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

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Abstract. The reaction of the functionalized mesoporous SBA-15 in absolute ethanol with copper (II) acetate afforded a novel Cu\textsuperscript{II}-Schiff base/SBA-15 catalyst. The compound Cu\textsuperscript{II}-Schiff base/SBA-15 was characterized by IR spectroscopy, small-angle X-ray diffraction (SAX), Energy Dispersive X-ray Spectroscopy (EDX), X-ray Absorption Near Edge Structure (XANES), Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM), and N\textsubscript{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 alkylene 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.

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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 (I) and copper (II), 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\textsuperscript{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\textsuperscript{II}-Schiff base/SBA-15 catalyst, and the recovery of the catalyst can be done easily.
several times without any significant loss of activity.

2. Results and discussion

Functionalized mesoporous SBA-15 was prepared by refluxing SBA-15/Pr-NH₂ 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 CuII-Schiff base/SBA-15 catalyst. The elemental analysis of the prepared CuII-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-NH₂, Schiff base/SBA-15, and CuII-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 νOH and δOH modes of silanol groups, respectively [38]. Moreover, the characteristic antisymmetric νSiO₃⁻ vibration bands of [SiO₄] units are observed at 1050-1200 cm⁻¹ [39]. The presence of a bond at 1650 cm⁻¹ in Schiff base/SBA-15 and CuII-Schiff base/SBA-15 is attributed to νH:C–N of the azomethine group [37,40].

The small angle XRD patterns of SBA-15/Pr-NH₂, SBA-15/Schiff base, and CuII-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° 2Θ that can be indexed to (100), (110), and (200) reflections in the hexagonal two-dimensional space group p6 nm for the mesoporous silica SBA-15 matrix [31,41]. Some loss in the intensities of the peaks was observed following the attachment of CuII-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 CuII-Schiff base/SBA-15 sample Figure 3(b). The X-ray diffraction patterns of SBA-15/Pr-NH₂, SBA-15/Schiff base, and CuII-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.

N₂ adsorption-desorption isotherms of SBA-15/Pr-NH₂, Schiff base/SBA-15, and CuII-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 mesopores [43]. The BET surface area, pore diameter, and pore volume of CuII-Schiff base/SBA-15 are smaller than those of Schiff base/SBA-15 and SBA-15/Pr-NH₂ 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 CuII-Schiff base/SBA-15 are shown in Figure 6. The peaks at
936.2 eV and 956.4 eV, respectively, are assigned to the transitions of Cu $2p_{3/2} - 4s$ (L$_{2}$) and $2p_{1/2} - 4s$ (L$_{2}$), and the presence of a bump-like feature at $\sim$ 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 silicons material, although Cu$^{II}$-Schiff base complex entered into the channels of functionalized SBA-15 [32].

### 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 3](image_url) - (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.

![Figure 4](image_url) - X-ray diffraction patterns of SBA-15/Pr-NH$_2$, SBA-15/Schiff base and Cu$^{II}$-Schiff base/SBA-15.

![Figure 5](image_url) - Nitrogen adsorption-desorption isotherms of SBA-15/Pr-NH$_2$, Schiff base/SBA-15-15, and Cu$^{II}$-Schiff base/SBA-15.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$d_{100}^{a}$ (nm)</th>
<th>$S_{BET}^{b}$ (m$^2$g$^{-1}$)</th>
<th>$V^{c}$ (cm$^3$g$^{-1}$)</th>
<th>$D_{BJH}^{d}$ (nm)</th>
</tr>
</thead>
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<tr>
<td>SBA-15/Pr-NH$_2$</td>
<td>5.179</td>
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<td>114.48</td>
<td>1.64</td>
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<td>Schiff base/SBA-15</td>
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<td>476.76</td>
<td>109.54</td>
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<td>387.55</td>
<td>89.04</td>
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$^{a}$ $d_{100}$ is the d(100) spacing; $^{b}$ $S_{BET}$ is the BET surface area; $^{c}$ $V$ is the total pore volume; $^{d}$ $D_{BJH}$ 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).

![Graph](image)

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

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.

![Images](image)

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

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst amount (mol%)</th>
<th>Catalyst amount (mg)</th>
<th>Temperature (°C)</th>
<th>Time (h)</th>
<th>Yield (%)\textsuperscript{a}</th>
<th>TON</th>
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<tr>
<td>1</td>
<td>-</td>
<td>0</td>
<td>70</td>
<td>18</td>
<td>0</td>
<td>0</td>
</tr>
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<td>2</td>
<td>0.1</td>
<td>1</td>
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<td>18</td>
<td>54</td>
<td>540</td>
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<tr>
<td>3</td>
<td>0.2</td>
<td>2</td>
<td>70</td>
<td>18</td>
<td>87</td>
<td>435</td>
</tr>
<tr>
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<tr>
<td>5</td>
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<td>2</td>
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<tr>
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<td>24</td>
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<td>435</td>
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</table>

\textsuperscript{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 CuI-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 CuI-Schiff base/SBA-15 catalyst.

In order to investigate CuI-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

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**Table 3.** Cycloaddition of benzyl halides with terminal alkynes in the presence of CuI-Schiff base/SBA-15.

<table>
<thead>
<tr>
<th>Entry</th>
<th>R₁</th>
<th>R₂</th>
<th>X</th>
<th>R₃</th>
<th>Yield (%)*</th>
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<td>H</td>
<td>Cl</td>
<td>Ph</td>
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<td>Ph</td>
<td>H</td>
<td>Cl</td>
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<td>H</td>
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<td>Br</td>
<td>Ph</td>
<td>97</td>
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<tr>
<td>10</td>
<td>Ph</td>
<td>Ph</td>
<td>Br</td>
<td>Ph</td>
<td>51</td>
</tr>
</tbody>
</table>

*Isolated yield.

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**Figure 8.** Recycling studies of the CuI-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 LECO instrument. 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 (APTM) 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 salicyldialdehyde 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 salicyldialdehyde, 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$_2$O (2 mL) alkyn (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 × 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

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References


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