Research Article

Biomass waste rice husk derived silica supported palladium nanoparticles: an efficient catalyst for Suzuki–Miyaura and Heck–Mizoroki cross-coupling reactions

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Abstract

Here, we report an inexpensive, versatile, and environmentally benign biomass waste rice husk derived amorphous silica-supported palladium (PdNPs/RH-SiO_2) nano-catalyst for Suzuki–Miyaura and Heck–Mizoroki cross-coupling reactions. The proposed catalyst was prepared in two steps. In the first step, amorphous SiO_2 obtained by calcination of rice husk and the following deposition of palladium nanoparticles by using the chemical reduction method in the second step. The physico-chemical properties of the catalysts were investigated by N_2 adsorption–desorption, XRD, XPS, ^{29}Si CP-MAS NMR, and TEM analysis. The palladium content in the catalysts has been determined by ICP-OES analysis. The 1% PdNPs/RH-SiO_2 exhibited excellent catalytic performance for Suzuki–Miyaura and Heck–Mizoroki C–C cross-coupling reactions to produce biaryl and stilbene compounds with >99% selectivity and excellent TON values (529 and 524). Furthermore, the catalyst is repeatedly used for four consecutive cycles without a significant drop in the yield.

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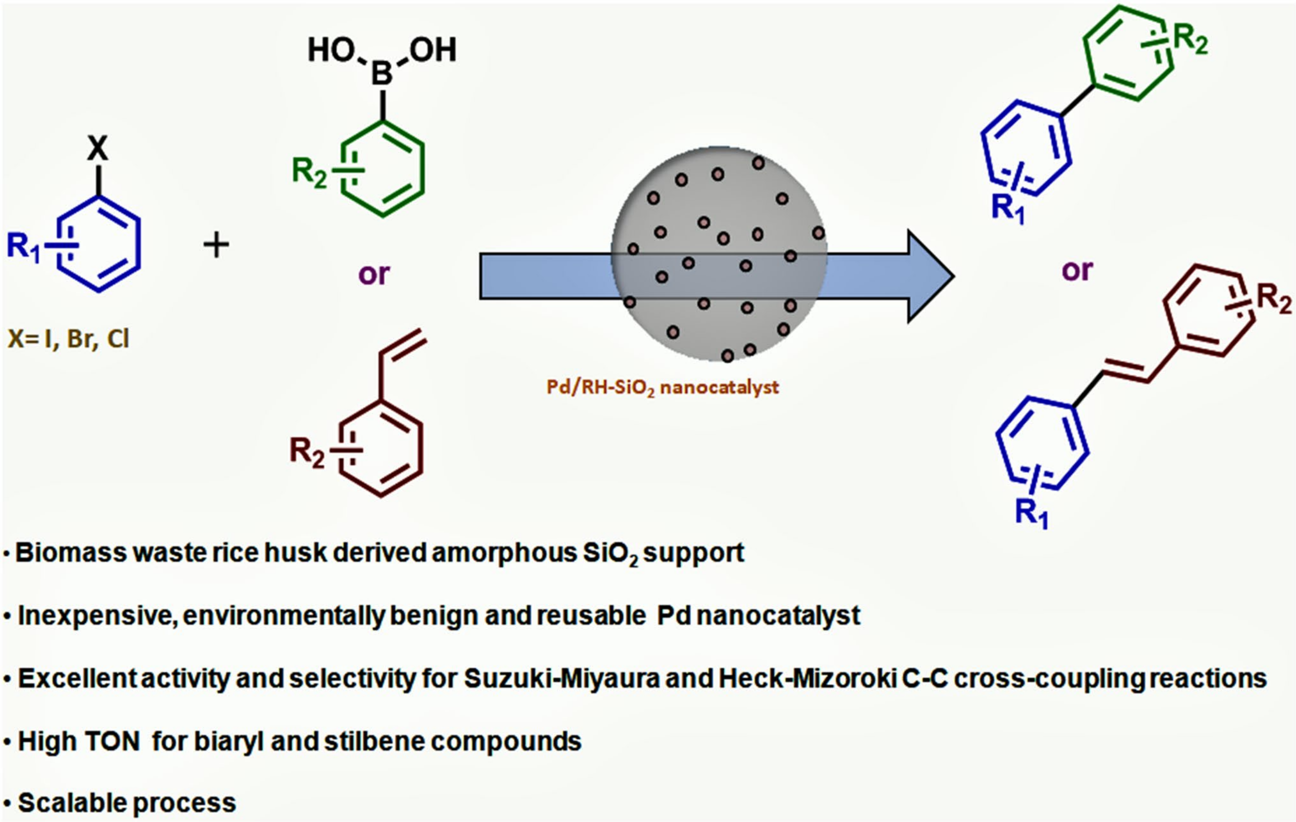
Graphic abstract



- Biomass waste rice husk derived amorphous SiO_2 support
- Inexpensive, environmentally benign and reusable Pd nanocatalyst
- Excellent activity and selectivity for Suzuki-Miyaura and Heck-Mizoroki C-C cross-coupling reactions
- High TON for biaryl and stilbene compounds
- Scalable process

Keywords Rice husk · SiO_2 · Palladium · C–C coupling · Suzuki · Heck

1 Introduction

Suzuki and Heck coupling reactions are the most powerful one-step methods for carbon–carbon bond formation in organic synthesis, especially these reactions are employed in the preparation of a large variety of complex organic molecules, having prevalent applications in pharmaceutical, crop-protection, polymers, materials, and fine chemical applications [1–12]. The current state-of-the-art process relies on precious homogeneous palladium complexes with a combination of sophisticated and sensitive ligands [13–15]. Despite their excellent activity, selectivity, and tolerant to broad substrate scope, the catalyst separation and recycling of Pd are the major obstacles for large scale applications [16]. Moreover, these catalytic processes require a tedious workup procedure for the isolation of the product, resulting in large amounts of waste, leading to the expensive manufacturing process [17]. More importantly, the contamination of Pd and ligand residues in the end product limits their application in pharmaceutical industries [9, 18]. In contrast to homogeneous catalysts, solid catalysts are often preferred due to their easy separation and reusability [12, 19]. In this regard, a commercially available Pd/C catalyst was employed for Suzuki and Heck coupling reactions and achieved up to 36,000 ton [20]. But, functional group tolerance and too much leaching of Pd/C are the major problems [21]. Therefore, the research has been directed towards the development of green and eco-friendly heterogeneous Pd catalysts for C–C coupling reactions. In this sense, several methods have been developed for the immobilization of Pd complexes on solid supports/polymers to combine the benefits of both homogeneous and heterogeneous catalysts [12, 22]. However, these catalysts are also encountered with several issues pertaining to activity/selectivity and leaching of palladium into the reaction medium [22]. In addition, several chemists have reported heterogeneous palladium catalysts on various supports such as metal oxides [22–27], silica [28–32], zeolites [33–35], carbon materials [36–38], polymers [39–43], MOFs [44–46] and others [47–53] to facilitate the recovery and reuse of precious Pd catalysts. But, the issues related to the use and cost of catalyst supporter stabilizers, reaction conditions, and reproducibility are questioning the practical applicability in the industrial point of view.

On the other hand, the replacement of fossil resources by renewable materials has been given the top priority in fuel/chemical industries. In recent years, the use of renewable feedstocks emerges as a promising strategy for the production of fuels, chemicals, and materials in a more sustainable approach [54–56]. In this regard, highly abundant and low-cost agricultural waste by-product rice husk has received particular attention in academia and industry. In general, rice husk is produced from rice, as 1-ton rice produces 0.2 ton rice husk. Hence, the mass production of rice in the world results a huge volume of rice husk, nearly 148 million metric tons of rice husk from 740 million metric tons of rice annually, and treating as a low-value fuel for bio-refineries [57]. Rice husk is mainly composed of cellulose (30–35%), hemicelluloses (20–25%), lignin (15–20%), and ash (10–15%). Interestingly, more than 90% of rice husk ash is in the form of hydrated amorphous silica. Since the high content of amorphous silica, rice husk is being considered as an excellent precursor for the preparation of nano and mesoporous silica materials [57–59]. Recently, rice husk derived carbon-supported catalysts have been developed and applied successfully for C–C coupling reactions [60, 61]. Therefore, the preparation of rice husk derived amorphous SiO_2 supported Pd catalysts is considered to be a green and low-cost approach for C–C coupling reactions.

Inspiring from the aforementioned works, herein, we demonstrate a simple and facile method for the preparation of inexpensive and environmentally benign biomass waste rice husk derived amorphous silica-supported palladium nano-catalyst (PdNPs/RH-SiO_2). These RH-SiO_2 supported Pd nanoparticles to create a stable and reusable catalyst for Suzuki–Miyaura and Heck–Mizoroki C–C cross-coupling reactions under mild reaction conditions.

2 Experimental section

2.1 Materials

Unless otherwise noted, all chemicals were purchased from M/s. Sigma–Aldrich and used as received. Gel-Silica (G-SiO_2) with 60–120 mesh purchased from M/s. SD Fine Chemicals Pvt. Ltd. Rice-Husk was obtained from the local rice mill, Telangana. 35.4% HCl purchased from M/s. Rankem Pvt. Ltd. Phenylboronic acid (98%) purchased from M/s. Alfa Aesar, sodium carbonate (99.5%), Hydrazine (99%) purchased from M/s. SD Fine Chemicals Pvt. Ltd.

2.2 Preparation of catalysts

2.2.1 Preparation of rice-husk derived silica support (RH-SiO_2)

RH-SiO_2 support was prepared according to the reported procedure with modifications and details are shown in Scheme 1 [57, 60]. In a typical procedure, a required amount of raw rice husk was added to 0.1 M HCl solution and stirred at 100 °C for 6 h. Then, the mixture was cooled down to room temperature, and the solids were filtered and washed with distilled water to reach the pH ~ 7. The resultant solids were oven-dried at 100 °C for 12 h. The dried solids were calcined at 600 °C for 3 h under airflow with a 90 ml/min flow rate and yielded the RH-SiO_2 support. The obtained silica was symbolized as RH-SiO_2.

2.2.2 Preparation of RH-SiO_2-supported palladium nanoparticles (PdNPs/RH-SiO_2)

The PdNPs/RH-SiO_2 catalysts with 0.5%, 1%, and 1.25% Pd on RH-SiO_2 support were prepared as per the reported method [62]. Typically, the required amount of $PdCl_2$ was dissolved in distilled water, and 2–3 drops of HCl were added. Then, the requisite amount of RH-SiO_2 support was added to the above solution and stirred at room

Scheme 1 Preparation of rice husk derived silica (RH-SiO_2)

temperature for 30 min. Subsequently, hydrazine hydrate was added drop wise under vigorous stirring for 1 h. The resulted reaction mixture was left for stirring for another 2 h, and the reaction mixture turns into black. The dark solids were filtered and washed several times with water followed by methanol and diethyl ether, respectively. The black solids were dried under vacuum at 100 °C for 12 h. In a similar procedure, 1% Pd on G-SiO_2 (1% Pd/G-SiO_2) and F-SiO_2 (1% Pd/FM-SiO_2) catalysts were prepared.

2.3 Catalytic activity

2.3.1 Procedure for Suzuki cross-coupling reaction

All reactions were performed in a 25 ml round bottom flask. In a typical experiment, Bromobenzene (1 mmol), phenylboronic acid (1.25 mmol), and Na_3PO_4 (1 mmol) were added to 2 ml EtOH:H_2O (1:1 v/v) solvent. Then, 20 mg of the respective catalyst was added to the reaction mixture and stirred at 80 °C for the required time. After the reaction, the catalyst was recovered by simple filtration and washed numerous times with ethyl acetate followed by drying.

2.3.2 Procedure for Heck–Mizoroki coupling reaction

A mixture of iodobenzene (1 mmol), styrene (1.2 mmol), Na_2CO_3 (1 mmol), and 20 mg of catalyst in 2 ml of DMF solvent was taken into 25 ml round bottom flask and stirred at 120 °C for the required time. After completion of the reaction, the reaction mixture cooled down to room temperature and diluted with ethyl acetate solvent. The catalyst was recovered by filtration and washed with ethyl acetate and dried.

The products of all the above reactions were analyzed and identified by HP-GC and GC–MS (QP-2010 model, M/s. Shimadzu Instruments, Japan) equipped with EB–5 MS capillary column (30 m × 0.25 mm × 0.25 μm).

3 Result and discussions

Pd/RH-SiO_2 nano-catalyst were prepared by a simple two-step method, (1) in the first step; rice husk biomass-derived SiO_2 support was obtained by calcination of rice husk biomass under airflow at 600 °C, (2) secondly, the palladium nanoparticles (PdNPs) were deposited on RH-SiO_2 support by chemical reduction with hydrazine hydrate.

3.1 Catalyst characterization

In order to understand the structure-activity of the 1% Pd/RH-SiO_2 nano-catalyst for selective C–C coupling reactions, the catalyst was extensively characterized

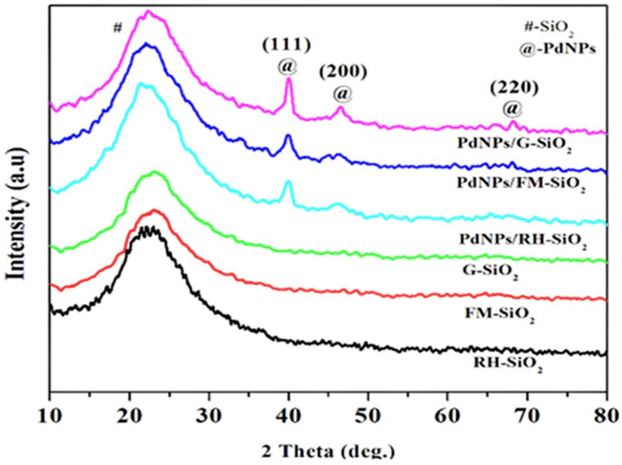


Fig. 1 Wide-angle XRD patterns of different SiO_2 and supported Pd catalysts

Table 1 Textural properties of different SiO_2 and supported Pd catalysts

Entry	Catalyst	S_{BET} (m^2/g)	v^a (cm^3/g)	d^b (nm)	Pd^c (wt%)	Pd^d (wt%)
1	RH-SiO_2	127	0.1	11.8	–	–
2	FM-SiO_2	318	0.3	3.2	–	–
3	G-SiO_2	552	0.5	3.1	–	–
4	1% PdNPs/RH-SiO_2	81	0.1	9.8	1	0.92
5	1% PdNPs/FM-SiO_2	238	0.1	3.0	1	0.94
6	1% PdNPs/G-SiO_2	218	0.3	3.0	1	0.91
7	0.5% PdNPs/RH-SiO_2	110	0.2	9.5	0.5	0.48
8	1.25% PdNPs/RH-SiO_2	95	0.2	9.7	1.25	1.17

[a] Pore volume

[b] Pore diameter

[c] From theoretical values

[d] From ICP-OES

with comprehensive analytical techniques such as XRD, XPS, BET, TEM, solid-state ^{29}Si CP-MAS NMR, and ICP-OES analysis.

3.1.1 N_2 adsorption–desorption analysis

The textural characteristics of various silica-based catalysts are determined by N_2 adsorption–desorption analysis. The BET surface area, pore-volume, and pore diameter and are depicted in Table 1. The commercially available Fumed-silica (F-SiO_2) and G-SiO_2 have the BET surface area of 552 and 318 m^2/g with 0.3, 0.5 cm^3/g pore volume and 3.2, 3.1 nm pore diameters (Table 1, entry 2 and 3). However, the rice husk derived SiO_2 support has a low BET surface area (127 m^2/g) and pore volume (0.1 cm^3/g), but a large pore diameter (11.8 nm) was noticed with respect to commercial SiO_2 supports (Table 1, entry 1). Further, a decrease in the surface area of all SiO_2 supports has been observed after the introduction of PdNPs. A similar trend has been monitored for pore volume and pore diameter, respectively (Table 1, entry 4–8). These results suggest the pore blockage by the deposition of PdNPs. The Pd content in the catalysts was determined by ICP-OES analysis, and the results are close to the theoretical values (Table 1, entry 4–8).

3.1.2 XRD analysis

The wide-angle XRD pattern of 1% Pd/RH-SiO_2, 1% Pd/G-SiO_2, and 1% Pd/F-SiO_2 nano-catalysts are shown in Fig. 1. The 1% Pd/RH-SiO_2 nanocatalyst exhibits a broad peak between 20° and 30° on the 2θ scale, which is a characteristic peak of amorphous silica. The 1% Pd/RH-SiO_2 nanocatalyst displays a diffracted peak at $2\theta = 40.1°$, $2\theta = 44.8°$ are referred to (111) (200) planes of palladium in zero oxidation state (JCPDS #05-0681). However, the peak corresponding to (220) plane is not observed, indicating the fine and homogeneous distribution of PdNPs throughout the SiO_2 matrix. The similar XRD patterns observed with G-SiO_2 and F-SiO_2 supported Pd nanocatalysts, respectively (Fig. 1).

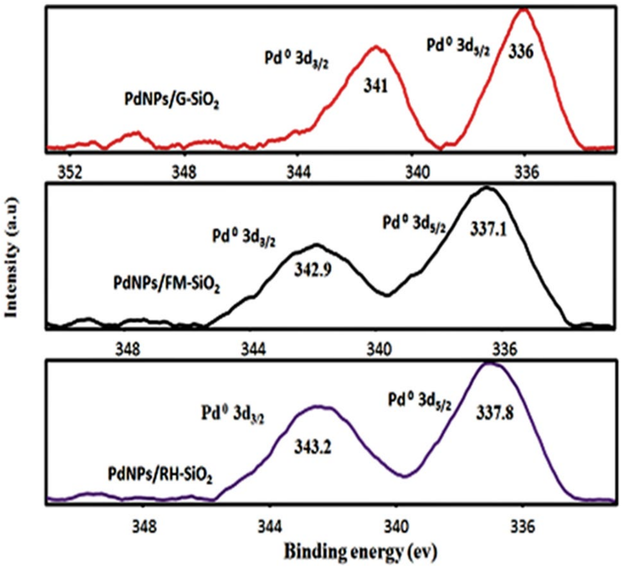


Fig. 2 XPS patterns of PdNPs/RH-SiO_2, PdNPs/FM-SiO_2, and PdNPs/G-SiO_2 catalysts

3.1.3 XPS analysis

XPS analysis was performed to ascertain the oxidation state of palladium and metal-support interactions in the different SiO_2 supported Pd catalysts, and the corresponding spectrum is shown in Fig. 2. As shown in Fig. 2, the Pd 3d spectra of 1% PdNPs/RH-SiO_2 catalyst display two peaks, the binding energies centered at 343.2 and 337.8 eV are attributed to $3d_{5/2}$ and $3d_{3/2}$ of palladium in zero oxidation state, which is consistent with the reported values for palladium in zero-valent [60]. In the case of 1% PdNPs/FM-SiO_2 and 1% PdNPs/G-SiO_2 catalysts, the Pd 3d peaks are shifted to lower binding energies (342.9, 337.1 eV and 341, 336 eV). These results are indicating that the 1% PdNPs/RH-SiO_2 nanocatalyst has strong metal-support (Pd–SiO_2) interactions.

3.1.4 Solid-state ^{29}Si CP-MAS NMR

The ^{29}Si CP-MAS NMR analysis provides information regarding the structural environment of silicon atoms in the SiO_2 matrix. The ^{29}Si CP-MAS NMR spectra of the different SiO_2 samples are shown in Fig. 3. The spectrum of

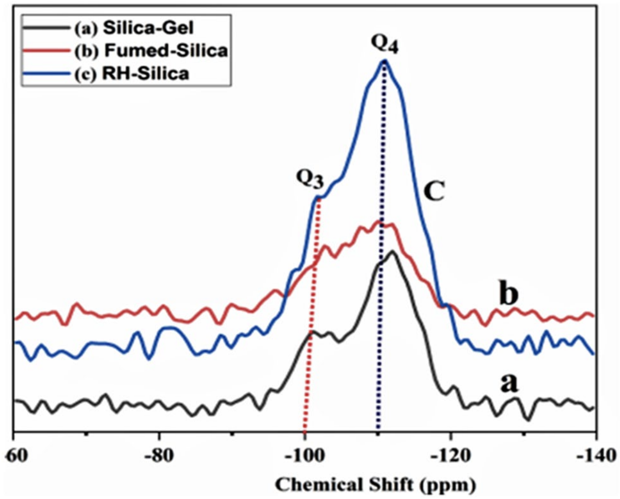


Fig. 3 ^{29}Si CP-MAS NMR of **a** G-SiO_2, **b** FM -SiO_2, and (c) RH-SiO_2

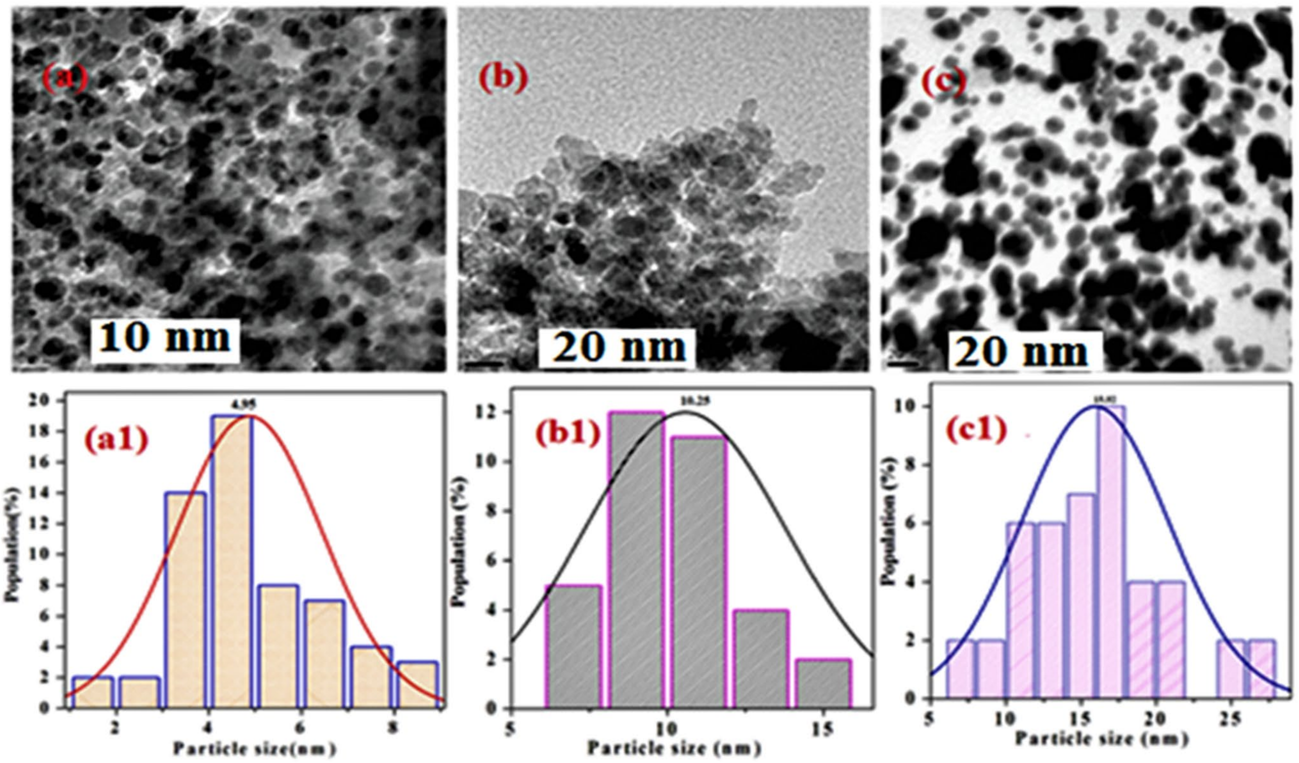


Fig. 4 TEM images of **a** 1PdNPs/RH-SiO_2, **b** 1PdNPs/FM-SiO_2, **c** 1PdNPs/G-SiO_2 catalysts

RH-SiO_2 can be fitted into two peaks at −100 and −110 ppm ascribed to silanol groups [Q_3, Si(Si–O)$_3$(OH)] and (Si–O)$_4$ of the silica framework [Q_4, Si(Si–O)$_4$] [63]. FM-SiO_2 and G-SiO_2 also exhibited the same NMR pattern (Fig. 3) but, the lines are with much larger line widths.

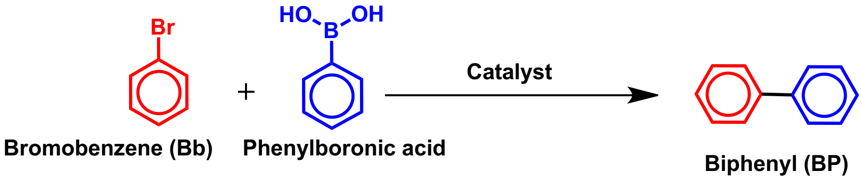
3.1.5 TEM analysis

The size and morphology of Pd nanoparticles in 1% PdNPs/RH-SiO_2, 1% PdNPs/FM-SiO_2, and 1% PdNPs/G-SiO_2 catalysts were investigated by using transmission electron microscopic (TEM) analysis, and the resultant TEM image is displayed in Fig. 4a. The Pd particles in 1% PdNPs/RH-SiO_2 catalysts are spherical with an average particle diameter in the range of 3–5 nm and uniformly dispersed throughout the RH-SiO_2 matrix. In the case of 1% PdNPs/G-SiO_2 and 1% PdNPs/FM-SiO_2 catalysts, the aggregation of Pd particles was observed in (Fig. 4b, c).

3.2 Catalyst screening

The catalytic activity of as-prepared 1% Pd/RH-SiO_2 nanocatalyst was systematically examined for the Suzuki–Miyaura cross-coupling reaction with bromobenzene (BB) and phenylboronic acids as model substrates and the corresponding results are shown in Table 2. Control experimental data shows that the reaction did not proceed in the absence of a catalyst (Table 2, entry 1). Similarly, no reaction was observed when SiO_2 supports were directly used as catalysts (Table 2, entry 2–4), indicating the need for active metal species to perform the reaction. The yield of biphenyl (BP) was only 42% with 1% PdNPs/G-SiO_2 catalyst, while the biphenyl yield was increased to 57% with 1% PdNPs/FM-SiO_2 catalyst (Table 2, entry 5 and 6). To our delight, the reaction with 1% PdNPs/RH-SiO_2 at 80 °C for 6 h using Na_3PO_4 base in H_2O: Ethanol solvent mixture, the yield was significantly increased to >99% and without the formation of any undesired side products (Table 2, entry 7). The remarkable catalytic activity of 1% PdNPs/RH-SiO_2 catalyst can be attributed to the formation of small-sized nanoparticles (3–5 nm) with uniform distribution on the RH-SiO_2 surface and strong metal-support interactions. In order to optimize the reaction parameters, the reaction has been performed in different solvents (Table 2, entry 8–10). In non-polar toluene solvent, only 41% yield obtained (Table 2, entry 8), while the yields were improved to 68–78% in polar DMF and ethanol solvents (Table 2, entry 9 and 10). The maximum biphenyl yield (>99%) was achieved in H_2O:Ethanol solvent mixture within the 6 h of reaction time (Table 2, entry 7). Next, we evaluated the effect of the base on the product yields. In general, the base plays a crucial role in

Table 2 Suzuki–Miyaura C–C cross-coupling reaction of bromobenzene (BB) and phenylboronic acids over different supported Pd catalysts



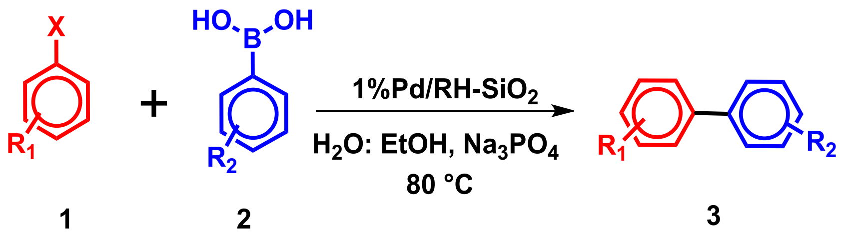
Entry	Catalyst	Conversion (%)	Selectivity (%)	TON
1	Blank	–	–	–
2[a]	RH-SiO_2	–	–	–
3[a]	G-SiO_2	–	–	–
4[a]	FM-SiO_2	–	–	–
5[a]	1% PdNPs/G-SiO_2	42	99	222.5
6[a]	1% PdNPs/FM-SiO_2	57	99	302
7[a]	1% PdNPs/RH-SiO_2	99	99	529.94
8[b]	1% PdNPs/RH-SiO_2	41	99	217.2
9[c]	1% PdNPs/RH-SiO_2	68	99	360.3
10[d]	1% PdNPs/RH-SiO_2	78	99	413.3
11[e]	1% PdNPs/RH-SiO_2	65	99	344.4
12[f]	1% PdNPs/RH-SiO_2	55	99	291.4
13[g]	1% PdNPs/RH-SiO_2	44	99	233
14[h]	1% PdNPs/RH-SiO_2	37	99	196.7
15[a]	0.5% PdNPs/RH-SiO_2	58	99	307.3
16[a]	1.25% PdNPs/RH-SiO_2	79	99	418.6

Reaction conditions: [a]Bromobenzene (1 mmol), Phenylboronic acid (1.25 mmol), catalyst (20 mg), Na_3PO_4 (1 mmol), 80 °C, 6 h. [b]Toulene, [c]ethanol, [d]DMF. [e]Na_2CO_3, [f]K_2CO_3, [g]CS_2CO_3, [h]Et_3N. TON-Turn over Number

the product yields and selectivity in Suzuki–Miyaura C–C coupling reactions [64]. From Table 2, we found that the reaction in inorganic bases proceeded smoothly than the organic base and obtained good to excellent desired product yields (Table 2, entry 11–14). Furthermore, the selectivity and yields depend on the strength of the base, as the yield was increased with decreasing the strength of the base. Further, we studied the effect of Pd loading on RH-SiO_2 support for the Suzuki cross-coupling reaction of bromobenzene (BB) and phenylboronic acid (Table 2, entry 15 and 16). With an increase, the Pd loading on the RH-SiO_2 support, the desired biphenyl product yields were also increased and obtained a maximum of >99% yield with 1% Pd loading (Table 2, entry 7). A further increase in the Pd loading, from 1 to 1.5 wt%, there is a significant drop in the biphenyl yield observed (Table 2, entry 16), which could be due to the aggregation of Pd nanoparticles on the surface of RH-SiO_2 support with increasing Pd loading.

With an optimized reaction condition in hand, Suzuki–Miyaura C–C cross-coupling of aryl halides and phenylboronic acids with a diverse functional group in the presence of 1% PdNPs/RH-$SiO_2$was evaluated, and the results are depicted in Table 3. The reaction with simple iodobenzene proceeds smoothly and obtained 99% conversion and selectivity within 3 h of reaction time, whereas the bromobenzene required 6 h reaction time (Table 3, entry 1 and 6). No reaction was observed with chlorobenzene (Table 3, entry 15). This result suggesting the iodobenzene has more reactivity than the Bromo and chlorobenzene, which is due to the –I is better leaving group than the –Br and –Cl groups. Next, we investigated the electronic effect of substituted aryl halides on the activity and selectivity of 1% PdNPs/RH-SiO_2 catalyst. The aryl halides with electron-withdrawing groups at *para*-position need short reaction times for complete conversion with 99% selectivity (Table 3, entry 4, 7, 10). In contrast, the electron-donating groups require a longer reaction time (Table 3, entry 3, 9, 14). Further, the aryl halides with electron-withdrawing/donating groups at *ortho*-position are less reactive than the *para*-position (Table 3, entry 2, 8, 11, 13). This phenomenon could be due to the substitute groups at the *ortho* position create a steric hindrance, which further restricts the reactivity of aryl halides. Also, the –OCH_3 substituted phenylboronic acids were

Table 3 Substrate scope of Suzuki cross-coupling over 1% PdNPs/RH-SiO_2 catalyst



Entry	X	R_1	R_2	Time (h)	Conversion (%)	Selectivity (%)	TON
1[a]	I	H	H	03	99	99	524.6
2	I	2-CH_3	H	24	93	99	492
3	I	4-CH_3	H	18	99	99	524.6
4	I	4-NO_2	H	05	99	99	524.6
5	I	H	-OCH_3	18	72	99	381
6	Br	H	H	06	99	99	524.6
7	Br	4-NO_2	H	08	99	99	524.6
8	Br	2-CH_3	H	24	68	99	360.3
9	Br	4-CH_3	H	24	99	99	524.6
10	Br	4-CHO	H	10	99	99	524.6
11	Br	2-CHO	H	10	75	99	397.4
12	Br	H	-OCH_3	24	99	99	524.6
13	Br	2,5-OCH_3	H	12	20	99	105
14	Br	4-OH	H	08	45	99	238.4
15[b]	Cl	H	H	12	–	–	–

Reaction conditions: Substituted iodobenzene = 1 mmol, substituted phenylboronic acid = 1.25 mmol, Pd = 0.0019 (20 mg) mmol, Na_3PO_4 = 1 mmol, solvent = 1 ml EtOH:H_2O (1:1) Temperature: 80 °C. X = a = Iodine, X = b = Chlorine. $R_2 = OCH_3$

successfully applied for the Suzuki–Miyaura C–C cross-coupling reaction in the presence of 1% PdNPs/RH-SiO_2 catalyst (Table 3, entry 5, 12).

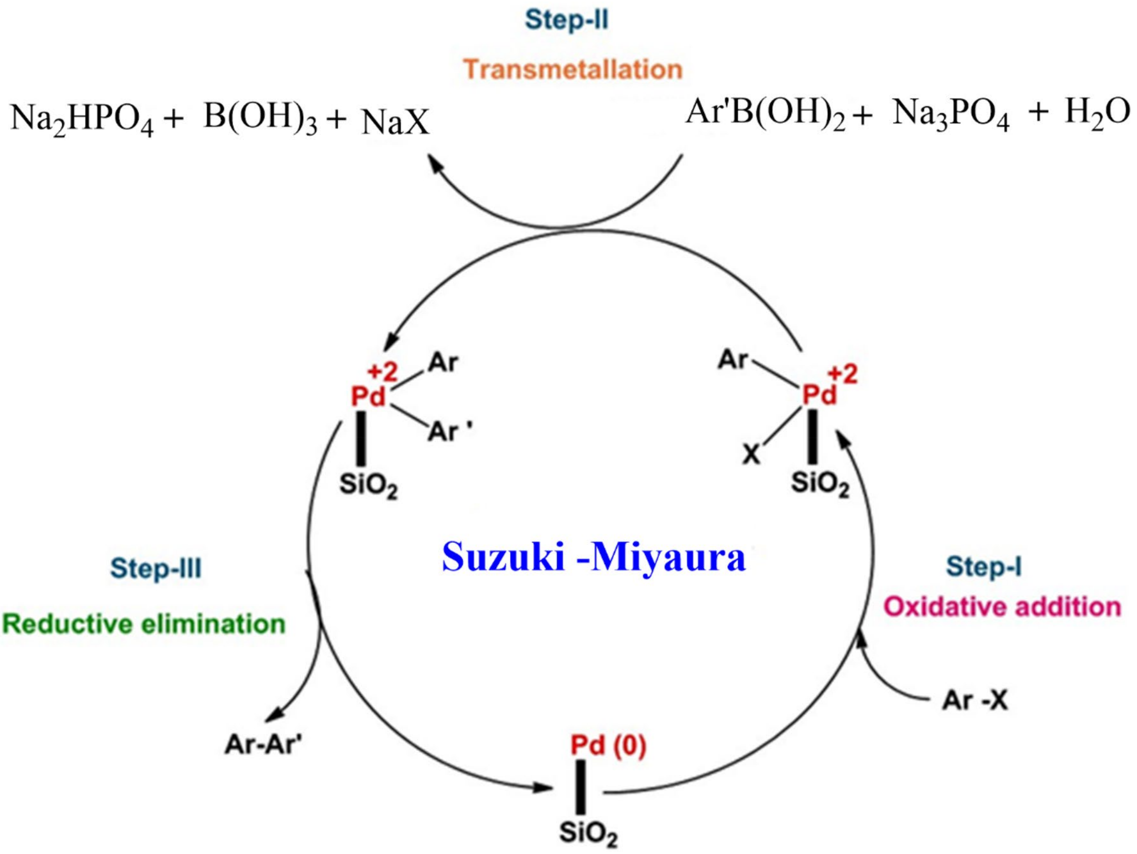
In the present context, the exact mechanism is not clear. However, according to the literature and the current results, we have proposed the plausible mechanism, as shown in Scheme 2. Initially, oxidative addition of aryl halide to Pd(0)/RH-SiO_2 (**I**) to form a phenyl Pd halide complex (**II**). Next, the trans-metalation step involves the transfer of phenyl group from phenylboronic acid to phenyl Pd halide complex (**II**) to form complex **III**. Finally, the reductive elimination step leads to the formation of the desired biphenyl product and regeneration of Pd(0)/RH-SiO_2 (**I**) catalyst.

3.2.1 Heck–Mizoroki coupling

Since the remarkable activity and selectivity of 1% PdNPs/RH-SiO_2 catalyst for C–C bond formation *via* Suzuki–Miyaura cross-coupling reaction of aryl halides with phenylboronic acids, we further investigated the activity of 1% PdNPs/RH-SiO_2 catalyst for Heck–Mizoroki coupling reaction of iodobenzenes with styrene for the preparation of stilbenes. The reactions were carried out at 120 °C in DMF solvent using Na_2CO_3 base over 1% PdNPs/RH-SiO_2 catalyst for required reaction time, and the results are shown in Table 4. The catalyst is tolerant of a variety of iodobenzene derivatives and afforded good yields of stilbenes with excellent selectivity (Table 4, entry 1–5).

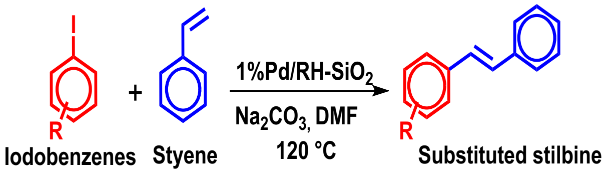
3.3 Reusability

To assess the stability and activity of the 1% PdNPs/RH-SiO_2 for Suzuki–Miyaura C–C cross coupling reaction of aryl bromide with phenylboronic acid, the catalyst was separated by centrifugation and washed several times with ethyl acetate followed by acetone solvents. The catalyst was vacuum dried at 60 °C, reused four times under the optimized reaction conditions (Fig. 5). Within repeated cycles, there is a little drop in the bromobenzene (Bb) conversion observed, but the selectivity of biphenyl (Bp) remains constant up to four successive cycles. Palladium leaching test was conducted by hot filtration method, in which the reaction was carried out for half of the reaction



Scheme 2 Proposed mechanism for Suzuki–Miyaura coupling over PdNPs/RH-SiO_2 catalyst

Table 4 Substrate scope of Heck-coupling over 1% PdNPs/RH-SiO_2 catalyst



Entry	R	Time (h)	Conversion (%)	Selectivity (%)	TON
1	H	12	99	99	524.6
2	4-NO_2	24	92	99	487.5
3	4-OCH_3	16	57	99	302
4	4-NH_2	20	99	99	524.6
5	3,4-OCH_3	14	42	99	222.5

Reaction conditions: Styrene (1.2 mmol), Iodobenzene (1 mmol), 1% PdNPs/RH-SiO_2 (20 mg, 0.0019 mmol), DMF (2 ml), Na_2CO_3 (1 mmol), 120 °C

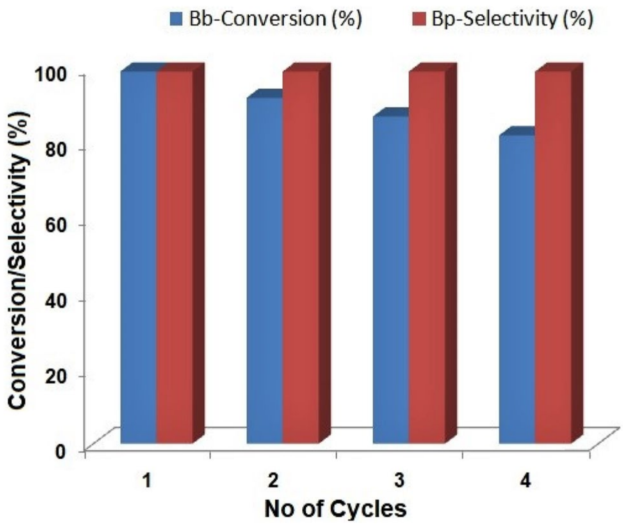


Fig. 5 Reusability of 1% PdNPs/RH-SiO_2 catalyst. Reaction conditions: Bromobenzene (Bb): 1 mmol, phenylboronic acid (1.25 mmol), catalyst (20 mg), Na_3PO_4 (1 mmol), 80 °C, 6 h

time (after 3 h) and separated the catalyst from the product mixture by centrifugation and continued the reaction for 6 h, but no conversion or product formation was observed. Further, the reaction solution was analyzed by ICP-OES and found no trace of Pd suggesting the no leaching of Pd nanoparticles during the reaction. From these results, it is concluded that this catalyst involves in a complex heterogeneous mechanism [52].

4 Conclusions

In summary, we have developed a green and environmentally benign biomass waste rice husk derived amorphous silica-supported palladium (1% PdNPs/RH-SiO_2) nanocatalyst *via* the deposition of PdNPs on rice husk derived amorphous silica obtained by chemical reduction method with an average particle size of 3–5 nm. This novel catalyst exhibits an excellent activity for Suzuki–Miyaura and Heck–Mizoroki C–C cross-coupling reactions for the selective preparation of biaryl and stilbene compounds under mild reaction conditions. Furthermore, the catalyst is tolerant of various functional groups under the optimized reaction conditions and reused four times for the Suzuki–Miyaura C–C coupling reaction of bromobenzene and phenylboronic acid. However, a little drop in the conversion was monitored, but the selectivity remains constant in all four cycles.

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Compliance with ethical standards

Conflict of interest The authors declare no conflict of interest.

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