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Novel heterogeneous catalyst systems based on Pd(0) nanoparticles onto amine functionalized silica-cellulose substrates [Pd(0)-EDA/SCs]: Synthesis, characterization and catalytic activity towards C-C and C-S coupling reactions in water under limiting basic conditions

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### **Graphical abstract**



### Highlights

- Synthesis and characterization of amine functionalized substrates [Pd(0)-EDA/SCs].
- Synergism of inorganic/organic properties to get silica/cellulose substrates.
- Base free or limiting base access to C-C and C-S couplings.
- Catalyst is recyclable up to five times with almost consistent activity.

### Abstract

Novel heterogeneous catalyst systems based on the immobilization of Pd(0) nanoparticles onto ethylene diamine functionalized silica-cellulose substrates [Pd(0)-EDA/SCs] are reported with a view to introduce new synthetic routes under base-free conditions. The base functionalized organic/inorganic hybrid provides specific basic sites for the reactions to occur under base-free or less basic conditions, and that too with excellent yields. Moreover, the

basic nitrogen sites present on the substrate can effectively stabilize and enhance the activity of Pd(0) nanoparticles by preventing their agglomeration and controlling their size. All the catalysts were characterized by TGA and FTIR analysis and the most active catalyst, [Pd(0)-EDA/SC-2] was further characterized by SEM, TEM, HRTEM, EDX, CHN and XRD studies. Additionally, it is shown that the Pd(0)-EDA/SCs exhibits excellent activity under limiting basic conditions for the C-C and C-S coupling reactions employing water as the "Green solvent". Furthermore, the novel catalyst could be recovered in a facile manner from the reaction mixture and could be reused up to five times without significant loss of catalytic activity.

## Keywords

Heterogeneous catalysis; Pd (0) nanoparticles; base functionalization; C-C and C-S couplings; Green solvent.

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### **1. Introduction**

From the standpoint of green chemistry, water is known to be a promising solvent and has received considerable attention in the area of organic synthesis **[1-5]**. Further, reactions in aqueous media offers key advantages such as rate enhancement and insolubility of the final products, which facilitates their isolation by simple filtration.

Inspired by the need for green and sustainable chemistry, palladium catalyzed reactions in aqueous media drew great interests of synthetic chemists [6-8]. Despite the remarkable utility of Pd catalysts in organic synthesis, they suffer from one significant drawback related to catalyst recovery and reuse, thus affecting the overall economics of the process. Therefore, developing a facile and expedient approach by using heterogeneous catalysts due to their easy handling, simple recovery and recycling is highly desirable [9]. Further, the use of palladium nanoparticles (Pd NPs) in catalysis is crucial as they mimic metal surface activation and catalysis at the nanoscale and thereby bring selectivity and efficiency to heterogeneous catalysis [10]. Although there is now considerable literature precedence for Pd catalysed transformations, the majority of the work has been carried out in the presence of organic or inorganic bases. Only a handful of reports focus on the use of base-free or less basic conditons for carrying out these transformations [11, 12].

commonly used inorganic bases (e.g.  $K_3PO_4$ ,  $Cs_2CO_3$ ) are poorly ionized in organic solvents and therefore, impede the necessary deprotonation step. Further, the organic bases are relatively expensive, hygroscopic and have to be stored and used under strictly dry conditions. These disadvantages may hamper the utility of the inorganic and organic bases in both Pd catalyzed reactions and other base-mediated organic transformations. To overcome these disadvantages, there is a great need to develop such catalyst systems which could efficiently limit the use of base in organic transformations. These days, base functionalised supports have been efficiently employed in heterogeneous catalysis for various organic synthesis [12-14].

The Pd catalyzed C-C bond formation via Suzuki-Miyaura reaction represents a viable protocol for rapid access to biaryls which have a broad and diverse range of applications from pharmaceuticals to material science [15]. Further, the synthesis of biologically important bis(heterocyclyl)methanes via C-C bond formation is also an important application of Pd NPs [16, 17]. Apart from C-C couplings, the formation of C-S bond for the synthesis of thioethers is also of utmost importance and is a key step in the synthesis of many organic molecules [18]. Majority of the developed protocols for the C-C and C-S bond formations genarally requires 2 or more equivalents of base [17, 19, 20]. In addition to this, the synthesis of thioethers involves the use of foul-smelling thiols, longer reaction times and harsh reaction conditions [1]. Thus, devising new environment friendly Pd catalysed strategies for the C-C and C-S bond formations avoiding the use of base or reducing the amount of base is highly enviable.

Owing to the exhaustive applications of Pd mediated processes, we became interested to explore new possibilities in catalyst design with more emphasis on base functionalised catalytic systems. Initially, to search for the suitable support, it is found that silicas [21] and activated carbons [22] are stable substrates for immobilization of Pd NPs, but in

recent years, several functionalised biopolymers such as cellulose has been efficiently used as catalyst support because of its hydrophilicity, chirality, biodegradability and broad chemical-modifying capacity [23]. The chemical modification of cellulose by incorporating the ethylene-1,2-diamine moiety as a pendant chain covalently bonded to the main polymeric framework provides more stability [24]. In order to further explore the applications of both organic and inorganic substrates, herein, we investigate that when the ethylene diamine functionalised cellulose is covalently bonded to silica, they can form a very stable bond with a high degree of organofunctionalisation. Moreover, the basic nitrogen sites present on the substrate increases the stability and activity of Pd NPs, and can work quite effectively under base-free or requiring very little amount of base in an aqueous media.

In this paper, we report the synthesis and characterization of novel heterogeneous catalyst systems based on the immobilization of palladium(0) nanoparticles onto ethylene diamine functionalized silica-cellulose substrates [Pd(0)-EDA/SCs] and explored their catalytic activities for C-C and C-S bond forming reactions in aqueous media under base-free or using very little amount of base.

### 2. Experimental

#### 2.1 Reagents and instrumentation

The chemicals used were purchased from Aldrich Chemical Company or Merck. The <sup>1</sup>H and <sup>13</sup>C NMR data were recorded in CDCl<sub>3</sub> on Bruker Avance III (400 MHz and 100 MHz). The FTIR spectra were recorded on Perkin-Elmer FTIR spectrophotometer. SEM images were recorded using FEG SEM JSM-7600F. Transmission Electron Micrographs (TEM) were recorded on Philips CM-200. High Resolution Transmission Electron Micrographs (MRTEM) were recorded on JEOL, JEM-2100F. X-ray diffratograms (XRD)

were recorded in 2 theta range of 10-80° on a Bruker AXSDB X-ray diffractometer using Cu Kα radiations. EDX analysis was carried out using OXFORD X-MAX JSM-7600. CHN analysis was recorded on ThermoFinnigan FLASH EA 1112 series. The amount of metal in catalyst was determined by AAS analysis using GBC Avanta-M atomic absorption spectrometer and thermal analysis was carried out on Linsesis STA PT-1000 make thermal analyzer. Microwave synthesizer used was manufactured by CEM (DISCOVER SYSTEM).

#### 2.2 Preparation of silica chloride

Firstly, activated silica (10 g) was charged to the three-neck flask (100 mL), equipped with a dropping funnel containing thionyl chloride (40 mL) and a gas inlet tube for conducting HCl over an absorbing solution of 10% NaOH. Thionyl chloride was added drop-wise over a period of 15 min at room temperature followed by stirring for 10 h at 80 °C. The untreated SOCl<sub>2</sub> was removed by distillation and the resulting silica chloride was vacuum dried at 90 °C to obtain as greyish white powder.

#### 2.3 Preparation of ethylene diamine functionalized cellulose (EDACel)

Cellulose (10 g) previously activated at 80 °C for 12 h was suspended in N,Ndimethylformamide (200 mL), followed by the slow addition of thionyl chloride (35 mL) at 80 °C, under mechanical stirring. After the addition was complete, stirring was continued for another 4 h. The cellulose chloride (CelCl) obtained was washed with several aliquots of dilute ammonium hydroxide solution (0.5 mol/L NH<sub>4</sub>OH) and the supernatant after each treatment was removed to bring the pH to neutral. To complete the washing, the suspension was exhaustively treated with distilled water (3×100 mL approx.). The solid was then separated by filtration and dried in vacuum at room temperature [24].

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A mixture of CelCl (5 g) and ethylene-1,2-diamine (25 mL) was stirred at 116 °C for 3 h. The reaction mixture was filtered through a sintered glass crucible and the solid was dried in vacuum at room temperature to afford EDACel as yellow powder.

2.4 Preparation of ethylene diamine functionalized silica-cellulose substrates (EDA/SCs)

A mixture of silica chloride and EDACel (8 g) was taken in three different ratios of 2:1, 1:1 and 1:2 respectively and magnetically stirred in CHCl<sub>3</sub> (35 mL) using triethyl amine (0.8 mL) at 60  $^{\circ}$ C for 12 h. Then, the three mixtures were filtered and washed with chloroform (3×10 mL) and water (3×10 mL) respectively, and dried under vacuum at room temperature to get light to dark yellow powders.

2.5 Preparation of Pd nanoparticles onto ethylene diamine functionalized silica-cellulose substrates [Pd(0)-EDA/SCs]

To a mixture of EDA/SCs (2.0 g) in H<sub>2</sub>O (12 mL), aqueous solution of PdCl<sub>2</sub> (0.19 g, 1.10 mmol, 3 mL) was added, and the mixture was stirred at room temperature for 8 h. Then, aqueous solution of NaBH<sub>4</sub> (1.50 mmol, 5 mL) was added slowly during 5 h. Finally, the mixture was filtered, and the residue was washed successively with H<sub>2</sub>O ( $3\times5$  mL) and CH<sub>3</sub>CN ( $3\times5$  mL), respectively, and dried under vacuum at room temperature to give the dark polymeric Pd(0) nanoparticles (**Scheme 1**).



**Scheme 1.** General procedure for the synthesis of Pd(0) NPs onto ethylene diamine functionalized silicacellulose substrates [Pd(0)-EDA/SCs.

#### 2.6 General procedure for the Pd(0)-EDA/SC-2 catalyzed Suzuki reaction

To a mixture of aryl halide (1 mmol), aryl/heteroaryl boronic acid (1.2 mmol), TBAB (0.25 mmol),  $K_2CO_3$  (0.25 mmol) and Pd(0)-EDA/SC-2 (0.2 g, 2.5 mol% Pd), double distilled water (5 mL) was added and the reaction mixture was stirred in a microwave synthesizer at 100 °C for an appropriate time (monitored by TLC) (**Scheme 2**). After completion, the reaction mixture was cooled to room temperature and filtered. The catalyst was washed with EtOAc (3×5 mL) followed by double distilled water (3×10 mL). It was dried at 100 °C for 1 h and could be used in subsequent reactions. The organic layer was washed with water and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Finally, the product was

obtained after removal of the solvent under reduced pressure followed by crystallization from a suitable solvent or passing through column of silica gel (EtOAc-pet. ether).



**Scheme 2.** Pd(0)-EDA/SC-2 catalyzed Suzuki coupling between arylhalides and boronic acids using water as solvent under microwave irradiation.

2.7 General procedure for the Pd(0)-EDA/SC-2 catalyzed synthesis of bis(heterocyclyl)methanes

To a mixture of C–H activated compound 3-methyl-1-phenyl-1H-pyrazol-5(4H)-one, dimedone or indole (2 mmol), aryl aldehyde (1 mmol) and Pd(0)-EDA/SC-2 (0.2 g, 2.5 mol% Pd), double distilled water (5 mL) was added and the reaction mixture was stirred at 100 °C for an appropriate time (monitored by TLC) (**Scheme 3**). After completion, the reaction mixture was cooled to room temperature and filtered. The product was extracted with hot ethyl acetate (approx. 70 °C,  $3 \times 10$  mL) followed by washing with double distilled water ( $3 \times 50$  mL). The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and the solvent was then removed under reduced pressure to get the crude product. Pure products were obtained after crystallization or by passing through column of silica gel using EtOAc-pet. ether as eluent. The catalyst was washed with EtOAc ( $3 \times 5$  mL) followed by double distilled water ( $3 \times 10$  mL). It was dried at 100 °C for 1 h for subsequent use.



Scheme 3. Pd(0)-EDA/SC-2 catalyzed synthesis of bis(heterocyclyl)methane derivatives in water at 100 °C.
2.8 General procedure for the Pd(0)-EDA/SC-2 catalyzed thioetherification of aryl halides

To a mixture of aryl halide (1 mmol), benzyl bromide (1.1 mmol),  $K_2CO_3$  (0.50 mmol), thiourea (1.2 mmol) and Pd(0)-EDA/SC-2 (0.2 g, 2.5 mol% Pd) in a round-bottom flask (25 mL), water (5 mL) was added and the reaction mixture was stirred at 100 °C for an appropriate time (**Scheme 4**). After completion of the reaction (monitored by TLC), the reaction mixture was diluted with ethyl acetate and filtered. The organic layer was washed with water (100 mL) and dried over anhydrus Na<sub>2</sub>SO<sub>4</sub>. Finally, the product was obtained after removal of the solvent under reduced pressure followed by crystallization or column chromatography on silica gel (EtOAc-pet. ether). The catalyst was washed with EtOAc (3×5 mL), double distilled water (3×10 mL) respectively and dried under vaccum for 1 h at 100 °C for further use.



**Scheme 4.** Pd(0)-EDA/SC-2 catalyzed one-pot thioetherification of arylhalides using thiourea as the source of sulfur.

### 3. Results and Discussion

### 3.1 Characterization of Pd(0) nanoparticles onto ethylene diamine functionalized silicacellulose substrates [Pd(0)-EDA/SCs]

Synthesis of the Pd(0)-EDA/SCs was achieved in four steps as depicted in Scheme 1. In this process, the silica chloride and 6-(2'-aminoethylamino)-6-deoxy-cellulose (EDACel) were taken in three different ratios of 2:1, 1:1 and 1:2 to prepare different EDA/SCs. Pd(0) NPs were then immobilized on EDA/SCs to get Pd(0)-EDA/SC-1 (prepared from 2:1 ratio of silica chloride and EDACel), Pd(0)-EDA/SC-2 (prepared from 1:1 ratio of silica chloride and EDACel), and Pd(0)-EDA/SC-3 (prepared from 1:2 ratio of silica chloride and EDACel), with a view to select the most active and selective heterogeneous catalyst which could efficiently work under base-free or less basic conditions. Among various catalysts screened, it was found that Pd(0)-EDA/SC-2 (prepared from 1:1 ratio of silica chloride and EDACel) was found to be most active and selective. All the three catalysts were characterised by Fourier Transform Infrared (FT-IR) spectroscopy and Thermogravimetric Analysis (TGA). The most active heterogeneous catalyst, Pd(0)-EDA/SC-2 was also characterised by Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), High Resolution Transmission Electron Microscopy (HRTEM), Energy Dispersive X-ray analysis (EDX), Carbon, Hydrogen and Nitogen analysis (CHN) and Powder X-ray Diffraction (XRD).

#### Fourier Transform Infrared analysis (FT-IR)

The FT-IR spectral analysis of Pd(0)-EDA/SCs was done to study the structure of EDA/SC. All the three catalysts i.e., Pd(0)-EDA/SC-1, Pd(0)-EDA/SC-2 and Pd(0)-EDA/SC-3 showed almost similar peaks in their corresponding FT-IR spectra due to the presence of same functionalities in them. The FT-IR spectra of Pd(0)-EDA/SC-2 (**Figure S1**, see **ESI**) showed bands in the range of 3700-3200 cm<sup>-1</sup> due to the surface -OH and -NH groups. The bands around 1105, 801 and 471cm<sup>-1</sup> were presumably due to the asymmetric stretching (v<sub>as</sub>), symmetric stretching (v<sub>s</sub>), and bending modes of Si–O–Si, respectively. The broad peak centered at 3434 cm<sup>-1</sup> was an envelope of streching vibrations for O-H of the adsorbed water, silanol groups, and N–H of the amino groups respectively. The characteristic bands around 2919 cm<sup>-1</sup> and 1633 cm<sup>-1</sup> were assigned to the stretching vibrations of the C-H of CH<sub>2</sub> groups and the bending vibrations of the –NH of the NH<sub>2</sub> groups respectively, both of which were associated with ethylene diamine modified silica-cellulose substrate.

#### Thermogravimetric analysis (TGA)

The stability of the Pd(0)-EDA/SCs was determined by TGA. The major weight losses of all the three catalysts are presented in **Table 1**. The difference between the thermal stabilities of the three catalysts may be due to the different ratios of inorganic/organic substates thus effecting the covalent bonding between the silica chloride and EDACel. The TGA curve of Pd(0)-EDA/SC-2 (**Fig. 1**) showed no appreciable weight loss up to 241 °C. The major weight loss from 241 to 300 °C was due to the decomposition of cellulose and chemisorbed material i.e. ethylene diamine groups from the Pd(0)-EDA/SC substrate. Thus, the catalyst is stable up to 241 °C and it is safe to carry out the reaction at 100 °C under heterogeneous conditions.

 Table 1. Characterization of ethylene diamine functionalized silica-cellulose

 substrates [Pd(0)-EDA/SCs] by thermal analysis

Entr	y Catalyst	TGA (°C)
		Loss of organic functionality
1	Pd(0)-EDA/SC-1	230-300
2	Pd(0)-EDA/SC-2	241-300
3	Pd(0)-EDA/SC-3	210-290

Thermal analysis was carried out on Linsesis STA PT-1000 make thermal analyzer with heating rate of 10  $\,^{\circ}C/min$ .



Fig. 1 TGA curve of Pd(0)-EDA/SC-2.

#### Scanning Electron Microscopy (SEM)

Scanning Electron Micrographs (**Fig. 2**) of Pd(0)-EDA/SC-2 were recorded to understand the morphological changes occur on the surface of EDA/SC. The SEM images showed that the catalyst was a homogeneous powder and Pd nanoparticles were uniformely distributed onto the surface of EDA/SC and most of the particles have quasi-spherical shape.



Fig. 2 SEM images of Pd(0)-EDA/SC-2

#### Transmission Electron Microscopy (TEM)

The TEM was performed to observe the morphology and distribution of palladium nanoparticles onto the surface of ethylene diamine functionalized silica-cellulose substrate [**Figure S2 (a and b),** see **ESI**]. From the TEM image (**a**), it was inferred that Pd(0)-EDA/SC-2 contained many small black spheres due to the presence of Pd(0) nanoparticles. Further, in image (**b**), Pd(0)-EDA/SC-2 shows the formation of molecular sieves which offers entrapment of metal particles inside the sieves of silica and cellulose, and thereby showing the phenomenon of host-guest relationship.

#### High Resolution Transmission Electron Microscopy (HRTEM)

In order to determine the size of the Pd nanoparticles, high resolution TEM images of Pd(0)-EDA/SC-2 were recorded **Fig. 3**. The histogram revealing the size distributions of Pd nanoparticles is proposed according to the data, which is obtained from the HRTEM image with an average size of 3.5 nm (**Figure S3**, see **ESI**).



Fig. 3 HRTEM images of Pd(0)-EDA/SC-2

Energy Dispersive X-ray (EDX) and Carbon Hydrogen Nitrogen (CHN) analysis

The elemental composition of Pd(0)-EDA/SC was determined by EDX analysis (**Figure S4**, see **ESI**). The EDX spectrum reveals the presence of Pd on EDA/SC. It also showed the presence of other elements like C, O, Si and Cl in EDA/SC. Moreover, the presence of nitrogen was also determined by CHN analysis.

#### Atomic Absorbption spectroscopy (AAS)

In order to evaluate the content of Pd supported on EDA/SC-2, the catalyst was analyzed using atomic absorption spectroscopy (AAS). The results indicated that the content of Pd loaded onto EDA/SC was 6.67 wt%.

X-ray Powder Diffraction (XRD)

Unequivocal evidence of Pd(0) nanoparticles onto EDA-SC was provided by XRD data (**Fig. 4**). The XRD data of Pd(0)-EDA/SC-2 revealed its metallic nature. Three reflection patterns, attributed to the planes (1 1 1), (2 0 0) and (2 2 0) are readily recognized from the XRD pattern, which could be indexed to a face-centered cubic (*fcc*) palladium [**25**]. These observations corresponds to the presence of Pd(0) nanoparticles onto the surface of EDA/SC.



Fig. 4 XRD spectrum of Pd(0)-EDA/SC-2.

#### 3.2 Catalyst testing for C-C bond formation

Activity of Pd(0)-EDA/SCs was tested for Suzuki coupling, and synthesis of bis(heterocyclyl)methanes via C-C bond formation. In order to optimize the reaction conditions for Suzuki coupling, 4-bromoacetophenone and benzene boronic acid were selected as test substrates and the reaction was carried out in water under microwave irradiation. We, then began our experiment by carrying out the reaction with test substrates using Pd(0)-EDA/SC-1, Pd(0)-EDA/SC-2 and Pd(0)-EDA/SC-3, with a view to find the best catalytic system for the Suzuki coupling. The results are presented in Table 2, which indicated that among the different catalysts screened, Pd(0)-EDA/SC-2 provided the best results in terms of reaction time, yield and selectivity. As our developed catalyst system [Pd(0)-EDA/SC-2] was base functionalised and since, our main motive was to carry out the Pd catalysed transformations under base-free conditions, we then examined Suzuki coupling under different conditions with respect to base and phase transfer catalyst, TBAB (Table 3). Initially, we carried out the Suzuki coupling in case of test substrates using Pd(0)-EDA/SC-2 in the absence of base, unfortunately poor results were obtained (35% yield after 0.5 h, **Table** 3, entry 1). It is well known that the addition of base is necessary to carry out the Suzuki coupling effectively, so K<sub>2</sub>CO<sub>3</sub> was selected as the base, since it is mild, inexpensive and

easily available. We then carry out the test reaction in the presence of base (0.10 mmol to 0.50 mmol, Table 3, entries 2-4), but the reaction didn't go to completion and the maximum yield obtained was only 55%. Since water was used as solvent, we then carried out the reaction using TBAB in order to increase the solubility of the reagents in water. Next, we carried the Suzuki reaction in the presence of Pd(0)-EDA/SC-2 using different amounts of base and TBAB (0.10 mmol to 0.50 mmol) (Table 3, entries 5-10). Without the presence of K<sub>2</sub>CO<sub>3</sub>, 47% of product was obtained using 0.25 mmol of TBAB (Table 3, entry 9). So, we further tried the test reaction using 0.5 mmol of TBAB without using any base (Table 3, entry 10), the results indicate that there is not much increase in yield as compared to 0.25 mmol of TBAB. On the basis of the results, we conclude that 0.25 mmol each of K<sub>2</sub>CO<sub>3</sub> and TBAB were required to carry out the reaction with excellent yield (92%, Table 3, entry 7). With these encouraging results, we had limited the amount of base in the presence of our base functionalised catalyst, Pd(0)-EDA/SC-2 from 200 mol% [19] to 25 mol%. Although, there is considerable literature precedence for Suzuki coupling, but till now, there is no report of Suzuki coupling performed using such a low amount of base, which justifies the role of Pd(0)-EDA/SC-2 as base functionalised catalyst system. Finally, to select the appropriate amount of Pd(0)-EDA/SC-2 the test reaction was carried using different amounts of the catalyst i.e. 0.050 g (1 mol% Pd), 0.10 g (1.5 mol% Pd), 0.15 g (2.0 mol% Pd), 0.2 g (2.5 mol% Pd) and 0.25 g (3 mol% Pd), and found that best results were obtained with 0.2 g (2.5 mol%). The results are shown in Fig. 5. From the results, it is clearly depicted that the addition of sole base in limited amount does not complete the reaction. However, with the addition of base functionalised Pd(0)-EDA/SC-2 and that too in appropriate amount acts synergistically with limited amount of base to complete the reaction with excellent yields. So, 0.2 g of catalyst was selected for carrying out the Suzuki coupling. Thus, optimum conditions selected were: aryl halide (1 mmol), aryl/heteroaryl boronic acid (1.2 mmol), K<sub>2</sub>CO<sub>3</sub> (0.25 mmol) TBAB

(0.25 mmol) and Pd(0)-EDA/SC-2 (0.2 g, 2.5 mol% of Pd) using distilled water as solvent under microwave irradiation (**Table 4**). The generality of the developed protocol was studied by choosing different aryl halides substituted with both electron-donating and electron-withdrawing groups, and good to excellent results were obtained (**Table 4**). Bromophenol and bromoaniline which were considered as poor substrates for the Suzuki coupling, also undergo reaction efficiently (**Table 4**, entries 6 and 7). Similar conditions were also successful for the synthesis of polyaryls (**Table 4**, entries 8 and 9). Heteroarylboronic acids which generally undergoes reaction slowly, also work efficiently using of Pd(0)-EDA/SC-2 in water (**Table 4**, entry 12). To highlight the applicability of the developed catalytic system, Suzuki reaction was also performed thermally under the same optimized reaction conditions and similar results were obtained (**Table 4**, entries 2, 3, 5 and 12).

 Table 2. Comparison of catalytic activities of ethylene diamine functionalized silica-cellulose substrates

 [Pd(0)-EDA/SCs] for C-C and C-S coupling reactions

Entry	Catalyst	Pd(0)-EDA/SC-1		Pd(0)-EDA/SC-2		Pd(0)-EDA/SC-3		
Liitiy	Reactions	Time (h)	Yield (%) <sup>d</sup>	Time (h)	Yield (%) <sup>d</sup>	Time (h)	Yield (%) <sup>d</sup>	
1.	Suzuki <sup>a</sup>	0.50	89	0.25	92	0.5	90	
2.	Bis(heterocyclyl) methanes <sup>b</sup>	2.0	88	1.5	90	2.5	86	
3.	Thioetherification <sup>c</sup>	7	83	6	88	8.5	82	

<sup>a</sup>Reaction conditions: 4-bromoacetophenone (1 mmol), benzeneboronic acid (1.2 mmol),  $K_2CO_3$  (0.25 mmol), TBAB (0.25 mmol), Pd(0)-EDA/SCs (2.5 mol% Pd) and water (5 mL) at 100 °C under microwave irradiation. <sup>b</sup>Reaction conditions: Benzaldehyde (1 mmol), 3-methyl-1-phenyl-1H-pyrazol-5(4H)-one (2 mmol), Pd(0)-EDA/SCs (2.5 mol% Pd) and water (5 mL) at 100 °C.

 $^{\circ}$ Reaction conditions: 4-bromobenzaldehyde (1 mmol), benzyl bromide (1.1 mmol), thiourea (1.2 mmol), K<sub>2</sub>CO<sub>3</sub> (0.5 mmol), Pd(0)-EDA/SCs ( 2.5 mol% Pd) and water (5 mL) at 100  $^{\circ}$ C

<sup>d</sup>Isolated yields.

Entry	Reaction	Optimization		Time (h)	Yield (%) <sup>e</sup>
		Base (mmol)	TBAB (mmol)		
1		-	-	0.5	35
2		0.10	-	0.5	40
3		0.25	-	0.5	50
4		0.50	-	0.5	55
5	Complet <sup>a</sup>	0.10	0.10	0.5	45
6	Suzuki	0.25	0.10	0.5	75
7		0.25	0.25	0.25	<b>92</b> <sup>d</sup>
8		0.50	0.25	0.25	92 <sup>d</sup>
9		-	0.25	0.5	47
10		-	0.50	0.5	52
11		0.10	-	1.0	91 <sup>d</sup>
12		0.25	-	1	93 <sup>d</sup>
13	Bis(heterocyclyl)methanes <sup>-</sup>	0.50	-	1	93 <sup>d</sup>
14		-	-	1.5	<b>90</b> <sup>d</sup>
15		_	-	8	25
16		0.25	-	8	60
17	Thioethers	0.50	-	6	$88^{\mathrm{d}}$
18		1.0	-	6	88 <sup>d</sup>

Table 3. Optimization of base ( $K_2CO_3$ ) for C-C and C-S couplings in the presence of ethylene diamine functionalized silica-cellulose [Pd(0)-EDA/SC-2]

<sup>a</sup>Reaction conditions: 4-bromoacetophenone (1 mmol), benzeneboronic acid (1.2 mmol),  $K_2CO_3$  ( x mmol), TBAB (x mmol), Pd(0)-EDA/SC-2 (0.2 g, 2.5 mol% Pd) and water (5 mL) at 100 °C under microwave irradiation.

<sup>b</sup>Reaction conditions: Benzaldehyde (1 mmol), 3-methyl-1-phenyl-1H- pyrazol-5(4H)-one (2 mmol),  $K_2CO_3$  ( x mmol), Pd(0)- EDA/SC-2 (0.2 g, 2.5 mol% Pd) and water (5 mL) at 100 °C.

<sup>c</sup>Reaction conditions: 4-bromobenzaldehyde (1 mmol), benzyl bromide (1.1 mmol), thiourea (1.2 mmol),  $K_2CO_3$ , (x mmol), Pd(0)-EDA/SC-2 (0.2 g, 2.5 mol% Pd) and water (5 mL) at 100 <sup>o</sup>C.

<sup>d</sup>Isolated Yields

<sup>e</sup>Column chromatography yields.

Entry	Substrate	Product	Time (min)	Yield (%) <sup>b</sup>
1.	Br		18	90
2.	H <sub>3</sub> C-C-Br	$H_3C-C$	15, 45°	92, 93 <sup>°</sup>
3.	NC Br		15, 40°	90, 90°
4.	H-C-Br	H-C-	17	90
5.	Ph-C-Br	Ph-C	15, 40 <sup>c</sup>	91, 92 <sup>c</sup>
6.	HO Br	но	35	85 <sup>d</sup>
7.	H <sub>2</sub> N-Br	H <sub>2</sub> N	35	82 <sup>d</sup>
8.	Br — Br		20	78
9.	Br		20	80
10.	CI	CI	20	79
11.	Br		25	75

Table 4.	Pd(0)-EDA/SC-2	catalyzed	Suzuki	coupling	between	arylhalides	and	boronic	acids	using	water	as
solvent un	der microwave irra	adiation <sup>a</sup>										

12. 
$$H_3C - C - C - Br = H_3C - C - S = 20, 60^{\circ}$$
 81, 83°

<sup>a</sup>Reaction conditions: aryl halide (1 mmol), benzeneboronic acid/2-thiophene boronic acid (1.2 mmol), K<sub>2</sub>CO<sub>3</sub> (0.25 mmol), TBAB (0.25 mmol), Pd(0)-EDA/SC-2 (0.2 g, 2.5 mol% Pd) and water (5 mL) at 100 °C under microwave irradiation.

<sup>b</sup>Isolated yields.

<sup>c</sup>Same conditions as (a) but under thermal conditions.

<sup>d</sup>The product was obtained after passing through column of silica gel and elution with EtOAc: pet ether (0.3-9.7).



**Fig. 5.** Effect of catalyst loading. Reaction conditions: 4-bromoacetophenone (1 mmol), benzeneboronic acid (1.2 mmol),  $K_2CO_3$  (0.25 mmol), TBAB (0.25 mmol), catalyst (0.05 g to 0.25 g) and water (5 mL) at 100 °C under microwave irradiation.

Our next endeavour was to extend the scope of Pd(0)-EDA/SC for the synthesis of bis(heterocyclyl)methanes. The reaction was carried out by stirring a mixture of 3-methyl-1phenyl-1H-pyrazol-5(4H)-one and benzaldehyde (test substrates) in the presence of Pd(0)-EDA/SC-1, Pd(0)-EDA/SC-2 and Pd(0)-EDA/SC-3 in water at 100 °C (Table 2). Again, Pd(0)-EDA/SC-2 was found to be the best catalyst for the synthesis of bis(heterocyclyl)methanes. Since our developed catalytic system, Pd(0)-EDA/SC-2 was base functionalised, so the influence of external base on the catalytic performance of this system was also investigated. The results are presented in Table 3, which indicated that with 0.25 mmol and 0.50 mmol of K<sub>2</sub>CO<sub>3</sub> in water, the product was obtained in 93% yield after 1 h.

However, in the absence of  $K_2CO_3$ , the product was obtained in 90% yield in 1.5 h (**Table 3**, entry 14). Although the reaction took a long time but we had significantly avoided the use of  $K_2CO_3$  in the presence of Pd(0)-EDA/SC-2 as base functionalised catalyst system. Again, optimization with respect to the amount of catalyst was done and found that 0.2 g of Pd(0)-EDA/SC-2 was sufficient to carry out the reaction efficiently in terms of reaction time and yield. With these encouraging results, we turn to explore the generality of the developed protocol using other C–H activated compounds such as dimedone and indole under the optimized reaction conditions. The reaction of C–H activated compounds such as pyrazolone, dimedone and indole was carried out with various aldehydes having both electron-releasing and electron-withdrawing groups and excellent results were obtained (**Table 5**).

Table 5.	Pd(0)-EDA/SC-2	catalyzed syntl	nesis of bis(het	erocyclyl)methane	e derivatives in	water at 100 °C <sup>a</sup>

Entry	Substrate	Product (1a-j)	Time/Yield (h) (%) <sup>b</sup>	Product (2a-j)	<b>Time/Yield</b> (h) (%) <sup>b</sup>	Product (3a-j)	Time/Yield (h) (%) <sup>b</sup>
1	н	Ph OH OH Ph 1a	1.5/90	он он 2a	2/89	HN Ja	3/87
2	Br H	Ph OH OH Ph 1b	1.2/88	Br OH OH 2b	1/85	Br HN HN 3b	2/89
3	CI H	CI N H N Ph OH OH Ph 1c	1.2/85	CI OH OH 2c	1.2/88	CI HN-3c	2/86

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<sup>&</sup>lt;sup>a</sup>Reaction conditions: aryl aldehyde (1 mmol), 3-methyl-1-phenyl-1H-pyrazol-5(4H)-one /dimedone/ indole (2 mmol), Pd(0)-EDA/SC-2 (0.2 g, 2.5 mol% Pd) and water (5 mL) at 100 °C. <sup>b</sup>Isolated Yields.

#### 3.3 Catalyst testing for C-S bond formation

Fascinated by the impressive performance of Pd(0)-EDA/SC-2 in C-C couplings, its catalytic activity was also tested for the thioetherification via C-S coupling reaction. The thioetherification of 4-bromobenzaldehyde was carried out using benzyl bromide and thiourea as sulphur source (test substrates) in the presence of Pd(0)-EDA/SCs. Again, water was used as a solvent. The screening of various catalysts allowed us to select Pd(0)-EDA/SC-2 as the most effective catalyst for one-pot thioetherification of aryl halides with thiourea and benzyl bromide in water at 100 °C (Table 2). Next, the reaction with test substrates was done in the presence of Pd(0)-EDA/SC-2 without using base. But unfortunately, in the absence of base, the yield of the product obtained was only 25% (Table 3, entry 15). So, we made a choice to add the base (K<sub>2</sub>CO<sub>3</sub>), and further optimization was done to select the minimum amount of base required for the complete conversion of reactants to products. The results are presented in Table 3, which indicated that 0.5 mmole of K<sub>2</sub>CO<sub>3</sub> showed the best performance, furnishing the desired product in quantitative yield (Table 3, entry 17). Compared with literature protocols [20], our catalyst Pd(0)-EDA/SC-2 successfully offers the thioetherification reaction to get completed in less basic conditions which validates our catalyst as base functionalised catalyst system. Using the optimized conditions and to evaluate the scope of the developed method, the present reaction was further extended to a broader range of substituted aryl halides (**Table 6**) and found that the reaction works well for both electron-donating and electron-withdrawing groups. In order to select the optimum amount of catalyst, reaction in case of test substrates was carried out with varying amounts of catalyst and found that 0.2 g of Pd(0)-EDA/SC-2 gave the best results in terms of reaction time and yield. In general, the reaction is clean, high yielding and leads to the synthesis of structurally diverse thioethers in a more practical and convenient way.

Entry	Aryl halide	Product	Time (h)	$\mathbf{Yield}(\mathbf{\%})^{\mathrm{b}}$	
1.	Br	S S	7.5	86	
2.	NC Br	NC S	6.0	88	
3.	H3COC	H <sub>3</sub> COC	7.0	87	
4.	H <sub>3</sub> COC Br	H <sub>3</sub> COC	7.0	88	
5.	OHC Br	OHC	6.0	88	
6.	онс — Сі	OHC S	7.0	86	
7.	HO	HO S S	8.5	81°	
8.	H <sub>2</sub> N-Br	H <sub>N</sub> N S	8.0	80°	
9.	Br	S C C	6.0	85	

 Table 6. Pd(0)-EDA/SC-2 catalyzed thioetherification of different aryl halides using thiourea under aqueous medium at 100 °C<sup>a</sup>.



<sup>a</sup>Reaction conditions: aryl halide (1 mmol), benzyl bromide (1.1 mmol), thiourea (1.2 mmol),  $K_2CO_3$ , (0.50 mmol), Pd(0)-EDA/SC-2 (0.2 g, 2.5 mol% Pd) and water (5 mL) at 100 °C. <sup>b</sup>Isolated yields.

<sup>c</sup>Column chromatographic yields.

In order to demonstrate the role of Pd(0)-EDA/SC-2 as the base functionalised heterogeneous catalyst, we performed the control experiments for the comparison of activity with other catalysts. The experiments were done in case of **Table 4**, entry 2; **Table 5**, entry 1 (1a) and **Table 6**, entry 5 and the results are summarised in **Table 7**. At first, the reactions were performed without catalyst (**Table 7**, entry 1) and found that no reaction was observed in each case. The reaction was also performed with  $PdCl_2$  (**Table 7**, entry 2) under homogeneous catalysis using 0.25 eq. of  $K_2CO_3$ . The reactions occurred but with less efficiency as compared to our base functionalized catalyst. Next, we employed various nano Pd(0) based heterogeneous catalysts. Again, the catalysts were less effective than our catalyst (**Table 7**, entries 3-5). These results clearly indicates that the base functionalization of Pd(0)-EDA/SC-2 played a significant role in catalysing the C-C and C-S coupling reactions with excellent yields.

Entry	Reactions	Suzi	Suzuki <sup>a</sup> Bis(heterocyclyl)methanes <sup>b</sup> Thioetherif		erification <sup>c</sup>		
	Catalyst	Time (min)	Yield (%) <sup>d</sup>	Time (h)	Yield (%) <sup>d</sup>	Time(h)	Yield(%) <sup>d</sup>
1.	No catalyst	15	NR <sup>e</sup>	1.5	traces	6	NR <sup>e</sup>
2.	PdCl <sub>2</sub>	15	60	1.5	85	6	35
3.	Cellulose Pd(0)	15	35	1.5	70	6	20
4.	Silica-Starch Pd(0)	15	36	1.5	78	6	20
5.	Silica-cellulose Pd(0)	15	40	1.5	80	6	25
6.	Pd(0)-EDA/SC-2	15	<b>92</b> <sup>f</sup>	1.5	<b>90</b> <sup>f</sup>	6	<b>88</b> <sup>f</sup>

**Table 7.** Control experiments for the comparison of activity of Pd(0)-EDA/SC-2 with other catalysts for the C-C and C-S coupling reactions

<sup>a</sup>Reaction conditions: 4-bromoacetophenone (1 mmol), benzeneboronic acid (1.2 mmol), K<sub>2</sub>CO<sub>3</sub> (0.25 mmol), TBAB (0.25 mmol), catalyst (2.5 mol% Pd) and water (5 mL) at 100 °C under microwave irradiation.

<sup>b</sup>Reaction conditions: Benzaldehyde (1 mmol), 3-methyl-1-phenyl-1H-pyrazol-5(4H)-one (2 mmol), catalyst (2.5 mol% Pd) and water (5 mL) at 100 °C.

<sup>c</sup>Reaction conditions: 4-bromobenzaldehyde (1 mmol), benzyl bromide (1.1 mmol), thiourea (1.2 mmol),  $K_2CO_3$  (0.5 mmol), catalyst (2.5 mol% Pd) and water (5 mL) at 100 <sup>o</sup>C

<sup>d</sup>Column chromatography yield.

<sup>e</sup>NR: No reaction.

<sup>f</sup>Isolated yield.

#### 3.4 Recyclabilty and heterogeneity

Recyclability of Pd(0)-EDA/SC-2 was investigated in case of **Table 4**, entry 2; **Table 5**, entry 1 (1a) and **Table 6**, entry 5. The catalyst was separated by filtration after completion of the reaction and again used for subsequent reactions after adding fresh substrates under similar conditions for five consecutive runs. The results are summarised in **Table 8**. It was found that catalyst could be recycled upto five consecutive runs without loss of significant activity. The thermogravimetric analysis and FTIR of the Pd(0)-EDA/SC-2 after 5th run indicated negligible change in the structure of catalyst. The slight loss of activity may be due to the microscopic changes on the surface of the catalyst. Moreover, the AAS analysis of the used Pd(0)-EDA/SC-2 after 5<sup>th</sup> run showed 6.58 wt%.

of Pd content, which indicated that a very small amount of the Pd metal was removed from the EDA/SC (fresh catalyst contains 6.67 wt% Pd). Recyclability in case of **Table 6**, **entry 5** also reveals that the catalyst successfully withstood the deactivation or poisoning in the presence of sulphur. Moreover, there is enough data in the literature to support, where palladium catalysts are able to withstand catalyst deactivation and form aryl-sulfur bonds in high-yielding transformations [26].

In order to rule out the possibility of leaching of Pd(0) NPs from the surface of the catalyst, we carried out the hot filtration test. The reaction in case of entry 2 (**Table 4**) has been carried out in the presence of Pd(0)-EDA/SC-2, until the conversion was 45% (7 min) and at that point, Pd(0)-EDA/SC-2 was filtered off at the reaction temperature. The liquid phase was then transfered to another flask and allowed to react, but no further significant conversion was observed. So, we conclude that there is no significant leaching of Pd(0) NPs from the surface of the substate, thus pointing to a catalysis of heterogeneous nature.

Catalytic	Suzuki	Bis(heterocyclyl)methanes	Thioetherification
runs	Yield (%) <sup>b</sup>	Yield (%) <sup>b</sup>	Yield(%) <sup>b</sup>
1.	92	90	88
2.	92	90	87
3.	91	90	87
4.	90	89	86
5.	90	88	85

Table 8. Recyclability of Pd(0)-EDA/SC-2 for the C-C and C-S coupling reactions<sup>a</sup>

<sup>a</sup>Reaction conditions [Suzuki coupling]: 4-bromoacetophenone (1 mmol), benzeneboronic acid (1.2 mmol),  $K_2CO_3$  (0.25 mmol), TBAB (0.25 mmol), Pd(0)-EDA/SC-2 (0.2 g, 2.5 mol% Pd) and water (5 mL) at 100 °C for 15 minutes under microwave irradiation; [bis(heterocyclyl)methanes]: benzaldehyde (1 mmol), 3-methyl-1-

phenyl-1H-pyrazol-5(4*H*)-one (2 mmol), Pd(0)-EDA/SC-2 (0.2 g, 2.5 mol% Pd) and water (5 mL) at 100 °C for 1.5 hours; [thioetherification]: 4-bromobenzaldehyde (1 mmol), benzyl bromide (1.1 mmol), thiourea (1.2 mmol),  $K_2CO_3$  (0.5 mmol), Pd(0)-EDA/SC-2 (0.2 g, 2.5 mol% Pd) and water (5 mL) at 100 °C for 6 hours. <sup>b</sup>Isolated yields.

### 4. Conclusion

In conclusion, we have developed novel catalyst systems based on the immobilization of Pd(0) NPs onto ethylene diamine functionalized silica-cellulose substrates for carrying out C-C and C-S coupling reactions in water. Compared with literature protocols, our catalyst system successfully offers the reactions to occur under base-free or less basic conditions and that too with excellent yields. Moreover, the developed catalyst system is highly active and recyclable upto five consecutive runs. Further use of this catalyst system for other palladium catalysed reactions is being carried out in our laboratory.

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