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Palladium nanoparticles supported on SiO₂ by chemical vapor deposition (CVD) technique as efficient catalyst for Suzuki–Miyaura coupling of aryl bromides and iodides: selective coupling of halophenols

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Nanoparticles of palladium were supported on SiO₂ by chemical vapor deposition technique. The obtained Pd nanocatalyst was characterized by various techniques. This catalyst was found to be very efficient for the selective cross-coupling of hydroxyl-substituted aryl iodides and bromide with arylboronic acids in water at room temperature to produce the corresponding hydroxyl-substituted biaryls. Coupling of phenylboronic acid with aryl iodides and bromides carrying substituents other than hydroxy group was also performed efficiently in refluxing ethanol. Copyright © 2012 John Wiley & Sons, Ltd.

Keywords: silica support; palladium nanoparticle; biphenyls; Suzuki-Miyaura reaction

Introduction

Cross-coupling reaction of aryl halides with arylboronic acids through the palladium-catalyzed Suzuki-Miyaura reaction is one of the most valuable methods for the synthesis of biaryl derivatives.^[1] This type of reaction is extensively applied in many synthetic transformations, such as natural products, pharmaceutical targets and conjugated materials.^[2] as well as in conducting polymers.^[3] Palladium complexes with different phosphine ligands are usually employed as catalysts in the traditional Suzuki-Miyaura reaction.^[4–7] However, some of these complexes have encountered problems such as sensitivity to both air and moisture and the possibility of P&bond;C bond degradation at elevated temperatures, and generally an inert atmosphere is required for their efficient manipulation and use. Moreover, their cost and toxicity limit their large-scale industrial application.^[8] As phosphine-free catalysis, Suzuki-Miyaura reaction using ligands such as N-heterocyclic carbenes,^[9] palladacycle species,^[10] palladium nanoparticles,^[11] and also techniques using microwave^[12] or ionic liquids,^[13] etc.^[14] in various solvents have been reported. From the standpoint of environmentally benign organic synthesis and easy recovery of the catalyst, development of immobilized palladium nanoparticles for generation of heterogeneous catalysts is challenging and important.^[15-17] In this line, a great deal of effort has been made to immobilize nano metals on different beds to increase the activity of heterogeneous catalytic systems owing to their higher surface area compared to bulk systems. Because of environmental and economic concerns, recently much effort has been directed towards using water as solvent for organic and organometallic reactions.^[18] Among functionalized biaryls, those substituted with hydroxyl groups are a class of important intermediates in the synthesis of natural products possessing biological activities.^[19]

These biarvls can be obtained by the Suzuki-Mivaura coupling of hydroxyl-substituted aryl halides and phenylboronic acid, catalyzed by palladium. The reaction represents an attractive alternative over other methods using organometallics because organoboranes are air- and moisture-stable with relatively low toxicity.^[20,21] Since halophenols show relatively low reactivity in the Suzuki-Miyaura reaction, there are only a few methods reported in the literature for synthesis of hydroxyl-substituted biaryls.^[22-31] 10% Pd/C has been used for this transformation, but the method can only be successfully applied for iodophenols at room temperature. The yield of the coupled product for bromophenol is low and the reaction time is long (12 h) and occurs at 50 °C.^[22] The use of other catalysts Is long (12 n) and occurs at 50° C.² The use of other catalysts such as Pd(II)/azetidine,^[23] Pd/Napht^{2.2+} (naphthidine di(radical cation),^[24] Pd/NaY zeolite,^[25] Pd/PS-*co*-PAEMA-*co*-PMAA,^[26] Pd(II)/ cationic 2,2-bipyridyl,^[27] Pd(OAc)₂/DBU,^[28] Pd/Sepiolit,^[29] Pd/C,^[22] Pd(II)/graphite oxide^[30] and Pd/CNT^[31] suffers from use of high temperatures (80–150 °C)^[24–28,30,31] and usually long reaction times (10–15 h).^[22,24,29–31] In the present work we wish to report the use of supported palladium nanoparticles on plate SiO₂ by a chemical vapor deposition (CVD) technique as an effective and reusable catalyst for the selective Suzuki-Miyaura coupling reactions of iodo- and bromophenols with phenyl and 4-fluorophenylboronic acids in water. This coupling reaction can also be performed efficiently for other substituted aryl halides in refluxing ethanol.

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Experimental

FT-IR spectra were run on a Shimadzu FTIR-8300 spectrometer. ¹H and ¹³C NMR spectra were recorded on a Brucker Avance DPX-250 MHz spectrometer using tetramethylsilane as internal standard and CDCl₃ as solvent. Scanning electron microscopy (SEM) was performed using a Philips XL-30 FEG instrument at 20 kV. Transmission electron microscopy (TEM) analyses were performed on a Philips model CM 10 instrument. X-ray diffraction (XRD) data were obtained with a Bruker AXS D8 Advance diffractometer. Reaction monitoring was carried out on silica gel analytical sheets or by gas chromatographic analysis using a 3 m length column packed with DC-200 stationary phase.

Preparation of Nano-Pd/SiO₂ by CVD Process^[32]

Plate SiO₂ (42.0 mmol, 2.50 g); 160-430 mesh, pore size diameter (type 60 GF₂₅₄) was placed inside the cooled collector (Fig. 1). A solution of palladium acetate (0.265 mg, 1.181 mmol) in 1-propanol (20 ml) was used as palladium source as shown in Fig. 1. The palladium acetate solution cell was heated to 70 °C with a temperature ramp of 10.0 °C min⁻¹, while argon was bubbled through the vessel containing the palladium acetate solution. This was then mixed with hydrogen and finally introduced to the CVD production line. This process led to the formation of palladium nanoparticles inside the guartz tube. The amounts of Pd aerosols were controlled by a piezoelectric vibrator positioned next to the bottom of the palladium acetate solution. The CVD-synthesized Pd nanoparticles were then passed through UV radiation and finally directed towards the cooled vessel for deposition on the silica substrate. The palladium nanoparticle-doped silica support was subsequently collected, sonicated in a sonication bath (frequency 100 MHz, 60 W) for ~20 min and washed with acetone. The catalyst was characterized



Figure 1. Characterization of Pd/SiO_2 including (A) SEM, (B) AFM and (C) voltage profile

by XRD, SEM, atomic force microscopy (AFM) and TEM. Inductively coupled plasma (ICP) analysis of the catalyst showed that the capacity of Pd was 0.471 mmol g^{-1} of SiO₂, which is equivalent to 5.0 weight percentage.^[32]

Preparation of Nano-Pd/SiO₂ by Solution Technique

Pd/SiO₂ catalyst (5%) was prepared according to the literature,^[33] with some modification as follows: 15.8 mmol, 0.95 g of plate SiO₂; 160–430 mesh, pore size diameter (type 60 GF₂₅₄) was added to an aqueous solution (100 ml) of Pd(NO₃)₂ (125 mg, 0.469 mmol) and magnetically stirred at room temperature. Then, an aqueous solution N₂H₄ (48.0 ml, 1.0 mmol) was added with stirring at room temperature. The black Pd(0) catalyst was formed immediately upon addition of hydrazine, which was filtered and washed thoroughly with water. The catalyst was characterized by SEM and TEM techniques. ICP analysis of the obtained catalyst showed that the Pd weight percentage on SiO₂ was 5%.

Typical Procedure for the Coupling of 4-lodophenol and Phenylboronic Acid Catalyzed with 5% Pd/SiO₂ in Water

A mixture of 5% Pd/SiO₂ (6.4 mg, 0.3 mol%), K₂CO₃ (400 mg, 3.0 mmol), phenylboronic acid (180 mg, 1.5 mmol), and 4-iodophenol (220 mg, 1.0 mmol) **2a** in H₂O (2.0 ml) was stirred magnetically at room temperature. TLC of the reaction mixture showed the completion of the reaction after 1.5 h. After completion, the catalyst was removed by filtration. The aqueous solution was either left for crystallization of the product or was extracted with CH₂Cl₂ (5 × 10 ml) and dried over anhydrous Na₂SO₄. 4-Phenylphenol **2b** was purified by crystallization from CH₂Cl₂ and petroleum ether (white crystals, 161 mg, 95% yield, m.p. 161 °C, (literature^[34] m.p. 165 °C). It was characterized by comparing its ¹H and ¹³C NMR spectra with those reported in the literature.

Typical Procedure for the Coupling of 1-Bromo-4-nitrobenzene and Phenylboronic Acid with 5% Pd/SiO₂ in Ethanol

Pd/SiO₂ (5%, 32 mg, 1.5 mol%), NaOH (60 mg, 1.5 mmol), phenylboronic acid (180 mg, 1.5 mmol), 1-bromo-4-nitrobenzene **8a** (202 mg, 1.0 mmol), and EtOH (2.0 ml) were placed in a 50 ml flask equipped with a magnetic stirring bar and refluxed. TLC of the reaction mixture showed the completion of the reaction after 15 min. After completion, the catalyst was filtrated off. The filtrate was concentrated and then purified by column chromatography over silica gel using *n*-hexane as eluent to afford highly pure 4-nitrobiphenyl **8b** (169 mg, 85% yield) as bright-yellow crystals, m.p. 116 °C, (literature^[35] m.p. 114–114.5 °C). The product was characterized by comparing its ¹H and ¹³C NMR spectra with the data reported in the literature.

Results and Discussion

We initially deposited palladium nanoparticles on plate SiO₂ by CVD method according to the procedure which was recently reported by two of us for deposition of Pd on nanotubes.^[32] In the designed CVD process, mentioned in the Experimental section, plate SiO₂ was used as a suitable solid substrate for coating by palladium nanoparticles.

To characterize the synthesized nano Pd/SiO_2 catalyst, various analytical techniques were used. Figure 1 shows the SEM, AFM and voltage profile images of Pd-supported SiO₂.

The TEM image of CVD-synthesized catalyst is shown in Fig. 2. Based on the information obtained from AFM and SEM images, the histogram of Pd-doped SiO₂ is presented in Fig. 3. According to this histogram, the average diameter of Pd nanoparticles was found to be ~35 nm. Also, the data obtained from TEM analysis confirmed the average size of nanoparticles to be ~30 nm.

Additional characterization was also applied to Pd-doped SiO₂ by patterned XRD technique. According to the XRD spectrum (Fig. 4), the strong peaks positioned at $2\theta = 41^{\circ}$, 48° , and 73° were related to the Pd(0) nanoparticles doped on the SiO₂ support.

We then studied the reaction of phenylboronic acid with 4-iodophenol in H_2O as a model reaction at room temperature



Figure 2. TEM of Pd-supported SiO₂ obtained by CVD technique



Figure 3. Histogram of Pd-doped SiO₂ based on AFM and SEM images



Figure 4. XRD patterns

in the presence of a different quantity of this catalyst and 3.0 molar equivalents of K_2CO_3 as a base (Scheme 1). The results are summarized in Table 1.

The type of silica gel was also found to affect the efficiency of the supported catalyst. As the results of Table 1 show, the Pd catalyst supported on plate SiO₂ with 160–430 mesh, pore size diameter 15–40 μ m (type 60 GF₂₅₄) (Table 1, entry 1) is more reactive than a similar one obtained using SiO₂ of 230–400 mesh, pore size diameter 37–63 μ m (Table 1, entry 4). Controlled experiments using Pd(OAc)₂ and Pd(OAc)₂ on bulk SiO₂ were also performed. The results obtained (Table 1, entries 6 and 7) show that Pd/SiO₂ prepared by CVD is much more reactive.

In order to have a comparison between reactivity of the supported nanopalladium on SiO_2 by this technique (CVD method) and the conventional chemical method, we also prepared 5 wt % nano-Pd on the plate SiO_2 by solution technique according to the literature.^[33] SEM and TEM of the obtained Pd/SiO₂ by this technique are shown in Fig. 5.

We then used this catalyst for the coupling reaction of 4-iodophenol and phenylboronic acid under the same reaction conditions as we used for the Pd/SiO₂ obtained by CVD technique (Table 1, entry 5). The obtained result shows that the catalyst obtained by CVD method was much more reactive. The lower reactivity of the nanopalladium catalyst obtained by solution technique compared to that obtained by CVD could be due to aggregation of the palladium nanoparticles, which is clearly demonstrated in its TEM image (Fig. 5). In comparison, the TEM image of the catalyst obtained by



Scheme 1. Suzuki–Miyaura cross-coupling reaction of 4-iodophenol with phenylboronic acid

Table 1. F	Reaction Perature	of 4- using	iodo g difl	pher feren	nol with photostatic supported	enylb d pal	ooronio ladium	c acid n nar	l in water a noparticles ^a	t
_									where the second	

Entry	of preparation	mol%	nme (n)	rieid" (%)
1	5% Pd/SiO ₂ (60 GF ₂₅₄)	0.3	1.5	95
	(160–430 mesh, pore size			
	diameter: 15–40 µm) / CVD			
2	5% Pd/SiO ₂ (60 GF ₂₅₄) / CVD	0.2	1.7	93
3	5% Pd/SiO ₂ (60 GF ₂₅₄) / CVD	0.1	2	93
4	5% Pd/SiO ₂ (230-400 mesh,	0.3	3.7	88
	pore size diameter:			
	37–63 μm) / CVD			
5	5% Pd/SiO ₂ type 60	0.3	8	85
	GF ₂₅₄ /solution technique ^[33]			
6	Bulk Pd(OAc) ₂	0.3	4	60
7	Bulk Pd(OAc) ₂ / bulk SiO ₂ ^c	0.3	4	65

^aReaction conditions: 4-iodophenol (1.0 mmol), phenylboronic acid (1.5 mmol), K_2CO_3 (3.0 mmol), catalyst in 2.0 ml H₂O. ^bIsolated yield.

^cReaction conditions are as mentioned in note 'a' in the presence of 2.86 mg SiO₂.



Figure 5. Microscopic images: (A) TEM and (B) SEM of palladium nanoparticles doped on SiO_2 by solution technique

CVD technique shows the well-separated nano-Pd supported on SiO_2 (Fig. 2).

Among different loading values of Pd/SiO₂ (Table 1, entries 1–3), 0.3 mol% was selected as the most suitable loading for this reaction.

The effect of solvent on the reaction of 4-iodophenol was also studied (Table 2). Among different solvents, H_2O was found to be the best choice for the reaction (Table 2, entry 7).

The effect of various bases on the coupling of 4-iodophenol was also studied. The results obtained showed that K_2CO_3 and Cs_2CO_3 acted as the most effective bases for this reaction (Table 3, entries 1 and 5).

Under our optimized reaction conditions (1.0 mmol of halophenol, 6.4 mg (0.3 mol%) of Pd/SiO₂, 3.0 mmol of K₂CO₃ and 2.0 ml of H₂O), the desired products were obtained in excellent yields from iodo- and bromophenols and phenylboronic acid at room temperature (Table 4, entries 3–6). The coupling reactions of 4-iodo- and 4-bromophenols were also successfully performed with 4-fluorophenylboronic acid at room temperature and 50 °C respectively (Table 4, entries 7–9).

When this catalyst was applied to aryl halides with substituents other than hydroxy group, such as &bond; CH_3 or &bond; OCH_3 , it was observed that the reaction times at room temperature were

Table 2.	Effect of different solvents on the coupling of 4-iodophenol
with pher	hylboronic acid at room temperature ^a

Entry Solvent		Time (h)		Isolated yield (%)		
		Room temperature	Reflux	Room temperature	Reflux	
1	THF	12	24	50	81	
2	Toluene	12	5	40	77	
3	CH₃CN	12	24	45	60	
4	CH_2CI_2	48	24	32	50	
5	DMF	12	12	65	90	
6	EtOH	12	12	60	83	
7	H ₂ O	1.5	—	95	—	

^aReaction conditions: 4-iodophenol (1.0 mmol), phenylboronic acid (1.5 mmol), K₂CO₃ (3.0 mmol), 5 wt% Pd/SiO₂ (0.3 mol%) in 2.0 ml solvent

Table 3. Effect of different bases on the reaction of 4-iodophenol at room temperature^a

Base	mmol of base	Time (h)	Isolated yield (%)
K ₂ CO ₃	3	1.5	95
NaOH	3	2.5	86
Na ₃ PO ₄ .12H ₂ O	3	6.8	85
KF.2H ₂ O	3	20	50
Cs ₂ CO ₃	3	1.3	96
Et_3N	3	4	82
K ₂ CO ₃	2	5	91
K ₂ CO ₃	1	11	94
	$\begin{array}{c} \text{Base} \\ \text{K}_2\text{CO}_3 \\ \text{NaOH} \\ \text{Na}_3\text{PO}_4.12\text{H}_2\text{O} \\ \text{KF}.2\text{H}_2\text{O} \\ \text{Cs}_2\text{CO}_3 \\ \text{Et}_3\text{N} \\ \text{K}_2\text{CO}_3 \\ \text{K}_2\text{CO}_3 \\ \text{K}_2\text{CO}_3 \end{array}$	Base mmol of base K2CO3 3 NaOH 3 Na3PO4.12H2O 3 KF.2H2O 3 Cs2CO3 3 Et3N 3 K2CO3 2 K2CO3 1	Base mmol of base Time (h) K2CO3 3 1.5 NaOH 3 2.5 Na3PO4.12H2O 3 6.8 KF.2H2O 3 20 Cs2CO3 3 1.3 Et3N 3 4 K2CO3 2 5 K2CO3 1 11

^aReaction conditions: 4-iodophenol (1.0 mmol), phenylboronic acid (1.5 mmol), base, 5 wt% Pd/SiO₂ (0.3 mol%) in 2.0 ml H_2O .

dramatically increased and the reactions were not completed (Table 4, entries 10 and 11). As far as we know, there are no reports in the literature on the selective coupling of halophenols; we therefore decided to take this advantage and apply it to the selective coupling of halophenols.

When we performed competitive reactions using binary mixtures of halophenols and aryl halides carrying substituents other than hydroxyl group with both $C_6H_5B(OH)_2$ and 4-F- $C_6H_4B(OH)_2$ under our optimized reaction conditions in water, high selectivity was observed and halophenols reacted preferentially (Table 5).

In order to gain some insight into the origin of the selectivity and discover the effect of solvent, we also performed the abovementioned competitive reactions in refluxing ethanol. In comparison with the reactions in water which occur at room temperature, the reactions in ethanol required refluxing conditions. However, again high selectivity was observed. On the basis of this observation, it can be concluded that the reaction is selective for halophenols independent of the nature of the solvent, reaction temperature, and the solubility effect. The observed selectivity may be explained based on the possibility of H-bonding between the hydroxyl groups of the silica and the phenolic ones. This interaction can bring closer the phenolic substrate and the complex obtained from the oxidative addition of aryl halide to Pd(0)/SiO₂ catalyst. The stability and recyclability of the catalyst were determined by using it in successive reactions and also by its thermal analysis. After reusing the catalyst four times in the coupling reaction of 4-iodophenol and phenylboronic Table 4. Nano Pd/SiO₂ catalyzes the coupling of halophenols and ArB(OH)₂ at room temperature^a



Entry	Halophenol	ArB(OH) ₂ (mmol)	Product	Time (h)	Isolated yield (%)
1	2-lodophenol 1a	PhB(OH) ₂ (1.5)	2-Phenylphenol 1b	12	64
2 ^b	2-lodophenol 1a	PhB(OH) ₂ (1.5)	2-Phenylphenol 1b	1	85
3	4-lodophenol 2a	PhB(OH) ₂ (1.0)	4-Phenylphenol 2b	3.5	82
4	4-lodophenol 2a	PhB(OH) ₂ (1.2)	4-Phenylphenol 2b	3	95
5	4-lodophenol 2a	PhB(OH) ₂ (1.5)	4-Phenylphenol 2b	1.5	95
6	4-Bromophenol 3a	PhB(OH) ₂ (1.5)	4-Phenylphenol 2b	2	89
7	4-lodophenol 2a	4-FC ₆ H ₄ B(OH) ₂ (1.5)	4-(4'-Fluoro)phenylphenol 3b	8	88
8 ^c	4-Bromophenol 3a	4-FC ₆ H ₄ B(OH) ₂ (1.5)	4-(4'-Fluoro)phenylphenol 3b	5	86
9 ^b	4-Bromophenol 3a	4-FC ₆ H ₄ B(OH) ₂ (1.5)	4-(4'-Fluoro)phenylphenol 3b	12.5	80
10 ^d	4-lodoanisol 4a	PhB(OH) ₂ (1.5)	4-Methoxybiphenyl 4b	8.5	48
11 ^d	4-lodotoluene 5a	PhB(OH) ₂ (1.5)	4-Methylbiphenyl 5b	8.5	33

^bThe reaction was performed at 50 °C.

^cThe reaction was performed in refluxing water.

^dYields were determined by gas chromatographic analysis.

Table	Table 5. Competitive reactions using binary mixtures of halophenols and other substituted aryl halides with PhB(OH) ₂ and 4-F-C ₆ H ₄ B(OH) ₂ ^a							
Entry	ArBr	Product	lsolated yield (%) in water / Time (h)	lsolated yield (%) in refluxing EtOH				
1	4-Bromophenol 3a 4-Bromoanisole 6a	4-Phenylphenol ^[47,51] 2b 4-Methoxybiphenyl ^[36,47–50] 4b	80 / 99	85 / 124				
2	4-Bromophenol 3a 4-Bromotoluene 7a	4-Phenylphenol ^[39,47,51] 2b 4-Methylbiphenyl ^[36,47,48] 5b	81 / 95	80 / 126				
3	4-Bromophenol 3a 1-Bromo-4- nitrobenzene 8a	4-Phenylphenol ^[34,47,51] 2b 4-Nitrobiphenyl ^[35,46–48,50] 8b	83 / 93	bb				
4	4-Bromophenol 3a 4-Bromotoluene 7a	4-(4'-Fluoro)phenylphenol 3b 4- (4'-Fluoro)phenyltoluene ^[37] 7b	83 / 9 ^c 4 ^c	78 / 125				
5	4-lodophenol 2a4-Bromotoluene 7a	4-Phenylphenol ^[34,47,51] 2b4-Methylbiphenyl ^[36,47,48] 5b	88 / 97	87 / 123				
aDeest		ather substituted and balide (10 model) when the work	a acticle and 4 Auguran	have de avanta a stal				

^aReaction conditions: halophenol (1.0 mmol), other substituted aryl halide (1.0 mmol), phenylboronic acid and 4-fluorophenylboronic acid (2.0 mmol), K_2CO_3 (3.0 mmol), 5 wt% Pd/SiO₂ (0.5 mol%, 10.6 mg) in 2.0 ml of solvent at room temperature.

^bNo reaction occurs in refluxing ethanol for both substrates.

^cThe reaction was performed in refluxing water.

acid, the coupled product was obtained in 95–89% yield but with some reaction time elongation from the first to the second run.

In order to determine the leaching of the catalyst, the reaction of 4-iodophenol and phenylboronic acid in the first run was stopped every 30 min, and the filtered solution was analyzed by ICP analysis. The results of ICP analysis did not show any appreciable amounts of Pd leaching. Analysis of the reaction after every run by ICP and TG showed only 0.81% of leached Pd. In support of the stability of the catalyst, in another set of experiments we also took the thermograms of the catalyst after every 30 min reaction time at the first run and after each run. The thermograms of the Pd-doped silica are shown in Fig. 6. According to thermograms B and C, the decrease to ~0.4% in the weight percentage at ~120°C is due to the desorption of water vapor from the nanocatalyst. Also, the slight enhancement in the weight percentages in all thermograms at around 180°C is due to the air oxidation of palladium nanoparticles, revealing the air stability and lack of significant leaching of Pd from the surface of silica. Also, a significant decrease (\sim 3.6%) in the weight percentage at a temperature of \sim 280 °C is related to desorption of the previously adsorbed organic molecules. The data obtained from thermal analysis can also be considered as further evidence for the lack of significant Pd leaching from the surface of the catalyst.

In order to show the efficiency of this nano-catalyst for the Suzuki– Miyaura coupling reaction of halophenols, we compared some of our results for the coupling of 4-bromophenol with those reported in the literature in Table 6. This comparison shows that our catalyst provides the highest isolated yield of the coupled product at the shortest reaction time and the lowest reaction temperature.

Since water was found to be a very suitable medium for the coupling of only halophenols, we decided to study the possibility

of using this new Pd nano-catalyst for the coupling of other substituted aryl halides using other solvents. In Table 7 the results obtained results for the coupling of 1-bromo-4-nitrobenzene in different solvents are shown. As demonstrated in Table 7, refluxing ethanol was found to be very suitable for the coupling of 1-bromo-4-nitrobenzene, and therefore this condition was extended to other aryl halides (Table 8). The results shown in Table 8 demonstrate that this





Entry	Solvent	Temp. (°C)	Catalyst	Time (h)	Isolated yield (%)	Ref.
1	H ₂ O	Room temp.	Pd/SiO ₂ (0.3)	2	95	a
2	H₂O	50	Azetidine-Pd(II) (0.01)	3	91	[23]
3	Dioxane	80	Pd/Napht ^{2.2+} (0.6)	15	48	[24]
4	DMA/H ₂ O (1:1)	100	Pd/NaY zeolite (0.001)	0.25	86	[25]
5	H ₂ O	90	Pd/ PS-co-PAEMA-co-PMAA (0.2)	1	99	[26]
6	H ₂ O	100	Pd(II)/cationic 2,2-bipyridyl (0.001)	1	99	[27]
7	EtOH/H ₂ O (1:1)	150	Pd(OAc) ₂ /DBU (0.4)	0.16	24	[28]
8	H₂O	Room temp.	Pd/sepiolite (0.1)	20	99	[29]
9	H ₂ O	50	Pd/C (0.3)	12	76	[22]
10	EtOH/H ₂ O (1:1)	80	Pd ²⁺ /GO (0.25)	17	96	[30]
11	H ₂ O	90	Pd/CNT (0.3)	10	99	[31]

^a Present	method.
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Table 7.	Table 7. Optimization of the different parameters for the coupling reaction of 1-bromo-4-nitrobenzene with phenylboronic acid ^a								
	O ₂ N Br B(OH) ₂ Nano Pd/SiO ₂ , Base O ₂ N Ph								
Entry	Solvent	Base (mmol)	Catalyst (mol%)	Temp. (°C)	Time (h)	Yield (%) ^b			
1	H ₂ O:EtOH (1:2)	K ₂ CO ₃ (3.0)	0.3	90	4.5	20			
2	H ₂ O:Dioxane (1:2)	K ₂ CO ₃ (3.0)	0.3	100	4	15			
3	H ₂ O:EtOH (1:2)	K ₂ CO ₃ (3.0)	1	90	4	90			
4	EtOH	K ₂ CO ₃ (3.0)	1	80	8	50			
5	DMF	K ₂ CO ₃ (3.0)	0.3	110	5	100			
6	DMF	K ₂ CO ₃ (3.0)	1	90	4	100			
7	DMF	K ₂ CO ₃ (3.0)	1	110	1	100			
8	EtOH	NaOH (3.0)	1	80	3.5	91			
9	DMF	NaOH (3.0)	1	110	0.25	100			
10	DMF	NaOH (3.0)	0.6	110	7	52			
11	DMF	Na ₃ PO ₄ .12H ₂ O (3.0)	1	110	4	100			
12	DMF	NaOH (1.5)	1	110	7.5	100			

^bGas chromatographic analysis.

Table 8. Suzuki–Miyaura reaction of phenylboronic acid with aryl halides^a

R: H, NO₂, CN, NH₂, CH₃, OCH₃, Cl X: Br, I

Entry	ArX	Ar-Ph	Time	Yield (%)
1	1-Bromo-4-nitrobenzene 8a	4-Nitrobiphenyl ^[35,46–48,50] 8b	15 min	85
2	4-Bromobenzonitrile 9a	4-Cyanobiphenyl ^[38,47] 9b	10 min	90
3	5-Bromopyrimidine 10a	5-Phenylpyrimidine ^[39] 10b	30 min	87
4	1-Bromo-4-chlorobenzene 11a	4-Chlorobiphenyl ^[40,48] 11b	60 min	88
5	3-Bromopyridine 12a	3-Phenylpyridine ^[41] 12b	90 min	80
6	4-lodoanisole 4a	4-Methoxybiphenyl ^[36,47–50] 4b	30 min	90
7	4-lodotoluene 5a	4-Methylbiphenyl ^[36,47,48] 5b	20 min	93
8	lodobenzene 13a	Biphenyl ^[42,48,50] 13b	10 min	97
9	1-lodo-4-nitrobenzene 14a	4-Nitrobiphenyl ^[35,47,48] 8b	5 min	98
10	4-lodoaniline 15a	4-Phenylaniline ^[43,48] 15b	30 min	75
11	2-lodotoluene 16a	2-Methybiphenyl ^[44,48] 16b	25 min	90
12	1-lodonaphthalene 17a	1-Phenylnaphthalene ^[43,48] 17b	25 min	72
13	2-lodo-5-nitrotoluene 18a	2-Phenyl-5-nitrotoluene ^[45] 18b	1 h	85
14 ^b	Bromobenzene 19a	Biphenyl ^[42,48,50] 13b	24 h	88
15 ^b	4-Bromotoluene 7a	4-Methylbiphenyl ^[36,47,48] 5b	24 h	78
16	1-Bromonaphthalene 20a	1-Phenylnaphthalene ^[43] 17b	4 h	80

^aReaction conditions: aryl halide (1.0 mmol), phenylboronic acid (1.5 mmol), 5 wt% Pd/SiO₂ (1.5 mol%, 32.0 mg), NaOH (1.5 mmol), EtOH (2.0 ml), reflux. ^bReaction conditions: aryl halide (1.0 mmol), phenylboronic acid (1.5 mmol), 5 wt% Pd/SiO₂ (1.5 mol%, 32.0 mg), NaOH (3.0 mmol), DMF (2.0 ml), 110 °C.

catalyst can be applied efficiently to the coupling of aryl bromides and iodides having both electron-withdrawing and donating groups as well as heteroaromatic compounds in refluxing ethanol.

We also performed the hot filtration test for the reaction of 1-bromo-4-nitrobenzene with phenylboronic acid in refluxing ethanol. ICP analysis of the filtrate showed only 1.1% of palladium leaching. The low leaching of the palladium from the catalyst shows that the reaction occurs mainly through a heterogeneous pathway.

Conclusion

In summary, adsorption of nano-palladium on SiO_2 by CVD technique provides an efficient and heterogeneous catalyst which works under very mild reaction conditions for the Suzuki– Miyaura coupling of halophenols ArX (X = Br, I) and phenylboronic acids. In addition, this catalytic system was found to be very selective for the coupling of halophenols, which can be considered a unique property for this catalyst.

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