FULL PAPER

Nanosilica-anchored Pd(II)-Schiff base complex as efficient heterogeneous catalyst for activation of aryl halides in Suzuki– Miyaura cross-coupling reaction in water

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Funding information UGC, New Delhi, India, SAD-DRS-I programme (2016–2021); UGC-BSR (RFSMS) Fellowship. A nanosilica (derived from rice husk)-anchored Pd(II)–Schiff base complex has been synthesized and characterized. This immobilized complex has been found to be a very effective and recyclable heterogeneous catalyst for the Suzuki–Miyaura cross-coupling reaction of various aryl halides with arylboronic acid in aqueous medium under mild conditions. The products were identified using ¹H NMR and mass spectral studies. This complex can be easily filtered out from the reaction medium and reused up to six times without significant loss of catalytic activity. Since the reaction proceeds under mild conditions in aqueous medium as well as the catalyst being recyclable, it provides an environmentally benign alternative route to the existing protocols for the Suzuki–Miyaura reaction.

KEYWORDS

aryl halides, arylboronic acid, rice husk, Schiff base, Suzuki-Miyaura

1 | INTRODUCTION

Schiff bases are some of the most widely explored ligands as they play a significant role not only in coordination but also in catalysis and synthetic organic chemistry. There are many Schiff base-containing Pd(II) complexes acting either as homogeneous or heterogeneous catalysts for cross-coupling reactions with excellent yields of products.^[1,2] Though homogeneous catalysts show very good activity, they are difficult to separate and rarely reusable, hence heterogeneous catalysts score better because of their easy separation from products, reusability and high stability if immobilized on a robust support like silica or alumina. In recent years, various reports have been published dealing with immobilization of palladium-based compounds on a variety of solid supports like silica,^[3-5] MCM-41,^[6,7] SBA-15,^[8,9] FSM-16,^[10] alumina,[11,12] etc. However, because of some specific characteristics like wide accessibility, ease of processing, low cost, high thermal stability and better surface reactivity, silica is one of the best and widely used supports for immobilization of transition metal compounds. One of the cheapest and most eco-friendly sources of silica is rice husk that

contains 90–97%^[13] silica and can be extracted using a very easy procedure.

The Suzuki–Miyaura reaction is one of the most widely studied, involving cross-coupling between aryl halides and arylboronic acid to give homoaryl and biaryl derivatives. Most of the available reports indicate the use of palladiumbased catalysts for such C–C coupling reactions with aryl bromides/iodides as substrates;^[3,14–18] however, there are only a few reports of aryl chlorides as substrates. Since aryl chlorides are easily available and economically more favourable than bromides and iodides, they may act as more suitable substrates in Suzuki–Miyaura reactions. Therefore, there is a need to develop new silica-supported palladium catalysts for efficient activation of aryl chlorides, preferably with low palladium loading but reusable for several reaction runs.

Here we report the synthesis of a reusable palladium compound with tetradentate Schiff base complex immobilized on rice husk-derived nanosilica and its evaluation as a heterogeneous catalyst in Suzuki–Miyaura cross-coupling reactions between aryl halides (including aryl chlorides) and arylboronic acid in aqueous media under mild reaction conditions.

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2 | EXPERIMENTAL

Nanosilica was derived from rice husk using a reported method^[19] and it was used for immobilization of the Pd(II)–Schiff base complex. The overall process is shown in Scheme 1.

To set up the reaction, a mixture of aryl halide (1 mmol), arylboronic acid (1.2 mmol), K_2CO_3 (2 eq.), catalyst (appropriate quantity) and solvent (6 ml) was taken in a 50 ml round-bottom flask and allowed to stir at the appropriate temperature. After completion of the reaction, the catalyst was separated by filtration and the residue was extracted from the filtrate using a water–ether mixture (1:3) followed by washing with brine and drying over Na₂SO₄. The products were isolated by column chromatography of the residue using ethyl acetate–hexane (1:9) as eluent.

3 | **RESULTS AND DISCUSSION**

3.1 | Characterization

The synthesized nanosilica and nanosilica-based materials were characterized using various analytical techniques, namely Fourier transform infrared (FT-IR) spectroscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM) coupled with energy-dispersive X-ray analysis (EDX), Brunauer–Emmett–Teller (BET) surface area measurement, elemental analysis and inductively coupled plasma atomic emission spectrometry (ICP-AES).

3.1.1 | FT-IR study

In the FT-IR spectra of nanosilica and (3-aminopropyl) triethoxysilane (APTES)-functionalized nanosilica, the peaks at 1629 and 3457.27 cm⁻¹ are assigned to OH bending and OH stretching, respectively. The FT-IR spectrum of APTES@nanoSiO₂ exhibits a new band at 1543 cm⁻¹ (γ NH₂) indicating grafting of APTES onto nanosilica (Fig. 1Sb). A new band observed at 1633.23 cm⁻¹ is assigned to ν C=N which indicates the formation of Schiff base anchored to nanosilica (Fig. 1Sc). In the FT-IR spectrum of the Pd(II)–Schiff base complex (Fig. 1Sd) new bands at 564 cm⁻¹ (ν P=N) and 557 cm⁻¹ (ν P-d-O) clearly indicate that Pd is coordinated through nitrogen and oxygen. Interestingly, it is observed that the ν C=N band is shifted from 1633.23 to 1624.32 cm⁻¹ on complexation. However, the FT-IR spectrum of Schiff base ligand L₁ (Figure 1) displays





FIGURE 1 FT-IR spectrum of Schiff base ligand (L1)

bands at 1636, 3446 (broad) and 1265 cm⁻¹, attributable to ν C=N, ν OH and ν C-O, respectively, confirming the formation of the Schiff base ligand.

3.1.2 | Elemental analysis

The elemental analysis data of free nanosilica, Schiff base of nanosilica, Schiff base ligand and the complex are presented in Table 1S.

3.1.3 | XRD, SEM-EDX and ICP-AES analyses

In the XRD pattern of amorphous nanosilica, a strong diffraction peak at $2\theta \approx 21.1^{\circ}$ indicates SiO₂ (Figure 2) and the diffraction pattern of nanosilica-immobilized Pd complex exhibits two new peaks at $2\theta = 38.09^{\circ}$ and 47.25° corresponding to the (111) and (200) lattice planes of face-centred



FIGURE 2 XRD patterns of (a) nanosilica and (b) Pd(II)–Schiff base complex

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cubic system of the Pd complex consistent with results reported previously.^[15,20]

The morphological change that occurs on the surface of nanosilica after loading of the Pd complex can be confirmed from the SEM images of the free nanosilica and supported Pd complex. It is observed that there is a significant decrease in the silica particle size in the presence of Pd which could be due to modification of surface morphology of silica due to immobilization of the Pd complex (Figure 3). The SEM–EDX results indicate the metal content along with the O, N and Si proportions and suggest the formation of metal complex with the anchored ligand in successive steps as shown in Figure 2S.

The ICP-AES analysis indicates that there is 0.068 mmol Pd content per 10 mg of the catalyst.



FIGURE 3 SEM images of (a) nanosilica, (b) Schiff base of nanosilica and (c) Pd(II)–Schiff base complex

TABLE 1 BET surface area measurement of nanosilica-based materials

Entry	Material	$S_{\rm BET} ({ m m}^2~{ m g}^{-1})$
1	Nanosilica	189.97 ^a
2	APTES@nanoSiO ₂	175.45 ^a
3	Schiff base anchored to nanosilica (L)	169.21
4	Pd(II)-Schiff base complex (C)	160

^aReported in Gogoi et al.^[19]

3.1.4 | Surface area measurement

The specific surface areas of the produced silica-based materials were calculated using the BET method. The gradual decrease in surface area (Table 1) from nanosilica to anchored Pd(II)–Schiff base complex is indicative of immobilization of the complex onto the nanosilica surface.

3.2 | Catalytic activity

We employed an aryl bromide (*p*-bromoanisole) and phenylboronic acid as model substrates in order to investigate the reaction conditions. At first, we conducted the reaction with various amounts of the catalyst, 5, 10, 15, 20 mg, and even in the absence of the catalyst. It is observed that 10 mg of catalyst is very efficient for the required conversion (Table 2, entry 2); however, no product is isolated in the absence of catalyst (Table 2, entry 9). The reaction was also performed in the absence of Pd metal (Table 2, entries 7 and 8), when no product can be isolated from the reaction mixture, clearly indicating the crucial role of Pd metal in the reaction.

The catalyst is less active at room temperature (*ca* 30 $^{\circ}$ C) producing only 55% yield after 5 h (Table 2, entry 5). Various solvents like C₂H₅OH, H₂O, ⁱPrOH, MeOH, CH₃CN and dimethylsulfoxide (DMSO) as well as various bases like K₂CO₃, Na₂CO₃, NaHCO₃ and Cs₂CO₃ were also tested in order to determine the optimum reaction conditions. Since water has high polarity index (9.0), bases are easily soluble in it, which activates the boronic acid. Thus, this may be the reason for obtaining the highest yield in water for the Suzuki coupling reaction (Table 2, entry 2). Furthermore, the best result is obtained in the case of 2 eq. of K₂CO₃ (entry 2). No product is obtained in the absence of base (entry 16). The reaction was also carried out with 1.5 and 2.5 eq. of K₂CO₃, which afford 78 and 98% yields, respectively (entries 17 and 18). Therefore, we carried out further reactions taking 2 eq. of K_2CO_3 as the optimum amount.

Next, we applied the optimized reaction conditions to various aryl bromides and arylboronic acid having either

TABLE 2 Optimization of Suzuki–Miyaura reaction of aryl bromide (p-bromoanisole) and phenylboronic acid at 50°C^a

MeO-Br + B(OH) ₂ Catalyst, base Solvent MeO-							
Entry	Catalyst (amount in mg)	Solvent	Base (eq.)	Time (h)	Yield (%) ^b		
1	Pd(II)–Schiff base complex (5)	H ₂ O	K ₂ CO ₃ (2)	1	70		
2	Pd(II)-Schiff base complex (10)	H ₂ O	K ₂ CO ₃ (2)	0.5	98		
3	Pd(II)-Schiff base complex (15)	H ₂ O	K ₂ CO ₃ (2)	0.5	98		
4	Pd(II)-Schiff base complex (20)	H ₂ O	K ₂ CO ₃ (2)	0.5	99		
5	Pd(II)-Schiff base complex (10)	H ₂ O	K ₂ CO ₃ (2)	5	55 ^c		
6	Pd(II)-Schiff base complex (10)	H ₂ O	K ₂ CO ₃ (2)	0.5	98 ^d		
7	Schiff base of nanosilica (20)	H ₂ O	K ₂ CO ₃ (2)	6	_		
8	Nanosilica (20)	H ₂ O	K ₂ CO ₃ (2)	6	_		
9	_	H ₂ O	K ₂ CO ₃ (2)	6	_		
10	Pd(II)-Schiff base complex (10)	C ₂ H ₅ OH	K ₂ CO ₃ (2)	3	67		
11	Pd(II)-Schiff base complex (10)	ⁱ PrOH	K ₂ CO ₃	2	71		
12	Pd(II)-Schiff base complex (10)	H_2O-^iPrOH (1:1)	K ₂ CO ₃ (2)	1	85		
13	Pd(II)-Schiff base complex (10)	CH ₃ CN	K ₂ CO ₃ (2)	2	80		
14	Pd(II)-Schiff base complex (10)	MeOH	K ₂ CO ₃ (2)	4	74		
15	Pd(II)-Schiff base complex (10)	DMSO	K ₂ CO ₃ (2)	5	65		
16	Pd(II)-Schiff base complex (10)	H ₂ O	_	6	_		
17	Pd(II)-Schiff base complex (10)	H ₂ O	K ₂ CO ₃ (1.5)	1	78		
18	Pd(II)-Schiff base complex (10)	H ₂ O	K ₂ CO ₃ (2.5)	0.5	98		
19	Pd(II)-Schiff base complex (10)	H ₂ O	Cs ₂ CO ₃ (2)	2.5	67		
20	Pd(II)-Schiff base complex (10)	H ₂ O	NaHCO ₃ (2)	2	65		
21	Pd(II)-Schiff base complex (10)	H ₂ O	Na ₂ CO ₃ (2)	2	67		

^aReaction conditions: aryl bromide (1 mmol), arylboronic acid (1.2 mmol), Pd catalyst (10 mg), K₂CO₃ (2 eq.), H₂O (3 ml), *ca* 50 °C in air unless otherwise noted. ^bIsolated yield.

^cRoom temperature.

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electron-withdrawing group or electron-donating group as coupling partner. The results are given in Table 3. It is found that aryl bromides with both electron-withdrawing and electron-donating groups underdo coupling reaction with arylboronic acid effectively to give products in high yields in water. In addition, the present protocol is also effective in the case of heteroaryl halide with 4-fluoroboronic acid (Table 3, entry 16). This procedure is found to be very useful and green resulting in excellent yields under mild reaction conditions.

To investigate the scope and limitations of the present catalytic system, we also conducted cross-coupling reactions using an aryl chloride under a similar set of conditions as with aryl bromides, when 25% yield is obtained even after 6 h of reaction time clearly indicating the low efficiency of the catalyst for aryl chlorides. However, when we used dimethylformamide (DMF)– H_2O (1:1) as solvent with 20 mg of catalyst loading at 65 °C, comparatively higher yield of product is obtained (Table 4, entry 7). Increasing the amount of base to 2.5 eq. does not affect the product yield (Table 4, entry 9). We also carried out the reaction by replacing the base with Cs₂CO₃ and Na₂CO₃, but this does not improve the yield (Table 4, entries 9 and 10).

In our next move, we carried out the reaction using aryl chlorides containing an electron-withdrawing group, such as p-chloroacetophenone (Table 5, entry 2), an electron-donating group, such as p-chloroanisole (entry 6), and an electron-neutral group, such as chlorobenzene (entry 3), with phenylbronic acid. Excellent yields of the desired biphenyl are achieved. However, on replacement of phenylboronic acid by p-methoxyboronic acid (entries 1 and 7) and pfluoroboronic acid (entry 5) no significant effect on the yield



$R_1 \xrightarrow{Br} B(OH)_2$ $Pd \text{ catalyst (10 mg), } K_2CO_3 (2 \text{ equiv.})$ $H_2O, 50 \ ^0C \qquad R_1 \xrightarrow{Pd} R_2$					
Entry	R ₁	R ₂	Product	Time (h)	Yield (%) ^b
1	4-MeO	Н	MeO-	1	98
2	4-MeO	4-MeO	MeO	1	100
3	4-MeO	3-Ме	MeO-	2	97
4	4-NO ₂	4-MeO	O ₂ N-OMe	3	95
5	4-NO ₂	Н	0 ₂ N-	3	92
6	4-CHO	Н	онс-	2	92
7	4-CHO	4-MeO	OHC - OMe	3	95
8	4-CH ₃ CO	4-MeO	H ₃ COC	3	93
9	4-Me	4-MeO	Me	2	96
10	4-NO ₂	4-F	O ₂ N-F	2	94
11	4-Me	3-Ме	Me-	4	97
12	Н	Н		0.5	100
13	4-MeO	2-Me	MeO	2	96
14	4-MeO	4-CHO	МеО-СНО	3	97
15	4-MeO	4-F	MeO-	3	95
16	N= N-Br	4-F	N N N	6	94

^aReaction conditions: aryl bromide (1 mmol), arylboronic acid (1.2 mmol), Pd catalyst (10 mg), K₂CO₃ (2 eq.), H₂O (3 ml), *ca* 50 °C in air. ^bIsolated yield.

MeO CI + B(OH) ₂ Catalyst, base Solvent MeO							
Entry	Catalyst (amount in mg)	Solvent	Base (eq.)	Time (h)	Yield (%) ^b		
1	Pd(II)-Schiff base complex (10)	H ₂ O	K ₂ CO ₃ (2)	6	25		
2	Pd(II)-Schiff base complex (10)	ⁱ PrOH	K ₂ CO ₃ (2)	6	56		
3	Pd(II)-Schiff base complex (10)	H_2O-^iPrOH (1:1)	K ₂ CO ₃ (2)	6	54		
4	Pd(II)-Schiff base complex (10)	DMF-H ₂ O (1:1)	K ₂ CO ₃ (2)	6	64		
5	Pd(II)-Schiff base complex (10)	DMF-H ₂ O (1:1)	K ₂ CO ₃ (2)	5	70 ^c		
6	Pd(II)-Schiff base complex (15)	DMF-H ₂ O (1:1)	K ₂ CO ₃ (2)	5	$70^{\rm c}$		
7	Pd(II)-Schiff base complex (20)	DMF-H ₂ O (1:1)	K ₂ CO ₃ (2)	5	74 ^c		
8	Pd(II)-Schiff base complex (20)	DMF-H ₂ O (1:1)	K ₂ CO ₃ (2.5)	5	74 ^c		
9	Pd(II)-Schiff base complex (20)	DMF-H ₂ O (1:1)	Cs ₂ CO ₃ (2)	6	65 ^c		
10	Pd(II)-Schiff base complex (20)	DMF-H ₂ O (1:1)	Na ₂ CO ₃ (2)	6	59 ^c		

^aReaction conditions: aryl chloride (1 mmol), arylboronic acid (1.2 mmol), K₂CO₃ (2 eq.), H₂O (3 ml).

^bIsolated yield.

°At 65 °C.

is observed. These results are quite significant for cross-coupling reactions of aryl chlorides with various arylboronic acids.

3.3 | Catalyst leaching and reusability

3.3.1 | Hot filtration test

The hot filtration test is an important method for checking whether a catalysed reaction is truly heterogeneous or not.^[21] We carried out a hot filtration test by taking p-

bromoanisole and phenylboronic acid as substrates. After 10 min, the reaction was stopped and the catalyst filtered off (20% yield determined using GC–MS), and the reaction was allowed to continue for a further 3 h without the solid catalyst (Figure 4). No catalytic activity could be seen in the filtrate (using GC analysis) which rules out the possibility of homogeneous/semi-heterogeneous catalysis. No Pd is leached into the solution, indicating the heterogeneous nature of our catalyst. To further establish this result, we performed ICP-AES analysis of the filtrate and no trace of Pd was found

 TABLE 5
 Suzuki–Miyaura reaction of aryl chlorides with various arylboronic acids^a

$R_1 \xrightarrow{CI} \qquad \qquad$						
Entry	R ₁	R ₂	Product	Time (h)	Yield (%) ^b	
1	4-Me	4-MeO	Me	5	62	
2	4-CH ₃ CO	Н	H ₃ COC	5	65	
3	Н	Н		4	85	
4	4-CHO	Н	онс-	5	68	
5	4-MeO	4-F	MeO-	5	67	
6	4-MeO	Н	MeO	5	74	
7	4-MeO	4-MeO	MeO	3	76	

^aReaction conditions: aryl chloride (1 mmol), arylboronic acid (1.2 mmol), Pd catalyst (20 mg), K₂CO₃ (2 eq.), DMF–H₂O (4 ml), *ca*. 65 °C in air. ^bIsolated yield.



FIGURE 4 Activity of the catalyst for the reaction between phenylboronic acid and 4-bromoanisole with hot filtration and without filtration

in the filtrate, supporting the absence of leaching of Pd and establishing the heterogeneous nature of the catalyst.

3.3.2 | Recyclability

The recyclability of the catalyst was investigated by choosing phenylboronic acid and 4-bromoanisole as coupling partner. Figure 5 shows that the nanosilica-anchored Pd(II)-Schiff base complex can be used for up to six consecutive cycles without any significant loss of its efficiency. Because of the solid nature of the catalyst, it is easily recoverable by centrifuging the reaction mixture after completion. The catalyst is reusable in a subsequent coupling reaction after thoroughly washing with water and ethyl acetate and drying. However, the reaction time increases slightly in successive cycles. Since there is no significant leaching of palladium during the catalysis and recovery, the slight gradual decrease in product yield after successive reuse may be due to physical loss of the amount of the catalyst. Moreover, the SEM-EDX analysis of the used catalyst (after the sixth cycle) shows the presence of Pd metal and the SEM image (Figure 6) is similar to that of the fresh catalyst.

To know the valance state of the catalyst after completion of a catalytic cycle, we performed solid-state UV–visible spectral analysis of the fresh catalyst and also of the catalyst



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FIGURE 6 SEM image of Pd complex (after sixth use)

recovered after completion of reaction (Figure 7). Results show that the valance of the nanosilica-anchored Pd(II)–Schiff base complex remains same after completion of the reaction under the same conditions. The appearance of peaks at 251 and 395 nm for fresh and used catalyst confirms that the Pd metal in the catalyst is in the +2 oxidation state.^[22]

We have also compared the catalytic activity of our catalyst with that of some previously reported catalysts,^[15,23,24] indicating the superior activity of our catalyst (Table 6).

4 | CONCLUSIONS

The novelty of the present work is that the catalyst is reusable up to six times and also it is active for both aryl chlorides and aryl bromides as one of the coupling partners with low catalyst loading. The catalyst exhibited a high activity in aqueous media under mild reaction conditions. Overall, the present protocol offers a mild, efficient and attractive alternative to the existing methods because of the use of green solvent and inorganic base and the broad substrate scope.



FIGURE 5 Recyclability of the catalyst

FIGURE 7 UV-visible spectra of (a) fresh catalyst and (b) used catalyst

TABLE 6 Comparison of catalytic activity of present catalyst with that of other previously reported supported Pd catalysts

Entry	Catalyst	Aryl halide	Yield (%), reaction time	Solvent	Temperature (°C), base	Ref.
1	Pd@imineSiO ₂	PhBr PhCl	100, 1 h No reaction	ⁱ PrOH–H ₂ O (1:1) ⁱ PrOH–H ₂ O (1:1)	27, Na ₂ CO ₃ 27, Na ₂ CO ₃	[15]
2	Pd ⁰ /SBA-15	PhBr PhCl	80.2, 4 h 60.0, 4 h	DMF DMF	110, NEt ₃ 110, NEt ₃	[21]
3	PdNP@SiO ₂ -PPh ₂	PhBr PhCl	94, 3 h 95, 5 h	ⁱ PrOH–H ₂ O (1:1) DMF	60, K ₂ CO ₃ 100, K ₂ CO ₃	[24]
4	Poly-NHC-2-Pd ²⁺	PhBr PhCl	99, 5 min 100, 3 h	EtOH-H ₂ O EtOH-H ₂ O	80, K ₃ PO ₄ ·3H ₂ O (3 eq.) 80, K ₃ PO ₄ ·3H ₂ O (3 eq.)	[23]
5	Pd(II)-Schiff base complex on rice husk-derived nanosilica support	PhBr PhCl	100, 0.5 h 85, 4 h	H ₂ O DMF-H ₂ O (1:1)	50, K ₂ CO ₃ (2 eq.) 65, K ₂ CO ₃ (2 eq.)	Present work

ACKNOWLEDGMENTS

The authors acknowledge SAIC-Tezpur University for carrying out SEM–EDX and CHN elemental analysis. The authors are also grateful to SAIF-Kochi for carrying out ICP-AES and ¹H NMR analyses of the products. The authors are grateful to UGC, New Delhi, India for financial support under the SAD-DRS-I programme (2016–2021). N.G. also thanks UGC, New Delhi for financial assistance in the form of UGC-BSR (RFSMS) Fellowship.

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How to cite this article: Gogoi N, Bora U, Borah G, Gogoi PK. Nanosilica-anchored Pd(II)-Schiff base complex as efficient heterogeneous catalyst for activation of aryl halides in Suzuki–Miyaura cross-coupling reaction in water. *Appl Organometal Chem.* 2016; e3686. doi: 10.1002/aoc.3686