



Silica-supported PEI capped nanopalladium as potential catalyst in Suzuki, Heck and Sonogashira coupling reactions

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ARTICLE INFO

Article history:

Received 23 August 2012

Received in revised form 2 January 2013

Accepted 23 January 2013

Available online xxx

Keywords:

Silica

Heterogeneous

Palladium

Polyethylenimine

Catalysis

ABSTRACT

We present the use of amine-functionalized silica ($\text{NH}_2\text{-SiO}_2$) as support for palladium nanoparticles (PdNPs) and the use of heterogeneous catalysts ($\text{Pd/NH}_2\text{-SiO}_2$) for the Suzuki, Heck and Sonogashira coupling reactions. The synthesized Pd catalyst is well characterized by XRD, HRTEM, BET, SEM-EDX, FT-IR, and UV–vis spectral techniques. It exhibits efficient catalytic activity for these coupling reactions without the assistance of ligand and copper salts.

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1. Introduction

The study of application of metal nanoparticles in catalysis, particularly, on organic transformations, has become a frontier area of research in nanocatalysis [1]. Heterogeneous catalysis is attractive for both laboratory and large-scale synthesis because of its advantages over homogeneous catalysis [2]. In fact, one of the challenging areas of research is heterogeneous catalysis with nanocatalysts supported on a solid surface [3]. Among the different metal nanocatalysts, palladium nanoparticles (PdNPs) have gained much reputation, because palladium is a versatile catalyst in modern organic synthesis and is widely used for a significant number of synthetic transformations [4] such as, Heck, Suzuki, Stille and Sonogashira cross coupling reactions [5–8].

Some types of traditional nanocatalysts include transition metal nanoparticles in colloidal suspension, and those adsorbed onto bulk supports [9–14]. Different types of stabilizers such as polymers [11,12,14,15], surfactants [16], dendrimers [17], as well as different types of ligands [18], have been used as capping agents to stabilize the nanoparticles. In the case of metal nanoparticles adsorbed onto bulk supports, a wide variety of support materials such as partially

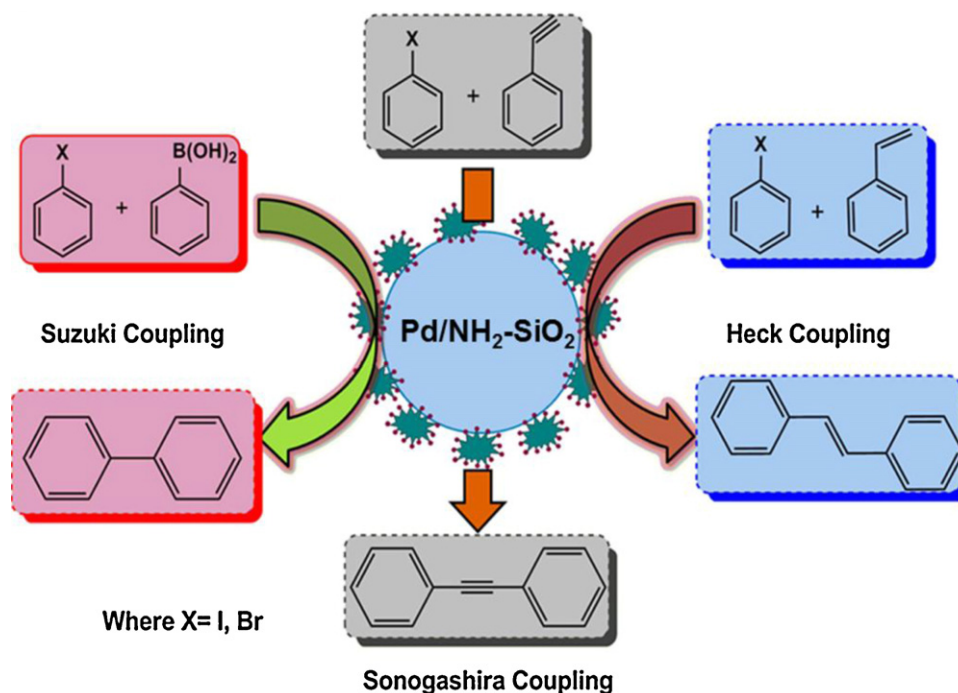
reduced graphene oxide (PRGO) [19], silica [13,20,21], titania [22], alumina [12,23], zeolites [24], resins [25] and carbon nanotubes (CNT) [26] have been used. In the absence of a suitable support, metal particle aggregates have reduced surface area and restricted control over particle size.

Among many supported NPs, silica-based PdNPs have several advantages and some of them are: (i) silica nanoparticles (SiNPs) are easy to synthesize at room temperature, (ii) SiNPs size can be easily tuned, (iii) easy adjustment of synthesis parameters leads to PdNPs with narrow size distribution ('monodispersed PdNPs'), (iv) SiNPs are stable in organic solvents, and (v) they are environmentally friendly materials. Due to these attractive features, $\text{Pd/NH}_2\text{-SiO}_2$ nanoparticles found widespread applications in the synthesis of C–C, C=C and C≡C coupling products. These Pd-catalyzed coupling reactions are ranked today amongst the most general transformations in organic synthesis, which have great industrial potential for the synthesis of chemicals, therapeutic drugs and their intermediates with promising industrial applications [27–32].

In the present work, we report a versatile methodology to prepare PdNPs that are immobilized on amine-functionalized silica nanoparticles ($\text{Pd/NH}_2\text{-SiO}_2$). The catalyst is designed with an aim to combine the property of highly branched polyethylenimine (PEI) to effectively immobilize and stabilize PdNPs for easy catalyst separation. The $\text{Pd/NH}_2\text{-SiO}_2$ is employed as an efficient catalyst in coupling reactions and its catalytic role is schematically represented in Scheme 1.

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Scheme 1. Suzuki, Heck and Sonogashira coupling reactions catalyzed by Pd/NH₂-SiO₂.

2. Experimental

2.1. Materials and methods

Palladium(II) acetate (Pd(CH₃COO)₂), polyethyleneimine (PEI, MW ~25,000), tetraethyl orthosilicate (TEOS, 98%), 3-aminopropyl triethoxysilane (APTES, 99%), ascorbic acid, phenylboronic acid, phenylacetylene, styrene, derivatives of iodo- and bromobenzene were purchased from Sigma–Aldrich and used as received. Water purified through a double distilled system was used.

The X-ray powder diffraction (XRD) pattern of the catalyst was taken using a XPERT-PRO diffractometer operated at a voltage of 40 kV and a current of 30 mA with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). High resolution TEM (HRTEM) images and the selected area electron diffraction (SAED) patterns were performed on a JEOL 3011 instrument with an accelerating voltage of 300 kV. The Pd/NH₂-SiO₂ was dispersed on ethanol solution under ultrasonic vibration for 20 min and one drop of the suspension evaporated onto a carbon-coated copper grid for HRTEM measurement. Detailed measurements of surface area were determined from nitrogen adsorption isotherm by the Brunauer–Emmett–Teller (BET) method and determination of the pore size distribution from adsorption branch by the Barrett–Joyner–Halenda (BJH) method. SEM observations were carried out on a JEOL JSM-6390 electron microscope. Detailed composition characterization of the Pd/NH₂-SiO₂ composites was carried out with energy-dispersive X-ray (EDX) analysis (equipped with the SEM). Ultraviolet–visible absorption spectral measurements were carried out with a SPECORDS100 diode-array spectrophotometer. FT-IR spectra of the purified SiNPs were recorded using a 8400 S Shimadzu FT-IR spectrometer in the region 4000–400 cm⁻¹ with a spectral resolution of 2 cm⁻¹. Solid samples were dispersed in dry KBr discs at room temperature.

Atomic force microscopy (AFM) (APE Research nanotechnology, AFM A100 SGS), working at 100 kV was used to measure the size of these nanoparticles. The samples were prepared by evaporating

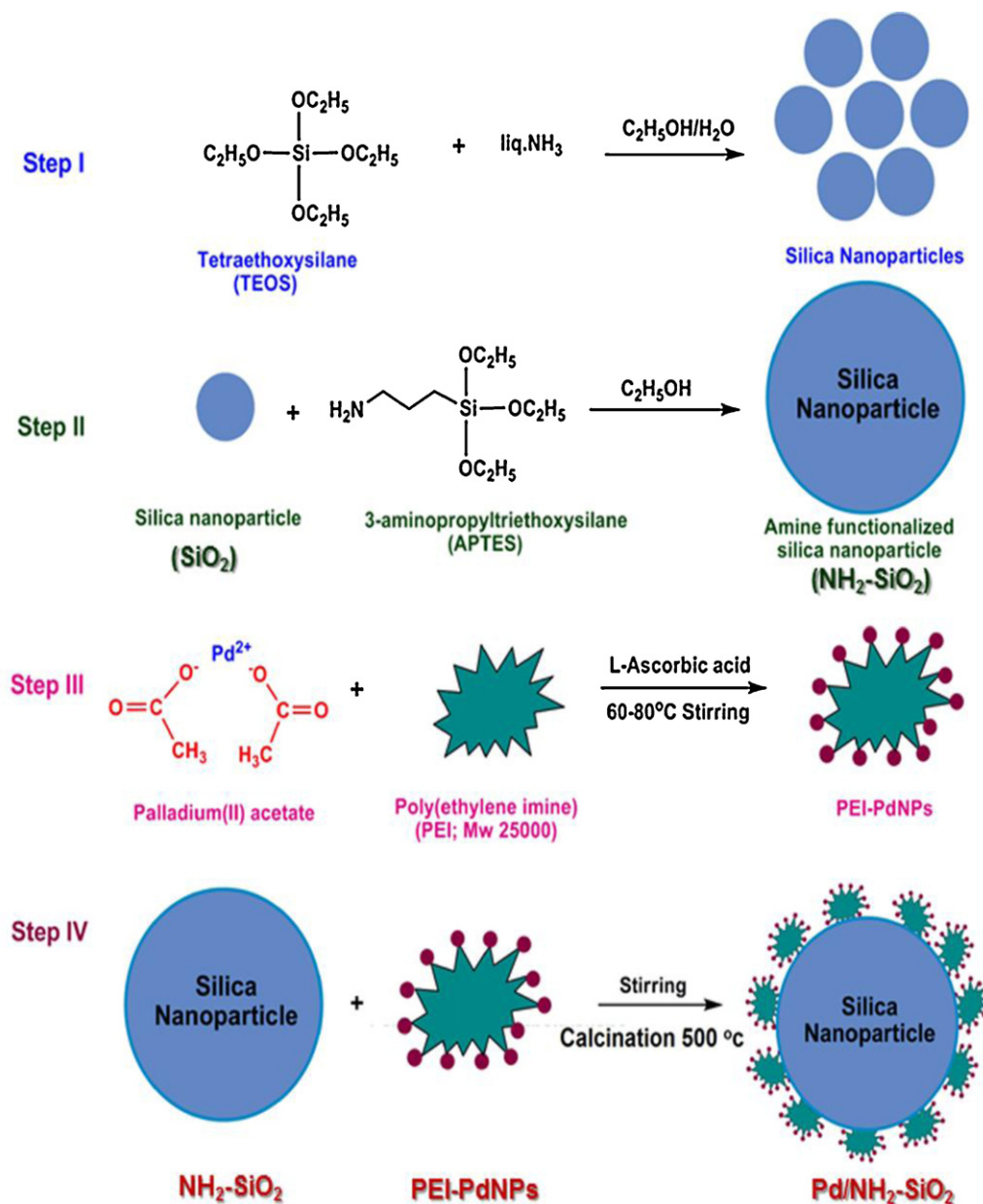
a drop of the dilute aliquot solution onto a thin glass plate. ¹H and ¹³C NMR data of products were acquired on a Bruker 300 MHz NMR spectrometer with CDCl₃ as the solvent.

2.2. Synthesis of amine functionalized silica supported PEI-PdNPs

The silica colloids were synthesized by using the Stöber synthesis method [33]. The PdNPs were synthesized by using palladium precursor (Pd(OAc)₂ and ascorbic acid reduction method similar to that described previously [34]. The PEI stabilized metal nanoparticles are prepared by the method described below [13,15,35–40]. The palladium precursor solution is prepared by mixing Pd(OAc)₂ (0.064 g) with 5.0 mL of PEI (1.0 wt.%) and then diluting to 25 mL with doubly distilled water. Aqueous solution of ascorbic acid (1.0 mL of 100 mM) is injected into the reaction mixture *via* syringe within few seconds. The synthesis of amine modified SiNPs [13] was added to PdNPs by stirring for 30 min and sonicated for 45 min. Dark black coloured PEI-PdNPs are bound on the surface of amine functionalized SiNPs with elapsing of reaction time, and the reaction continued for 2.5 h. Finally, the particles are washed with ethanol, centrifuged and dried under vacuum at RT and calcinated at 500 °C for 8 h and stored in a closed container. The entire synthetic procedure is given in Scheme 2.

2.3. Suzuki coupling reaction

To halobenzene (1.0 mmol), phenylboronic acid (1.2 mmol), K₂CO₃ (276 mg, 2.0 mmol), tetrabutylammonium bromide (TBAB) (161 mg, 0.5 mmol) and Pd/NH₂-SiO₂ 0.05 mol% are added to a 25 mL round-bottom flask equipped with a magnetic stirrer bar. About 2.0 mL of H₂O is added and the reaction mixture is stirred at 60–70 °C for 2–3 h. After the reaction, the Pd/NH₂-SiO₂ is separated by centrifugation and washed with diethyl ether (20 mL) followed by deionized water (20 mL). The collected Pd/NH₂-SiO₂ is dried and reused for the next run. The aqueous phase is extracted with diethyl



Scheme 2. Schematic representation of four-step process for the synthesis of Pd/NH₂-SiO₂.

ether (20 mL) and the combined organic phases are concentrated and purified with thin layer chromatography (TLC, SiO₂).

2.4. Heck coupling reaction

To a suspension of halobenzenes (1.0 mmol), styrene (1.2 mmol), K₂CO₃ (2.0 mmol) and Pd/NH₂-SiO₂ (0.05 mol%) are added to a 25 mL round-bottom flask equipped with a magnetic stirrer. 5.0 mL of distilled dry DMF is added and the reaction mixture is stirred at 110 °C with heating on an oil bath for 4–6 h. The reaction is monitored by TLC (or GC if necessary). On completion of the reaction, the mixture is filtered and the filtrate poured into water (50 mL) and extracted with CH₂Cl₂ (3 × 15 mL). The combined organic phases are dried over Na₂SO₄ or MgSO₄, filtered and evaporated in vacuum. The mixture is then purified by column chromatography over silica gel or recrystallization to afford a product with high purity.

According to the above procedure after the completion of the reaction, the suspension is cooled down to room temperature and filtered off. The Pd/NH₂-SiO₂ is washed with DMF, water and acetone. It is dried under vacuum and then used in the next reaction cycle with a new portion of reagents without any pretreatment. Characterization of the products is performed by comparison of their ¹H and ¹³C NMR data with those of the authentic samples

2.5. Sonogashira coupling reaction

To a 50 mL round-bottom flask equipped with a magnetic stirrer under N₂ atmosphere, ethylene glycol (3.0 mL) is added to the Pd/NH₂-SiO₂ (0.05 mol%), K₂CO₃ (2.0 mmol, 276 mg), aryl halide (1.0 mmol) and phenylacetylene (2.0 mmol) and the mixture is heated at 120–130 °C for the appropriate reaction time. After the completion of the reaction, the reaction mixture is extracted with ethyl acetate or diethyl ether (25 mL) and the upper organic phase is separated and evaporated. Further purification is performed by

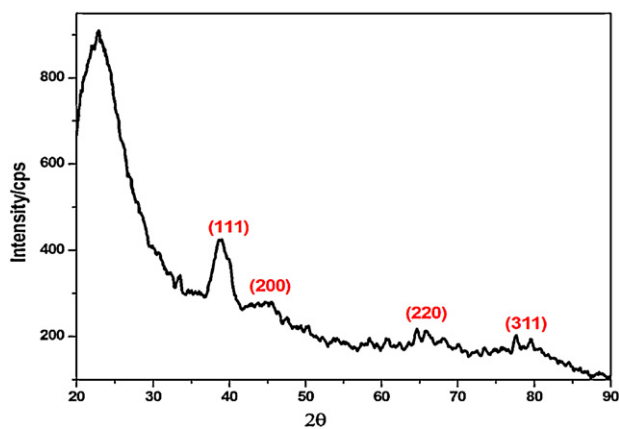


Fig. 1. The XRD patterns of the Pd/NH₂-SiO₂ catalyst.

column chromatography (EtOAc/*n*-hexane) to obtain the desired coupling product. For the recycling test, the recovered catalyst is further washed sufficiently with ethanol followed by water.

3. Results and discussion

3.1. XRD results

Powder XRD diffraction patterns of Pd/NH₂-SiO₂ exhibit a broad reflection corresponding to the amorphous silica support as shown in Fig. 1.

Four additional reflections are found in the XRD pattern that could be attributed to elemental palladium, in good agreement with the JCPDS 46-1043 file [41]. All materials prepared exhibit a similar XRD pattern. Of note is the absence of any other reflections in the diffractogram, indicating the absence of significant quantities of the Pd precursor on the support.

The peaks are observed in XRD pattern 2θ values at 40°, 45°, 68.3° and 81.5°. These peaks correspond to the [1 1 1], [2 0 0], [2 2 0] and [3 1 1] planes of a fcc lattice, respectively, indicating that the synthesized PEI-PdNPs have the fcc structure, which is confirmed by HRTEM images [42,43].

3.2. HRTEM analysis

Synthesis of SiNPs and modification or functionalization with amine group on the surface of SiNPs is discussed in our previous report [13]. HRTEM images of monodisperse spheres of bare SiNPs (SiO₂) and amine functionalized SiNPs (NH₂-SiO₂) show homogeneous size with a smooth surface. Fig. 2 displays representative HRTEM images of the highly branched polymer (PEI) capped PdNPs prepared by using ascorbic acid as the reducing agent described above. From the HRTEM images we measured particle size of small PdNPs, an average size of 5–10 nm with spherical morphologies.

The direct observation of the PdNPs supported on the SiNPs could be obtained by HRTEM analysis. The HRTEM images of the Pd/NH₂-SiO₂ (Fig. 3a–c) revealed that PdNPs are adsorbed or covalently attached to the surface of the silica colloids [10]. They were well dispersed homogeneously on the surface of SiO₂ without the obvious aggregation phenomenon. An EDX analysis confirmed the presence of palladium and silicon in Pd/NH₂-SiO₂ as shown in Fig. 3d.

3.3. BET surface area studies

Nitrogen adsorption and desorption isotherms on all the samples at 77 K are measured to characterize their pore textural properties including BET surface area, pore volume and pore size distribution. Physicochemical properties of the NH₂-SiO₂ and Pd/NH₂-SiO₂ are given in Table 1.

To verify the changes of the surface area and porous characteristics the pure NH₂-SiO₂ and PdNPs immobilized NH₂-SiO₂ samples are evaluated by N₂ sorption analysis as shown in Supporting

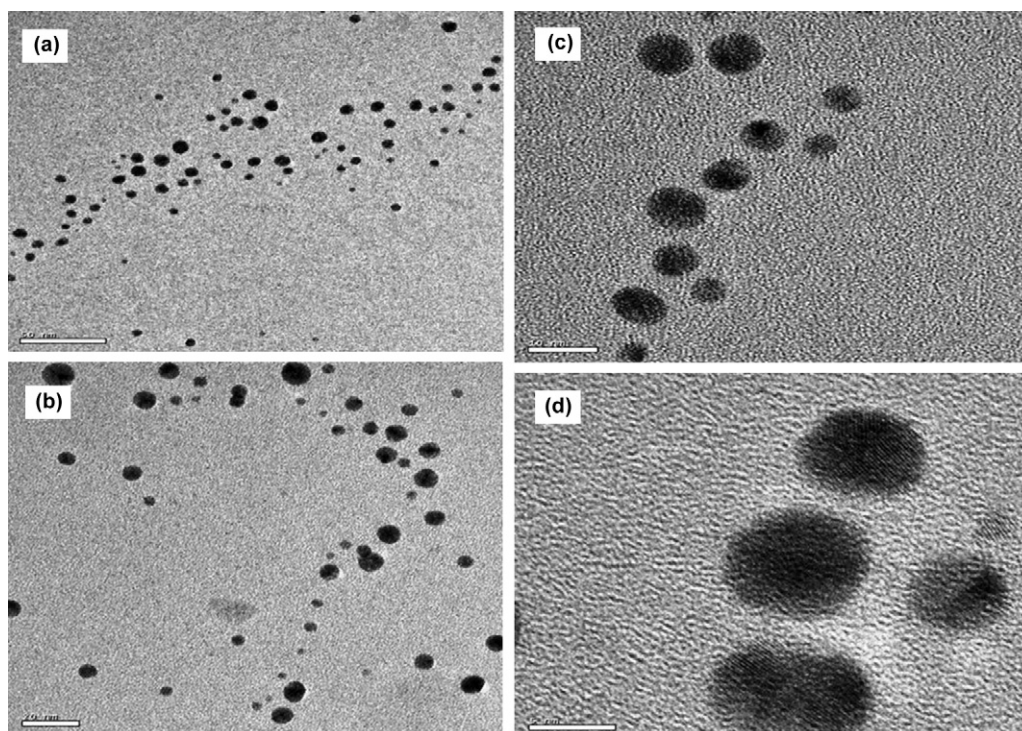


Fig. 2. HRTEM images of PEI capped PdNPs. Scale bars (a) 50 nm, (b) 20 nm, (c) 10 nm and (d) 5 nm.

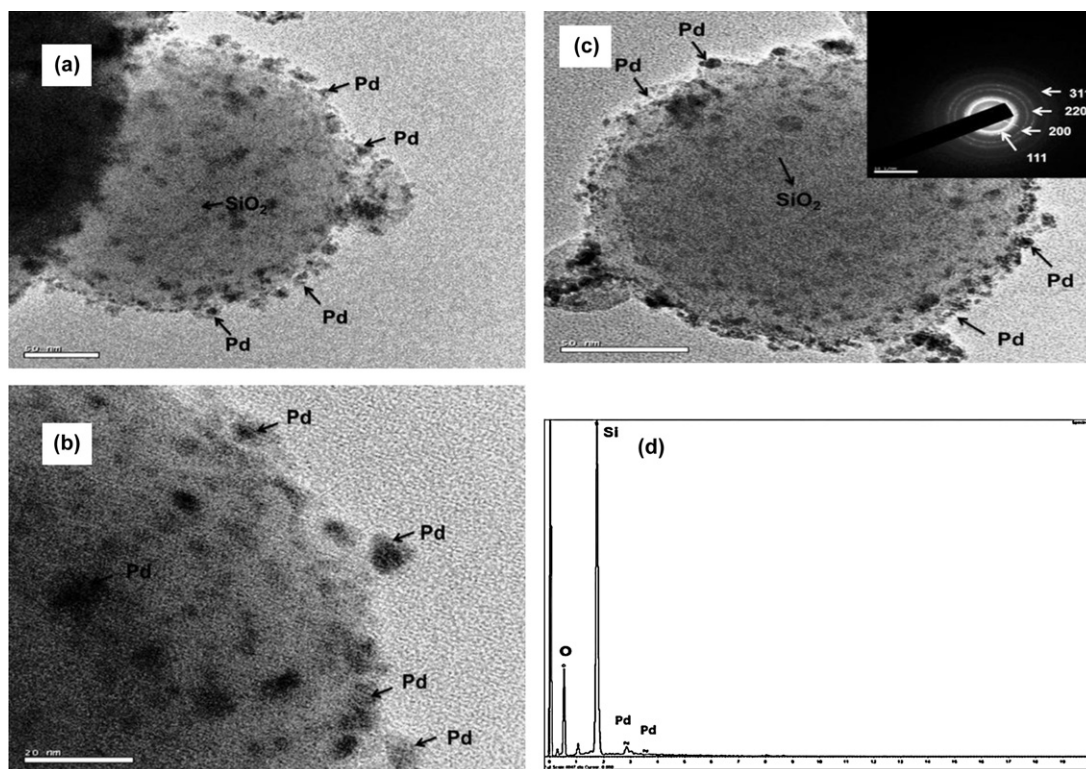


Fig. 3. HRTEM photographs of (a–c) correspond to the different images of the representative Pd/NH₂-SiO₂; (d) EDX analysis and inset of (c) shows SEAD spectrum of Pd/NH₂-SiO₂.

information, Fig. S5. The BET surface area of the NH₂-SiO₂ is 110.8 m² g⁻¹ whereas that of the catalyst Pd/NH₂-SiO₂ is in the 87.8 m² g⁻¹, respectively. The corresponding isothermal curves of 1.0 wt.% Pd, belonging to type IV sorption isotherms [44] with hysteresis loop of type H1 according to the IUPAC classification is given in Supporting information, Fig. S5.

The specific surface areas of the samples are estimated by the BET method in the relative pressure range of 0.05–0.20 from nitrogen desorption isotherms [45], and the pore size distribution is determined by the BJH (Barrett–Joyner–Halenda) method. The specific surface area of the silica decreases from 110.08 m² g⁻¹ to 87.08 m² g⁻¹ for Pd/NH₂-SiO₂ due to the immobilization of PdNPs, which may result from the deposition of PdNPs on the surface of silica.

The small hysteresis of the composite indicates less mesoporosity present in the NH₂-SiO₂. From the N₂ sorption analysis, it is known that the total pore volume is reduced from 0.60 cm³ g⁻¹ for NH₂-SiO₂ to 0.17 cm³ g⁻¹ for Pd/NH₂-SiO₂. This is due to pore blockages of metal particles during impregnation and/or calcination step. The same types of effects are observed for Pd/Al₂O₃ and Pt/TiO₂ nanocatalysts [46,47]. Since the Pd catalysts tested, their nitrogen adsorption–desorption isotherms did not vary with respect to bare carriers and the BET area only decreased slightly upon palladium incorporation [48,49]. Finally, all the adsorption/desorption isotherms are of type IV as per IUPAC classification,

and the hysteresis loops in the isotherms suggest the presence of mesopores in NH₂-SiO₂.

3.4. SEM analysis

The scanning electron microscopy (SEM) images of SiNPs synthesized by Stöber method are shown in the Supporting information Fig. S6. The SiNPs have very uniform spherical morphology and monodispersed distribution. The mean diameter of these particles is ~180 nm, with very little distribution, and representative electron micrographs obtained are presented in the Supporting information, Fig. S6.

3.5. UV–vis absorption spectroscopy

Heating played a critical role in the synthesis of the PEI-PdNPs, from the reduction of Pd²⁺ to Pd⁽⁰⁾ with ascorbic acid as the reducing agent. At 95 °C, the PEI-Pd²⁺ solution turned to transparent light brown as soon as ascorbic acid is added, indicating rapid reduction of Pd²⁺ and formation of fine PdNPs. UV–vis absorption spectroscopy is used to monitor the complete reduction of Pd²⁺ to Pd⁽⁰⁾ state [50–52].

The Pd²⁺ is mixed with 1.0 wt.% of PEI and stirred for 15–20 min to form dark coloured solution of PdNPs. Pd²⁺ (yellow) is reduced, step-by-step, to Pd⁽⁰⁾ (dark black) during the reaction: (a) Pd²⁺ salt

Table 1
Physicochemical properties of the NH₂-SiO₂ and Pd/NH₂-SiO₂ catalyst.

Sample	Pd content (wt.%)	BET surface area (m ² g ⁻¹)	Langmuir surface area (m ² g ⁻¹)	t-Plot external surface area (m ² g ⁻¹)	Average pore diameter (nm)	Pore volume (cm ³ g ⁻¹)
NH ₂ -SiO ₂	–	110.8	186.9	106.9	33.0	0.60
Pd/NH ₂ -SiO ₂	1.0	87.8	142.4	76.5	25.2	0.17

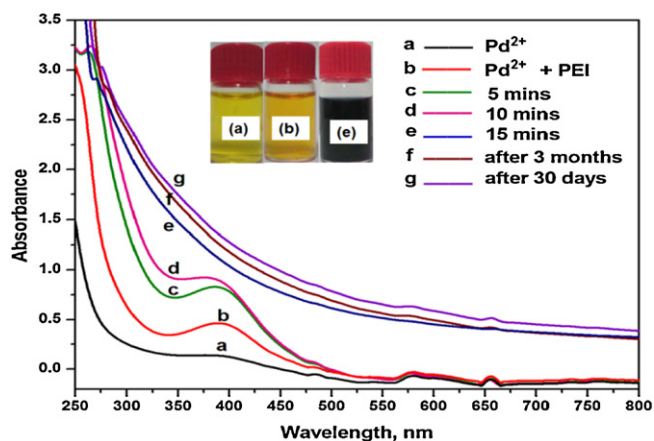


Fig. 4. UV-vis absorption spectra of PEI stabilized PdNPs. (For interpretation of the references to colour in text, the reader is referred to the web version of this article.)

only, (b) mixture of Pd²⁺ and PEI, (c) at approximately 15 min (d and e). After about 15 min, the absorption peak disappeared completely, which indicated that Pd²⁺ is entirely reduced to Pd⁽⁰⁾ as shown in Fig. 4e and f.

The increasing scattering absorbance at wavelengths between 300 and 800 nm with time reveal full conversion of Pd²⁺ to Pd⁽⁰⁾. The synthesized PEI capped PdNPs are stable for 30 days (Fig. 4g) and 3 months (Fig. 4f), respectively. Both spectra feature a continual increase of absorbance at shorter wavelengths characteristic of nanosized palladium, which can account for the overall dark black colour appearance of the dispersion [51]. Although both spectra show virtually identical profiles, it is observed that there is a slight decrease in the overall absorbance recorded after 3 months in comparison to that after 30 days.

3.6. FT-IR spectroscopy

FT-IR spectra of pure SiO₂, amino modified silica (NH₂-SiO₂) and Pd/NH₂-SiO₂ are recorded in the regions 4000–400 cm⁻¹. The FT-IR spectral assignments of dried and calcined samples of pure SiO₂, NH₂-SiO₂ and PdNPs coated amine functionalized silica (Pd/NH₂-SiO₂) are shown in Supporting information, Fig. S8.

The 2929 and 2856 cm⁻¹ bands are assigned to ν_{CH} of the -CH₂ groups, and the bands at 1544 cm⁻¹ and 1542 cm⁻¹ to δ_{NH} of the -NH₂ groups, both of which are associated with amino modified (NH₂-SiO₂) and Pd/NH₂-SiO₂ skeleton, respectively. The strong peaks at 1076 and 790 cm⁻¹ are due, respectively, to ν_{asym} (Si-O) and ν_{sym} (Si-O) of the Pd/NH₂-SiO₂ skeleton [13,53,54]. Moreover, the presence of the amino groups confirms the formation of the amine-modified particles. The broad peak centred at 3400 cm⁻¹ is an envelope of ν_{O-H} for the adsorbed water, silanol groups, and ν_{N-H} of the amino groups. It should be pointed out here that the band corresponding to the Si-OH group appears at 960 cm⁻¹ as a shoulder (arrow) of the 1076 cm⁻¹ Si-O-Si skeleton peak, and is little weaker than that found ever in the conventional SiO₂ particles that exhibit a clear and well-defined peak of the Si-OH groups [13].

3.7. Suzuki coupling reaction of different aryl halides

Generally, the palladium-catalyzed Suzuki coupling reaction is performed under an inert atmosphere because the catalytic species are sensitive to oxygen or moisture. Nowadays, the Suzuki reaction is probably one of the most popular Pd-catalyzed coupling reactions [55]. This reaction involving heterocycles is of interest to the pharmaceutical industry because of the special biological

activities displayed by the hetero biaryl compounds [56]. We first tested Pd/NH₂-SiO₂ in the Suzuki reaction of aryl iodides with phenylboronic acid in water and the observed results are summarized in Table 2.

We used water (water was necessary to favour the solubility of phenyl boronic acid and base) as the reaction medium for environmental benefit [57]. Tetrabutylammonium bromide, a phase transfer agent is added to enhance the reactivity in aqueous medium. Various substituted (-CH₃, -OCH₃, -COCH₃ and -NO₂) iodo- and bromobenzenes were coupled with arylboronic acid in the presence of 0.05 mol% of Pd/NH₂-SiO₂ at 60–70 °C to afford the corresponding products in good to excellent yields (Table 2, entries 1–6).

Suzuki cross coupling reactions of various aryl halides carried out using the Pd/NH₂-SiO₂ catalyst, produced the coupling products close to 90% yield, except for 4-iodotoluene (82%, Table 2, entries 2–6). The aryl bromides give executable product yields (70–92%, Table 2, entries 1–6). Overall, the Pd/NH₂-SiO₂ shows excellent catalytic activity in the reaction of 4-bromopyridine with pyridin-4-ylboronic acid to give low yield (85%) compared with phenylboronic acid. Phenylboronic acid reacts faster than the pyridin-4-ylboronic acid because of solubility of the latter in water.

The feasibility of recycling the catalyst is also examined. After the reaction, the Pd/NH₂-SiO₂ is simply recovered by ultracentrifugation followed by washing with ethanol and drying in vacuum for 2–3 days. However, we observe that the catalytic activity of vacuum dried Pd/NH₂-SiO₂ is decreased only slightly in the third cycle. Nearly quantitative amounts of Pd/NH₂-SiO₂ (up to 96–78%) could be recovered from each run. In a test of third cycle, the catalyst could be reused with reduced amount of its catalytic activity. The slight reduction in yield is probably due to loss of some catalyst at the time of filtration.

The recovered Pd/NH₂-SiO₂ after the third run had no obvious change in structure according to the HRTEM images in comparison with the fresh Pd/NH₂-SiO₂ see Supporting information, Fig. S4).

3.8. Effect of solvents and bases on Suzuki coupling reaction

Generally, Suzuki-Miyaura coupling reactions are carried out with the assistance of phosphine ligands along with Pd [58]. However, Pd-catalyzed Suzuki coupling under phosphine-free conditions is a topic of considerable interest because of both economic and environmental reasons [59].

Another limitation of Suzuki-Miyaura coupling is that cheaper aryl bromides are less reactive than aryl iodides. In order to determine the optimal reaction conditions, various types of bases were screened and the results shown in the Supporting information, Table S9. Among the bases examined for the reaction of 4-iodobenzene with phenylboronic acid, K₂CO₃ was found to be most suitable because it gave the highest product yield.

Badone et al. [60] have reported that, when water was used as the solvent, the addition of one equivalent of TBAB to the reaction mixture greatly accelerates the reaction. We also observed that aryl bromides and iodides can be coupled with phenylboronic acid to yield biaryls fairly rapidly (1 h) and in good yields. The role of the ammonium salt is thought to be twofold. Firstly, it facilitates solvation of the organic substrates in the solvent. Secondly it enhances the rate of the coupling reaction by activating the boronic acid towards reaction by formation of a boronate complex [ArB(OH)₃]₂[R₄N]⁺ [61].

3.9. Proposed mechanism for Suzuki reaction

The proposed mechanism for the Suzuki coupling reaction is shown in Scheme 3.

Table 2
Results of Suzuki coupling of aryl halides with phenylboronic acid.^a

Entry	Reactants	Products	Time (h)	Yield (%) ^b
1			1	96 (X = I); 90 (X = Br) ^d
2			3 (5)	82 (X = I); 70 (X = Br) ^c
3			3 (5)	90 (X = I); 87 (X = Br) ^f
4			45 min (5)	93 (X = I); 82 (X = Br) ^c
5			4 (6)	92 (X = I); 85 (X = I) ^c
6 ^e			6	85 ^c

^a Reaction conditions: aryl halide (1.0 mmol), aryl boronic acid (1.2 mmol), Pd/NH₂-SiO₂ (0.05 mol%), TBAB (0.5 mmol), H₂O (2.0 mL).

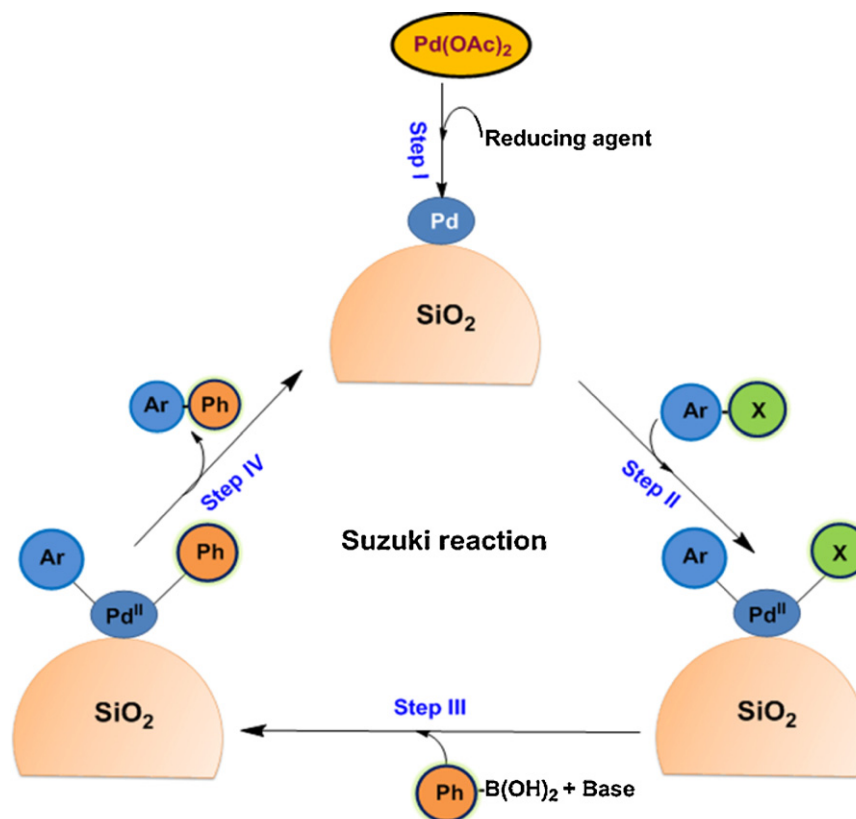
^b Yields were determined from the mass of biaryl products after column chromatography.

^c Reaction temperature: 60–70 °C.

^d Reusability of the Pd/NH₂-SiO₂ for 1st, 2nd and 3rd runs of yields is 96%, 87% and 78%, respectively.

^e Pyridineboronic acid is used.

^f 100 °C.



Scheme 3. Possible mechanism of Suzuki coupling reaction.

Table 3
Comparison of other catalyst systems on Suzuki reaction of halobenzenes with phenylboronic acid.

Entry	Catalysts ^a	Size (nm)	Mol (%)	Time (h)	Temp (°C)	Solvent	Yield (%)
1	Au-G [64]	2–3	1.0	4	100	H ₂ O	85
2	Fe ₃ O ₄ -Bpy-Pd(OAc) ₂ [65]	6–20	15 mg	6	80	Toluene	>99
3	Pd/NiFe ₂ O ₄ [66]	100–300	0.1	5	90	DMF:H ₂ O (1:1)	97
4	Pd/NiFe ₂ O ₄ [71]	10–12	50 mg	30	110	DMF	97
5	Pd/NiFe ₂ O ₄ [72]	>50	0.08	4	80	NMP:H ₂ O (5:2)	97
6	Pd-Fe ₃ O ₄ nanocrystals [67]	36	1.0	24	>80	DME:H ₂ O (3:1)	99
7	Pd/G [68]	7–9	0.3	10	~80	H ₂ O:EtOH (1:1)	>99
8	Pd/GO [68]	12–18	0.3	10	~80	H ₂ O:EtOH (1:1)	>99
9	Pd-SBA-15 [69]	1.5	0.5	30 min	100	H ₂ O:EtOH (3:2)	21
10	Pd-SBA-16 [77]	10–25	0.01	5	50	EtOH	99
11	Fe ₃ O ₄ -Pd ⁽⁰⁾ [70]	8–10	5.0	24	50	DMF	54
12	Ru/Al ₂ O ₃ [73]	2–3	5.0	12	60	DME:H ₂ O (1:1)	96
13	LDH-Pd ⁽⁰⁾ [78]	4–6	1.0	10	100	1,4-Dioxane:H ₂ O (5:1)	93
14	Diatomite-Pd ⁽⁰⁾ [79]	20–100	0.1	20 min	110	DME:H ₂ O (1:1)	95
15	Polyoxometalate-Pd ⁽⁰⁾ [74]	15–20	0.01	12	80–85	H ₂ O:EtOH (1:4)	92
16	MES-IMes (20%)-Pd [84]	>20	0.5	24	80	Isopropyl alcohol	78
17	Organostannoxane-Pd ⁽⁰⁾ [61]	4.3	5.0 mg	4	110	Toluene	95
18	Pd/SiO ₂ [76]	>100	100 mg	12	100	CH ₃ CN:H ₂ O (3:1)	>90
19	SiO ₂	>100	0.05	12	60–70	H ₂ O	Trace ^b
20	NH ₂ -SiO ₂	>100	0.05	12	60–70	H ₂ O	Trace ^c
21	Pd/NH ₂ -SiO ₂	5–6	0.05	1	60–70	H ₂ O	96 ^d

^a References.

^{b–d} Reaction conditions as exemplified in the experimental procedure, where G, graphene; GO, graphene oxide; DMF, dimethylformamide; DME, dimethyl ether; NMP, *N*-methyl-2-pyrrolidone; CH₃CN, acetonitrile, respectively.

In **Step I**, the formation of PdNPs is shown from the source Pd(OAc)₂ using ascorbic acid as the reducing agent. It is believed that Pd⁽⁰⁾ is the catalytic species and that the reaction proceeds through the usual interaction of aryl halide and silica supported Pd⁽⁰⁾ to form the aryl-palladium halide complex [Ar-(Pd²⁺)-X] as shown in **Step II**. The aryl-palladium halide complex then couples with arylboronic acid, (Ph-B(OH)₂) in the presence of a base to produce the aryl-Pd(II) intermediate [Ar-(Pd²⁺)-Ph] in **Step III**, and finally providing the biaryl product (Ar-Ph) via the reductive elimination of Pd²⁺ to Pd⁽⁰⁾ as in **Step IV**, outlined in **Scheme 3**. The coupling reaction does not proceed at all in the absence of PdNPs [62,63].

3.10. Comparison with other catalyst systems on Suzuki reaction

A number of articles describing the use of supported PdNPs or composites as catalysts for Suzuki reaction have been published [61,64–81]. Most of these studies employed phenylboronic acid with bromo- and iodoarenes in C–C coupling reactions with yields altered from 21% to 99% as shown in **Table 3**.

The iron oxide (Fe₂O₃) supported PdNPs show good catalytic activity in the Suzuki reaction of iodobenzene with phenylboronic acid to form biaryls (**Table 3**, entries 2–8 and 12–15). The Pd/NiFe₂O₄ nanocatalyst [66] is of very large size (100–300 nm) compared to other catalysts systems. The novelty of the present study is that the Suzuki reaction has been carried out in the presence of Pd/NH₂-SiO₂ with water as the solvent, to develop a green and low-cost strategy [61].

Comparison of our results with those of some of the recently published methods using different nanocatalysts for Suzuki coupling is of worth consideration [61,64–76]. The procedure followed by us provides significant advantages in terms of reaction time, simplicity of operation, and yields of products compared to other catalytic systems. In addition, this procedure provides the products without assistance of any copper salts and ligands.

3.11. The role of the Pd/NH₂-SiO₂ on Heck coupling reactions

The Heck coupling, often referred to as the Mizoroki–Heck reaction, first reported by Heck in 1968, is the alkenylation of aromatic compounds through the reaction of substituted aromatics (halides,

triflates, or diazonium derivatives called the Matsuda–Heck reaction, etc.) with alkenes [80–82]. The Pd/NH₂-SiO₂ catalyst is also examined for a series of Heck coupling reactions in DMF solvent by using bromo and iodoarenes with styrene. The results are listed in **Table 4**.

As shown in **Table 4**, all of the obtained products are *trans*-isomers, which are identified by ¹H NMR analysis. When aryl bromides are used as the starting materials, good conversion is also obtained with K₂CO₃ as the base (**Table 4**, entries 5–7). When we used dibromoarenes (**Table 4**, entries 6 and 7), 2.4 mmol of styrene is required to complete the reaction to afford good yields, 92% and 90%, respectively.

3.12. Effect of solvents and bases on Heck coupling reactions

The activity of the NH₂-SiO₂ supported Pd nanocatalyst is first examined in the Heck coupling reaction of different aryl halides with styrene and the results are collected in **Table 4**. In a model reaction, the coupling of iodobenzene with styrene is initially studied. In the process of coupling reaction the choice of solvent and base is crucial, so these parameters are optimized and the results are summarized as shown in the **Supporting information, Table S10**. It is found that the best system is DMF as the solvent and K₂CO₃ as the base using 0.05 mol% of Pd/NH₂-SiO₂ at 120 °C to give 95% of yield. Further studies were continued in DMF as a solvent offering a higher yield (95%). The results collected in **Table S11 (Supporting information)** illustrate the effect of different bases and solvents on the reaction. With K₂CO₃ and Cs₂CO₃, an increase in yield (95% and 93%) was noted. Much better results were found when DMF or EtOH was used, DMF being superior to EtOH. However, the use of a tertiary amine instead of K₂CO₃ leads to a decrease in the yield from 90% to 85% (**Table S11**, entry 5).

3.13. Proposed mechanism for Heck reaction

The possible mechanism for the Pd/NH₂-SiO₂ catalyzed Heck reaction is shown in **Scheme 4** [75,83,84].

The process starts from reduction of Pd(OAc)₂ and formation of Pd⁽⁰⁾ nanoparticles (**Step I**). The oxidative addition of aryl halide to a silica supported nano Pd⁽⁰⁾ to form a complex is a key step in Heck reaction. Activation of aryl halide [Ar-X] via oxidative addition

Table 4
Results of various Heck coupling reactions catalyzed by Pd/NH₂-SiO₂ catalyst.^a

Entry	Reactants	Products	Time (h) ^b	Yield (%) ^c
1			2	95 (X = I) ^d ; 91 (X = Br)
2			3	89
3			4	80
4			5	85
5			3	90
6			6	92 ^e
7			6	90 ^e

^a Reaction conditions: aryl halide (1.0 mmol), styrene (1.2 mmol), Pd/NH₂-SiO₂ (0.05 mol%), base (2.0 mmol) and DMF (3.0 mL).

^b Reaction temperature: 110 °C.

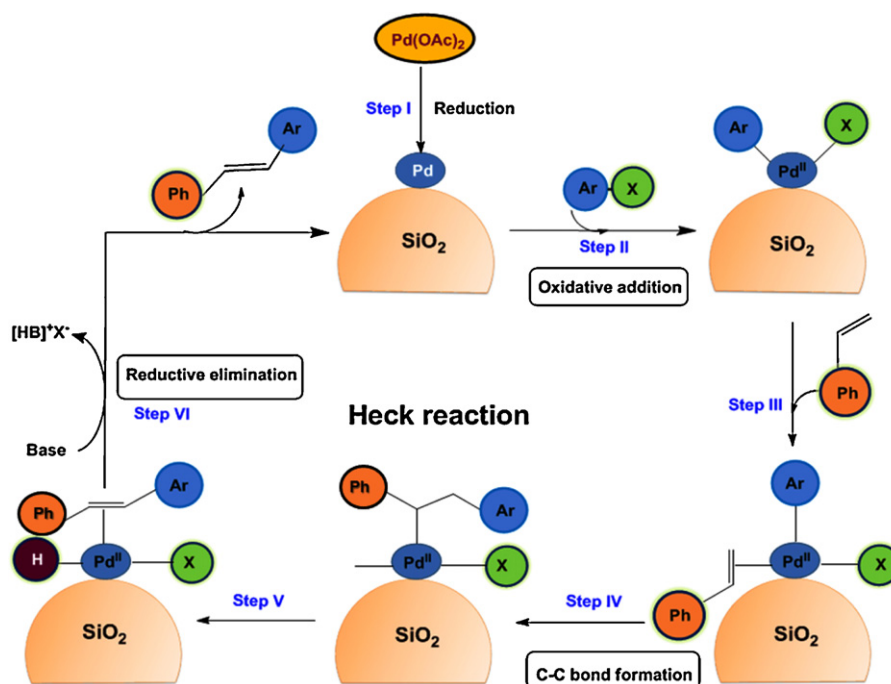
^c Yield were determined from the mass of biaryl products after column chromatography.

^d Reusability of the Pd/NH₂-SiO₂ for 1st, 2nd and 3rd runs 95%, 88% and 70%, respectively.

^e Styrene 2.4 mmol used.

produces a Pd(II) complex [Ar–Pd²⁺–X] with aryl and halide ligands coordinated to the palladium metal as shown in **Step II**. The formed complex next reacts with olefin forming an π -olefin complex (**Step III**). The olefin bonded to palladium undergoes a migratory

insertion forming a new C–C bond, followed by β -hydride elimination (**Steps IV and V**) and removal of the final product (**Step VI**), arylated olefin from the coordination sphere of palladium. Palladium remains, after this stage, in the form of a hydrido complex



Scheme 4. Possible mechanism of Heck coupling reaction.

Table 5
Comparison of other catalyst systems in Heck reaction of halobenzenes with styrene.

Entry	Catalysts ^a	Size (nm)	Mol (%)	Time (h)	Temp (°C)	Solvent	Yield (%)
1	NHC-Pd/SBA-16-IL [77]	10–20	0.01	40	140	NMP	94
2	Ni(O)NPs [101]	>100	0.02	16	140	H ₂ O	78
3	Polyaniline/Ni ⁽⁰⁾ [102]	1.52	5.0	15–20	130	DMF	95
4	[Pd]-APTS-Y [89]	4–5	0.075 g	2	120	DMAC	95
5	Pd/(C@(Au@Fe)) [90]	250–300	0.25	4	100	DMF	98
6	Hollow Pd-Fe [91]	200	0.02	24	90	H ₂ O	95
7	Pd/C [92]	2.4–23	0.01	2–3	80–140	NMP	88
8	Pd/(SiO ₂ /Fe ₃ O ₄) [93]	100	15 mg	12	80–90	CH ₃ CN:H ₂ O (1:3)	71
9	Fe ₃ O ₄ -NH ₂ -Pd [94]	35	5.0	10	130	NMP	>99
10	PIC-PdNPs [95]	2.6–2.7	1.0	20	80	H ₂ O	99
11	Pd/PS-IL[Cl] [96]	4–6	0.2	6	100	H ₂ O	42
12	Ru/Al ₂ O ₃ [73]	2–3	5.0	12	135	DMF	91
13	LDH-Pd ⁽⁰⁾ [81]	4–6	3.0	0.5	130	NMP	95
14	Diatomite-Pd ⁽⁰⁾ [79]	20–100	0.1	2	120	DME:H ₂ O (1:1)	92
15	Pd/C nanofiber [97]	40–150	0.01	10	120	NMP	95
16	Pd ⁽⁰⁾ MCM-41 [100]	3–4	0.05 g	24	100	DMF	90
17	PVP-Pd/SiO ₂ [98]	20–25	0.5	1.0	120	DMF	93
18	Polyoxometalate-Pd ⁽⁰⁾ [99]	20	63 mg	2.0	100	DMF	93
19	SiO ₂	>100	0.05	12	110	DMF	Trace
20	NH ₂ -SiO ₂	>100	0.05	12	110	DMF	Trace
21	Pd/NH ₂ -SiO ₂	5–6	0.05	2	110	DMF	95

^a References.

^{b-d} Reaction conditions as exemplified in the experimental procedure, where PIC, polyion complex; DMF, dimethylformamide; DME, dimethyl ether; NMP, *N*-methyl-2-pyrrolidone; DMAC, *N,N*-dimethyl acetamide; CH₃CN, acetonitrile, respectively.

and is converted back to the initial form by reaction with a base acting as H–X acceptor (Scheme 4) [85].

3.14. Comparison with other catalyst systems on Heck reaction

The Heck reaction is one of the most versatile tools in modern synthetic chemistry and has great potential for future industrial applications [5,53,75,83]. However, heterogeneous palladium catalysts suffer from reusability, due to either aggregation or leaching of the particles from the supports during the reaction.

Therefore, we are interested in evaluating the performance of our nanocatalyst (Pd/NH₂-SiO₂) compared to other reported systems for arylation of styrene with iodobenzene (Scheme 4). Comparison of the activity of various heterogeneous nanocatalysts on the Heck reaction of bromobenzene with styrene is listed in Table 5.

Different kinds of support have large impact on the dispersion of PdNPs. Also, the interaction between PdNPs and support is different, which has great influence on the stability of Pd.

It seems that most of the reactions are conducted in DMF medium (Table 5, entries 3, 5, 12 and 16–18). Due to its wide liquid temperature range, good chemical and thermal stability (even at its boiling point, 153 °C), high polarity and wide solubility range for both organic and inorganic compounds, this unique versatile and powerful chemical has been used as a solvent in a wide variety of synthetic procedures, including preparation of colloids, and many types of organic chemical reactions [86,87]. Our catalyst system performed in a very short time to complete the reaction (2 h) to afford moderate yield (95%).

3.15. Effect of solvents and bases on Sonogashira coupling reactions

The coupling of aryl halides with terminal acetylenes catalyzed by palladium and other transition metals, commonly termed as Sonogashira cross-coupling reaction, is one of the most important and widely used sp²–sp carbon–carbon bond formation reactions in organic synthesis, frequently employed in the synthesis of

Table 6
Results of Sonogashira coupling reactions catalyzed by Pd/NH₂-SiO₂ catalyst.^a

Entry	Reactants	Products	Time (h) ^b	Yield (%) ^c
1			2	98 (X=I); 93 (X=Br) ^d
2			3	90
3			4	85
4			5	92

^a Reaction conditions: aryl halide (1.0 mmol), phenylacetylene (1.5 mmol), Pd/NH₂-SiO₂ (0.05 mol%), base (2.0 mmol) and ethylene glycol (3.0 mL).

^b Reaction temperature: 120–130 °C.

^c Isolated yields of pure product after column chromatography.

^d Reusability of the Pd/NH₂-SiO₂ for 1st, 2nd and 3rd runs 98%, 90% and 80%, respectively.

natural products, biologically active molecules, heterocycles, molecular electronics, dendrimers and conjugated polymers or nanostructures [88].

The products of Sonogashira coupling reaction were obtained in good to excellent yields as shown in Table 6.

The coupling of iodobenzene with phenylacetylene afforded a very good yield (98%) of diphenylacetylene when it was conducted in the ethylene glycol at 125 °C temperature (Table 6, entry 1). The bromobenzene was found to be less efficient than iodobenzene (Table 6, entry 1), due to the electronic effects on the reactions were limited [2,88].

Remarkably, we carried out the coupling between 4-iodoanisole and phenylacetylene (Table 6, entry 3) to 85% yield, but 4-iodoacetophenone (Table 6, entry 4) reacts with phenylacetylene to yield (92%) compared to iodobenzene (98%), respectively.

The effect of different solvents upon the reaction of iodobenzene (1.0 mmol) with phenylacetylene (2.0 mmol) as a model reaction in the presence of K_2CO_3 (2.0 mmol) and 0.05 mol% of the Pd/ NH_2 - SiO_2 catalyst at 125 °C is studied and shown in Supporting information, Table S11. The results show that ethylene glycol (EG) is a suitable solvent for the reaction. EG is thermally stable, not so expensive with a low toxicity [103] and possesses negligible vapour pressure. Ethylene glycol is highly soluble in water, and can be easily separated from the organic phase by addition of water to the reaction mixture.

3.16. Proposed mechanism for Sonogashira reaction

This proposed mechanism of Sonogashira reaction is similar to the Heck coupling reaction as shown in Scheme 5.

The active nano Pd⁽⁰⁾ catalyst, obtained on reduction from a Pd(II) precursor, enters a catalytic cycle where subsequent oxidative addition of an aryl halide occurs. This process is followed by adduct alkylation to give the aryl alkynyl derivative of

palladium which regenerates Pd⁽⁰⁾ by the reductive elimination of substitution product (Steps I–VI). Various metal nanoparticles (e.g., Pd, Ti, and Ru) were also prepared by virtue of the formation of metal–carbon (M–C≡) single bonds [104–106].

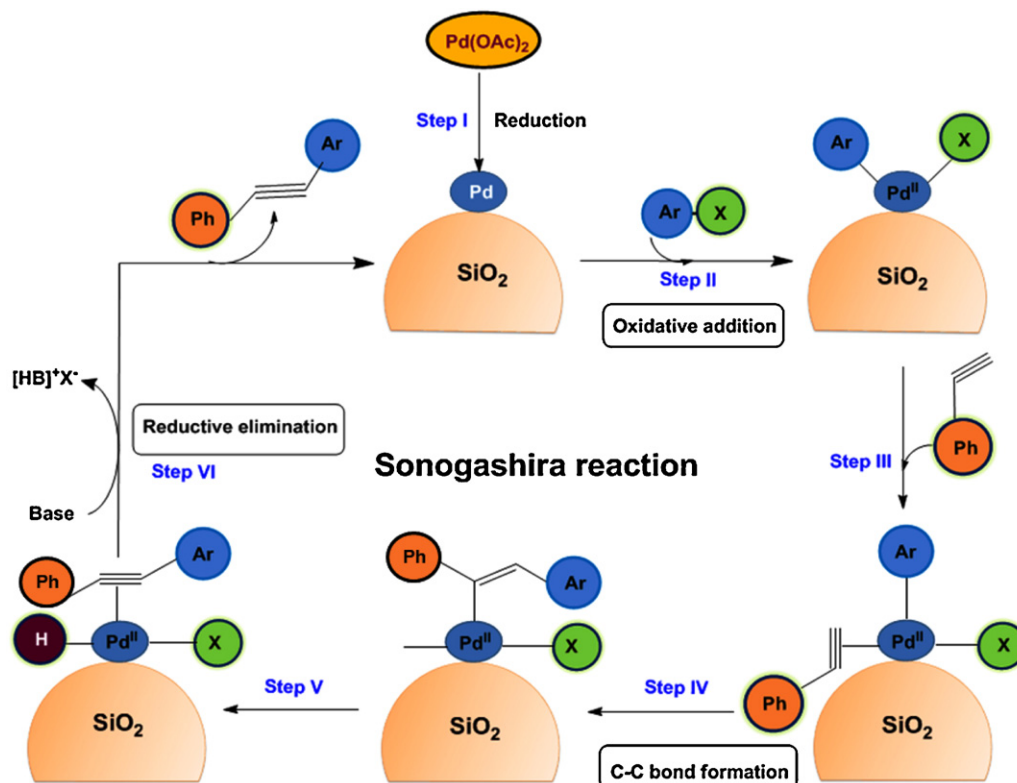
3.17. Comparison with other catalyst systems on Sonogashira reaction

Comparison of the activity of various heterogeneous nanocatalysts on the Sonogashira reaction of iodo- and bromobenzene with phenylacetylene published in the literature are listed in Table 7.

Hyeon and co-workers synthesized Pd/Ni bimetallic nanoparticles with a cheap metal core (Ni) and a noble metal shell (Pd), which can be used on Sonogashira coupling reactions [107]. The toxic organic solvent diisopropylamine (DIA) or toluene, however, has been used for this reaction. A high temperature was maintained >120 °C to complete the reaction (Table 7, entries 2, 8 and 10).

Lanthana (La_2O_3) supported AuNPs [117] were used for Sonogashira coupling reactions of iodobenzene and phenylacetylene to yield both the desired Sonogashira cross-coupling product (diphenylacetylene) and the two homocoupling side products (diphenyldiacetylene and biphenyl) are identified. But in our case no byproducts are observed. Cu_2O [115] and Pd-containing bimetallic hollow nanospheres [111] are successfully used to catalyze the Sonogashira reaction, but one of the drawbacks is the reaction proceeded with assistance of co-catalysts and ligand (CuI and PPh_3). But our system is used without assistance of any copper and other ligands for the reaction.

The temperature range from 30 to 140 °C has been the most commonly used reaction condition to Sonogashira transformations using different types of palladium catalysts as shown in Table 7. Indeed, it has previously been reported that the Sonogashira reaction using phosphine-based catalysts could occur at 80 °C [111].



Scheme 5. Possible mechanism of Sonogashira coupling reaction.

Table 7
Comparison of other catalyst systems on Sonogashira reaction of halobenzenes with phenylacetylene.

Entry	Catalysts ^a	Size (nm)	Mol (%)	Time (h)	Temp (°C)	Solvent	Yield (%)
1	Pd–Ni [106]	2–3	2.0	2	80	Toluene	92
2	Au/Ag/Pd [107]	4.2–4.4	0.5	2	140	DMF:H ₂ O (3:1)	99
3	Gelatin–Pd [108]	4–7	0.05 g	45 min	100	PEG	90
4	PdCo bimetallic hollow nanospheres [109]	60–90	0.05	6	80	H ₂ O	92
5	CoFe ₂ O ₄ –NH ₂ –Pd-complex [110]	30–40	1.0	2	80	DMF	93
6	Rh/Al ₂ O ₃ [111]	2.0	100 mg	24	120	DMF	57
7	PS–PdO [112]	2.3	1.5	6	80	H ₂ O	99
8	Cu ₂ O [113]	10	10	24	135–140	DMF	96
9	Pd ⁽⁰⁾ /[bbim]BF ₄ [114]	3–8	0.02	15 min	30	Acetone	85
10	La ₂ O ₃ –Au ⁽⁰⁾ [115]	20	30 mg	160	145	DMF	0.41
11	LDH–Pd ⁽⁰⁾ [78]	4–6	1.0	30–48	80	THF:H ₂ O (1:1)	95
12	PVP–Pd ⁽⁰⁾ [116,117]	7.0	1.06 mg	6	80	EtOH	95
13	Pd/MOF-5 [118]	3–6	3.0 wt.%	3	80	MeOH	86
14	Ru/Al ₂ O ₃ [32]	2–3	5.0	24	90	CH ₃ CN	85
15	Fe ₃ O ₄ [119]	<30	11 mg	35	125	EG	92
16	SiO ₂	>100	0.05	12	120	EG	Trace ^b
17	NH ₂ –SiO ₂	>100	0.05	12	120	EG	Trace ^c
18	Pd/NH ₂ –SiO ₂	5–6	0.05	1	120	EG	98 ^d

^a References.

^{b–d} Reaction conditions as exemplified in the experimental procedure, where DMF, dimethylformamide; MOF, metal organic framework; PEG, polyethylene glycol; EG, ethylene glycol; CH₃CN, acetonitrile, respectively.

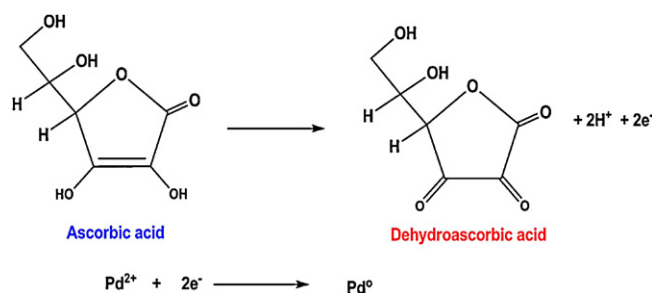
The effect of temperature on the reaction was therefore addressed. Experimental results show that pure (SiO₂) and amine modified silica (NH₂–SiO₂) afforded trace amount of product (Table 7, entries 16 and 17). In the present study the Sonogashira reaction was carried out in EG using 0.05 mol% palladium catalyst to give 98% yield which was achieved after 1 h at the reaction temperature of 120 °C.

The most effective temperature range for the Sonogashira reaction using the immobilized palladium catalyst used here was in good agreement with the literature as shown in Table 7. The effect of catalyst concentration on the reaction was then studied, using EG as the solvent and K₂CO₃ as the base at 120 °C. As with previous reports, the higher the catalyst concentration (Table 7, entries 3, 8, 11–13 and 18) used, the higher was the reaction rate. It was observed that 98% conversion was achieved after 1 h at the palladium concentration of 0.05 mol%. The catalyst concentrations used in this study were comparable to those of several previous reports covering different aspects of the Sonogashira reaction [118], where the palladium concentrations varied from less than 0.05 mol% to more than 5.0 wt.%, depending on the nature of the catalysts as well as the substrates as shown in Table 7.

It could be rationalized based on the fact that the homocoupling of phenylacetylene increased significantly at 1.0 mol% catalyst, leaving no phenylacetylene for the cross-coupling reaction. It is therefore decided to use 0.05 mol% catalyst for further experiments. The recovered Pd/NH₂–SiO₂ after the third run had no obvious change in structure according to the HRTEM images in comparison with the fresh Pd/NH₂–SiO₂ (see Supporting information, Fig. S4). The low activity of Pd/NH₂–SiO₂ may be due to low Pd dispersion on the surface of SiO₂ after recovery from the third cycle. The HRTEM images also reveal that Pd/NH₂–SiO₂ is very stable and capable of producing catalytic activity. These results indicate that the present catalyst on NH₂–SiO₂ support Pd/NH₂–SiO₂ is good for Suzuki, Heck and Sonogashira coupling reactions.

3.18. The role of ascorbic acid as reducing agent

Aqueous solution of ascorbic acid (vitamin C) has been widely used as a reducing agent [119]. To prevent oxidation, the reaction solutions are carefully deoxygenated and the entire process is performed under rigorous protection of inert gas in many reported studies [120]. Synthesis of the PEI stabilized PdNPs in aqueous solution using ascorbic acid as the reducing agent at room temperature



Scheme 6. Reduction reaction of Pd²⁺ with ascorbic acid.

is investigated. A standard electrode potential of ascorbic acid is ($E^{\circ} = 0.058$ V) for dehydroascorbic acid/ascorbic acid as shown in Scheme 6.

During the synthesis process, ascorbic acid plays a role as reducing agent, and in the storage, excessive ascorbic acid is essential to avoid oxidation of PdNPs. The antioxidant properties of ascorbic acid come from its ability to scavenge free radicals and reactive oxygen molecule, accompanying the donation of electrons to give the semi-dehydroascorbate radical and dehydroascorbic acid as shown in Scheme 6. It is capable of reducing Pd²⁺ into PdNPs and their redox potential is $E^{\circ} = 0.915$ V at room temperature. Therefore, ascorbic acid serves as a reducing agent for the synthesis of small PdNPs and this reaction can be completed without protective gas [119,121]. The brief 10 min heating played a critical role in the synthesis of the PdNPs, i.e., reduction of Pd²⁺ to Pd⁽⁰⁾ with ascorbic acid. At 95 °C, the PEI–Pd²⁺ solution is turned to transparent dark black as soon as ascorbic acid is added indicating rapid reduction of Pd²⁺ and formation of fine PdNPs as given in Scheme 6.

4. Conclusions

We have demonstrated that the synthesized amine modified silica supported palladium nanoparticles (Pd/NH₂–SiO₂) can successfully be employed in the Suzuki, Heck and Sonogashira coupling reactions. The silica supported PdNPs synthesized using highly branched PEI as a capping agent and ascorbic acid as a reducing agent in aqueous solution are characterized by XRD, HRTEM, BET, SEM-EDX, FT-IR, and UV–vis spectral techniques. Though the Suzuki cross-coupling reaction is carried out in aqueous media, Heck and Sonogashira coupling reactions are conducted in DMF

and ethylene glycol, respectively. As far as we know the catalytic system described here seems to be a very simple, efficient and green method for the synthesis of very important organic compounds from readily available organic compounds as the starting materials.

Acknowledgements

P.V. acknowledges University Grants Commission (UGC), New Delhi for a SRF position under Meritorious Fellowship Scheme. S.R. thanks Department of Science and Technology (DST) and University Grants Commission-Basic Scientific Research (UGC-BSR), New Delhi for the financial support.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcata.2013.01.021>.

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