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Nicotine functionalized-silica palladium (II) complex: a highly efficient, environmentally benign and recyclable nanocatalyst for C-C bond forming reactions under mild conditions

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An environmentally friendly silica-grafted nicotine-based palladium(II) complex was successfully prepared and evaluated for the first time as novel and efficient nanocatalyst in C-C bond forming reactions. Grafted-nicotine in this catalytic system plays an important role, and as an effective ligand and a quaternary ammonium salt demonstrates an efficient stabilizing effect on the Pd(II) species by a synergistic effect of coordination and electrostatic interactions. The catalyst was well characterized by FT-IR, CHN, XRD, TEM, SEM–EDX, ICP and TG analysis, and demonstrated a highly efficient catalytic activity in the reaction system under phosphine-free and low Pd loading conditions, and the coupled products were produced in good to excellent yields. Furthermore, the catalyst can be easily recovered and reused without a significant loss of activity. Copyright © 2016 John Wiley & Sons, Ltd.

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Keywords: mizoroki–heck reaction; suzuki–miyaura reaction; magnetic nanoparticles; *n*-heterocyclic carbenes

Introduction

Nowadays, a great deal of progress has been attained in improving the reaction conditions and designing efficient and environmentally benign catalytic systems for the metal-catalyzed aryl-nucleophile bond forming reactions.[1–4] Combinations of transition-metal salts and ligands have been described as highly efficient catalytic systems for the synthesis of C-C, C-N, and also C-O bonds.[5,6] The development of green chemistry in the synthesis routes which reduce contamination and pollution in chemical synthesis has attracted much attention in recent years.[7] There are diversity of competitive methodologies for the synthesis of aryl-nucleophile bonds with various sources of C-, O-, N-, P-, and S-nucleophiles.[8]

Heterogeneous catalysis is noteworthy for both academic and industrial synthesis due to its advantages over homogeneous catalysis.[9–13] The immobilization of catalyst on the solid-support improves the catalyst stability and facilitates the separation and recovery of catalyst from reaction media.

In heterogeneous catalysis research, recent attention has been concerned with the stabilization of nano-catalysts on a solid surface.[14–17] A number of important studies have been focused on development of the supported nano-catalysts manufactured by reacting a functionalized surface with available functional groups on the catalyst atoms.

Palladium -based catalysts are powerful for the formation of carbon-nucleophile bonds, which have excessive applications in both laboratory and large-scale synthesis.[18–20] In view of modern synthesis, the non-renewable use of expensive palladium-based catalysts is less valuable, in particular, for industrial scale production. In recent years, palladium-based nanocatalysts stabilized on the solid surface have been widely applied as efficient catalysts for the important reactions involving low catalyst loadings under mild and environmentally friendly conditions.[21,22] Nano-scale particles usually display distinctive properties in comparison with their bulk materials and the isolated atoms in catalytic reactions.[23,24]

The novel supported palladium nano-catalysts can be used in a variety of reactions, including Sonogashira and Suzuki carbon–carbon coupling reactions.[25–28]

The construction of carbon–carbon bonds is important in the production of pharmaceuticals, and natural and industrial products.[29,30]

The pd.-catalyzed Suzuki–Miyaura cross-coupling reaction is a considerable procedure for carbon–carbon bond formation, especially for the synthesis of biaryl compounds, which are used as the building blocks for most of the pharmaceuticals, natural products and advanced materials.[31,32]

Introduction of a triple bond into aromatic systems via cross-coupling of aryl/alkyl halides and terminal alkynes.[28,33]

Quaternary ammonium and phosphonium salts combined with metals such as palladium and copper have been successfully applied for chemical synthesis.[34] The efficiency of these systems is due to the involvement of metal nanoparticles stabilized by quaternary salts and/or the formation of a new catalytic systems.[35–37]

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The Sonogashira coupling reaction is a powerful synthetic method for the formation of C(sp)-C(sp2) bonds by the Niu et al.[38] have applied Multiwalled Carbon Nanotubes-containing quaternary salts to support Au nanoparticles. Wang et al.[39] reported a click-imidazolium-modified copolymer as a solid support to stabilize the pd.- NPs.

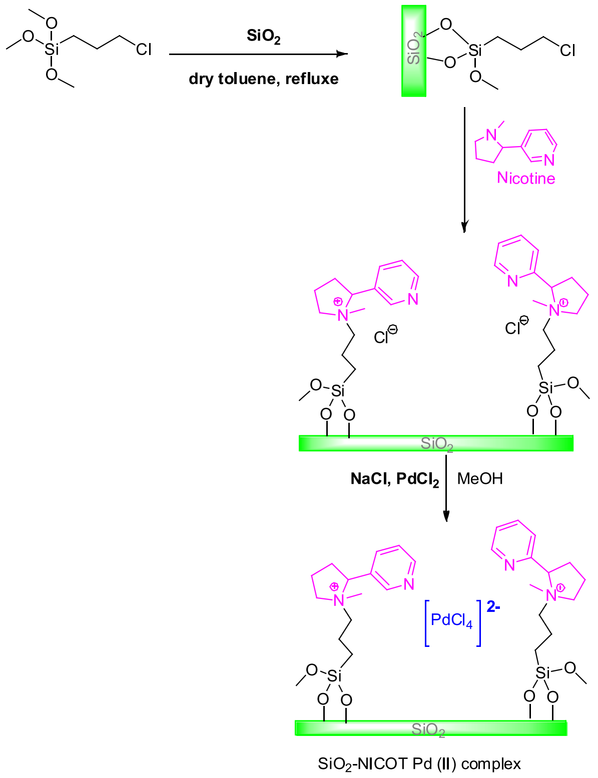
Recently, we have used benzyl nicotinium chloride as the promoter in metal-catalyzed C-C and C-S coupling reactions.[40–42] We have also reported the investigation of a series of nicotine-based ammonium salts as catalysts for chemical fixation of carbon dioxide into cyclic carbonates, and it was found that monobenzylnicotinium bromide showed a much higher activity than dibenzylnicotinium bromide.[43]

In continuation of our recent studies on the development of eco-friendly catalytic protocols,[44,45] herein, we report the synthesis and characterization of a nicotine-functionalized silica supported Pd complex as a recyclable solid catalyst. This new catalyst system having a synergistic effect of coordination and electrostatic interactions was found to be efficient in palladium-catalyzed C-C bond formation.

Results and discussion

In this work, we have reported the synthesis and characterization of a *N*-donor quaternary ammonium-based palladium complex and evaluated its catalytic activity in the Suzuki and Sonogashira cross coupling reactions.

As shown in Scheme 1, at first, activated SiO_2 reacts with 3-chloropropyl trimethoxysilane in dry toluene. Then, the modified silica treats with nicotine in acetonitrile solvent to obtain the silica-nicotine (SiO_2-NICOT) support. In the next step, this support reacts with $PdCl_2$ to achieve SiO_2-NICOT Pd (II) complex.



Scheme 1. The nanocatalyst preparation.

The products SiO_2-NICOT and SiO_2-NICOT Pd (II) complex were separated and washed several times with ethanol and acetone and were characterized by FT-IR (Figure. 1). In the FT-IR spectrum depicted in Figure 1, the characteristic peaks of C = N stretching (1640 cm^{-1}), C = C stretching (1691 cm^{-1}), C–H stretching (3010–2900 cm^{-1}), CH_2 bending (1460 cm^{-1}), Si–C stretching (1212 cm^{-1}), and Si–O stretching (1050–1110 cm^{-1}) vibrations are assignable to the SiO_2-NICOT.

The presence of the organic phase in the SiO_2-NICOT support was also confirmed by elemental analysis (CHN). Accordingly, the amount of grafted nicotine based on the nitrogen content was found to be 0.43 mmol/g.

By the SEM–EDX analysis of SiO_2-NICOT Pd (II) complex(Figure 2), the presence of palladium phase was well confirmed.

The content of palladium in the case of SiO_2-NICOT Pd (II) was measured by ICP, which was 0.4%.

Further characterization of SiO_2-NICOT-Pd(II) complex was done by transmission electron microscopy (TEM). As shown in Figure 3, the TEM micrographs of catalyst show well-defined dispersion of nano-sized palladium particles in the catalyst matrix. From histogram, the nanoparticles size mostly are about 30 nm.

Sasaki et al.[46] have prepared and characterized a series of immobilized metal ion-containing imidazolium based quaternary salts (ImmM-QSs) on silica surfaces. They found that the immobilized metal ion-imidazolium salts were more active than

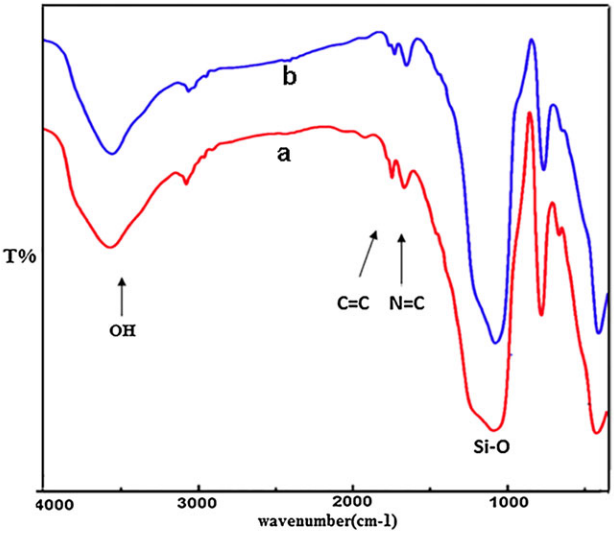


Figure 1. FT-IR spectrum of: SiO_2-NICOT (a) and SiO_2-NICOT-Pd (b).

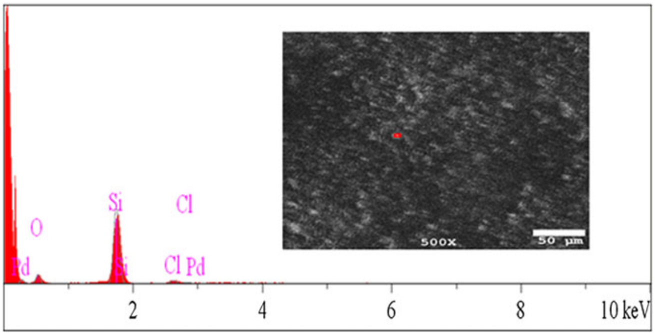


Figure 2. SEM–EDX spectra of catalyst.

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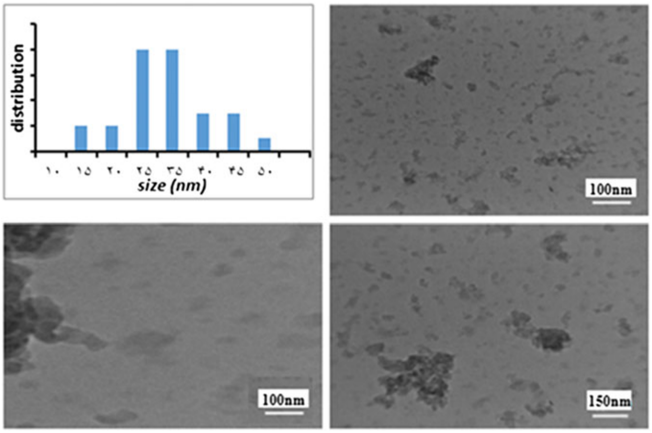


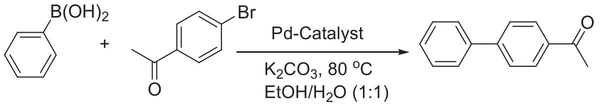
Figure 3. TEM images and particle size distribution results for SiO_2-NICOT Pd (II) catalyst.

similar systems unsupported on silica, and in all of the studied ImmM-QSs, no metal–metal bond was observed. They reported that in the structures of immobilized metal ion-imidazolium salts (M = Ni^{2+}, Cu^{2+}, Zn^{2+},Mn^{2+}, Pd^{2+} and Co^{2}) the metal ions as MCl_4 species are held between two imidazolium ions on the surface of SiO_2. Based on this report, we have suggested the immobilization of $PdCl_4$ species combined with nicotinium ions on the silica support in this work.

The resulted catalyst was stable and its catalytic activity as a solid-catalyst was investigated in Suzuki and Sonogashira cross coupling reactions.

First, we optimized the catalyst preparation by investigation of activity of the resulted catalyst. For this, we prepared two catalysts with 4% and 0.4% of palladium content (the amount of palladium was determined by ICP) and the activity of both catalyst was examined in Suzuki reaction. A comparison of the reaction results showed that the catalytic performance is strongly influenced by the palladium content of catalyst. It was found that by the reaction of bromoacetophenone with phenyl boronicacid in the present of K_2CO_3 and EtOH/H_2O at 80 °C, the use of catalyst with a lower Pd loading gave 80% of coupled product, whereas the catalyst with a higher Pd loading (0. 4%) resulted in 50% conversion, at the same conditions (Table 1). Hence, the effect of palladium content on the catalytic activity of catalyst was examined, and it was found that lower content showed much higher activity, probably being ascribed to the dispersity and size of the palladium species embedded in the catalyst matrix. Therefore, we chose the catalyst with 0.4% of Pd-content for further studies as optimized catalyst.

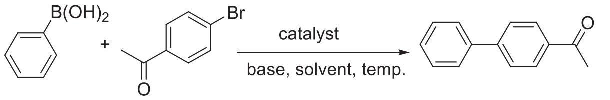
Table 1. Optimization of catalyst preparation in Suzuki reaction of bromoacetophenone with phenylboronicacid in the presence of SiO_2-NICOT-Pd (II) [a]



Entry	Catalyst (mol%)	Yield [b] (%)
1	0.07 (4% Pd-content)	53
2	**0.07** (**0.4%** Pd-content)	**80**

[a] The reaction conditions: bromoacetophenone (1.0 mmol), phenyl boronicacid(1.2 mmol), base (2 equiv.) solvent (2.0 mL) for 2 h.
[b] GC yield

Table 2. Optimization of Suzuki reaction of bromoacetophenone with phenyl boronicacid in the presence of SiO_2-NICOT-Pd(II)[a]



Entry	Solvent	T (°C)	Base	Catalyst (mol%)	Yield [b].%
1	EtOH/H_2O	50	K_2CO_3	0.07	65
2	H_2O	50	K_2CO_3	0.07	50
3	EtOH/H_2O	80	K_2CO_3	0.07	80
4	**EtOH/H_2O**	**80**	**K_2CO_3**	**0.1**	**97**
5	EtOH/H_2O	80	KOH	0.1	97
6	EtOH/H_2O	80	$NaHCO_3$	0.1	97

[a] The reaction conditions: bromoacetophenone (1.0 mmol), phenylboronic acid (1.1 mmol) and solvent (2.0 mL) for 2 h.
[b] GC yield

We explored the catalytic properties of SiO_2-NICOT-Pd (II) in the Suzuki reaction under various conditions. At first, base, solvent and reaction temperature were examined in the coupling reaction of 4-bromoacetophenone (1.0 mmol) and phenyl boronicacid (1.2 mmol), as model reaction of Suzuki cross-coupling.

Two green solvent system such as H_2O and EtOH /H_2O, were examined, and EtOH /H_2O was chosen. It was also found that the reaction temperature and the amount of catalyst have important influence on this reaction. The kind of base has no effect on reaction (Table 2 entries 4–6).

These optimized reaction conditions were used for Suzuki reaction of different aryl halides. As it is demonstrated in Table 3, aryl halides with electron withdrawing substituents and lower steric hindrance, gave higher yields than the derivatives containing electron-donating groups and higher steric hindrance.

The activity of this catalyst in the Sonogashira reaction was also studied. In order to optimize reaction conditions, the reaction of 4-Iodoanisol with phenylacetylene was chosen as a model reaction and the effect of different bases and solvents, was studied (Table 4). It seems that KOH has acted better than other bases and EtOH/H_2O (1:1) showed better result as solvent. The reactions at different temperatures were also examined and 50 C was selected as the optimized conditions. Also the amount of catalyst was studied. Finally, 0.07 mol% of catalyst was chosen as the optimized catalyst loading.

Under the optimized reaction conditions (Table 4, entry 7), various aryl bromides reacted with phenyl acetylene and produced Sonogashira products (Table 5). In this reaction system , similar to the Suzuki coupling, aryl halides with electron withdrawing substituents and lower steric hindrance gave higher yields than the derivatives contain electron-donating groups and higher steric hindrance. Also, the reaction condition is mild.

The reusability of catalyst is an essential subject in the field of catalysis from economic and environmental points of view that is commonly attributed to its stability. We surveyed the possibility of recovery and reuse of the SiO_2-NICOT-Pd(II) catalyst using the Suzuki reaction of bromoacetophenone and phenyl boronicacid as the substrates under the same conditions reported in Table 3.

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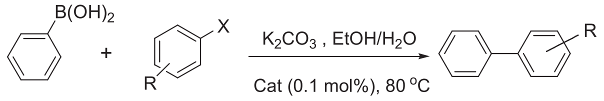
Table 3. Suzuki–Miyaura cross coupling of aryl halides and phenyl boronic acid in the presence of SiO$_2$-NICOT-Pd [a]



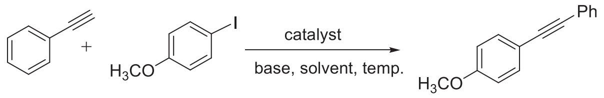
Entry	X	R$_1$C$_6$H$_4$X	Time (h)	Yield(%)[b]
1	Br	4-NO$_2$	2.5	93
2	Br	2-NO$_2$	4.5	84
3	Br	4-Cl	4	75
4	Br	2-Cl	4.5	60
5	Br	H	2.5	83
6	Br	4-OMe	2	88
7	Br	4-OCH$_3$	2	97
8	Br	3-OCH$_3$	2	92
9	Br	2-OCH$_3$	3	80
10	Br	4-CN	1	95
11	Br	4-CHO	3	94
12	Br	3-Cl	4.5	65
13[c]	I	4-OMe	1.5	80
14[c]	I	3-NO$_2$	1	65

[a] The reaction was carried out with aryl halide (1.0 mmol), phenyl boronic acid (1.1 mmol) using K$_2$CO$_3$ (2 eq) and EOH: H$_2$O (1:1) 2 mL in the presence of catalyst (0.1 mol % of Pd) at 80 °C.

[b] GC yield

[c] Room temperature

Table 4. Optimization of Sonogashira reaction of 4-Iodoanisol with phenyl acetylene in the presence of SiO$_2$-NICOT-Pd [a]

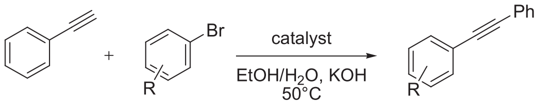


Entry	Solvent.	Base	T (C)	Catalyst (mol%)	Yield(%)[b]
1	EtOH/H$_2$O	K2CO3	r.t	0.1	32
2	EtOH/H$_2$O	K2CO3	50	0.1	55
3	EtOH/H$_2$O	K3PO4	50	0.1	70
4	EtOH/H$_2$O	KOH	50	0.1	90
5	H$_2$O	KOH	50	0.1	40
6	H$_2$O	KOH	80	0.1	53
7	**EtOH/H$_2$O**	**KOH**	**50**	**0.07**	**88**
8	EtOH/H$_2$O	KOH	50	0.04	45

[a] The reaction was carried out with 4-Iodoanisol (1.0 mmol), phenyl acetylene (1.1 mmol) and solvent (2.0 mL) for 3 h.

[b] isolated yield

Table 5. Sonogashira cross coupling of aryl halides and phenylacetylene in the presence of SiO$_2$-NICOT-Pd[a]



Entry	R	Time(h)	Yield(%)[b]
1	4-NO$_2$	1.5	93
2	2-NO$_2$	3	70
3	4-COCH$_3$	3	90
4	4-CN	1	94
5	4-OMe	2	85
6	H	2	65

[a] The reaction was carried out with aryl halide (1.0 mmol), Phenylacetylene (1.1 mmol) using KOH (2 eq) and EOH: H$_2$O (1:1) 2 mL in the presence of 0.7 mol % of Pd-catalyst at 50 C.

[b] GC yield

Table 6. Recyclability of catalyst in the Suzuki reaction [a]

Run	Yield (%)	Run	Yield(%)[b]
1	97	4	91
2	95	5	88
3	91	6	87

[a] The reaction was carried out with bromoacetophenone (1.0 mmol), phenyl boronicacid (1.2 mmol), base (2 equiv.) solvent (2.0 mL) for 20 min.

[b] GC yield

After each reaction-run, the catalyst was separated by centrifugation, washed with ethanol and acetone and dried. Then, the resulting catalyst was reused directly for the next run without further purification. As showed in Table 6, the catalyst was reused six times without significant loss of activity.

The recovered catalyst was invesigated using FT-IR and XRD analysis. In IR spectrum, no remarkable changes were found in the catalyst structure after six times reused (supporting information F1).

Figure 4 shows the XRD patterns of fresh and recovered catalyst. As seen in the Figure 4a, no characteristic peaks of metallic palladium was observed in the XRD pattern of fresh catalyst, confirming the presence of palladium species as the Pd(II) complexes in the catalyst system. In this pattern, the characteristic peak of amorphous SiO$_2$ at $2\theta = 22°$ is clear.

After using the catalyst in the reaction, the catalyst color turned to black, which shows the formation of metallic palladium in the catalyst during the reaction. Sharp peaks at $2\theta = 40.1$ and 46 in the XRD pattern of recovered catalyst (Figure 4b) confirmed the formation of metallic palladium (Pd (0)) in the catalyst after using in the reaction.

To realize that the leaching is occurred or not, catalyst remove from mixture of reaction during the reaction. With removing catalyst during reaction, reaction doesn't proceed more over and this observation confirmed that no leaching has occurred in during reaction.

Experimental

General

All chemicals were purchased from Merck Chemical Co. (Germany) and Sigma-Aldrich and were used without any purifications. The FT-IR spectra were recorded on a Jasco-680 (Japan) spectrophotometer and reported in cm^{-1} (diluted with KBr). The X-ray

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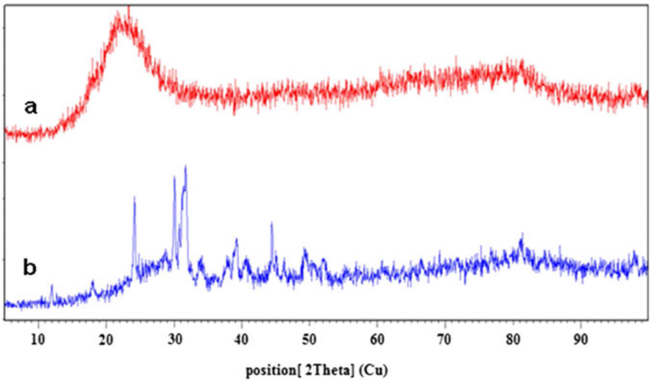

Figure 4. XRD pattern of the fresh catalyst (a) and recovered catalyst (b).

diffraction (XRD) patterns were measured by a Philips X'pert X-ray powder diffractometer. The metal content of the complex was assessed by inductively coupled plasma (ICP). TGA curve was obtained with a heating rate of 10 °C/min under nitrogen atmosphere. The transmission electron microscopy (TEM) images were obtained using Philips CM10 microscope.

General procedure for synthesis of SiO_2-NICOT-Pd(II) nanocatalyst

Scheme 1 summarizes the synthetic route to the SiO_2-NICOT-Pd(II) nanocatalyst. Activated SiO_2 was prepared by adding SiO_2 gel (150–230 mesh; 5 g) in HCl 37% (20 mL) for one day to obtained active silica gel, and then washed with deionized water several times until the pH of the filtrate achieve about 7. And the obtained product was dried at 150 °C overnight in vacuum oven. In a round bottom flask equipped with magnetic stirrer and condenser, a mixture of active silica gel (1 g) and 3-chloropropyltrimethoxysilane (0.4 mmol, 0.74 mL) was refluxed in dry toluene (100 mL) at 110 °C for 72 hours. After that, the solids were separated from the reaction mixture by centrifuge, washed with ethanol and methanol several times and dried under vacuum at 70 °C to obtain chloropropyl-SiO_2 gel.

The chloropropyl-SiO_2 gel and nicotine (NICOT, 0.8 ml, 5 mmol) were added in a round bottom flask equipped with magnetite stirrer and condenser, and the mixture was refluxed in acetonitrile (30 ml) at 80 °C for 40 hours. The mixture was filtered and washed with ethanol and acetone, then dried in room temperature to obtained SiO_2-NICOT.

The final catalyst SiO_2-NICOT-Pd were obtained as light brown solid by addition of Na_2PdCl_4 (5 mg $PdCl_2$ and 2 mg NaCl in methanol) to SiO_2-NICOT (0.7 g) in methanol solvent at room temperature for 24 h. Palladium content was determined 0.4% by ICP. Another catalyst with higher Pd content (4%) was prepared similarly by addition of Na_2PdCl_4 (17 mg $PdCl_2$ and 6.6 mg NaCl in methanol) to 0.24 g of SiO_2-NICOT support in methanol solvent.

General procedure for Suzuki cross-coupling reaction by SiO_2-NICOT-Pd(II) nanocatalyst

In a round-bottomed flask equipped with a condenser and a magnetic stirrer, phenyl boronicacid (1.2 mmol), aryl halide (1.0 mmol), K_2CO_3 (2 eq) and catalyst (1 mol % Pd) were mixed in EtOH-H_2O (1:1, 2 mL). The mixture was stirred at 80 °C under air atmosphere. The progress of the reaction was monitored by TLC (n-hexan/ethyl acetate, 5:1) and GC. After completion of the reaction, the mixture was cooled to room temperature CH_2Cl_2 (15 mL) was added and the catalyst was separated by centrifuge. The organic phase was washed with H_2O (3 × 10 mL), dried over $CaCl_2$, and the solvent was evaporated by rotary. The product was isolated by column chromatography (n-hexane / ethyl acetate, 5:1. The substituted biphenyls synthesized in this work are known compounds and were characterized by their IR, ^1H and ^{13}C NMR spectra, which have been reported previously in the literature.[47–54]

General procedure for Sonogashira cross-coupling reaction by SiO_2-NICOT-Pd(II) nanocatalyst

In a round-bottomed flask equipped with a magnetic stirrer, phenyl acetylene (1.2 mmol), aryl halide (1.0 mmol), catalyst (0.7 mol % Pd) and KOH (2 eq.) in EtOH-H_2O (1:1, 2 mL) was stirred under air atmosphere at 50 °C. The progress of the reaction was monitored by TLC (n-hexan/ethyl acetate, 5:1) and GC. After completion of the reaction, CH_2Cl_2 (15 mL) was added and the catalyst was separated by centrifuge. The organic layer was washed with water (3 × 10 mL) and dried over $CaCl_2$. The product was isolated by column chromatography (n-hexane / ethyl acetate, 5:1) to obtain the corresponding products in to 65–93% yields. The arylalkyne products were known compounds and were characterized by their IR, ^1H and ^{13}C-NMR spectra which have been reported previously in the literature.[54–56]

Conclusions

In this work we have reported synthesis and characterization of SiO_2-NICOT-Pd(II) nanocatalyst and investigated its application in Suzuki and Sonogashira cross coupling reaction in mild condition. Excellent yields in short time have been archived using this catalyst. In addition, the catalyst could be reused in a facile manner from the reaction mixture and recycled for the several times.

Acknowledgements

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