

Palladium-Alumoxane Framework as a Novel and Reusable Nanocatalyst for Suzuki–Miyaura, Stille and Heck Cross Coupling Reactions

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Abstract Herein for the first time, a Schiff base alumoxane-supported palladium (SBA-Pd°) were successfully synthesized and reported as a new mesoporous nanocatalyst for C–C cross coupling reactions. The SBA-Pd° nanocatalyst could be dispersed in poly(ethylene glycol) and showed excellent catalytic activity for Suzuki–Miyaura, Stille and Heck coupling reactions. In addition, the nanocatalyst could be recovered and reused several times without significant loss of its catalytic activity. Pd leaching from SBA-Pd° is very negligible for this coupling reaction.

Graphical Abstract



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1 Introduction

Palladium (Pd) is the most convenient and widely used metal as an effective catalyst for $C(sp^2)-C(sp^2)$ coupling reactions. In the meantime, the Pd-catalyzed Suzuki-Miyaura coupling reaction is an excellent method for the synthesis of biaryl compounds, which have found important role in the synthesis of agrochemicals, pharmaceuticals, and natural products [1-7]. Traditionally, copious Pd complexes have been utilized as homogeneous catalysts in the presence of various ligands for coupling reaction [8-11]. Despite of higher activity of homogeneous catalysts, utilizing them has been accompanied by some challenges such as: difficult separation from reaction mixture, weak reusability and contamination of products [12]. Providing heterogeneous catalyst through immobilization of Pd species on solid supports facilitates minimizing contamination, separation and reusability of expensive catalysts. In this regard, various solid supports have been used for heterogenization of catalysts such as polymers, zeolites, silica, carbon nanotubes and metal-organic frameworks (MOFs) [13-20].

Pd leaching from the supports causes to the lower reactivity for some heterogeneous catalyst than homogeneous ones. Therefore, the nature of supports is an important factor in Pd heterogeneous catalysis and there is a need to utilize novel supports to obtain more effective catalysts [21]. Carboxylate–alumoxane is a versatile compound which has been introduced as a novel support for heterogonous catalysts. Carboxylate alumoxanes with general formula $[Al(O)_x (OH)_y(O_2CR)_z]_n$, 2x + y + z = 3 are prepared through the reaction of boehmite (γ -AlOOH) and carboxylic acids. The surface of the alumoxanes is covered with covalently bound carboxylate groups. The physical and chemical properties of the alumoxane can be affected by the type of carboxylic acid, and range from water soluble powders to hard solids that are resistant to acids, bases and organic solvents [22-24]. As a precursor for alumoxane synthesis, Boehmite is a metastable phase of aluminium oxide with oxide-hydroxide bonds which commonly used as supporting matrix [25, 26]. The advantages of alumoxane as a catalyst support are included the low price of boehmite and the availability of an almost infinite range of carboxylic acids [27]. Zirconocene complex supported by para-hydroxybenzoate-alumoxane (PHBA) were reported as novel catalyst for olefin polymerization [28]. In another study, Pd was immobilized on the boehmite through tannic acid and used as a highly active catalyst for hydrogenation of olefins [26].

In recent decades, the Suzuki–Miyaura, Stille and Heck reactions have been introduced as effective C–C coupling methodologies [29–32]. Nevertheless, there is no significant works about application of alumoxanes in the catalysis field especially for coupling reactions. Currently there is no report about using the alumoxane supports for Suzuki–Miyaura, Stille and Heck coupling reactions. In this work for the first time we report the successful synthesis of paladium–alumoxane through covalent bonding of Pd-Schiff base carboxylic acid on boehmite nanoparticles and using them as a new nanocatalyst for the coupling reaction (Fig. 1).

2 Experimental

2.1 Reagents and Materials

Palladium(II) acetate, $Al(NO_3)_3 \cdot 9H_2O$ and other chemicals were all analytic reagents and purchased from Merck, Sigma-Aldrich, Fluka and Fisher chemical Companies.

2.2 Instrumentation

The X-ray powder diffraction (XRD) of the nano materials were carried out on a Philips PW 3040 X-ray diffractometer with Cu K α source ($\lambda = 1.5406$ Å) in a range of Bragg's angle (10°–100°) at 25°C. Scanning electron microscope (SEM) images were taken using FE-SEM MIRA3 TESCAN microscope (acceleration voltage 30 kV) that equipped with an energy dispersive X-ray detector (EDS) for the chemical composition analysis. Transmission electron microscopy (TEM) images were taken by a JEOL-2100 microscope. Fourier-transform infrared (FTIR) spectra were recorded with KBr pellets at room temperature (Bruker alpha, German). The NMR spectra were recorded on a Bruker AVANCE DPX-400 (400 MHz for ¹H). Chemical shifts are given in ppm (δ) relative to internal TMS and coupling constants Jare reported in Hz. TG-DTA analysis was carried out using a STA PT-1000 instrument in N₂ atmosphere at a heating rate of 10° C min⁻¹. Nitrogen sorption measurement was measured on a Belsorp mini II apparatus at 77 K. Prior to the measurements, all the samples were degassed at 373 K in a vacuum line for 5 h. The content of Pd was estimated using an inductively coupled plasma atomic emission spectrometer (ICP-OES simultaneous, Varian VISTA-PRO Model). The ultrasonication of solutions has been done by ultrasonic bath (240 W-35 kHz, SONREX, DT52 H model made by the Bandelin, Germany).

2.3 Catalyst Preparation

2.3.1 Preparation of Boehmite Nano Particles (Bo)

Boehmite nanoparticles (Bo) were synthesized via previously reported procedure [25]. In brief, NaOH solution (6.5 g in 50 mL distilled water) was slowly added to a solution of hexahydrated Aluminium nitrate (20 g in 30 mL distilled water) by vigorous stirring. Then obtained precipitate was subjected to mixing in the ultrasonic bath for 3 h at the



Fig. 1 Stepwise synthesis of palladium-alumoxane (SBA-Pd°) from boehmite schematically

room temperature, filtered and washed with distilled water. The precipitate was kept in the oven at 220 °C for 4 h.

2.3.2 Preparation of Schiff-Base (SB)

Schiff base (SB) was synthesized according to literature [33]. Briefly, salicylaldehyde (12.2 g, 0.1 mol) was slowly added to a stirred solution of para-aminobenzoic acid (13.7 g, 0.1 mol in 100 mL ethanol) and the mixture was stirred for 30 min at room temperature. The precipitated yellow Schiff-base was filtered and recrystallized with methanol to obtain SB.

2.3.3 Preparation of Schiff-Base Alumoxane (SBA)

The amount of 2 g Boehmite (Bo) powder added to a stirred solution of Schiff-base SB (0.266 g, 0.001 mol in 50 mL Dimethylformamide) and the resulting mixture was refluxed for 17 h. Then the yellow precipitation of resulting Schiff-Base alumoxane (SBA) was filtered off and washed thoroughly by ethanol and methanol, and dried at 70 °C.

2.3.4 Preparation of Pd°-Schiff-Base Alumoxane (SBA-Pd°)

At 100 mL round-bottom flask, 0.5 g of SBA powder and 0.023 g (0.0001 mol) palladium(II) acetate were dispersed into 40 mL methanol and closed its lid. The mixture was stirred for 24 h at ambient temperature. Then the orange precipitate was filtered off and washed several time with methanol to obtain SBA-Pd²⁺ complex. In continuous, 0.3 g dry SBA-Pd²⁺ complex was dispersed in 30 mL methanol at a 100 mL round-bottom flask and then 1 mL of hydrazine hydrate was added slowly over 5 min under constant stirring. The reduction of Pd²⁺ to Pd^o started immediately, and the color changed from orange to black (Fig. 1). The resulting black SBA-Pd^o was collected and washed with distilled water for several times and then dried in oven at 70 °C.

2.4 General Procedure for Suzuki–Miyaura Reaction

A test tube equipped with a magnetic stirrer bar was charged with aryl halides (1 mmol), sodium tetraphenylborate (171 mg, 0.5 mmol), Na_2CO_3 (318 mg, 3 mmol), SBA-Pd° catalyst (10 mg) and 2 mL solvent (PEG). The reaction mixture was heated for the required time at 80 °C until reaction completed (the progress of reaction was monitored by TLC). Then the mixture was cooled to room temperature. The catalyst was separated by filtration, washed by acetone and dried in oven.

The organic layer was extracted with Et_2O (3 mL, four times) from PEG filtrate in a separating funnel by aid of

adding water. Finally the solvent was evaporated to give the corresponding biaryl product.

The ¹H NMR spectra were used for characterization of biaryl products. Some selected ¹H NMR data for entries 4 and 8 (Table 3) are in good agreement with those previously reported.

2.4.1 4-Methoxy-1,1'-Biphenyl

¹H NMR (400 MHz, CDCl₃): $\delta_{\rm H}$ (ppm)=7.61–7.57 (m, 4H), 7.48–7.44 (t, 2H, *J*=7.6 Hz), 7.35–7.31 (tt, 1H,



Fig. 2 FT-IR spectra of a Bo, b SB, c SBA, d SBA-Pd^{2+} and e SBA-Pd^{\circ}

J = 1.2, 7.6 Hz), 7.05–7.02 (dt, 2H, J = 8.8, 2.4 Hz), 3.90 (s, 3H).

2.4.2 4-Chloro-1,1'-Biphenyl

¹H NMR (400 MHz, $CDCl_3$): δ_H (ppm)=7.61–7.59 (m, 2H), 7.58–7.55 (m, 2H), 7.52–7.44 (m, 4H), 7.43–7.39 (tt, 1H, J=6, 1.6 Hz).

2.5 General Procedure for Stille Reaction

A test tube equipped with a magnetic stirrer bar was charged with aryl halides (1 mmol), triphenyltin chloride (192.7 mg, 0.5 mmol), Na_2CO_3 (318 mg, 3 mmol), SBA-Pd° catalyst (10 mg) and 2 mL solvent (PEG). The reaction mixture was heated for the required time at 80 °C. Progress of reaction was monitored by TLC. Then

the mixture was cooled to room temperature. The catalyst was separated by filtration, washed by acetone and dried in oven. The organic layer was extracted with Et_2O (3 mL, four times) from PEG filtrate in a separating funnel by aid of adding water. Finally the solvent was evaporated to give the corresponding biaryl product.

The ¹H NMR spectra were used for characterization of biaryl products. Some selected ¹H NMR data for entries 1 and 6 (Table 5) are in good agreement with those previously reported.

2.5.1 1,1'-Biphenyl

¹H NMR (400 MHz, CDCl₃): $\delta_{\rm H}$ (ppm) = 7.63–7.65 (m, 4H), 7.41–7.51 (m, 4H), 7.37–7.41 (tt, 2H, J = 7.6, 1.2 Hz).



Fig. 3 N₂ adsorption–desorption isotherms and the corresponding pore size distributions for boehmite nanoparticles (\mathbf{a} , \mathbf{b}), SBA-Pd° (\mathbf{c} , \mathbf{d})

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Table 1 Surface properties of SBA-Pd° and boehmite precursor	Sample	Specific surface area $(m^2 g^{-1})$		Specific pore volume (cm ³ g ⁻¹)		Pore diameter (nm)	
precuisor		SBET	SBJH	Vtot (BET)	V (BJH)	Dav	D (BJH)
	Boehmite	2.28	2.48	0.0125	0.0125	22	1.21
	SBA-Pdo	315.26	269.24	0.345	0.310	4.37	1.21

2.5.2 4-Nitro-1,1'-Biphenyl

¹H NMR (400 MHz, CDCl₃): $\delta_{\rm H}$ (ppm)=8.32–8.35 (dt, 2H, J=8.8, 2.4 Hz), 7.76–7.79 (dt, 2H, J=8.8, 2.4 Hz), 7.65–7.68 (m, 2H), 7.51–7.56 (m, 2H), 7.46–7.50 (tt, 1 H, J=7.6, 2.4 Hz).

2.6 General Procedure for Heck Reaction

A test tube including aryl halide (1 mmol), butyl acrylate (153.8 mmol, 1.2 mmol), Na_2CO_3 (318 mg, 3 mmol), SBA-Pd° (10 mg) and PEG (2 mL) was stirred in 100 °C and the completion of the reaction was monitored by TLC. After completion, the mixture was cooled to room temperature and the catalyst was separated by filtration, washed by acetone and dried in oven. The organic layer was extracted with Et₂O (3 mL, four times) from PEG filtrate



Fig. 4 XRD spectra of a Bo, b SBA and c SBA-Pd°

in a separating funnel by aid of adding water. Finally the solvent was evaporated to give the corresponding product.

The ¹H NMR spectra were used for characterization of products. Some selected ¹H NMR data for entries 4 and 5 (Table 7) are in good agreement with those previously reported.

2.6.1 (E)-Butyl 3-(4-Methoxyphenyl)Acrylate

¹H NMR (400 MHz, $CDCl_3$): δ_H (ppm) = 0.97 (t, J = 7.2 Hz, 3H), 1.43 (sex, J = 6.8 Hz, 2H), 1.67 (quint, J = 6.8 Hz, 2H), 3.89 (s, 3H), 4.24 (t, J = 6.4 Hz, 2H), 6.33 (d, J = 16 Hz, 1H), 6.92 (d, J = 8.8 Hz, 2H), 7.49 (d, J = 8.8 Hz, 2H), 7.64 (d, J = 15.6 Hz, 1H).

2.6.2 Butyl Cinnamate

¹H NMR (400 MHz, $CDCl_3$): δ_H (ppm) = 1.05 (t, J = 7.8 Hz, 3H), 1.46 (six, J = 2 Hz, 2H), 1.74 (quint, J = 3.2 Hz, 2H), 4.25 (t, J = 6.4 Hz, 2H), 6.49 (d, J = 16 Hz, 1H), 7.40 (m, 3H), 7.43 (m, 2H), 7.73 (d, J = 16 Hz, 1H).

3 Results and Discussion

3.1 Catalyst Characterization

3.1.1 FT-IR Analysis

Fourier transform infrared spectroscopy (FT-IR) is an adequate technique for the determination of the molecular structure of organic–inorganic materials. Therefore, FT-IR spectra were recorded for Bo, SB, SBA, SBA-Pd²⁺ and SBA-Pd° (Fig. 2). In the spectrum of Bo (Fig. 2a), two strong peaks at 3092 and 3316 cm⁻¹ are related to the stretching vibration of Al–OH. Also the tow frequencies 1071 and 1166 cm⁻¹ are allocated to the symmetrical bending vibrations of hydrogen bands between Al–OH groups at the surface of boehmite. The three bands of 741, 615 and 482 cm⁻¹ also refer to the Al–O–Al vibration modes [25]. The frequency peaks of 1385 and 1637 cm⁻¹ are related to the stretching vibration of the nitrate impurity and absorbed water in the crystal structure consecutively.

In the spectrum of SB (Fig. 2b), the strong peak at 1703 cm^{-1} was related to stretching vibrations of C=O

Fig. 5 SEM images of **a** Bo, **b** SBA and **c** SBA-Pd°



groups and the broad peak at range of $2480-3000 \text{ cm}^{-1}$ was referred to stretching vibrations of acidic OH. These peaks of carboxylic groups were eliminated when reacted with boehmite through carboxylate formation (Fig. 2b).

In the spectrum of SBA (Fig. 2c), the emersion of several peaks in $1200-1800 \text{ cm}^{-1}$ region is assigned of carboxylate-alumoxane formation through the covalent

bonding between boehmite (Bo) and Schiff base (SB). Two peaks emerged in 1492 and 1560 cm⁻¹ are referred to symmetrical and asymmetrical stretching vibrations of bidentate carboxylate bonding respectively. Also the peak of 1626 cm⁻¹ is related to vibrations of unidentate carboxylate bonding [22, 34]. Schiff bases displays the imine (C=N) vibrations in the band of 1663 cm⁻¹

Fig. 6 Negative SEM images of **a** SBA, **b** SBA-Pd° in various magnifications



which vanished in Fig. 2b because of overlapping. Also stretching vibrations of the phenolic C–O is observed at 1282 cm⁻¹. Finally the peaks of 1600 and 1417 cm⁻¹ are refer to the vibrations of sp² C=C in the aromatic rings for SBA [35]. In the spectra of SBA-Pd²⁺ and SBA-Pd^o (Fig. 2d, e), it can be seen to decrease in intensity of ligand peaks that is related to chelation of Pd²⁺ at the surface of SBA. It seems that chelation caused to the high rigidity and decreasing in bond vibrations. Also a shift to lower wave number has been observed for C=N (1663 cm⁻¹) upon chelation. This shows that it may be considered as a center of chelation to Pd [35].

The presence of boehmite index peaks in the other spectra may be considered as existence of free Al– OH groups that cannot be reacted with Schiff base SB because of some spherical hindrances.

3.1.2 Specific Surface Area

The nitrogen adsorption–desorption isotherms and pore size distribution of boehmite (Bo) precursor and SBA-Pd° are illustrated in Fig. 3. It can be seen from Fig. 3a, c, these nano materials indicate a typical type IV isotherm (defined by IUPAC), which are identified as mesoporous materials. Pore size distributions (Fig. 3b, d) are indicated the micro and meso porosity in both of them which there is decreasing in pore size for SBA-Pd° versus Bo precursor.

All data obtained by Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) method are presented in Table 1. The Bo precursor with average pore diameter 22 nm contained a specific surface area (S_{BET}) of 2.28 m² g⁻¹ and a specific pore volume of 0.0125 cm³ g⁻¹. Despite being nanoparticles, Bo has shown the very low specific surface area which can be result of the sever agglomeration between their particles. In contrast, SBA-Pd° with average pore diameter 4.37 nm has shown the



Fig. 7 SEM-EDS data of a Bo, b SBA, c SBA-Pd° and d schematic of Pd° nano particles immobilized on SBA nano flakes

specific surface area (S_{BET}) of 315.26 m² g⁻¹ and a specific pore volume of 0.345 cm³ g⁻¹. These could be sign of decrease in agglomeration through alumoxane formation as a framework for Pd nanoparticles. In fact attachment of schiff base at the surface of Bo nanoparticles caused to disintegrate agglomerates and formation of nano flake frameworks with the high surface area. The D_{av} for SBA-Pd° indicated meso porosity while D_{BJH} values showed the micro porosity for them.

3.1.3 X-Ray Diffraction

X-ray diffraction (XRD) is a useful and versatile technique for the phase analysis and determination of the crystal structure of materials. Hence, X-ray diffraction patterns were recorded for Bo, SBA and SBA-Pd° (Fig. 4). XRD pattern of Bo (Fig. 4a) shows broad peaks at $2\Theta = 14^{\circ}$, 28.1°, 38.5°, 45.7°, 49.2°, 51.2°, 55.2°, 61°, 64.3°, 67°, 68.3°, 72° and 81°corresponding to diffraction lines (020), (120), (031), (131), (051), (220), (151), (080), (231), (002), (171), (251) and (271), respectively which can be identified obviously as orthorhombic boehmite γ -AlOOH (JCPDS card 21-1307). The broad and less intense diffraction peaks of Bo reveals that Bo had lower crystallinity.

XRD pattern of SBA (Fig. 4b) exhibited the same diffraction lines of Bo with sharper and more intense peaks. It may be considered as inadequate functionalization of boehmite with Schiff-base molecules due to some spherical hindrances. On the other hand, augmentation in sharpness and intensity of SBA peaks indicates its higher crystallinity versus Bo.

Also diffraction pattern of SBA-Pd° (Fig. 4c) exhibited the same diffraction lines of SBA with the same peaks sharpness. With further observation, it can be seen some small differences in SBA-Pd° versus SBA. These differences in XRD patterns are referred to the small Pd° nanoparticles with good dispersion were formed in the SBA-Pd°, which is confirmed by following SEM images. The diffraction lines related to Pd° species clearly cannot be Fig. 8 TEM images of Bo (a)

and SBA-Pd° catalyst (b)



observed in the SBA-Pd $^{\circ}$ pattern because of weak intensity of the Pd $^{\circ}$ peaks and overlapping with SBA lines.

Pd species in the SBA-Pd° spectrum exhibited peaks at $2\Theta = 40.2^{\circ}$, 46.42° , 68.04° , 82.05° and 87.3° corresponding to diffraction lines (111), (200), (220), (311) and (222), respectively. However the presence of Pd° can be detected only in the lines of (111) and (200).

3.1.4 SEM and TEM Investigation

The morphological and structural characterizations of Bo, SBA and SBA-Pd° were studied by SEM (Fig. 5). It can be observed that Bo sample (Fig. 5a) was mainly composed of nanoparticles. These Bo nanoparticles were agglomerated due to presence of OH groups at their surfaces and tendency to hydrogen bonding among them.

Comparison between the SEM images of Bo (Fig. 5a) and SBA (Fig. 5b) reveals that the morphological features are changed significantly by SBA formation from Bo. It can be seen that SBA sample was composed of nano flakes with irregular shapes, about 20–30 nm thickness and 50–100 nm across. It seems that rearrangement of boehmite (Bo) crystallites with Schiff-base (SB) interactions caused to formation of 2-D morphology of nano flakes. Figure 5c shows the SEM images of SBA-Pd° nanocatalyst which approves well dispersion of the Pd° nanoparticles at the surface of SBA-Pd° nano flakes.

The Fig. 6 obviously shows the negative SEM images of SBA and SBA-Pd° in various magnifications. The presence of spherical Pd° nanoparticles (approximate particle size about 5 nm) are approved by comparing between Fig. 6a, b. As shown in Fig. 6b, the spherical





Pd° nanoparticles are formed in the surface of SBA nano flakes.

SEM-EDS analysis for Bo investigates the presence of the expected elements in the structure of Boehmite, namely C, O, Al (Fig. 7a). Furthermore, SEM-EDS data for SBA also reveals the presence of N element which refers to the Schiff-base molecules (Fig. 7b). SEM-EDS analysis for SBA-Pd° also indicates the presence of Pd° nanoparticle on the surface of SBA supports with the weight present about 5.38 w% (Fig. 7c). The immobilization of spherical Pd° nanoparticles on the surface of SBA support has been shown schematically in Fig. 7d.

Figure 8 shows the TEM images of boehmite nanoparticles (a) and SBA-Pd° (b). It can be seen that boehmite nanoparticles with average particle size 10-30 nm have shown an orthorhombic structure. Also Fig. 8b confirmed the distribution of Pd° nanoparticles at the surface of SBA-Pd° which is quite consistent with the SEM images. It can be seen the spherical Pd nanoparticles at the surface of nano flakes formed a mesoporous structure.

3.1.5 Thermal Analysis (TG-DTA)

The thermal behavior of the SBA-Pd° nanocatalyst was studied by thermo gravimetric-differential thermal analysis (TG-DTA). The TG curve in Fig. 9a presents a minor weight loss (mass change: 0.78%, 0.097 mg) at 190 °C initially, which was followed by a weight increase immediately. The DTA curve shows an endothermic peak at 190 °C that can be related to dehydroxylation process of free OH groups in SBA-Pd°. Generally dehydroxylation process starts about 200 °C for boehmite (γ -AlOOH) structure [25].

As can be seen from Fig. 9b, the weight loss in the first stage may be related to the dehydroxylation process and increasing in the weight can be due to the recapturing of OH by Pd.

The TG curve in Fig. 9a also presents a major weight loss (mass change: 11%, 1.364 mg) started at 406 °C. The DTA curve also shows an exothermic peak at 450 °C that can be referred to the combustion process of schiffbase groups in SBA-Pd°. According to the second weight loss, the amount of these organic groups was calculated 0.451 mmol g^{-1} . Therefore it can be concluded that SBA-Pd° nano catalyst is thermally stable up to 406 °C. The calculation based on the second stage weight loss show that the percentage of Pd° in SBA-Pd° nano catalyst is 4.85 w%.

3.1.6 Palladium Content

Amount of loaded Pd on SBA-Pd° catalyst was evaluated by inductively coupled plasma-optical emission spectrometry (ICP-OES) to be 15.7×10^{-5} mol g⁻¹ (1.67 w% Pd). We performed the hot filtration test to confirm the heterogeneous nature of the nano catalyst. The solid nano catalyst was removed by hot filtration after 47% of the reaction was completed and the liquid phase of the reaction mixture (4-bromonitrobenzene, NaPh₄B, PEG and Na₂CO₃) was kept in reaction conditions (80 °C) for another 60 min. The negligible increase in the amount of product was observed (only 1%). This result indicates

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that Pd leaching from SBA-Pd $^{\circ}$ is very negligible for coupling reaction.

3.2 SBA-Pd° Catalytic Studies

The catalytic performance of SBA-Pd° was evaluated in the carbon–carbon coupling reaction of aryl halides with sodium tetraphenylborate, triphenyltin chloride and butyl acrylate. In our primary experiments, Suzuki–Miyaura coupling reaction between 4-bromonitrobenzene and sodium tetraphenylborate in the presence of catalytic amounts of SBA-Pd° was chosen as a model reaction to optimize the effects of base, solvent, temperature and amount of nanocatalyst. The results of optimization conditions are presented in Table 2. At the beginning, Na₂CO₃ was used as base and PEG as solvent in the presence of 4–11 mg of SBA-Pd° at 80 °C.

The best results were achieved using 10 mg $(0.157 \times 10^{-5} \text{ mol g}^{-1})$ of the nanocatalyst (Table 2, entry 8). By increasing the amount of the nanocatalyst, no

Table 2Optimization ofSuzuki–Miyaura couplingreaction over the SBA-Pd° nanocatalyst

NO ₂	+	Na ⁺ B-	SBA-Pd° nai Base, Solve	no catalyst ent, Temp.	\frown	}—NO₂
Entry	Solvent	Base	Catalyst (mg)	Temp (°C)	Time (h)	Yield (%) ^a
1	PEG	Na ₂ CO ₃	_	80	2	_
2	PEG	Na ₂ CO ₃	4	80	3	_
3	PEG	Na ₂ CO ₃	5	80	3	17
4	PEG	Na ₂ CO ₃	6	80	3	42
5	PEG	Na ₂ CO ₃	7	80	3	64
6	PEG	Na ₂ CO ₃	8	80	2	75
7	PEG	Na ₂ CO ₃	9	80	2	81
8	PEG	Na ₂ CO ₃	10	80	2	95
9	PEG	Na ₂ CO ₃	11	80	2	96
10	PEG	NaHCO ₃	10	80	2	78
11	PEG	NaOAc	10	80	2	38
12	PEG	KH_2PO_4	10	80	2	31
13	PEG	NaOH	10	80	2	-
14	PEG	K ₂ CO ₃	10	80	2	_
15	H ₂ O	Na ₂ CO ₃	10	80	2	83
16	DMF	Na ₂ CO ₃	10	80	2	8
17	DMSO	Na ₂ CO ₃	10	80	2	_

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Reaction conditions: 4-bromonitrobenzene (202 mg, 1 mmol), NaPh4B (171 mg, 0.5 mmol), PEG (2 mL), and 3 mmol base

25

45

60

95

4

4

2

1

^aIsolated yield

PEG

PEG

PEG

PEG

Na₂CO₃

Na₂CO₃

Na₂CO₃

Na₂CO₃

10

10

10

10

18

19

20

21

_

30

95

remarkable improvement in yield was observed (Table 2, entry 9). Afterward studies focused on the effect of other bases on the coupling reaction (Table 2, entry 10–14). The results showed that Na_2O_3 was still the more effective base among the bases to perform a high yield of the product. The optimization was continued in various solvents such as DMSO, H₂O and DMF instead of PEG to study solvent effects (Table 2, entries 15–17). Changing the solvent did not provide any improvement in the reaction yield and showed that protic solvents (PEG, H₂O) were more effective than aprotic solvents (DMF, DMSO). It may be related to the effective interactions between Al–OH groups in SBA-Pd° and protic solvent. Also PEG as a phase transfer catalyst, can enhance the solubility of NaBPh₄ and Na₂CO₃, as well as promote basicity of Na₂CO₃. Effect of various temperatures were examined in ranging from 25 to 95 °C (Table 2, entries 8, 18–21) and it was revealed that the coupling reaction proceeds efficiently at 80 °C (Table 2, entry 8). Afterward, we successfully utilized the optimized conditions (SBA-Pd° as catalyst, Na₂CO₃ as base in PEG

Table 3Suzuki–Miyauracoupling reaction with arylhalides and NaPh4B catalyzedby SBA-Pd°

R	X +	P°C R					
Entry	Aryl halide	Time (min)	Yield (%) ^a	M.p. (°C)		TON	$TOF(h^{-1})$
				Found	Reported		
1	I—	20	96	67–69	68–70 [<mark>36</mark>]	611	1834
2	H ₃ C-	60	92	43–45	44-46 [36]	586	586
3	СООН	70	90	109–110	111–113 [37]	573	491
	⟨I						
4	MeOI	75	93	86–88	88–90 [36]	592	474
5	BrBr	20	93	67–69	68–70 [36]	592	1777
6	O ₂ N————————————————————————————————————	120	95	110–112	112–114 [36]	605	302
7	NC-	140	93	83–84	85–86 [38]	592	254
8	Cl-	60	94	75–76	77–79 [36]	599	599
9	H ₃ C-	60	92	43–45	44-46 [36]	586	586
10	HO—	140	89	161–163	163–164 [38]	567	243
11	Br	8 h	63	Colorless oil	Colorless oil [39]	401	50
12	Cl	4 h	78	67–69	68–70 [36]	497	124
13		10 h	35 ^b	83–84	85–86 [38]	111	11

Reaction conditions: aryl halides (1 mmol), NaPh₄B (171 mg, 0.5 mmol), PEG (2 mL), Na₂CO₃ (318 mg, 3 mmol), SBA-Pd° catalyst (10 mg, 0.157 mol%) and 80 °C.

^aIsolated yield

^bContaining 20 mg nano catalyst and 95 °C reaction temperature



Fig. 10 Scheme of the Suzuki–Miyaura coupling mechanism by SBA-Pd $^{\circ}$

solvent) for the Suzuki–Miyaura coupling reaction of different aryl halides to obtain the corresponding biaryls (Table 3).

As expected for aryl iodides, coupling reaction gave excellent yields in the shorter times (Table 3, entries 1–4). Aryl bromides as well as aryl iodides indicates high reactivity in high yields but relatively shows higher reaction times versus aryl iodides (Table 3, entries 5–11). The reactions of aryl chlorides were carried out in more difficult conditions which relatively gave lower yields versus other aryl halides (Table 3, entries 12–13). The mechanism of the Suzuki–Miyaura coupling reaction by SBA-Pd° catalyst has been shown schematically in the Fig. 10.

In order to demonstrate the broad application of SBA-Pd° as a catalyst, the Stille reaction were studied. For optimizing the reaction and obtain the best catalytic system, the reaction of iodobenzene (1 mmol) with triphenyltin chloride (0.5 mmol) was chosen as a model reaction, and was evaluated effect of parameters such as base, solvent, temperature and amount of SBA-Pd° (Table 4).

I	+		SBA-Pd°nar Base, Solve	no catalyst ent, Temp.		
Entry	Solvent	Base	Catalyst (mg)	Temp (°C)	Time (min)	Yield (%) ^a
1	PEG	Na ₂ CO ₃	_	80	120	_
2	PEG	Na ₂ CO ₃	4	80	30	Trace
3	PEG	Na ₂ CO ₃	5	80	30	21
4	PEG	Na ₂ CO ₃	6	80	30	38
5	PEG	Na ₂ CO ₃	7	80	30	56
6	PEG	Na ₂ CO ₃	8	80	10	72
7	PEG	Na ₂ CO ₃	9	80	10	83
8	PEG	Na ₂ CO ₃	10	80	10	96
9	PEG	Na ₂ CO ₃	11	80	10	97
10	PEG	NaHCO ₃	10	80	10	75
11	PEG	NaOAc	10	80	10	45
12	PEG	KH ₂ PO ₄	10	80	10	36
13	PEG	K ₂ CO ₃	10	80	10	-
14	H ₂ O	Na ₂ CO ₃	10	80	10	80
15	DMF	Na_2CO_3	10	80	10	26
16	DMSO	Na ₂ CO ₃	10	80	10	15
17	PEG	Na ₂ CO ₃	10	25	300	68
18	PEG	Na ₂ CO ₃	10	40	75	73
19	PEG	Na ₂ CO ₃	10	60	35	84
20	PEG	Na ₂ CO ₃	10	120	3	97

Reaction conditions: Iodobenzene (204 mg, 1 mmol), triphenyltin chloride (193 mg, 0.5 mmol), PEG (2 mL), and 3 mmol base

^aIsolated yield

Table 4Optimization of Stillecoupling reaction over theSBA-Pd° nano catalyst



 Table 5
 The Stille coupling reaction with aryl halides and Ph3SnCl catalyzed by SBA-Pd°

Reaction conditions: aryl halides (1 mmol), triphenyltin chloride (193 mg, 0.5 mmol), PEG (2 mL), Na₂CO₃ (318 mg, 3 mmol), SBA-Pd° catalyst (10 mg, 0.157 mol%) and 80 °C.

^aIsolated yield

As expected, no product is obtained in the absence of SBA-Pd° (Table 4, entry 1). Initially, the effect of various solvents in model reaction revealed that PEG gives the best yields in compared with other solvents (Table 4, entries 14–16). Like the Suzuki reaction, the optimum amount of catalyst were achieved 10 mg $(0.157 \times 10^{-5} \text{ mol g}^{-1})$ of the SBA-Pd° (Table 4, entry 8). By increasing the amount of the nanocatalyst, no remarkable improvement in yield was observed (Table 4, entry 9). Also the results revealed that Na₂O₃ was still the more effective base among the bases (Table 4, entries 10–13) to perform a high yield of the product. Finally the effect of various temperatures were examined in ranging from 25 to 120 °C (Table 4, entries 8, 17–20) and it was observed that the reaction proceeds efficiently at 80 °C (Table 4, entry 8). Also it is found that unlike the Suzuki reaction, SBA-Pd° has been able to carry out the Stille reaction at the room temperature and the lower times' reaction. Therefore, the best results are obtained in PEG solvent at 80 °C in the presence of 10 mg (0.157 mol%) of SBA-Pd°



Fig. 11 Scheme of the Stille coupling mechanism by SBA-Pd°

and using Na₂CO₃ (Table 4, entry 8). After obtaining the optimum conditions, various aryl halides were utilized in Stille reaction in order to obtain the corresponding biaryls (Table 5). A variety of aryl halides (including Cl, Br and I) with electron-donor and electron-withdrawing substituents were catalyzed by SBA-Pd° to obtain the corresponding biphenyls in excellent yields and lower times.

As expected in compared to aryl chlorides, aryl iodides and aryl bromides react in shorter times. The mechanism of the Stille coupling reaction by SBA-Pd° catalyst has been shown schematically in the Fig. 11.

In addition to the Suzuki and Stille reactions, the SBA-Pd° also shows applicable performance in the Heck reaction. So we examined the SBA-Pd° catalyzed Heck reaction through the coupling of butyl acrylate with various aryl halides. Therefore, the reaction of butyl acrylate and iodobenzene was selected as a model to optimize conditions. Table 6 illustrates the catalytic activity of SBA-Pd° for Heck reaction in various conditions of base, solvent, temperature and amount of catalyst. The optimum result is observed in PEG solvent at 100 °C in the presence of 10 mg (0.157 mol%) of SBA-Pd° and using Na₂CO₃ (Table 6, entry 7).

After optimization of conditions, various aryl halides were investigated in Heck reaction in order to obtain the corresponding biaryls (Table 7). A variety of aryl halides (including Cl, Br and I) with electron-donor and electronwithdrawing substituents were catalyzed by SBA-Pd° to obtain the corresponding biphenyls in good performance. The mechanism of the Heck coupling reaction by SBA-Pd° catalyst has been shown schematically in the Fig. 12.

+	-o~~~	SBA-Pd [°] nano cata Base, Solvent, Te	mp.	~ Å	\wedge
Solvent	Base	Catalyst (mg)	Temp (°C)	Time (min)	Yield (%) ^a
PEG	Na ₂ CO ₃	_	100	180	-
PEG	Na ₂ CO ₃	5	100	50	26
PEG	Na ₂ CO ₃	6	100	40	34
PEG	Na ₂ CO ₃	7	100	30	44
PEG	Na ₂ CO ₃	8	100	20	63
PEG	Na ₂ CO ₃	9	100	20	85
PEG	Na ₂ CO ₃	10	100	20	91
PEG	Na ₂ CO ₃	11	100	20	92
PEG	NaHCO ₃	10	100	35	45
PEG	NaOAc	10	100	35	35
PEG	KH_2PO_4	10	100	35	19
H_2O	Na ₂ CO ₃	10	100	35	Trace
DMF	Na ₂ CO ₃	10	100	35	53
DMSO	Na ₂ CO ₃	10	100	35	42
PEG	Na ₂ CO ₃	10	80	120	70
	+ Solvent PEG PEG PEG PEG PEG PEG PEG PEG PEG PEG	+ O Solvent Base PEG Na2CO3 PEG Na4CO3 PEG Na4CO3 PEG Na2CO3 DMF Na2CO3 PEG Na2CO3 PEG Na2CO3	+ \bigcirc SBA-Pd'nano cata Base, Solvent Base, Solvent, Te Base, Solvent Base, Solvent, Te PEG Na2CO3 - PEG Na2CO3 5 PEG Na2CO3 6 PEG Na2CO3 7 PEG Na2CO3 7 PEG Na2CO3 9 PEG Na2CO3 10 PEG Na2CO3 10 PEG Na2CO3 10 PEG Na2CO3 10 PEG Na0Ac 10 PEG Na2CO3 10	\bullet	$+ \underbrace{ \begin{array}{c} \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$

 Table 6
 Optimization of Heck

 coupling reaction over the
 SBA-Pd° nano catalyst

Reaction conditions: Iodobenzene (204 mg, 1 mmol), butyl acrylate (153.8 mg, 1.2 mmol), PEG (2 mL), and 3 mmol base

^aIsolated yield

Table 7The Heck couplingreaction with aryl halides andbutyl acrylate catalyzed bySBA-Pd°

R	+	SBA-Pd [°] nano catalys Na ₂ CO ₃ / PEG /100 °C	R R		\sim
Entry	Aryl halide	Time (min)	Yield (%) ^a	TON	$TOF(h^{-1})$
1	I	20	91	579	1738
2	H ₃ C-	45	95	605	806
3	СООН	95	83 ^b	528	333
4	MeOI	65	96 ^b	611	564
5	Br	390	85	541	83
6	O ₂ N-Br	80	90	573	429
7	NCBr	110	89	566	309
8	H ₃ CBr	1220	84 ^b	535	26
9	HOBr	135	90 ^b	573	254
10	Br	1560	72 ^b	458	2.7
11	NC-Cl	1440	89 ^b	566	3.7

Reaction conditions: aryl halides (1 mmol), butyl acrylate (153.8 mg, 1.2 mmol), PEG (2 mL), Na_2CO_3 (318 mg, 3 mmol), SBA-Pd° catalyst (10 mg, 0.157 mol%) and 100 °C. ^aIsolated yield

^bReaction was carried out at 120 °C

3.3 Reusability of Catalyst

In order to commercial applications, the recovery and reusability of the catalyst are very important factors. Therefore, after the reaction completion, SBA-Pd° recovered by centrifugation, thoroughly washed with methanol and water and after drying in oven, it can be reused for next coupling reactions including the Suzuki–Miyaura, Stille and Heck. It was found that SBA-Pd° has been recovered and reused without remarkable loss of its reactivity at least for six runs (Fig. 13). The average isolated yield for six runs is 93, 94.3 and 88.6% in the Suzuki, Stille and Heck reaction respectively.

The amount of Pd leaching was evaluated by ICP-OES analysis of recycled nano catalyst. The result indicated negligible changes of Pd contents $(15.7 \times 10^{-5} \text{ mol g}^{-1})$, only 1% leaching was observed.

3.4 Catalyst Comparison

The activity of this nanocatalyst is presented by comparison our results on the Suzuki coupling of bromobenzene with the previously reported heterogeneous catalysts in the literature (Table 8). This comparison reveals that SBA-Pd is comparable or may be better in some terms of reaction (Pd mol%, temperature, time and yield) than the other reported catalysts. Furthermore, this nano catalyst in terms



Fig. 12 Scheme of the Heck coupling mechanism by SBA-Pd°

of price, stability and toxicity is can be better than the other catalysts. Unlike the Alumoxane frameworks, some expensive materials such as MCM-41, SBA-15, polymers or MWCNT which have been used as catalyst support, requires high temperature, a lot of time or tedious conditions to prepare.

4 Conclusion

In summary, SBA-Pd° as a new mesoporous nanocatalyst was synthesized and characterized. Analysis data confirmed the synthesized schiff-base alumoxane with nano flakes morphology formed the stable framework for Pd nanoparticles which can be thermally stable up to 406 °C. Also the Pd° percentage in nano catalyst were indicated (1.67 w%; 15.7×10^{-5} mol g⁻¹). The SBA-Pd° showed excellent catalytic activity and high reusability for the Suzuki–Miyaura,



Table 8 Comparison of SBA-Pd° nano catalyst for the C-C coupling of bromobenzene with previously reported procedure

Entry	Substrate	Reagent	Catalyst type	Pd mol%	Time (min)	Temp (°C)	Yield (%)	References
1	Ph–Br	Ph-B(OH) ₂	Fe ₃ O ₄ @SiO ₂ -NH ₂ -Pd	1	480	100	95	[40]
2	Ph–Br	Ph-B(OH) ₂	SiO ₂ -imidazole-Pd	1.62	180	95	95	[41]
3	Ph–Br	Ph-B(OH) ₂	Pd(II)-sepiolite	0.001	1440	130	65	[42]
4	Ph–Br	Ph-B(OH) ₂	Pd-Schiff base@MWCNT	0.1	180	60	98	[43]
5	Ph–Br	Ph-B(OH) ₂	Pd doped KF/Al ₂ O ₃	10	240	100	60	[44]
6	Ph–Br	Ph-B(OH) ₂	Pd@SBA-15/SH	0.05	35	80	97	[45]
7	Ph–Br	Ph-B(OH) ₂	SiO ₂ /TEG/Pd	0.75	720	110	86	[<mark>46</mark>]
8	Ph–Br	Ph-B(OH) ₂	Hydroxyapatite@ Pd	0.002	240	120	80	[47]
9	Ph–Br	Ph ₄ BNa	Polystyrene@ Pd ²⁺	1	18	120	90	[20]
10	Ph–Br	Ph ₄ BNa	Schiff base alumoxane-Pd	0.157	20	85	93	This work

Fig. 13 Reusability of SBA-Pd° in the coupling reaction of iodobenzene (1 mmol) with **a** NaBPh₄ (0.5 mmol) and **b** Ph₃SnCl (0.5 mmol) and **c** butyl acrylate (1.2 mmol) under reaction conditions Stille and Heck reactions. This nanocatalyst is effective for reaction of various aryl halides (including chlorides, bromides and iodides) with NaBPh₄, Ph₃SnCl and butyl acrylate. In addition, this nanocatalyst could be recovered and reused at least for six times without significant loss of catalytic activity. Pd leaching from SBA-Pd° is very negligible for this coupling reaction.

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