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Palladium-free and phosphine-free Sonogashira coupling reaction of aryl halides with terminal alkynes catalyzed by boehmite nanoparticle-anchored Cu(I) diethylenetriamine complex

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Abstract In this work, a novel diethylenetriamine-functionalized-boehmite nanoparticle-supported Cu(I) catalyst is synthesized. The catalyst prepared is then characterized by FT-IR spectroscopy, scanning electron microscopy, transmission electron microscopy, X-ray diffraction spectroscopy, and inductively coupled plasma techniques. The catalyst prepared shows great activity in the Sonogashira coupling reaction of aryl halides with terminal alkynes in DMF under an argon atmosphere. Moreover, it could be removed from the reaction mixture by means of simple filtration and used again for up to six runs without an appreciable loss in its activity.

Keywords Boehmite nanoparticles · Palladium-free · Sonogashira reaction · Aryl halide

Introduction

From the time it was discovered in 1975, Sonogashira coupling reaction has been widely applied to the synthesis of both the synthetically and biologically significant aryl acetylenes [1, 2]. This reaction generally makes use of $Pd(PPh_3)_2Cl_2$ or $Pd(PPh_3)_4$ and copper(I) iodide as the catalytic system, which is not favored for industrial applications because of the high price of palladium [3, 4]. From the

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standpoint of modern organic synthesis, employing costly palladium catalysts and the demand for a copper (I) salt as a co-catalyst is less appealing, particularly for industrial-scale syntheses. Consequently, some studies of great importance have concentrated on the invention of new palladium- and phosphine-free catalytic systems with notable activities [5–8]. According to these research works, various catalytically active metals have been proposed for the Sonogashira coupling reactions, which include the ionic complexes of cobalt [9], iron [10], silver [11], nickel [12], ruthenium [13, 14], and gold [15, 16] with different ligands. Moreover, the use of copper salts and complexes have attracted much attention for these types of coupling reactions due to their lower toxicity and price. Recently, various phosphine-free ligands such as *N*,*N*-dimethylglycine [17], 1,10-phenanthroline [18], 1,4-diazabicyclo[2.2.2]-octane (DABCO) [19], *N*,*N*′-dimethylethylenediamine (DMEDA) [20], 1,1′-binaphthyl-2,2′-diol (rac-BINOL) [21], diamines [22], pyrimidines [23], ß-diketones [24], 8-hydroxyquinoline [25], and salicylic acid [26] have been investigated for this purpose. However, in most of the procedures employed, either a high loading of copper salts or complexes have been used or they have been applicable only to special substrates. Furthermore, the question remains how to activate the less reactive aryl bromides and chlorides for the Sonogashira cross-coupling reactions under phosphine- and palladium-free conditions. Additionally, the copper-catalyzed Sonogashira reactions are conducted using a catalyst produced in situ by mixing the copper salts with excess free ligands. Although these procedures are reasonably beneficial in both the small-scale and process chemistry operations, they suffer from many disadvantages. For instance, an excess amount of ligand frequently stops the activity of the catalytic system, it is not cost-efficient, and it gives rise to a lot of problems in the succeeding purification of the reaction product from the reaction mixture. As a consequence, the establishment of a new catalytic system that is readily available, eco-friendly, easily separable, and mild is still a challenge in modern synthesis.

The heterogeneous metal-supported catalysts have acquired much interest due to their operational benefits in comparison with their homogeneous counterparts [27–29]. Nevertheless, only a few examples of the Sonogashira reactions with heterogeneous copper supported catalysts have been reported in the literature. Rothenberg and co-workers have introduced cross-coupling of aryl halides with alkynes using copper nano-clusters as the catalyst in DMF at 110 °C for 24 h [30]. Biffis et al. [31] have reported copper(II) oxide and copper particles supported on alumina as effective pre-catalysts for the Sonogashira coupling reactions of aryl iodides in toluene at 110 °C. Furthermore, Saha and co-workers have proposed successful Sonogashira reactions of alkynes with cis- and trans-styrenyl bromides catalyzed by a heterogeneous hydroxyapatite-supported Cu(I) catalyst in DMF at 120 °C [32]. Recently, Zhao et al. [33] have reported the Schiff base-pyridine bidentate copper (I) complex anchored onto MCM-41, which shows high reactivity and recyclability in a Sonogashira reaction. Although these procedures all give good product yields, on the one hand, some are sluggish and require at least 24 h and high temperature for completion, and, on the other hand, as mentioned earlier, the reactions have to be conducted in a relatively great quantity of copper.

Boehmite is an aluminum oxide hydroxide (γ-AlOOH) mineral, a constituent of aluminum ore bauxite comprising additional hydroxyl groups on its surface. Among the various techniques used for the production of boehmite nanoparticles (BNPs), the hydrothermal-assisted sol–gel method has some benefits such as production in a one-pot process and processing at low temperatures. The most encouraging property of the hydrothermal-processed BNPs is the development of a highly crystalline single-phase product with no organic residues [34]. Our strategy for the establishment of a multi-purpose heterogeneous catalyst was based upon the notion of immobilizing an organometallic complex onto the BNPs since using the BNPs catalyst frequently provides an increased catalytic activity due to its high surface area.

Recently, Ghorbani et al. [35–37] have reported some heterocyclic synthetic reactions catalyzed by BNPs. Moreover, Mirzaee et al. [38–40] have reported the epoxidation of different olefins using oxosulfate vanadium(IV) and hexacarbonyl molybdenum complexes anchored onto the amine and/or Schiff base functionalized BNPs. We have recently reported the use of unfunctionalized BNPs for the synthesis of highly substituted imidazoles [41] and 3,4-dihydropyrimidin-2-(1*H*)-ones [42]. These results encouraged us to establish an additional application for BNPs toward advanced chemical conversions, particularly the carbon–carbon bond formation reactions.

In continuation of our interest in the generation of new catalysts for the C–C bond formation reactions [43–46], herein we report the synthesis and characterization of the boehmite nanoparticle-anchored Cu(I) diethylenetriamine complex [BNPs-DETA-Cu(I)], and demonstrate its use in the Sonogashira coupling reactions in DMF at 70 °C. This catalyst exhibits a high activity in the coupling reactions of various aryl halides. Moreover, the simplicity of its recovery and its notable recycling effectiveness make it an appropriate system for coupling reactions.

Experimental

General

Materials and methods

Solvents and reagents were supplied from Merck or Fluka and used without any further purification. Gas chromatographic (GC) analyses were performed using an Agilent Technologies 6890N chromatograph equipped with a flame ionization detector (FID). Powder X-ray diffraction (PXRD) patterns were collected on a Philips PW-1800 or STOE diffractometer with Cu Kα radiation. Scanning electron microscopy (SEM) studies were conducted on a MIRA3TESCAN-XMU instrument. Transmission electron microscopy (TEM) was performed using a JEOL JSM-6360LV transmission electron microscope. Brunauer–Emmett–Teller (BET) surface area and porosity of nanoparticles were determined with a micromeritics ASAP 2000 automatic analyser. Thermogravimetric analysis (TGA) curves were recorded using a BAHR STA 503.

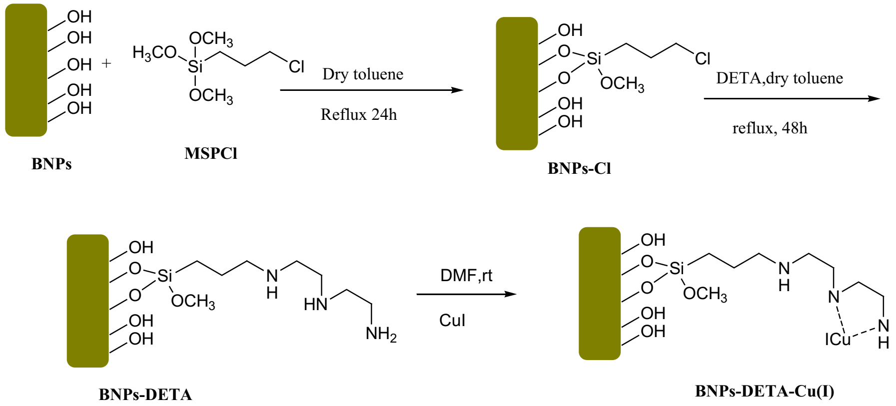
Preparation of catalyst

(a) *Preparation of BNPs* Aluminium 2-butoxide was synthesized from aluminium and 2-butanol according to the general method used for the synthesis of aluminium alkoxides. Aluminium alkoxide thus prepared was vacuum-distilled in order to obtain a high-quality aluminium alkoxide precursor. For the hydrothermal-assisted hydrolysis, according to an earlier report [41], aluminium-2-butoxide (2 M, 10 mL) in 2-butanol was placed in a 300 mL stainless steel autoclave that contained 50 mL deionized water. The autoclave was heated for 5 h at 100 °C in an oven. After cooling the autoclave, the powder produced was filtered off and dried at 100 °C overnight. This powder was used as the catalyst in the organic reactions.

(b) *Preparation of BNPs-Cl* For the preparation of the functionalized BNPs, 1.00 g BNPs was refluxed with MSPCl (400.0 µL, 2.2 mmol) in dry toluene (50.0 mL) for 24 h (Scheme 1). The functionalized BNPs (BNPs-Cl), as a white solid, was filtered off, washed three times with dry toluene, and dried at 100 °C overnight.

(c) *Preparation of BNPs-DETA* 1.00 g BNPs-Cl was refluxed with diethylenetriamine (320 µL, 3 mmol) in dry toluene (50.0 mL) for 48 h (Scheme 1) in order to replace the terminal chlorine atoms. Finally, diethylenetriamine functionalized BNPs (BNPs-DETA) was filtered off, washed three times with dry toluene, and dried at 100 °C.

(d) *Loading with CuI* In a 50 mL round-bottom flask, BNPs-DETA (1.00 g) was mixed with CuI (0.1 g, 1.6 mmol) in DMF (5 mL). The mixture was stirred for 5 h under an N_2 atmosphere at room temperature. Then it was filtered, and the solid obtained was washed with dry toluene and dried at 100 °C overnight to give BNPs-DETA-Cu(I). The copper loading of BNPs-DETA-Cu(I) was 3.2% (0.5 mmol g^{-1}), determined by inductively coupled plasma (ICP).



Scheme 1 Preparation of BNPs-DETA-Cu(I)

Sonogashira coupling reaction

The typical reaction was carried out with a terminal alkyne (1.0 mmol), an aryl halide (1.0 mmol), Et_3N (2.0 mmol), and the catalyst (0.1 g, 0.05 mmol based on Cu) in DMF (3.0 mL). The reaction mixture was stirred for 10 h at 70 °C under an Ar atmosphere. After completion of the reaction, the mixture was filtered to recover the catalyst. The catalyst was washed with dry toluene, vacuum dried, and stored for a new run. After GC analysis, the solvent was removed under vacuum, and the crude product was subjected to silica gel column chromatography using $CHCl_3/CH_3OH$ (97:3) as eluent to afford the pure product.

Catalyst recycling

In a typical experiment, after recovering the catalyst from the reaction mixture under the optimum conditions, it was washed several times with dry toluene, and then used in the same procedure under the same conditions.

Results and discussion

BNPs-DETA-Cu(I) was synthesized as shown in Scheme 1, wherein the first step is the synthesis of BNPs via a hydrothermal-assisted sol–gel process [34]. The second step is the preparation of BNPs-Cl by grafting 3-(tri-methoxy silyl) propyl chloride (MSPCl) on the surface of BNPs by refluxing the mixture of BNPs and MSPCl in dry toluene for 24 h [37].

Elemental analysis shows that the carbon content of BNPs-Cl was 10.25%, which means that 2.1 mmol/g of pending groups were covalently bonded to the surface of 1.00 g BNPs (Table 1). We also determined the loading level of Cl by potentiometric titration of the chlorine content. For this purpose, 0.03 g of the sample was added to 5.0 mL of deionized water and titrated by Ag^+ standard solution using a potentiometer (Model: LT, Lutron, PH-207). The results showed that the loading level of Chlorine was ~ 2.1 mmol g^{-1}. In the third step, the pending chlorine atoms of BNPs-Cl were changed to amine by refluxing with

Table 1 Elemental analysis of BNPs, BNPs-DETA, and BNPs-DETA-Cu(I) samples

Entry	Sample	Analysis	C%	H%	N%	Cu%
1	BNPs	CHN	NF	NF	NF	–
2	BNPs-Cl	CHN	10.25	4.24	–	
3	BNPs-DETA	CHN	29.31	5.49	6.90	–
4	BNPs-DETA-Cu(I)	ICP	–	–	–	3.2
5	BNPs-DETA-Cu(I)	ICP	–	–	–	3.12[a]

NF not found

[a] Recycled catalyst

diethylenetriamine (DETA) in toluene for 48 h to afford BNPs-DETA. The loading amount of the DETA ligand on BNPs was determined by the C, H, and N elemental analysis, which reveals that the DETA loading is around 1.64 mmol/g or near 78% of pending chlorine atoms were changed to DETA by this reaction (Table 1). Finally, BNPs-DETA and CuI were stirred in DMF at room temperature for 5 h to generate the BNPs-immobilized copper(I) complex [BNPs-DETA-Cu(I)]. The loading amount of copper salt was determined by ICP. The details of the analysis data are presented in Table 1, which reveals that the loading of copper is approximately 0.5 mmol/g.

The FT-IR spectra for (a) BNPs, (b) BNPs-Cl, (c) BNPs-DETA, and (d) BNPs-DETA-Cu(I) are shown in Fig. 1. The broad band observed in 3086–3369 cm^{-1} in all samples typically indicates the stretching vibrations of the boehmite surface hydroxyl groups accompanied by a low intensity band in 1073–1155 cm^{-1} due to its bending vibrations. The absorption band at around 1630 cm^{-1} in all samples is due to the adsorbed water molecules. The new bands observed in the ranges of 2864–2932 and 1384–1474 cm^{-1} for BNPs-Cl, BNPs-DETA, and BNPs-DETA-Cu(I) correspond to the CH_2 stretching and bending vibrations, respectively. The newly generated band at 1557 cm^{-1} in BNPs-DETA and BNPs-DETA-Cu(I) corresponds to the N–H bending vibrations in amine grafted groups [47]. The NH_2 stretching vibration in the FT-IR spectrum of these amine-grafted samples should be seen in 3135 cm^{-1} , but it is masked with a broad band for the hydroxyl group stretching vibrations of BNPs in this region.

The PXRD pattern for BNPs confirmed its crystallization as a single-phase boehmite (Fig. 2a). The PXRD patterns for BNPs-DETA and BNPs-DETA-Cu(I) (Fig. 2b, c) confirm the retention of the crystalline structure after the functionalization and metal loading. Calculation of the particle size from the PXRD pattern using the Scherer equation showed 10-nm particles for all the three samples without any change during functionalization and metal loadings. This is confirmed by the transmission electron microscopy images for BNPs and BNPs-DETA-Cu(I) (Fig. 3), which show needle-shaped particles up to 30-nm long and 5-nm

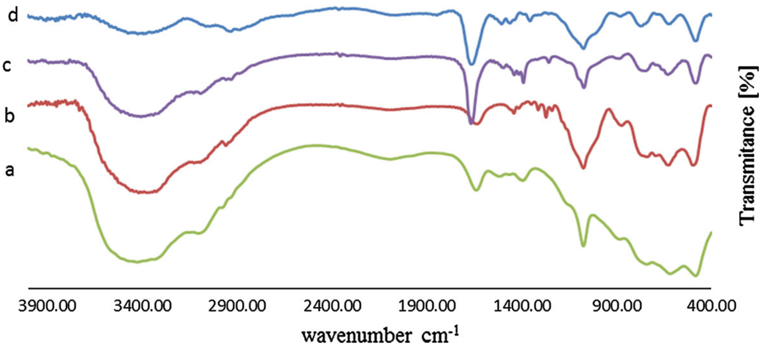


Fig. 1 FT-IR spectra for BNPs (*a*), BNPs-Cl (*b*), BNPs-DETA (*c*), and BNPs-DETA-Cu(I) (*d*)

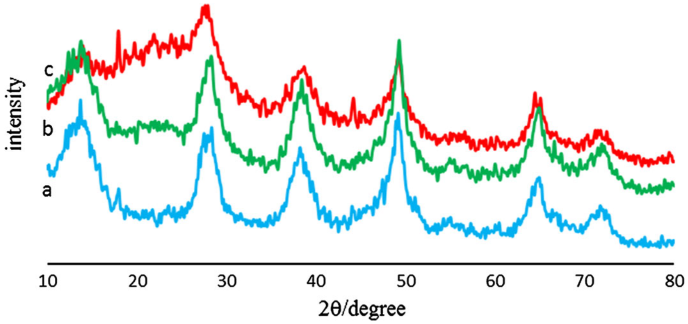


Fig. 2 PXRD patterns for BNPs (*a*), BNPs-DETA (*b*), BNPs-DETA-Cu(I) (*c*)

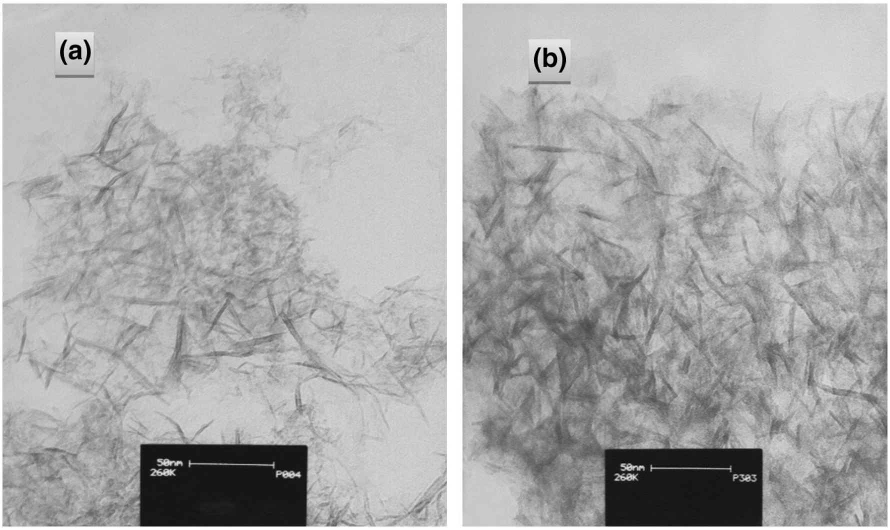


Fig. 3 Transmission electron microscopy (TEM) images for BNPs (**a**) and BNPs-DETA-Cu(I) (**b**)

wide. The surface area of the boehmite nanoparticles was 326 m^2/g, according to the BET experiment.

In order to reveal the surface morphological changes of these samples, the scanning electron microscopy (SEM) studies were engaged. The SEM micrographs for the BNPs and BNPs-DETA-Cu(I) samples are shown in Fig. 4. We were delighted to find that the rod-shaped morphology of BNPs was replicated for the BNPs sample (Fig. 4a). The coagulate particles of BNPs were also seen in the BNPs-DETA-Cu(I) sample (Fig. 4b) but the surface morphology was changed after metal loading. The EDX analysis of BNPs-DETA-Cu(I) (Fig. 5) also confirmed the presence of Cu, I, Al, Si, O, and C atoms on the surface of this sample.

Figure 6 shows the TG/DTA thermogram of the BNPs-DETA-Cu(I) catalyst. There are three important weight-loss regions in the TG curve. The first one is below 100 °C accompanied by an endothermic peak in the DTA curve, which should be related to the

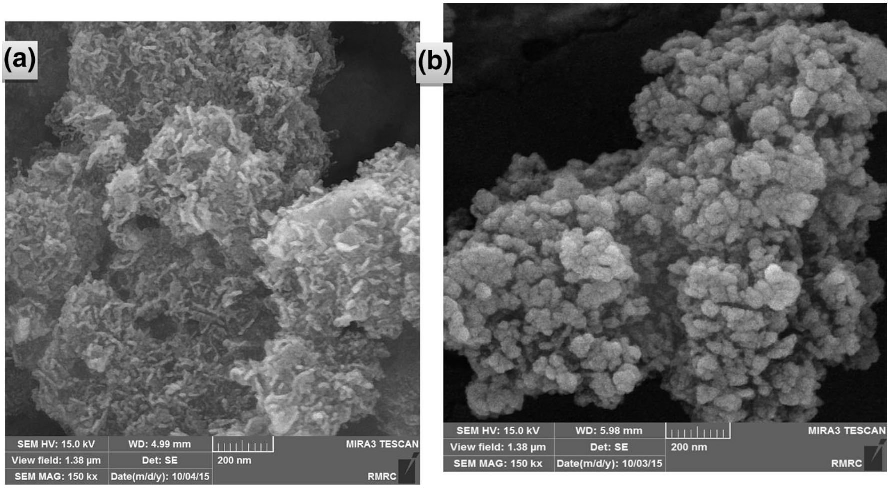


Fig. 4 Scanning electron microscopy (SEM) images for BNPs (**a**) and BNPs-DETA-Cu(I) (**b**)

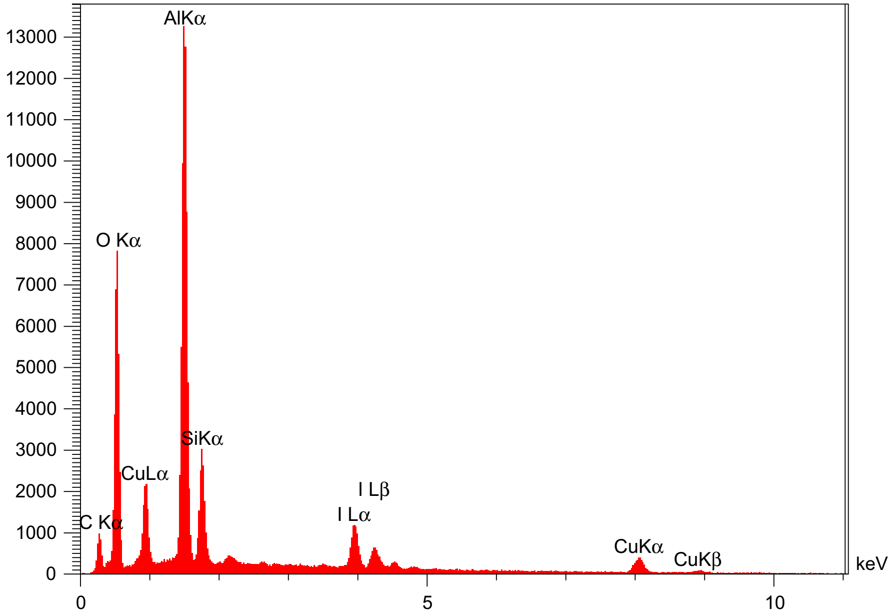


Fig. 5 EDX analysis of BNPs-DETA-Cu(I)

elimination of physically adsorbed water. Another weight loss is in the temperature range of 110–360 °C accompanied by two exothermic peaks in the DTA curve, which may be related to the decomposition of the organic residue anchored onto the surface of BNPs-DETA-Cu(I). The last weight loss was observed in the temperature range of

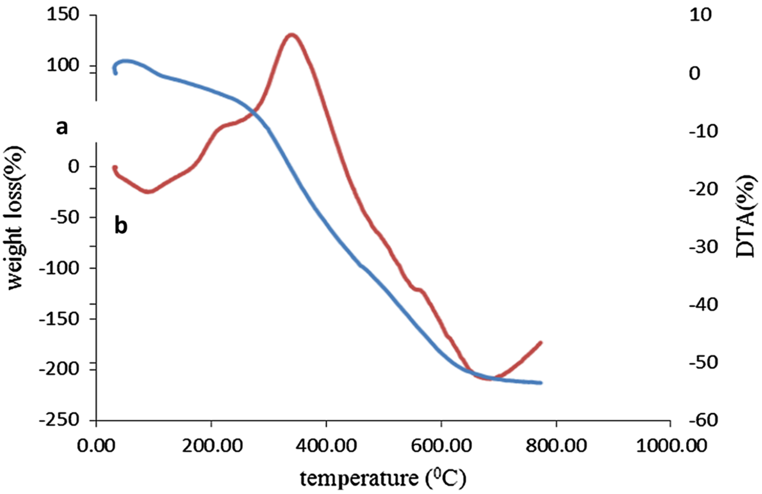


Fig. 6 TG/DTA thermogram of BNPs-DETA-Cu(I) catalyst

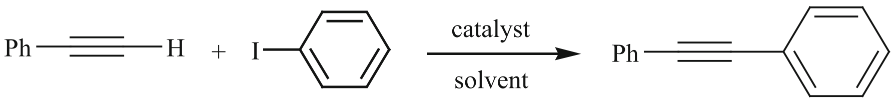
470–560 °C accompanied by another endothermic peak in the DTA curve, which could be related to the dehydroxylation of BNPs and the crystallization of γ-alumina.

Catalytic activity

To test the catalytic activity of BNPs-DETA-Cu(I) in the Sonogashira reaction, the reaction between phenylacetylene and iodobenzene was chosen as a model reaction using 5.0 mol% of the catalyst in DMF at 70 °C under an Ar atmosphere. The influences of different parameters were examined to obtain the best possible combination. The parameters included solvent, base, reaction temperature, and catalyst concentration. As shown in Table 2 (entries 1–4), the coupling reaction yields were susceptible to temperature changes with 5.0 mol% catalyst in DMF. The increase in temperature up to 70 °C led to an excellent yield (95%) after 10 h heating (Table 2, entry 3). Decreasing the loading of the catalyst to 2.0 mol% lowered the yield dramatically (Table 2, entry 5). However, increasing the amount of catalyst to 10 mol% showed no substantial improvement in the yield (Table 2, entry 6).

The effect of various solvents was then investigated. The model reaction was examined in the presence of 5.0 mol% of the catalyst at 70 °C in several solvents including CH_3CN, THF, EtOH, and 1,4-dioxane (Table 2, entries 7–10). Among all these solvents, DMF was found to be the best one, affording the highest yield (Table 2, entry 3). Moreover, when the reaction was carried out under solvent-free conditions, the targeted product was obtained with a low yield (Table 2, entry 11). Our next study focused on the effect of a base on the model reaction. Among the bases examined, Et_3N was found to be the most effective one (Table 2, entry 3). Diisopropyl ethylamine (DIPEA), pyrrolidine, and pyridine also gave good yields (Table 2, entries 12–14), whereas inorganic bases such as Na_2CO_3 and KOH were

Table 2 Investigation of effects of catalyst, solvents, base, and temperature on Sonogashira coupling reactions



1a **2a** **3a**

Entry	Solvent	Base	Catalyst (mol%)	Temp. (°C)	Yield (%)[a]
1	DMF	Et_3N	5	r.t.	Trace
2	DMF	Et_3N	5	50	40
3	DMF	Et_3N	5	70	95
4	DMF	Et_3N	5	90	95
5	DMF	Et_3N	2	70	45
6	DMF	Et_3N	10	70	95
7	CH_3CN	Et_3N	5	70	20
8	THF	Et_3N	5	70	35
9	EtOH	Et_3N	5	70	40
10	1,4-Dioxane	Et_3N	5	70	30
11	–	Et_3N	5	70	25
12	DMF	DIPEA[b]	5	70	80
13	DMF	Pyrrolidine	5	70	85
14	DMF	Pyridine	5	70	83
15	DMF	Piperidine	5	70	65
16	DMF	Cs_2CO_3	5	70	73
17	DMF	K_2CO_3	5	70	68
18	DMF	Na_2CO_3	5	70	55

Table 2 continued

Entry	Solvent	Base	Catalyst (mol%)	Temp. (°C)	Yield (%)[a]
19	DMF	KOH	5	70	35
20[c]	DMF	Et_3N	5	70	NF
21[d]	DMF	Et_3N	5	70	63

Reaction conditions: phenylacetylene (1.0 mmol), phenyl iodide (1.0 mmol), base (2 mmol), solvent (3.0 mL). Reaction time (10 h)

NF not found

[a] GC yield

[b] Diisopropyl ethylamine

[c] In the presence of BNPs

[d] Hot filtration, after 5 h

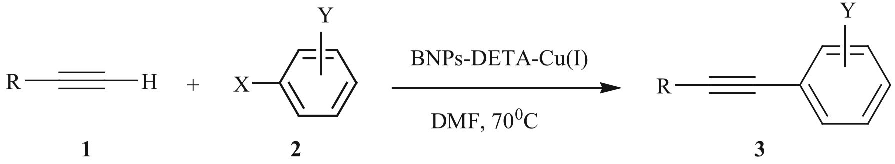
substantially less effective (Table 2, entries 18 and 19). To find out the roles of BNPs and BNPs-DETA-Cu(I) during the Sonogashira coupling reaction, the model reaction was examined in the presence of BNPs. As shown in Table 1, in the presence of BNPs, Sonogashira coupling could not be achieved (Table 2, entry 20). Thus, the optimized reaction conditions for this Sonogashira coupling reaction were BNPs-DETA-Cu(I) (5.0 mol%) in DMF using Et_3N as base at 70 °C under an Ar atmosphere for 10 h (Table 2, entry 3).

Under the optimized reaction conditions, the scope of the reaction was explored with various terminal alkynes and aryl halides. As shown in Table 3, the coupling of phenylacetylene with phenyl iodide took place smoothly at 70 °C in the presence of 5 mol% of the catalyst to give a quantitative yield of diphenylacetylene (entry 1). It could be concluded that aryl iodides bearing an electron-donating or electron-withdrawing group were obtained in high yields. For example, the Sonogashira coupling reaction of phenylacetylene with *p*-nitroiodobenzene, *p*-chloroiodobenzene, *p*-iodo toluene, and *p*-iodoanisol gave the corresponding biarylacetylenes in 97, 96, 92, and 90% yields, respectively (Table 3, entries 2–5). When the less reactive acetylene, 1-hexyne, 1-octyne, and propargyl alcohol were used, the coupling product was produced efficiently. The coupling of para-substituted iodobenzene having nitro, chloro, and methyl groups took place with 1-hexyne or 1-octyne to give the corresponding products in high yields (Table 3, entries 7–9 and 11–13). The coupling reaction of propargyl alcohol with the more reactive electron-withdrawing *p*-nitroiodobenzene gave a good yield (90%) (entry 15). Under the same conditions, the less active electron-rich *p*-iodotoluene produced a lower yield (entry 16).

To extend the scope of our work, we next investigated the coupling of various aryl bromides with terminal alkynes. As expected, aryl iodides were more reactive than aryl bromides, and the substituent effects in the aryl iodides appeared to be less significant than in the aryl bromides. However, as shown in Table 3, a high catalytic activity was observed in the coupling of unactivated aryl bromides such as *p*-nitrobromobenzene (entries 18, 23, 25, and 27), as well as activated *p*-nitroiodobenzene (entries 2, 7, 11, and 15). Although aryl iodides and bromides were found to be effective substrates, unfortunately, this catalyst failed to produce biaryl compounds when chlorobenzene was used as a substrate (Table 3, entries 29 and 30). The low reactivity of chlorides resulted from the strength of the C–Cl bond, whose bond dissociation energy was 96 kcal/mol [48].

We also investigated the recyclability of BNPs-DETA-Cu(I) using the coupling reaction of iodobenzene with phenylacetylene. As shown in Fig. 7, the recovered catalyst was added to the reaction mixture under the same conditions for five cycles without significant losses in the yield and catalytic activity. In addition, copper leaching from the supported catalyst was determined. The copper content (3.12 wt%) of the recovered catalyst remained just about the same as the fresh catalyst, indicating that Cu leaching was negligible (Table 1, entry 4). Hot filtration test was also conducted and confirmed negligible leaching in this catalytic protocol because by removing the catalyst in the middle of reaction progress after 5 h, the reaction stopped and the yield did not raised anymore (Table 2, entry 21). In addition, in this catalytic coupling reaction a single product with high yield was produced which

Table 3 Sonogashira reactions of terminal alkynes with aryl halides



Entry	R	X	Y	Product	Yield (%)[a]
1	Ph	I	Ph	**3a**	95
2	Ph	I	4-NO_2–C_6H_4–	**3b**	97 (94)
3	Ph	I	4-Cl–C_6H_4–	**3c**	96
4	Ph	I	4-CH_3–C_6H_4–	**3d**	92 (90)
5	Ph	I	4-OCH_3–C_6H_4–	**3e**	90
6	*n*-C_4H_9	I	Ph	**3f**	85
7	*n*-C_4H_9	I	4-NO_2–C_6H_4–	**3g**	88
8	*n*-C_4H_9	I	4-Cl–C_6H_4–	**3h**	86 (82)
9	*n*-C_4H_9	I	4-CH_3–C_6H_4–	**3i**	83
10	*n*-C_6H_{13}	I	Ph	**3j**	90
11	*n*-C_6H_{13}	I	4-NO_2–C_6H_4–	**3k**	92
12	*n*-C_6H_{13}	I	4-Cl–C_6H_4–	**3l**	87
13	*n*-C_6H_{13}	I	4-CH3-C6H4-	**3m**	85
14	CH_2OH	I	Ph	**3n**	87
15	CH_2OH	I	4-NO_2–C_6H_4–	**3o**	90 (87)
16	CH_2OH	I	4-CH_3–C_6H_4–	**3p**	85
17	Ph	Br	Ph	**3q**	80
18	Ph	Br	4-NO_2–C_6H_4–	**3r**	88 (85)

Table 3 continued

Entry	R	X	Y	Product	Yield (%)[a]
19	Ph	Br	4-Cl–C_6H_4–	**3s**	90
20	Ph	Br	4-CH_3–C_6H_4–	**3t**	82
21	Ph	Br	4-OCH_3–C_6H_4–	**3u**	85
22	*n*-C_4H_9	Br	Ph	**3v**	88
23	*n*-C_4H_9	Br	4-NO_2–C_6H_4–	**3w**	93 (91)
24	*n*-C_6H_{13}	Br	Ph	**3x**	90
25	*n*-C_6H_{13}	Br	4-NO_2–C_6H_4–	**3y**	95 (92)
26	CH_2OH	Br	Ph	**3z**	82
27	CH_2OH	Br	4-NO_2–C_6H_4–	**3aa**	89
28	CH_2OH	Br	4-CH_3–C_6H_4–	**3ab**	80
29	Ph	Cl	Ph	**3ac**	35
30	Ph	X	Y	**3ad**	40

Numbers in parentheses are isolated yields

Reaction conditions: alkyne (1.0 mmol), aryl halide (1.0 mmol), [BNPs-N-CuI] (0.05 mmol), Et_3N (2.0 mmol), 10 h, 70 °C, Ar atmosphere

[a] GC yield

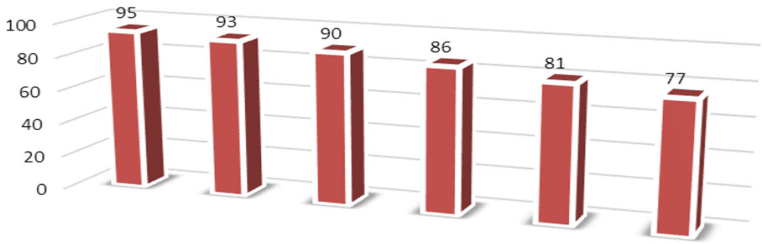
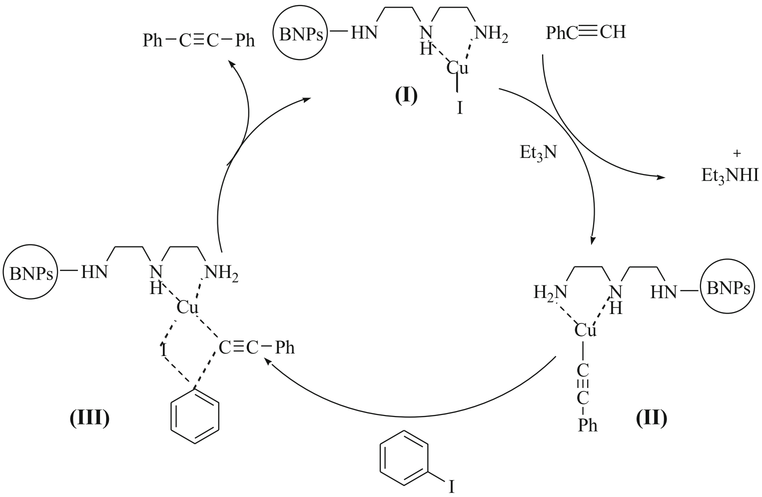


Fig. 7 Synthesis of product **1** catalyzed by recycled catalyst



Scheme 2 Proposed mechanism

along with above results could proposed the presence of static single type active center in this catalytic protocol according to the Eremin, and Ananikov report [49].

We suggest that a terminal alkyne coordinates to the copper (I) species BNPs-DETA-CuI (**I**) to provide a BNPs-immobilized copper acetylide (**II**) under the basic conditions. Then intermediate (**II**) reacts with the aryl halide via a four-centered transition state (**III**) [50] to afford the desired coupling product (**3**) and regenerate BNPs-DETA-CuI (**I**) (Scheme 2).

Conclusion

We described the synthesis and characterization of a novel diethylenetriamine-functionalized-boehmite nanoparticle-supported Cu(I). The catalyst was characterized by various methods including XRD, TEM, SEM, EDX, and FT-IR spectroscopy. The catalytic efficacy of the BNPs-DETA-Cu(I) catalyst was evaluated in Sonogashira coupling reactions, which led to better yields under moderate conditions compared with those given in the literature. Furthermore, aryl iodides and aryl bromides showed high yields, satisfactory in Sonogashira coupling reactions, using this catalyst. The recycling experiments showed that the catalyst could be used for several times without a significant loss in its catalytic activity.

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