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# Heterogeneous O–arylation of nitroarenes with substituted phenols over copper immobilized mesoporous silica catalyst<sup>#†</sup>

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<sup>†</sup>Electronic supplementary information (ESI) available: Results of catalytic reactions in specific condition in tabular form, PXRD, and TEM and SEM images of virgin and recovered catalyst, N<sub>2</sub> sorption data, graphical presentation of O-arylation reaction of phenol in five successive runs, <sup>1</sup>H and <sup>13</sup>C NMR spectra and HRMS plots of the isolated products.

# For Table of contents entry



A heterogeneous mesoporous silica based copper catalyst has been designed for O–arylation of phenol using nitroarene as electrophile which affords unsymmetrical diarylether. The catalyst shows high efficiency for catalyzing reaction as reflected in high turnover frequency. Catalyst can be recycled up to 5 times without any significant loss of catalytic activity.

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#### Abstract

Highly porous and robust mesoporous silica, SBA–15 has been subjected for post-synthesis modification for anchoring of copper through Schiff base moiety formation in it using silicon alkoxide route. Hybrid porous material has been fully characterized by powder–XRD, electronic spectra, EPR, thermogavimatric analysis, N<sub>2</sub> sorption measurement, TEM and SEM/EDS study. Efficiency of the catalyst has been assessed in O–arylation reaction using various substituted phenols and nitroarenes in heterogeneous condition. Catalytic coupling reaction efficiently produces unsymmetrical diarylethers. Impressive capability to activate substrates having electron–donating or electron–withdrawing substituent and to afford high turnover frequency in catalytic reactions made the catalyst highly desirable.

# Introduction

Diarylethers has received much attention because of their natural biological activity and their importance in polymer industries.<sup>1</sup> Among the various synthetic methods of diarylethers, transition metal catalyzed C–O bond formation has become a general procedure for the direct synthesis of these compounds.<sup>2</sup> Many of these transformations utilize aryl halides,<sup>2</sup> arylboronic acids<sup>3</sup> or arenes<sup>4</sup> as coupling partners. Recently, Chen and co–workers introduced homogeneous copper catalyzed C–O bond formation reaction using cheap nitroarene as arylating regent.<sup>5</sup> Very recently, we have reported a homogeneous copper Schiff base complex catalyzed coupling of nitroarenes with phenols to produce diaryl ethers.<sup>6</sup> But for large–scale applications, heterogeneous catalyst is highly desirable because of the ease of handling, simple

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recovery/recycling of the catalyst and minimization of unnecessary toxic wastes.<sup>7</sup> Furthermore. designing of heterogeneous catalytic system with comparable efficiency to that of homogeneous catalyst is a challenge. Phan et al. reported a heterogeneous Cu-based metal-organic framework (MOF) for the coupling reaction of phenols with nitroarenes.<sup>8</sup> Further exploration in this area allows us to endeavor a new heterogeneous system that is highly active towards C-O coupling reaction in entirely leaching free condition. The role of the support in heterogeneous catalytic reaction is a prime factor and for that matter a support may change activity/or selectivity of the catalyst towards reaction.<sup>9</sup> Large pore mesoporous silica SBA-15, with larger surface area (BET)<sup>10</sup> and higher thermal stability owing to thick walls is considered as good candidate for catalytic support.<sup>11</sup> Large pore size facilitates the synthesis of active metal center inside the pore and easy diffusion of bulky reactants and products during catalytic reactions. To this end Schiff-base transition metal complexes has been studied widely due to their potential application in catalyzing various catalytic reactions<sup>12</sup> and ease of loading of Schiff-base moiety onto porous silica.<sup>13</sup> Besides ligands which afford electron-rich metal complexes are necessary to reach a high degree of efficiency.<sup>14</sup>

Herein we report, a first example of a heterogeneous copper Schiff–base modified SBA–15 catalyst, S@Cu (see Experimental Section) for C–O coupling reaction using nitroarene as coupling partner. The recoverable and reusable catalyst displays high turnover frequency (TOF) by employing sub–stoichiometric amount of catalyst.

# **Experimental section**

# Materials

CuCl<sub>2</sub>·2H<sub>2</sub>O, tetraethyl orthosilicate (TEOS, 98%), the nonionoic surfactant Pluronic P123, 3– [2-(2-(Aminoethylamine)ethylamino]propyl-trimethoxysilane (AEPTS), pyridine-2-aldehyde and all other reagents were purchased either from Sigma-Aldrich/Fluka or Alfa-Aesar and were used as received without further purification. Solvents were purchased from Merck (India) and were distilled and dried before use.

#### **Physical measurements**

Mesoporous materials were characterized by small angle powdered X-ray (SAX) diffraction study. Small angle X-ray patterns of all powdered samples were taken in the  $2\theta$  range of  $2^{\circ}$  to  $10^{\circ}$  at a rate of  $2^{\circ}$  min<sup>-1</sup> in steps of  $0.02^{\circ}$  (Bruker D8 Advance diffractometer) using Cu–Ka radiation. Perkin–Elmer 240C elemental analyzer was used to collect microanalytical data (C, H and N). Fourier transform-infrared spectra on KBr pellets spectra were measured on a Perkin–Elmer L1600300 FTIR spectrometer. The solid state diffuse reflectance UV–Vis spectra were recorded by UV-2401 PC SHIMADZU spectrophotometer in the wavelength range of 200-800 nm. EPR spectra of both the catalysts were collected from JEOL JES-FA200 ESR SPECTROMETER. The copper content of catalyst was determined by a Perkin Elmer A–Analyst 200 atomic absorption spectrometer (AAS). The BET surface area and total pore volume of the mesoporous samples were determined by an Autosorb-iQ (Quantachorme Inc.) gas sorption system. Prior to analyses, all the samples were degassed at 130 °C under vacuum until a final pressure of  $10^{-2}$  Torr was reached to evacuate the physically adsorbed moisture. The transmission electron micrograph (TEM) of samples was obtained by JEOL-TEM-2010 electron microscopes with an acceleration voltage of 200 kV. Scanning electron microscopic (SEM) images were recorded on ZEISS EVO 18 (Special edition) and energy dispersive X-ray

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scattering (EDS) analysis of samples (with gold coating) was recorded on OXFORD EDS8100. TG/DTA thermograms were recorded on a Perkin Elmer (Singapore) Pyris Diamond TG/DTA unit with N<sub>2</sub> carrier gas flowing at a rate of 150 mL min<sup>-1</sup> and the heating rate was programmed at 4 °C min<sup>-1</sup>. All products of the catalytic reactions were collected and purified by column chromatographic method and characterized by elemental analysis (using Perkin–Elmer 240C elemental analyzer) and comparison of their NMR and Mass spectra with those reported in the literature. Reactions were monitored by TLC and NMR spectra recorded in CDCl<sub>3</sub> or in DMSO–d<sub>6</sub> on a Bruker Avance DPX 300 NMR (300 MHz) spectrometer. Mass spectra were measured on a Waters XEVO–G2QTOF#YCA351 high resolution Mass Spectrometer.

#### **Catalyst preparation**

#### Inclusion of amine groups into SBA-15

Mesoporous silica material, SBA–15 was synthesized following a method described in literature.<sup>15</sup> In a typical experiment [Scheme S1(a)], SBA–15 (calcined, 0.2 g), dry toluene (15 mL) and AETPS (0.5 mL) was stirred at 70 °C for 24 h under N<sub>2</sub> atmosphere. The white solid thus formed, named S@Am, was filtered, washed with dry toluene for several times followed by dry dichloromethane and dried in air.

### Generation of Schiff–base moiety in S@Am

0.05 g of S@Am was refluxed with pyridine–2–aldehyde (0.07 g) in methanol (10 mL) for 6 h at 65 °C in air [Scheme S1(b)]. The resulting yellowish solid was then collected by filtration and was dried in a desiccator. The as–synthesized products were denoted as S@SB.

#### Preparation of catalyst S@Cu

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Finally, the S@Cu was prepared by refluxing S@SB (0.07g) with CuCl<sub>2</sub>·2H<sub>2</sub>O (0.086 g, 0.5 mmol) in methanol (12 mL) at 65 °C for 6 h under air [Scheme S1(c)]. The green solid thus formed was filtered, washed with methanol using Soxhlet and dried under vacuum. The Cu content (measured from AAS) of the catalyst found to be 1.58 (wt.%) (0.025 mol.%). Elemental analysis showed N:Cu was 4.1.

#### General experimental procedure for the C–O coupling reactions

0.003 g of catalyst S@Cu (0.025 mol%) was added to a round-bottom flask containing a DMF (3 mL) solution of phenol (0.094 g, 1 mmol), 4-nitrobenzaldehyde (0.166 g, 1.1 mmol) and  $K_2CO_3$  (0.391 g, 1.2 mmol). Reaction mixture was refluxed at 100 °C for 8 h. The conversion was monitored by TLC (thin layer chromatography) method. After 8 h the reaction mixture was cooled to room temperature and the mixture was extracted with water and dithyl ether (2 × 15 mL). The organic layers thus collected were combined and washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (mesh 60–120) using an n-hexane/ethyl acetate mixture as the eluent to give the desired product. The product was characterized by <sup>1</sup>H, <sup>13</sup>C–NMR, HRMS and elemental analysis then compared with literature data.

#### Hot filtration test

The reaction mixture of phenol (1.0 mmol),  $K_2CO_3$  (1.2 mmol), and S@Cu (3 mg) in dry DMF (3 mL) with *p*-nitrobenzaldehyde (1.1 mmol) was refluxed at 100 °C under air and the progress of the reaction was monitored by TLC. After completion of reaction ~30%, catalyst was separated at the reaction temperature by filtration (Whatman 1, 10 µm); further  $K_2CO_3$  (1.2

mmol) was added to the reaction solution and stirred at 100 °C for another 8 h. Progress of the reaction was examined by TLC analysis.

#### **Preparation of PNA-SBA-15**

Anchoring of AEPTS into SBA–15 has been achieved according to method mentioned above [Scheme S1(a)]. The white solid, S@Am was then refluxed with *p*–nitroacetophenone (5 mmol, 0.8 g) in 10 mL methanol for 6 h at 65 °C. The resulting yellowish solid PNA–SBA–15 was then collected by filtration and dried in desiccator (Scheme S2).

#### Three phase test

A solution of phenol (1 mmol), *p*–nitrobenzadehyde (1.1 mmol), and K<sub>2</sub>CO<sub>3</sub> (1.2 mmol) in 3 mL DMF was stirred in the presence of 0.003 g of S@Cu and 1 g of PNA–SBA–15 at 100 °C for 8 h. Reaction mixture was collected by filtration and workup in the usual manner, then the residual portion was hydrolyzed with 2 N aqueous HCl solution (1.7 mL HCl in 8.5 mL H<sub>2</sub>O) for 3 h under a refluxing condition and isolated as *p*–nitroacetophenone. Both the resulting solutions were analyzed by GC and <sup>1</sup>H NMR.

# **Results and discussion**

#### **Catalyst characterization**

Small angle X–ray diffraction patterns of S@Am, S@SB and S@Cu are shown in Fig. 1. Patterns demonstrated typical three diffraction lines<sup>16</sup> in  $2\theta$  range 0.9 to 1.8 with a very strong  $d_{100} = 101.32$  Å and two small diffraction peaks for the 110 and 200 planes confirming a well–defined 2D hexagonal mesoporous structure.<sup>17</sup> A progressive decrease in the intensity and Published on 28 March 2016. Downloaded by Middle East Technical University (Orta Dogu Teknik U) on 28/03/2016 11:46:20.

slight increase in *d*-spacing was observed which is associated with the sequential modification of the pore of SBA-15. The intensity reduction may be mainly due to contrast matching between the silicate framework and organic moieties present in the channels of SBA-15.<sup>18</sup>



Fig. 1 Powder XRD patterns of (a) S@Am, (b) S@SB, (c) S@Cu.

Fig. 2 depicts the FTIR spectra of S@SB and S@Cu. IR spectrum of S@SB exhibits a band at 1645 cm<sup>-1</sup> due to C=N bond stretching frequency of imine bond. A shift of imine C–N stretching towards lower frequency region (1632 cm<sup>-1</sup>) was observed upon metalation (Fig. 2b) indicating the coordination of azomethine nitrogen to the copper ion. The solid–state electronic spectra (Fig. 3a) of the species S@SB showed three absorption maxima at *ca*. 215, 250 and 319 nm which could be attributed to intra ligand charge transfer transitions. Upon complex formation intra ligand charge transfer bands shifted towards higher wavelength region and a relatively weak band appeared at *ca*. 648 nm is assigned to d–d transitions (Fig. 3b).<sup>19</sup>



Fig. 2 FTIR spectra of a) S@SB, b) S@Cu.



Fig. 3 Diffuse reflectance UV–Vis spectra of a) S@SB, b) S@Cu.

Fig. 4 displays the X-band EPR spectrum of S@Cu. The principle g values calculated by the usual methods from EPR spectra are in agreement with those reported for other copper(II)

Schiff base complexes.<sup>20</sup> The  $g_{\parallel}$  and  $g_{\perp}$  values of S@Cu are *ca*. 2.283 and 2.077, respectively. The catalyst features  $g_{\parallel} > g_{\perp} > 2.0023$  which clearly suggest the characteristic of square planar geometry in copper(II) complexes.<sup>21</sup>



Fig. 4 EPR spectrum of S@Cu.

 $N_2$  sorption isotherms and pore size distribution plots for SBA–15, S@Am, S@SB and S@Cu are shown in Figs. 5A and B, respectively. All plots are of typical of type IV isotherm (according to the IUPAC nomenclature), with an H2–type hysteresis loop, which is characteristic of the mesoporous materials. BET surface area of SBA–15 is 1431 m<sup>2</sup> g<sup>-1</sup> with mesopore volume of 1.62 cm<sup>3</sup> g<sup>-1</sup>. The average pore diameter is calculated to be 31 Å using the NLDFT method. A gradual decrease in the BET surface area [Fig. 5A], pore volume, and pore diameter [Fig. 5B] could be observed at each stage of modification (Table S1).<sup>22</sup> This indicates that the immobilization of the copper(II) complex has taken place substantially inside the pore channels of SBA–15.



Fig. 5 A) Nitrogen sorption isotherms of a) SBA–15, b) S@Am, c) S@Cu and B) pore size distribution plot of a) SBA–15, b) S@Am, c) S@Cu.

TEM images of SBA–15 and S@Cu are shown in Fig. 6. When electron beam falls on the catalyst perpendicular to the pore axis, the pores are seen to be arranged in patches composed of regular rows, as has been interpreted by Chenite *et al.*<sup>23</sup> Both the SBA–15 matrix and catalyst showed open–ended lamellar type (Fig. 6a and 6b) arrangement. TEM image provides strong evidence that the long–range ordering of the support framework is retained even after the immobilization of the copper(II) Schiff base complex in the mesoporous silica matrix.

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Fig. 6 TEM Images of A) SBA-15 and B) catalyst, S@Cu.

All the SEM images shown in Fig. 7A revealed the similar worm–like morphology typical for SBA type mesoporous materials.<sup>24</sup> This also suggest that no significant changes of the external surface morphology occurred upon inclusion of Schiff–base of the copper(II) complex into porous matrix. The EDS elemental analysis indicated the presence of copper and chlorine in catalyst whereas those atoms are absent in SBA–15 (Fig. 7B). The ratio of Cu:Cl obtained from EDS was close to 1:1 ratio which supports the proposed structure of copper Schiff-base complex inside the pore as shown in Scheme S1.







Fig. 7B EDS patterns of a) SBA-15, b) S@Cu.

TG curve (Fig. 8) of S@Cu shows a weight loss between room temperature and 160 °C while DTA curve shows a broad endothermic peak in the temperature range 100-200 °C. Upon further heating, the catalyst showed thermal stability up to ~ 200 °C and then a steady mass loss was obtained upto ~ 700 °C which corresponds to an exothermic peak centered at ~ 550 °C in its corresponding DTA curve. The first mass loss seemed to be due to removal of adsorbed water and solvent molecules, while the second mass loss may be due to decomposition of the organically modified framework.

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Fig. 8 TG–DTA curve of S@Cu.

#### **Catalytic activity**

In order to get optimal conditions for C–O cross coupling reaction we first examined the influences of different parameters *e.g.* solvent, base, reaction temperature, % Cu loading in catalyst, reaction time etc. Our objective was to develop a protocol that requires minimum amount of catalyst for smooth C–O cross coupling reaction and that tolerate a wide range of functional groups on both coupling partners. We first screen the optimized conditions for reaction of phenol with *p*–nitrobenzaldehyde and the results are summarized in Table S2. As the catalyst is thermal and air stable, inert atmosphere was not employed. It is noteworthy that the coupling reaction does not proceed without copper catalyst (Table S2, entry 1). Of the different solvents investigated, DMF was the most suited for catalytic reaction (Table S2, entry 2). While finding out the suitable base to be used in this coupling reaction it is noticed that when finely

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powdered Cs<sub>2</sub>CO<sub>3</sub> was used, excellent arylated product was obtained (Table S2, entry 11) due to the enhanced basicity of  $C_{s_2}CO_3^{25}$  However, the use of  $K_2CO_3$  will be more economic than that of Cs<sub>2</sub>CO<sub>3</sub> for large scale production. Other bases such as KOH, Na<sub>2</sub>CO<sub>3</sub>, CH<sub>3</sub>COONa, tert-BuOK, and DABCO showed a slower formation of 4-phenoxybenzaldehyde after 8 hours (Table S2, entries 9–14). Cheap K<sub>2</sub>CO<sub>3</sub> showed a satisfactory yield and was chosen for the O-arylation reaction (Table S2, entry 2). Reaction temperature and time also has great influence on the coupling reactions. Reaction at 60 °C produced low yield (Table S2, entry 15) even after 20 h. With increase of temperature yield increased and gave a maximum of product yield at 100 °C whereas upon further increase in temperature yield decreased gradually. This is due to formation of some unwanted non-isolable by-products (Table S2, entry 16). Thus the optimized reaction conditions were found to be  $K_2CO_3$  (as the base) and DMF (as the solvent) at 100 °C under air. To study the catalytic efficacy of S@Cu, we controlled the copper loading in the catalyst by varying the amount of CuCl<sub>2</sub>·2H<sub>2</sub>O in the Schiff–base complex formation as shown in Fig. S1. A maximum conversion was achieved with 0.025 mol% of catalyst in 8 hours. Notably isolated yields were not up to the mark with lower concentrations of catalyst. Additionally, increasing the catalyst concentration beyond 0.025 mol% did not enhance the reaction rate significantly. Thus the optimum conditions for the catalytic reaction were as follows: K<sub>2</sub>CO<sub>3</sub> (base), DMF (solvent), 0.025 mol% catalyst and a reaction temperature of 100 °C. Reactions in the presence S@Am+CuCl<sub>2</sub>·2H<sub>2</sub>O, S@SB+CuCl<sub>2</sub>·2H<sub>2</sub>O, CuCl<sub>2</sub>·2H<sub>2</sub>O were also investigated under optimum condition to understand the competence of S@Cu as a catalyst (Table S2, entries 17–19).

With the optimal condition in hand we investigated the catalytic activity of S@Cu for various aryl alcohols with nitroarenes containing diverse functional groups. The results obtained

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in test reactions demonstrate that the electronic properties of the phenols affect the product yield (Table 1). Substituted phenols possessing electron donating methyl groups accelerate the reaction to yield products in a greater amount in comparison to simple phenols (Table 1, entries 1a,c and 1k,l). However, p-methylphenol showed a higher yield than m- and o-methylphenol indicating that the yield is also affected by the steric effects of substitution (Table 1, entries 11-n). It is worth noting here that the TOF reached *ca*. 165  $h^{-1}$  in the case of *p*-methylphenol which completes the reaction in 8 h (Table 1, entry 1c). Here the *p*-methoxy substituent in phenol acts similarly like *p*-methyl group towards the coupling reaction as shown in Table 1, entry 1d. The substitution in nitroarenes has an impact on the reaction kinetics. Aryl nitro containing the  $p-NO_2$  and  $o-NO_2$  group gave 99% and 92% yield, respectively, while reacts with *p*-methylphenol, probably due to electronic and steric hindrance, but TOFs still exceeded 165  $h^{-1}$ and 153  $h^{-1}$  (Table 1, entries 1c and 1d), respectively. *p*-nitrobenzonitriles showed more product yields than *p*-nitrobenzaldehyde (Table 1, entries 1f-h). The coupling reactions of electron-deficient phenols with aryl halides have been challenging as the corresponding phenolates are weak nucleophiles.<sup>26</sup> But the results presented here demonstrate that p-nitrobenzonitrile can behave as a strong electrophile in the O-arylation of *p*-hydroxyacetophenone and can afford moderate yields (58%) with TOF 77  $h^{-1}$  (Table 1, entry 1j).

Table 1 S@Cu catalysed O-arylation reaction of nitroarene with aryl alcohols.<sup>a</sup>

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<sup>*a*</sup> Reaction condition: Aryl alcohol (1.0 mmol), nitroarene (1.1 mmol),  $K_2CO_3$  (1.2 mmol), 0.003 g catalyst (Cu content: 0.025 mol%), DMF (3 mL) at 100 °C for 8 h. <sup>*b*</sup> Isolated yield. <sup>*c*</sup> TOF = mol. product/ (mol.Cu × time) (unit in h<sup>-1</sup>).

In search of efficient heterogeneous catalysts for the C–O cross coupling reactions, we have undertaken few comparison studies. Recently, Li *et al.* reported the O–arylation of p–hydroxyacetophenone with p–fluorobenzonitrile in DMF media at a temperature of 90 °C under a N<sub>2</sub> atmosphere.<sup>27</sup> Buchwald and his group also studied the reactivity of some electron–deficient phenols in C–O coupling reactions at 100–110 °C.<sup>26</sup> However, in all the above reported processes aryl halides were used as electrophiles. In contrast catalyst S@Cu efficiently catalyzed the same reaction using nitroarene as electrophile at 100 °C and the TOF of the reaction becomes 77 h<sup>-1</sup>. Phan *et al.* reported for O–arylation of phenol with p–nitrobenzaldehyde using 3 mol% of heterogeneous Cu<sub>2</sub>(BDC)<sub>2</sub>(DABCO) manifested TOF *ca.* 17 h<sup>-1.8</sup> While in our case reaction could proceed with 0.025 mol% of S@Cu and procure TOF *ca.* 152 h<sup>-1</sup>.

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#### Hot filtration test

To ascertain the catalysis is indeed heterogeneous we have performed hot filtration test.<sup>28</sup> After hot filtration the residual activity of the supernatant solution was studied. It was found that coupling reactions do not proceed further as the catalyst was removed by filtration (Fig. S2). Atomic absorption spectrometric analysis (sensitivity up to 0.001 ppm) of the supernatant solution collected by filtration also confirmed the absence of copper in the liquid phase. The above results suggest that copper was not being leached out from the solid support and the catalyst is indeed heterogeneous.

#### Three phase test

Three phase test is one of the important tests to ascertain the true heterogeneity of the copper based catalyst<sup>19,22</sup> for O–arylation reaction using a designed aryl nitro in usual condition as described in Scheme S3. In the case of the immobilized aryl nitro, no reaction was observed on support and no *p*–phenoxyacetophenone was detected. If there be any leaching of Cu from the catalyst, anchored *p*–nitroacetophenone would have also participated in the above–described reaction. We found remained *p*–nitroacetophenone as unreacted, while the soluble *p*–nitrobenzaldehyde substrate converted to *p*–phenoxybenzaldehyde as expected for O–arylation reaction, indicating the presence of an active heterogeneous catalyst.

#### Separation and reuse of catalyst

For recycling study the first O-arylation reactions were performed with phenol, p-nitrobenzaldehyde and K<sub>2</sub>CO<sub>3</sub>, maintaining the optimized reaction conditions. After the every cycle, the catalyst was recovered by centrifugation and then washed thoroughly with (9:1)

acetonitrile–water mixture. Recovered catalyst was dried under vacuum at 100 °C overnight. Atomic absorption spectrometric analysis of the recovered catalysts confirmed that the copper content of the S@Cu remained virtually the same (~1.56 wt%). Performance of the recycled catalyst up to five successive runs is shown in Fig. S3. In addition, recovered catalyst was thoroughly checked by X–ray powder diffraction (Fig. S4), FTIR spectra (Fig. S5), TEM (Fig. S6) and SEM study (Fig. S7). All these studies convincingly supported the structural integrity of the compound.

# Conclusion

In essence, we have successfully synthesized a new mesoporous silica based copper Schiff base catalyst by post–synthetic modification method. The catalyst facilitates the C–O coupling reaction to go smoothly encompassing a broad range of functional groups. Notably, the catalysts are efficient enough to activate electron–deficient phenols towards O–arylation reactions. This leaching resistant catalyst shows high TOF values for synthesis of diarylethers using cheap nitroarene as electrophile. O–arylation can be undertaken in open flask reaction which makes the procedures easily accessible for synthesis of a variety of important compounds.

# Supporting information

Supporting information may be found in the online version of this article.

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