FULL PAPER



Applied Organometallic WILEY Chemistry

Boehmite@SiO₂@ Tris (hydroxymethyl)aminomethane-Cu(I): a novel, highly efficient and reusable nanocatalyst for the C-C bond formation and the synthesis of 5-substituted 1H-tetrazoles in green media

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Funding information Ilam University In this work, a versatile protocol was introduced for the preparation of a new Cu(I) supported complex on Silica supported boehmite nanoparticles (Boehmite@SiO₂@Tris-Cu(I)). The structure of the catalyst was comprehensively characterized using Fourier transform infrared spectroscopy (FT-IR), X-Ray Diffractometer (XRD), energy-dispersive X-ray spectroscopy (EDS), inductively coupled plasma atomic emission spectroscopy (ICP), X-ray mapping, thermogravimetric analysis (TGA) and scanning electron microscopy (SEM) techniques. The catalytic activity of this catalyst was studied in the Suzuki cross-coupling reaction and synthesis of 5-substituted 1H-tetrazole derivatives in ethanol and PEG-400 respectively as green solvents. In this sense, simple preparation of the catalyst from the commercially available materials, high catalytic activity, simple operation, short reaction times, high yields and use of green solvent are some advantages of this protocol. Finally, it is worth mentioning that this nanocatalyst was easily recovered, and reused for several times without significant loss of its catalytic efficiency. In addition, stability of the catalyst after recycling was confirmed by FT-IR technique.

K E Y W O R D S

5-substituted 1H-tetrazole, Boehmite@SiO_2@Tris-cu(I), C-C cross coupling, reusable catalyst, Suzuki reaction

1 | INTRODUCTION

Since the discovery of carbon–carbon coupling (C–C) by Akira Suzuki and Norio Miyaura in 1979,^[1] this type of reaction together with the Heck, Stille, Sonogashira and Buchwald–Hartwig reactions has revolutionized the world of organic synthesis.^[2–4] The C–C bond formations are the most important synthetic transformations in industry and in current researches.^[5,6] These types of reactions are of important in the preparation of natural products,^[7] drugs and pharmaceutical compounds,^[8] polymers,^[2,9] herbicides^[3] and industrially important starting materials.^[6] In order to understand the importance of C–C coupling reactions, it should be noted that, in 2010, the Nobel Prize for Chemistry was awarded to Suzuki, Negishi and Heck for their ground breaking contributions on Pd-catalyzed cross-coupling reactions in the organic synthesis.^[10–12] In the context of C–C coupling reactions, transition metal supported on heterogeneous nanoparticles as catalysts are the most relevant type of catalytic systems due to their high reactivity and selectivity in coupling processes in spite of this fact, the metal presents a high superficial energy, which makes them prone to aggregation.^[5,6] The use of copper catalysts for this transformation is still interesting from an industrial perspective because copper is cost-effective and less toxic than other transition metals.^[13–18]

Tetrazoles are an important class of heterocyclic compounds.^[19-22] Recently, organic compounds containing tetrazole moiety have attracted increasing attention due to their wide range of applications in various areas of science.^[23,24] Especially in medicinal chemistry,^[25] tetrazole rings have been utilized as bioisosteres for carboxyl groups owingto their similar properties. Therefore, the tetrazole moiety could be found in pharmaceutical materials, such as antihypertensive, antineoplastic, antibiotic, antiviral and antiallergic drugs. They have also been used in agrochemicals, as ligands in coordination chemistry, and in materials science.^[26] Numerous methods have been developed for the synthesis of tetrazoles,^[20,27,28] they have been generally synthesized by [3 + 2]-cycloaddition reaction between nitriles and azides in the presence of various transition metal catalysts, such as Pd,^[20,28,29] Ni.^[22,30,31] and iron compounds.^[32-34] Methods for the synthesis of 5-substituted 1H-tetrazoles from aldoximes or aldehydes in the presence of copper (II) catalysts have also been reported.^[35] However, some methods have disadvantages such as the need for toxic metals and explosive azide sources.^[19,35-37] The use of copper catalysts for this transformation is still interesting from an industrial point of view; because copper is cheaper and less toxic than other transition metals.^[38,39] The most representative Cu catalysts are homogenous Cu complexes coordinated with different organic ligands and providing excellent yields.^[40] However, the homogenous Cu complexes suffer from significant drawbacks; including, the difficulty of separation and recovery of Cu complexes from the reaction system, high costs and the potential environmental pollution.^[41-43]

However, separation, purification, and reusability of homogeneous catalysts are tedious process.^[44-47] On the other hand, easy separation and consecutive reusability of heterogeneous catalyst makes their consideration for industrial and laboratorial aims.^[48,49] Due to the unique dimensions and size, physical properties, easy recyclability, large specific surface area,^[5,6,49,50] make them as a perfect candida in catalysis science.^[13,51-55] During the past years, the use of recyclable heterogeneous catalysts (prepared by supporting solid support via homogenous precursors) has received great attention in organic synthesis.^[5,6,47,49,50,56] In recent years boehmite have attracted viable attention as potential solid support for the nano scaled heterogenization of homogeneous catalysts.^[6] This nano structural material can be prepare from inexpensive, commercially available and non-toxic substrates in aqueous media under air conditions.^[6,57–59] Boehmite nanoparticles has outstanding properties that make it as ideal heterogeneous support: such as high surface area, easy modification *via* cross linking of organic compounds and high thermal and physical stability in reaction media.

In this research project, we have designed a new nano structural catalyst using boehmite as solid support (Boehmite@SiO₂@Tris-Cu(I)). The catalytic activity of this catalyst has been examined in the Suzuki C-C Cross coupling and synthesis of 5-substituted 1H-tetrazole derivatives.

2 | EXPERIMENTAL

2.1 | Synthesis of Boehmite@SiO₂@Triscu(I) NPs

In the first step boehmite nanoparticles was prepared according to the our previously reported method.^[6] The obtained boehmite nanoparticles (1 g) was dispersed in water (10 ml) and ethanol (50 ml) by sonication for 30 min, Under continuous stirring, PEG (5.36 g), ammonia solution (10 ml) and TEOS (2 ml) were respectively added into the suspension, and continuously reacted for 38 hr at room temperature. Then, the product (Boehmite@SiO₂) was filtered and washed with ethanol and distilled water and dried at room 60 °C. Then, 1 g of boehmite@SiO₂ NPs was dispersed diffused in toluene (50 ml), and 3 ml of 3-chloropropyltrimethoxysilane was add to vessel and stirred at 90 °C at reflux conditions for 24 hr. Then the obtained NPs (Boehmite@SiO₂@*n*-Pr-Cl) isolated by simple filtration and Washed by EtOH for several times and dried at 40 °C. To immobilization of Tris (Tris (hydroxymethyl)aminomethane) ligand on the surface of boehmite nanoparticles, 1 gr of prepared Boehmite@SiO₂@*n*-Pr-Cl was dispersed in water (50 ml) for 30 min and 2.5 mmol of Tris was add to the reaction mixture and stirred for 24 hr at 100 °C under N₂ as inert atmosphere at reflux conditions. Then the obtained Boehmite@SiO2@Tris NPs was separated by simple filtration. Washed with hot water for several times and dried at 50 °C. Finally, The Cu was grafted on the heterogenized ligand by the reaction of Boehmite@SiO₂@Tris (1 g) with CuCl (2.5 mmol) in EtOH at reflux condition for 24 hr under N₂ as inert atmosphere. Then the obtained Boehmite@SiO2@Tris-Cu(I) NPs was separated by simple filtration. Washed with hot water and hot EtOH unsupported CuCl substrates and dried at 60 °C.

2.2 | General procedure for the Suzuki reaction catalyzed by Boehmite@SiO₂@Tris-cu(I) NPs

A mixture of aryl halides (1 mmol), phenylboronic acid (1.2 mmol) and K_2CO_3 (1.5 mmol) in the presence of Boehmite@SiO₂@Tris-Cu(I) NPs (0.25 mol %) was dissolved in ethanol and stirred at reflux conditions for appropriate time shown in Table 2. The progress of reaction was monitored by TLC in *n*-Hexane. After the completion of reaction, the mixture was cooled down to room temperature, the catalyst was separated by simple filtration and the product was washed with EtOAc and water, and organic layer was dried over anhydrous sodium sulfate (about 1.5 g). Then ethyl acetate was evaporated and the pure products was obtained in good to excellent yields.

2.3 | General procedure for the synthesis of 5-substituted 1H-tetrazole derivatives catalyzed by Boehmite@SiO₂@Triscu(I) NPs

A mixture of sodium azide (1.3 mmol) and arylnitrile (1 mmol) in the presence of Boehmite@SiO₂@Tris-Cu(I) NPs (0.20 mol %) was dissolved in PEG (2 ml) and stirred vigorously at 120 °C for the required time. The progress of reaction was monitored by TLC. After the completion of reaction, the mixture was cooled down to room temperature, Then, HCl (4 N, 10 ml) was add to the mixture was added and after blending for 30 seconds, the catalyst was separated by simple filtration and the product was washed with EtOAc and water, and organic layer was dried over anhydrous sodium sulfate (about 1.5 g). Then the ethyl acetate was evaporated to give the desired tetrazole derivatives.

2.4 | Selected spectral data

The copies of ¹H NMR spectral data for some of prepared compounds can be found in the Supporting information.

5-(4-Chlorophenyl)-1H-tetrazole: ¹H NMR (500 MHz, CDCl₃) δ 8.34–8.02 (m, 2H), 7.52–7.35 (m, 2H) ppm. **1-(4-(1H-tetrazol-5-yl)phenyl)ethanone:** ¹H NMR (500 MHz, CDCl₃) δ 8.25–8.12(m, 2H), 7.26, 2.68 (m, 2H), 2.68 (s, 3H) ppm.

3 | RESULTS AND DISCUSSION

3.1 | Catalyst preparation

Initially, the silica coated Boehmite nanoparticles reacted with 3-choloropropyltriethoxysilane (Boehmite@SiO₂@*n*-

Pr-Cl NPs).^[28] In order to prepare Boehmite@SiO₂@Tris NPs, Tris ligand has been grafted on Boehmite@SiO₂@*n*-Pr-Cl NPs via substitution reaction of NH₂ with terminal Cl groups. Finally, the catalyst was synthesized by the reaction of Boehmite@SiO₂@Tris with CuCl (Scheme 1). The structure of resulting material has been characterized by FT-IR, XRD, EDS, ICP, X-ray mapping, TGA and SEM techniques.

3.2 | Catalyst characterizations

The FT-IR spectra of a) Boehmite NPs, b) Boehmite@SiO₂ NPs, c) Boehmite@SiO2@n-Pr-Cl NPs, d) Boehmite@ SiO₂@Tris support and e) Boehmite@SiO₂@Tris-Cu(I) heterogenized metallic complex are shown in Figure 1. As shown in the FT-IR spectrum of the boehmite nanoparticles (Figure 1a), two strong bands at 3295 cm^{-1} (asymmetrical mode) and 3,086 (symmetrical mode) are attributed to the O-H bonds on the surface of boehmite nanoparticles. In FT-IR spectra a-e, several peaks at 480, 618 and 743 cm^{-1} were observed that they are related to the absorption of Al–O bonds.^[61] In the 1,072 and 770 cm⁻¹ spectral region of the FT-IR spectra (Figure 1 b-e): an overlap of the asymmetric and symmetric stretching vibration of the Si-O-Si bonds with Al-O and OH ... OH stretching vibration leads to band broadening. In the spectrum of Boehmite@n-Pr-Cl (Figure 1c), the immobilization of (3-Chloropropyl)trimethoxysilane group was confirmed by C-H stretching vibration appearing at $2830-2960 \text{ cm}^{-1}$.

As shown in the FT-IR spectrum of Boehmite@ SiO_2 @Tris support (Figure 1d), the successful substitution reaction of NH₂ with terminal Cl groups on the modified surface of boehmite nanoparticles was confirmed through the presence of absorption bands in the range of 1,516 and 1,086 cm⁻¹ is assigned to C–N and N–H vibration bands, respectively.^[62] More importantly, the bending vibration of NH₂ near 1,516 cm⁻¹ in the FT-IR spectrum of Boehmite@SiO₂@Tris support (Figure 1d), is shifted to lower wavenumber in the Boehmite@SiO₂@Tris-Cu(I) NPs (Figure 1e) that confirmed the coordination of nitrogen atom of amino groups to Cu.

In order to see the coordination of Cu organic moieties, FIR spectrum of Boehmite@SiO₂@Tris-Cu(I) NPs was studied (Figure 2). The FIR confirms a detailed description of the IR-active low-frequency modes (frequency region below 700 cm⁻¹), and it can provide information on the metal–ligand vibrations. The coordination of the –NH and –OH groups is further substantiated by the appearance of additional band in the 420 cm⁻¹ corresponding to the stretching vibrations of Cu–N^[63,64] and a band at 620 cm⁻¹ assigned to the



SCHEME 1 Stepwise preparation of Boehmite@SiO₂@Tris-Cu(I) nanocatalyst

vibration of Cu–O.^[65] The results show a reasonably good agreement with the available literature data.^[66]

The XRD diagram of a) Boehmite NPs, b) Boehmite@ SiO₂ NPs, c)Boehmite@SiO₂@n-Pr-Cl NPs, d) Boehmite@ SiO₂@Tris support and e) Boehmite@SiO₂@Tris-Cu(I) were shown in Figure 3. The XRD pattern of Boehmite NPs (Figure 3a), shows major peaks at 2θ values at 14.83, 28.83, 39.12, 49.69, 51,12, 55.62, 65.36, 67.71 and 72.80, which are in agreement with the standard boehmite XRD spectrum, and all peaks strongly confirmed the crystallization of boehmite nanoparticles in orthorhombic unit cells.^[6] The results of XRD patterns of Boehmite@ SiO₂ NPs (Figure 3b) reveal that the surface modification of the boehmite nanoparticles does not lead to their phase change. After adding tetraethyl orthosilicate (TEOS), some couriers may be eliminated or peak intensity may be reduced as seen in the spectrum. In the literature, after adding TEOS some of couriers dropped or moved, also the broad peaks around $2\theta = 20 - 27^{\circ}$ are typical for existence of amorphous SiO₂. The PXRD patterns for Boehmite@SiO₂@n-Pr-Cl NPs, Boehmite@SiO₂@Tris and Boehmite@SiO2@Tris-Cu(I) (Figure 3c-e), exhibited the same diffraction lines but sharper and more intense than Boehmite@SiO2. This result confirmed the crystalline structure retained after the functionalization and metal loading. Also, several new peaks appeared at

 2θ = 30.97 °, 32.47 °, 38.42 ° and 39.67° showing clear immobilization of the Tris-Cu(I) complex on the surface of Boehmite@SiO₂ NPs.^[11]

The elemental composition of the prepared catalyst (Boehmite@SiO2@Tris-Cu(I)) was studied using energydispersive X-ray spectroscopy (EDX), which exhibit the presence of Al, Si, O, C, N and Cu species in its structure (Figure 4). The results confirmed the successful immobilization of tris (hydroxymethyl)aminomethane-Cu(I) on the boehmite NPs (Figure 4).

Moreover, in order to extend the scope of catalysts characterization, the exact amount of Cu in Boehmite@ SiO₂@Tris-Cu(I) NPs was examined by ICP-OES technique. The immobilized amount of Cu catalyst on Boehmite@ SiO₂@Tris NPs was found to be 1.79×10^{-3} mmol g⁻¹.

X-Ray Mapping analysis of Boehmite@SiO2@Tris-Cu(I) NPs confirmed the homogeneous distributions of Al, Si, O, C, N and Cu atoms on the surface of nanoparticles (Figure 5). It can be concluded from the figure that the copper has evenly dispersed on the surface of Boehmite@SiO2@Tris support.

The thermal stability of the Boehmite@SiO₂@Tris-Cu(I) nanomaterial was also investigated by thermogravimetric analysis (TGA) (Figure 6). The TGA curve of Boehmite@SiO₂@Tris-Cu(I) NPs shows three steps of weight loss. The weight loss about 3.74% below



FIGURE 2 FIR spectra of a) Boehmite@SiO₂@Tris-Cu(I) NPs and (b) recycled Boehmite@SiO2@Tris-Cu(I) NPs

200 °C corresponds to desorption of physiosorbed and chemosorbed solvents.^[6] The weight loss between 200 and 600 °C in the next steps is mainly attributed to the oxidative decomposition of both n-Propyl linker and tris (hydroxymethyl)aminomethane ligand located in the Boehmite@SiO2@Tris-Cu(I) framework. The results

FIGURE 3 XRD curves of a) Boehmite NPs, b) Boehmite@SiO2 NPs, c) Boehmite@SiO2@n-Pr-Cl NPs, d) Boehmite@SiO2@Tris NPs and e) Boehmite@SiO2@Tris-Cu(I) NPs

indicate that Tris-Cu(I) catalytic complex has been successfully grafted on to the surface of Boehmite@SiO2 NPs.^[6,49]

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620.68 86.

618:46

491.82

66

625.6 568.1

500

80

[%]



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FIGURE 4 EDX pattern of Boehmite@SiO2@Tris-Cu(I) NPs

For additional study on the surface morphology of copper supported on Boehmite@SiO2@Tris catalyst, we used SEM analysis. The shapes and dimensions of the particles can be seen in Figure 7. As expected, the SEM image of prepared nanocatalyst illustrated that the

particles size was quietly valuable and is about 21.95-28.80 nm. On the other hand, the SEM results are in good agreement with XRD patterns in which nano sized catalyst was shown using characteristic peaks.

3.3 | Catalytic study

As a part of this research, it was decided to study the catalytic effect of Boehmite@SiO2@Tris-Cu(I) in organic reactions including the synthesis of tetrazoles and Suzuki C-C cross coupling reactions.

In order to find the best reaction conditions for Suzuki reaction in the presence of Boehmite@SiO2@ Tris-Cu(I) NPs, the coupling of iodobenzene and phenylboronic acid was selected as a model reaction and the results are summarized in Table 1. In order to optimize the reaction conditions, we examined different reaction parameters including different amounts of Boehmite@SiO2@Tris-Cu(I) NPs, solvent, base and temperature (Scheme 2). As shown in Table 1, the reaction did not proceed in the absence of catalyst even after 2 days (Table 1, entry 1). In the next step, effect of



FIGURE 5 The X-ray map analysis Boehmite@SiO2@Tris-Cu(I) NPs

FIGURE 6 TGA curves of Boehmite@SiO2@Tris-Cu(I) NPs



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SCHEME 2 Optimization of reaction conditions for Boehmite@SiO2@Tris-Cu(I) NPs catalyzed the Suzuki C-C cross-coupling reaction of iodobenzene with phenylboronic acid

different amounts of catalyst were studied in which inferior results were obtained using <0.25 mol % of the catalyst on the basis of Cu loading (Table 1, entries 2-8). However, when 0.025 mol% of the catalyst was used, excellent biphenyl yields were obtained (Table 1, entry 8). In the next step, various types of solvents such as EtOH, PEG-400, DMF, DMSO, H₂O, EtOH:H₂O (1:1), Dioxane and solvent- free conditions were explored (Table 1, entries 8-15) and the best results were obtained with EtOH (Table 1, entry 8). Then, the effect of various bases was investigated and K₂CO₃ was selected as the most effective base. Moreover, the effect of different temperatures studied, which the reflux condition was selected as the best temperature conditions (Table 1, entries 19-22). As shown in Table 1, aryl halide (1 mmol), phenylboronic acid (1.2 mmol) in the presence of the 0.25 mol % of the catalyst based on Cu loading in EtOH under reflux conditions was found to be the ideal reaction conditions for the formation of the corresponding biphenyl products.

In order to explore the generality of this procedure, the catalytic activity of Boehmite@SiO2@Tris-Cu(I) NPs in the synthesis of a wide range of biphenyl derivatives, bearing various functional groups, was examined under the optimized conditions (Scheme 3). The summarized

Entry	Catalyst (mol%)	Solvent	Base	Temperature (°C)	Time (min)	Yield (%) ^a
1	-	EtOH	K ₂ CO ₃	reflux	2 days	NR
2	0.15	EtOH	K_2CO_3	reflux	60	Trace
3	0.03	EtOH	K_2CO_3	reflux	60	41
4	0.05	EtOH	K_2CO_3	reflux	60	57
5	0.10	EtOH	K_2CO_3	reflux	60	72
6	0.15	EtOH	K_2CO_3	reflux	60	85
7	0.20	EtOH	K ₂ CO ₃	reflux	60	93
8	0.25	EtOH	K ₂ CO ₃	reflux	60	98
9	0.25	PEG-400	K ₂ CO ₃	80	60	64
10	0.25	DMF	K ₂ CO ₃	80	60	88
11	0.25	DMSO	K ₂ CO ₃	80	60	91
12	0.25	H ₂ O	K_2CO_3	reflux	60	81
13	0.25	EtOH:H ₂ O (1:1)	K_2CO_3	reflux	60	87
14	0.25	Dioxane	K_2CO_3	reflux	60	31
15	0.25	Solvent free	K ₂ CO ₃	reflux	60	NR
16	0.25	EtOH	Na ₂ CO ₃	reflux	60	89
17	0.25	EtOH	Et ₃ N	reflux	60	86
18	0.25	EtOH	-	reflux	60	NR
19	0.25	EtOH	K ₂ CO ₃	25	60	NR
20	0.25	EtOH	K ₂ CO ₃	40	60	51
21	0.25	EtOH	K ₂ CO ₃	60	60	79
22	0.25	EtOH	K ₂ CO ₃	70	60	81

TABLE 1 Optimization of the reaction conditions for the Suzuki C-C cross coupling of iodobenzene with phenylboronic acid

^aIsolated yield.

results in Table 2 show that the target products were afforded in moderate to excellent yields. As the results shown various ortho-, meta-, and para-substituted aryl halides; including, aryl iodide, aryl bromides and aryl chlorides having both electron-withdrawing and electron-donating groups such as NO₂, NH₂, CN, CF₃, CH₃ and OCH₃ produced their pure corresponding derivatives in good to excellent yields. However, it is worth mentioning that the reaction time of the aryl halides with electron-donating groups on the aromatic ring was longer than aryl halides with electron-withdrawing groups. Moreover, the Suzuki C-C cross-coupling of phenylboronic acid with aryl iodide and aryl bromides was easier than aryl chlorides. In order to show the chemoselectivity of this new catalytic system, the reaction of 1-bromo-4-chloro

benzene was also investigated in which the bromide group showed more reactivity (Tables 2 entry 8). This selectivity allows to remain an active halide site for further functionalization.

The cyclic mechanism of Suzuki reaction in the presence of Boehmite@SiO₂@Tris-Cu(I) NPs has been shown in the Scheme 4 based on the previously reported mechanisms.^[5] The general catalytic cycle for Suzuki cross coupling reaction involves three fundamental steps: oxidative addition, transmetalation, and reductive elimination as demonstrated in Scheme 4, The oxidative addition of aryl halides to Boehmite@SiO₂@Tris-Cu(I) complex is the initial step to give intermediate 1. In the next step under the participation of base, an organoborane compound reacts with intermediate 1 in transmetalation

 $R_{11}^{r_1} \xrightarrow{X} + \bigcup_{K_2CO_3, EtOH, Reflux} R_{R_1}^{r_2} \xrightarrow{Boehmite@SiO_2@Tris-Cu(I)} R_{R_2}^{r_2}$

SCHEME 3 Boehmite@SiO₂@Tris-Cu(I) NPs catalyzed the Suzuki cross-coupling of various aryl halides with phenylboronic acid for the synthesis of biphenyl products

TABLE 2 Catalytic Suzuki C-C cross-coupling of various aryl halides with phenylboronic acid in the presence of catalytic amounts of Boehmite@SiO₂@Tris-Cu(I), in EtOH at 80 °C

					Melting point	
Entry	Aryl halide	Product	Time (min)	Yield (%) ^{a,b}	measured	literature
1			60	98	61–63	62-64 ^[28]
2	Me	Ме	100	96	43–44	43-45 ^[28]
3	MeO	MeO	160	97	81-83	82-85 ^[28]
4	U OMe	OMe	200	90	Oil	Oil ^[60]
5	Br		160	87	62–64	62-64 ^[28]
6	Me Br	Ме	120	95	43–45	43-45 ^[28]
7	NC		80	88	84–86	82-84 ^[28]
8	CI Br	ci	300	90	72-73	70–72 ^[60]
9	O ₂ N Br	0 ₂ N-	50	94	111-113	111–114 ^[28]

(Continues)

TABLE 2 (Continued)

anometallic

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					Melting point	
Entry	Aryl halide	Product	Time (min)	Yield (%) ^{a,b}	measured	literature
10			200	91	67–68	62-64 ^[28]
	CI					
11			100	87	111-112	111-113 ^[60]
	O ₂ N	0 ₂ N-				

^aIsolated yield.

^bReaction conditions: aryl halide (1 mmol), phenylboronic acid (1.2 mmol) and K_2CO_3 (1.5 mmol), Boehmite@SiO_2@Tris-Cu(I) NPs (0.25 mol %), in EtOH (3 ml) at 80 °C (Reflux conditions).



SCHEME 4 Proposed mechanism for the Suzuki reaction in the presence of catalyzed by Boehmite@SiO₂@Tris-Cu(I) NPs



SCHEME 5 Optimization of reaction conditions for Boehmite@SiO₂@Tris-Cu(I) NPs catalyzed the reaction of sodium azide and benzonitrile

to afford intermediate 2. This is followed by reductive elimination to give the desired product and regenerate the original Boehmite@SiO₂@Tris-Cu(I) species.

The next part of the study focused on the utility of this nanocatalyst for the synthesis of tetrazole derivatives. In order to find the best reaction conditions for the synthesis of 5-substituted tetrazoles in the presence of Boehmite@SiO2@Tris-Cu(I) NPs, the reaction of benzonitrile and sodium azide (NaN₃) was selected as a model reaction (Scheme 5). The results are summarized in Table 3. In order to optimize the reaction conditions, we examined different reaction parameters; including, type of solvent, different amounts of catalyst and/or NaN₃, and the effect of temperature on the reaction efficiency. Initially, the amount of the catalyst was optimized, which the best results was obtained with 0.20 mol% of the catalyst. It is worth mentioning that the reaction did not proceed in the absence of Boehmite@SiO₂@Tris-Cu(I) NPs even after 8 hr (Table 3, entry 1). Subsequently, the influence of different solvents was examined and, the highest yield was achieved using PEG. Then, the effect of various temperatures on the out-come of reaction was investigated and the best result was obtained at 120 °C. Finally, the amount of NaN₃ was optimized that was observed the best amount is 1.3 mmol. As shown in Table 3, the optimal amounts and conditions is 0.20 mol% of Boehmite@SiO2@Tris-Cu(I) heterogenized complex in PEG-400 at 120 °C using 1.3 mmol of NaN₃.

In order to investigate the scope and generality of this procedure, various benzonitriles bearing different electron-withdrawing or electron-donating substituents were reacted with sodium azide under the optimized reaction conditions (Scheme 6). The results are summarized in Table 4. The experimental results show that various benzonitriles produced their corresponding 5-substituted 1H-tetrazole derivatives in good to excellent yields. However, it is worth mentioning that the reaction

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TABLE 3 Optimization of the reaction conditions for Boehmite@SiO₂@Tris-Cu(I) NPs catalyzed the reaction of sodium azide and benzonitrile

Entry	Catalyst (mol%)	Solvent	NaN ₃ (mmol)	Temperature (°C)	Time (min)	Yield (%) ^a
1	-	PEG-400	1.3	120	8 h	NR
2	0.5	PEG-400	1.3	120	120	48
3	0.10	PEG-400	1.3	120	120	63
4	0.15	PEG-400	1.3	120	120	83
5	0.17	PEG-400	1.3	120	120	89
6	0.20	PEG-400	1.3	120	120	95
7	0.25	PEG-400	1.3	120	120	95
8	0.20	PEG-400	1.3	120	120	93
9	0.20	EtOH	1.3	120	120	NR
10	0.20	H ₂ O	1.3	120	120	NR
11	0.20	Glycerol	1.3	120	120	NR
12	0.20	DMF	1.3	120	120	25
13	0.20	DMSO	1.3	120	120	47
14	0.20	Dioxane	1.3	120	120	46
15	0.20	Solvent free	1.3	120	120	N.R
16	0.20	PEG-400	1.3	25	120	N.R
17	0.20	PEG-400	1.3	40	120	N.R
18	0.20	PEG-400	1.3	60	120	Trace
19	0.20	PEG-400	1.3	80	120	33
20	0.20	PEG-400	1.3	90	120	57
21	0.20	PEG-400	1.3	100	120	81
22	0.20	PEG-400	1.3	110	120	89
23	0.20	PEG-400	1.2	120	120	90
24	0.20	PEG-400	1.1	120	120	82
25	0.20	PEG-400	1	120	120	67

^aIsolated yield.



time of the benzonitriles with electron-donating groups on the aromatic ring was longer than benzonitriles with electron-withdrawing groups. In order to show the chemoselectivity of this new catalytic system, the reaction of terephthalonitrile with sodium azide under the optimized reaction conditions was also investigated in which the only one of cyanide group was reacted and the corresponding pure 5-(4-cyanophenyl)-1H-tetrazole product obtained in 89 yield (Tables 4 entry 8). This selectivity allows an active benzonitrile site remain for further functionalization.

A plausible mechanism is shown in Scheme 7.^[31,67] Initially, interaction of nitrogen atom of nitrile with Cu

 $R \stackrel{fi}{\square} \stackrel{CN}{\longrightarrow} + NaN_3 \xrightarrow{\text{Boehmite@SiO}_2@Tris-Cu(I)}{PEG-400, 120 °C, then HCl} R \xrightarrow{N} H$

forms intermediate A, which accelerates the cyclization step. In fact, Boehmite@SiO₂@Tris-Cu(I) act as a Lewis acid, which activates the nitrile groups via coordination. Hence, it enhances the electrophilic character of cyanide group, which then reacts with sodium azide to form the intermediate B. Acidic work up, affords C and D.

3.4 | Recyclability of the catalyst

Reusability of catalysts provides an important advantage in industrial applications. Therefore, the recoverability and reusability of Boehmite@SiO₂@Tris-Cu(I) has been

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TABLE 4 Catalytic synthesis of 5-substituted 1H-tetrazole derivatives from the reaction of various arylnitriles with sodium azide in the presence of Boehmite@SiO₂@Tris-Cu(I) NPs in PEG-400 at 120 °C

					Melting point (°C)	
Entry	Arylnitrile	Product	Time (min)	Yield (%) ^{a,b}	measured	literature
1	CN CN		120	95	211-214	211-214 ^[21]
2	CN NO ₂	HO	130	97	149–152	149–150 ^[27]
3	O ₂ N CN	O ₂ N	110	97	217-220	215-218 ^[27]
4	CI CN		60	91	129-132	128–130
5	CI		70	95	261–263	258–260 ^[27]
6	Br	Br	80	98	266-267	266–267 ^[27]
7	Ac	o → → → → → → → → → → → → →	480	93	173–176	176–178 ^[27]
8	CN		60	92	224–226	226 ^[27]
9	HOCN	HO	80	97	233-235	234-235 ^[21]

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TABLE 4 (Continued)

					Melting point (°C)	
Entry	Arylnitrile	Product	Time (min)	Yield (%) ^{a,b}	measured	literature
10			110	89	254-257	192-193 ^[27]
	NC					

^aIsolated yield.

^bReaction conditions: Arylnitrile (1 mmol), NaN₃ (1.3 mmol) Boehmite@SiO₂@Tris-Cu(I) NPs (0.20 mol %), PEG-400 (2 mL) at 120 °C.



the experiment, the reaction system was cooled down to room temperature and the catalyst was separated from the solution *via* simple filtration, washed with acetone, air-dried and, finally, reused for the next run. As shown in Figure 8, the recycling process was repeated for five cycles with a slight decrease in the activity of the catalyst.



2000

1500

Wavenumber cm-1

3000

3500

2500

584

500

1000



FIGURE 10 FIR spectra of a) Boehmite@SiO₂@Tris-Cu(I) NPs and b) recycled Boehmite@SiO₂@Tris-Cu(I) catalyst

Also, in order to consider the stability of the catalyst after recycling, the recycled catalyst has been characterized by FT-IR and FIR techniques. The Figure 9 and 10 show the FT-IR and FIR spectrums of fresh and spent Boehmite@SiO₂@Tris-Cu(I) NPs, respectively. IR analysis shown that the catalyst is stable during the reaction.

3.5 | Hot filtration test

Also, the heterogeneity of Boehmite@SiO₂@Tris-Cu(I) in the reaction mixture was studied using the hot filtration test. The hot filtration test was performed for the Suzuki cross-coupling reaction on the model reaction under the optimal reaction conditions. After half time of reaction, the reaction was terminated, and corresponding product obtained in 57% of yield. Then, the reaction was repeated, and at the half time of the reaction, the catalyst was separated by simple filtration from the reaction mixture and the filtrate was allowed to react further (in the absence of catalyst). We found that only a trace conversion (<3%) of the coupling reaction was happened upon the heating of the catalyst-free solution for another half time of reaction.

4 | CONCLUSION

In this study, we described a simple strategy to immobilize a novel Cu (I) complex on the modified-surface of Boehmite nanoparticles. The prepared nanocatalyst was characterized by FT-IR, XRD, EDS, ICP, X-ray mapping, TGA and SEM techniques. The activity of the catalyst was tested in Suzuki crss-coupling reaction and the synthesis of 5-substituted 1H-tetrazole derivatives. This new method offers several advantages; including, green conditions, high yield, short reaction time, simple work-up procedure, ease of separation, and recyclability of the catalyst.

ACKNOWLEDGMENTS

This work was supported by the research facilities of Ilam University, Ilam, Iran.

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How to cite this article: Ghorbani-

Choghamarani A, Aghavandi H, Mohammadi M. Boehmite@SiO₂@ Tris (hydroxymethyl) aminomethane-Cu(I): a novel, highly efficient and reusable nanocatalyst for the C-C bond formation and the synthesis of 5-substituted 1H-tetrazoles in green media. *Appl Organomet Chem.* 2020;e5804. https://doi.org/10.1002/aoc.5804