Scientia Iranica C (2018) 25(3), 1335–1343

SCIENTIA
IRANICA

Sharif University of Technology
**Scientia Iranica**
*Transactions C: Chemistry and Chemical Engineering*
http://scientiairanica.sharif.edu

# SBA-15-supported copper (II) complex: An efficient heterogeneous catalyst for azide-alkyne cycloaddition in water

**M. Bagherzadeh[a,*], H. Mahmoudi[a], M. Amini[b], S. Gautam[c], and K.H. Chae[d]**

a. *Department of Chemistry, Sharif University of Technology, Tehran, P.O. Box 11155-3615, Iran.*
b. *Department of Chemistry, Faculty of Science, University of Maragheh, Maragheh, Iran.*
c. *University Institute of Chemical Engineering & Technology (SSB UICET), Panjab University Chandigarh, 160-014, India.*
d. *Advanced Analysis Center, Korea Institute of Science and Technology, Seoul 136-791, South Korea.*

Received 18 January 2017; received in revised form 28 June 2017; accepted 12 February 2018

**KEYWORDS**
Mesoporous SBA-15;
Copper complex;
Azide-alkyne cycloaddition;
Triazole;
Heterogeneous catalyst.

**Abstract.** The reaction of the functionalized mesoporous SBA-15 in absolute ethanol with copper (II) acetate afforded a novel Cu$^{II}$-Schiff base/SBA-15 catalyst. The compound Cu$^{II}$-Schiff base/SBA-15 was characterized by IR spectroscopy, small-angle X-ray diffraction (SAX), Energy Dispersive X-ray Spectroscopy (EDXS), X-ray Absorption Near Edge Structure (XANES), Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM), and $N_2$ adsorption/desorption studies. Further, the catalytic activity of this well-defined material was tested in three-component Copper-catalyzed Azide-Alkyne Cycloaddition (CuAAC) reactions to obtain 1,4-disubstituted-1,2,3-triazoles in good to excellent yields from an organic halide, sodium azide, and alkyne in water as a green solvent. More importantly, the catalyst can be recovered and reused efficiently up to five consecutive cycles with negligible loss of catalytic activity.

## 1. Introduction

The Copper-catalyzed Azide-Alkyne Cycloaddition (CuAAC) for the synthesis of 1,2,3-triazole derivatives is one of the most attractive [1] and fundamental reactions [2] in nature [3-6] and synthetic organic chemistry [7-13]. Both copper (0) and copper (I), containing compounds, have recently emerged as effective catalysts in 1,3-dipolar azide-alkyne cycloaddition [14-24]. However, these compounds are prone to redox processes; hence, it is desirable to protect and stabilize the active copper catalysts during CuAAC-cycloaddition reaction [25]. This limitation can be overcome by utilizing a Cu(II) catalyst [26-28].

Mesoporous SBA-15, as an interesting mesoporous silica material, has attracted considerable attention [29] due to its ordered pore diameter [30], large specific surface areas [31], uniform-sized pores [32], thicker walls [33], high hydrothermal stability [33], high surface-to-volume ratio [31], variable framework compositions [34], and ease of modification [35] by utilizing available surface silanol groups to immobilize a homogeneous catalyst to minimize the leaching of the active component [31,32,34-36]. Herein, the synthesis of SBA-15 to anchor Cu$^{II}$-Schiff base complex through an organic linker (3-aminopropyl)trimethoxysilane was reported. The 1,3-dipolar azide-alkyne cycloaddition reaction proceeds with a Cu$^{II}$-Schiff base/SBA-15 catalyst, and the recovery of the catalyst can be done easily

---

*. *Corresponding author. Tel.: +98 21 66165354;*
*E-mail address: bagherzadeh@sharif.edu (M. Bagherzadeh)*

doi: 10.24200/sci.2018.20197

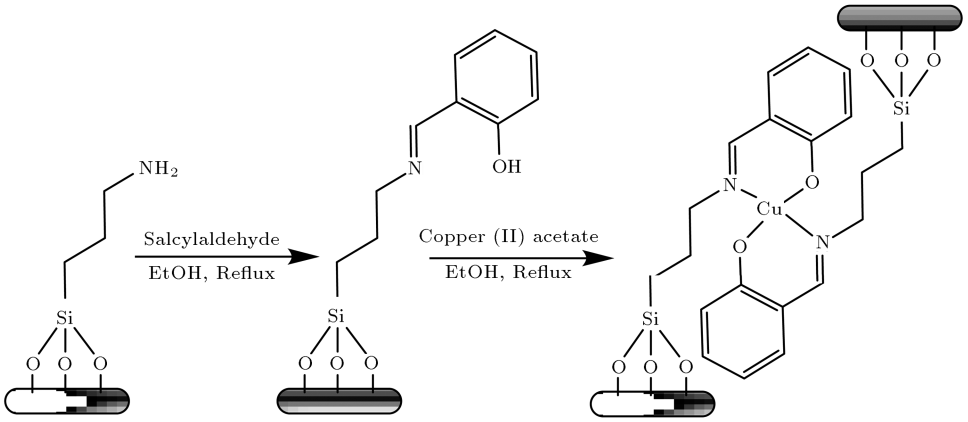


**Figure 1.** Preparation steps of $Cu^{II}$-Schiff base/SBA-15 catalyst.

several times without any significant loss of activity.

## 2. Results and discussion

Functionalized mesoporous SBA-15 was prepared by refluxing SBA-15/Pr-$NH_2$ with salicylaldehyde. The subsequent reaction of the functionalized mesoporous SBA-15 in absolute ethanol with copper (II) acetate led to the formation of a novel $Cu^{II}$-Schiff base/SBA-15 catalyst. The elemental analysis of the prepared $Cu^{II}$-Schiff base/SBA-15 catalyst showed 3.13% for the weight percentage of Cu, 13.97% for C, and 1.69% for N. Elemental analysis demonstrated that the molar ratios of N/Cu and C/Cu were ~2.47 and ~23.76, respectively, affirming the coordination of two Schiff base ligands on the SBA-15 with copper (II) ions as shown in Figure 1 [37].

### *2.1. Catalyst's characterization*

The FTIR spectra of SBA-15/Pr-$NH_2$, Schiff base/SBA-15, and $Cu^{II}$-Schiff base/SBA-15 are shown in Figure 2. According to the FTIR spectrum, the bands at 3450 (very broad) and 1650 $cm^{-1}$ are attributed to $\nu_{\text{O-H}}$ and $\delta_{\text{O-H}}$ modes of silanol groups, respectively [38]. Moreover, the characteristic antisymmetric $\nu_{\text{Si-O-Si}}$ vibration bands of [$SiO_4$] units are observed at 1050–1200 $cm^{-1}$ [39]. The presence of a bond at 1650 $cm^{-1}$ in Schiff base/SBA-15 and $Cu^{II}$-Schiff base/SBA-15 is attributed to $\nu_{\text{H-C=N}}$ of the azomethine group [37,40].

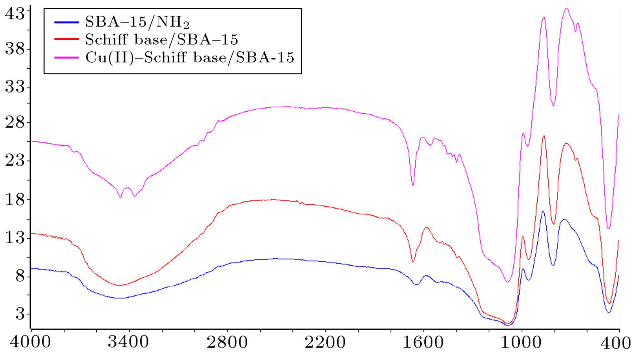
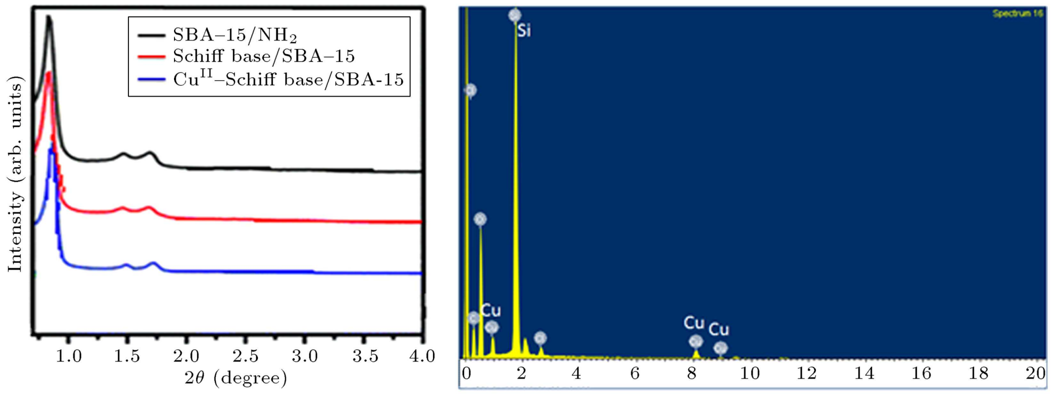


**Figure 2.** FT-IR spectra of SBA-15/Pr-$NH_2$, Schiff base/SBA-15, and $Cu^{II}$-Schiff base/SBA-15.

The small angle XRD patterns of SBA-15/Pr-$NH_2$, SBA-15/Schiff base, and $Cu^{II}$-Schiff base/SBA-15 are shown in Figure 3. XRD patterns display three well-resolved peaks in the low angle range at 0.5-4° $2\Theta$ that can be indexed to (100), (110), and (200) reflections in the hexagonal two-dimensional space group p6 mm for the mesoporous silica SBA-15 matrix [31,41]. Some loss in the intensities of the peaks was observed following the attachment of $Cu^{II}$-complex, revealing that silylation indeed occurred inside the channels of SBA-15 [42]. The SAX patterns confirm that the high mesoscopic order of the compounds was not destroyed in the multi-step synthesis procedure. Energy Dispersive X-ray Spectroscopy (EDXS) confirms the presence of 4.06% copper in $Cu^{II}$-Schiff base/SBA-15 sample Figure 3(b). The X-ray diffraction patterns of SBA-15/Pr-$NH_2$, SBA-15/Schiff base, and $Cu^{II}$-Schiff base/SBA-15 showed a similar pattern, indicating that the structure of SBA-15 was not changed with the addition of the complex into the channels of SBA-15, Figure 4.

$N_2$ adsorption-desorption isotherms of SBA-15/Pr-$NH_2$, Schiff base/SBA-15, and $Cu^{II}$-Schiff base/SBA-15 show type IV isotherms with hysteresis loops (Figure 5), related to capillary condensation steps, characteristic of the mesoporous materials with uniformly sized mesoporous [43]. The BET surface area, pore diameter, and pore volume of $Cu^{II}$-Schiff base/SBA-15 are smaller than those of Schiff base/SBA-15 and SBA-15/Pr-$NH_2$ mesoporous silica, suggesting that the complex is present inside the pores of the support material, because it is well known that the introduction of the complex in porous supports shows a decrease in its specific surface area and pore volume (Table 1) [44].

Cu L-edge XANES spectra for $Cu^{II}$-Schiff base/SBA-15 are shown in Figure 6. The peaks at



(a) (b)

**Figure 3.** (a) Small-Angle X-ray diffraction (SAX) patterns of SBA-15/Pr-NH$_2$, SBA-15/Schiff base and Cu$^{II}$-Schiff base/SBA-15. (b) EDXS analysis of the final compound Cu$^{II}$-Schiff base/SBA-15.

936.2 eV and 956.4 eV, respectively, are assigned to the transitions of Cu $2p_{3/2} - 4s$ ($L_3$) and $2p_{1/2} - 4s$ ($L_2$), and the presence of a bump-like feature at ~ 940.5 eV signifies the existence of copper with oxidation state 2+ in the sample [45,46].

Figure 7(a) and (b) illustrates SEM and 7(c) and (d) TEM images of Cu$^{II}$-Schiff base/SBA-15 to confirm the high mesoscopic order of the compound. This catalyst displays parallel channels with the highly ordered pores arranged in a 2D-hexagonal p6 mm-resembling structure, thus confirming the retention of the physical structure of the siliceous material, although Cu$^{II}$-Schiff base complex entered into the channels of functionalized SBA-15 [32].

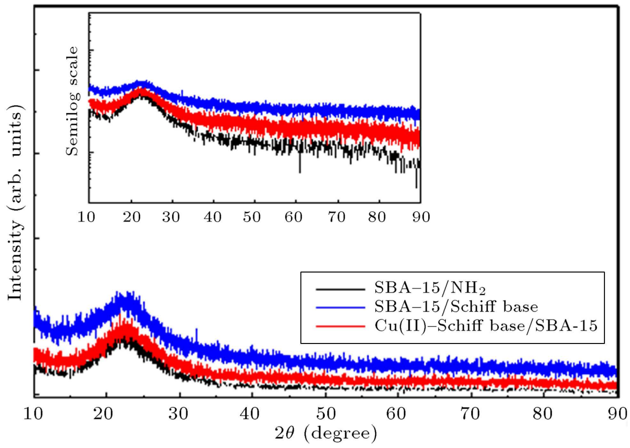


**Figure 4.** X-ray diffraction patterns of SBA-15/Pr-NH$_2$, SBA-15/Schiff base and Cu$^{II}$-Schiff base/SBA-15.

## 2.2. *Catalytic activity*

The Cu$^{II}$-Schiff base/SBA-15 catalyst was shown to be efficient in the multi-component 1,3-dipolar cycloaddition of terminal alkynes and organic azides yielded in situ from sodium azide and different organic halides. Phenylacetylene and benzyl chloride were chosen as starting compound models to optimize the reaction conditions (Table 2). Interestingly, water as a "green" solvent was used for all cycloaddition reactions. Initially, optimization of the reaction was performed by varying the catalyst loading. As shown in Table 2,

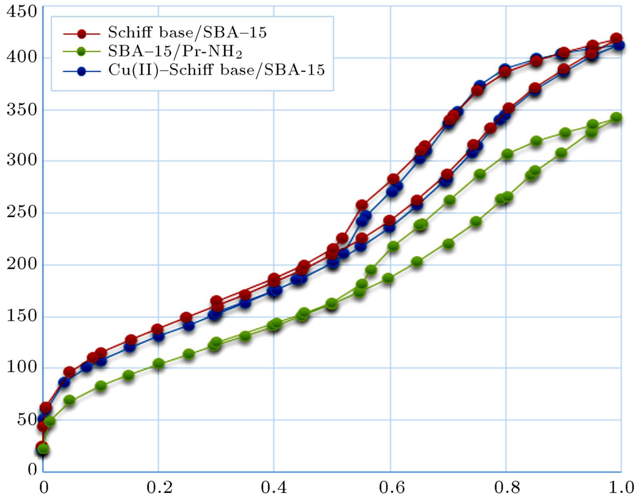


**Figure 5.** Nitrogen adsorption-desorption isotherms of SBA-15/Pr-NH$_2$, Schiff base/SBA-15-15, and Cu$^{II}$-Schiff base/SBA-15.

**Table 1.** Surface characteristics of SBA-15/Pr-NH$_2$, Schiff base/SBA-15, and Cu$^{II}$-Schiff base/SBA-15.

| **Compound** | $\mathbf{d_{100}}$$^a$ **(nm)** | $\mathbf{S_{BET}}$$^b$ **($m^2g^{-1}$)** | **V**$^c$ **($cm^3g^{-1}$)** | $\mathbf{D_{BJH}}$$^d$ **(nm)** |
|---|---|---|---|---|
| SBA-15/Pr-NH$_2$ | 5.179 | 498.27 | 114.48 | 1.64 |
| Schiff base/SBA-15 | 5.338 | 476.76 | 109.54 | 1.64 |
| Cu$^{II}$-Schiff base/SBA-15 | 5.435 | 387.55 | 89.04 | 1.21 |

$^a$d$_{100}$ is the d(100) spacing; $^b$S$_{BET}$ is the BET surface area;

$^c$V is the total pore volume; $^d$D is the average pore diameter.

in the absence of a catalyst, no product was obtained after 18 h (entry 1). The best result was achieved when the catalyst amount was 0.2 mol% (entry 8). With a further increase of the catalyst amount to 0.5 mol%, no further improvement in the product yield was observed (entry 4). At temperatures higher than room temperature, a significant improvement in the product yield was not found (entries 5,6). The yield of cycloaddition product 1-benzyl-4-phenyl-1H-1,2,3-triazole monotonously increased with increasing reaction time up to 18 h. After the determination of the best reaction condition, CuAAC reactions were carried out with various azides and alkynes to produce the corresponding 1,4-disubstituted-1,2,3-triazoles. The results are summarized in Table 3. The substitution of electron donating or electron withdrawing groups on the phenyl ring of benzyl halides and phenylacetylenes did not have a meaningful effect on the reaction

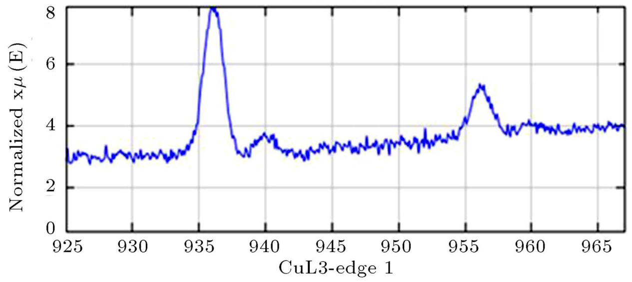
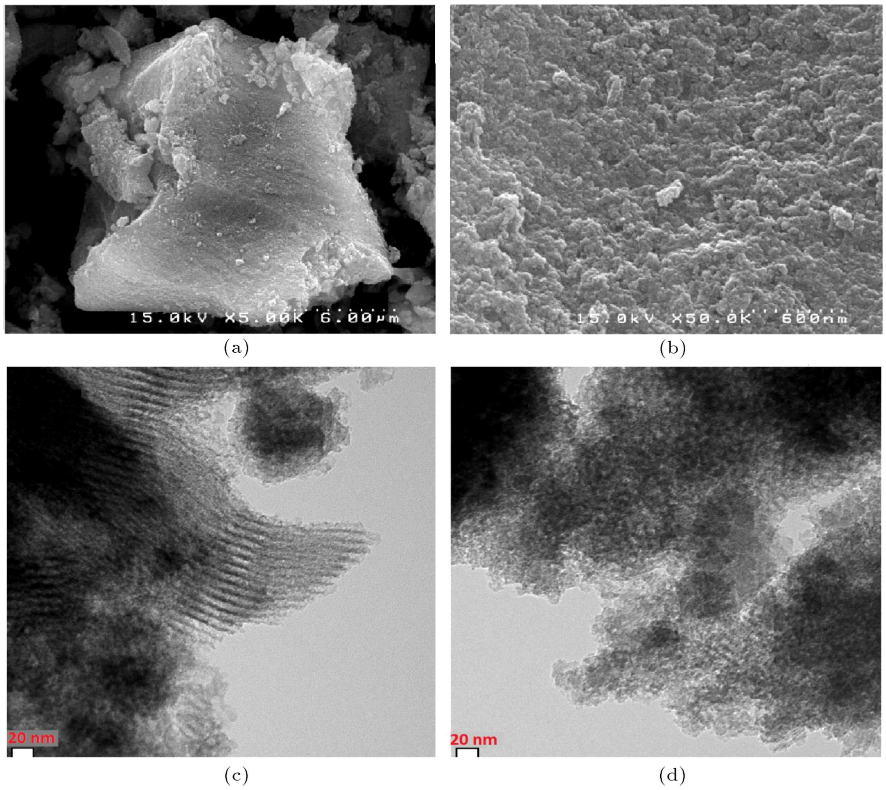


**Figure 6.** The copper L-edge XANES spectra for Cu$^{II}$-Schiff base/SBA-15



(a) (b)

(c) (d)

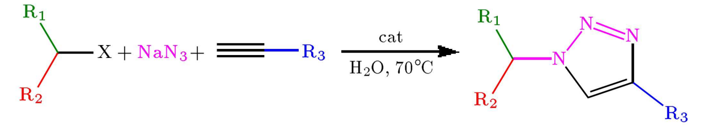
**Figure 7.** (a) and (b) SEM images, (c) and (d) TEM images of Cu$^{II}$-Schiff base/SBA-15.

**Table 2.** The effect of reaction conditions on the azide-alkyne cycloaddition.

| Entry | Catalyst amount (mol%) | Catalyst amount (mg) | Temperature (°C) | Time (h) | Yield (%)[a] | TON |
|---|---|---|---|---|---|---|
| 1 | – | 0 | 70 | 18 | 0 | 0 |
| 2 | 0.1 | 1 | 70 | 18 | 54 | 540 |
| 3 | 0.2 | 2 | 70 | 18 | 87 | 435 |
| 4 | 0.5 | 5 | 70 | 18 | 86 | 172 |
| 5 | 0.2 | 2 | r.t. | 18 | 0 | 0 |
| 6 | 0.2 | 2 | 80 | 18 | 87 | 435 |
| 7 | 0.2 | 2 | 70 | 8 | 53 | 265 |
| **8** | **0.2** | **2** | **70** | **12** | **85** | **425** |
| 9 | 0.2 | 2 | 70 | 24 | 87 | 435 |

[a] Isolated yield.

**Table 3.** Cycloaddition of benzyl halides with terminal alkynes in the presence of Cu$^{II}$-Schiff base/SBA-15.



| Entry | R$_1$ | R$_2$ | X | R$_3$ | Yield (%)$^a$ |
|---|---|---|---|---|---|
| 1 | Ph | H | Cl | Ph | 87 |
| 2 | 4-Me-Ph | H | Cl | Ph | 84 |
| 3 | 2-Me-Ph | H | Cl | Ph | 69 |
| 4 | 4-NO$_2$-Ph | H | Cl | Ph | 85 |
| 5 | Ph | H | Cl | 4-MeO-Ph | 79 |
| 6 | Ph | H | Cl | 4-Me-Ph | 81 |
| 7 | Ph | H | Br | Ph | 97 |
| 8 | Ph | H | Br | 4-MeO-Ph | 93 |
| 9 | Ph | H | Br | 4-Me-Ph | 94 |
| 10 | Ph | Ph | Br | Ph | 51 |

$^a$Isolated yield.

outcome (entries 2-6). Furthermore, steric hindrance of the ortho substituents on benzyl chlorides affected the progress of the reaction, and benzyl chloride substituted with a methyl group at the ortho position had less product yield than the para derivative (entries 2 and 3). Due to the weak C-Br bond compared to C-Cl bond [47], replacement of benzyl chloride with benzyl bromide appears to have a decisive effect on the catalytic activity, as benzyl bromide reacted to give the corresponding 1,2,3-triazole products in good to excellent yields (entries 7-10).

Repeated use of a catalyst is an important parameter in its evaluation [48]; thus, recoverability and reusability of Cu$^{II}$-Schiff base/SBA-15 were investigated. The amounts of both the catalyst and reactants were increased by five-fold, and the experiment was performed under the previous reaction conditions. After the reaction, the catalyst was recovered by centrifugation, washed three times with water and ethanol, dried at 60°C, and subjected to a new cycle of reaction. The results indicated that the used material was also active as a catalyst for five times without a dramatic loss of catalytic performance (Figure 8).

After the last run, the catalyst was separated from the reaction mixture, washed several times with ethanol, and dried at 60°C. The FTIR spectra of the separated catalyst were recorded at room temperature, and this spectrum was compared to the fresh catalyst spectrum (Figure 9). This comparison showed no major changes, indicating good stability of Cu$^{II}$-Schiff base/SBA-15 catalyst.

In order to investigate Cu$^{II}$-Schiff base/SBA-15 leaching into the azide-alkyne cycloaddition of phenylacetylene and benzyl chloride as a model reaction, the reaction stopped at half the reaction time (6 h) and the catalyst was completely filtered from the solution. Subsequently, the rest of the reaction mixture

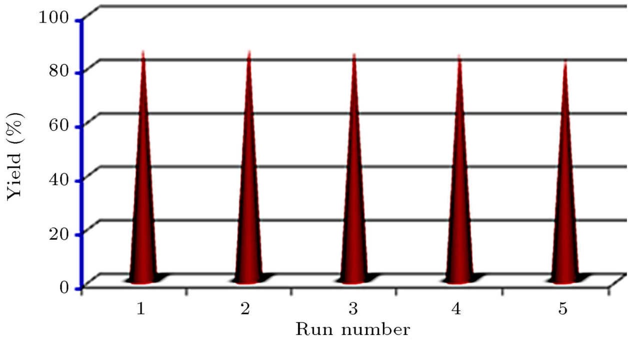


**Figure 8.** Recycling studies of the Cu$^{II}$-Schiff base/SBA-15 catalyst in the azide-alkyne cycloaddition reaction.

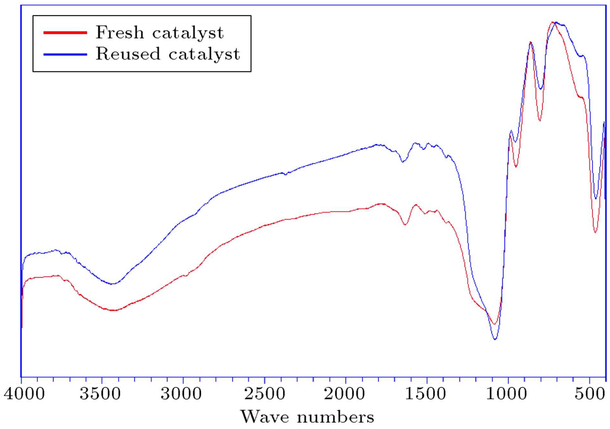


**Figure 9.** FT-IR spectra of fresh (red line) and reused (blue line) catalyst.

in the absence of catalyst was allowed to stir for another period of half of the reaction time. Almost no amount of the cycloaddition product was obtained after catalyst separation. These results showed that $Cu^{II}$-Schiff base/SBA-15 is truly heterogeneous, and catalyst leaching is negligible under these conditions.

## 3. Experimental section

### 3.1. Materials and methods

Chemicals and solvents were purchased from Merck and Sigma-Aldrich and were used without further purification. FT-IR spectrum was obtained using a Bruker tensor 27 FT-IR spectrophotometer using KBr disks at room temperature. TEM measurements were carried out on pristine and irradiated samples at 200 kV using FEI, Tecnai F20 G2 TEM. The morphologies of the products were observed further by scanning electron microscopy (SEM, FEI XL-30 FEG) with Energy-Dispersive X-ray spectroscopy (EDX) for percentage composition. The XANES investigation was done at NSRRC, Hsinchu, Taiwan. Nitrogen adsorption isotherms at $-196°$C were measured using Belsorp mini II Instrument. The mesostructured materials were degassed at 100°C for 15 h prior to each adsorption measurement. The copper content of the catalyst was determined by a Perkin-Elmer AA-300 Inductively Coupled Plasma–Atomic Emission Spectroscopy (ICP-AES). Elemental analysis, for Carbon, Hydrogen, and Nitrogen (CHN), was undertaken on a lecotruspec elemental analyzer. The $^1$H NMR spectra of the catalytic product in $CDCl_3$ were obtained using a Bruker FT-NMR 500 MHZ spectrometer.

### 3.2. Catalyst preparation

The ordered mesoporous silica was prepared following the previously published procedure with small changes in reagents [29,31]. In the reactor chamber equipped with a mechanical stirrer, 4.0 g Pluronic copolymer P123 was dissolved in 120 mL of 2.0 M HCl under constant stirring. After 2 h, 30 mL of water and, then, 39.8 mmol of tetraethyl orthosilicate (TEOS) were added dropwise into the solution of P123. Then, 1.23 mmol of (3-aminopropyl) trimethoxysilane (APTMS) was poured into the above mixture. All the steps were kept in water bath at 40°C. The mixture continued being stirred for 24 h; then, it was held at 100°C in a Teflon-lined autoclave. After 24 h, the white resultant solid was recovered by filtration and washed with ethanol. To remove the occluded P123, the product was extracted by Soxhlet extraction with ethanol for 48 h and, then, dried at 60°C. This substance was identified as SBA-15/Pr-$NH_2$.

Modification of the mesoporous channels was carried out by refluxing 0.8 g of SBA-15/Pr-$NH_2$ with 5 mmol of salicylaldehyde in 25 mL of ethanol for 24 h under uniform stirring. The resulted yellowish solid, SBA-15/Schiff base, was centrifuged, washed with ethanol to remove unreacted salicylaldehyde, and dried at 60°C. At last, the catalyst was synthesized by adding 3 mmol of copper (II) acetate to the suspension of the SBA-15/Schiff base (0.6 g) in 20 mL of ethanol; then, the mixture was refluxed under invariable stirring. After 24 h, the resulted material was filtered, washed with ethanol, and dried in an oven at 60°C.

### 3.3. General procedure for azide-alkyne cycloaddition

For the suspension of $Cu^{II}$-Schiff base/SBA-15 catalyst (0.2 mol%) in $H_2O$ (2 mL) alkyne (0.5 mmol), the organic halide (0.55 mmol) and $NaN_3$ (0.55 mmol) were added. The reaction mixture was warmed to 70°C and stirred for 12 h. Then, water (5 mL) was added to the resulting mixture, and a product was extracted with EtOAc ($2 \times 10$ mL). The collected organic phases were dried over anhydrous $MgSO_4$, and the solvent was removed under reduced pressure to give the corresponding triazoles, which did not require any further purification.

## 4. Conclusion

In summary, the present study illustrated the feasibility and applicability of utilizing the $Cu^{II}$-Schiff base/SBA-15 material to catalyze the azide-alkyne cycloaddition for the synthesis of the corresponding $1,2,3-$triazoles through $1,3-$dipolar cycloaddition of terminal alkynes with organic azides generated in situ from sodium azide and different organic halides in the presence of water. The process is environmentally friendly and uses an easily available solvent to produce excellent yields. Furthermore, the recyclability and reusability of catalyst for up to five consecutive cycles in the reaction of phenylacetylene and benzyl chloride substrates without any significant loss of efficiency indicate the potential of the $Cu^{II}$-Schiff base/SBA-15 as an efficient catalyst.

## Acknowledgements

The first author acknowledges the research council of the Sharif University of Technology for the research funding of this work.

## References

1. Evans, R.A. "The rise of azide-alkyne 1,3-dipolar 'click' cycloaddition and its application to polymer science and surface modification", *Aust. J. Chem.*, **60**, pp. 384-395 (2007).
2. Spruell, J.M. *The Power of Click Chemistry for Molecular Machines and Surface Patterning: Power of Click Chemistry for Molecular Machines and Surface Patterning*, *Springer* (2011).

3. Hein, C., Liu, X.-M., and Wang, D. "Click chemistry, a powerful tool for pharmaceutical sciences", *Pharm. Res.*, **25**, pp. 2216-2230 (2008).

4. Moses, J.E. and Moorhouse, A.D. "The growing applications of click chemistry", *Chem. Soc. Rev.*, **36**, pp. 1249-1262 (2007).

5. Thirumurugan, P., Matosiuk, D., and Jozwiak, K. "Click chemistry for drug development and diverse chemical-biology applications", *Chem. Rev.*, **113**, pp. 4905-4979 (2013).

6. Witczak, Z.J. and Bielski, R., *Click Chemistry in Glycoscience: New Developments and Strategies*, Wiley (2013).

7. Padwa, A., *1,3-Dipolar Cycloaddition Chemistry*, Wiley (1984).

8. Amini, M., Naslhajian, H.F., Farnia, S.M., Kyoung Kang, H., Gautam, S., and Chae, K.H. "Polyoxomolybdate-stabilized $Cu_2O$ nanoparticles as an efficient catalyst for the azide-alkyne cycloaddition", *New J. Chem.*, **40**, pp. 5313-5317 (2016).

9. Donnelly, K.F., Petronilho, A., and Albrecht, M. "Application of 1,2,3-triazolylidenes as versatile NHC-type ligands: synthesis, properties, and application in catalysis and beyond", *Chem. Commun.*, **49**, pp. 1145-1159 (2013).

10. Haldon, E., Nicasio, M.C., and Perez, P.J. "Copper-catalysed azide-alkyne cycloadditions (CuAAC): an update", *Org. Biomol. Chem.*, **13**, pp. 9528-9550 (2015).

11. Becer, C.R., Hoogenboom, R., and Schubert, U.S. "Click chemistry beyond metal-catalyzed cycloaddition", *Angew. Chem. Int. Ed.*, **48**, pp. 4900-4908 (2009).

12. Mekhzoum, M.E.M., Benzeid, H., Qaiss, A.E.K., Essassi, E.M., and Bouhfid, R. "Copper(I) confined in interlayer space of montmorillonite: A highly efficient and recyclable catalyst for click reaction", *Catal. Lett.*, **146**, pp. 136-143 (2016).

13. Domini, C., Álvarez, M., Silbestri, G., Cravotto, G., and Cintas, P. "Merging metallic catalysts and sonication: A periodic table overview", *Catalysts.* **7**, p. 121 (2017).

14. Faraji, M., Amini, M., and Anbari, A.P. "Preparation and characterization of $TiO_2$-nanotube/Ti plates loaded $Cu_2O$ nanoparticles as a novel heterogeneous catalyst for the azide-alkyne cycloaddition", *Catal. Commun.*, **76**, pp. 72-75 (2016).

15. Akbari, A., Arsalani, N., Amini, M., and Jabbari, E. "Cube-octameric silsesquioxane-mediated cargo copper Schiff base for efficient click reaction in aqueous media", *J. Mol. Catal. A: Chem.*, **414**, pp. 47-54 (2016).

16. Meldal, M. and Tornøe, C.W. "Cu-catalyzed azide–alkyne cycloaddition", *Chem. Rev.*, **108**, pp. 2952-3015 (2008).

17. Hein, J.E. and Fokin, V.V. "Copper-catalyzed azide-alkyne cycloaddition (CuAAC) and beyond: new reactivity of copper(i) acetylides", *Chem. Soc. Rev.*, **39**, pp. 1302-1315 (2010).

18. Jin, T., Yan, M., and Yamamoto, Y. "Click chemistry of alkyne-Azide cycloaddition using nanostructured copper catalysts", *Chem. Cat. Chem.*, **4**, pp. 1217-1229 (2012).

19. Woo, H., Kang, H., Kim, A., Jang, S., Park, J., Park, S., Kim, B.-S., Song, H., and Park, K. "Azide-alkyne huisgen [3+2] cycloaddition using CuO nanoparticles", *Molecules*, **17**, p. 13235 (2012).

20. Rostovtsev, V.V., Green, L.G., Fokin, V.V., and Sharpless, K.B. "A Stepwise huisgen cycloaddition process: Copper(I)-Catalyzed regioselective Ligation of azides and terminal alkynes", *Angew. Chem. Int.* Ed., **41**, pp. 2596-2599 (2002).

21. TornØe, C.W., Christensen, C., and Meldal, M. "Peptidotriazoles on solid phase: [1,2,3]-triazoles by regiospecific copper(I)-catalyzed 1,3-dipolar cycloadditions of terminal alkynes to azides", *J. Org. Chem.*, **67**, pp. 3057-3064 (2002).

22. Shamim, T. and Paul, S. "Silica functionalized Cu(I) as a green and recyclable heterogeneous catalyst for the huisgen 1,3-dipolar cycloaddition in water at room temperature", *Catal. Lett.*, **136**, pp. 260-265 (2010).

23. Wan, L. and Cai, C. "Multicomponent synthesis of 1,2,3-triazoles in water catalyzed by silica-immobilized NHC-Cu(I)", *Catal. Lett.*, **142**, pp. 1134-1140 (2012).

24. Amini, M., Hassandoost, R., Bagherzadeh, M., Gautam, S., and Chae, K.H. "Copper nanoparticles supported on $CeO_2$ as an efficient catalyst for click reactions of azides with alkynes", *Catal. Commun.*, **85**, pp. 13-16 (2016).

25. Presolski, S.I., Hong, V.P., and Finn, M.G., "Copper-catalyzed azide-alkyne click chemistry for bioconjugation", in *Current Protocols in Chemical Biology*, John Wiley & Sons, Inc (2009).

26. Amini, M., Bayrami, A., Marashi, M.N., Arab, A., Ellern, A., and Woo, L.K. "Synthesis, structure, and catalytic properties of copper, palladium and cobalt complexes containing an N,O-type bidentate thiazoline ligand", *Inorg. Chim. Acta.*, **443**, pp. 22-27 (2016).

27. Mohammed, S., Padala, A.K., Dar, B.A., Singh, B., Sreedhar, B., Vishwakarma, R.A., and Bharate, S.B. "Recyclable clay supported Cu (II) catalyzed tandem one-pot synthesis of 1-aryl-1,2,3-triazoles", *Tetrahedron.*, **68**, pp. 8156-8162 (2012).

28. Jlalia, I., Gallier, F., Brodie-Linder, N., Uziel, J., Augé, J., and Lubin-Germain, N. "Copper(II) SBA-15: A reusable catalyst for azide-alkyne cycloaddition", *J. Mol. Catal. A: Chem.*, **393**, pp. 56-61 (2014).

29. Alavi, S., Hosseini-Monfared, H., and Siczek, M. "A new manganese (III) complex anchored onto SBA-15 as efficient catalyst for selective oxidation of cycloalkanes and cyclohexene with hydrogen peroxide", *J. Mol. Catal. A: Chem.*, **377**, pp. 16-28 (2013).

30. Katiyar, A., Yadav, S., Smirniotis, P.G., and Pinto, N.G. "Synthesis of ordered large pore SBA-15 spherical particles for adsorption of biomolecules", *J. Chromatogr. A.*, **1122**, pp. 13-20 (2006).

31. Bagherzadeh, M., Zare, M., Salemnoush, T., Özkar, S., and Akbayrak, S. "Immobilization of dioxomolybdenum (VI) complex bearing salicylidene 2-picoloyl hydrazone on chloropropyl functionalized SBA-15: A highly active, selective and reusable catalyst in olefin epoxidation", *Appl. Catal., A.*, **475**, pp. 55-62 (2014).

32. Bagherzadeh, M., Zare, M., Amini, M., Salemnoush, T., Akbayrak, S., and Özkar, S. "Epoxidation of olefins catalyzed by a molybdenum-Schiff base complex anchored in the pores of SBA-15", *J. Mol. Catal. A: Chem.*, **395**, pp. 470-480 (2014).

33. Zhang, F., Yan, Y., Yang, H., Meng, Y., Yu, C., Tu, B., and Zhao, D. "Understanding effect of wall structure on the hydrothermal stability of mesostructured silica SBA-15", *J. Phys. Chem. B.,* **109**, pp. 8723-8732 (2005).

34. Stevens, W.J.J., Lebeau, K., Mertens, M., Van Tendeloo, G., Cool, P., and Vansant, E.F. "Investigation of the morphology of the mesoporous SBA-16 and SBA-15 materials", *J. Phys. Chem. B.,* **110**, pp. 9183-9187 (2006).

35. Enumula, S.S., Gurram, V.R.B., Kondeboina, M., Burri, D.R., and Kamaraju, S.R.R. "$ZrO_2$/SBA-15 as an efficient catalyst for the production of [gamma]-valerolactone from biomass-derived levulinic acid in the vapour phase at atmospheric pressure", *RSC Adv.*, **6**, pp. 20230-20239 (2016).

36. Mohammadi Ziarani, G., Lashgari, N., and Badiei, A.R. "Green synthesis of spiro[indoline-3, 9'-xanthene]trione derivatives using sulfonic acid functionalized SBA-15 as a new nanoporous acid catalyst", *Sci. Iran.* **20**, pp. 580-586 (2013).

37. Bhunia, S., Saha, D., and Koner, S. "MCM-41-supported oxo-vanadium (IV) complex: A highly selective heterogeneous catalyst for the bromination of hydroxy aromatic compounds in water", *Langmuir*, **27**, pp. 15322-15329 (2011).

38. Alba, M.D., Luan, Z., and Klinowski, J. "Titanosilicate mesoporous molecular sieve MCM-41: synthesis and characterization", *J. Phys. Chem.*, **100**, pp. 2178-2182 (1996).

39. Jitianu, A., Crisan, M., Meghea, A., Rau, I., and Zaharescu, M. "Influence of the silica based matrix on the formation of iron oxide nanoparticles in the $Fe_2O_3$-$SiO_2$ system, obtained by sol-gel method", *J. Mater. Chem.*, **12**, pp. 1401-1407 (2002).

40. Bagherzadeh, M., Ataie, S., Mahmoudi, H., and Janczak, J. "Synthesis, structure characterization and study of a new molybdenum Schiff base complex as an epoxidation catalyst with very high turnover numbers", *Inorg. Chem. Commun.*, **84**, pp. 63-67 (2017).

41. Beck, J.S., Vartuli, J.C., Roth, W.J., Leonowicz, M.E., Kresge, C.T., Schmitt, K.D., Chu, C.T.W., Olson, D.H., Sheppard, E.W., McCullen, S.B., Higgins, J.B. and Schlenker, J.L. "A new family of mesoporous molecular sieves prepared with liquid crystal templates", *J. Am. Chem. Soc.*, **114**, pp. 10834-10843 (1992).

42. Joseph, T., Deshpande, S.S., Halligudi, S.B., Vinu, A., Ernst, S. and Hartmann, M. "Hydrogenation of olefins over hydrido chlorocarbonyl tris-(triphenylphosphine) ruthenium (II) complex immobilized on functionalized MCM-41 and SBA-15", *J. Mol. Catal. A: Chem.*, **206**, pp. 13-21 (2003).

43. Ying, J.Y., Mehnert, C.P., and Wong, M.S. "Synthesis and applications of supramolecular-templated mesoporous materials", *Angew. Chem. Int. Ed.*, **38**, pp. 56-77 (1999).

44. Srivastava, R., Srinivas, D., and Ratnasamy, P. "Sites for $CO_2$ activation over amine-functionalized mesoporous Ti(Al)-SBA-15 catalysts", *Microporous Mesoporous Mater.*, **90**, pp. 314-326 (2006).

45. Gurevich, A.B., Bent, B.E., Teplyakov, A.V., and Chen, J.G. "A NEXAFS investigation of the formation and decomposition of CuO and $Cu_2O$ thin films on Cu(100)", *Surf. Sci.*, **442**, pp. L971-L976 (1999).

46. Sharma, A., Varshney, M., Park, J., Ha, T.-K., Chae, K.-H., and Shin, H.-J. "XANES, EXAFS and photocatalytic investigations on copper oxide nanoparticles and nanocomposites", *RSC Adv.*, **5**, pp. 21762-21771 (2015).

47. Shaik, S.S. and Pross, A. "$SN_2$ reactivity of $CH_3X$ derivatives. A valence bond approach", *J. Am. Chem. Soc.*, **104**, pp. 2708-2719 (1982).

48. Massah, A.R., Kalbasi, R.J., Toghiani, M., Najafabadi, B.H., and Adibnejad, M. "Hydrotalcite as an efficient and reusable catalyst for acylation of phenols, amines and thiols under solvent-free conditions", *E-J. Chem.,* **9**, pp. 2501-2508 (2012).

## Biographies

**Mojtaba Bagherzadeh** is a Professor at the Chemistry Department of Sharif University of Technology. He obtained his PhD degree in Inorganic Chemistry from Shiraz University in 1998. His research interests include metal complex catalyzed oxidations of organic compounds, synthesis of inorganic complexes, biomimetic catalytic systems, and experimental and theoretical mechanistic studies of catalytic reactions.

**Hamed Mahmoudi** received his BS degree in Applied Chemistry from Razi University in 2011 and MS degree in Inorganic Chemistry from the Sharif University of Technology in 2013, where he has been working since 2013 on his doctoral degree project. His research interest is mainly focused on the synthesis of multifunctional homogeneous and heterogeneous catalysts for catalytic transformation in a green medium.

**Mojtaba Amini** is an Associate Professor of Inorganic Chemistry at University of Maragheh. He obtained his PhD degree in Inorganic Chemistry from Sharif University of Technology in 2011. His research interest is mainly focused on the synthesis of novel homogeneous and heterogeneous catalysts for oxidation reactions, Heck and Suzuki coupling reactions, cycloaddition reactions, and also preparation of polyoxometalete nanoclusters and nanoparticles.

**Sanjeev Gautam** is an Assistant Professor at the Chemistry Department of the Panjab University Institute of Engineering and Technology. His research interest is mainly focused on preparation and electronic structure investigation of various nanoparticles.

**Keun Hwa Chae** is an Assistant Professor at the Chemistry Department of The Korea, Institute of Science and Technology. His research interest is mainly focused on the characterization and electronic structure studies of various nanoparticles.