) model with slit pore geometry, respectively. The metal loading was measured by inductively coupled plasma – optical emission spectrometry (ICP-OES, Optima 7300DV, USA). The thermal stability of the samples was evaluated by thermogravimetric analysis (TGA, SCINCO thermal gravimeter S-1000, Japan) under an Argon (Ar) atmosphere over the temperature range, 30–700 ^{o}C in flowing argon at a heating rate of 5 ^{o}C min^{-1}. Transmission electron microscopy (TEM) was performed using a CM200 UT (Philips, Germany) instrument. The catalytic reaction conversions were analyzed gas chromatography (GC, Agilent Technologies, 7890A, USA) fitted with a HP-5 capillary column and a flame ionization detector. The nuclear magnetic resonance (NMR, VARIAN UNITYINOVA (USA) and JEOL 400 MHz instruments (USA)) spectra were recorded in tetramethylsilane as the internal standard and $CDCl_3$ as a solvent. High resolution X-ray photoelectron spectroscopy (XPS, Thermo scientific, USA) was performed using a monochromatic Al Kα X-ray source and a hemispherical analyzer.

General procedure for the Ullmann coupling of *O*-arylation reaction

In a typical procedure, a mixture of aryl halide (1 mmol), phenol (1.2 mmol), Cs_2CO_3 (2 mmol), Cu@MCTP-1 (100 mg, which contains 2.68 wt.% of Cu as determined by ICP-OES) in

DMF (3 mL) was placed in a 25 mL round bottom flask. The reaction was conducted at 130 °C in an oil bath with magnetic stirring for various reaction times. After the reaction, the reaction mixture was cooled to room temperature, and diluted with ethyl acetate (10 mL). The catalyst was then centrifuged, the supernatant was extracted with distilled water, and the organic layer was dried over anhydrous sodium sulfate. The organic solvent was removed under reduced pressure and the resulting residue was purified by column chromatography to provide the desired pure product.

Results and discussion

The synthesis procedure and physic-chemical properties of the MCTP-1 is given in our previous publication.[32] The synthetic strategy of Cu@MCTP-1 in this study involves the simple preparation of a mixture of MCTP-1 and Cu(II) ions from $Cu(NO_3)_2 \cdot 3H_2O$, and the subsequent chemical reduction of the immobilized Cu(II) ions to Cu(0) NPs. A uniform distribution of nano-sized Cu NPs in Cu@MCTP-1 was confirmed by PXRD, TGA, XPS, N_2 adsorption-desorption isotherms, TEM, and ICP-OES analyses.

The crystallinity of the Cu@MCTP-1 was examined by PXRD in the range, 4 to 80° 2θ (Figure 1). The two broad diffraction peaks at 10.3° and 21.8° 2θ suggest the potential stacking of triazine linkage (001) plane.[24a] The strong Bragg reflection peaks are observed at 43.38°, 50.48° and 74.13° 2θ, which were assigned to the (111), (200) and (220) sets of lattice planes of the face centered cubic (fcc) structures of Cu, respectively. The oxide forms of the Cu phase peaks were not observed in PXRD, which clearly pointed out that the produced Cu NPs are present in the fully-reduced Cu(0) state. TGA of Cu@MCTP-1 exhibited good thermal stability up to 260 °C (Figure 2).

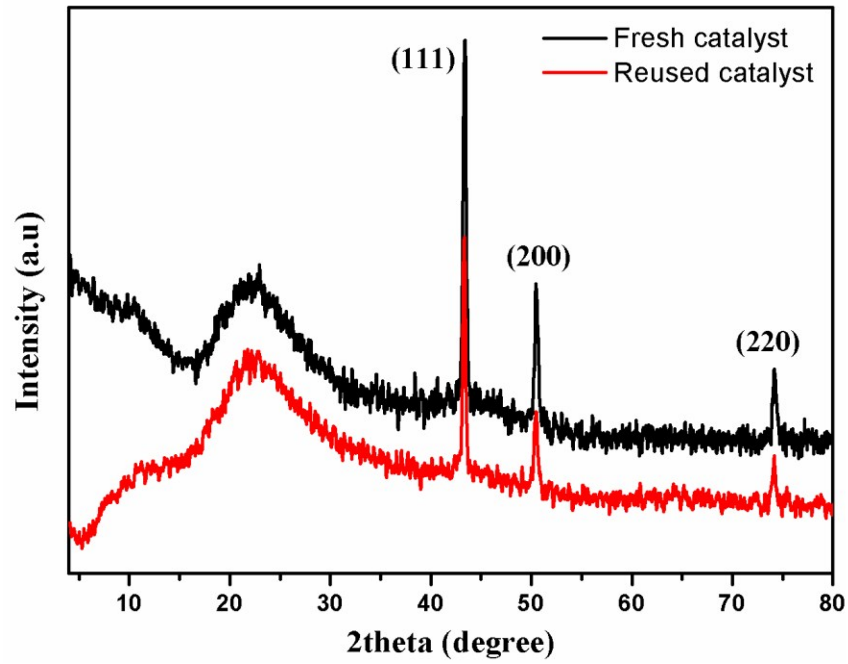


Figure 1. Powder XRD pattern of the fresh and reused Cu@MCTP-1

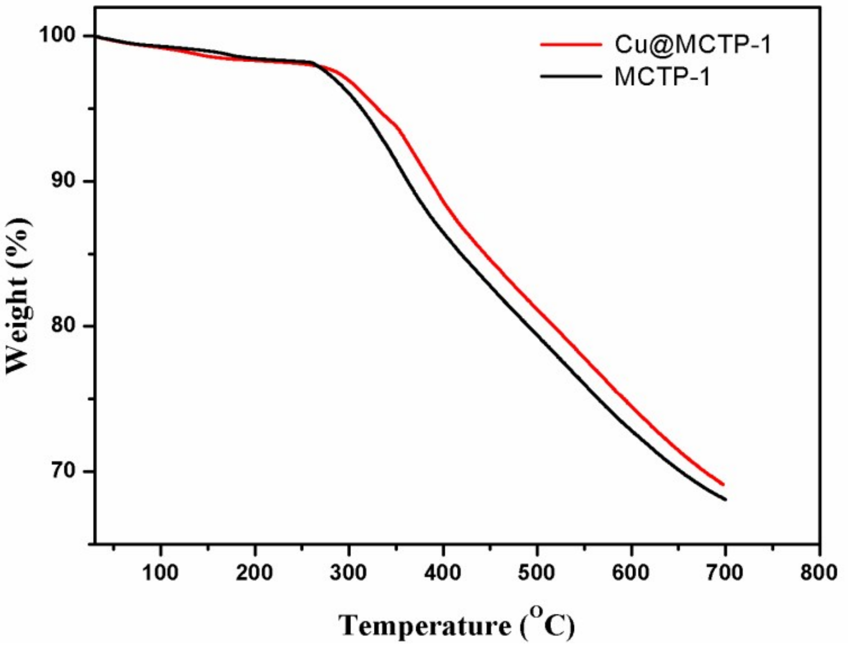


Figure 2. TGA curves of MCTP-1 and fresh Cu@MCTP-1

The oxidation state of Cu and the strong affinity between Cu and N in triazine in MCTP-1 were confirmed by XPS (Figure 3). In the fresh Cu@MCTP-1, two strong binding energy peaks at 952.3 and 932.5 eV were assigned to Cu $2p_{1/2}$ and Cu $2p_{3/2}$ level of Cu(0), respectively. In addition, the difference between the binding energy peaks of 19.8 eV (between Cu $2p_{1/2}$ and Cu $2p_{3/2}$ level) and the absence of a Cu $2p_{3/2}$ satellite peak around 942 eV also confirmed the formation of Cu NPs and that all the particles were present in the pure Cu(0) state.[33] The triazine-unit N 1s core level was previously reported at 398.8 eV.[34] The observed nitrogen 1s core level binding energy at 400.1 and 400.0 eV, respectively, of the fresh and reused (Figure 3b) catalyst clearly showed that Cu metals are strongly bound to triazine nitrogen species in MCTP-1.

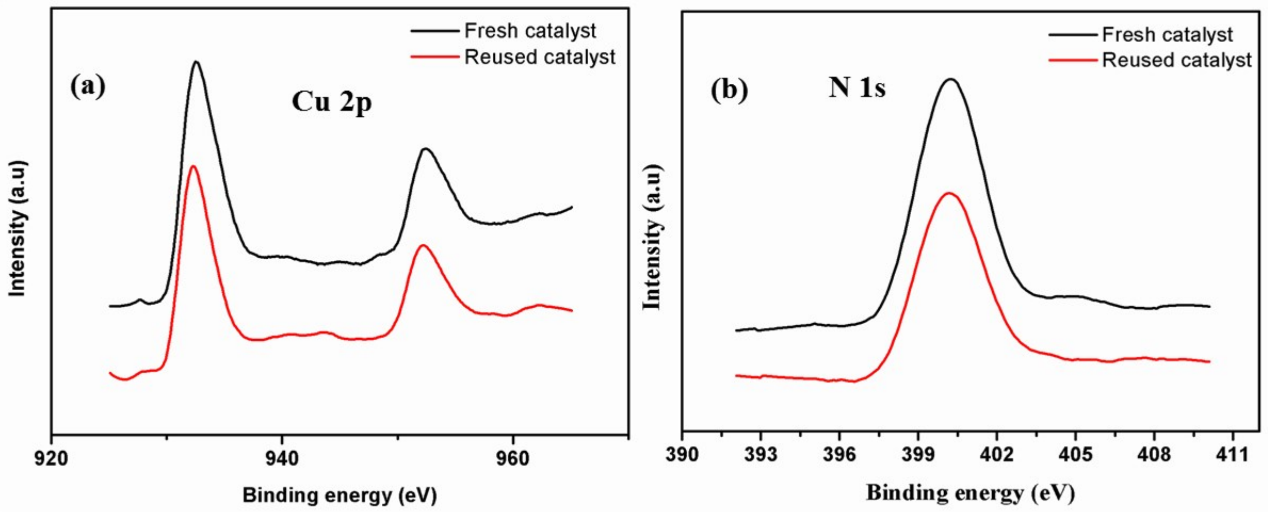


Figure 3. XPS of fresh and reused Cu@MCTP-1 catalyst (a) Cu 2p and (b) N 1s core levels

The N_2 adsorption-desorption isotherm of the fresh and reused Cu@MCTP-1 catalyst at 77 K showed a type I isotherm with steep N_2 uptakes in the low pressure region (Figure 4), which indicated a microporous structure. Table 1 lists the resulting textural properties of Cu@MCTP-1. The fresh and reused catalyst BET surface areas were 1002 and 1034 m^2g^{-1}, respectively, which were estimated from the 0.01 - 0.05 relative P/P_0 pressure region of the adsorption isotherms. The hysteresis in the isotherms in Figure 4 is reported elsewhere.[24a,35] This is probably due to the flexibility, amorphous nature of the polymers with soft pore walls and pore shape effect, which lead to irreversible desorption.

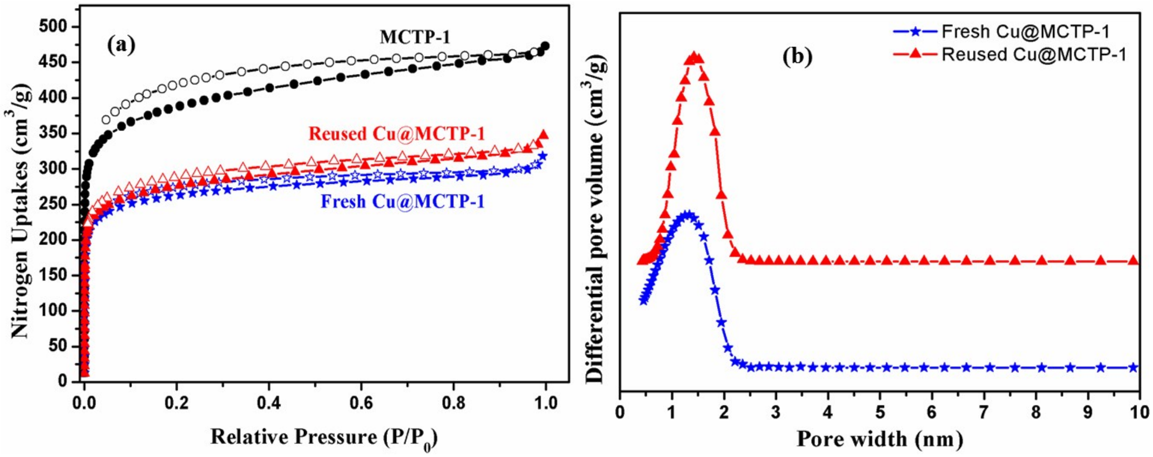


Figure 4. (a) N_2 adsorption (solid) – desorption (empty) isotherm of MCTP-1 (black), fresh Cu@MCTP-1 (blue) and reused Cu@MCTP-1 (red) catalyst, and (b) pore size distribution of fresh and reused Cu@MCTP-1 catalyst

Table 1. N_2 isotherm properties of MCTP-1, fresh and reused Cu@MCTP-1

Sample	S_{BET} (m^2g^{-1})	Total V_{pore} (cm^3g^{-1})	Pore width (nm)
MCTP-1	1459	0.73	1.51
Fresh Cu@MCTP-1	1002	0.58	1.34
Reused Cu@MCTP-1	1034	0.60	1.40

The morphology and particle size of Cu NPs supported on MCTP-1 was confirmed by TEM (Figure 5), which revealed a narrow particle size distribution ranging from 2.0 to 6.0 nm with a mean particle size of 3.0 nm, and the Cu particles were highly dispersed on MCTP-1. From ICP-OES, the fresh Cu@MCTP-1 was found to contain *ca.* 2.68 wt.% of Cu NPs.

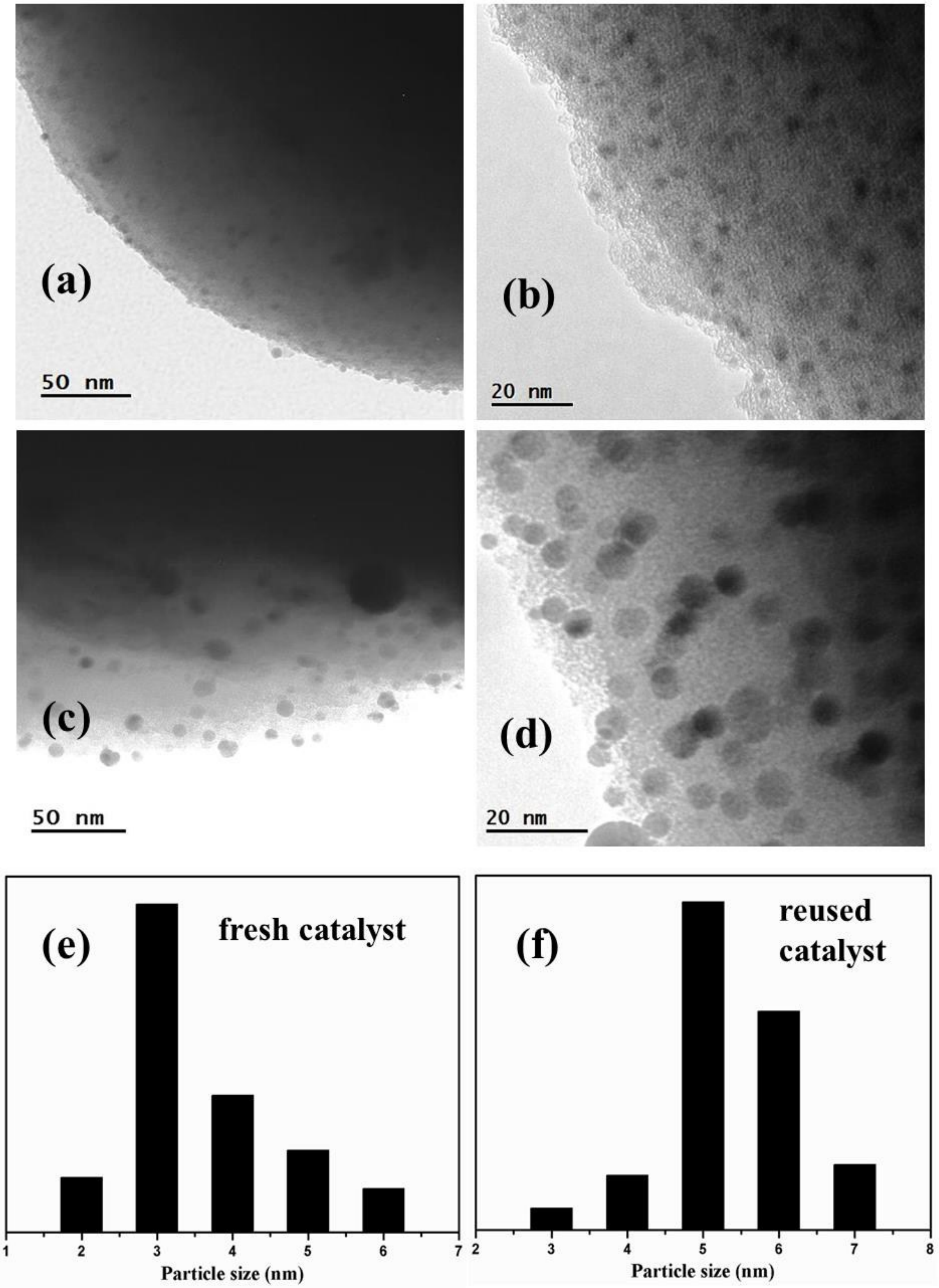


Figure 5. TEM image of the fresh Cu@MCTP-1 (a & b), the recovered Cu@MCTP-1 after the fifth runs (c & d) and particle size distribution plot of fresh (e) and reused Cu@MCTP-1 (f)

The catalytic property of Cu@MCTP-1 was examined in the Ullmann coupling of *O*-arylation using phenols with aryl iodides and bromides (Scheme 2). In the initial study to establish the optimized reaction conditions, the experiments were conducted with the cross coupling of phenol and iodobenzene as model substrates with different solvents and bases. The detailed results of these experiments are listed in Table 2. Without a catalyst or with MCTP-1 alone, the reaction did not proceed in 24 h, clearly establishing the active role of Cu in this Ullmann coupling reaction (Table 2, entries 1-2). When the reaction was carried out with the homogeneous Cu salt catalysts, the reaction proceeded very slowly and only resulted in poor yields (Table 2, entries 3-5). The reaction with Cu@MCTP-1 in DMF, however, produced the diaryl ether product in 94% yield (Table 2, entry 6). Apparently, the efficacy of the base is critical for achieving a good product yield, because the reaction did not proceed without a base (Table 2, entry 7). The effect of different bases was screened in this reaction system (Table 2, entries 8-11). After testing five different bases (Cs_2CO_3, K_2CO_3, Na_2CO_3, $NaHCO_3$ and NaOAc), Cs_2CO_3 gave superior results and the corresponding diaryl ether product was observed in 94% yield, due to the higher basicity and rapid dissociation of the intermediate cesium phenoxide. Polar and nonpolar solvents (dioxane and toluene) were screened to determine the solvent effects in this reaction. When polar solvents such as DMF, DMSO, DMAc and ACN, were used, the products were observed in 94%, 77%, 89%, and 58% yields (Table 2, entries 12-14), respectively. The nonpolar dioxane and toluene solvents were less active in this reaction (Table 2, entries 15-16). The reaction temperature also plays an important role in the yield of the reaction (Table 2, entry 17). As the reaction temperature was decreased from 130 to 100 ^{o}C, the product yield also decreased gradually. In addition, a higher product yield was achieved with 100 mg of catalyst than with 60 or 80 mg of catalyst (Table 2, entry 18). Finally, the cross coupling reaction was examined at reaction different times (0, 4, 8, 12, 16, 20, and 24 h), and the yield was 0, 25, 47, 63, 75, 85, and 94%, respectively (Figure 6a). For further investigation of the Cu@MCTP-1 catalysis, the following set of reaction conditions was selected: Cs_2CO_3 as a base and Cu@MCTP-1 (100 mg) as a catalyst in DMF at 130 ^oC for 24 h.

Table 2. Optimization of the reaction condition for the Ullmann coupling of *O*-arylation[a]

Entry	Base	Solvent	Conversion (%)[b]
1[c]	Cs_2CO_3	DMF	0
2[d]	Cs_2CO_3	DMF	0
3[e]	Cs_2CO_3	DMF	22
4[f]	Cs_2CO_3	DMF	13
5[g]	Cs_2CO_3	DMF	11
6	Cs_2CO_3	DMF	94
7	-	DMF	0
8	K_2CO_3	DMF	53
9	Na_2CO_3	DMF	26
10	$NaHCO_3$	DMF	12
11	NaOAc	DMF	17
12	Cs_2CO_3	DMSO	77
13	Cs_2CO_3	DMAc	89
14	Cs_2CO_3	ACN	58
15	Cs_2CO_3	Dioxane	8
16	Cs_2CO_3	Toluene	19
17	Cs_2CO_3	DMF	52[h], 81[i]
18	Cs_2CO_3	DMF	83[j], 65[k], 33[l]

[a] Reaction Conditions: Iodobenzene (1 mmol), phenol (1.2 mmol), base (2 mmol), solvent (3 mL), Cu@MCTP-1 (100 mg), 130 ^oC, 24 h; [b] GC conversion based on iodobenzene; [c] Without Cu@MCTP-1; [d] MCTP-1 alone; [e] $CuCl_2$; [f] $Cu(NO_3)_2.3H_2O$; [g] $CuSO_4.5H_2O$; [h] 100 ^oC; [i] 120 ^oC; [j] 80 mg of catalyst; [k] 60 mg of catalyst; [l] 40 mg of catalyst.

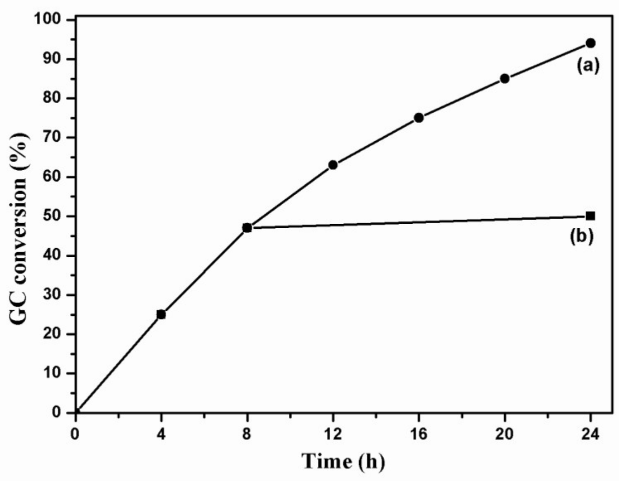


Figure 6. (a) Time interval plot for the coupling of iodobenzene with phenol over Cu@MCTP-1 and (b) after removing the catalyst at 47% product formation

The reaction of phenol with various substituted aryl iodides also produced to excellent product yields (Table 3, entries 1-12). Furthermore, the electron-withdrawing groups in the *para*-position of the iodo substrates reacted more readily with phenols to give slightly higher yields of the corresponding products (Table 3, entries 4-9) compared to the *para*- or *meta*-substituted electron-donating iodo substrates (Table 3, entries 2, 3, 10 & 11), but the *ortho*- substituted 2-nitroiodobenezene gave somewhat lower yield due, probably to steric hindrance (Table 3, entry 12). On the substrates containing either chloro- or fluoro- group in iodobenzene, phenol coupled selectively only with the iodo-sides (Table 3, entries 6-7).

The catalyst efficiency was examined further with less reactive aryl bromides under the same reaction conditions. Here, the same type of electronic effect was observed as in aryl iodides, and gave the products in 77-86% yield (Table 3, entries 13-17). In a further set of experiments, the reaction between substituted phenols and various aryl iodides were examined. In this case, the electron donating groups on the phenol reacted more readily with iodobenzene than the electron withdrawing groups on the phenol (Table 3, entries 18-27). Interestingly, heterocyclic 4-iodopyridine and 1,4-diiodobenzene coupled easily with phenol, which gave the corresponding products in 89 and 83% yield, respectively (Table 3, entries 28-29). The coupling products of diaryl ethers were characterized by NMR spectroscopy and the corresponding data are presented in the supporting information.

Table 3. Diversity of Cu@MCTP-1 catalyzed *O*-arylation of aryl halides with various phenols[a]

Entry	Phenols (1)	Aryl halides (2)	Products (3)	Yield of 3 (%)[b]
1	C_6H_5-OH (1a)	C_6H_5-I (2a)	3a	94
2	1a	4-CH_3-C_6H_4-I (2b)	3b	89
3	1a	4-CH_3O-C_6H_4-I (2c)	3c	87
4	1a	4-NO_2-C_6H_4-I (2d)	3d	96
5	1a	4-NC-C_6H_4-I (2e)	3e	94
6	1a	4-F-C_6H_4-I (2f)	3f	97
7	1a	4-Cl-C_6H_4-I (2g)	3g	95
8	1a	4-CH_3CO-C_6H_4-I (2h)	3h	93
9	1a	4-CF_3-C_6H_4-I (2i)	3i	91
10	1a	3-CH_3-C_6H_4-I (2j)	3j	88
11	1a	3-CH_3O-C_6H_4-I (2k)	3k	85
12	1a	2-NO_2-C_6H_4-I (2l)	3l	71
13	1a	C_6H_5-Br (2m)	3a	82
14	1a	4-CH_3-C_6H_4-Br (2n)	3b	79
15	1a	4-CH_3O-C_6H_4-Br (2o)	3c	77
16	1a	4-NO_2-C_6H_4-Br (2p)	3d	85
17	1a	4-NC-C_6H_4-Br (2q)	3e	86
18	4-CH_3-C_6H_4-OH (1b)	2a	3b	95
19	4-CH_3O-C_6H_4-OH (1c)	2a	3c	93
20	4-NO_2-C_6H_4-OH (1d)	2a	3d	78
21	1b	2b	3m	90
22	1b	2j	3n	89
23	1c	2h	3o	88
24	1d	2d	3p	84
25	1d	2h	3q	82
26	4-F-C_6H_4-OH (1e)	2f	3r	84
27	4-NC-C_6H_4-OH (1f)	2f	3s	86
28	1a	4-iodopyridine (2r)	3t	89
29[c]	1a	1,4- I-C_6H_4-I (2s)	3u	83

[a]Reaction Conditions: Aryl halides (1 mmol), phenols (1.2 mmol), Cs_2CO_3 (2 mmol), DMF (3 mL), Cu@MCTP-1 (100 mg), 130 ^{o}C, 24 h; [b]Isolated yields; [c]200 mg of Cu@MCTP-1.

To check for the possibility of Cu leaching from the Cu@MCTP-1 solid support to the solution and confirm that the catalysis is truly heterogeneous in nature, a hot filtering experiment proposed by Sheldon was carried out using iodobenzene and phenol as the substrates under optimized conditions (Figure 6b). The reaction was quenched after an 8 h reaction, and the catalyst was removed by centrifugation. The supernatant solution was further subjected to reaction at 130 ^{o}C for the remaining period of time (16 h). After the reaction time, the mixture was cooled and extracted with ethyl acetate to identify the product and yield. Practically no further conversion was detected in the supernatant solution, which clearly supported that the catalysis is heterogeneous in nature.

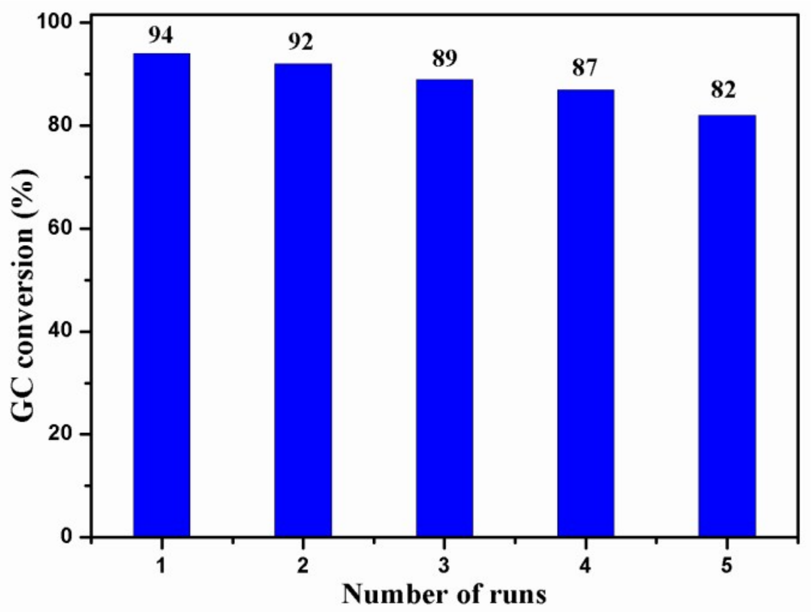


Figure 7. Recycling test of Cu@MCTP-1 catalyst towards the Ullmann coupling of phenol with iodobenzene

Easy product separation and reusability of the catalyst are highly desirable for industrial applications. The catalyst reusability was assessed in the coupling reaction of *O*-arylation between iodobenzene and phenol under the optimized reaction conditions (Figure 7). The catalyst was recovered by centrifugation after each experiment, washed with DMF followed by water to remove the base. The catalyst was dried under vacuum at 100 ^{o}C for 2 h, and the recovered catalyst was used for the next four consecutive runs. As shown in Fig. 7, the conversion of iodobenzene steadily decreased after each runs. Subsequently, the recovered catalyst stability was examined by PXRD, TEM, XPS, ICP-OES, and BET surface area measurement (N_2 adsorption-desorption isotherm) analyses. The PXRD pattern (Figure 1) of the reused catalyst showed similar set of peaks to those of the fresh one and no additional peaks were observed, which indicates that the recovered catalyst is highly stable even after the fifth runs. The TEM analysis of the recovered Cu@MCTP-1 catalyst after the 5th run (Figure 5) showed that the size of the Cu particles have grown slightly to 3.0-7.0 nm with a mean particle size of 5.0 nm reflecting mild agglomeration. Similar finding was reported for Pd on a porous covalent triazine polymer support.[28] The XPS spectra of the reused catalyst revealed two strong binding energy peaks at 952.1 eV and 932.3 eV respectively, and no impure (Cu^{2+} state) satellite peak was observed, suggesting that the Cu NPs are not oxidized in the catalytic reaction and all the Cu particles are present in the zero valence state (Figure 3a). The reused Cu@MCTP-1 catalyst had shown a BET surface area (1034 m^2g^{-1}) slightly higher than the fresh catalyst (1002 m^2g^{-1}). According to the TEM analysis of the used Cu@MCTP-1, Cu particles have somewhat grown in size, which could have made more pore interior exposed. In addition, The Cu content at the fifth cycle, however, was 2.55 wt.% as measured by ICP-OES analysis, which indicates minute leaching of Cu particle from the external surface of the material. The Cu NPs might have detached from the Cu@MCTP-1 through attrition of the catalysts particles caused by magnetic stirring during the long reaction time. Despite the minor limitation, the catalyst could be reused at least five times.

Conclusion

A simple and economical method for preparing a catalyst comprised of Cu NPs immobilized on an organic porous polymer MCTP-1 with high nitrogen content was reported for the first time. This Cu@MCTP-1 showed excellent catalytic activity in the Ullmann coupling of *O*-arylation under optimized conditions and the system provided a wide range of diaryl ethers from various phenols and aryl halides. The catalyst was reusable for up to five consecutive runs with a slight decrease in product yield and the heterogeneity of the catalyst was proven by the Sheldon test. Further applications of this catalyst to other chemical transformations are currently underway.

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Graphical Abstract

Synthesis of copper nanoparticles supported on a microporous covalent triazine polymer: an efficient and reusable catalyst for *O*-arylation reaction

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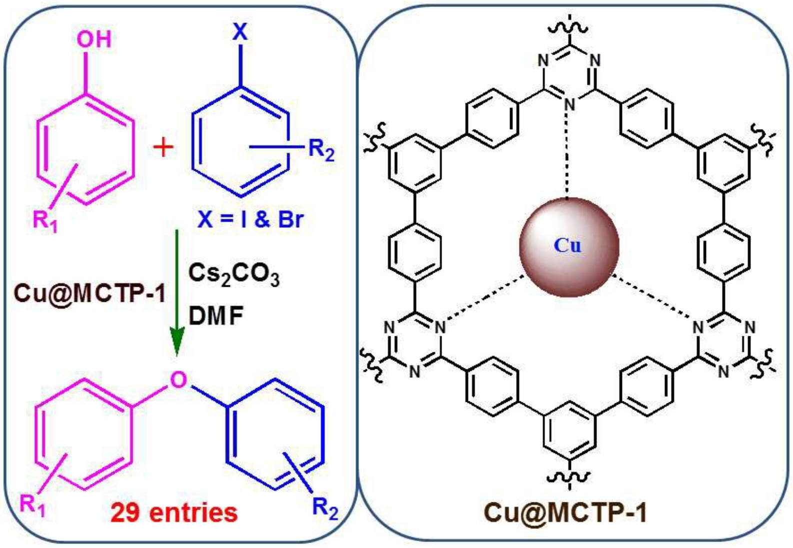

Cost-effective synthesis of Cu NPs immobilized on microporous covalent triazine polymer was evaluated as catalyst for Ullmann coupling of *O*-arylation.