Journal of Molecular Catalysis A: Chemical 386 (2014) 78–85

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

Cu(II)-anchored functionalized mesoporous SBA-15: An efficient and recyclable catalyst for the one-pot Click reaction in water

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ARTICLE INFO

Article history:
Received 1 November 2013
Received in revised form 29 January 2014
Accepted 31 January 2014
Available online 10 February 2014

Keywords:
Mesoporous material
SBA-15
Cu(II) anchored
One-pot
Click reaction.

ABSTRACT

A new pyridine-imine functionalized mesoporus silica (SBA-15) has been synthesized through the Schiff-base condensation of 3-aminopropyl functionalized SBA-15 with 2-pyridinecarboxaldehyde followed by the grafting of Cu(II) onto it resulting a new Cu@PyIm-SBA-15 material. 2D-hexagonally ordered mesophases of the material are analyzed by small-angle powder X-ray diffractions (PXRD) and transmission electron microscopic (TEM) image analyses. The Cu(II)-anchored mesoporous material, Cu@PyIm-SBA-15 showed excellent catalytic activity towards the one pot click reaction between azides formed *in situ* from the corresponding amines and acetylenes in water at 0 °C to room temperature resulting a wide variety of 1,4-disubstituted 1,2,3-triazoles. The catalyst has been recycled for five cycles without any appreciable loss of catalytic activity and also without any appreciable Cu-leaching, suggesting a future potential of this novel mesoporous catalyst for the synthesis of 1,4-disubstituted 1,2,3-triazoles.

1. Introduction

Organically functionalized mesoporous materials have received considerable attention since past decades because these materials have excellent potentiality as environmentally benign catalysts [1–12], hosts of nanomaterials [13,14], sensors [15–17], optoelectronic devices [18–22], drug delivery [23], etc. These organically functionalized materials have gained particular importance as supports for various metal salts in designing novel heterogeneous catalysts due to their exceptionally high surface area, wide and controllable pore opening in nanoscale dimension, easy product separation and excellent recycling efficiency [1–11]. Among them mesoporous organosilicas and related nanomaterials have been extensively used as heterogeneous catalysts through grafting or immobilizing metal complexes within the nano channels [24–27].

On the other hand "Click" reaction between azides and alkynes leading to the formation of 1,4-disubstituted 1,2,3-triazoles has received widespread attention since its discovery by Sharpless and his co-workers in 2001 [28,29]. 1,2,3-Triazoles are found to possess wide applications in several research fields like synthetic organic chemistry [30–34], biological chemistry [35,36], medicinal chemistry [37–39] and material chemistry [40–42]. Hence several methods have been developed for the synthesis of 1,2,3-triazoles using various catalytic systems like copper nanoparticles [43], copper nanoclustures [44], Cu(II)/Cu(0) comproportionation [45], mixed Cu/Cu-oxide nanoparticles [46–48], *in-situ* reduction of Cu(II) salts to Cu(I) salts [49,29,50–52] etc. But the major disadvantages associated with these homogeneous copper catalysts are the difficulties to recover and reuse for successive reaction cycles and the possibility of metal contamination with the end product. To overcome these serious issues, various solid-supports like zeolites [53], polymers [54,55], carbon [44], silica [56] etc. have been employed to synthesize the corresponding heterogeneous copper catalysts by immobilizing the active metal ions onto the solid supports.

Herein, we report the synthesis of a new Cu(II) anchored functionalized SBA-15 type mesoporous silica and utilized it to catalyze the "Click" reaction. The mesoporous silica SBA-15 was first amine functionalized using 3-aminopropyltriethoxysilane (3-APTES), which was then subjected to undergo Schiff base condensation reaction with 2-pyridinecarboxaldehyde to form a new imine functionalized mesoporous SBA-15. Grafting of copper

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http://dx.doi.org/10.1016/j.molcata.2014.01.027

acetate on the surface of this imine functionalized mesoporous SBA-15 resulted in Cu@PyIm-SBA-15 material.

On the other hand one pot procedure for the synthesis of 1,2,3-triazoles through the reaction between *in-situ* generated azides from its corresponding amines and acetylenes is highly desirable and economical as this avoids the isolation step of azides. Several one pot procedures for the synthesis of 1,2,3-triazoles have been developed using various copper catalysts [57–64]. Most of them used alkyl halide as the starting material, but the main challenge is to start with aromatic precursors like anilines, aryl halides or aryl boronic acids. Few such methodologies have been developed for the synthesis of 1,2,3-triazoles but, most of them uses costly reagents or organic solvents/ligands/high temperature, etc., which are not acceptable in the context of green chemistry. Here we report a green one pot procedure for the synthesis of 1,2,3-triazoles by the so-called click reaction between aryl azides formed *in situ* from anilines and acetylenes over Cu@PyIm-SBA-15 catalyst at 0 °C to room temperature (Scheme 1) to form a wide range of 1,4-disubstituted 1,2,3-triazoles.

2. Experimental

2.1. General

Pluronic P123 (EO20PO70EO20, EO = ethylene oxide, PO = propyleneoxide, M_{av} = 5800), tetraethoxyorthosilicate (TEOS), 3-aminopropyl triethoxysilane (3-APTES), copper acetate and all acetylene derivatives were purchased from Sigma-Aldrich. All the reagents were analytical grade and used as such without further purification. Solvents were purified and dried according to standard procedures. Thin layer chromatography was carried out by using commercial (MERCK) plates with silica gel 60 F_{254}

2.2. Synthesis of catalyst

The reaction pathways for the synthesis of mesoporous Cu@PyIm-SBA-15 is outlined in Scheme 2.

2.2.1. Synthesis of mesoporous SBA-15 (1)

Mesoporous SBA-15 was synthesized by following the reported procedure [18]. P123 (4 g), 2.0 (M) aq. HCl (120 mL) and distilled water (15 mL) were stirred at room temperature for 4 h. Then TEOS (8.5 g) was added drop wise to the solution of P123 at 40 °C for 24 h. Then, a synthesized gel was thus formed, which was then loaded in a 500 mL scaled polypropylene bottle using Teflon tape and was kept at 100 °C for 24 h under static condition. Solid white product was formed and separated by filtration, washed with distilled water, dried in air. Then the product was calcined at 500 °C for 5 h.

2.2.2. Synthesis of 3-amino propyl functionalized SBA-15 (2)

The calcined SBA-15 (2 g) was refluxed with 3-aminopropyltriethoxysilane (3-APTES) (3.6 g) in toluene for 18 h. The resulting white solid was filtered, washed thoroughly with ethanol and finally dried in air.

2.2.3. Synthesis of SBA-15 supported imine ligand (3)

2-Pyridinecarboxaldehyde (3 mL) was added to a mixture of 3-amino propyl functionalized SBA-15 (1.8 g) in super dry ethanol (90 mL) in a 250 mL round bottomed flask. The reaction mixture was stirred at 60 °C for 24 h. Then it was filtered. The resulting light yellow solid was washed with toluene and then further washed with ethanol to remove any unreacted aldehyde. It was dried in a hot-air oven at 90 °C for overnight to furnish the corresponding SBA-15 supported imine material (3).

2.2.4. Synthesis of Cu@ImPy-SBA-15 (4)

One gram of SBA-15 supported imine material (3) was suspended in absolute ethanolic (20 mL) solution of copper acetate (0.2 g) and was kept under refluxing condition for 12 h. The reaction mixture was cooled at room temperature. Then the resulting brown material, Cu@ImPy-SBA-15 was filtered out, washed thoroughly with ethanol and dried under vacuum.

2.3. Elemental analysis of the catalyst

The copper content in the Cu@ImPy-SBA-15 catalyst was determined by using a Varian, USA, AA240 atomic absorption spectrophotometer (AAS). The amount of metal was determined by stripping the bound metal from the support followed by the analysis of the metal ion by using an atomic absorption spectrophotometer. Copper content in the catalyst was 1.19 wt%. The copper content in Cu@ImPy-SBA-15 after five reaction cycles has also been measured.

2.4. Characterizations of Cu@ImPy-SBA-15

Powder X-ray diffraction patterns of the pure SBA-15 and functionalized materials were recorded on a Bruker D-8 Advance diffractometer operated at 40 kV voltage and 40 mA current using Cu K_α (λ = 0.15406 nm) radiation. TEM analysis was carried out by using a JEOL 2010 TEM operated at 200 kV. The EPR (electron paramagnetic resonance) spectra of the fresh and used Cu@PyIm-SBA-15 catalyst were recorded for the solid sample at room temperature using a JES-FA200 ESR spectrometer (JEOL).

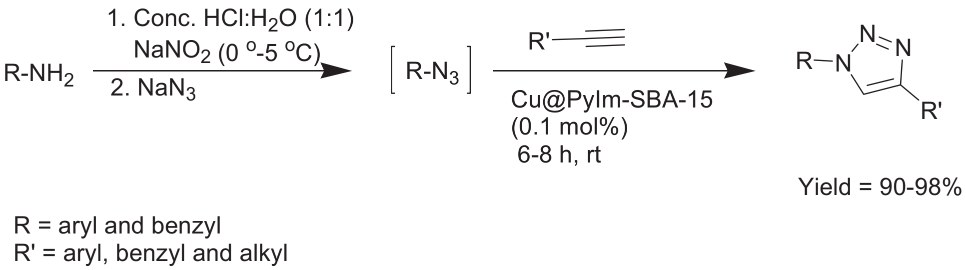
2.5. Experimental procedure for the synthesis of 1,4-disubstituted 1,2,3-triazole

Aniline (0.5 g, 5.4 mmol) was placed into a 25 mL round bottomed flask which was then put in an ice water bath (0–5 °C). Subsequently, a mixture of conc. HCl–H_2O (1.3 mL: 1.3 mL) was added to it and the mixture was stirred for 1 min. $NaNO_2$ (0.392 g, 5.7 mmol), dissolved in 1 mL of water, was first cooled at 0–5 °C and then added to the reaction mixture drop wise. After 2 min stirring, sodium azide (0.416 g, 6.4 mmol) was added and stirred for 5 min. Then phenylacetylene (0.46 g, 4.6 mmol) and Cu@PyIm-SBA-15 (0.025 g, 0.1 mol%) were added to the reaction mixture followed by stirring at room temperature for 6 h (TLC). When the reaction was over, the water layer was decanted off and the reaction mixture was dissolved in ethanol. Then the catalyst was filtered through a sintered glass-bed (G-4), and washed with water (3 × 4 mL) followed by ethanol (3 × 3 mL) and acetone (2 × 4 mL). The product was purified by a simple crystallization from ethanol to furnish the corresponding triazole, 1,4-diphenyl-1*H*-[1,2,3]triazole, as a white solid (Yield = 98%), TOF = 163 h^{-1}, mp 183–185 °C; IR (KBr) 3120, 1598, 1502, 1481, 1451, 1228, 1056, 758 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.37 (*t*, *J* = 7.5 Hz, 1H), 7.44–7.47 (*m*, 3H), 7.54 (*t*, *J* = 7.5 Hz, 2H), 7.79 (*d*, *J* = 8 Hz, 2H), 7.92 (*d*, *J* = 8 Hz, 2H), 8.2 (*s*, 1H).

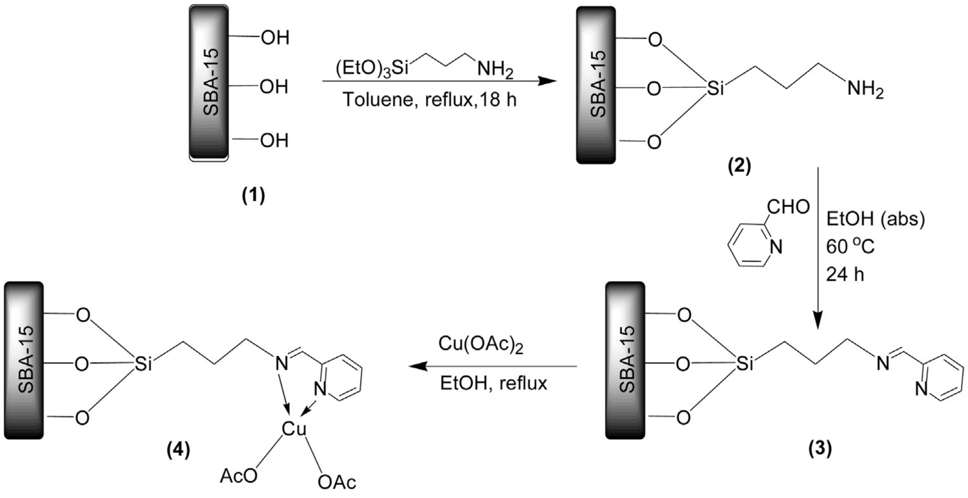
3. Results and discussion

3.1. Characterizations of Cu@ImPy-SBA-15

The heterogeneous catalyst, Cu@PyIm-SBA-15 was synthesized via surface functionalization of mesoporus SBA-15 with 3-aminopropyltriehoxysilane (3-APTES) followed by Schiff-base condensation of surface–NH_2 group with 2-pyridinecarboxaldehyde. Then $Cu(OAC)_2$ was subjected to react with Schiff-base anchored SBA-15 catalyst to yield Cu@PyIm-SBA-15 as shown in Scheme 2.



Scheme 1. Cu@PyIm-SBA-15 catalyzed one-pot Click reaction.



Scheme 2. Synthesis of Cu@PyIm-SBA-15 catalyst.

3.1.1. *Nanostructure of Cu@PyIm-SBA-15*

The small angle X-ray diffraction pattern of Cu@PyIm-SBA-15 material has been shown in Fig. 1. Very strong intensity peak centred at $2\theta = 0.92$ is due to the diffraction of 1 0 0 plane of mesostructure is very clearly observed. This is followed by other two weak intensity peaks, corresponding to the 2 0 0 and 2 1 0 planes of 2D-hexagonal planes of the ordered mesophase of the SBA-15 type material [65,66]. The intensity of the latter diffraction planes decreased from pure mesoporous silica SBA-15 material due to the disturbance of ordered mesostructure after grafting of the organic scaffold and copper. The *d* spacing for the mesophase is *ca.* 9.80 nm. Considerable increase in the pore wall thickness in the Cu@PyIm-SBA-15 material compared to pure SBA-15 is observed. This could be attributed to the homogeneous grafting of organic moiety and Cu(II) at the surface of the mesopore.

3.1.2. *TEM studies*

The TEM image of Cu@PyIm-SBA-15 is shown in Fig. 2. As seen from the Image 2D array of pore channels are quite clear together hexagonal arrangement of pores (white spots) of dimension *ca.* 7.0 nm, which are uniformly spread throughout the specimen. Further, no agglomeration of metallic Cu is observed in the entire grid,

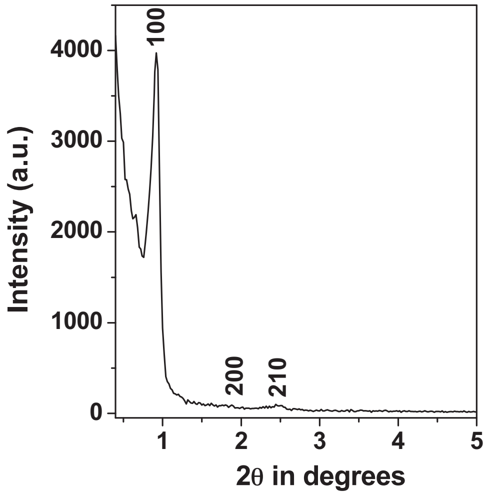


Fig. 1. Small angle X-ray diffraction pattern of Cu@PyIm-SBA-15.

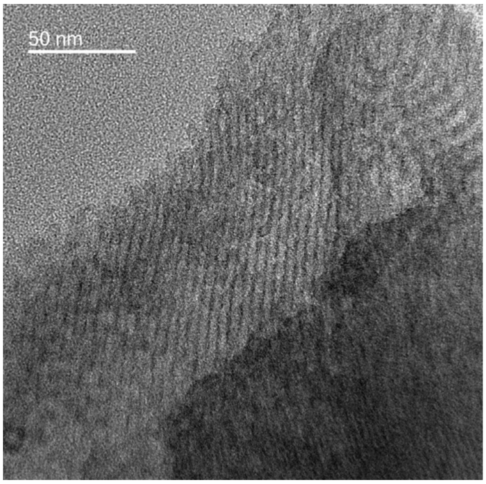


Fig. 2. TEM image of Cu@PyIm-SBA-15.

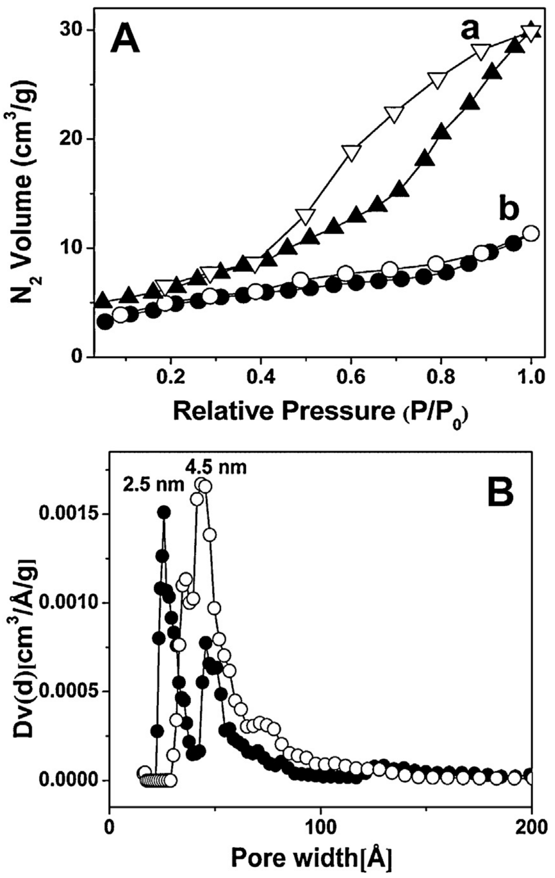


Fig. 3. A: N_2 adsorption/desorption isotherms of Cu@PyIm-SBA-15 (a), and used Cu@PyIm-SBA-15 (b). Adsorption points are marked with filled triangles or circles whereas those for desorptions are marked by empty triangles or circles. B: Respective pore size distributions employing NLDFT model.

suggesting uniform anchoring of Cu(II) species at the surface of the pyridine-imine functionalized SBA-15 material.

3.1.3. Surface area and porosity

N_2 adsorption/desorption isotherms of the Cu@PyIm-SBA-15 before and after the catalytic reactions are shown in Fig. 3. These sorption isotherms are typical type IV. A large hysteresis loop in the 0.5 to 0.8 P/P_0 range is observed for the fresh sample. The BET surface areas of the fresh and reused Cu@PyIm-SBA-15 samples were 21.0 $m^2 g^{-1}$ and 13.5 $m^2 g^{-1}$, respectively. Their respective pore size distributions using non-local density functional theory (NLDFT) method shown in Fig. 3B, which suggests that mesopores with peak pore dimensions of *ca.* 4.5 nm and 2.5 nm, respectively. Decrease in the BET surface area and peak pore size is observed for the reused catalyst, however mesostructure has been preserved.

3.1.4. EPR data

The X-band EPR spectra of the fresh and used Cu@PyIm-SBA-15 catalyst are shown in Fig. 4. The spectrum shows four well-defined hyperfine lines which arises due to the coupling of the unpaired electron with the nuclear spin of copper(II). Moreover, it was also clear that the EPR spectrum of the used catalyst was very similar to that of the fresh catalyst which indicates that Cu remains in the +2 oxidation state throughout the reaction.

3.2. Catalytic activity

Detailed catalytic investigations were carried out using this Cu(II)-anchored functionalized mesoporous SBA-15 catalyst (Cu@PyIm-SBA-15) for the one-pot Click reaction. We first chose water as the reaction medium as it is environmentally benign for the one pot click reaction between phenyl azides formed *in situ* from anilines and phenyl acetylene at 50 ^{0}C using high Cu loaded sample (5 mol% Cu). To our delight the reaction was successful leading to the formation of the 1,4-diphenyl 1,2,3-triazole in 98% yield. To optimize the reaction conditions in water a series of experiments varying the mol% of Cu in the catalyst, temperature and time for the representative reaction were carried out. The results are summarized in Table 1. Progress of the reaction for the preparation of 1,4-diphenyl 1,2,3-triazole with time at different temperatures has been given in supporting information, Figure S3.

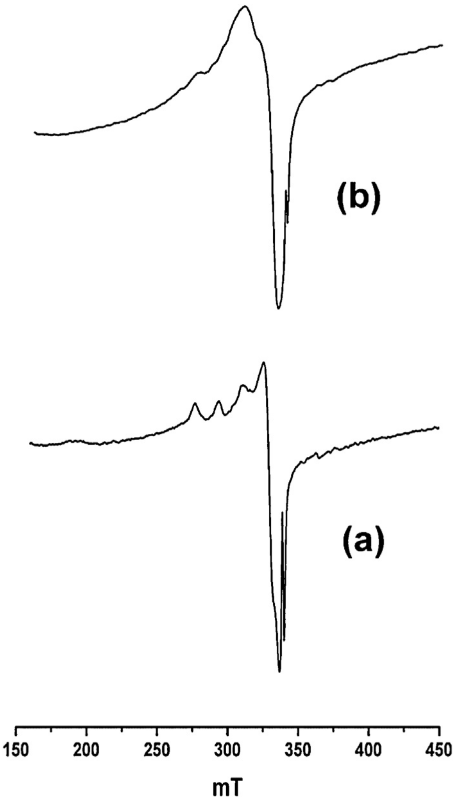


Fig. 4. The X-band EPR spectrum of Cu^{+2} in (a) fresh and (b) used catalyst.

The best result was obtained using 0.1 mol% of Cu in the catalyst Cu@PyIm-SBA-15 at room temperature for 6 h for the second step (Table 1, entry 8). No product was obtained in absence of

Table 1
Optimization of the reaction conditions for the synthesis of 1,4-disubstituted 1,2,3-triazoles[a].

Entry cat.	(Cu mol%)	Temperature (°C)[b]	Time (h)	Yield[c] (%)
1	5	50	8	98
2	2	50	8	98
3	1	50	8	98
4	0.1	50	8	98
5	0.05	50	8	92
6	0.1	40	8	98
7	0.1	rt	8	98
8	0.1	rt	6	98
9	0.1	rt	5	85
10	–	–	6	–
11	0.1	40	6	98

[a] Reaction conditions: Aniline (5.4 mmol), conc. $HCl:H_2O = 1:1$, $NaNO_2 = 5.7$ mmol, $NaN_3 = 6.4$ mmol, alkyne = 4.6 mmol, Cu@PyIm-SBA-15 = 0.1 mol% of Cu

[b] Temperatures refer to the second step

[c] Yields refer to those of isolated pure products

catalyst, Cu@PyIm-SBA-15. At first diazotization of aniline was carried out using conc. HCl and $NaNO_2$ in water medium at 0–5 °C, then sodium azide (NaN_3) was added to form the corresponding phenyl azide. After 5 min of stirring, phenyl acetylene and Cu@PyIm-SBA-15 catalyst were added and the reaction mixture was stirred at room temperature for additional 6 h (progress of the reaction was monitored through TLC). After the completion of reaction, water was decanted and the solid product was crystallized from environmentally benign ethanol to provide the pure product (NMR). Thus the use of huge amount of hazardous organic solvents in the work-up and column chromatography stages was avoided.

A variety of substituted azides formed *in situ* from the corresponding amines were reacted with a variety of acetylenes to produce the corresponding 1,4-disubstituted 1,2,3-triazoles. The results are summarized in Table 2. A wide range of diversely substituted azides formed *in situ* from their corresponding amines were subjected to react with phenyl acetylenes (Table 2, entries 1–5). Both electron withdrawing (4-NO_2) and donating (4-OMe) group substituted anilines reacted to equal extent with phenyl acetylene under the said reaction conditions (Table 2, entries 2 and 4). Sterically hindered (2-I) aniline reacted smoothly with phenyl acetylene (Table 2, entry 3). Benzyl amine also reacted with phenyl acetylene without any difficulty to produce the corresponding 1-benzyl-4-phenyl 1,2,3-triazole (Table 2, entry 5).

A variety of substituted acetylenes were also employed to react with different substituted azides formed *in situ* from the corresponding amines (Table 2, entries 6–14). Both electron withdrawing (CN, F) (Table 2, entries 6 and 7) and electron donating (OMe) (Table 2, entry 10) group substituted phenyl acetylene reacted smoothly with variety of azides to form the corresponding triazoles. Biphenyl acetylene (Table 2, entries 8 and 9) and napthyl acetylene (Table 2, entry 10) also participated in the click reaction. Interestingly, when 2-nitro-phenylazide formed *in situ* from 2-nitro-aniline was subjected to react with excess (1.5 equiv) of 1,4-diethynyl benzene, only the mono triazole product was formed keeping the other acetylene moiety intact (Table 2, entry 11). This implies that the reaction is chemoselective. Heteroaryl substituted acetylene, 2-ethynyl pyridine also reacted smoothly with benzyl azide formed *in situ* from benzyl amine to form the corresponding triazole containing pyridine moiety (Table 2, entry 12). Significantly aliphatic acetylene, propergyl alcohol also reacted with 3-chloro aniline and 4-nitro aniline without any difficulty (Table 2, entries 13 and 14). Both the electron donating and electron withdrawing substituents on both the amine and acetylene moieties do not show any significant influence on the outcome of the reaction and they all were competable with the reaction condition. All *ortho*, *meta* and *para* substituted anilines reacted almost uniformly with acetylenes. Generally, the reactions are quite clean and high yielding. Most significantly no column chromatography was required for the purification of products as they can be easily crystallized from ethanol. Thus the use of hazardous organic solvents in the entire process could be avoided. Atomic absorption spectroscopy (AAS) showed that the final product does not contain even a trace amount of copper, suggesting strongly bound Cu(II) sites at the surface of Cu@PyIm-SBA-15.

The IR, ^1H NMR spectroscopic data of the triazole products are in good agreement with those of the authentic compounds reported earlier. Reaction in gram scale also provided the uniform result. This procedure was followed for all the reactions in Table 2. Most of these products are known compounds and are identified by a comparison of their spectroscopic data with those previously reported (see references in Table 2). The products which are not reported earlier were characterized through FT IR, ^1H NMR and ^{13}C NMR spectroscopic analysis (Table 2, entries 8 and 9, supporting information).

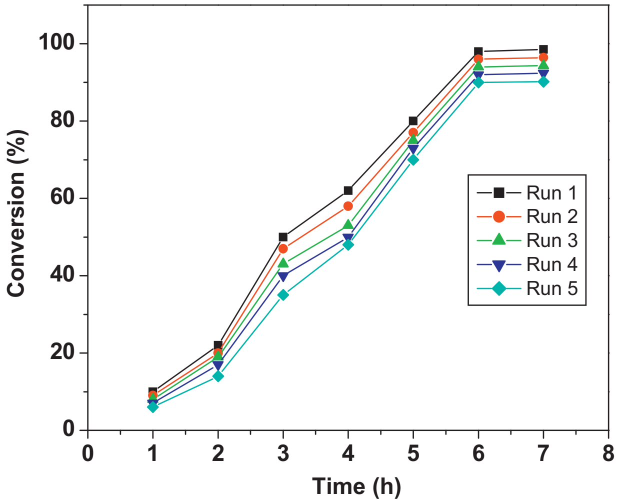


Fig. 5. Kinetic plot of recycling test of catalyst (Cu@PyIm-SBA-15) in the Click reaction of phenyl azide formed from aniline with phenyl acetylene.

3.2.1.1. 4-(Biphenyl-4-yl)-1-(3-chlorophenyl)-1H-1,2,3-triazole (Table 2, entry 8)

White solid (92%), mp 210–212 °C, IR (KBr) 3109, 1593, 1479, 1450, 1394, 1226, 1037, 885, 840, 815, 783, 761, 678 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.30 (*d*, *J* = 5 Hz, 1H), 7.37 (*t*, *J* = 5 Hz, 1H), 7.44–7.50 (*m*, 4H), 7.51–7.53 (*m*, 2H), 7.58–7.61 (*m*, 1H), 7.64–7.73 (*m*, 2H), 7.90 (*s*, 1H), 8.05 (*d*, *J* = 5 Hz, 1H), 8.22 (*s*, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 120.9, 125.6, 126.4 (2C), 127.1 (2C), 127.7, 127.8 (2C), 128.1, 129.0 (2C), 129.1, 130.5, 131.0, 135.8, 138.0, 140.6. Anal. Calcd for $C_{20}H_{14}ClN_3$: C, 72.40; H, 4.25; N, 12.66%. Found: C, 72.46; H, 4.22; N, 12.67%.

3.2.1.2. 4-(Biphenyl-4-yl)-1-(2-nitrophenyl)-1H-1,2,3-triazole (Table 2, entry 9)

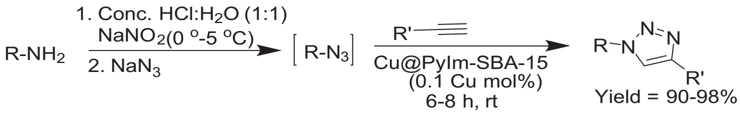
Yellow solid (93%), mp 203–205 °C, IR (KBr) 3134, 1604, 1591, 1537, 1479, 1423, 1359,1311, 1240, 1029, 850, 802, 767, 746, 727 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.35–7.38 (*m*, 1H), 7.47 (*t*, *J* = 8 Hz, 2H), 7.69–7.75 (*m*, 4H), 7.80–7.85 (*m*, 1H), 7.98 (*d*, *J* = 7 Hz, 2H), 8.10 (*s*, 1H), 8.12 (*s*, 1H); ^{13}C NMR(100 MHz, $CDCl_3$) 121.1, 125.7, 126.5 (2C), 127.2 (2C), 127.7, 127.8 (2C), 128.1, 128.8, 129.0 (2C), 130.4, 130.9, 133.9, 140.7, 141.6, 144.6, 148.3. Anal. Calcd for $C_{20}H_{14}N_4O_2$: C, 70.17; H, 4.12; N, 16.37%. Found: C, 70.12; H, 4.26; N, 16.35%.

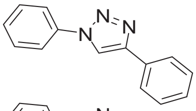
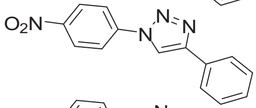
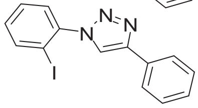
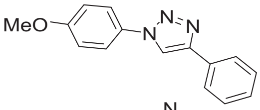
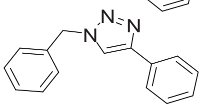
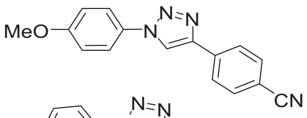
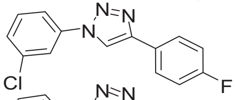
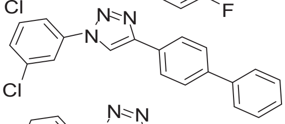
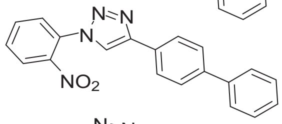
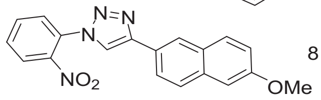
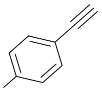
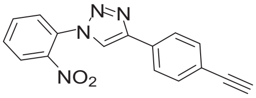
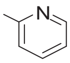
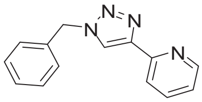
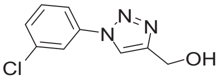
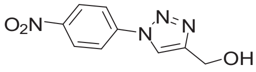
3.3. Recycling of catalyst

For a heterogeneous catalyst, it is important to examine its ease of separation, recoverability and reusability. The reusability of the mesoporous Cu@PyIm-SBA-15 catalyst was investigated in “Click” reaction between phenyl azide formed *in situ* from aniline and phenyl acetylene (Table 2, entry 1). After the first cycle of the reaction catalyst was recovered by simple filtration through a sintered glass-bed (G-4) and washed with ethanol followed by acetone which was then dried in an oven at 100 °C. The performance of the recycled catalyst for the representative reaction was tested with time (h) up to five successive runs and the corresponding kinetic plot is shown in Fig. 5. This diagram clearly suggests that the catalytic efficacy of the recovered catalyst remained almost the same for several reaction cycles.

We have also compared the recyclability of the Cu@PyIm-SBA-15 catalyst with Cu@SBA-15, which bear no surface grafted Schiff-base imine ligand for the representative synthesis of 1,4-diphenyl-1*H*-[1,2,3]triazole. It was found that over Cu@SBA-15 the catalytic activity start reducing from the second cycle itself and

Table 2
One pot click reaction between azides formed *in situ* from corresponding amines and acetylenes catalyzed by Cu@PyIm-SBA-15 in [68,69] water.



Entry	R	R'	Product	Time	Yield[a] (%)	Ref
1	C_6H_5-	C_6H_5-		6	98	52
2	4-NO_2-C_6H_4-	C_6H_5-		7	98	62
3	2-I-C_6H_4-	C_6H_5-		7	97	52
4	4-OMe-C_6H_4-	C_6H_5-		8	95	57
5	$C_6H_5CH_2$-	C_6H_5-		6	98	57
6	4-OMe-C_6H_4-	4-CN-C_6H_4-		8	96	68
7	3-Cl-C_6H_4-	4-F-C_6H_4-		7	94	55
8	3-Cl-CH_4-	4-Ph-C_6H_4-		7	92	
9	2-NO_2-C_6H_4-	4-Ph-C_6H_4-		7	93	
10	2-NO_2-C_6H_4-	6-OMe-$C_{10}H_6$-		8	96	55
11	2-NO_2-C_6H_4-			8	96	55
12	$C_6H_5CH_2$-			7	92	52
13	3-Cl-C_6H_4-	-CH_2OH		6	90	69
14	4-NO_2-C_6H_4-	-CH_2OH		6	96	65

[a]Yield refers to those of isolated pure products.

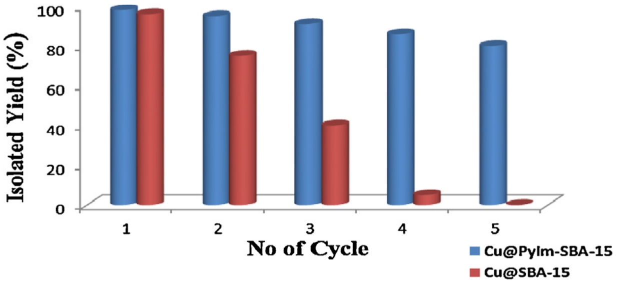


Fig. 6. Comparison of recyclability between Cu@PyIm-SBA-15 and Cu@SBA-15.

after third cycle there is a drastic reduction of product yield (Fig. 6). This result suggested the superiority of our Cu-grafted functionalized mesoporous material over Schiff-base ligand free Cu@SBA-15 catalyst. Retention of the catalytic activity could be largely due to strong binding of the catalytically active Cu(II) sites at the mesopore surface via coordination bonds through imine-N and pyridine-N donor sites (Scheme 2).

3.4. Heterogeneity test

To examine whether copper was being leached out from the solid support to the solution, a typical test was performed in the click reaction between aniline and phenyl acetylene with our supported Cu@PyIm-SBA-15 catalyst. For the various proof of heterogeneity, a test was carried out by filtering catalyst from the reaction mixture 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 reaction mixture, reaction 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 (below detection limit of AAS) in the liquid phase. Thus, results of the above test suggested that Cu was not being leached out from the solid catalyst during the reactions.

It is also evident from the electron paramagnetic resonance (EPR) spectrum of the fresh and used Cu@PyIm-SBA-15 catalyst (Fig. 4) that copper remains in +2 oxidation state throughout the reaction. Moreover we also did not found the formation of even a trace amount of dimer of alkyne in any reaction which generally forms via Cu(I) catalysis. Hence, it can be assumed that our reaction may proceed in a similar pathway catalyzed by Cu^{+2}, postulated by Pitchumani et al. [67].

4. Conclusion

In conclusion, we have developed a new pyridine-imine functionalized mesoporous SBA-15 material Cu@PyIm-SBA-15 and it has been employed as an efficient catalyst for the synthesis of 1,4-disubstituted 1,2,3-triazoles through one-pot click reaction between azides formed *in situ* from the corresponding amines and acetylenes in water at 0 °C to room temperature. The methodology offers several advantages like one-pot synthesis of a wide range of triazole derivatives starting from amines, reaction in water, very low catalyst loading (0.1 Cu mol%) with very high yields of the products. Further, there is no need of external energy, i.e. heat or microwave as the reactions proceed smoothly at room temperature in the absence of any hazardous organic solvents, easy product purification and high recyclability of the catalyst make the procedure green and cost effective. To the best of our knowledge Cu-supported functionalized mesoporous materials have not been explored as catalyst in the one-pot synthesis of triazole derivatives starting from amines and hence we believe that this result would make an important contribution to the existing methods for triazole synthesis.

Acknowledgement

SMI acknowledges the Council of Scientific and Industrial Research (CSIR) and Department of Science and Technology (DST), New Delhi, India for funding. We acknowledge DST for providing support to the University of Kalyani under Purse and FIST programme. AB wishes to thank DST-SERB, New Delhi for extramural project grant and DST Unit on Nanoscience for providing instrumental facilities. MP wishes to thank CSIR, New Delhi for Senior Research Fellowships.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata.2014.01.027.

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