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Triazole-Functionalized Silica Supported Palladium(II) Complex: A Novel and Highly Active Heterogeneous Nano-catalyst for C–C Coupling Reactions in Aqueous Media

Abdol Reza Hajipour[1,2] · **Fatemeh Mohammadsaleh**[1]

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Abstract

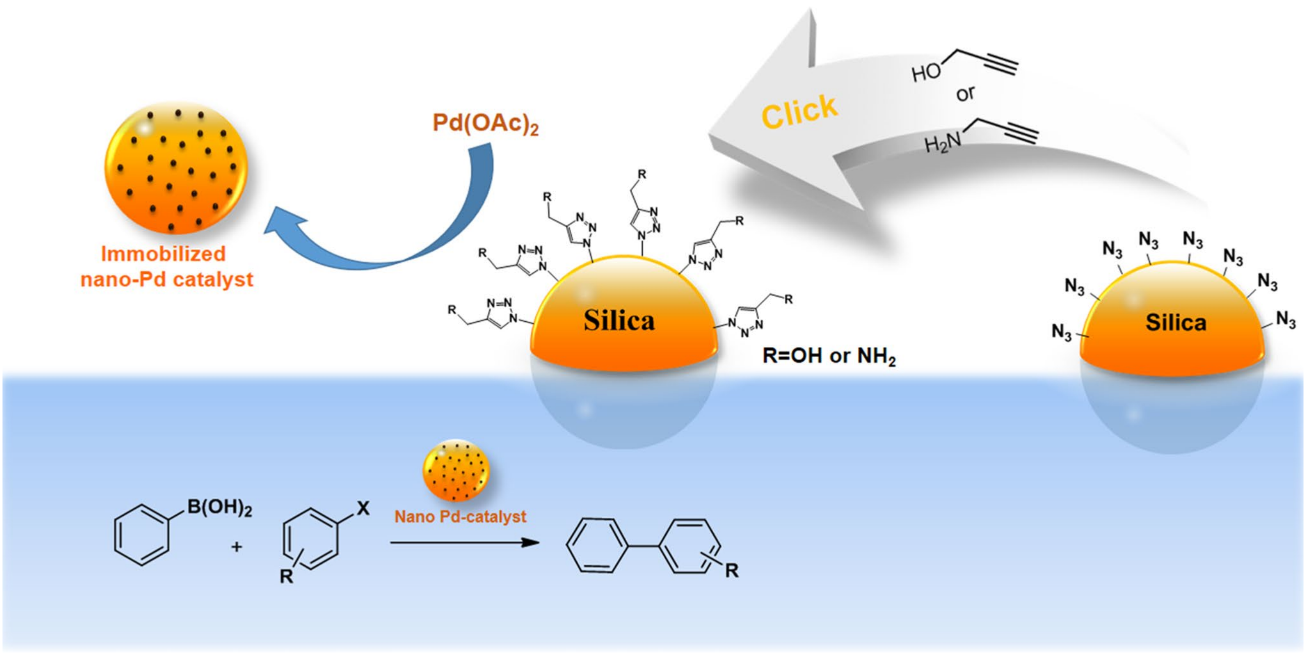
Two novel triazole-modified silica supports A and B were successfully prepared via "click" reaction of azide-functionalized SiO_2 with propargyl alcohol (A) and propargyl amine (B), in which the click-triazole as an important functional entity, in addition to a molecular linker, provides capabilities of metal coordination as an excellent chelator. Treatment of the resulting click-supports with $Pd(OAc)_2$ afforded the click-catalysts A and B, which were well characterized and evaluated in Suzuki–Miyaura coupling in terms of activity and recyclability in H_2O/EtOH solvent. The catalyst A showed more reasonable results and so, was applied as a highly efficient and recyclable catalyst in the coupling reactions of various aryl halides with phenylboronic acid under phosphine-free and low Pd loading conditions.

Graphical Abstract

Two novel nano pd-catalysts were successfully prepared by immobilization of $Pd(OAc)_2$ onto the silica supports containing the nitrogen-rich triazole chelators and were investigated in Suzuki–Miyaura coupling in aqueous solvent.

Electronic supplementary material The online version of this article (https://doi.org/10.1007/s10562-018-2316-5) contains supplementary material, which is available to authorized users.

Extended author information available on the last page of the article



Keywords Heterogeneous catalysis · Click chemistry · Triazoles · Coupling reaction

1 Introduction

The copper(I)-catalyzed azide–alkyne 1,3-dipolar cycloaddition (CuAAC) reaction known as a highly useful example of "click chemistry", which has been proved to be a powerful synthetic tool in molecular conjugation chemistry [1–8].

1,2,3-Triazoles are nowadays an important class of *N*-heterocyclic compounds, which have shown numerous applications in all aspects of bioconjugation, drug discovery, and materials science [9–11]. This nitrogen-rich unit has a large dipole moment, and in the recent years, different studies have shown that 1,2,3-triazoles are able to coordinate a metal center as the ligand [12, 13]. Such property make an important role for triazoles in the catalysis field, especially in metal-based catalysis. The clicked 1,2,3-triazole as the *N*-donor ligand can form chelates with metal ions and stabilize catalytic sites. Recently, some researchers have demonstrated the coordination of metal ions with the 1,2,3-triazolyl group via the nitrogen atoms in single-crystal structures [12, 14–19]. Figure 1 shows some examples using 1,2,3-triazole-derived ligands reported by other groups.

Scrivanti et al. synthesized the triazole ligand **1** for the palladium-catalyzed Suzuki–Miyaura coupling reactions [15]. A variety of triazole-based N4 tetradenate ligands **2** was reported by Hao and Wang [16], and Mn(II) complexes containing these ligands showed efficient catalytic activities in the epoxidation of various aliphatic terminal olefins with peracetic acid. Astruc et al. designed 2-pyridyl-1,2,3-triazole ligands **3** that were powerful stabilizing ligands for palladium-catalyzed C–C coupling reactions [20]. Messerle et al. prepared two new bidentate pyrazolyl–triazolyl donor ligands **4** and investigated the catalytic activity of rhodium(I) and iridium(I) complexes containing these N–N′ ligands for the intramolecular cyclization of alkenamines and nonterminal alkynamines [21].

Metal-catalyzed cross-coupling reactions are one of the challenging areas of research in modern organic synthesis [22, 23]. There are variety of competitive methods for the synthesis of carbon–carbon and carbon–heteroatom bonds

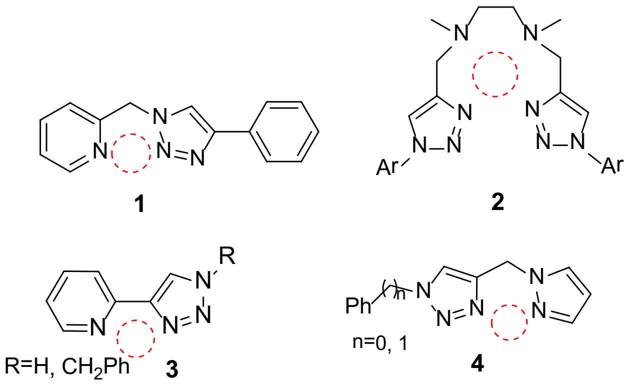


Fig. 1 Examples of 1,2,3-triazolyl ligands used in metal catalysis

including combinations of transition metals and ligands as the efficient catalytic systems [24]. The palladium-catalyzed coupling reactions are ranked nowadays among the most general transformations in organic synthesis, which have great applications in both academic and industrial settings [25]. In traditional protocols, catalysts used in these reactions are based on homogeneous palladium complexes [26]. Although these homogeneous catalysts have many advantages, they have some significant limitations in terms of the separation and recycling. In view of modern organic synthesis, the non-renewable use of expensive palladium catalysts is less constructive, in particular, for industrial scale synthesis. Additionally, leaching the metal to the products and contamination of product with ligands is always one of the most important problems of these catalysts. In contrast, Pd catalyst immobilized on a support can be easily separated from reaction media through centrifuge or simple filtration and successfully reused [27–29]. The solid-supported catalysts produce a heterogeneous catalyst and improve catalyst stability, which have newly attracted much interest owing to the increasing environmental concern [30]. 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 surface [31, 32].

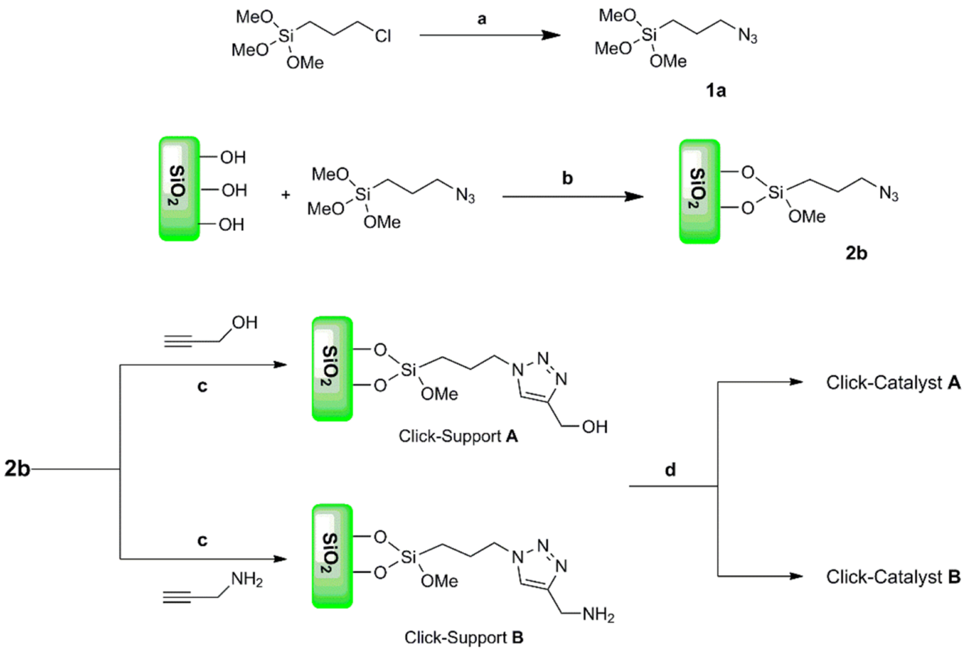
"Click" chemistry-based surface modification has recently received much attention, especially in the design of metal based heterogeneous catalysts [20, 33–35]. Some researcher groups have successively modified the surface of various solid supports via the "click" rout [36]. The 1,2,3-triazole grafted on this supports, as an important functional unit, in addition to a molecular linker, could provide capabilities of hydrogen bonding as both a donor and an acceptor, metal coordination, and π–π interactions in this click-modified supports [13]. This nitrogen-rich heterocyclic compound, has drawn considerable attention for the catalyst immobilization as a highly stable linker or/and a chelator to graft catalysts onto the supports. Ding and co-workers have reported a SBA-15-supported palladium catalyst containing a triazole framework via the click reaction, and its application for the aerobic oxidation of alcohols [33]. Luo et al. have successfully prepared a magnetic nanoparticle-supported nano-palladium catalyst via a "click" route [34]. They evaluated the efficiency of this catalyst in Suzuki–Miyaura coupling in terms of activity and recyclability in aqueous ethanol solvent.

Recently, Shen et al. have reported the single crystal structure of a Pd click-catalyst, in which the glycosyl pyridyl-triazole coordinates with palladium in a bidentate (N,N) coordination mode [37]. They applied this click catalyst in palladium-catalyzed C–C coupling reactions such as Suzuki–Miyaura coupling, Heck and Sonogashira reaction.

Sangtrirutnugul et al. have also prepared the Pd(II) complexes containing 1,2,3-triazol ligands and described their crystal structures [38]. Catalytic studies of these click catalysts exhibited moderate to high activity for Suzuki–Miyaura coupling.

The palladium-catalyzed Suzuki cross-coupling is a powerful synthetic procedure for C–C bond formation via coupling of aryl halides with arylboronic acids to provide biaryl derivatives, which are used as the building blocks in the synthesis of natural products, pharmaceuticals and advanced materials [39–45].

Scheme 1 Synthesis of silica-supported nano-palladium click-catalyst **A** and **B**. *Reaction conditions* (a) CH_3CN, NaN_3, TBAB, 80 °C 24 h; (b) toluene, reflux, 24 h; (c) Cu_2O, H_2O/MeOH, r.t., 3 days; (d) toluene, $Pd(OAc)_2$, r.t., 24 h



In continuation of our efforts to design and discover new catalytic systems [46–48], we have herein focused on click-modification of silica support and immobilization of palladium catalyst to prepare an effective and recyclable heterogeneous nano-palladium catalyst for cross coupling reactions. Initially, the surface of silica was functionalized with azide group and then reacted via a "click" route with propargyl amine or propargyl alcohol as the alkyne section to construct the click- modified silica support. Then, immobilization of palladium(II) acetate into the resulting click-supports gave palladium-based solid catalysts **A** and **B**, which were comparatively investigated in terms of their catalytic activity and recycling for Suzuki–Miyaura coupling reactions. The detailed route is shown in Scheme 1.

2 Experimental

2.1 Synthesis of Azide- Functionalized Silica Support

First, 3-chloropropyltrimethoxysilane was converted to the 3-azidopropyltrimethoxysilane according to the method reported by Ding et al. [33], 3-chloropropyltrimethoxysilane (0.92 mL, 5 mmol) was added to a solution of NaN_3 (0.46 g, 7 mmol) and tetrabutylammonium bromide (TBAB, 0.32 g, 1 mmol) in dry acetonitrile (30.0 mL) under nitrogen atmosphere, and the mixture was heated under reflux for 24 h. After cooling, the solvent was removed under reduced pressure. The residue was then diluted in Et_2O (20 mL) and the mixture was filtered and washed with Et_2O. The combined solvent was removed to give 3-azidopropyltrimethoxysilane, and the flask charged with 50 mL dry toluene for further reaction with SiO_2 gel. Activated silica was prepared 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 until the pH of the filtrate was higher than 6 and dried at 150 °C for 8 h. The fresh activated silica (2 g) was suspended in the above solution of 3-azidopropyltrimethoxysilane in toluene, and the suspension was refluxed under nitrogen for 24 h. After cooling, the silica particles were collected by filtration and washed thoroughly with toluene, methanol and finally with acetone. The resulting solid was dried under vacuum at 60 °C to give azide- functionalized silica support. The formation of 3-azidopropyltrimethoxysilane and the successful attachment of azide group onto the surface of silica was confirmed according to FT-IR spectra (Figs. S1 and S2).

2.2 Synthesis of Click-Supports A and B

Azide- functionalized silica (0.5 g) and Cu_2O (0.02 g) were mixed in 30 mL H_2O/MeOH (1:1), and then an excess amount of propargyl alcohol (for the support **A**) or propargyl amine (for the support **B**) was added. The reaction mixture was stirred at room temperature for 3 days. After completion, the solid particles were filtered, washed several times with methanol, water, HCl solution (5% solution in water), water and acetone, and finally dried at 60 °C under vacuum. The solid was obtained as a withe powder for the click-support **A** and a light brown powder for the click-support **B**.

2.3 Synthesis of Click-Catalysts A and B

A mixture of the click-support (**A** or **B**, 0.3 g) and palladium acetate (0.2 mmol, 0.045 g) were stirred in dry toluene (10 mL) at room temperature for 30 h. After the complexation, the solid phase was separated by centrifugation, washed thoroughly with toluene and acetone several times in order to remove any adsorbed palladium on the surface, and finally allowed to dry at room temperature.

2.4 General Procedure for Suzuki–Miyaura Coupling Reaction

Aryl halide (1 mmol), K_2CO_3 (2.0 mmol), phenylboronic acid (1.2 mmol), click-catalyst **A** (0.2 mol%) and 3 mL H_2O/EtOH (1:1, V/V) were mixed in a round-bottom flask equipped with condenser and under an air atmosphere. The mixture was heated in an oil bath at 70 °C (for the aryl bromides) and stirred continuously during the reaction and monitored by thin-layer chromatography (TLC) and gas chromatography (GC). After the reaction was complete, the mixture was diluted with EtOH. The catalyst was separated by centrifugation, washed with EtOH/H_2O and then reused for recycling experiments without further pretreatment. Then, the coupled product was extracted with EtOAc and the organic phase was dried over $MgSO_4$, filtered and concentrated. The residue was purified by recrystallization or silica gel column chromatography (*n*-hexane:EtOAc), and was characterized.

3 Results and Discussion

Silica-supported nano-palladium click-catalysts **A** and **B** were prepared following the route shown in Scheme 1. The all processes of click modification and catalyst immobilization were investigated by FTIR analysis. At first, the silica was functionalized with azide group through a simple

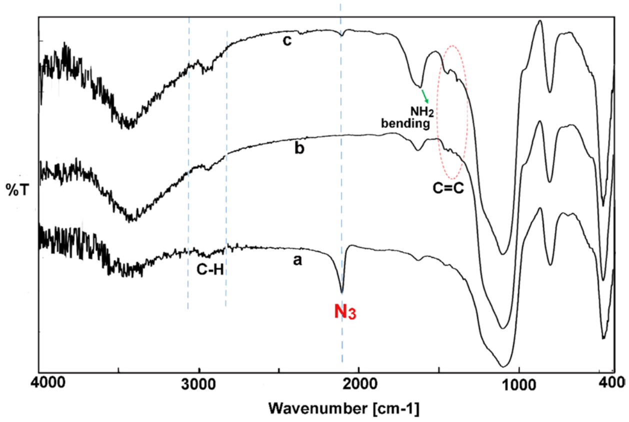


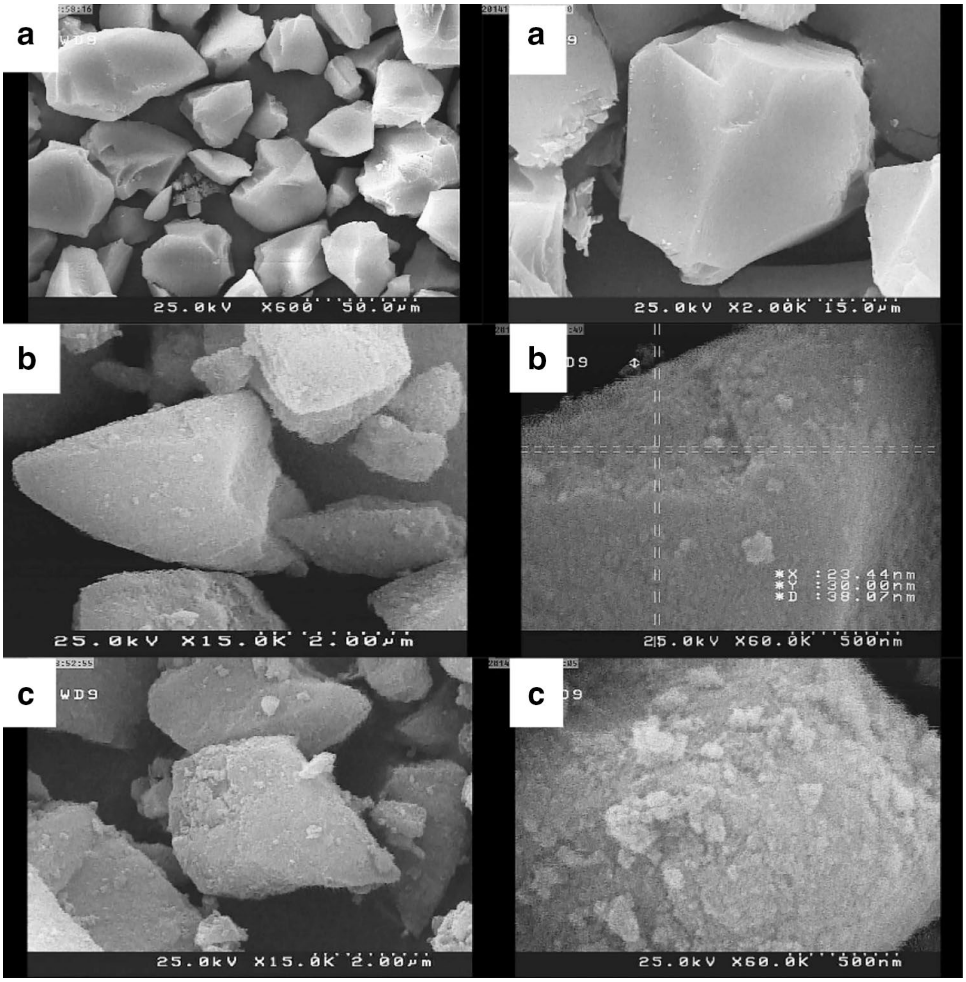
Fig. 2 FTIR spectra of azide-functionalized silica (*a*), click-support **A** (*b*) and click-support **B** (*c*)

procedure to achieve click-capability, and the presence of azide group was confirmed by the appearance of the N_3 band at 2100 cm^{-1} in FT-IR spectra (Figs. S1 and S2). The resulting azide-functionalized silica was treated with an excess of propargyl alcohol or propargyl amine in the presence of Cu_2O catalyst in aqueous methanol. During the "click" reaction, azide groups react with alkyne sections to obtain click-supports **A** and **B** containing the 1,2,3-triazole units. The nearly complete conversion of all azide groups was confirmed by FTIR spectra, which showed disappearance of the absorption band at 2100 cm^{-1} attributed to the N_3 (Fig. 2). The amount of click-ligand grafted onto the surface of silica was estimated by elemental analysis of the nitrogen content using click-supports **A** and **B**, and were found to be 1.0 and 0.95 $mmolg^{-1}$, respectively.

The resulting click-supports were further treated with $Pd(OAc)_2$ in toluene at room temperature to afford the desired solid click-catalysts **A** and **B**, meanwhile, their palladium loading was respectively measured to be 0.38 and 0.31 $mmolg^{-1}$ by inductively coupled plasma (ICP).

Field emission scanning electron microscopy (FE-SEM) images in Fig. 3 demonstrate a comparison of the surface morphology and the particles distribution in virginal silica, click-catalysts **A** and **B**. As shown in the FE-SEM micrographs, the surface morphology of virginal silica was clearly changed after click-modification and catalyst immobilization.

Fig. 3 FE-SEM images of virginal silica (**a**), click-catalysts **A** (**b**) and **B** (**c**)



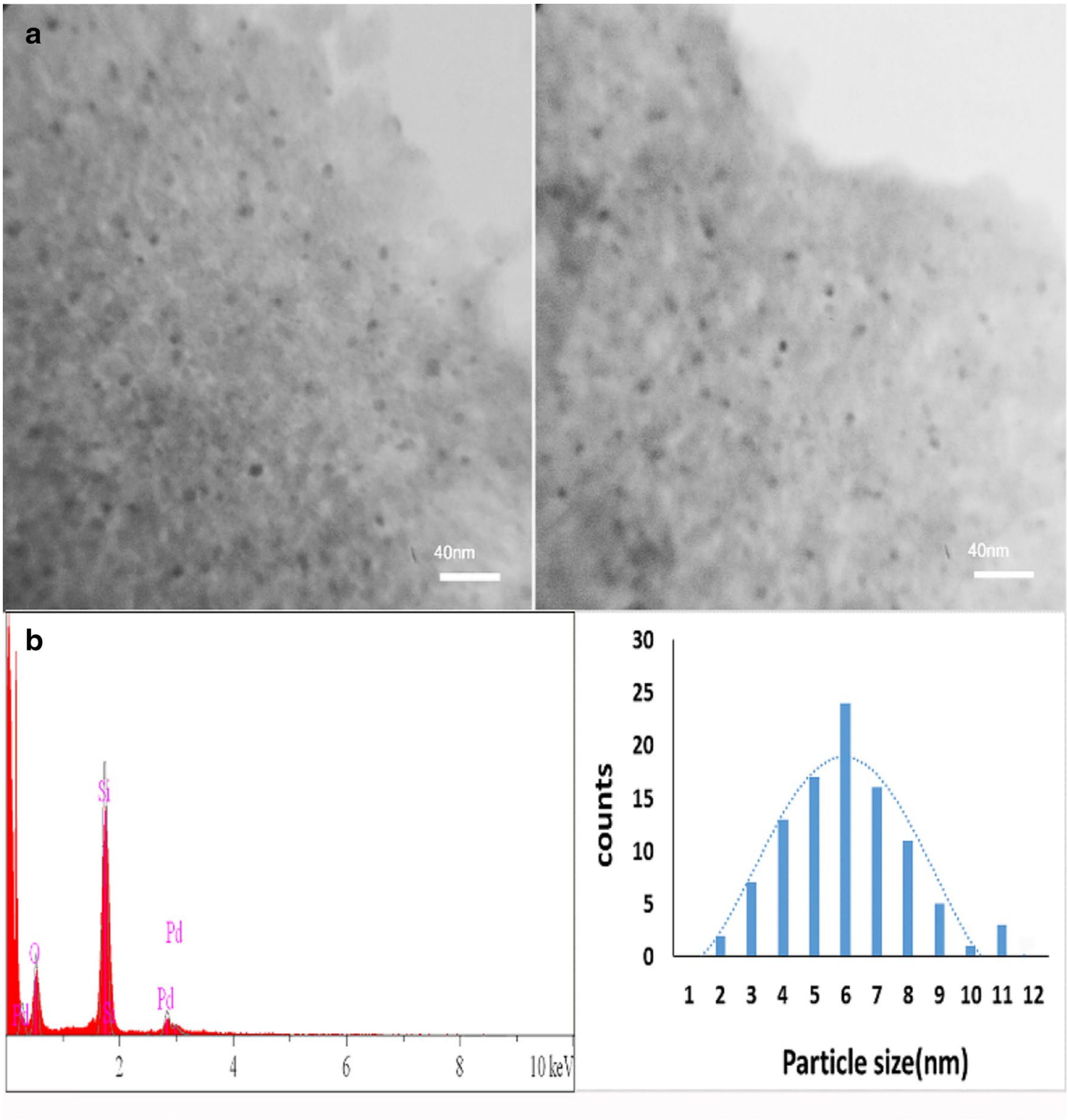


Fig. 4 TEM images (**a**) and EDX spectrum (**b**) of the click-catalyst **A**

In addition to the conventional SEM images, the meaningful pictures of the element distribution of the surface of click-catalyst **A** were provided by EDX mapping (Fig. S3).

Chelation of the click-ligand grafted on the silica surface with palladium(II) ions prevent the aggregation of particles in the catalyst system. Transmission Electron Microscopy (TEM) image of the click-catalyst **B** in the Fig. 4 shows the distribution of particles and confirm that the nano-sized particles have been well distributed throughout the catalyst system, and the nanoparticle average size was found to be about 5–6 nm. The presence of palladium complexes is appearing as black spots. By the SEM-EDX analysis the presence of palladium in the catalyst was approved (Fig. 4b).

To further investigation of the catalysts **A** and **B**, efficiency of these catalysts was evaluated in the Suzuki–Miyaura cross-coupling reactions.

At first, the coupling of 4-bromonitrobenzene and phenylboronic acid was chosen as the model reaction to begin this investigation. It was found that by employing click-catalysts **A** or **B** (0.2 mol%), K_2CO_3 and mixed solvent EtOH/H_2O (50:50) at 70 °C, the corresponding biaryl was obtained in 100% yield (GC-yield) after 30 min. This result demonstrates that both catalysts are effective in this reaction system.

Despite the excellent catalytic efficiency of the click-catalysts in the first use, we carried out further investigations

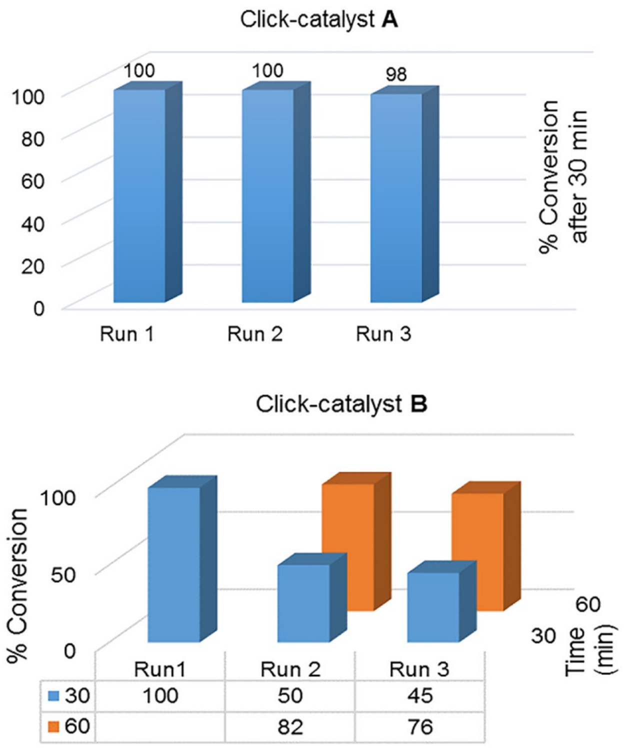


Fig. 5 The reusability results of the click-catalysts **A** and **B**. *Reaction conditions* 4-nitrobromobenzene (1 equiv.), phenylboronic acid (1.2 equiv.), H_2O/EtOH (1:1), K_2CO_3 (2 equiv.), 70 °C. GC conversion

focusing on their reusability and the catalyst recycling. The recovery of catalyst becomes an important factor due to economic and environmental concerns, especially for expensive metal catalysts such as Pd. Therefore, the recyclability of these click-catalysts was examined by using the above model reaction by simple filtration and washing with EtOH/H_2O. These recycling studies have shown that the catalyst **A** could be readily recovered and reused several times without significant loss of activity. However, the catalyst **B** could be also recycled, although a slight reduction in the yield of the coupled product and an increase in the reaction time were observed (Fig. 5).

As a result, click-catalyst **A** showed the better performance and the more reasonable reusability than those of the click-catalyst **B**, and could successfully reused up to five cycles.

Next, we checked the Pd leaching for the click-catalysts. Importantly, no significant leaching of the Pd could be detected during the experiments as ascertained by ICP analysis of click-catalysts after recycling from reaction mixture, indicating that the reactions are truly heterogeneous in nature. Hence, metal leaching does not seem to be the reason of the activity shortcoming of click-catalyst **B** during the recycling experiments.

X-Ray reflective diffraction (XRD) of catalysts was carried out before and after use in reaction system to get detailed information about the architecture of the novel click-catalysts **A** and **B** (Fig. 6). The XRD patterns of both catalysts before using show only characteristic peaks of amorphous SiO_2 at $2\theta = 22°$, and no characteristic peaks for Pd (0) nanoparticles are observed. The XRD pattern of catalyst **A** after five times use and recycling from the reaction media displays the slight appearance of new peaks attributed to Pd (0) species, which verifies in situ formation of partially metallic palladium nanoparticles during the reaction. However, in the XRD pattern of catalyst **B** after using and recovery there was no appearance of new peaks. It indicates that the Pd(II) complexes on the surface of solid catalysts could be still maintained after use in the reaction.

Based on these results two catalysts **A** and **B** exhibit different behaviors and properties, which can probably be due to the difference of their structures.

1,2,3-Triazoles having several donor sites are potentially powerful chelator for metal coordination [49]. In the nitrogen-coordination mode of triazoles, DFT calculations have shown that N_3 is a better donor compared to N_2 [50]. However, as shown in Scheme 2, when there are other donor sites nearby, synergetic coordination through N_3 and additional donor site is possible to form a bi- or poly-dentate chelator [49, 51–53]. Tale et al. have recently reported 1, 2, 3-triazol-4-yl methanol-based ligands as the accelerator in copper catalyzed azide–alkyne cycloaddition (CuAAC) reaction [54]. They found that, the presence of hydroxymethyl (–CH_2OH) moiety along with electron releasing substituent on the terminal benzene ring of 1, 2, 3-triazole in these click-ligands, has favorable effect on the rate enhancement of the CuAAC.

Based on these reports, we assumed synergetic coordination of N-atom of triazolyl ligand and OH or NH_2 groups present in the structure of studied catalysts to palladium that leads to the formation of Pd(II) complexes on the support surface.

Further characterization of the click-catalysts **A** and **B** was performed by UV–Vis diffuse reflectance spectroscopy, as shown in Fig. 7. We studied the UV–Vis spectra of click-supports and the resulting catalysts after complexation in the range of 200–800 nm. The UV–Vis spectra of Pd-catalysts show a slight red shift compared with their corresponding supports, which could confirm palladium complexation and suggests that palladium existing on the solid supports with a coordinated mode. Before the metallation reactions, the click-supports **A** and **B** showed a distinct π–π* transition around 250–300 nm. The wide band in the range of 350–400 nm after coordination is probably due to the n→π* transition or to the ligand-to-metal charge-transfer transition (LMCT).

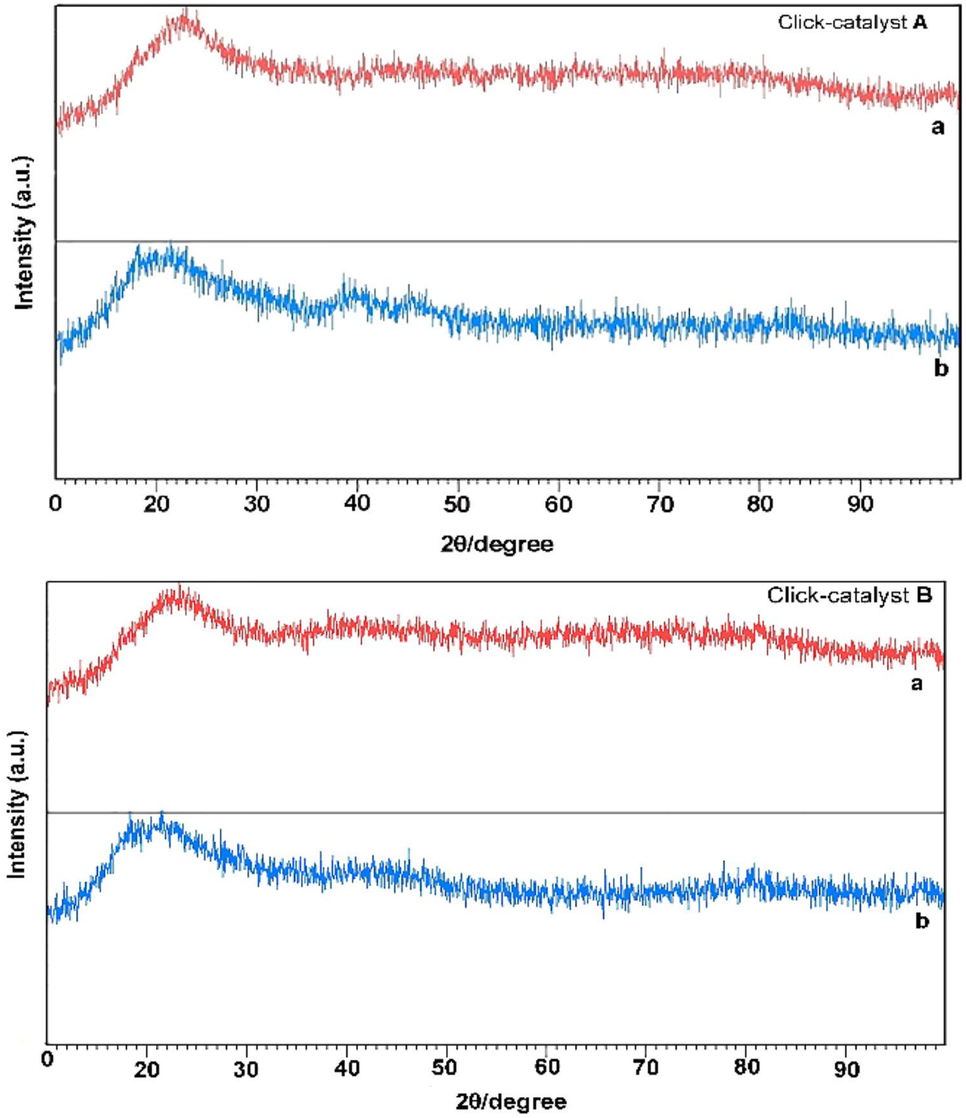
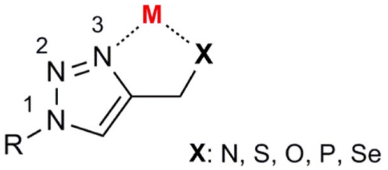


Fig. 6 XRD pattern of the fresh (*a*) and recovered click-catalysts A and B (*b*)



Scheme 2 The coordination mode of chelating triazole with transition metal (M)

Although both studied catalysts showed relatively good performance, but we chose click-catalyst **A** as the superior catalyst and hence, continued further studies using this catalyst. Figure 8 shows the FTIR spectrum of the catalyst **A** compared with the FTIR spectra of click-support **A** and pure $Pd(OAc)_2$. The spectrum of catalyst **A** showed the characteristic bands of (COO) at 1562 and 1410 cm^{-1}, evidencing the presence of OAc groups.

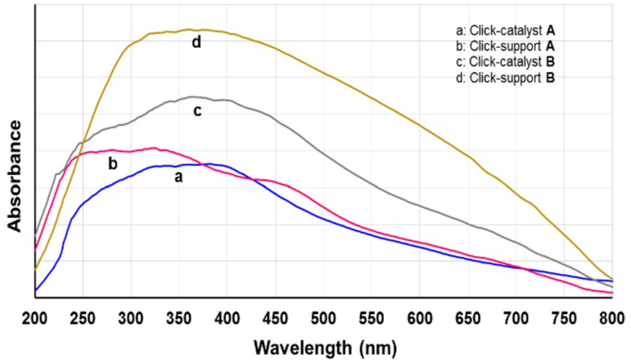


Fig. 7 UV–Vis spectra of click-catalyst **A** (*a*), support **A** (*b*), catalyst **B** (*c*) and support **B** (*d*)

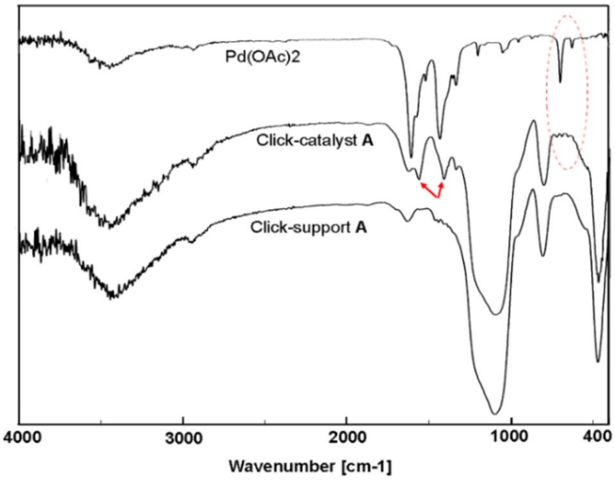


Fig. 8 FTIR spectra of click-support **A**, catalyst **A** and Pd(OAc)$_2$

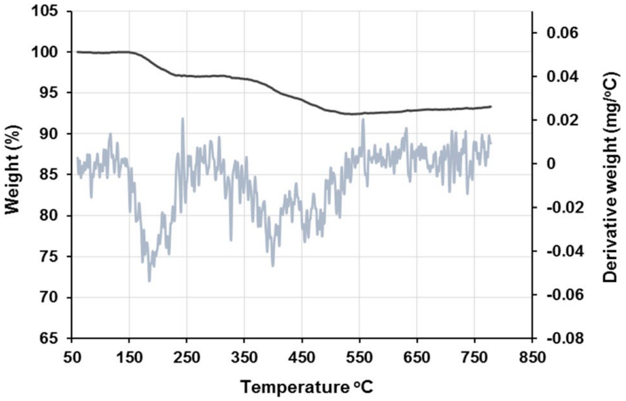


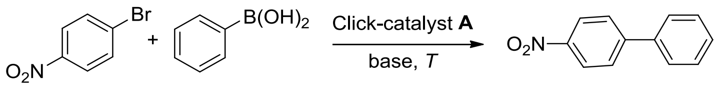
Fig. 9 TGA/DTA analysis of click-catalyst **A**

Thermogravimetric (TG) analysis was used to study the thermal behaviour and stability of the supported click-catalyst **A** (Fig. 9). The measurement was carried out in the temperature range of 60–800 °C with a heating rate of 20 °C min^{-1} under nitrogen atmosphere. As shown in the TG curve, an initial weight loss of 2.7% is observed up to 150 °C, which is due to the elimination of water adsorbed onto the silica. Thermal degradation of the catalyst attributed to the decomposition of the organic groups on the silica surface occurred after 300 °C, which revealed the excellent thermal stability. Hence, the click-catalyst **A** found to be very stable and could be used within a broad temperature range.

As already observed for the catalyst **A**, this showed excellent catalytic activity and recyclability in Suzuki cross-coupling reaction of 4-bromonitrobenzene and phenylboronic acid as the model reaction in green solvent H_2O/EtOH (50:50) at 70 °C. Being encouraged we attempted to optimize the reaction conditions, and examined the effect of various reaction parameters such as base and temperature on the yields and reaction times of a series of screening experiments carried out by using the above model reaction as summarized in Table 1.

Due to green chemistry and environmental concerns, only water and alcohol was chosen as solvent in all experiments. The advantage of the aqueous mixed-solvents might be attributed to the good solubility of the organic reactants and the inorganic base. Among the different bases tested such as K_2CO_3, KOH and K_3PO_4, K_2CO_3 and KOH were found to act as the effective bases (Table 1, entries 1–3), that we continue our work with k_2CO_3. The reaction temperature and the catalyst loadings were also examined for the title reaction. The yield of the model reaction increased when the reaction was conducted at 70 °C (Table 1, entries 2, 5). A catalyst loading of 0.2 mol% was found to be optimal

Table 1 Optimization of the reaction conditions for the Suzuki–Miyaura coupling

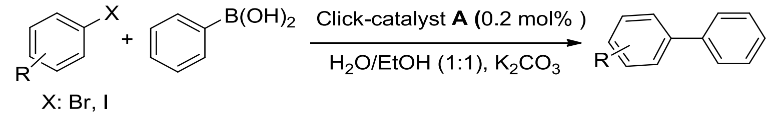


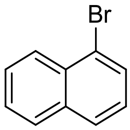
Entry	Base	Catalyst (mol%)	*T* (°C)	*t* (min)	Yield (%)[a]
1	K_3PO_4	0.2	70	30	20
2	K_2CO_3	0.2	70	30	100
3	KOH	0.2	70	30	100
4	None	0.2	70	30	Trace
5	K_2CO_3	0.35	RT	300	Trace
6	K_2CO_3	none	70	60	–
7	K_2CO_3	0.1	70	30	82

Reaction conditions 4-nitrobromobenzene (0.5 mmol), Phenylboronic acid (0.52 mmol), H_2O/EtOH (1:1) 3 mL, base (2 equiv.)

[a] GC yield

Table 2 Scope of aryl halides in Suzuki–Miyaura coupling reaction with phenylboronic acid



Entry	R (X)	T (°C)	t (min)	Yield (%)[a]	TON[b]	TOF (min^{-1})[c]
1	4-NO_2 (Br)	70	30	97	485	16.2
Run2			30	97	485	16.2
Run3			30	94	470	15.7
Run4			90	90	450	5
Run5			90	81	405	4.5
2	4-NO_2 (I)	RT	20	97	485	24.25
3	4-OCH_3 (I)	RT	20	95	475	23.75
4	4-$COCH_3$ (I)	RT	20	95	475	23.75
5	3-NO_2 (I)	RT	20	96	480	24
6	H (I)	RT	20	91	455	22.75
7	4-$COCH_3$ (Br)	70	20	97	485	24.25
8	4-OCH_3 (Br)	70	50	95	475	9.5
9	H (Br)	70	45	90	450	10
10	4-COH (Br)	70	30	93	465	15.5
11	4-CN (Br)	70	30	95	475	15.8
12	4-Cl (Br)	70	30	93	465	15.5
13	4-NO_2 (Cl)	70	120	–	–	–
14	2-Cl (Br)	70	50	90	450	9.3
15		70	60	80	400	6.7

Reaction conditions aryl halide (1 mmol), phenylboronic acid (1.2 mmol), K_2CO_3 (2 mmol), solvent 3 mL

[a] Isolated yield

[b] Turnover number (TON) calculated as moles of product formed/moles of catalyst used

[c] Turnover frequency (TOF) calculated as moles of product formed/moles of catalyst used per min

(Table 1, entries 2, 6, 7) by employing various amounts under optimized conditions. A lower catalyst concentration usually led to slow reactions, increasing the amount of catalyst shortened the reaction time.

After optimization, catalyst **A** was applied to the Suzuki coupling of aryl halides with phenylboronic acid, and a various aryl iodides and bromides reacted efficiently to give the corresponding biaryl derivatives in good to excellent yields.

As shown in Table 2, electron-poor as well as electron-rich aryl halides proceeded effectively to afford the coupled products. This catalyst was compatible with a wide range of functional groups such as nitro, methoxy, cyano and carbonyl on the aryl halides. All aryl iodides were rapidly converted to the corresponding Suzuki products at room temperature in excellent yields. However, Aryl bromides required heat to react with phenylboronic acid and afforded the corresponding products at 70 °C. Additionally, 4-chloronitrobenzene was chosen as the challenging substrates, however, the catalytic system was less effective even when prolonged reaction time (Table 2, entry 13).

As previously reported by other groups, different catalytic systems based on palladium catalysts combined with the triazole ligand promote the Pd-catalyzed reactions such as coupling or oxidation reactions [20, 33, 34]. Reaction temperature, reaction rate and selectivity are important factors that must be considered in this transformations, especially for heterogeneous catalysts in addition to their stability and reusability. The present catalytic method was compared with some procedures reported for the Suzuki–Miyaura reaction of 4-iodoanisole with phenylboronic acid in published literatures, and the results have been shown in Table 3. Of course, the reaction conditions are different, but the catalyst used in this study might

Table 3 Comparison of catalytic activities with literature examples for the Suzuki reaction between 4-iodoanisole and phenylboronic acid

Entry	Catalyst (mol%)	Reaction conditions	Yield (%) Ref.	TOF[a]
1	PS-btsu-Pd(II) complex (0.5)	H_2O + MeOH (1:1)/RT/LiOH·H_2O/4 h	90 [55]	0.75
2	2-Pyridyl-1,2,3-triazole-Pd(II) complex (0.5)	EtOH:H_2O (7.5 mL:5 mL)/RT/K_2CO_3/48 h	77 [20]	0.038
3	$[Pd(OAc)_2]_n$@dendrimer, $\mathbf{11_3}$ (0.5)	EtOH:H_2O (7.5 mL:5 mL)/50 °C/K_2CO_3/48 h	96 [20]	0.067
4	Pd(0)-Montmorillonite clay (0.07)	H_2O/60 °C/K_2CO_3/1 h	94 [56]	22.3
5	Hollow Fe3O4-NH2-Pd (1.0)	EtOH/80 °C/K_2CO_3/30 min	96 [57]	3.2
6	Cellulose acetate (CA)/Pd(0) (0.5)	H_2O/100 °C/K_2CO_3/3 h	97 [58]	1.1
7	Fe3O4@PUNP-Pd (0.1)	H_2O/90 °C/K_2CO_3/1 h/Argon atmosphere	96 [59]	16
8	Present work	EtOH:H_2O (1:1)/RT/K_2CO_3/20 min	95	23.75

[a] Turnover frequency (TOF) calculated as moles of product formed/moles of catalyst used per min

be one of the best catalysts with regards to lower reaction time and temperature.

Click-surface modification and the use of triazole units as the stable linker and excellent ligand, especially for the design of efficient and phosphine-free solid-supported metal based catalysts will be interesting to follow in the near future in view of modern organic synthesis owing to novel design and facile synthesis of these systems.

4 Conclusion

In conclusion, we have prepared two new silica supported palladium catalyst **A** and **B** via a ‘‘click’’ route, in which the click-triazole acts as a stable linker as well as an excellent chelator to immobilize Pd(II) complex on the silica surface. Both solid catalysts exhibited a promising catalytic activity towards the Suzuki–Miyaura coupling reactions without any added ligand under aerobic conditions, however, the catalyst **A** showed a better outcome in terms of recovery and catalyst recycling compared with the catalyst **B**. Hence, we employed the catalyst **A** as an outstanding heterogeneous palladium catalyst for the coupling reactions of various aryl halides with phenylboronic acid to provide a variety of substituted aromatic biaryls in good to excellent yield. Currently, we are investigating the “click” modification of the carbon- and polysaccharide-based supports such as graphene oxide and chitosan for catalyst immobilization, which could be advanced topics in the green heterogeneous catalysis research.

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Affiliations

Abdol Reza Hajipour[1,2] · **Fatemeh Mohammadsaleh**[1]

✉ Abdol Reza Hajipour
haji@cc.iut.ac.ir

[1] Pharmaceutical Research Laboratory, Department of Chemistry, Isfahan University of Technology, 84156 Isfahan, Islamic Republic of Iran

[2] Department of Pharmacology, Medical School, University of Wisconsin, 1300 University Avenue, Madison, WI 53706-1532, USA