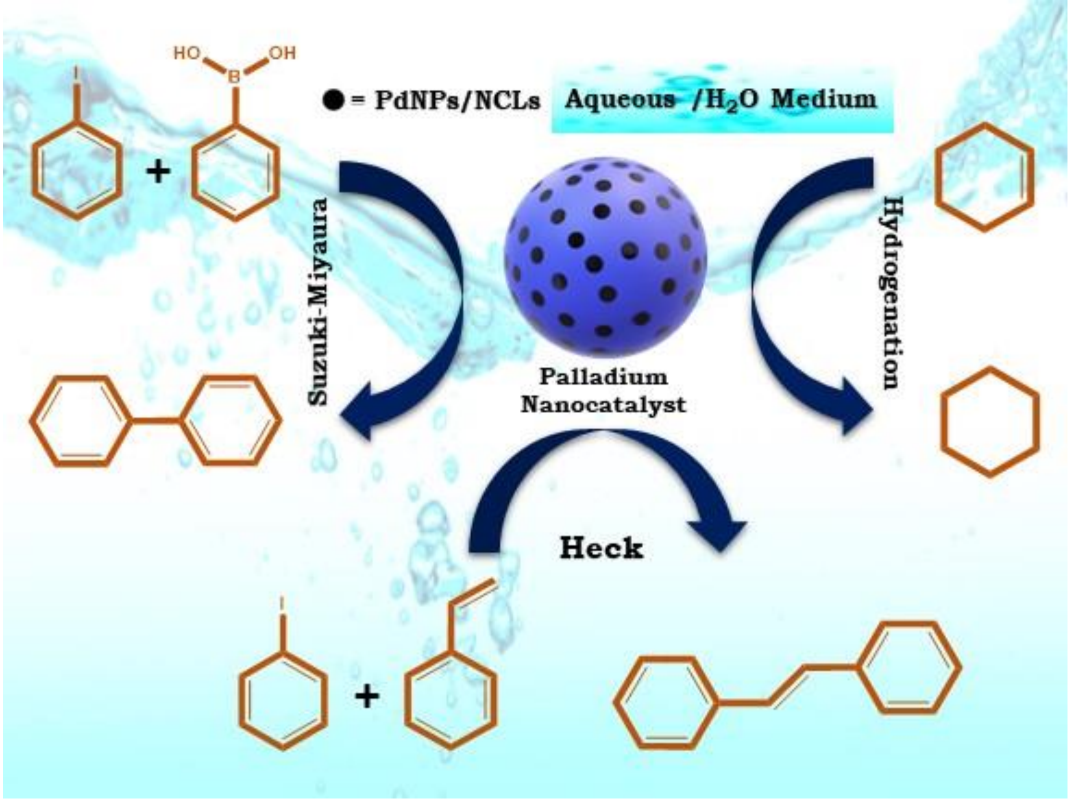
Summary of thesis entitled

Development of Stabilized Palladium Nanocatalysts Based on Heteropoly acids and Their Applications in some Organic Transformations



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By

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Introduction

Developing chemical reactions catalyzed by palladium-based materials have gained noble recognition because its unique properties make it intensively investigated, prevalent and permits real exploitation [1] dominantly over Pt, Au, Ir etc. Moreover, its ability to activate and facilitates industrially important molecules without getting incorporated in to the final product is the most considerable factor. However, especially in case of Pd nanocatalysts (PdNCs), the associated key issues are the aggregates formation during the catalyst synthesis or the reaction due to its ultra-small size and high surface energy [2, 3]. To overcome the same, different stabilizing agents such as phosphorus base ligands, dendrimers, polyvinyl pyridine, cyclodextrin, surfactants, ionic liquids and carbene complexes, and most of these are highly expensive and toxic organic ligands [3-5].

The use of such ligands can be avoided by the replacement of some other materials, able to stabilize PdNCs into either its lowest oxidation state or highest oxidation state, depending on the noble metal. In advancement to this, heteropoly acids (HPAs) are the excellent candidates for the same because they are the unique class of inorganic compounds having discrete metal–oxygen cluster composed of transition metals of group V and VI in high oxidation states and their anionic form is also known as polyoxometaltes. They are very fascinating and excellent as stabilizing agent for Pd nanoparticles/clusters (PdNPs/PdNCLs), due to their number of convergent properties such as robust oxoanionic nature, its negative charges, large relative sizes, stability, reducing and encapsulating agent [6, 7].

The direct use of HPAs stabilized PdNCs is often associated with tedious catalyst recovery as HPAs are homogeneous in polar solvent [8, 9], material deactivation and reduced efficiency in organic transformations. To overcome, a much simpler method is to support/anchor the such materials with different supports such as inorganic materials, organic polymers, metal organic frameworks (MOFs) and membranes, and for the same zirconia was selected due to its number of advantages.

As a catalytic efficiency evaluation, C-C cross coupling (Suzuki-Miyaura and Heck) as well as hydrogenation reactions were selected due to their great industrial importance. For example, C-C cross coupling are used to synthesize natural products, perfumery intermediates, active pharmaceutical ingredients, advance materials and food products [10]. Whereas, hydrogenation of aromatics and aliphatics provides the precursors for the production of edible fats from liquid oils, petroleum industry, numerous processes involved in the manufacture of gasoline and petrochemical products, pharmaceutical and food industries. On these lines, the objectives of thesis were proposed.

Objectives of the work

- To synthesize Palladium nanocatalysts (PdNCs) stabilized by Zirconia supported TPA/LTPA (12-tungstophosphoric acid/mono lacunary tungstophosphoric acid) using ion exchange method.
- To design stabilized Palladium nanocatalyts (PdNCs) based on TPA/LTPA using salt method
- To convert above synthesized homogeneous nanocatalysts into heterogeneous by supporting/anchoring onto ZrO_2/SiO_2.
- To characterize all synthesized nanocatalysts by various techniques such as EDX, FT-IR, TGA, ^{31}P MAS NMR, XPS, Powder XRD, BET Surface Area, SEM, TEM, HRTEM and STEM
- To use the synthesized catalysts for C-C coupling (Suzuki-Miyaura and Heck) and hydrogenation under mild conditions (aqueous medium and water medium)

- To study different reaction parameters such as substrate to catalyst ratio, temperature, pressure, time and solvent for maximum conversion as well as product selectivity
- To study the sustainability of the catalyst by multiple regeneration and characterization
- To study reaction mechanism
- To compare the efficiency of all the catalysts and to propose the best method of designing as well as catalyst for the said reactions

The work is divided into two parts based on synthesis

Part A: Ion Exchange Method

Chapter 1	**PdNPs Stabilized by Zirconia Supported TPA: Synthesis, Characterization and Applications to C-C coupling and Hydrogenation**
Chapter 2	**PdNPs Stabilized by Zirconia Supported LTPA: Synthesis, Characterization and Applications to C-C coupling and Hydrogenation**

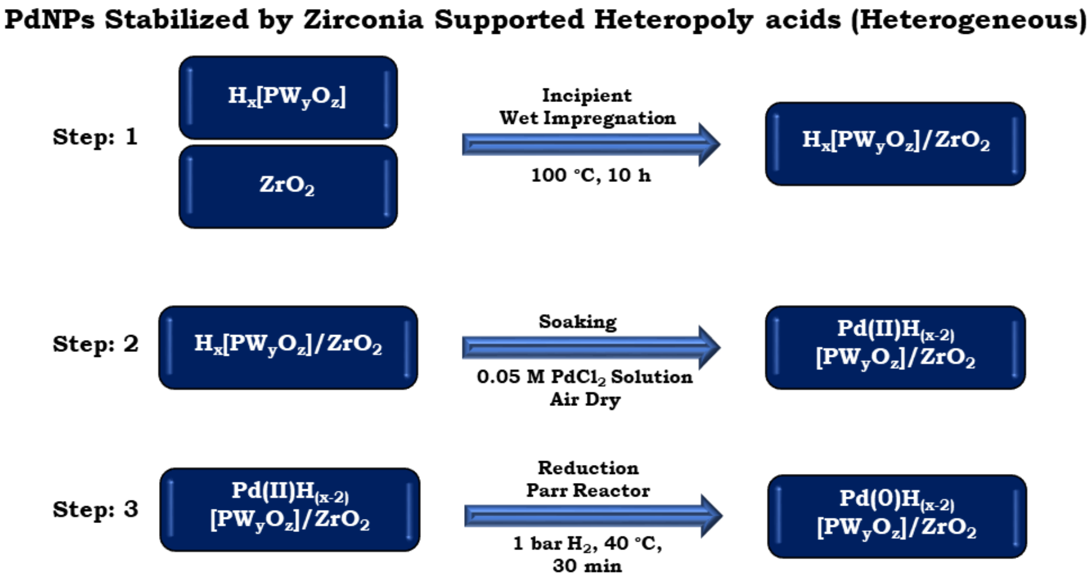
Part B: Salt Method

Chapter 1	**Stabilized PdNCLs by TPA: Synthesis, Characterization and Applications to C-C coupling and Hydrogenation**
Chapter 2	**Zirconia Supported Stabilized PdNCLs by TPA: Synthesis, Characterization and Applications to C-C coupling and Hydrogenation**
Chapter 3	**Zirconia Supported Stabilized PdNCLs by LTPA: Synthesis, Characterization and Applications to C-C coupling and Hydrogenation**
Annexure	**Silica Encapsulated Stabilized PdNCLs by TPA: Synthesis, Characterization and Applications to C-C coupling and Hydrogenation**

Part A: Ion Exchange Method

Designing of catalyst by ion exchange method

Ion exchange method is consisting of three steps for the synthesis of PdNPs stabilized by zirconia supported TPA/LTPA. *Step-I*: TPA/LTPA is supported on zirconia by incipient wet impregnation method. *Step-II*: Exchange of available counter protons by Pd using soaking method. *Step-III*: Finally, this Pd exchanged zirconia supported TPA/LTPA is converted to stabilized PdNPs by reducing in Parr reactor. Synthetic scheme by ion exchange method is given in scheme 1, where, $H_x[PW_yO_z]$ = 12-tungstophosphoric acid, TPA ($H_3PW_{12}O_{40}$) or Mono lacunary tungstophosphoric acid, LTPA ($H_7PW_{11}O_{39}$).



Scheme 1 Synthetic scheme for stabilized PdNPs via ion exchange method.

Chapter 1: PdNPs Stabilized by Zirconia Supported TPA: Synthesis, Characterization and Applications to C-C coupling and Hydrogenation

To design the catalyst, the advantage of available counter protons of zirconia supported 12-tungstophosphoric acid was exploited. Zirconia (ZrO_2) [11] and zirconia supported 12-tungstophosphoric acid (TPA/ZrO_2) were synthesized by following the same method reported by us. Palladium (II) was deposited on supported 12-tungstophosphoric acid via exchanging the available protons of TPA [12]. 1 g of TPA/ZrO_2 was soaked with 25 mL 0.05 M aqueous solution of $PdCl_2$ for 24 h with stirring. The solution was filtered, washed with distilled water in order to remove the excess of palladium and dried in air at room temperature. The resulting brown catalyst was designated as Pd(II)-TPA/ZrO_2. Then, synthesized catalyst was charged in a Parr reactor under 1 bar H_2 pressure, at 40 °C for 30 min to reduce Pd(II) to Pd(0). After that catalyst was removed from reactor and kept in air to attain the room temperature. The obtained black catalyst was designated as Pd-TPA/ZrO_2. The same procedure was followed for the synthesis of Pd/ZrO_2.

Results and Discussion

The synthesized materials were characterized by EDX, TGA, BET, FT-IR, ^{31}P MAS NMR, powder XRD, XPS, TEM, HRTEM and STEM.

The gravimetric analysis shows 0.4 wt% of Pd in Pd(II)-TPA/ZrO_2 [13]. EDX values of W (16.87 wt%) and Pd (0.47 wt%) are in good agreement with calculated one (16.91 wt% of W, 0.4 wt% of Pd). TGA curve of Pd-TPA/ZrO_2 shows the 13% weight loss up to 150 °C due to the loss of adsorbed water molecules. No weight loss is observed up to 500 °C indicating the stability of the catalyst up to 500 °C. The FT-IR spectrum of Pd-TPA/ZrO_2 shows the characteristic bands at 824, 945 and 1056 cm^{-1} corresponding to stretching vibration for W-O-W, W=O and P=O but with significant shift, may be due to the change in the environment. Here, additional band corresponding to Pd-O band is not observed, this may be due to the merging of band with Zr-O.

XPS of Pd-TPA/ZrO_2 shows very intense peak at binding energy 532 eV corresponds to the direct overlap peak between $Pd3p_{3/2}$ and O1s peaks at binding energy 532 eV, which is in good agreement with the reported one [14], and cannot be assigned to confirm the presence of Pd(0). The instrument generated full spectra, supporting the presence of Pd(0). This is further confirmed by recording the high resolution Pd3d spectrum which showed a low intense spin orbit doublet peak at binding energy 335.6 eV and 340.2 eV correspond to $Pd3d_{5/2}$ and $Pd3d_{3/2}$, confirming the presence of Pd(0) [15-17]. Two additional high intense peaks at binding energy 331 eV and 345 eV attributed to $Zr3p_{3/2}$ and $Zr3p_{1/2}$, respectively [18]. Pd-TPA/ZrO_2 also showed a single spin-orbit pair at binding energy 35.7 and 37.7 eV (spin-orbit splitting, 2.0 eV) confirming no reduction of W during the synthesis [16, 19]. SAED image indicates the non-crystalline and uniform distribution of Pd(0) in the synthesized catalyst. TEM images show the dark uniform suspension in the amorphous nature of the catalyst. This indicates the high dispersion of PdNPs over the surface of the catalyst. TEM micrographs of the Pd-TPA/ZrO_2 are displayed in figure 1(a-c). SAED image 1a indicates the non-crystalline dispersion of PdNPs in the synthesized catalyst. Image 1(b-c) shows the dark uniform suspension in the amorphous nature of the catalyst indicating the high dispersion of PdNPs onto surface of support. To further confirm, HRTEM micrographs were also recorded as shown in figure 1(d-f), which clearly shows the uniform dispersion of PdNPs throughout the morphology, without aggregates formation, confirming the stabilization of PdNPs by TPA. STEM Also confirmed the same.

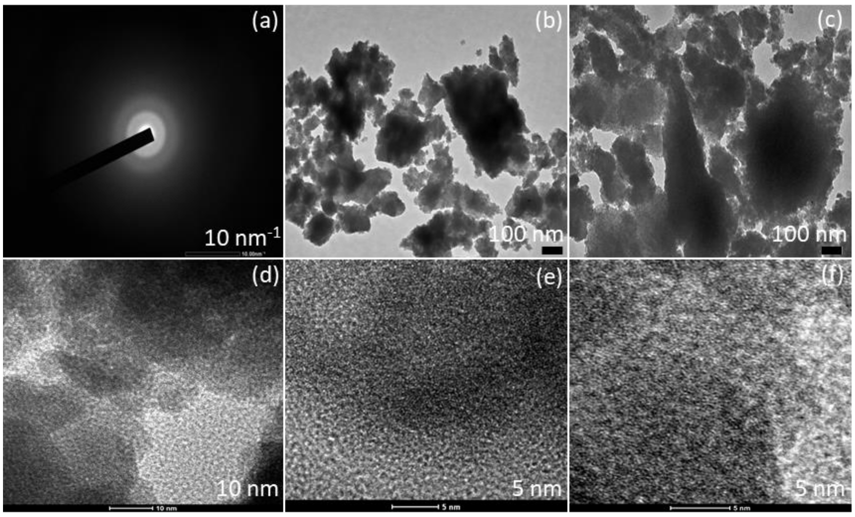


Figure 1 (a) SAED, (b-c) TEM and (d-f) HRTEM images of Pd-TPA/ZrO_2.

The increase in surface area of the Pd(II)-TPA/ZrO_2 (169 m^2/g) as compared to that of TPA/ZrO_2 (146 m^2/g) indicates high uniform dispersion of the Pd onto surface of TPA/ZrO_2. It is very interesting to note down that there is a drastic increase in the value of surface area of Pd-TPA/ZrO_2 (203 m^2/g) as compared to that of Pd(II)-TPA/ZrO_2 (169 m^2/g), conforming the reduction of Pd(II) to Pd(0) and in good agreement with the known fact that nanoparticles have higher surface area than the parent one.

The XRD patterns of TPA/ZrO_2 and Pd-TPA/ZrO_2 catalysts were recorded. The XRD pattern of TPA/ZrO_2 does not show any characteristic diffraction line indicating that a high dispersion of TPA in a non-crystalline form on the surface of ZrO_2. In XRD patterns of Pd- TPA/ZrO_2, absence of any crystalline peak corresponds to Pd(0), is due to the low concentration of Pd(0) on the surface of the catalyst as well as high dispersion of PdNPs on the surface of TPA/ZrO_2.

Catalytic activity

SM coupling

(i) Aqueous medium

The catalytic efficiency of the catalyst was evaluated towards Suzuki-Miyaura (SM), Heck and hydrogenation reactions. For SM, iodobenzene (1.96 mmol) and phenylboronic acid (2.94 mmol) were selected as the test substrates and effect of different reaction parameters such as palladium concentration, time, temperature, base, solvent and solvent ratio were studied to optimize the conditions for maximum conversion (Figure 2).

Initially, the reactions were carried out by varying the catalyst amount (Figure 2a) in the range of 25-5 mg with concentration of Pd(0) in the range of 37.4×10^{-4} mmol (0.192 mol%) to 1.88×10^{-4} mmol (0.0096 mol%), respectively. Which indicated that very low concentration (0.0096 mol%) of Pd(0) is sufficient for the maximum % conversion. The influence of time on catalytic conversion indicates that 30 min is sufficient for maximum 99 % conversion (Figure 2b). The effect of temperature was assesed between 60 to 90 °C and 99 % conversion was obtained at 80 °C (Figure 2c). Effect of various bases was also carried out and obtained results represented K_2CO_3 as optimized base (Figure 2d).

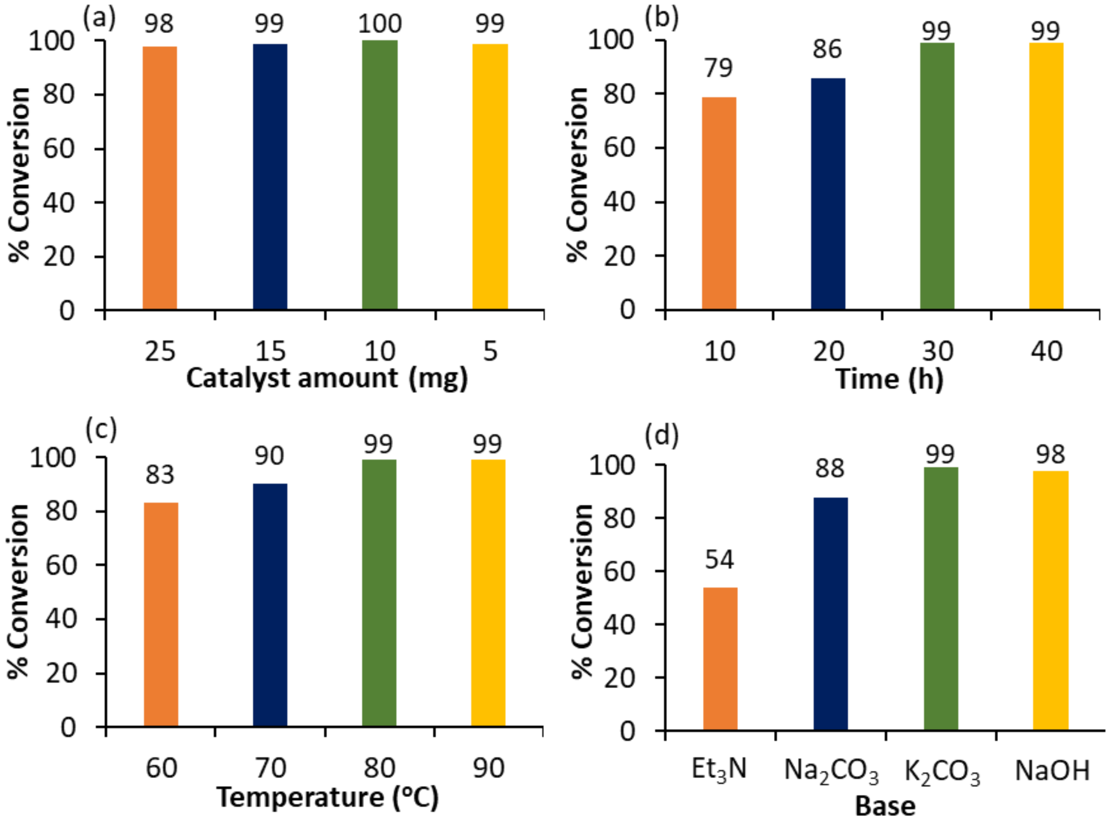


Figure 2 Optimization of parameters for SM coupling. Reaction conditions: (a) Effect of catalyst amount- K_2CO_3 (3.92 mmol), EtOH: H_2O (3:7 mL), time (30 min), temperature (80 °C); (b) Effect of time- catalyst (5 mg), K_2CO_3 (3.92 mmol), EtOH: H_2O (3:7 mL), temperature (80 °C); (c) Effect of temperature- catalyst (5 mg), K_2CO_3 (3.92 mmol), EtOH: H_2O (3:7 mL), time (30 min); (d) Effect of base- catalyst (5 mg), base (3.92 mmol), EtOH: H_2O (3:7 mL), time (30 min), temperature (80 °C).

Effect of solvent study showed that ethanol is highly efficient compared to other solvent. Finally, the effect of solvent to water (Ethanol: H_2O) ratio was studied and obtained results showed that (3:7) mL ratio was the optimum one for maximum 99 % conversion.

From the above study, the optimized conditions for the maximum % conversion (99) are: iodobenzene (1.96 mmol), phenylboronic acid (2.94 mmol), K_2CO_3 (3.92 mmol), conc. of Pd (1.88×10^{-4} mmol, 0.0096 mol%), substrate/catalyst ratio (10429/1), C_2H_5OH:H_2O (3:7 mL), time (30 min), temperature (80 °C). The calculated TON is 10,325 and TOF is 20,650 h^{-1}.

(ii) Water medium

Similarly, effect of different reaction parameters was studied and the optimized conditions for the maximum % conversion (89) are: iodobenzene (1.96 mmol), phenylboronic acid (2.94 mmol), K_2CO_3 (3.92 mmol), conc. of Pd (1.88×10^{-4} mmol, 0.0096 mol%), substrate/catalyst ratio (10,429/1), H_2O (6 mL), time (1 h), temperature (100 °C). The calculated TON is 9282 and TOF is 9282 h^{-1}.

Heck coupling

To evaluate the efficiency of the catalyst for heck coupling, iodobenzene (0.98 mmol) and styrene (1.47 mmol) were selected as test substrates. As described in SM coupling, in present case also, effect of all parameters were studied.

The optimized conditions for the maximum % conversion (99) are: iodobenzene (0.98 mmol), styrene (1.47 mmol), K_2CO_3 (1.96 mmol), conc. of Pd (1.13×10^{-3} mmol, 0.115 mol%), substrate/catalyst ratio (869/1), DMF:H_2O (3:2 mL), time (6 h), temperature (100 °C). The calculated turnover number (TON) is 860 and turnover frequency (TOF) is 143 h^{-1}.

Hydrogenation

(i) Cyclohexene hydrogenation

To evaluate the efficiency of the catalyst for hydrogenation, cyclohexene (9.87 mmol) was selected as test substrate. Effect of different reaction parameters such as palladium concentration, time, temperature, pressure and solvent were studied to optimize the conditions for maximum conversion.

The optimized conditions for the maximum % conversion (96) are: cyclohexene (9.87 mmol), H_2O (50 mL), conc. of Pd (7.52×10^{-4} mmol, 0.0076 mol%), substrate/catalyst ratio (13130/1), time (4 h), temperature (80 °C) and H_2 pressure (10 bar). The calculated TON is 12,604 and TOF is 3151 h^{-1}.

(ii) Crotonaldehyde hydrogenation

Similar to cyclohexene case, here also, effect of various reaction parameters were studied and optimized conditions for the maximum % conversion (89) are: crotonaldehyde (9.87 mmol), H_2O (50 mL), conc. of Pd(0) (7.52×10^{-4} mmol, 0.0076 mol%), substrate/catalyst ratio (13130/1), temperature (80 °C), H_2 pressure (8 bar) and time (4 h). The calculated TON is 11744 while the TOF is 2936 h^{-1}.

In all the reactions, control experiments were carried out with TPA, ZrO_2, TPA/ZrO_2, $PdCl_2$, Pd/ZrO_2 and Pd-TPA/ZrO_2 under optimized conditions in order to understand the role of each component, and results that TPA, ZrO_2 and TPA/ZrO_2 were inactive toward the reactions. Almost same conversion was found in the case of $PdCl_2$, Pd/ZrO_2 and Pd-TPA/ZrO_2 in all reactions. This indicates that Pd is real active species responsible for the reactions.

Leaching and Heterogeneity test indicated the stabilization of PdNPs by TPA and does not allow to leach it into the reaction mixture, making it a true heterogeneous catalyst to recycle and reuse. Here, withholding of active species onto support during the reaction show that present catalyst is of category C [20] and truly heterogeneous in nature.

Recyclability and sustainability study showed the gradual decrease in the % conversion in case of Pd/ZrO_2 during all the reactions, confirming the leaching of active species PdNPs from the support. In contrast, Pd-TPA/ZrO_2 did not show any appreciable change in the % conversion up to five cycles for all reactions, indicating that the catalyst was stable, heterogeneous, can be regenerated and reused for further catalytic runs also. Here, TPA plays an important role by stabilizing PdNPs and makes the system sustainable.

In order to check the stability, the regenerated catalyst was characterized by EDS, XRD, BET and XPS. EDX values of Pd (0.46 wt%) and W (16.90 wt%) of regenerated Pd-TPA/ZrO_2 is in good agreement with values of fresh catalyst (16.87 wt% of W, 0.47 wt% of Pd) confirming no emission of Pd as well as TPA from ZrO_2. Identical XRD spectra of fresh and regenerated catalysts revealed the retention of highly dispersed nature of the catalyst. Absence of any characteristic peaks regarding Pd aggregates as well as TPA clearly indicates the sustainability of the catalyst during the reaction. XPS of regenerated Pd-TPA/ZrO_2 is displayed in figure 3. The spectrum of regenerated catalyst is found to be identical with fresh one, confirms the retention of Pd(0) active species as well as W(VI), which did not undergo reduction during the reaction, indicating the sustainability of the catalyst.

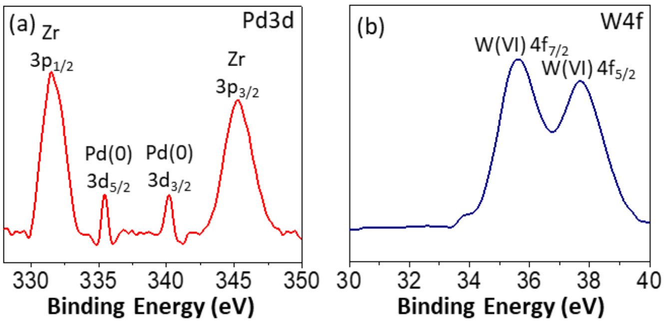


Figure 3 XPS spectra of regenerated catalyst.

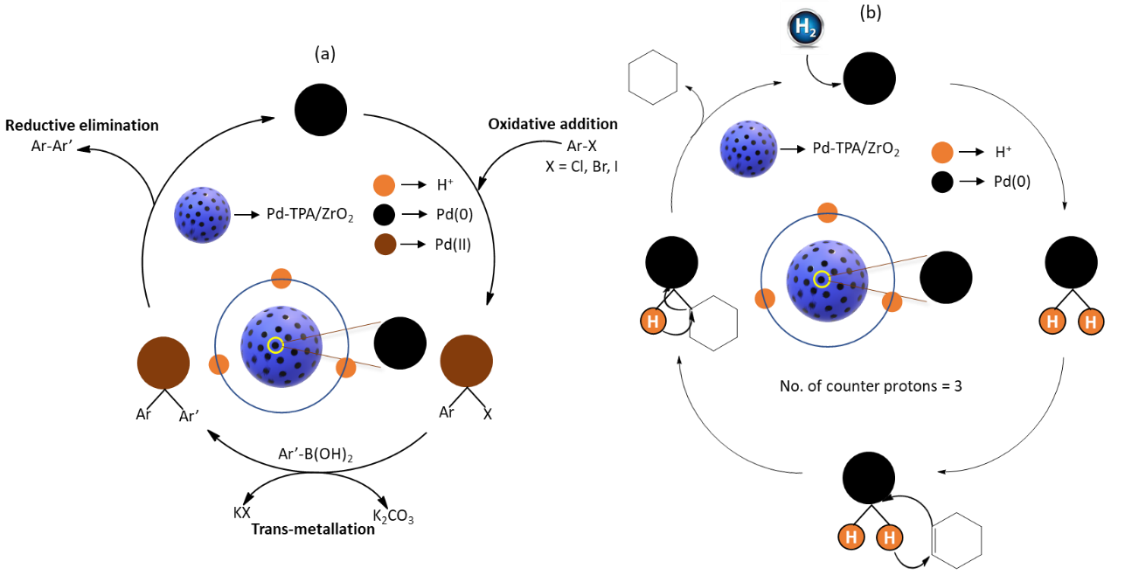
The viability of the catalyst was evaluated towards substrates having different functionality and obtained results confirmed the high activity of the catalyst towards the said reactions. Catalytic activity of the present catalyst is compared with reported catalysts for all reactions and obtain results indicate that the present catalytic system is best one of all reported one in terms of activity under mild reaction conditions.

Plausible mechanism

C-C coupling

In the present work, we are expecting the well-known mechanism, which involves oxidative addition, transmetallation and reductive elimination [21]. During oxidative addition and transmetallation steps, we could not isolate the Pd(II) species due to the high rate of the reaction. The steric and electronic characteristics of TPA are important for catalysis. In general, oxidative addition is governed by electronic factors, whereas the transmetallation and reductive elimination processes are controlled by a mixture of both electronic and steric effect [22]. Thus, TPA would achieve a suitable balance between these two factors. The plausible mechanism for the C-C coupling is shown in scheme 2.

Hydrogenation

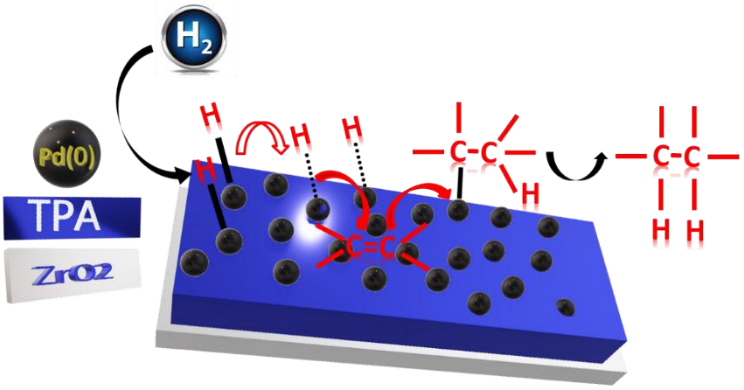


Scheme 2 Plausible mechanism for (a) C-C coupling and (b) for hydrogenation.

It is well known that in case of Pd catalyzed hydrogenation, mechanism is governed by palladium hydride (Pd-H) formation. In present system, we are also expecting the same mechanism in which molecular hydrogen initially gets adsorbed onto Pd surface to form Pd-H. This formed species subsequently tranfer the hydrogen to unsaturate bond of prely adsorbed substrate over the surface to form product. The plausible mechanism for cyclohexene hydrogenation is shown in scheme 2.

Crotonaldehyde hydrogenation

In case of crotonaldehyde hydrogenation, we achieved single selective product that is butyraldehhyde instead of product mixture. There might be two reasons for the selective reduction of C=C bond. (i) The presence of only water as a solvent instead of any organic solvent as discussed above. Here, the absence of organic solvent would not activate C=O bond and selectively produce butyraldehyde only. To check the same, we have carried out the same reaction under optimized condition using EtOH: H_2O (20:30) mL as a solvent. Obtained results showed 91 % conversion with 60 % butyraldehyde and 40 % crotylalcohol selectivity, indicating the activation of C=O bond for hydrogenation due to the presence of EtOH as solvent. (ii) The high adsorption capacity of the catalyst towards the substrates and initially formed products [23-25]. In present case, initially formed product butyraldehyde get adsorbed on the surface of the catalyst, and did not allow it to desorb for further hydrogenation to generate other product butanol. Hence, we are expecting the well-known mechanism for both the reactions. The proposed mechanism for both the reactions is shown in scheme 3.



Scheme 3 Plausible mechanism for crotonaldehyde hydrogenation.

Chapter 2: PdNPs Stabilized by Zirconia Supported LTPA: Synthesis, Characterization and Applications to C-C coupling and Hydrogenation

Palladium was deposited on LTPA/ZrO_2 via exchanging the available protons of LTPA following the same method as discussed in chapter 1 and characterized by various physico-chemical techniques. The catalytic efficiency of the catalyst was evaluated towards SM, Heck and hydrogenation reaction and optimized reaction parameters are as follows:

SM coupling: The optimized conditions for the maximum % conversion (99) are: iodobenzene (1.96 mmol), phenylboronic acid (2.94 mmol), K_2CO_3 (3.92 mmol), conc. of Pd (6.77×10^{-4} mmol, 0.035 mol%), substrate/catalyst ratio (2897/1), $C_2H_5OH:H_2O$ (3:7 mL), time (30 min), temperature (90 °C). The calculated TON is 2868 and TOF is 5736 h^{-1}.

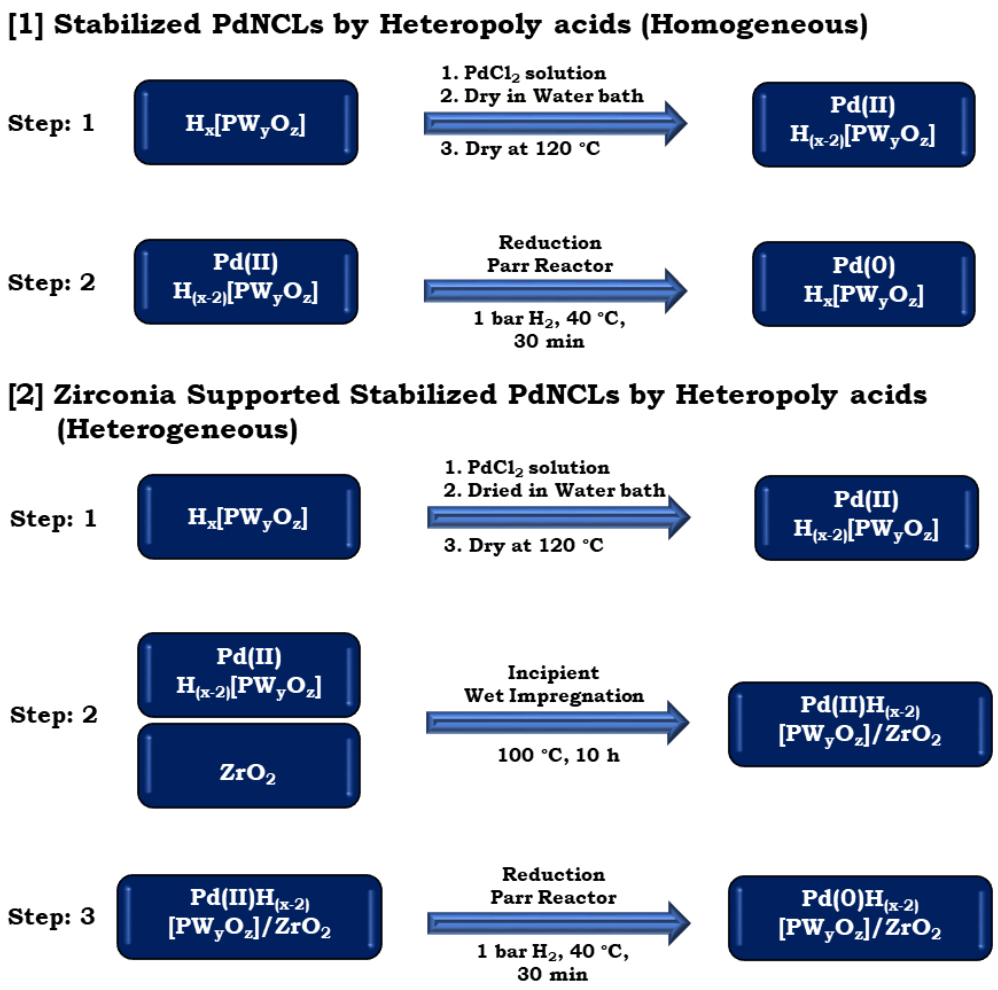
Heck coupling: The optimized conditions for the maximum % conversion (96) are: iodobenzene (0.98 mmol), styrene (1.47 mmol), K_2CO_3 (1.96 mmol), conc. of Pd (2.03×10^{-3} mmol, 0.207 mol%), substrate/catalyst ratio (483/1), DMF:H_2O (3:2 mL), time (6 h), temperature (100 °C). The calculated turnover number (TON) is 464 and turnover frequency (TOF) is 77 h^{-1}.

Hydrogenation: The optimized conditions for the maximum % conversion (96) are: cyclohexene (9.87 mmol), H_2O (50 mL), conc. of Pd (3.38×10^{-4} mmol, 0.0034 mol%), substrate/catalyst ratio (29177/1), time (2 h), temperature (50 °C) and H_2 pressure (10 bar). The calculated TON is 28010 and TOF is 14005 h^{-1}.

Part B: Salt Method

Designing of catalyst by salt method

This method involves two steps for the synthesis of TPA/LTPA stabilized PdNCLs as homogeneous. *Step-I*: The saturated solutions of TPA/LTPA and $PdCl_2$ are mixed in stoichiometric amount to form Pd(II) salt of TPA/LTPA by evaporation, followed by drying. *Step-II*: Finally, this salt is converted to stabilized PdNCLs by reducing in Parr reactor. This homogeneous counter-part, Pd(II)TPA/LTPA salt can be heterogenized by supporting it over zirconia by incipient wet impregnation method as discussed in general introduction (Scheme 4).



Scheme 4 Synthetic scheme for stabilized PdNCLs via salt method.

Chapter 1: Stabilized PdNCLs by TPA: Synthesis, Characterization and Applications to C-C coupling and Hydrogenation

Palladium tungstophosphate was synthesized by salt method as reported in the literature [26] with modification. 1 g of 12-tungstophosphoric acid (TPA) was dissolved in minimum amount of distilled water followed by the addition of a stoichiometric amount of aqueous $PdCl_2$ (58.6 mg) solution dropwise. The resulting mixture was aged for 1 h at 80 °C and the excess water was evaporated to dryness on the water bath. The resulting material was oven dried at 120 °C overnight to obtain brown coloured salt, designated as PdHTPA. In this step, available protons of TPA get replaced by Pd(II) in stoichiometric amount. Finally, PdHTPA was reduced under 1 bar H_2 pressure at 40 °C for 30 min in Parr reactor and the obtained black coloured catalyst was designated as PdTPA. The synthesized material was characterized by EDX, TGA, FT-IR, ^{31}P MAS NMR, powder XRD, XPS and TEM.

To evaluate the efficiency of PdTPA as homogeneous catalyst, SM, Heck and hydrogenation reactions were carried out. Preliminary study showed the leaching of Pd from the PdTPA during the reactions. The catalyst is homogeneous and shows the high efficiency for said reactions. However, the obtained negative result of leaching made us to redesign the catalyst to overcome the sustainability issue.

To overcome this problem, the synthesized material was supported on Ziconia support…

Chapter 2: Zirconia Supported Stabilized PdNCLs by TPA: Synthesis, Characterization and Applications to C-C coupling and Hydrogenation

A series of catalysts, containing 10-40 % of PdHTPA supported onto ZrO_2 was synthesized by incipient wet impregnation method and post reduction method. The study on effect of loading showed superior activity of 30 % PdTPA/ZrO_2 (Later, PdTPA/ZrO_2). Hence, only PdTPA/ZrO_2 was characterized by EDX, TGA, BET, FT-IR, ^{31}P MAS NMR, powder XRD, XPS, TEM, HRTEM and STEM, and its catalytic efficiency was evaluated towards C-C coupling and hydrogenation as discussed in earlier chapters. The optimized conditions are as follows.

SM reaction: The optimized conditions for the maximum % conversion (96) are: iodobenzene (1.96 mmol), phenylboronic acid (2.94 mmol), K_2CO_3 (3.92 mmol), conc. of Pd (3.76×10^{-4} mmol, 0.0192 mol%), substrate/catalyst ratio (5215/1), C_2H_5OH: H_2O (3:7 mL), 30 min, 90 °C. The calculated TON is 5006 and TOF is 10012 h^{-1}.

Heck coupling: The optimized conditions for the maximum % conversion (96) are: iodobenzene (0.98 mmol), styrene (1.47 mmol), K_2CO_3 (1.96 mmol), conc. of Pd (1.13×10^{-3} mmol, 0.115 mol%), substrate/catalyst ratio (869/1), DMF:H_2O (3:2 mL), time (6 h), temperature (100 °C). The calculated TON is 834 and TOF is 139 h^{-1}.

Hydrogenation: The optimized conditions for the maximum % conversion (94) are: cyclohexene (9.87 mmol), H_2O (50 mL), conc. of Pd (1.50×10^{-3} mmol, 0.015 mol%), substrate/catalyst ratio (6565/1), time (4 h), temperature (80 °C). The calculated TON is 6171 and TOF is 1543 h^{-1}.

Chapter 3: Zirconia Supported Stabilized PdNCLs by LTPA: Synthesis, Characterization and Applications to C-C coupling and Hydrogenation

As discussed in chapter-2, in this system also, catalyst was synthesized, characterized and catalytic efficiency was evaluated towards C-C coupling and hydrogenation as discussed in earlier chapters. The optimized conditions are as follows.

SM coupling: The optimized conditions for the maximum % conversion (99) are: iodobenzene (1.96 mmol), phenylboronic acid (2.94 mmol), K_2CO_3 (3.92 mmol), conc. of Pd (3.81×10^{-4} mmol, 0.0194 mol%), substrate/catalyst ratio (5150/1), C_2H_5OH:H_2O (3:7 mL), time (30 min), temperature (90 °C). The calculated TON is 5099 and TOF is 10198 h^{-1}.

Heck coupling: The optimized conditions for the maximum % conversion (98) are: iodobenzene (0.98 mmol), styrene (1.47 mmol), K_2CO_3 (1.96 mmol), conc. of Pd (1.14×10^{-3} mmol, 0.117 mol%), substrate/catalyst ratio (858/1), DMF:H_2O (3:2

mL), time (6 h), temperature (100 °C). The calculated TON is 841 and TOF is 140 h^{-1}.

Hydrogenation: The optimized conditions for the maximum % conversion (96) are: cyclohexene (9.87 mmol), H_2O (50 mL), conc. of Pd (1.52×10^{-3} mmol, 0.0154 mol%), substrate/catalyst ratio (6484/1), time (5 h), temperature (80 °C) and H_2 pressure (10 bar). The calculated TON is 6224 and TOF is 1245 h^{-1}.

Comparison of activity

In order to check the activity order, coupling and hydrogenation reactions were carried out over all synthesized catalysts Pd-TPA/ZrO_2, Pd-LTPA/ZrO_2, PdTPA/ZrO_2 and PdLTPA/ZrO_2 using similar active amount of Pd under identical experimental conditions and obtained results are compared in terms of % conversion, TON/TOF (Table 1).

Table 1 % Conversion, TON/TOF for C-C coupling

Catalyst	% Conversion	TON/TOF (h^{-1})	No. of counter protons	Total acidic sites (Bulk acidity) (mequiv./g)
Pd-TPA/ZrO_2	**[a]99** **[b]99**	**[a]10325/20650** **[b]860/143**	**3**	**4.2**
PdTPA/ZrO_2	[a]86 [b]96	[a]8865/17730 [b]834/139	3	4.7
PdLTPA/ZrO_2	[a]92 [b]97	[a]9595/19190 [b]843/140	2	4.4
Pd-LTPA/ZrO_2	[a]62 [b]70	[a]6466/12932 [b]608/101	7	5.1

[a]**SM coupling:** iodobenzene (1.96 mmol), phenylboronic acid (2.94 mmol), K_2CO_3 (3.92 mmol), conc. of Pd (0.0096 mol%), substrate/catalyst ratio (10429/1), C_2H_5OH: H_2O (3:7) mL, temperature (80 ˚C), time (30 min). [b]**Heck coupling:** iodobenzene (0.98 mmol), styrene (1.47 mmol), K_2CO_3 (1.96 mmol), (3.92 mmol), conc. of Pd (0.115 mol%), substrate/catalyst ratio (869/1), DMF: H_2O (3:2) mL, temperature (100 ˚C), time (6 h).

Table 1 shows that among all, Pd-TPA/ZrO_2 is highly active for both the reactions and this can be explained on the basis of total acidic sites (Bulk acidity).

The activity order of all catalysts towards C-C cross coupling is:

Activity order	**Pd-TPA/ZrO_2**	**>>**	**PdLTPA/ZrO_2**	**>>**	**PdTPA/ZrO_2**	**>>**	**Pd-LTPA/ZrO_2**
No. of Counter protons	**3**		**2**		**3**		**7**
Total acidic sites	**4.2**		**4.4**		**4.7**		**5.1**

It shows that the nanocatalyst synthesized by exchange method is better.

Hydrogenation

Obtained results (Table 2) show that Pd-LTPA/ZrO_2 is highly active amongst all synthesized catalysts. This can be explained on the basis of number of counter protons.

Table 2 % Conversion, TON/TOF for hydrogenation

Catalyst	% Conversion	TON/TOF (h^{-1})	Number of Protons
Pd-TPA/ZrO_2	15	4,377/2189	3
Pd-LTPA/ZrO_2	**96**	**28,010/14005**	**7**
PdTPA/ZrO_2	14	4085/2042	3
PdLTPA/ZrO_2	8	2334/1167	2

Reaction conditions: cyclohexene (9.87 mmol), conc. of Pd (0.0034 mol%), substrate/catalyst ratio (29177/1), H_2O (50 mL), temperature (50 °C), H_2 pressure (10 bar), time (2 h).

Activity order of the catalysts:

Activity order	**Pd-LTPA/ZrO_2**	**>>**	**Pd-TPA/ZrO_2**	**≡**	**PdTPA/ZrO_2**	**>>**	**PdLTPA/ZrO_2**
No. of Counter protons	**7**		**3**		**3**		**2**

Here also, the nanocatalyst synthesized by ion exchange method is found to be superior as compared to that by salt method.

Main Conclusion

- We have successfully synthesized and characterized Pd nanocatalysts stabilized by parent (TPA) and vacant tungstophosphoric acid (LTPA) by two different routs
- Catalytic activity of all the catalysts were evaluated towards C-C cross coupling (SM and Heck) as well as hydrogenation
- For all reactions, exchanged method for the designing of the catalysts was found to be better. For C-C cross coupling Pd-TPA/ZrO_2 whereas for hydrogenation Pd-LTPA/ZrO_2 was found to be better
- Finally, our study agrees with our assumption that NPs and NCLs depicts almost similar catalytic activity for organic transformations

In order to study the role of the support, we have chosen another acidic metal oxide-based support, SiO_2*.*

Annexure: Silica encapsulated Stabilized PdNCLs by 12-tungstophosphoric acid: Synthesis, characterization and applications C-C coupling and hydrogenation

A series of materials, containing 10-40 % of Pd(II)TPA encapsulated in SiO_2 was synthesized as discussed in chapter-2 and characterized by various physico-chemical techniques. The catalytic efficiency of the catalyst was evaluated towards SM, Heck and hydrogenation reaction and optimized reaction parameters are as follows:

SM coupling: The optimized conditions for the maximum % conversion (94) are: iodobenzene (1.96 mmol), phenylboronic acid (2.94 mmol), K_2CO_3 (3.92 mmol), conc. of Pd (3.76×10^{-4} mmol, 0.0192 mol%), substrate/catalyst ratio (5215/1), $C_2H_5OH:H_2O$ (3:7 mL), time (30 min), temperature (90 °C). The calculated TON is 4902 and TOF is 9804 h^{-1}.

Heck coupling: The optimized conditions for the maximum % conversion (94) are: iodobenzene (0.98 mmol), styrene (1.47 mmol), K_2CO_3 (1.96 mmol), conc. of Pd (1.13×10^{-3} mmol, 0.115 mol%), substrate/catalyst ratio (869/1), DMF:H_2O (3:2 mL), time (6 h), temperature (100 °C). The calculated turnover number (TON) is 817 and turnover frequency (TOF) is 136 h^{-1}.

Hydrogenation: The optimized conditions for the maximum % conversion (97) are: cyclohexene (9.87 mmol), H_2O (50 mL), conc. of Pd (1.50×10^{-3} mmol, 0.023 mol%), substrate/catalyst ratio (4377/1), time (4 h), temperature (50 °C) and H_2 pressure (8 bar). The calculated TON is 4245 and TOF is 1061 h^{-1}.

Comparison study of PdTPA/ZrO_2 and PdTPA/SiO_2

In order to compare the activity of the catalysts, both coupling and hydrogenation reactions were carried out under identical experimental conditions. Obtained results (Table 3) are compared in terms of % conversion, TON/TOF.

Table 3 Effect of support on conversion % conversion, TON/TOF

Catalyst	Total acidity (mequi./g)	SM coupling		Heck coupling		Hydrogenation		Surface area (m^2/g)
		% Conv.	TON/ TOF	% Conv.	TON/ TOF	% Conv.	TON/ TOF	
PdTPA/ZrO_2	4.7	**96**	**5006/ 10012**	**96**	**834/ 139**	60	2627/ 657	202
PdTPA/SiO_2	5.1	94	4902/ 9804	94	817/ 136	**97**	**4245/ 1061**	322

Reaction conditions: *SM coupling*- iodobenzene (1.96 mmol), phenylboronic acid (2.94 mmol), K_2CO_3 (3.92 mmol), conc. of Pd (0.0192 mol%), substrate/catalyst ratio (5215/1), C_2H_5OH: H_2O (3:7 mL), time (30 min), temperature (90 °C); *Heck coupling*- iodobenzene (1.96 mmol), phenylboronic acid (2.94 mmol), K_2CO_3 (3.92 mmol), conc. of Pd (0.115 mol%), substrate/catalyst ratio (869/1), DMF: H_2O (3:2 mL), time (6 h), temperature (100 °C); *Hydrogenation*- Cyclohexene (9.87 mmol), conc. of Pd (0.023 mol%), substrate/catalyst ratio (4377/1), H_2O (50 mL), time (4 h), temperature (50 °C), H_2 pressure (8 bar).

In case of C-C coupling, the results show that PdTPA/ZrO_2 is more active compared to PdTPA/SiO_2. This can be explained on the basis of total acidic sites. Whereas in case of hydrogenation, PdTPA/SiO_2 is more active than PdTPA/ZrO_2. This can be explained on the basis of surface area. Activity order of the catalysts is:

C-C Coupling: **PdTPA/ZrO_2 > PdTPA/SiO_2**

Hydrogenation: **PdTPA/SiO_2 >> PdTPA/ZrO_2**

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