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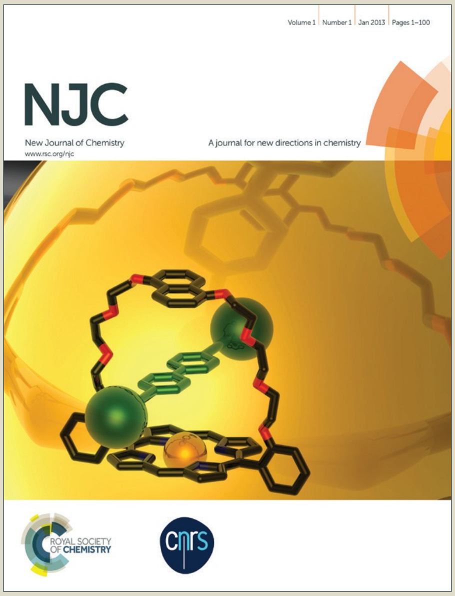

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DABCO-functionalized silica-copper (I) complex: a novel and recyclable heterogeneous nanocatalyst for palladium-free Sonogashira cross-coupling reaction

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DABCO-functionalized silica supported copper(I)-based nanocatalyst was successfully prepared using a novel and simple rout, in which the DABCO as an important functional entity acts as both a stable linker and a excellent chelator. Initially, Cu(II) ions were fixed in DABCO-functionalized SiO_2 matrix via complex formation with *N*-groups of DABCO, subsequently this Cu(II)-DABCO@SiO_2 composite as a precursor reacted with NaI in methanol solvent at room temperature under aerobic conditions to produce the DABCO-functionalized silica-copper (I) complex (catalyst **A**). This catalyst was well characterized by FT-IR, CHN, XRD, FE-SEM, TEM, EDX, ICP-AES and TG analysis, and was found to be efficient and recyclable for C-C bond formation reaction in palladium-free copper-catalyzed Sonogashira coupling of aryl halides with phenylacetylene. Grafted DABCO having a synergistic effect of coordination and electrostatic interactions, plays an important role in this catalyst system and as an effective ligand and a quaternary ammonium salt, demonstrates an efficient stabilizing effect on the Cu(I) species.

Introduction

Metal-catalyzed cross-coupling reactions are one of the challenging areas of research in modern organic synthesis.[1] There are variety of competitive methods for the synthesis of carbon–carbon and carbon–heteroatom bonds including combinations of transition metals and ligands as the efficient catalytic systems. Palladium is the most popular metal used for cross-coupling reactions in both academic and industrial settings,[1, 2] however, in modern organic synthesis, researchers have focused their studies on palladium-free conditions and development of inexpensive transition-metal catalysts such as cobalt,[3] nickel,[4] and copper,[5, 6] with different ligands.

Coupling of aryl halides with terminal acetylenes in Sonogashira reaction is one of the most applicable metal-catalyzed carbon–carbon cross-coupling reactions.[7, 8] Csp2-Csp coupling between aryl halides and terminal aryl- and alkyl-alkynes affords the corresponding substituted internal alkynes, which are extremely valuable intermediates in organic synthesis and the building blocks of a wide range of pharmaceuticals, natural products and biologically active molecules.[8-10]

Recently, many studies have been conducted toward employing copper-only catalytic systems in coupling reactions, in particular, for Sonogashira-type couplings[11] A number of copper-based catalytic systems have been proposed, including bis(μ-iodo)bis((-)-sparteine)dicopper(I) catalyst,[12] Cu(I)/amino acid,[13] CuI/dabco,[14] CuCl/N-Benzyl DABCO,[11] CuCl/monobenzyl nicotinium[15] and Cu(I)/diamine.[16]

It should be noted that the above reaction has been performed in a homogeneous media. Although the catalytic activity of homogeneous catalysts is higher compared to heterogeneous catalyst, the reaction in a homogeneous phase has many problems such as separation and purification of the target product from the reaction mixture, thermal sensitive, high toxicity, difficult and expensive recovery for reuse of the catalyst.[17, 18] These problems bring serious damage to the environment and costly for the industry. Additionally, leaching the metal to the products and contamination of product with ligands is always one of the most important problems of homogeneous catalysts. In contrast, Pd catalyst immobilized on a support can be easily separated from reaction media through centrifuge or simple filtration and successfully reused.[19] The solid-supported catalysts produce a heterogeneous catalyst and improve catalyst stability, which have newly attracted much interest owing to the increasing environmental concern.[20] Supported catalysts are manufactured by reacting a functionalized support with available and suitable functional groups on the catalyst atoms. Numerous methodologies have been reported for the modification of various supports.[18, 21, 22]

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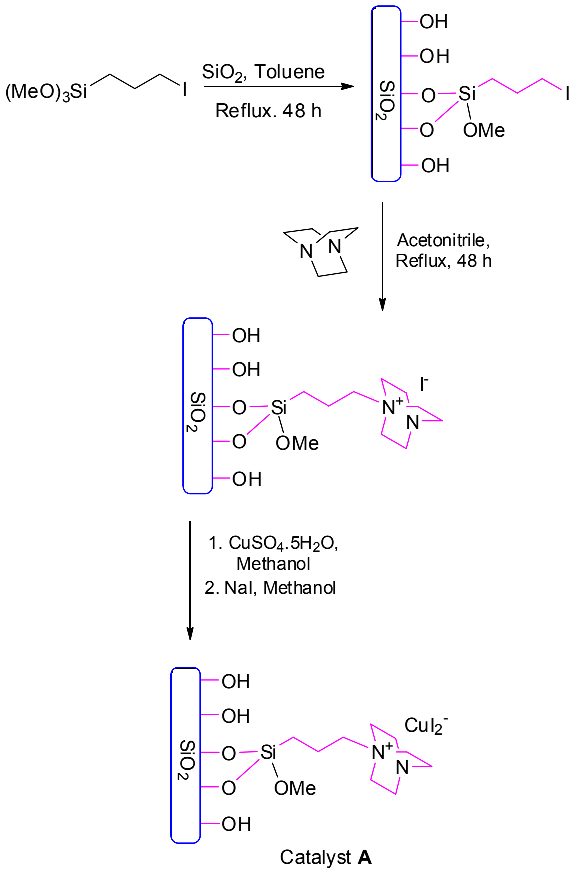
Heterogeneous catalysts provides large enough surface for the reaction using various substrates such as silica, [23, 24] polymers, [25, 26] alumina, [27, 28] zeolites, [29, 30] carbon nanotube [31-34] and etc. The stabilizers are generally chosen consistent with nature of metallic species and reaction media. Ligands,[37, 38] polymers,[39, 40], ionic liquids (ILs)[33, 41, 42] and dendrimers[23] have been developed as common metal-stabilizers in literature, in which the metallic species have been immobilized by coordination, electrostatic, steric or their synergetic interactions.

The development of a new catalytic system that is eco-friendly, available, mild and easily separable was useful. Our goal is the development of a range of efficient and green copper-based catalysts for cross-coupling reactions.

In continuation of our recent investigations on the synthesis and applications of efficient and eco-friendly green solid catalysts,[25, 43-45] herein, we prepared a silica supported copper (I) catalyst in which 1,4-diazabicyclo[2,2,2]octane (DABCO) was used as a stabilizer and immobilizer ligand. This copper-catalyst was found to be an efficient and recyclable nanocatalyst for Sonogashira coupling of aryl halides with phenylacetylene giving quantitative yields.



Scheme 1. Synthesis process of Cu(I)-DABCO@SiO_2 (catalyst **A**)

Results and Discussion

Preparation and characterization of the catalyst A

The DABCO was grafted on the surface of silica according to our previous work.[43] First, 3-iodopropyl trimethoxysilane reacts with activated silica gel in dry toluene. Then, the modified silica treated with DABCO in acetonitrile solvent to obtain the silica-DABCO support.

In the FT-IR spectrum depicted in Fig 1, the characteristic peaks of C–H stretching (2958, 2900 cm^{-1}), CH_2 bending (1465 cm^{-1}), C–N (1390 cm^{-1}) and Si–O stretching (1050, 1110 cm^{-1}) vibrations are assignable for the DABCO@SiO_2.

The presence of the organic phase in the silica-support was also confirmed by elemental analysis (EA). The amount of DABCO-ligand grafted onto the surface of silica was determined by EA based on the nitrogen content, and were found to be 0.35 $mmolg^{-1}$.

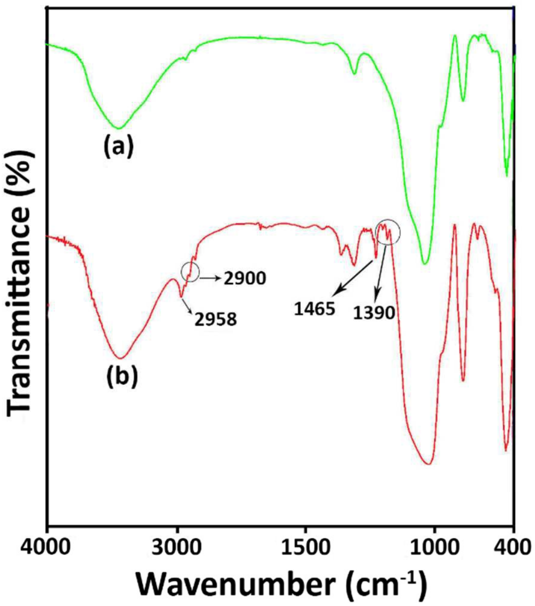


Fig 1. FTIR spectra of SiO_2 (a) and DABCO@SiO_2 (b).

The production process of CuI onto the silica-DABCO support was performed according to the following reaction.[46]

$$2Cu^{2+} + 4I^{-} \rightarrow 2CuI + I_2$$

At first, the Cu^{2+} ions were immobilized onto the silica-DABCO support, wherein a light green solid was produced. Then, the resulting solid was treated with NaI in methanol solvent. During this process, the colour of mixture changed to yellow. This colour change indicates that the Cu^{2+} ions have successfully reacted with NaI and can be attributed to the production of I_2 in the reaction mixture.

Here, the reduction stage takes place onto the SiO_2 surface, and the copper(II) ions which are chelating with *N*-groups of DABCO grafted on silica are reduced and therefore, a

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composite of DABCO-functionalized silica with CuI species is formed.

The copper content of final solid product was analyzed by the inductively coupled plasma atomic emission spectroscopy (ICP-AES) that was obtained about 9%.

As shown in Fig. 2, the XRD pattern of as-prepared Cu(I)-DABCO@SiO_2 composite indicates diffractions of CuI particles, containing several peaks that are clearly distinguishable and all of them can be perfectly indexed to crystalline CuI particles. The peak positions are in good agreement with those for CuI crystals reported in references (JCPDS card No. 83-1105). These results confirm that Cu(II) ions in the precursor have successfully been reduced to crystalline CuI particles embedded in silica-DABCO matrix.

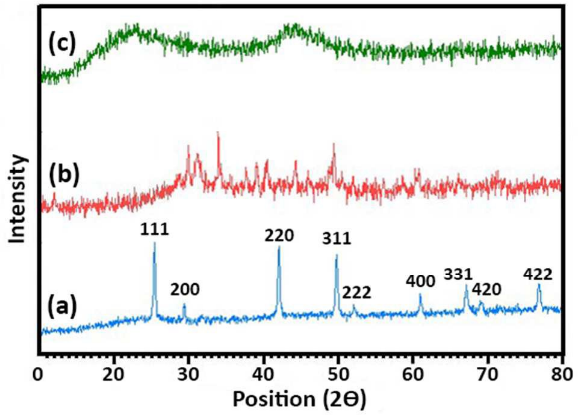

Fig 2. XRD pattern of the fresh catalyst **A** (a), the recovered catalyst **A** after third cycle (b) and the reactivate catalyst A after the treatment with NaI.

The surface morphology of catalyst **A** was studied using field emission scanning electron microscopy (FE-SEM). As can be seen in Fig 3, the FE-SEM micrographs clearly show the distribution of particles in the surface of catalyst. By the EDX analysis, the presence of copper, nitrogen and iodide in the catalyst composite was also proved (Fig 3B).

In this catalyst system, the DABCO grafted on silica surface as a quaternary ammonium salt containing a coordinating center, plays an important role and increases the stability of Cu(I) non stable species during the production process. The immobilized Cu(I) species are stabilized by synergistic effect of coordination and electrostatic interactions.

Coordination bonds with *N*-groups of grafted DABCO and also electrostatic interactions with quaternary salt section prevent the aggregation of CuI particles in the catalyst network.

Fig 4 depicts the TEM (Transmission Electron Microscopy) images of the catalyst **A**. TEM micrographs show clearly the distribution of particles and confirm that nano-sized particles have been well dispersed in the catalyst matrix. The black spots and translucent parts show nanoparticles and DABCO-SiO_2 support, respectively.

To investigate the thermal stability, thermo gravimetric analysis (TGA) of catalyst **A** was measured between 25-800 °C under nitrogenous atmosphere at a heating rate of 10 °C/min. As shown in Fig 5, the first mass loss, at around 100 °C, was probably due to the elimination of water molecules adsorbed onto the surface of silica material. The second phase of weight loss occurred between 330-480 °C, and then has a mild mass loss till 750 °C. These results indicate that the thermal stability of the catalyst **A** is considerable and catalyst is stable up to 300 °C.

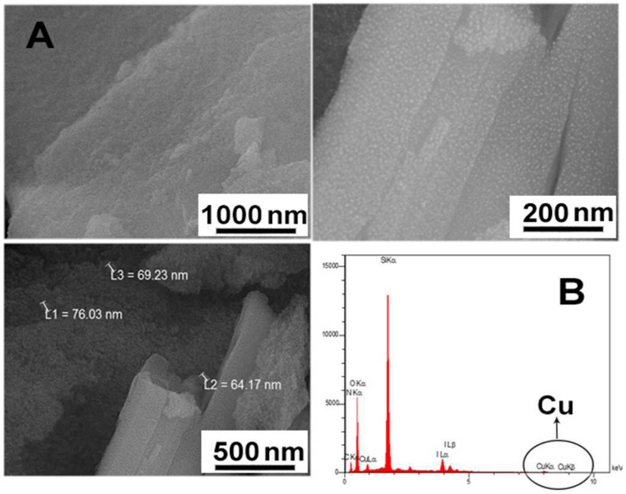

Fig 3. FE-SEM images and SEM-EDX spectrum of catalyst A.

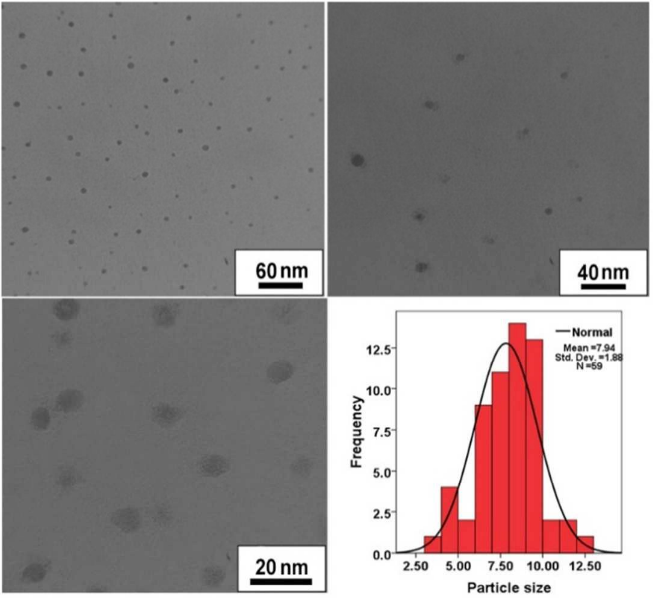

Fig 4. TEM images of catalyst **A**.

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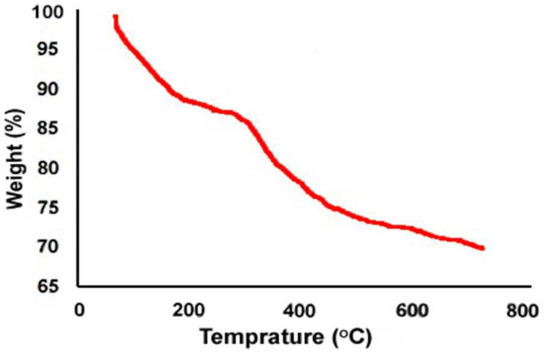

Fig 5. TGA analysis of the catalyst **A**.

Catalytic activity

The efficiency of this catalyst was evaluated in Sonogashira cross-coupling reactions of aryl halides with phenylacetylene. In order to optimize the reaction conditions, we examined the effect of various reaction parameters such as solvent, base, and temperature on the yields and reaction times of a series of screening experiments carried out for the cross-coupling of 4-iodoanisole with phenylacetylene as a model reaction (Table 1).

Table1. Optimization of the reaction conditions for the Sonogashira cross-coupling reaction.[a,b]

Entry	Catalyst [mol%]	Solvent	*T* [°C]	Base	*t* [h]	Yield [%]
1	-	DMF	135	K_2CO_3	6	-
2	DABCO@SiO_2	DMF	135	K_2CO_3	6	-
3	Cu(II)-DABCO@SiO_2 [10 mol %]	DMF	135	K_2CO_3	6	Trace
4	Cat **C** [10 mol %][c]	DMF	135	K_2CO_3	6	25
5	Cat **A** [10 mol %]	DMF	135	K_2CO_3	2	83
6	Cat **A** [10 mol %]	H_2O	100	K_2CO_3	6	-
7	Cat **A** [10 mol %]	EtOH	80	K_2CO_3	6	-
8	Cat **A** [10 mol %]	MeCN	80	K_2CO_3	6	-
9	Cat **A** [10 mol %]	PEG	135	K_2CO_3	5	60
10	Cat **A** [10 mol %]	DMSO	135	K_2CO_3	4	71
11	Cat **A** [10 mol %]	DMF	80	K_2CO_3	4	Trace
12	Cat **A** [10 mol %]	DMF	100	K_2CO_3	4	25
13	Cat **A** [10 mol %]	DMF	120	K_2CO_3	4	56
14	Cat **A** [10 mol %]	DMF	135	K_3PO_4	2	74
15	Cat **A** [10 mol %]	DMF	135	Li_2CO_3	2	57
16	**Cat A [10 mol %]**	**DMF**	**135**	**KOH**	**2**	**93**
17	Cat **A** [5 mol %]	DMF	135	KOH	2	73
18	Cat **A** [15 mol %]	DMF	135	KOH	2	95

[a] Reaction conditions: 4-iodoanisole (0.1 mmol), phenylacetylene (0.11 mmol), base (2 eq.), solvent (2 mL) under N_2 atmosphere. [b] GC yield. [c]CuI salt was directly grafted onto the DABCO@SiO_2 support.

Among the different solvents tested such as H_2O, Ethanol, MeCN, DMF, PEG, and DMSO, DMF gave the best result. Screening of different bases such as K_3PO_4, K_2CO_3, KOH, and Li_2CO_3 revealed KOH as the most effective base. Temperature showed a critical role in this catalytic system. The yield of the model reaction increased when the reaction was conducted at 135 °C.

We also optimized the catalyst loading, employing various amounts of catalyst for the cross-coupling reaction. The best result was obtained when the model reaction was carried out with 10 mol% of the catalyst. The results showed that the optimized conditions were as follows: DMF solvent, KOH as the base, 135 °C (Table 1, entry 16).

As shown in Table 1 (entry 3), efficiency of Cu(II)-DABCO@SiO_2 (Cat B) as catalyst was also investigated in this reaction system. It was found that treatment of 4-iodoanisole with phenylacetylene under optimized reaction conditions afforded only trace amount of the corresponding Sonogashira product. This result implied that Cu(I) species or related complexes play a key role in the catalytic cycle and serve as the active catalyst.

To obtain more information on the effects of the methodology used for catalyst preparation on the catalytic activity, the CuI was directly grafted onto the DABCO@SiO_2 support such that the CuI salt reacted with DABCO@SiO_2 in DMF solvent at room temperature (Cat. C). The activity of the obtained catalyst in this method was examined using of 4-iodoanisole with phenylacetylene as model reaction under the optimized conditions, and the corresponding coupled product was obtained only in 25% yield after 6 h (Table 1, entry 4).

After optimizing the reaction conditions, the catalyst **A** was applied to the Sonogashira coupling of various aryl halides with phenylacetylene (Table 2). The corresponding alkyne products were produced in moderate to excellent yields. The electronic and steric effects on the yields and reaction times was examined in this reaction system. This catalyst was compatible with a wide range of functional groups such as nitro, cyano, methoxy and carbonyl on the aryl halides.

Aryl halides substituted with electron-withdrawing groups in comparison with electron-donating substituents gave better conversions in shorter reaction times.

As can be seen in Table 2, all aryl iodides were rapidly converted to the corresponding Sonogashira products in

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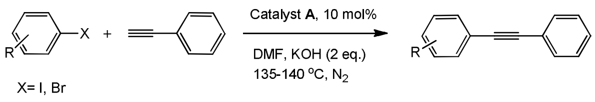
Table 2. Sonogashira cross coupling of various aryl halides in the presence of catalyst **A**[a,b]



Entry	R	X	Time (h)	Yield (%)
1	4-MeO	I	2	93
2	4-CN	I	2	95
3	H	I	2	94
4	4-NO_2	I	2	98
5	3-NO_2	I	2	98
6	4-MeCO	I	2	97
7	4-Me	I	2	95
8	3-Me	I	2	94
9	H	Br	6	40
10	4-Br	Br	6	55
11	4-CHO	Br	6	60
12	4-NO_2	Br	6	65
13	4-CN	Br	6	53
14	4-MeCO	Br	6	58
15	4-MeO	Br	6	-
16	4-CN	Cl	12	-
17	4-NO_2	Cl	12	-

[a] Reaction conditions: aryl halide (1 mmol), phenylacetylene (1.1 mmol), KOH (2 eq) and DMF (3 mL). [b] GC yield.

excellent yields. The reactivity of aryl bromides was lower than that of the aryl iodides and they required longer times giving lower yields. Aryl chlorides were inactive in this reaction system.

Reusability of the Catalyst A

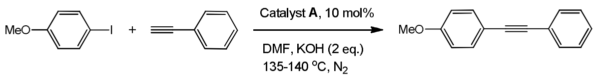
The recyclability of catalyst is an important topic in the green heterogeneous catalysis research that is commonly attributed to its stability. We examined the possibility of recovery and reuse of the catalyst **A** using the Sonogashira reaction between phenylacetylene and 4-iodoanisole as the substrates under optimized reaction conditions.

A series of reactions were carried out in order to investigate the catalyst reusability. At first, this study was done in accordance with conventional methods reported in the literature. In this method, after each run, the catalyst was separated by centrifugation from the reaction mixture, washed with methanol, dried at room temperature and then used directly for the next cycle. The results showed that the recovered catalyst could be reused only for 3 times with major decrease in catalytic activity (Table 3-A). Fig 2 (b) demonstrates XRD pattern of the catalyst **A** recovered from the third cycles. Based on this XRD analysis, the crystal structure of CuI particles in the catalyst **A** has been destroyed after using in the reaction system.

As discussed earlier, the Cu(I) species are active catalytic sites in this reaction system, hence, to increase the ability of recovery and recyclability of the catalyst A, it is necessary to re-produce the active Cu(I) species in the recovered catalyst. For this, the catalyst which was separated by centrifugation from the reaction mixture after each run, washed with methanol, dried at room temperature and then was treated with NaI in methanol solvent at room temperature for 5 h. Afterward, the resulting solid was separated, washed with methanol, dried at room temperature and reused for the next catalytic cycle. As seen in the Table 3, the efficiency of reactivate catalyst was significantly improved by this method (Table 3 B). We also characterized the reused catalyst after the reactivation treatment by XRD analysis. As shown in Fig 2 (c), an X-ray amorphous pattern was observed in this case, which is probably due to the destroyed-crystal structure and the size distribution of CuI nanoparticles in the reactivate catalyst.

The TEM images of recovered catalyst A were also investigated. As shown in Fig 6, TEM micrographs indicate that the nano-sized particles have been well distributed in the recovered catalyst, and therefore, it can be realize that the nano-sized particles in the catalyst **A** was preserved after using in the reaction media.

Table 3. The reusability results for catalyst **A**



Method A[a]			Method B[b]		
Run	Time (h)	Yield (%)	Run	Time (h)	Yield (%)
1	2	93	1	2	93
2	2	75	2	2	90
3	2.5	55	3	2.5	86
4	2.5	25	4	2.5	80
5	3	-	5	3	78

[a] In method A, after each reaction-run, the catalyst was separated by centrifugation from the reaction mixture, washed, dried and then, used directly for the next cycle.

[b] In method B, after each run, the catalyst which was separated by centrifugation from the reaction mixture was re-activated via reaction with NaI and then, washed, dried and reused for the next catalytic cycle.

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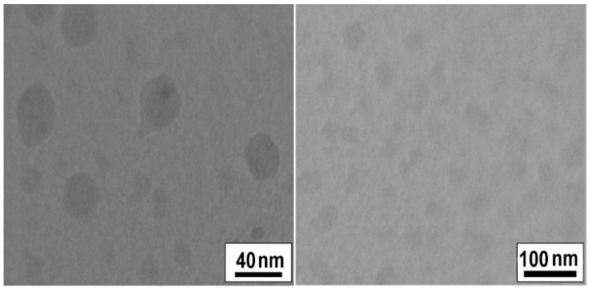

Fig 6. TEM of recovered catalyst **A**.

The present catalytic method was compared with some procedures published for the Sonogashira reaction of 4-iodoanisole with phenylboronic acid in literatures, and the results have been shown in Table 4. Evidently, the reaction conditions are different, but the most important benefits of this study are contributed to the advantages of heterogeneous catalysis such as easy separation, efficient recycling, minimization of metal contamination and low cost.

Table 4. Comparison of catalytic activities with literature examples for the Sonogashira reaction between 4-iodoanisole and phenylacetylene

Entry	Catalyst [ref]	Reaction conditions	Yield (%)
1	[N-Benzyl DABCO][Cu_4Cl_5][11]	DMF / 135 °C / K_2CO_3/ 4.5 h/ N_2	90
2	Cu_2I_2((-)-sparteine)$_2$[12]	DMF / 110 °C / Cs_2CO_3/ 6 h/ N_2	97
3	CuI/DABCO[14]	DMF / 135 °C / Cs_2CO_3/ 6 h/ N_2	98
4	[Monobenzyl nicotinium][Cu_4Cl_5][15]	DMF / 140 °C / $K_3PO_4.3H_2O$/ 8 h/ N_2	88
5	Cu(I)/diamine[16]	dioxane / 100 °C / K_2CO_3/ 24 h	76
6	Present Catalyst	DMF / 135 °C / KOH/ 2 h/ N_2	93

To date, several mechanisms for copper-catalyzed Sonogashira coupling reactions have been proposed in the literatures.

Monnier et al [47] have reported a Cu(I)/Cu(III) mechanistic pathway via an oxidative addition/reductive elimination catalytic cycle, in which a four coordinate Cu(III) intermediate undergoes reductive elimination to expel the coupled product.

Another mechanism has been reported by Bolm et al [48] in which the coupling reaction may proceed by a concerted breaking of the aryl halide bond and formation of the new C-C bond.

Conclusions

In summary, we successfully developed the inexpensive and heterogeneous catalytic system DABCO-functionalized silica-grafted CuI nanoparticles (catalyst **A**) for the Sonogashira cross-coupling reactions of various aryl halides with phenylacetylene. The Cu(II) ions were initially fixed in the DABCO-functionalized silica, then reacted with NaI as a reducing agent to afford the CuI species which have immobilized as nano-scale in the silica matrix. This nanocatalyst was found to be efficient in the Sonogashira reaction system and could be successfully recovered from the reaction mixture.

Experimental

Preparation of DABCO functionalized-silica (DABCO@SiO_2)

3-iodopropyl@SiO_2 was synthesized by the method described in our previous work.[43] At first, the silica was activated by immersing SiO_2-gel (150–230 mesh; 5 g) in concentrated HCl for 24 h to hydrolyze the surface Si–O–Si bonds to Si–OH, and then washed with deionized water several times and dried at 120 °C for 10 h. The fresh activated silica (2 g) was suspended in a solution of 3-iodopropyl trimethoxysilane (1.96 ml, 10 mmol) in toluene, and the reaction mixture was refluxed under N_2 for 48 h. After cooling to room temperature, the mixture was diluted with toluene, and the solid particles were collected by filtration and washed thoroughly with toluene and acetone and dried under vacuum at 60 °C to obtain 3-iodopropyl@SiO_2.

The as-prepared 3-iodopropyl@SiO_2 (1.0 g) was suspended in 30 mL of acetonitrile and then, DABCO (1.0 g, 9 mmol) was added. The mixture was refluxed for 24 h. After cooling, the reaction mixture was filtered and washed several times with acetone, and methanol and dried in vacuum to afford DABCO@SiO_2 as a white powder. The successful attachment of DABCO group onto the surface of silica was confirmed according to FT-IR spectra.

Preparation of catalyst A

The as-prepared DABCO@SiO_2 (0.5 g) was dispersed in 15 ml methanol by sonication at room temperature for 15 min. In another beaker, a solution of $CuSO_4.5H_2O$ (0.125 g in 15 mL methanol) was prepared and this solution was added dropwise into the above suspension under stirring. The mixture was stirred at room temperature for 5 h.

Then, the reaction mixture was centrifuged (6000 rpm) and the resulting solid washed with methanol several times to remove impurities and dried. A light green product was obtained in this step that this colour-change confirms the immobilization of Cu^{2+} ions onto the surface of DABCO@SiO_2 support.

In the next stage, the obtained light green solid (Cu(II)-DABCO@SiO_2) was dispersed in 15 mL methanol by stirring at room temperature and a solution of NaI (1.5 mmol in 15 mL methanol) was added dropwise into this mixture under

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stirring. The reaction mixture was stirred at room temperature for 5 h. During this process, the colour of the mixture changed to light yellow. Afterward, the solid product was isolated by centrifugation and washed with methanol several times to remove impurities and dried at room temperature. The production of CuI particles onto the DABCO@SiO_2 support was confirmed by XRD analysis of the final product.

General process for sonogashira cross-coupling reaction

Aryl halide (1 mmol), phenylacetylene (1.1 mmol, 0.11 ml), KOH (2 mmol, 0.112 g), DMF (3 mL) and 10 mol % of catalyst A were mixed in a round bottom flask equipped with a condenser under N_2 atmosphere. The mixture was heated in an oil bath at 135-140 °C and followed by gas chromatography (GC) and thin-layer chromatography (TLC). After the reaction was complete, or when the progress of the reaction had stopped, the cooled resulting mixture was diluted by adding with EtOAC and H_2O. The coupled product was extracted with EtOAc and the organic phase was dried over $CaCl_2$, filtered and concentrated. The residue could be purified by silica gel column chromatography (hexane:EtOAc). The arylalkyne products were known compounds and were characterized by ^{1}H NMR, ^{13}C NMR and FTIR.

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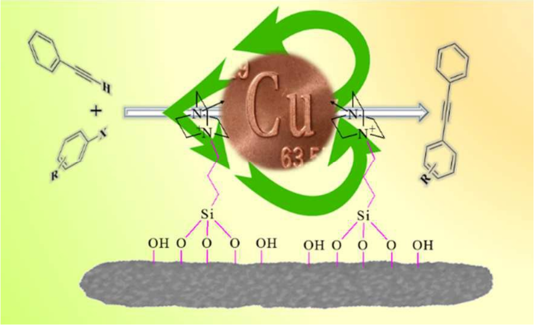
Graphical Abstract



Nano-CuI stabilized in functionalized-DABCO silica matrix was prepared, characterized and evaluated as a new heterogeneous nanocatalyst in copper-catalyzed Sonogashira coupling