

SBA-15-supported-dithizone-copper(I): An efficient heterogeneous catalyst for synthesis of 1,4-disubstituted 1,2,3-triazoles in water

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ABSTRACT

In this work, the SBA-15-supported dithizone-copper(I) [SBA-15-dtz-Cu(I)] complex as a new heterogeneous catalyst is prepared for the first time. The catalyst prepared is characterized by the FT-IR spectroscopy, SEM, and ICP techniques. This reusable heterogeneous catalyst can be used in the click reactions for the green and facile synthesis of 1,4-disubstituted 1,2,3-triazoles *via* a one-pot three-component reaction of benzyl chloride derivatives, terminal alkynes, and sodium azide in the water at 60 °C. A synthetic technique offering numerous advantages including environmentally friendly, high-to-excellent reaction yields, operational simplicity, short reaction times, reusability of the catalyst, and lack of an organic solvent was developed.

Keywords: 1,2,3-Triazol, Heterogeneous catalyst, Click reaction, Terminal alkyne.

1. Introduction

Over the last decade, much interest has been shown in the synthesis of 1,2,3-triazole units. Apart from pharmaceutical applications, where these units are important for their biological activity or as an amide bond isoster, they are also important in material science and chemical biology [1, 2]. The Huisgen 1,3-dipolar cycloaddition reaction is the result of the studies carried out by Huisgen, he was the first scientist who studied the synthesis of 1,2,3-triazoles, involving the reaction of an azide with an alkyne to give 1,4- and 1,5-disubstituted triazole regioisomers [3, 4].

Several methodologies including transition metals have been developed to control the regioselectivity of the reaction [5-8]. In principle, the copper(I)-catalyzed cycloaddition reaction of azides and alkynes (further abbreviated as CuAAC), developed by Sharpless [9] and Meldal [10], allowed the formation of 1,4-regioisomer (Scheme 1).

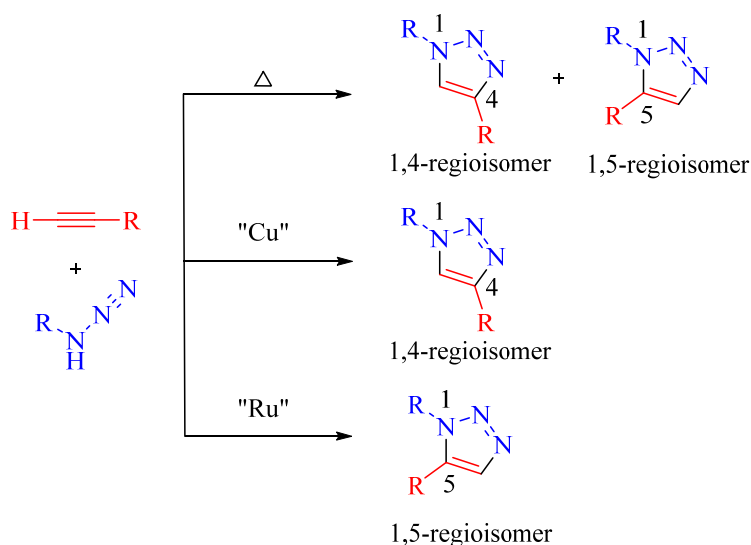
The effect of CuAAC reactions on the synthesis of 1,2,3-triazole derivatives under light conditions is now considered as the most efficient, highly regioselective, and biocompatible method. Moreover, it has been deeply used in many different organic synthetic reactions.

In order to make the CuAAC reactions functional, many efforts have been made, concentrating on discovering new and more significant synthetic strategies [11-13]. In CuAAC reactions, copper has an outstanding role in the construction of 1,2,3-triazole derivatives. On the basis of the work of Sharpless and Meldal, different copper sources such as Cu (I) [14-19], Cu(OAc)₂ [20], CuOTfC₆H₆ [21], [Cu(CH₃CN)₄]PF₆ [22], and [Cu(phen)(PPh₃)₂]NO₃ [23] have been tested. Moreover, in recent years, in order to synthesize triazoles, many other methods have been suggested [24-26]. Although these simple procedures are feasible for many reactions, they have a major drawback; recovery of the homogenous copper complexes after completion of the reaction is very difficult. Since the removal of trace amounts of metal contaminants from the products is necessary, particularly in the pharmaceutical industry, copper catalysts should be fully separated from the products. Thus, the heterogeneously-catalyzed procedures are advantageous for such reactions.

During the past few years, copper ions have been immobilized onto a large variety of solid supports including agarose [27], clay [28], chitosan [29], silica [30], and graphene [31] that assist in controlling reactivity and selectivity besides the advantage of easy workability.

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Scheme 1. Regioselectivity of the 1,3-dipolar cycloaddition reaction of an azide and an alkyne.

In organic synthesis, so many different solvents are used. However, water, as a solvent, is rather non-toxic, safe, most eco-friendly, and most economical. At intervals, it has been proved that compared with organic solvents, water has higher reactivity and selectivity, which is the direct result of its significant hydrogen bonding potential. The above-mentioned characteristics are the real reason behind the potentials of water causing it to be considered as a solvent, a catalyst, and most importantly, a reactant, unlike those seen by the conventional organic solvents [32]. Therefore, we expanded our research works [33-35] and reached a simple procedure for the one-pot synthesis of 1,4-disubstituted 1,2,3-triazoles from alkynes, sodium azide, and benzyl chloride, catalyzed by the SBA-15-anchored Cu(I) dithizone complex [SBA-15-dtz-Cu(I)] as a non-poisonous, eco-friendly, and reusable solid catalyst in water (Scheme 2).

2. Experimental

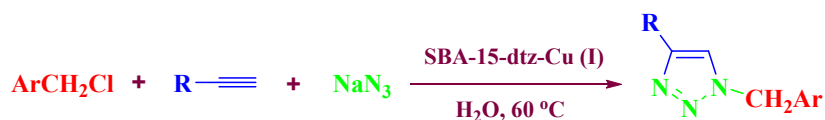
The solvents and reagents used were all supplied from Merck, Fluka or Aldrich. The reaction progress and the purity of compounds were monitored by TLC using analytical silica gel plates (Merck 60 F250). Melting points were determined using an electro-thermal C14500 apparatus. The micro-analyses were performed on a Perkin-Elmer 240-B micro-analyzer. The scanning electron microscopy (SEM) studies were conducted on a VEGA TESCAN instrument.

2.1. Preparation of SBA-15

The synthesis of SBA-15 was performed following a well-known procedure [36]. In brief, Pluronic P123 (4.0 g) was dissolved in water (50 mL), and the resulting solution was stirred for more than 5 h at room temperature (RT). After that 120 mL of hydrochloric acid solution (2 M) was added to the solution and it was left for nearly 2 h. Then TEOS (8.5 g) was added to the resulting solution and it was stirred for 24 h at 35 °C. This mixture was then kept without stirring for 24 h at 80 °C. After all these stages, the reaction was complete. Then the solid product obtained was washed with deionized water and it was air-dried overnight. Using a Soxhlet apparatus, P123 has vanished with hot ethanol/water (3:2) after 24 h, and the resulting precipitate was dried overnight at 100 °C.

2.2. Preparation of SBA-15-(CH₂)₃-Cl

To a 250 mL round-bottomed flask, anhydrous n-hexane (96 mL), SBA-15 (4.8 g), and 3-chloropropyl trimethoxysilane (CPTMS) (5 g) were introduced. The resulting solution was refluxed for 24 h under a nitrogen atmosphere, after which, the resulting solid SBA-15-(CH₂)₃-Cl was filtered and washed with n-hexane for several times and dried under vacuum at 80 °C for 10 h. The elementary analysis showed that the carbon content of SBA-Cl was 7.6%, which meant that 1.58 mmol/g of the pending groups were covalently bonded to the surface of 1.00 g SBA.



Scheme 2. Synthesis of 1,4-disubstituted 1,2,3-triazoles catalyzed by [SBA-15-dtz-Cu(I)].

2.3. Preparation of SBA-15-dtz

SBA-15-(CH₂)₃-Cl (3 g) and dithizone (7.0 mmol, 0.18 g) were added to a 250 mL round-bottomed flask containing DMF (20 mL) and equipped with a magnetic stirrer bar. The reaction mixture was stirred for 30 h at 100 °C, filtered, washed thoroughly with ethanol, and dried under vacuum for 12 h to obtain SBA-15-dtz. The elementary analysis also showed that the nitrogen content was 1.2%, which revealed that the dithizone loading, around 0.21 mmol/g or nearly 13% of the pending chlorine atom, was changed to dithizone by this reaction.

2.4. Immobilization of CuI on the surface of SBA-15-dtz

The dithizone-functionalized SBA-15 (SBA-15-dtz) (3.0 g) was treated with ethanol (50 mL) for 30 min. An ethanolic solution of CuI (5.0 mmol, 1.0 g) was added and the resulting mixture was refluxed for 15 h under an argon atmosphere. The resulting brown solid impregnated with the metal complex was filtered and washed with ethanol to obtain SBA-15-dtz-Cu(I). The copper loading of SBA-15-dtz-Cu(I) was 1.08% (0.17 mmol/g), determined by the inductively coupled plasma (ICP) technique.

2.5. General procedure for the synthesis of 1,4-disubstituted 1,2,3-triazoles (4a-n)

A round-bottomed flask was charged with an organic halide (1.0 mmol), a terminal alkyne (1.0 mmol), SBA-15-dtz-Cu(I) (0.1 g, 0.002 mmol of Cu), NaN₃ (1.2 mmol, 0.08 g), and water (3.0 mL). The reaction

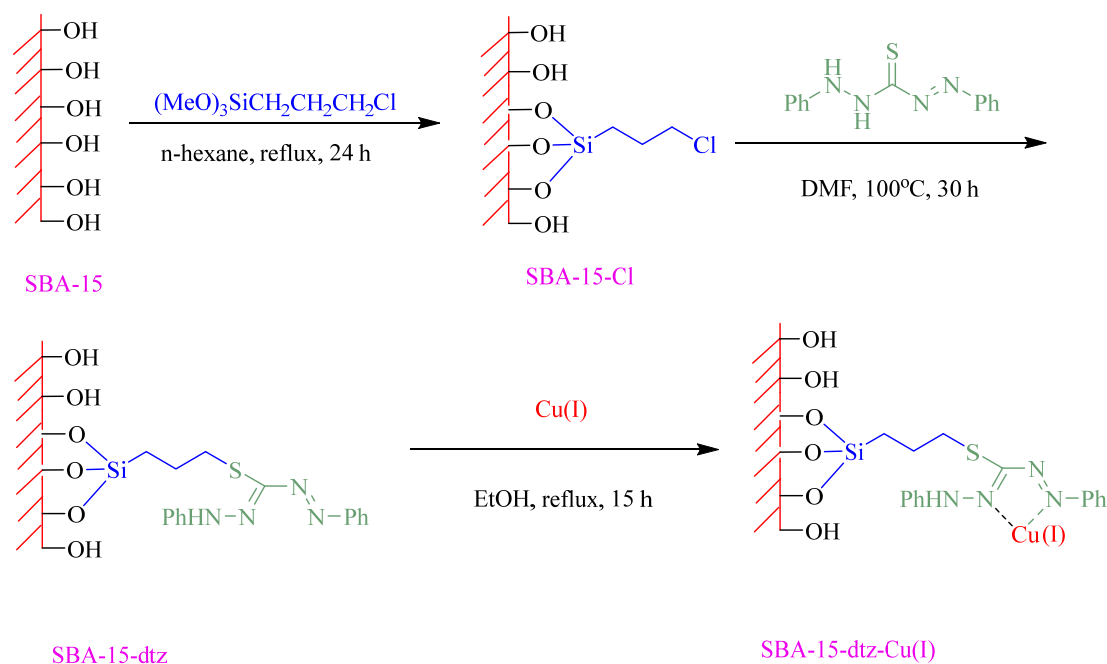
mixture was stirred at 60 °C (the reaction progress was monitored by TLC). After completion of the reaction, warm ethanol (3 × 20 mL) was used to separate the catalyst. Finally, the purified residue was extracted by crystallization from ethanol to give the desired product (Table 2). To recover the catalyst, the separated catalyst was washed with acetonitrile (5 mL) twice and reused after drying.

3. Results and Discussion

In continuation of our recent success in the introduction of new catalysts [37-39], herein we wish to report the synthesis of a Cu(I) complex supported on dithizone-functionalized SBA-15 [SBA-15-dtz-Cu(I)] as a novel and efficient catalyst for the C-N bond formation in click reactions under mild reaction conditions (Scheme 3).

3.1. Catalyst characterization

The FT-IR spectra were recorded separately at different stages of the catalyst preparation (Fig. 1). Curve A in this figure is the spectrum of SBA-15. The absorption bands at 464, 802, 1090, and 1384 cm⁻¹ are assigned to the asymmetric and symmetric stretching vibrations of the mesoporous framework (Si-O-Si). The O-H stretching vibration bands appeared at 3433 cm⁻¹. The FT-IR spectrum for SBA-15-*n*Pr-Cl (Fig. 1 (b)), in addition to the SBA-15 characteristic bands, showed new bands at 2925 cm⁻¹, which were assigned to the $\bar{\nu}$ (C-H) stretching of the grafted CPTMS group.



Scheme 3. Preparation of [SBA-15-dtz-Cu(I)].

Curve C shows the stretching vibrations at 1654 cm^{-1} (C=N) SBA-15-dtz. The $\bar{\nu}$ (N-H) stretching vibration in the FT-IR spectrum of SBA-15-dtz should be seen in 3421 cm^{-1} but it has been masked with a broad band for the hydroxyl group stretching vibrations of SBA-15 in this region. Curve D shows the FT-IR spectrum of the catalyst after adsorption of Cu(I) onto SBA-15-dtz. The morphological changes in the catalyst were

investigated by scanning electron microscopy (SEM) of a single bead of pure SBA and the SBA-15-dtz-Cu(I) complex. As expected, the presence of Cu caused changes in the polymer particle size and surface roughness (Fig. 2).

EDX analysis (Fig. 3) also confirmed the presence of copper atoms on the surface of SBA-15-dtz-Cu(I) in addition to the carbon, oxygen, and silicon atoms.

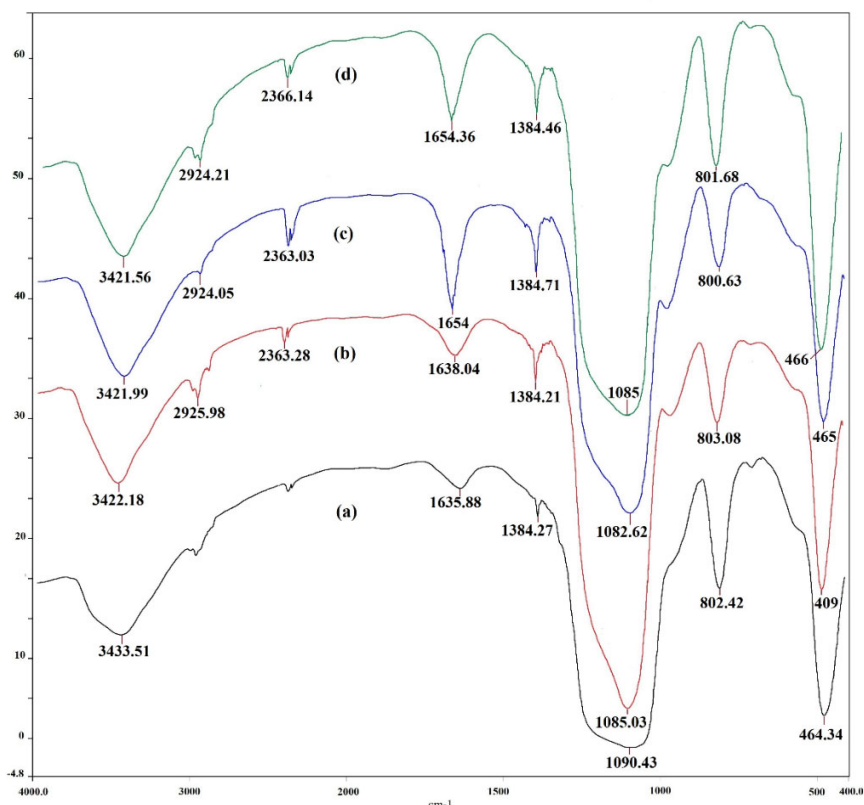


Fig. 1. FT-IR spectra for (a) SBA-15, (b) SBA-15-nPr-Cl, (c) SBA-15-dtz, and (d) SBA-15-dtz-Cu(I).

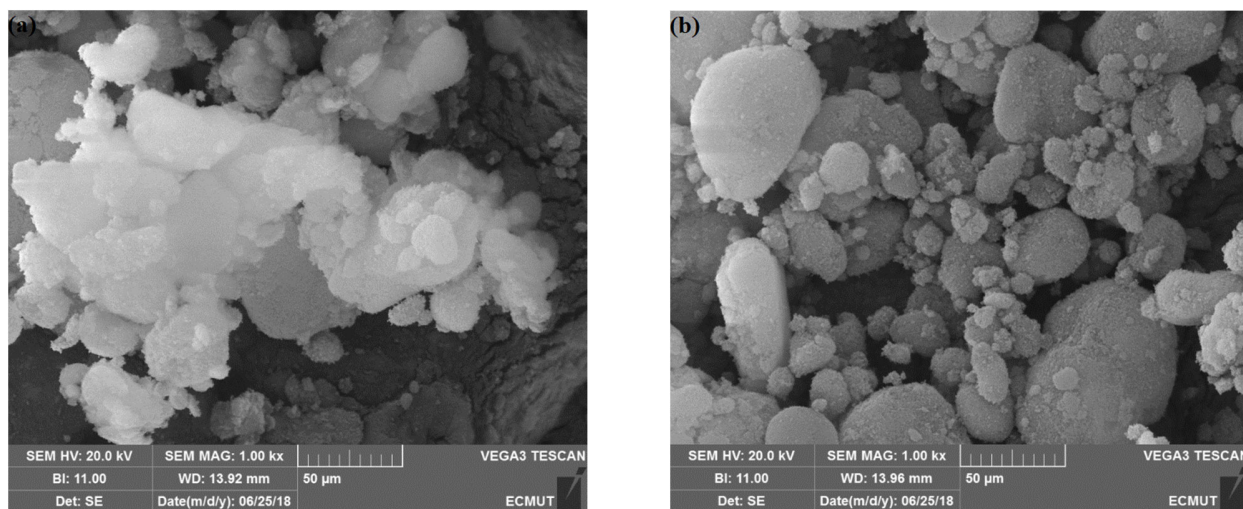


Fig. 2. SEM images for SBA-15 (a) and SBA-15-dtz-Cu(I) (b).

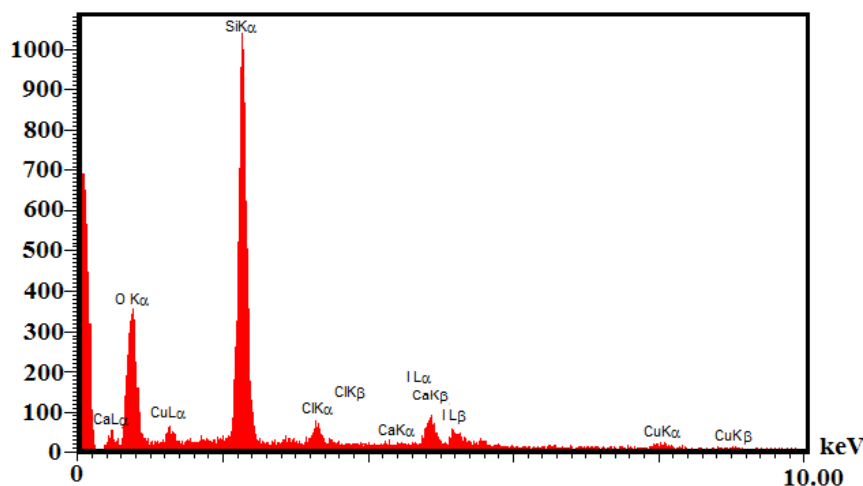


Fig. 3. EDX analysis of SBA-15-dtz-Cu(I).

Fig. 4 showed low and high angle XRD patterns of SBA-15 (a): SBA-15-dtz (b) and SBA-15-dtz-Cu(I) (c); this confirms the mesoporous structure of SBA-15 and deposition of

copper nanoparticles on its surface. These patterns also showed that the structure of catalysts did not disturb during functionalization and metal deposition.

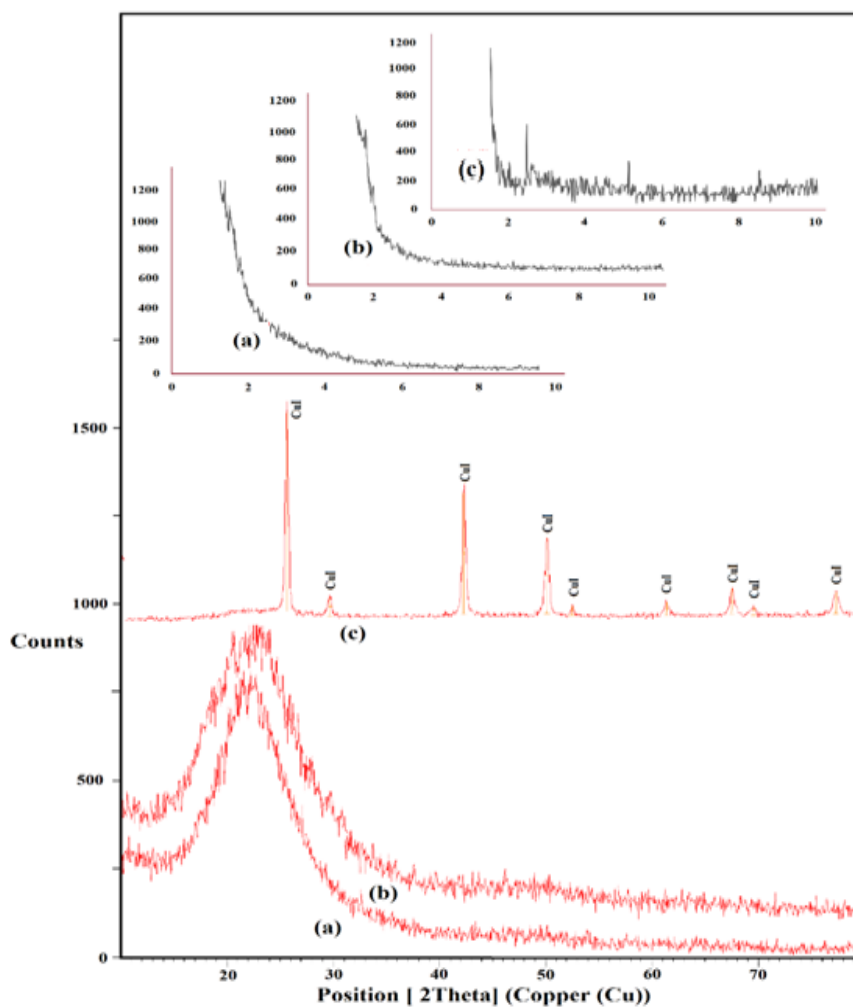


Fig. 4. High and low angle XRD patterns of SBA-15 (a): SBA-15-dtz (b) and SBA-15-dtz-Cu(I) (c).

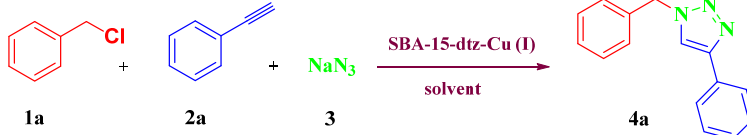
3.2. Catalytic activity

Preliminary experiments were performed using the reaction of benzyl chloride with sodium azide and phenylacetylene, as a model reaction, in the presence of SBA-15-dtz-Cu(I) (0.2 mol%). The reactions were performed using various solvents including CH₃CN, toluene, ethanol, methanol, H₂O, THF, 1,4-dioxan, DMF, acetone, CH₂Cl₂, CCl₄, and in solvent-free conditions. As shown in Table 1, when H₂O was used as the solvent (Table 1, entry 5), the highest reaction yield was obtained. Notably, the reaction gave lower yields when the reaction was performed under solvent-free conditions (Table 1, entry 12). The parameters including the reaction temperature and catalyst concentration were then investigated. It was found that 0.2 mol% of [SBA-15-dtz-Cu(I)] was the optimum condition (Table 1, entry 5). Increasing the amount of catalyst did not increase the reaction yield (Table 1, entry 13). Decreasing the loading of the catalyst to 0.1 mol% reduced the yield dramatically (Table 1, entry 14). Moreover, when the reaction was carried out in the

absence of a catalyst, only a trace amount of the desired product **4a** was obtained, even after the reaction time was prolonged to 5 h (Table 1, entry 15). Also, the effect of temperature on the reaction yield was checked, and the results obtained were tabulated in Table 1. It is obvious that at room temperature, a low yield is obtained (Table 1, entry 16). An increase in the temperature up to 95 °C did not improve the reaction yield (Table 1, entry 17).

With the optimal conditions in hand (0.2 mol% of catalyst), the scope of [SBA-15-dtz-Cu(I)]-catalyzed one-pot click reactions was investigated for a variety of benzyl chloride derivatives and alkynes. The results obtained are summarized in Table 2. A broad scope of different benzyl chloride derivatives containing electron-donating or electron-withdrawing substituents was tested, and 1,4-disubstituted 1,2,3-triazoles **4** were obtained in high-to-excellent yields. As shown in this table, benzyl chlorides with an electron-donating group on the benzene ring (Table 2, entries 3, 13 and 14) were carried out at shorter reaction time.

Table 1. Optimization of the reaction conditions for the synthesis of 1-benzyl-4-phenyl-1*H*-1,2,3-triazole **4a**.^a



Entry	Solvent	Catalyst (mol%)	Temp. (°C)	Time (h)	Yield (%) ^b
1	CH ₃ CN	0.2	reflux	3	65
2	Toluene	0.2	80	3	47
3	EtOH	0.2	reflux	2	90
4	MeOH	0.2	reflux	2	85
5	H ₂ O	0.2	80	1	98
6	THF	0.2	reflux	1	25
7	1,4-dioxan	0.2	reflux	2	38
8	DMF	0.2	80	3	56
9	Acetone	0.2	reflux	3	80
10	CH ₂ Cl ₂	0.2	reflux	5	55
11	CCl ₄	0.2	reflux	5	45
12	Solvent-free	0.2	80	5	20
13	H ₂ O	0.4	80	1	96
14	H ₂ O	0.1	80	4	80
15	H ₂ O	No catalyst	80	5	Trace
16	H ₂ O	0.2	r.t	5	45
17	H ₂ O	0.2	95	1	94

^aReaction conditions: Benzyl chloride (1.0 mmol), a terminal alkyne (1.0 mmol), NaN₃ (1.2 mmol, 0.08 g), catalyst (0.2 mol%), solvent (4 mL).

^bIsolated yield.

Table 2. Synthesis of 1,4-disubstituted 1,2,3-triazoles **4**.^a

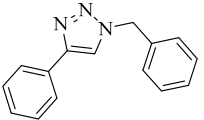
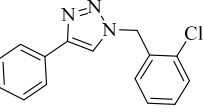
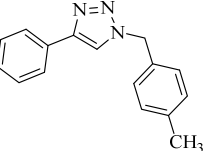
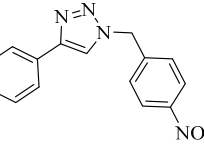
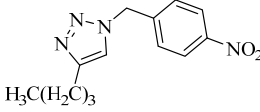
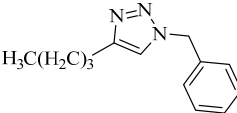
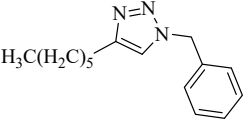
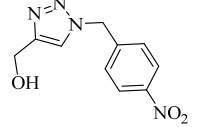
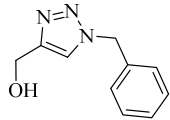
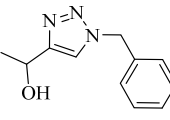
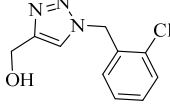
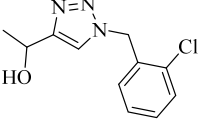
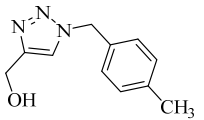
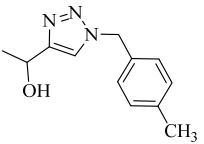
$\text{ArCH}_2\text{Cl} + \text{R}-\text{C}\equiv\text{C} + \text{NaN}_3 \xrightarrow[\text{H}_2\text{O}, 60^\circ\text{C}]{\text{SBA-15-dtz-Cu(I)}} \text{R}-\text{N}=\text{N}-\text{C}(\text{Ar})-\text{N}=\text{N}-\text{CH}_2\text{Ar}$											
Entry	Ar	Alkyne	Time (h)	Product	Structure	Yield (%) ^b	TON	TOF	m.p. (°C)		Ref.
									Found	Reported	
1	Ph	Ph-C≡C	1	4a		98	490	490	127-129	128-129	[40]
2	2-Cl-C ₆ H ₅ -	Ph-C≡C	1	4b		85	425	425	58-60	59-61	[41]
3	4-Me-C ₆ H ₅ -	Ph-C≡C	1	4c		88	440	440	105-107	106-108	[42]
4	4-NO ₂ -C ₆ H ₅ -	Ph-C≡C	2	4d		87	435	217	154-156	154-155	[43]
5	4-NO ₂ -C ₆ H ₅ -	H ₃ C(H ₂ C) ₃ -C≡C	2	4e		90	450	225	59-61	60-61	[43]
6	Ph	H ₃ C(H ₂ C) ₃ -C≡C	3	4f		82	410	136	61-62	60-62	[44]

Table 2. (Continued).

7	Ph	$\text{H}_3\text{C}(\text{H}_2\text{C})_5\text{—}\equiv$	3	4g		82	410	136	61-62	60-62	[44]
8	4-NO ₂ -C ₆ H ₅ -	$\text{HOH}_2\text{C—}\equiv$	2	4h		90	450	225	124-127	125-126	[43]
9	Ph	$\text{HOH}_2\text{C—}\equiv$	1	4i		91	455	455	74-76	78-80	[45]
10	Ph	$\text{H}_3\text{C}(\text{HO})\text{HC—}\equiv$	2	4j		79	395	197	76-78	81-83	[46]
11	2-Cl-C ₆ H ₅ -	$\text{HOH}_2\text{C—}\equiv$	1	4k		78	390	390	110-112	110-112	[47]
12	2-Cl-C ₆ H ₅ -	$\text{H}_3\text{C}(\text{HO})\text{HC—}\equiv$	1	4l		80	400	400	56-59	59-61	[47]
13	4-Me-C ₆ H ₅ -	$\text{HOH}_2\text{C—}\equiv$	1	4m		83	415	415	83-84	86-88	[48]
14	4-Me-C ₆ H ₅ -	$\text{H}_3\text{C}(\text{HO})\text{HC—}\equiv$	1	4n		86	430	430	47-49	47-49	[49]

^aReaction conditions: Benzyl chloride (1.0 mmol), a terminal alkyne (1.0 mmol), NaN₃ (1.2 mmol, 0.08 g), [SBA-15-dtz-Cu(I)] (0.2 mol%), H₂O (4 mL), 60 °C.

^bIsolated yield.

A proposed mechanism for the synthesis of 1,2,3-triazole **4a** from benzyl chloride, sodium azide, and phenyl acetylene catalyzed by [SBA-15-dtz-Cu(I)] is shown in Scheme 4; a) formation of copper(I) acetylide (A); this step occurs through a π -alkyne copper complex intermediate; b) the azide is activated by coordination of copper(I) to framing intermediate (B); c) the first C–bond formation affords the six-membered ring copper(III) metallacycle (C); d) cyclization takes place to yield the copper triazole intermediate (D); e) proteolysis of the Cu–C bond gives the triazole product **4a** and regenerates the catalyst [50].

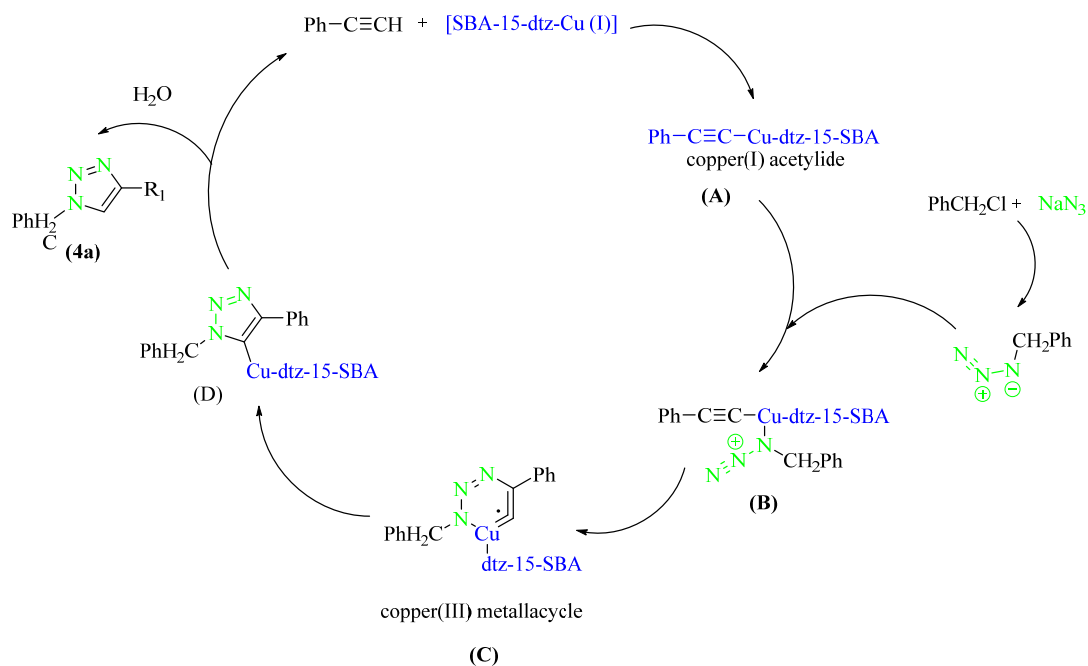
3.4. Catalyst reusability

We also investigated the recyclability of [SBA-15-dtz-Cu(I)] using the reaction of benzyl chloride, sodium azide, and phenyl acetylene in the water at 80°C. The catalyst was recovered by simple filtration and reused over 5 runs without a significant loss in its activity. We found that the product yield decreased slightly from 98 to 89% over five recycling runs.

A comparative study of the reaction conditions for the synthesis of 1,2,3-triazole **4a** using the methods given in Table 4 demonstrates that the proposed protocol is actually better than several other ones. Most of the listed methodologies suffer from some limitations such as long reaction times, harsh reactions, and the use of organic solvents.

4. Conclusions

We have developed an environmentally friendly method for the synthesis of 1,4-disubstituted 1,2,3-triazoles using SBA-15-dtz-Cu(I) as an efficient, new, and reusable catalyst. This method offers several advantages such as shorter reaction time, cleaner reaction, reusability of the catalyst, and high reaction yield. Moreover, this innovative heterogeneous catalyst could be easily separated and reused for at least 5 repeated cycles without a considerable loss in its catalytic activity.



Scheme 4. Proposed mechanism.

Table 4. Synthesis of 1,2,3-triazol **4a** using different catalysts and reaction conditions.

Entry	Catalyst	Solvent	Time (h)	Temp. (°C)	Yield (%)	Ref.
1	CuSO ₄	t-BuOH/H ₂ O	6	65	96	[51]
2	CuFe ₂ O ₄	H ₂ O	3	70	93	[40]
3	Cu-Al ₂ O ₃	H ₂ O	8	RT	92	[52]
4	CuO Hollow Nanospheres	DMSO	3	150	100	[53]
5	SBA-15-dtz-Cu (I)	H ₂ O	1	60	98	This work

Acknowledgments

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