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ARTICLE

Efficient one pot click synthesis of *β*-hydroxy-1,2,3-triazoles catalyzed by copper(I)@phosphorated SiO_2 via multicomponent reaction in aqueous media

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Hossein Naeimi* and Vajihe Nejadshafiee

Copper (I)-modified SiO_2, especially Cu(I)@Phosphorated SiO_2 (CPSi) have been found to catalyze effectively the multi-component synthesis of *β*-hydroxy-1,2,3-triazoles from a variety of epoxides and alkynes in water. This novel heterogeneous catalyst is easily recycled and reused several times. The formation of the product proceed two reaction steps in one pot through a mechanism that involves in situ generated organic azide intermediate and followed by rapid ring closure of this intermediate with terminal alkynes to form *β*-hydroxy-1,2,3-triazole derivatives. The pure products were significantly obtained in high yields and short reaction times.

Introduction

1,2,3-Triazoles are special interest because they exhibit useful biological activities, such as anti HIV [1], anti-bacterial [2], anti-allergy [3–5]. Also 1,2,3-triazole derivatives are used in industrial applications such as herbicide, fungicides, corrosion retarding agents, dyes and solar cells [6–8].

The formation of 1,2,3-triazole derivatives was proceeded through the Huisgen 1,3-dipolar cycloaddition of organic azides and alkyens using CuAAC as catalyst [9–12]. In recent years multi-component click synthesis of *β*-hydroxy-1,2,3-triazoles have been developed via in situ azidolysis of epoxides in the presence of the alkynes and different heterogeneous catalysts with source of copper in water [13–15]. One-pot synthesis of 1,2,3-triazoles from epoxides, linked to the dipolar cycloaddition with azide and alkynes has been reported through some heterogeneous catalytic system such as; copper (I)-modified zeolites (8 mol %)/H_2O [16], copper nanoparticles on activated carbon [17,18], porphyrinato copper nanoparticles (5 mol %)/H_2O[19], Cu[N^2,N^6-bis(2-hydroxyphenyl) pyridine-2,6-dicarbox-amidate]H_2O (5 mol %)/ascorbic acid (20 mol %)/H_2O[20] and $CuSO_4.5H_2O$/sodium ascorbate/H_2O[15]. It is worth noting that synthesis of *β*-hydroxy-1,2,3-triazoles in water, the solvent used by nature for biological chemistry, which can make synthetic processes cheaper, safer and greener.

In continuation of pioneering works in this field on development of efficient method using reusable supports of heterogeneous copper catalysts[21–27], here in we wish to report an efficient, three-component click reaction protocol for synthesis of *β*-hydroxy-1,2,3-triazoles from sodium azide, epoxides, and non-activated terminal alkynes using safe, mild and environmentally friendly modified SiO_2 (silica gel) as a novel heterogeneous catalyst.

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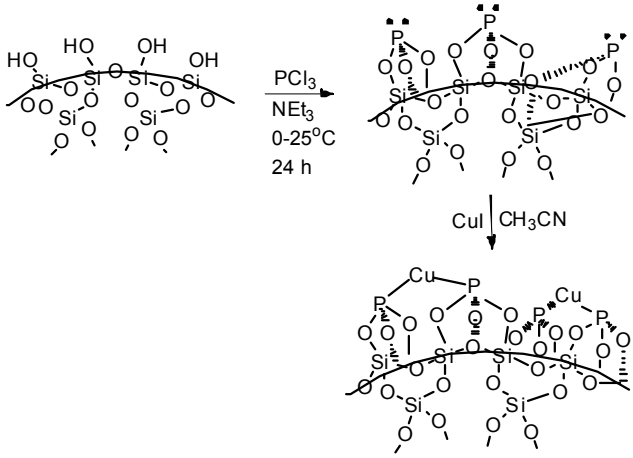
Results and Discussion

Preparation and characterization of the catalyst

Initially, it was modified the surface of SiO_2 (silica gel) with phosphorous via the reaction of PCl_3 and activated silica gel in flowing nitrogen and using Et_3N as a base source at temperature 0-25 °C. The next step, a mixture of CuI and Phosphorated SiO_2 in acetonitrile solvent was heated at 60 °C for 24 h (Scheme 1).



Scheme 1 Preparation of Cu(I)@ Phosphorated SiO_2 from activated SiO_2 (silica gel).

The structures of phosphorated SiO_2 and Cu(I)@ phosphorated SiO_2 were characterize by Fourier transform infrared spectroscopy (FT-IR), energy dispersive spectrometer (EDS), X-ray diffraction (XRD) and atomic absorption spectroscopy (AAS) analyses.

The FT-IR results for activated SiO_2, phosphorated SiO_2 and CPSi are shown in Fig. 1. FT-IR of the core silica gel (Fig. 1-a) shows a broad band around 1250-1101 cm^{-1}, corresponding to asymmetric stretching of Si-O-Si. The bands at 802 and 469 cm^{-1} may be attributed to the bending vibration of the Si-O-Si bonds. The band at 966 cm^{-1} corresponds to symmetric stretching vibration of Si-OH. The broad absorption band around 3433 cm^{-1} can be related to the absorption of Si-OH on surface, which provides opportunities for forming the hydrogen bonding.

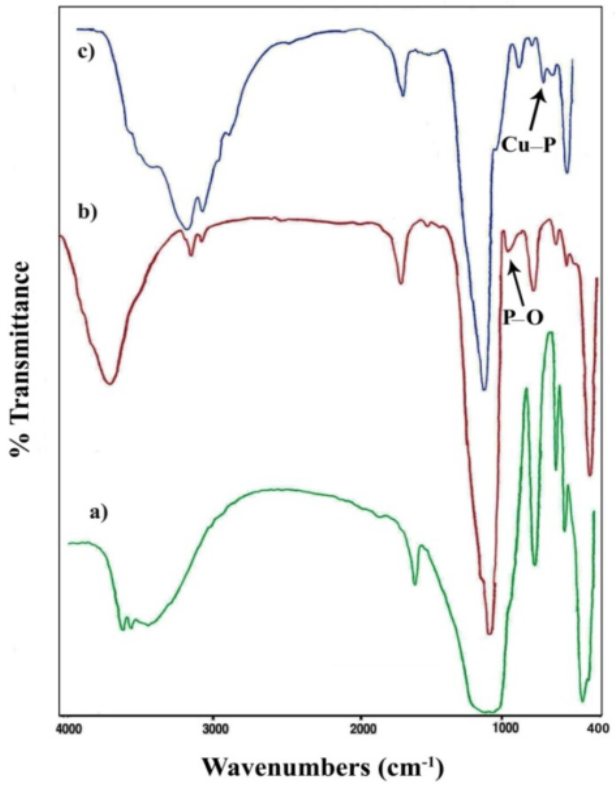


Figure 1 FT-IR spectra of a) SiO_2 (Silica gel), (b) phosphorated SiO_2 and Cu(I)@ phosphorated SiO_2 framework

The FT-IR spectra (Fig. 1-**b,c**) of phosphorated SiO_2 and CPSi are almost the same as that to support the core silica gel. Furthermore, characteristic weak peaks regarding to framework of these modified silicas are observed at wave numbers 959.69 and 619.98 cm^{-1} that can be related to the stretching vibrations of P-O and Cu-P[28] bonds, respectively. The EDS analysis of phosphorated SiO_2 and CPSi catalyst are confirmed the presence of phosphorus and copper on their regions (Fig. 2).

The XRD diffractogram of CPSi shows significant peaks due to copper supported on the phosphorated SiO_2 (Fig. 3). The sharp intense peaks at 29.76, 42.45 and 50.18 show that Cu(I) particles with an irregular shape confined inside the irregular surface of phosphorated SiO_2.

The diffraction and dispersive patterns of the phosphorated SiO_2 and CPSi are illustrated that Cu(I) is highly dispersed on the phosphorated SiO_2 framework. The loading of copper was determined using AAS and shows a loading at 0.075 ± 0.01 mmol g^{-1}.

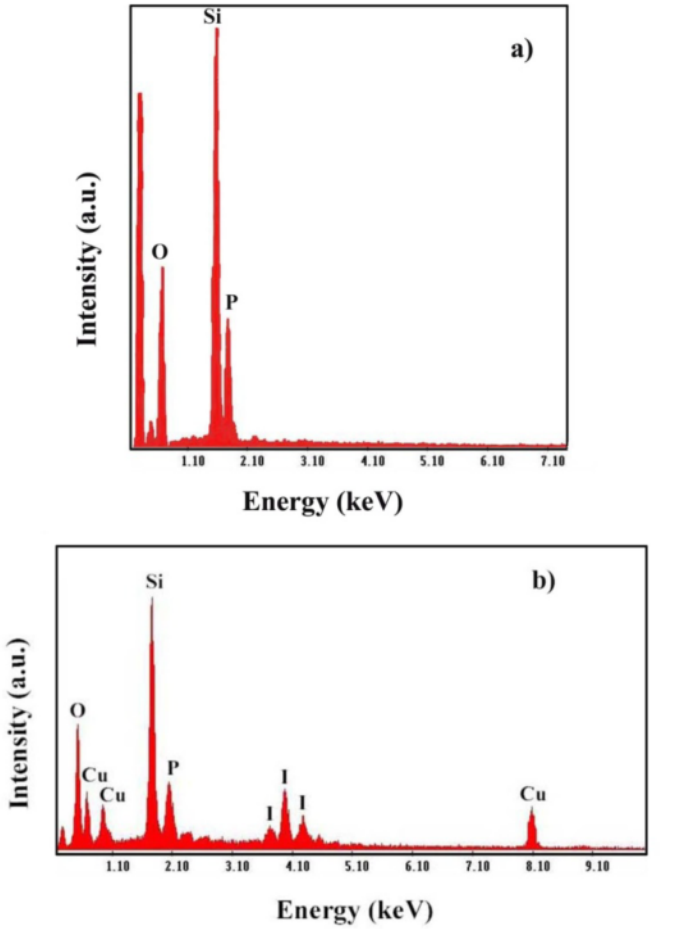


Figure 2 EDS patterns of a) phosphorated SiO_2 and b) Cu(I)@ phosphorated SiO_2 framework.

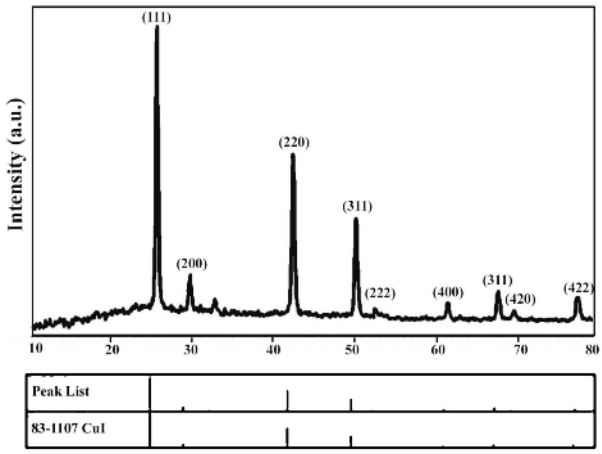


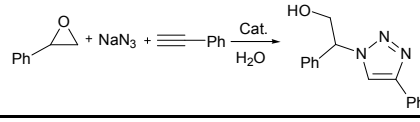
Figure 3 The XRD pattern of CuI supported on phosphorated SiO_2 framework.

Application of CPSi as a catalyst in the click reaction

In this research, three-component synthesis of *β*-hydroxy-1,2,3-triazoles from the treatment of epoxides, alkynes and

sodium azide in the presence of CPSi as catalyst in water media was carried out. Initially, in order to optimize the catalyst amount, the reaction of styrene oxide, phenyl acetylene and sodium azide using various amounts of catalyst were performed (Scheme 1). The results are indicated in (Table 1). As can be seen in this Table, the optimized amount of catalyst in the reaction was obtained 0.64 mol % (35 mg) of catalyst. All reactions were performed with 0.64 mol % of the copper loading being 12-fold lower than the lowest previously published by others [14,18,19,29].

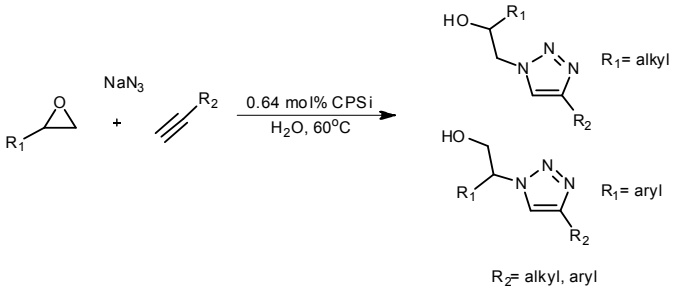
Table 1 The optimization of Cu(I)@Phosphorated SiO_2 as catalyst[a].



Entry	Cat. amount (g)	Cu (mol %)	T(h)	Yield[b] (%)
1	25	0.46	2.5	78
2	30	0.55	1.80	81
3	35	0.64	1	94
4	40	0.74	1	94

[a] Reaction condition: **1** (1 mmol), **2** (1 mmol), NaN_3 (1.1 mmol), CPSi , H_2O.
[b] Isolated yields.

In ascertain to the limitation and development of the reaction, a series of commercially available epoxides and alkynes were subjected to the azidolysis and cycloaddition processes in the presence of optimized amount of catalyst in water at 60 °C (Scheme 1).

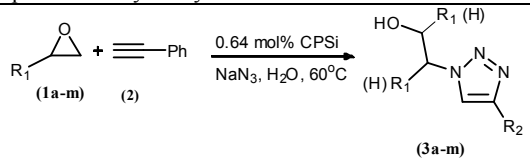


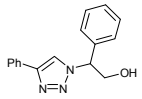
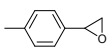
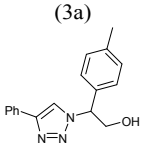
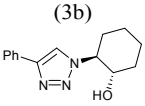
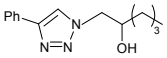
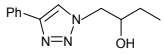
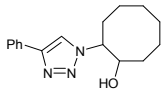
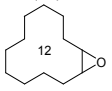
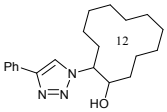
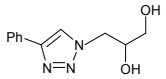
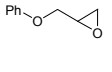
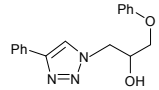
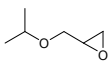
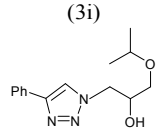
Scheme1 Three-component synthesis of *β*-hydroxy-1,2,3-triazoles.

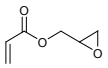
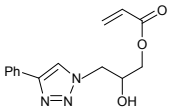
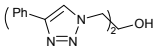
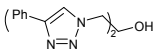
The results related to the reaction of different epoxides with phenylacetylene and sodium azide were summarized in Table 2. The reaction of aryl-substituted epoxides **1a** and **1b** was quickly reacted with phenylacetylene (Table 1, entries 1, 2), to give triazoles **3a** and **3b**, in high yield and short reaction time correspondingly. Then, we explored the reactivity of alkyl-substituted oxiranes with phenylacetylene (Table 1, entries 3-5) that these epoxides were shown to be reluctant to react in lower yields and higher reaction times than the aryl-substituted epoxides. Moreover, cyclooctene oxide **(1f)** and cyclododecene oxide **(1g)** were not reacted and remained unchanged even after extended heating and reaction time until 24 h (Table 2, entries 6, 7). 2,3-epoxypropan-1-ol was unexpectedly shown that to be poorly reactive, giving only a trace of adducts of the alkyne (entry 8).

In contrast, the corresponding benzylated derivative was reacted as well as the aryl substituted derivatives (Table 1, entry 9), revealing the significance of electronic effects in these series. Triazole **3j** was obtained from alkyl-substituted epoxide **1j** in good yield and moderate reaction time at 60°C, but epoxide **1k** gained the high reaction time and yields less than epoxide **1j**, due to the electron withdrawing effect of carbonyl group in the structure of epoxide **1k**.

Table 2 Three component synthesis of *β*-hydroxy-1,2,3-triazoles from epoxides catalyzed by CPSi in water[a]

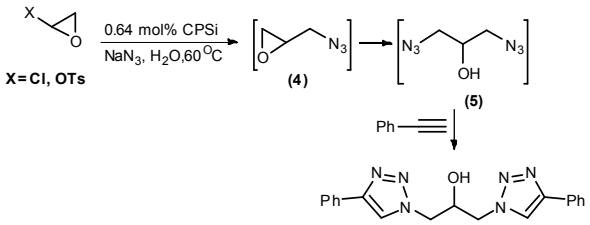


Entry	Epoxide	T(h)	Triazol	Yield[b] (%)	TON[c]
1	 (1a)	1	 (3a)	94	46.5
2	 (1b)	0.75	 (3b)	95	47.5
3	 (1c)	3.5	 (3c)	87	43.5
4	 (1d)	5.5	 (3d)	84	42
5	 (1e)	3.5	 (3e)	88	44
6	 (1f)	24	 (3f)	-	-
7	 (1g)	24	 (3g)	-	-
8	 (1h)	24	 (3h)	trace	-
9	 (1i)	1.5	 (3i)	89	44.5
10	 (1j)	2	 (3j)	83	41.5

11	 (1k)	8	 (3k)	80	40
12[d]	 (1l)	4	 (3l)	76	38
13	 (1m)	2	 (3m)	81	40.5

[a] Reaction condition: **1** (1 mmol), **2** (1 mmol), NaN_3 (1.1 mmol), CPSi (0.64 mol %), H_2O, 60 °C.
[b] Isolated yields.
[c] TON: Mole of formed *β*-hydroxy-1,2,3-triazole per mole of catalyst.
[d] The reaction was done with 1:2:2 mol ratio of epoxide, alkyne and NaN_3 respectively.

Epichlorohydrin (1l) and (2S)-(+)-2,3-epoxypropyltoluene-4-sulfonate (1m) were reacted as well as aryl epoxides in term of yield and reaction time. It was observed that bis-triazoles can be obtained from the predictable ring opening of epoxides 1l and 1m; nevertheless, the new epoxide 4 and the diazido alcohol 5 were initially formed as intermediates (Scheme 2). The formation of bis-triazoles 3l and 3m in this reaction can be due to the presence of good leaving groups (Cl, OTs) in the early epoxides. Furthermore, it was confirmed the structures of these products by ^{1}H NMR and ^{13}C NMR spectra.

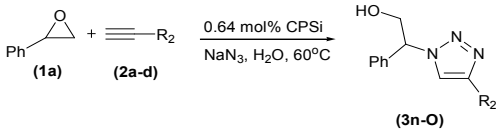


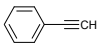
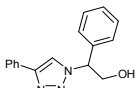
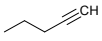
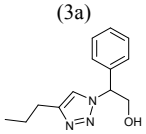
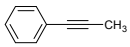
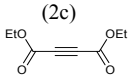
Scheme 2 The formation of bis-triazoles **3l** and **3m** in the presence of CPSi as catalyst.

The reactivities of various alkynes were then examined by presenting them to the reaction with styrene oxide under the same condition (Table 3). It was observed that: (a) phenylacetylene was reacted in this reaction with high activity (Table 3, entry 1).

The methodology was verified to be like wise effective for alkyl-substituted alkyne such as, pent-1-yne (2b), which manifested the same reactivity pattern (Table 3, entry 2). (b) Usage of the disubstituted alkynes in this method, led to the formation of only product resulted from the ring opening of epoxide without to form any triazole product[16] (Table 3, entries 3, 4).

Table 3 Three-component synthesis of *β*-hydroxy-triazoles from styrene oxide and different alkynes catalyzed by CPSi in water[a]



Entry	Epoxide	T(h)	Triazol	Yield[b] (%)	TON
1	 (2a)	1	 (3a)	93	46.5
2	 (2b)	2	 (3n)	88	44
3[d]	 (2c)	24		90	-
4[d]	 (2d)	24		90	-

[a] Reaction condition: **1** (1 mmol), **2** (1 mmol), NaN_3 (1.1 mmol), CPSi (0.64 mol %), H_2O, 60 °C.
[b] Isolated yields.
[c] TON: Mole of formed *β*-hydroxy-1,2,3-triazole per mole of catalyst.
[d] Yields of isolated products is related to the intermediate resulted from ring opening of epoxide.

Stability and recycling the catalyst

The process of catalyst preparation is simple and the catalyst was handled in air. Furthermore, the progress of the reaction could be visually pursued. In the end of reaction, the *β*-hydroxytriazoles were in the core of the solid sheltered by the catalyst when a sphere-shaped solid at the surface of a clear and colorless solution was observed. It is valuable mentioning that, although a small amount of catalyst was utilized, it could be simply recovered by filtration (after treating with methanol) and reused. We recorded a progressive decrease in quantitative yield of *β*-hydroxytriazole 3a along five sequential cycles that a fair isolated yield of 73 % was recorded after the five cycles (Fig. 4).

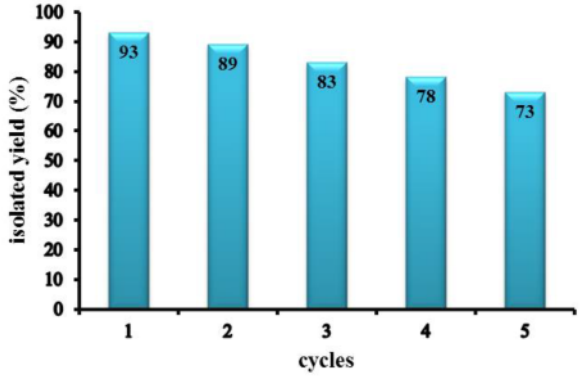
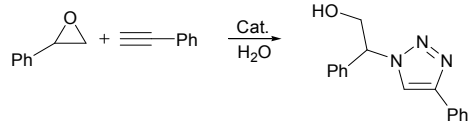


Figure 4 Recyclability of the CPSi catalyst in the synthesis of the triazole 3a.

Comparison of the CPSi catalyst with other catalysts

Recently, a variety of copper catalysts were prepared via addition of the prepared copper (I) particles to the different supports. Also, we carried out a comparative study on the activity of the Cu@(I)Phosphorated SiO_2 with different catalysts to the reaction of styrene oxide (1a), phenylacetylene **(2a)**, and sodium azide in the optimized condition (Table 4). However, the Cu(I)@ Phosphorated SiO_2, was shown to be more active, a low copper loading and short reaction time (0.64 mol %) in comparison with the other catalysts (Table 4, entries 5, 6 vs 1-4).

Table 4 Three component synthesis of *β*-hydroxy-triazoles from epoxides catalyzed by copper on different supports

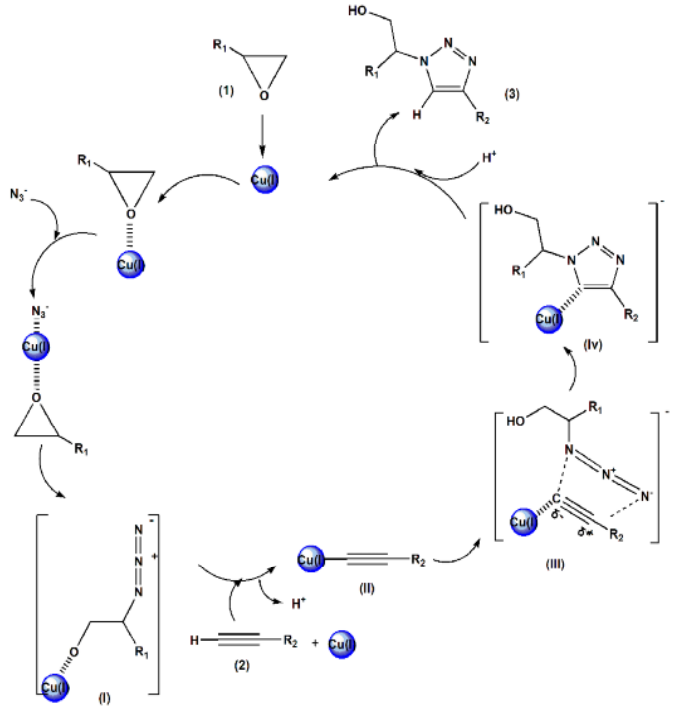


Entry	Catalyst	Catalyst amount (mol %)	t (°C)	T (h)	Yield (%)
1	CuNPs/C[a]	0.5	70	8	93
2	Cu^{I}-Zeolite[b]	8	25	20	77
3	T(*o*-Cl)PPCu-MWCNT[c]	5	25	0.8	95
4	T(*o*-Cl)PPCu[d]	5	25	1.5	93
5	Cu(I)@ phosphorated SiO_2[e]	0.64	60	1	94
6	Cu(I)@ phosphorated SiO_2[e]	0.64	25	3.5	86
7	Cu(I)/SiO_2[f]	0.64	80	6	32
8	P/SiO_2	35[g]	80	24	0

[a] Copper nanoparticles on activated carbon, Ref. [17].
[b] Zeolite loading of 20 mg (ca. 0.08 mmol Cu(I)), Ref. [16].
[c] Multi-walled carbon nanotube, Ref. [19].
[d] Cu [N^2, N^6-bis(2-hydroxyphenyl)pyridine-2,6-dicarboxamidate], Ref. [20].
[e] Catalyst loading of 35 mg (ca. 0.64 mol % Cu(I)).
[f] 35 mg of Cu(I)/SiO_2
[g] 35 mg of P/SiO_2

The proposed mechanism

Our mechanistic proposal for the formation of *β*-hydroxy-1,2,3-triazole includes 2 pathways in which CPSi has a twofold catalytic role as a bifunctional catalyst, which combines two reactions as one-pot ring opening and 1,3-dipolar cycloaddition. Firstly, the participation of a metal azide as the catalytically active species suggests that the mechanism of epoxide ring opening involves azide delivery from the catalyst as well as epoxide activation by the CPSi catalyst. While the phenylacetylene using up and also the generation of CPSi-acetylide intermediate (II) and the disappearance of the 2-azido-1-phenylethanol intermediate (I) were checked by thin layer chromatography (TLC) runs of the reaction mixture, we found that 2-azido-1-phenylethanol is fastly formed. Moreover, the intermediate (II) facilitates the 1,3-dipolar cycloaddition between the C≡C bond of the intermediate (II) and simultaneous generated azide (III), to produce the triazole (IV) along with Cu-C bond formation. In the end, protonolysis of the Cu-C bond of intermediate (IV) by aqueous media to afford the analogous *β*-hydroxy-1,2,3-triazole **3** and regenerates the catalyst (Scheme 3). This result highlights the double responsibility in the three-component synthesis of *β*-hydroxytriazoles that CPSi can take part in the ring opening reaction and in the 1,3-dipolar cycloaddition from epoxides and alkynes (Scheme 4).



Scheme 3 Proposed mechanism of Cu(I)@phosphorated SiO_2 catalyst for the synthesis of *β*-hydroxy-1,2,3-triazole in a one pot and three-component reaction.

Conclusion

We have demonstrated that copper particles were catalyzed the click reaction for synthesis of *β*-hydroxy-1,2,3-triazoles from epoxides, terminal alkynes and sodium azide under mild conditions. The improved methodology is regiospecific with admiration to both the azidolysis of the epoxide and the 1,3-dipolar cycloaddition as follows: (a) aryl-substituted oxiranes lead to primary *β*-hydroxytriazoles; (b) alkyl-substituted oxiranes give rise to secondary *β*-hydroxytriazoles; (c) bis-triazoles are only produced from epoxides when having exclusively a leaving group at the alfa-position; and (d) non-terminal alkynes are inactive in this reaction. In addition, the catalyst is utilized at a low copper loading (0.64 %), also it could be recovered and reused along five cycles, providing in

high yield, by a simple procedure and short experimental time. Furthermore, the products are solid and easily isolated from the reaction mixture by a simple purifications process. Finally, it was concluded that the used catalyst has a lot of significant such as; eco-friendly, easy preparation, recyclable catalyst with its well-active sites providable at a low copper loading in the multicomponent reaction.

Experimental section

Chemicals

Mesoporous silica gel (average pore diameter 60 Å), anhydrous copper (I) iodide, Phosphorous trichloride, epoxides, alkynes and sodium azide were purchased from Fluka, Aldrich and Merck.

Apparatus

IR spectra were obtained as KBr pellets on a Perkin-Elmer 781 spectrophotometer and on an impact 400 Nicolet FT-IR spectrophotometer. ^{1}H NMR and ^{13}C NMR were recorded in $CDCl_3$ solvents on a Bruker DRX-400 spectrometer with tetramethylsilane as internal reference. Melting points obtained with a Yanagimoto micro melting point apparatus are uncorrected. Holland Philips X pert X-ray powder diffraction (XRD) diffractometer (CuKα radiation, λ= 0.154056 nm), at a scanning speed of 2°/min from 10° to 100° (2∅) was employed for characterization of the heterogeneous catalyst. The purity determination of the substrates and reaction monitoring were accomplished by TLC on silica-gel polygram SILG/UV 254 plates (from Merck Company).

Typical Procedure for the Preparation of Cu(I)@ Phosphorated SiO_2

In a well-dried 10 mL Schlenk flask equipped with a septa and magnetic stirrer bar, mesoporous silica gel (average pore diameter 60 Å) was activated for 24 h at 150 °C before undergoing chemical surface modification. PCl_3 (5.7 mmol, 5mL) added slowly to a suspension of SiO_2 (1g silica gel) in dry triethylamine (3 mL) as base, under nitrogen atmosphere. The resulting mixture was at 0 °C for 4 h and subsequently kept at room temperature for 24 h. Then, the solid materials were filtered off and the residue was washed with dry $CHCl_3$ and dried under vacuum overnight to give phosphorated silica. Next step, CuI (0.26 mmol, 0.05 g) was added to phosphorated silica (1 g) in dry CH_3CN (5mL). The resulting mixture was refluxed for 24 h, filtered, and the solid successively washed with CH_3CN (15 mL) and dried under vacuum overnight.

General Procedure for the Synthesis of β-Hydroxytriazoles from Epoxides catalyzed by Cu(I)@ Phosphorated SiO_2 in Water

NaN_3 (72 mg, 1.1 mmol), the epoxide (1 mmol), and the alkyne (1 mmol) were added to suspension of Cu(I)@ Phosphorated SiO_2 (35 mg, 0.64 % Cu) in H_2O (3 mL). The reaction mixture was warmed to 60 °C and monitored by TLC until total conversion of the starting materials. After completion of the reaction, the solid product was collected from the reaction mixture. In order to separate the catalyst, the product was dissolved in hot methanol, subsequently, the whole mixture was directly passed through a sintered glass filter funnel, and the solvent was removed in vacuo to give the corresponding β-hydroxytriazoles **3**, which did not require any further purification.

2-Phenyl-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)ethanol (3a). Pale yellow solid: mp. 125.0 -127.0 °C, Lit [17] (mp. 125.5-127.0 °C). IR (KBr): ν= 693, 758, 1045, 1079, 1242, 1436, 1463, 1493, 1595, 2928, 3064, 3087, 3140, 3346. ^{1}H NMR(400 MHz, $CDCl_3$) δ= 7.81-7.79 (m, 3 H), 7.70 (s, 1H), 7.43-7.39 (m, 6 H) 7.34 (s, 1H), 5.68 (dd, ^{3}J(H,H)= 8 Hz, ^{3}J=3.9 Hz, 1H), 4.68-4.61 (dd, 1H, ^{3}J(H-H)= 12.4 Hz, ^{3}J(H-H)= 7.6), 4.26-4.21 (dd, 1H, ^{3}J(H-H)= 14.4 Hz, ^{3}J(H-H)= 3.6), 3.22 (t, J(H, H) = 6.8 Hz; 1H, OH).

2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)-1-*p*-tolylethanol (3b). Yellow solid: mp. 125.0 °C-127.0 °C, Lit [15] (mp. 124.0-126.0 °C). IR (KBr): ν= 696, 724, 755, 1047, 1075, 1008, 1185, 1220, 1380, 1457, 1496, 2927, 3029, 3092, 3418. ^{1}H NMR(400 MHz, $CDCl_3$) δ= 7.69-7.66 (m, 3 H), 7.39 (m, 3H), 7.27-7.21 (m, 3 H) , 5.68-5.66 (dd, ^{3}J(H,H)= 8 Hz, ^{3}J=3.2 Hz, 1H), 4.66-4.61 (dd, 1H, ^{3}J(H-H)= 12.6 Hz, ^{3}J(H-H)= 8.4), 4.24-4.20 (dd, 1H, ^{3}J(H-H)= 9 Hz, ^{3}J(H-H)= 3.6), 2.38(s, 3H), 2.36 (t, J(H, H) = 2.8 Hz; 1H).

2-(4-Phenyl-1*H*-1,2,3-triazol-1-yl) cyclohexanol (3c).Yellow solid: mp. 168.0 -171.0 °C, Lit [17] (mp. 168.0-171.0 °C). IR (KBr): ν= 699, 768, 713, 1053, 1083, 1234, 1441, 2858, 2937, 3119, 3307. ^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.79 (s, 1H), 7.74-7.72 (m, 2H), 7.40-7.37 (m, 2H) 7.33-7.30 (s, 1H), 4.19-4.09 (m, 3H), 4.01-1.90 (m, 4H), 2.25-2.22 (m, 2H), 1.51-1.26 (m, 2H).

1-(4-phenyl-1*H*-1,2,3-triazol)hexan-2-ol (3d). Cream solid: mp. 92.0 -94.0 °C, Lit [15] (mp. 91.0-93.0 °C). IR (KBr): ν= 694, 764, 1087, 1138, 1227, 1463, 2862, 2925, 2959, 3141, 3248, 3408. ^{1}H NMR(400 MHz, $CDCl_3$) δ= 7.85 (s, 1H), 7.77-7.75 (m, 2H), 7.42-7.40 (m, 2H), 7.34-7.32 (m, 1H) , 4.52-4.49 (m, 2H), 4.29-4.24 (m, 1H), 4.15-4.13 (m, 1H), 1.57-1.51 (m, 3H), 1.44-1.37 (m, 3H), 0.95-0.92 (t, 3H). ^{13}C NMR (400 MHz, $CDCl_3$) δ= 147.27, 130.33, 128.78, 128.06, 125.53, 121.16, 70.44, 56.34, 34.17, 30.77, 28.01, 22.59, 13.99.

1-(4-phenyl-1*H*-1,2,3-triazol-1-yl)butan-2-ol (3e). White solid: mp. 110.0 -111.0 °C. IR (KBr): ν= 694, 763, 982, 1078, 1136, 1228, 1457, 1617, 2926, 2962, 3139, 3254, 3419. ^{1}H NMR(400 MHz, $CDCl_3$) δ= 7.87 (s, 1H), 7.81-7.79 (m, 2H), 7.44-7.40 (m, 2H), 7.34 (m, 1H) , 4.55-4.51 (dd, 1H, ^{3}J(H-H)= 14 Hz), 4.33-4.29 (dd, 1H, ^{3}J(H-H)= 13.8 Hz, ^{2}J(H-H)= 7.6), 2.66-2.65(d, ^{3}J(H-H)= 4.4, 1H), 1.66-1.53 (m, 2H), 1.09-1.05 (t, 3H). ^{13}C NMR (400 MHz, $CDCl_3$) δ= 147.44, 130.40, 128.82, 128.12, 125.61, 121.09, 71.86, 55.84, 27.48, 9.81.

1-phenoxy-3-(4-phenyl-1*H*-1,2,3-triazol-1-yl)propan-2-ol (3i). Pale yellow solid: mp. 125.0 -127.0 °C, Lit [19] (mp. 125.5-126.0 °C). IR (KBr): ν= 691, 755, 982, 1043, 1245, 1494, 1595, 2867, 2927, 3087, 3429. ^{1}H NMR(400 MHz, $CDCl_3$) δ= 7.89 (s, 1H), 7.75-7.73 (m, 2H), 7.41-7.38 (m, 2H), 7.32-7.27 (m, 3H) , 7.02-6.93 (m, 1H), 6.93-6.91 (m, 2H), 4.75-4.73 (m, 1H), 4.56-4.54 (m, 2H), 4.23-4.04 (m, 2H), 3.95-3.76 (m, 1H).

3-isoproxy-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)propan-1-ol (3j). Yellow solid: mp. 61.0 -63.0 °C. R (KBr): ν= 695, 765, 924, 975, 1078, 1127, 1228, 1373, 1468, 2866, 2973, 3062, 3138, 3425. ^{1}H NMR(400 MHz, $CDCl_3$) δ= 7.91 (s, 1H), 7.79-7.77 (m, 2H), 7.42-7.38 (m, 2H), 7.34-7.30 (m, 1H) , 4.61-4.57 (dd, 1H, ^{3}J(H-H)= 12 Hz, ^{2}J(H-H)= 2.8), 4.64-4.41 (dd, 1H, ^{3}J(H-H)= 14 Hz, ^{2}J(H-H)= 4), 4.22 (m, 1H), 3.64-3.58 (m, 1H), 3.53-3.50 (dd, 1H, ^{3}J(H-H)= 8 Hz, ^{3}J(H-H)= 4.4), 3.40-3.36 (dd, 1H, ^{3}J(H-H)= 10 Hz, ^{3}J(H-H)= 4), 1.16-1.17 (t, 6H). ^{13}C NMR (400 MHz, $CDCl_3$) δ= 131.55, 130.36, 129.94, 129.21, 126.72, 122.49, 73.59, 70.45, 70.18, 54.49, 23.14.

2-hydroxy-3-(4-phenyl-1*H*-1,2,3-triazol-1-yl)propyl acrylate (3k). Livid solid: mp. 101.0 -103.0 °C. IR (KBr): ν= 692, 756, 1044, 1246, 1494, 1596, 2925, 3087, 3425. ^{1}H NMR(400 MHz, $CDCl_3$) δ= 7.91 (s, 1H), 7.79-7.77 (m, 1H), 7.43-7.40 (m, 2H), 7.35-7.31 (m, 2H) , 7.02-6.99 (t, 1H), 6.93-6.91 (m, 2H), 4.22 (m, 1H), 3.64-3.58 (m,

1H), 4.07-3.98 (m, 1H), 3.38-3.37 (m, 1H). ^{13}C NMR (400 MHz, $CDCl_3$) δ= 158.25, 147.29, 130.10, 129.63, 128.86, 128.19, 125.56, 121.66, 121.40, 121.14, 114.57, 68.98, 68.70, 53.52.

1,3-bis(5-phenyl-1*H*-1,2,3-triazol-1-yl) propan-2-ol (3l, 3m). Green solid: mp. 233.0 -236.0 ^{o}C, Lit [16] (mp. 233.0-236.0 ^{o}C). IR (KBr): ν= 688, 724, 763, 1074, 1125, 1278, 1464, 1729, 2860, 2928, 2959. ^{1}H NMR (400 MHz, DMSO) δ= 8.54 (s, 1H), 7.84 (m, 2H), 7.44-7.43 (m, 2H), 7.32-7.31 (m, 1H), 5.81 (m, 1H), 4.62-4.56 (d, 1H), 4.40 (m, 2H). ^{13}C NMR (400 MHz, DMSO) δ= 147.71, 132.42, 130.51, 129.68, 129.41, 127.11, 126.72, 124.12, 69.91, 54.84.

2-phenyl-2-(4-propyl-1*H*-1,2,3-triazol-1-yl)ethanol (3n). Pale yellow solid: mp. 62.0 -64.0 ^{o}C. IR (KBr): ν= 697, 760, 1070, 1281, 1456, 1726, 2854, 2925, 3062, 3367. ^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.82 (s, 1H), 7.71 (m, 1H), 7.55-7.54 (m, 1H), 7.46-7.33 (m, 3H) , 4.24-4.18 (m, 2H), 1.69-1.8 (t, 1H), 1.43-1.40 (m, 1H), 1.32-1.26 (m, 4H), 0.94 (m, 3H).

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