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# Fluorapatite-Supported Palladium Catalyst for Suzuki and Heck Coupling Reactions of Haloarenes

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**Abstract:** A fluorapatite-supported palladium catalyst (PdFAP) was synthesized by treatment of fluorapatite (prepared by incorporating the basic species fluoride ion into apatite *in situ* by co-precipitation) with bis(benzonitrile)palladium(II) chloride in acetone. The catalyst displayed high catalytic activity for Suzuki coupling of aryl iodides and bromides with boronic acids at room temperature and chloroarenes at 130 °C in the presence of tetrabutylammonium bromide to give biaryls in excellent yields. Heck olefination of chloroarenes was also successfully carried out by this catalyst. PdFAP was recovered quantitatively by simple filtration and reused with consistent activity. PdFAP was well characterized by XRD, FTIR, XPS, ICP-AES, $CO_2$ TPD and CHN elemental analysis.

**Keywords:** chloroarenes; fluorapatite-supported palladium catalyst; Heck olefination; heterogeneous catalyst; room temperature; Suzuki coupling

## Introduction

Palladium-catalyzed Suzuki and Heck olefinations of aryl halides have become one of the most powerful tools in organic synthesis for the construction of carbon-carbon bonds. Cross-coupling of aryl halides or triflates with organoboronic acids in the presence of palladium and base to synthesize biaryl compounds is known as the Suzuki–Miyaura reaction.[1] Biaryl compounds are important intermediates for pharmaceuticals,[2] herbicides,[3] chiral ligands for catalysis[4] and in materials science.[5] Arylation or vinylation of olefins is universally referred to as the Heck olefination. Heck olefination products are widely used in the preparation of materials,[6] natural products,[7] drugs and pharmaceuticals[8] and in bioorganic chemistry.[9] Naproxen, a non-steroidal anti-inflammatory drug,[10] ethyl 4-methoxycinnamate, a key intermediate for diltiazem hydrochloride, a typical calcium antagonist,[11] octyl methoxycinnamate,[12] a widely used UV-absorber, and prosulfuron, a sulfonylurea herbicide are prepared on industrial scales using the Heck olefination reaction.[13]

Generally, Suzuki and Heck cross-coupling reactions are carried out using homogeneous palladium catalysts, such as $Pd(PPh_3)_4$ and $Pd_2(dba)_3$ or palladium(II) salts,[14] along with phosphines, phosphates, carbenes or thioether ligands.[15] The use of such electron-donating phosphine ligands is undesirable because of their toxicity and air- as well as moisture-sensitivity. Moreover, phosphines and their palladium complexes are prone to decompose so that excesses of phosphine and palladium are required which increases the cost of the process. However, a new class of Pd(II) complexes having Pd-carbon σ bonds, e.g., palladacycle complexes,[16] PCP pincer-type complexes,[17] and N-heterocyclic carbenes (NHCs),[18] have led to a significant breakthrough in this area.

Despite the synthetic elegance and high turnover numbers, the non-reusability of the precious palladium precludes wide synthetic applications in the pharmaceutical industry. In view of the above, it is desirable to develop a ligand-free and reusable catalytic system.

Heterogeneous catalysis is particularly attractive as it allows the production and ready separation of large quantities of products with the use of a small amount of catalyst. In recent years, numerous heterogeneous supported palladium catalyst such palladium on charcoal,[19] palladium on magnesium oxide,[20] palladium on simple oxides such as silica,[21] alumina or titania,[21,22] Pd/Nb-MCM-41,[21] Pd/polymeric materials,[23] Pd/zeolites,[24] alkali-exchanged sepiolite,[25] basic zeolites[26] and mixed oxides[27], Pd/C,[28] Pd-sepiolite,[29] polymer-supported Pd catalysts,[30] Pd-immobilized complexes on a solid support such as Pd-phosphine on MCM-41 zeolite,[31] and oxime-carbapalladacycle[32] were successfully employed in Heck and Suzuki cross-coupling reactions. Earlier, we reported the effective Heck-, Suzuki-, Sonogashira-, and Stille-type coupling

reactions of chloroarenes using an Mg-Al layered double hydroxides-supported nanopalladium catalyst.[33]

Apatites are metal basic phosphates for which the chemical formula is $M_{10}(PO_4)_6(OH)_2$ [M = divalent metal] and the most typical apatite is calcium hydroxyapatite: $Ca_{10}(PO_4)_6(OH)_2$ (CaHAP). CaHAP has attracted wide attention due to its versatile applications in the field of bioceramics, chromatographic adsorbents and acid-base catalysis. It has been well established that the $Ca^{2+}$ sites of CaHAP can be replaced by divalent cations such as $Sr^{2+}$, $Ba^{2+}$, $Pb^{2+}$, $Cd^{2+}$ etc.[34] Kaneda and co-workers have demonstrated the utility of CaHAP as a solid support for Ru and Pd to perform many organic transformations that include oxidation of alcohols and Heck and Diels–Alder reactions.[35] Fluorapatites (FAP) are basic metal phosphates for which the chemical formula is $M_{10}(PO_4)_6(F)_2$ (CaFAP) [M = divalent metal].

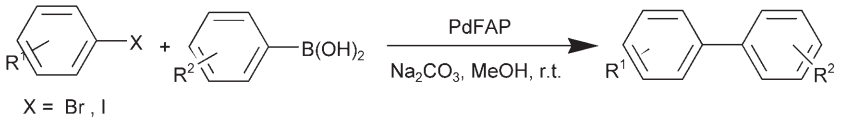
Recently, Kaneda et al. reported the preparation of two types of PdHAP by selecting appropriate Ca/P molar ratios to give the stoichiometric $Ca_{10}(PO_4)_6(OH)_2$ (Ca/P = 1.67, HAP-0) hydroxyapatite and the non-stoichiometric $Ca_9(HPO_4)(PO_4)_5(OH)$ (Ca/P = 1.50, HAP-1) Ca-deficient hydroxyapatite.[35d] The treatment of the HAP-0 with an acetone solution of $PdCl_2(PhCN)_2$ yielded the hydroxyapatite-bound Pd complex, PdHAP-0, while the PdHAP-1 complex was obtained using HAP-1 by the same method. Suzuki and Heck coupling reactions with bromo- and iodoarenes at 130 °C were efficiently performed with PdHAP-1 using NMP as solvent[35e] in comparison to PdHAP-0.

In an effort to develop a new heterogeneous system, we turned our attention towards the exploration of highly basic fluorapatite (FAP) as a support. A basic support will stabilize and provide adequate electron density to palladium. In this direction, Hell et al. reported[36a] Heck coupling reactions using a highly basic Pd/Mg-La mixed oxide. Later Jiang et al. reported[36b] that basic Pd/LDH-F exhibited better activity in Heck coupling than Pd-LDH-$CO_3$. Very recently, we reported the preparation of recyclable, heterogeneous Cu-exchanged fluorapatite and copper exchanged *tert*-butoxyapatite catalysts, by incorporating the basic species $F^-$/*t*-$BuO^-$ into apatite *in situ* by co-precipitation and subsequent exchange with Cu(II) for the *N*-arylation of imidazoles and other heterocycles with chloroarenes and fluoroarenes (EW) with good to excellent yields.[36c] We have also explored the *N*-arylation of heterocycles with bromo- and iodoarenes using Cu-exchanged fluorapatite.[36d] Thus, in continuation of our work on fluorapatite, we herein report the preparation of a recyclable, heterogeneous fluorapatite-supported palladium catalyst (PdFAP) by treatment of fluorapatite with $PdCl_2(PhCN)_2$ in acetone for Suzuki coupling of bromo- and iodoarenes with boronic acids at room temperature (Scheme 1) and chloroarenes at 130 °C in presence of TBAB to give biaryls in excellent yields (Scheme 2). The Heck olefination of bromo- and chloroarenes was also successfully carried out by this catalyst.

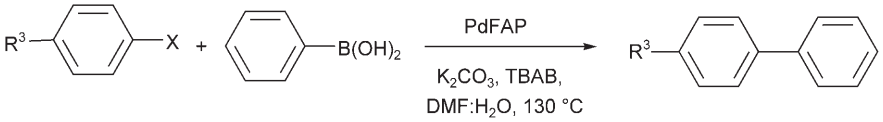
## Results and Discussion

Fluorapatite (FAP) was synthesized according to the literature procedure and was well characterized by XRD, FTIR, XPS, ICP-AES, $CO_2$ TPD and CHN elemental analysis.

Treatment of the FAP with an acetone solution of $PdCl_2(PhCN)_2$ for 3 h at room temperature yielded the hydroxyapatite-bound Pd complex. The palladium content was measured as 0.023 mmol $g^{-1}$ using ICP-




**Scheme 1.**




**Scheme 2.**

AES. The XRD peaks for PdFAP were similar to those of the parent fluorapatite (Figure 1).

XPS spectra were recorded for PdFAP catalyst. A survey scan of the PdFAP catalyst showed peaks char-

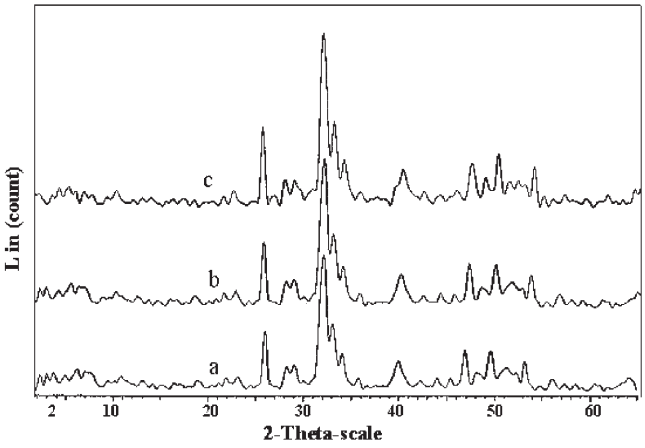



**Figure 1.** XRD spectra of a) FAP, b) PdFAP, c) used PdFAP.

acteristic of C 1s (285 eV), Ca 2p (349 eV), O 1s (532 eV), P 2p (135 eV), F 1s (685 eV) and Pd 3d (337 eV). XPS high resolution narrow scan of Pd showed peaks at 337.8 eV and 343.1 eV which are due to Pd $3d_{5/2}$ and Pd $3d_{3/2}$ respectively in the +2 oxidation state and the atomic ratio of Pd to Cl is 1:2 (whereas XPS of Pd on HAP showed peaks at 338 eV and 343.2 eV, respectively**)**. Pd in the +2 oxidation state was further confirmed by diffused-reflectance UV/Vis spectra (peak at 325 nm). No signals assignable to ν(CN) bands were observed in IR spectroscopy, suggesting that a PhCN moiety arising from the Pd precursor was not present in the catalyst (Figure 3), moreover, the absence of carbon and nitrogen atoms in PdFAP was observed by CHN elemental analysis. Inductively coupled plasma (ICP) analysis revealed that no Ca was present in the filtrate after palladium loading which clearly demonstrates that isomorphic substitution of Pd with Ca did not occur in organic solvent and that it is bound on the surface of FAP, which is similar to that reported by Kaneda et al.[35d] previously with HAP. The basic site distribution was measured by pulse chemisorption of $CO_2$ using 10% $CO_2$ in He through a six-port valve followed by TPD of $CO_2$. The basicity of the PdFAP catalysts is nearly six times higher as compared to PdHAP (Figure 2).

## Catalytic Suzuki Coupling of Iodo- and Bromoarenes with Arylboronic Acids

To explore the potential activity of such a highly basic PdFAP catalyst, we subjected the catalyst to Suzuki coupling of iodo-, bromo- and chloroarenes with vari-

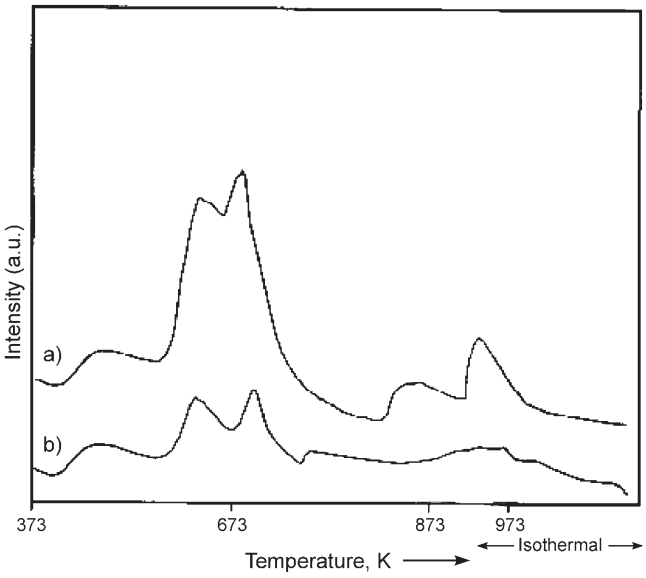



**Figure 2.** $CO_2$ TPD patterns of a) PdFAP(desorption of $CO_2$ is 67 μmoles/g), b) PdHAP (desorption of $CO_2$ is 11 μmoles/g).

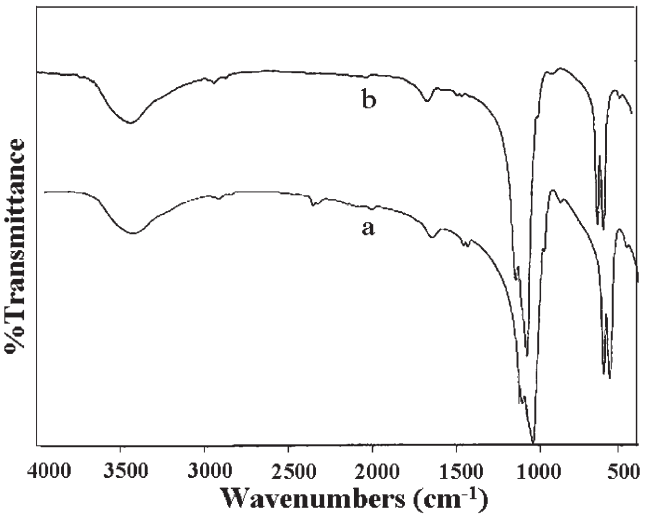
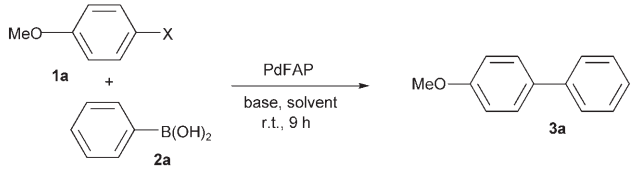



**Figure 3.** FTIR spectra of a) FAP and b) PdFAP.

ous arylboronic acids. In an effort to develop a better catalytic system, various reaction parameters were studied for the preparation of 4-methoxybiphenyl by the reaction of 4-bromoanisole with phenylboronic acid at room temperature and the results are summarized in Table 1. The solvent has a pronounced effect in these reactions out of which methanol has been proven to the best solvent, ethanol and water gave moderate yields whereas ethanol and water in a ratio of 1:1 was proven to be equally good as methanol as the solvent. *n*-Butanol and isopropyl alcohol were also tested and gave poor yields of 4-methoxybiphenyl. Among the various bases screened in methanol, the relatively weak and less expensive $Na_2CO_3$ gave

**Table 1.** Effect of solvent and base in Suzuki coupling of **1a** and **2a** catalyzed by PdFAP.[a]




| Entry | Solvent | Base | Yield [%][b] |
|---|---|---|---|
| 1 | *n*-butanol | $Na_2CO_3$ | 15 |
| 2 | isopropyl alcohol | $Na_2CO_3$ | 26 |
| 3 | ethanol | $Na_2CO_3$ | 70 |
| 4 | methanol | $Na_2CO_3$ | 91, 90,[c] 72[d] |
| 5 | water | $Na_2CO_3$ | 50 |
| 6 | ethanol/water (1:1) | $Na_2CO_3$ | 87 |
| 7 | methanol/water (1:1) | $Na_2CO_3$ | 89 |
| 8 | methanol | $K_2CO_3$ | 70 |
| 9 | methanol | NaOAc | 31 |
| 10 | methanol | $NaHCO_3$ | 84 |
| 11 | methanol | $Ag_2CO_3$ | 7 |

[a] *Reaction conditions:* **1a** (1 mmol), **2a** (1.5 mmol), base (2 mmol), solvent (3 mL), PdFAP (50 mg) or $1.15\times10^{-3}$ mmol of Pd.
[b] Isolated yields.
[c] Yield after third cycle.
[d] PdFAP (25 mg) or $5.75\times10^{-4}$ mmol of Pd was used.

the best result. The control reaction conducted under identical conditions and devoid of PdFAP gave no coupled product, despite a prolonged reaction time. PdFAP was recovered quantitatively by simple filtration and reused. PdFAP shows consistent activity even after the third cycle (Table 1, entry 4). To check the heterogeneity of the catalyst, a reaction between 4-bromoanisole and phenylboronic acid was terminated at 20% conversion (1 h) and the catalyst separated by simple filtration. The reaction was continued for additional 12 h and the conversion remained almost unchanged. These studies clearly demonstrate that no leaching of palladium has taken place from the catalyst and throughout the reaction palladium is bounded to the support. Moreover, the absence of palladium in the filtrate was also confirmed by ICP-AES, which reiterates that there is no leaching of palladium from the support.

During the course of the reaction, (in the period of a few minutes after reaction started) the color of the catalyst changed to gray. XPS and UV-VIS-DRS spectra were recorded for the used catalyst. An XPS high resolution narrow scan of the used PdFAP catalyst showed peaks at 335.5 eV and 340.0 eV for Pd $3d_{5/2}$ and Pd $3d_{3/2}$, respectively, which clearly indicates that Pd in the used catalyst is reduced to Pd(0) (Figure 4). This was further confirmed by diffused-reflectance UV/VIS spectra in which peak at 325 nm corresponding to Pd in the +2 oxidation state had disappeared. When the used PdFAP was subjected to XRD analysis, the diffraction line at $2\theta = 40^{o}$ was intensified over the parent FAP (which has peacks over the same diffraction line). This clearly confirms that the catalyst was reduced to Pd(0) during the reaction. The average size of the nanopalladium particles in the used PdFAP catalyst was measured from transmission electron microscope(TEM) images and found to be in the range of 15–20 nm which are molecularly dispersed on the support (Figure 5).

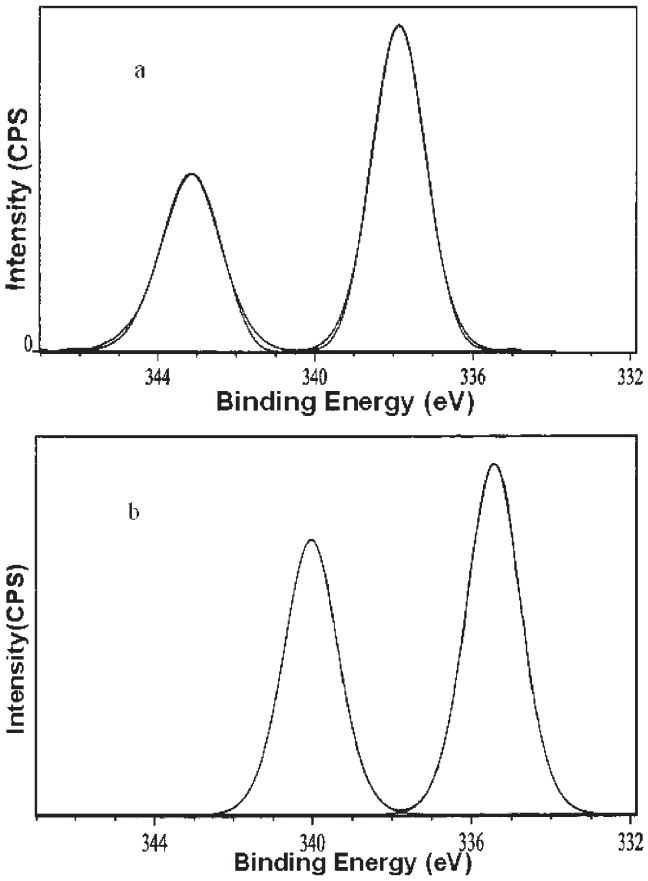



**Figure 4.** XPS spectra of a) $Pd^{2+}$ in PdFAP, b) Pd(0) in used PdFAP catalyst.

We chose a variety of structurally divergent iodo- and bromoarenes possessing a wide range of functional groups to understand the scope and the generality of the PdFAP-promoted Suzuki reaction to afford biaryls at room temperature and the results are summarized in Table 2. Among the various iodo- and bromoarenes tested in coupling with phenylboronic acid, deactivated electron-rich bromoarenes such as 4-bromotoluene and 4-bromoanisole (Table 2, entries 6 and 7) underwent smooth reaction with good yields over a long duration of time compared with iodoarenes and activated electron-poor bromoarenes (Table 2, entries 1–5 and 8–10) which took hardly 2–5 h for completion of the reaction with excellent yields to give the corresponding biaryls. In order to expand the scope of the methodology, a variety of substituted ar-

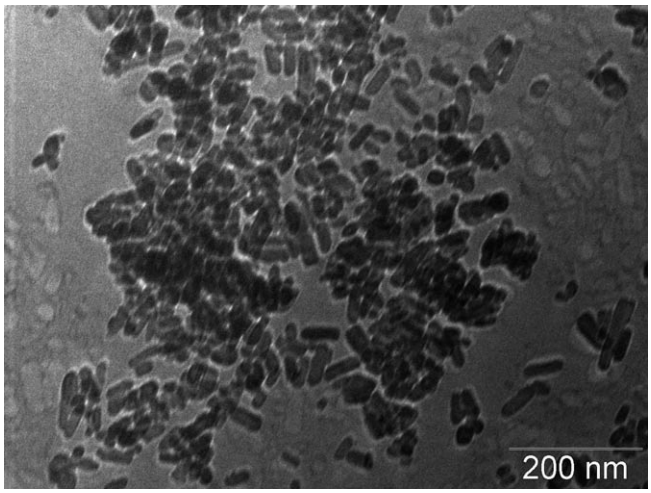



**Figure 5.** TEM image of the used PdFAP catalyst after the Suzuki reaction of bromoanisole with phenylboronic acid

ylboronic acids were successfully coupled with 4-iodoanisole and the results are summarized in Table 3. Arylboronic acids with electron-donating groups such as methyl, methoxy groups (Table 3, entries 1, 2 and 7) underwent smooth reaction with excellent yields in a short period of time compared to those with electron-withdrawing groups (Table 3, entries 3, 4 and 6) present in the arylboronic acid ring.

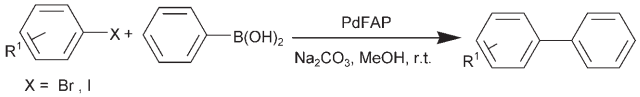
### Catalytic Suzuki Coupling of Chloroarenes with Phenylboronic acid

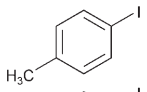
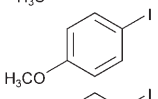
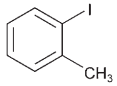
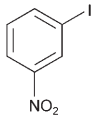
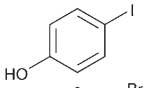
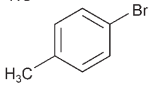
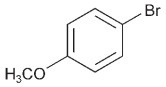
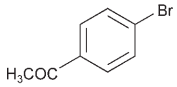
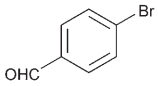
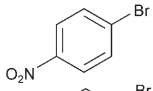
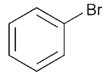
Impressed with the results from iodo- and bromoarenes, we further tried to extend the scope of PdFAP catalyst to activate chloroarenes (Table 4). In an effort to develop a better catalytic system, various solvents and bases were studied for the preparation of 4-acetylbiphenyl by the reaction of 4-chloroacetophenone with phenylboronic acid. DMF: water in the ratio of 50:1 and $K_3PO_4$ in the presence of 30 mol% of TBAB afforded good yields of 4-acetylbiphenyl. The presence of an electron-donating group in the chloroarene retards the reaction whereas an electron-withdrawing moiety acts oppositely by facilitating the oxidative addition step.

### Heck Olefination

We further extended the scope of our PdFAP catalyst to Heck olefination of bromo- and chloroarenes. To identify the best catalytic system for the Heck olefination of styrene with bromo- and chloroarenes, a variety of bases were screened and it was found that PdFAP catalyst with sodium acetate (3 equivs.) afforded good yields of arylated olefins in DMF at 130 °C. The catalytic activity of chloroarenes without TBAB was very low and was significantly improved in the presence of 30 mol% TBAB. The control reaction conducted under identical conditions but devoid of PdFAP gave no coupled product, despite a prolonged reaction time. PdFAP was recovered quantitatively by simple filtration and reused and shows consistent activity even after the third cycle.

**Table 2.** PdFAP-catalyzed Suzuki coupling of iodo- and bromoarenes with phenylboronic acid.[a]

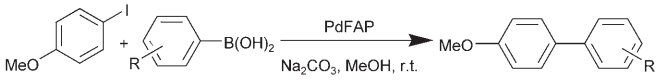


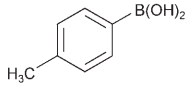
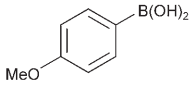
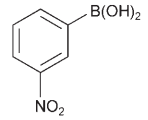
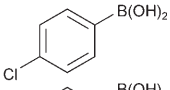
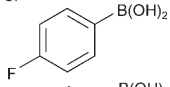
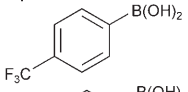
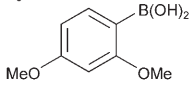
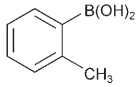

| Entry | Aryl Halides | Time [h] | Yield [%][b] |
|---|---|---|---|
| 1 |  | 4 | 92, 36[d] |
| 2 |  | 4 | 94 |
| 3 |  | 4.5 | 86 |
| 4 |  | 4 | 89 |
| 5 |  | 3 | 93 |
| 6 |  | 9 | 90 |
| 7 |  | 9 | 91, 11[d] |
| 8 |  | 3 | 96 |
| 9 |  | 3 | 95 |
| 10 |  | 5 | 86 |
| 11 |  | 7 | 91[c] |

[a] *Reaction conditions:* aryl halide (1 mmol), phenylboronic acid (1.5 mmol), $Na_2CO_3$ (2 mmol), PdFAP (50 mg) or $1.15 \times 10^{-3}$ mmol of Pd, MeOH (3 mL), room temperature.
[b] Isolated yields.
[c] Instead of phenylboronic acid, 4-methylphenylboronic acid was taken.
[d] PdHAP catalyst ($1.15 \times 10^{-3}$ mmol of Pd) was used.

**Table 3.** PdFAP-catalyzed Suzuki coupling of 4-iodoanisole with various arylboronic acids.[a]

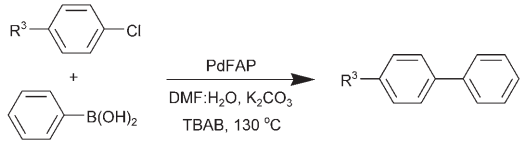



| Entry | Aryl Halides | Time [h] | Yield [%] [b] |
|---|---|---|---|
| 1 |  | 8 | 97 |
| 2 |  | 5 | 94 |
| 3 |  | 24 | 60 |
| 4 |  | 24 | 77 |
| 5 |  | 10 | 92 |
| 6 |  | 10 | 74 |
| 7 |  | 10 | 85 |
| 8 |  | 10 | 99 |

[a] *Reaction conditions:* 4-iodoanisole (1 mmol), arylboronic acid (1.5 mmol), $Na_2CO_3$ (2 mmol), PdFAP (50 mg) or $1.15\times10^{-3}$ mmol of Pd, MeOH (3 mL), room temperature.

[b] Isolated yields.

**Table 4.** PdFAP-catalyzed Suzuki coupling of aryl chlorides with phenylboronic acid.[a]




| Entry | $R^3$ | Time [h] | Yield [%] [b] |
|---|---|---|---|
| 1 | $NO_2$ | 6 | 94 |
| 2 | CN | 6 | 92 |
| 3 | $COCH_3$ | 6 | 94 |
| 4 | H | 30 | 45 |
| 5 | $OCH_3$ | 30 | 32 |

[a] *Reaction conditions:* aryl chloride (1 mmol), boronic acid (1.5 mmol), $K_2CO_3$ (2 mmol), PdFAP (125 mg) or $2.8\times10^{-3}$ mmol of Pd, TBAB (0.3 mmol), DMF:$H_2O$, 50:1-(5 mL), 130 °C.

[b] Isolated yields.

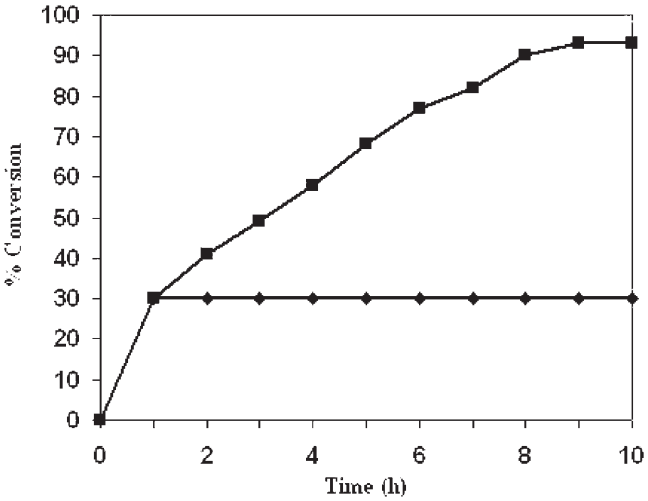


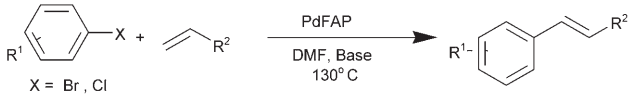

**Figure 6.** Activity profile for bromobenzene a) with catalyst (-■-) and b) with filtrate (-◆-).

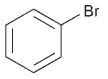
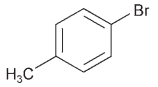
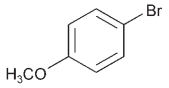
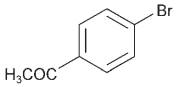
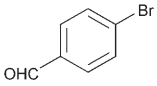
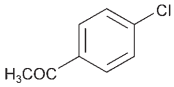
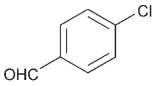
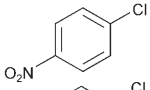
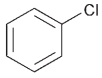
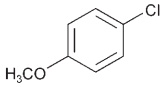
To check the heterogeneity of the catalyst two separate experiments were conducted between bromobenzene and styrene. In the first experiment, for every one-hour interval of time (up to 10 h) a sample (in hot condition) was collected and subjected to GC and ICP-AES analysis. In all the samples the Pd content was found to be within 0.5 to 0.7 ppm. A plot between conversion and reaction time is shown in Figure 6a. In the second experiment, the reaction was terminated at 30% conversion and the catalyst separated by hot filtration. The reaction was continued with the filtrate for additional 10 h and the conversion remained almost unchanged as can be seen from Figure 6b. These studies clearly demonstrate that slight leaching of palladium has taken place from the catalyst (which is not active Pd as confirmed by second experiment) and the reaction proceeds *via* a heterogeneous path. Thus the palladium is bounded to the support throughout the reaction.

We chose a variety of structurally divergent bromo- and chloroarenes possessing a wide range of functional groups to understand the scope and generality of the PdFAP-promoted Heck olefination reaction with styrene to form *trans*-stilbenes and the results are summarized in Table 5. The products are obtained with moderate to excellent yields and with >97% *trans*-selectivity. The olefination of the deactivated electron-rich haloarenes took longer times (Table 5, entries 2, 3 and 10) compared to that of activated electron-poor haloarenes (Table 5, entries 4–8). Thus, the reactivity of these bromo- and chloroarenes in the coupling reactions, which is in the order, activated

**Table 5.** PdFAP-catalyzed Heck olefinations of bromo- and chloroarenes.[a]




| Entry | Aryl Halides | $R^2$ | Time [h] | Yield [%][b] |
|---|---|---|---|---|
| 1 |  | $C_6H_5$ | 10 | 93, 87[c] |
| | | $CO_2CH_3$ | 24 | 91 |
| | | $CO_2CH_2CH_3$ | 24 | 89 |
| 2 |  | $C_6H_5$ | 28 | 84 |
| 3 |  | $C_6H_5$ | 28 | 82 |
| 4 |  | $C_6H_5$ | 24 | 95 |
| 5 |  | $C_6H_5$ | 24 | 91 |
| 6 |  | $C_6H_5$ | 24 | 92[d] |
| 7 |  | $C_6H_5$ | 24 | 91,[d] 45[e] |
| 8 |  | $C_6H_5$ | 24 | 92,[d] 89[e] |
| 9 |  | $C_6H_5$ | 36 | 32[d] |
| 10 |  | $C_6H_5$ | 36 | 29[d] |

[a] *Reaction conditions:* aryl halide (1 mmol), olefin (1.2 mmol), NaOAc (3 mmol), PdFAP (50 mg) or $1.15 \times 10^{-3}$ mmol of Pd , DMF (5 mL), 130 °C.
[b] Isolated yields.
[c] Yield after third cycle.
[d] TBAB (0.3 mmol), PdFAP (125 mg) or $2.8 \times 10^{-3}$ mmol of Pd was used.
[e] Molten TBAB (10 mmol) was used as solvent.

electron-poor haloarenes > non-activated electron-neutral haloarenes > deactivated electron-rich haloarenes, is correlated to the nucleophilicity of the aromatic ring.

In order to expand the scope of the methodology, other alkenes such as methyl acrylate and ethyl acrylate were successfully coupled with bromobenzene to give the corresponding arylated alkenes in good yields (Table 5, entry 1).

## Conclusion

A fluorapatite-supported palladium catalyst (PdFAP) was synthesized by treatment of fluorapatite (prepared by incorporating basic species $F^-$ into apatite by *in situ* by co-precipitation) with $PdCl_2(PhCN)_2$ in acetone and displayed high catalytic activity for Suzuki coupling of aryl iodides and bromides with boronic acids at room temperature and chloroarenes at 130 °C in presence of TBAB to give biaryls in excellent yields. Heck olefinations of chloroarenes were also successfully carried out with this catalyst. PdFAP was recovered quantitatively by simple filtration and reused with consistent activity. PdFAP was well characterized by XRD, FTIR, XPS, ICP-AES, $CO_2$ TPD and CHN elemental analysis. This high catalytic activity is due to the basic support (fluorapatite) which stabilizes and provides adequate electron density to palladium. The noticeable merits of PdFAP catalyst are: 1) the Suzuki reaction with iodo- and bromoarenes can be performed at room temperature, 2) the catalyst is a potential candidate to activate chloroarenes for Suzuki coupling, especially electron-donating chloroarenes, and 3) Heck coupling of chloroarenes can also be performed.

## Experimental Section

### General Remarks

FT-IR spectra were recorded on a Perkin–Elmer spectrophotometer. $^1$H NMR spectra were recorded on Bruker (300 MHz) and Varian Gemini (200 MHz) spectrometers using $CDCl_3$ as solvent and TMS as the internal standard. XPS spectra were recorded on a Kratos AXIS 165 with a dual anode (Mg and Al) apparatus using the Mg Kα anode. X-ray powder diffraction (XRD) data were collected on a Simens/D-5000 diffractometer using Cu Kα radiation. The particle size and external morphology of the samples were observed on a Philips TECNAI F12 FEI transmission electron microscope. Diffuse reflectance UV/VIS spectra for samples as KBr pellets were recorded on a GBC Cintra 10$^e$ UV-VIS spectrometer in the range 200 to 800 nm with a scan speed 200 nm per minute. GC analysis was performed using a Shimadzu GC-2010 and ZB-5 capillary column. All known compounds were characterized by comparing their physical data with those in the literature. Solvents used for the experiments were dried and distilled according to literature procedures. All the reactants were commercially available and used without purification.

### Preparation of Palladium Fluorapatite (PdFAP)

Calcium fluorapatite $[Ca_{10}(PO_4)_6(F)_2]$ was synthesized according to the literature procedure.[37] CaFAP (2 g) was stirred in 150 mL acetone solution of $PdCl_2(PhCN)_2$ ($2.67 \times 10^{-4}$ mol) at 25 °C for 3 h. The obtained slurry was filtered, washed with acetone and dried under vacuum, yielding PdFAP (Pd content: 0.023 mmol per gram).

### Typical Procedure for Suzuki Coupling of Bromo- and Iodoarenes using PdFAP as Catalyst

4-Methylbromobenzene (1 mmol), phenylboronic acid (1.5 mmol), $Na_2CO_3$ (3 mmol), PdFAP (50 mg) or $1.15\times10^{-3}$ mmol of Pd, and methanol (3 mL) were charged in a 10-mL round-bottom flask and stirred at room temperature under a nitrogen atmosphere. After the completion of the reaction (as monitored by TLC), the catalyst was filtered and reused. The filtrate was diluted with ethyl acetate and washed with 10% aqueous NaOH solution and finally with saturated aqueous NaCl solution. The organic layer was dried with $Na_2SO_4$ and concentrated to get the crude productwhich was subjected to column chromatography to afford the pure product.

### Typical Procedure for Suzuki Coupling of Aryl Chlorides Using PdFAP as Catalyst

Aryl chloride (1 mmol), phenylboronic acid (1.5 mmol), $K_2CO_3$ (3 mmol), TBAB (0.3 mmol), PdFAP (125 mg) or $2.8\times10^{-3}$ mmol of Pd, and DMF:$H_2O$, 50:1 (5 mL) were charged in a 10-mL round-bottom flask and stirred at 130 °C. After the completion of the reaction (as monitored by TLC), the catalyst was filtered. The filtrate was treated with ethyl acetate (20 mL) and washed with water. After removing the solvent, the crude material was chromatographed on silica gel (100–200 mesh) to afford the corresponding biaryl.

### General Procedure for Heck Olefination with PdFAP

An olefin (1.2 mmol), haloarene (1 mmol), PdFAP (50 mg) or $1.15\times10^{-3}$ mmol of Pd, sodium acetate (3 mmol), TBAB (0.3 mmol) (in case of aryl chlorides) and 5 mL of DMF were charged in a round-bottom flask and stirred at 130 °C for 24–36 h under a nitrogen atmosphere. After completion of the reaction (as monitored by TLC), the catalyst was centrifuged, the centrifugate was treated with ethyl acetate (20 mL) and washed with water. After removing the solvent, the crude material was chromatographed on silica gel (100–200 mesh) to afford the corresponding *trans*-olefin.

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