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Palladium Ion Catalysed Oxidative C–C Bond Formation Reactions in Arylboronic Acid: Application of Cordierite Monolith Coated Catalyst

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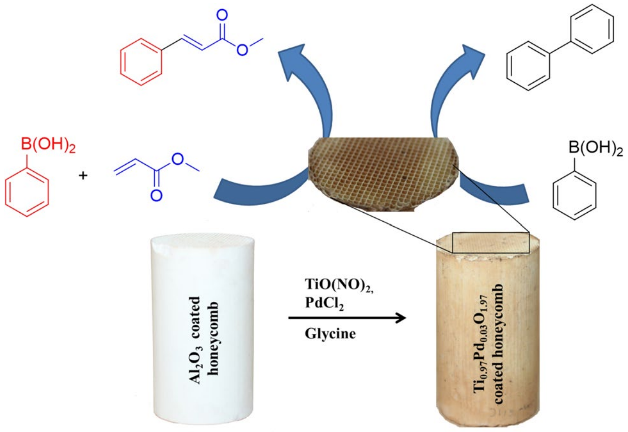
Abstract

Catalytic efficiency of palladium ion substituted in TiO_2, $Ti_{0.97}Pd_{0.03}O_{1.97}$ is successfully exploited for the oxidative homocoupling of arylboronic acid and oxidative Heck coupling reactions between arylboronic acid and olefins. The reaction protocol provides direct approach to synthesize biphenyls and cinnamates from moderate to good yield with good functional group tolerance. As a result, 11 symmetrical biaryls and 14 cinnamates were synthesized from readily available arylboronic acids. $Ti_{0.97}Pd_{0.03}O_{1.97}$ powder catalyst is synthesized by solution combustion method and characterized by powder X-ray diffraction. The C–C bond formation reactions were carried out by catalyst cartridge method using $Ti_{0.97}Pd_{0.03}O_{1.97}$ catalyst coated cordierite monolith. Coating of the catalyst on a cordierite monolith enhanced the applicability of the catalyst and made handling and recycling of the catalyst very easy. Catalyst was recovered and recycled for eight times in both homocoupling and oxidative Heck coupling reactions. The turnover number for both the reactions found to be 443 and 424, respectively.

Graphic Abstract



Keywords Cordierite monolith · Noble metal ionic catalyst · Homocoupling · Oxidative heck reaction · Heterogeneous catalyst · $Ti_{0.97}pd_{0.03}O_{1.97}$

1 Introduction

Biphenyls are building blocks which exhibit a wide range of chemical and physical properties in advanced materials, pharmaceuticals, polymers and natural products [1–8]. Several methodologies have been developed to synthesize both symmetrical and unsymmetrical biaryls [9–12]. Arylboronic acid represents one of the most reliable

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substrate for the synthesis of the class of biphenyls via palladium catalysed homocoupling reaction because of their non-toxic nature, stability and broad tolerance of functional groups. Since arylboronic acids are commercially available, the oxidative homocoupling of these compounds is widely spread method to synthesize biaryls [13–17]. Various protocols have been developed using transition metal catalysts as emerging methodology [18–21]. Palladium has gained very much attention in coupling reactions such as Suzuki coupling reaction, Stille coupling, Negishi coupling and many more from past few decades [22–25]. But these reactions have economical obstacle due to aryl halide or other organometallic reagents.

Another standard synthetic tool to construct C–C bond is Heck coupling reaction from aryl halides and olefins [26–33]. These arylated olefins are present in pharmaceuticals, natural products and advanced organic materials [26–33]. Despite wide range of applications of this reaction, the drawbacks for these reactions are harsh reaction condition, inert atmosphere and production of hydrogen halides [26–35]. Olefins can also be arylated by use of many organometallic arylated reagents such as tin [36–38], silicon [39], and antimony [40–44]. But these reagents and their by-products are highly toxic and difficult to separate from the final product. Therefore, oxidative Heck coupling reaction emerged as very good synthetic tool to synthesize arylated olefins from organoboronic acid and olefins. It required mild reaction condition compared to conventional Heck reaction. The oxidative Heck coupling reaction was first described by Heck in 1975 [31]. The reaction mechanism has shown that an oxidant is required for efficient coupling of olefins with arylboronic acids [45–51]. Recent protocols have shown the usage of molecular oxygen as an oxidant [52–54]. Pure oxygen, however limit the utility of technology for large scale production. Thus, if atmospheric air could be utilized as the palladium reoxidant, allowing a simple open-vessel protocol, the value of the transformation should increase significantly. In 2006, Jung published base free oxidative Heck coupling reaction [55]. Till date, only few palladium(II) system have been used in the oxidative Heck coupling reaction without base [56–59]. In order to get satisfactory result in oxidative Heck coupling reaction, employment of nitrogen or phosphorous based ligands are necessary [59–62]. The current diversity of arylboronic acids, low toxicity, their stability in air and moisture has made oxidative Heck coupling a popular building block in organic reactions [55–62]. Although many successes have been achieved, many of the C–C coupling reactions uses homogeneous catalysts. Compared to homogeneous catalysis, heterogeneous catalysis offers numerous advantages of recoverability, recyclability, easy to-handle and enhanced stability. Furthermore to think that, complete recovering of heterogeneous catalysts are also tedious process such as filtration and centrifugation which leads to loss of expensive catalysts. Therefore, easily separable catalysts are still highly desirable.

Noble metal ionic catalyst has gained much attention in recent years [63]. Pd^{2+} ion substituted in reducible oxides such as CeO_2 and TiO_2 are very good catalysts toward many gas phase reactions such as CO oxidation, NO_x reduction, H_2 and O_2 recombination and hydrocarbon oxidation [63–67]. Among these two reducible oxides, $Ti_{1-x}Pd_xO_{2-x}$ $(x = 0.005$ to $0.03)$ are found to be excellent CO oxidation catalysts even at room temperature compared to same amount of Pd in CeO_2 [65]. Pd ion could be substituted in TiO_2 forming stoichiometric solid solution $Ti_{1-x}Pd_xO_{2-x}$ $(x = 0.005$ to $0.03)$ with Pd in +2 oxidation state leaving an oxide ion vacancy per Pd ion [65]. TiO_2 crystallizing in anatase structure is catalytically active, which is a cheaper reducible oxide support and non-toxic compared to CeO_2. Single phase compounds of the type $Ti_{1-x}Pd_xO_{2-x}$ $(x = 0.005$ to $0.03)$ have been prepared by solution combustion method where 0.5 to 3% of Ti is substituted by Pd ion. Materials are nano crystalline with 5 to 10 nm size so that large surface area is exposed for catalysis. $Ti_{1-x}Pd_xO_{2-x}$ $(x = 0.005$ to $0.03)$ showed high catalytic activity in $H_2 + O_2$ recombination reaction over cordierite monolith honeycomb material [67].

As an effort to develop the application of palladium substituted TiO_2 catalyst, here we report $Ti_{0.97}Pd_{0.03}O_{1.97}$ catalysed oxidative homocoupling and oxidative Heck coupling reactions. Homocoupling of arylboronic acid can be done in presence of mild reagents such as K_2CO_3 as base, $K_2S_2O_8$ as oxidant and acetone–water mixture as solvents. Similarly, we report oxidative Heck coupling reaction. This reaction can be performed under extremely mild conditions, with the use of 1,10-phenanthroline ligand and mixture of toluene-water as solvents, without any oxidant and base. In both reactions catalyst is highly tolerant to various functional groups at all positions on the aryl unit. We have shown efficiency of catalyst in both the reactions for several cycles in recycling process. Handling of powder catalyst could be avoided by coating it over cordierite monolith. Employing cordierite monolith honeycomb material in organic reactions is the uniqueness of this work. On each honeycomb monolith material, 25 mg catalyst was coated, which account for only 0.97 mg (9.2 µmol) of palladium active site in the catalyst.

2 Experimental

2.1 General

X-ray diffraction pattern of catalyst was recorded on a Bruker X-ray diffractometer. NMR spectra were recorded on 400 MHz spectrometers in $CDCl_3$, tetramethylsilane (TMS; $\delta = 0.00$ ppm) served as an internal standard for ^1H NMR. The corresponding residual non-deuterated solvent signal

($CDCl_3$; $\delta = 77.00$ ppm) was used as internal standard for ^{13}C NMR. Column chromatography was carried out by packing glass columns with silica gel 230–400 mesh or 100–200 mesh and thin-layer chromatography was carried out using SILICA GEL GF-254. All reagents and reactants were procured from commercial suppliers. Solvents used for work up and chromatographic procedures were purchased from commercial suppliers and used without further purification.

2.2 Synthesis, Coating and Characterization of Catalyst

Synthesis of $Ti_{1-x}Pd_xO_{2-x}$ ($x = 0$, 0.01, 0.02, 0.03) powder catalyst is reported earlier [65, 68]. Briefly, the catalyst $Ti_{0.97}Pd_{0.03}O_{1.97}$ was synthesized from titanium tetraisopropoxide ($Ti(OC_3H_7)_4$), palladium chloride and glycine by solution combustion method. Initially, $TiO(NO_3)_2$ was prepared in a beaker from titanium tetraisopropoxide (9.7 mmol). 2.7569 g of titanium tetraisopropoxide was added to a beaker containing distilled water (~ 40 mL), it precipitated and settled at the bottom of the beaker. Remaining distilled water has been decanted from the beaker to separate the precipitate. Nearly 3 mL of concentrated HNO_3 was added to dissolve the precipitate and the clear solution is $TiO(NO_3)_2$. $PdCl_2$ (53.1 mg, 0.3 mmol) and glycine (0.80835 g, 10.78 mmol) were dissolved in the same beaker using 0.5–1 mL of conc. HCl and 15 mL of water. Solution was transferred to crystallizing dish and kept for combustion inside a 350 °C pre-heated muffled furnace for 20 min. Then dish was removed, allowed to cool to room temperature and collected the powder catalyst. The catalyst was ground nicely to fine powder and characterized by PXRD. Similarly, $Ti_{0.98}Pd_{0.02}O_{1.98}$ and $Ti_{0.99}Pd_{0.01}O_{1.99}$ were synthesized and characterized by PXRD by varying the quantity of starting materials.

The combustion reaction is given by:

$9(1 - x)TiO(NO_3)_2 + 10(1 - x) C_2H_5NO_2 + 9xPdCl_2 \; 9Ti_{1-x}Pd_xO_{2-} + 20(1 - x) CO_2 + 14(1 - x) N_2 + (25 - 34x) H_2O + 18xHCl$: $x = 0.01$, 0.02, 0.03.

X-ray diffraction patterns were recorded on a Bruker X-ray diffractometer at a scan rate of 0.015°/s with a step size in the 2θ range between 10° and 85°. There are no Pd or PdO peaks in the X-ray diffraction pattern which confirmed that Pd ion has substituted in the TiO_2 lattice.

XPS of Pd/TiO_2 before and after reaction were recorded with a SPECS spectrometer using non-monochromatic AlKα radiation (1486.6 eV) as an X-ray source operated at 150 W (12 kV, 12.5 mA). The binding energies reported here were referenced with C 1s peak at 284.6 eV. Individual core level spectra were recorded with a pass energy of 40 eV and step increment of 0.05 eV. For XPS analysis, samples were made into thin pellets of 9 mm diameter, mounted on the sample holders and placed into a load-lock chamber with an ultra-high vacuum (UHV) of 8.0×10^{-8} mbar for 5 h in order to desorb any volatile species present on the surface. After 5 h, the samples were transferred into the analyzing chamber with UHV of 5.0×10^{-10} mbar one by one and XPS were recorded.

Coating of $Ti_{0.97}Pd_{0.03}O_{1.97}$ catalyst over cordierite monolith: γ-Al_2O_3 was coated over monolith before coating the catalyst, to increase the surface area and adhesion. 15 mmol (3.18 g) of $Al(NO_3)_3$ and 9 mmol (0.675 g) of glycine were taken as starting materials. Solution of starting materials was made in a beaker using 80 mL of water. Pre-weighed monolith was dipped in the solution and kept inside 350 °C preheated muffled furnace for combustion. After 20–30 min, monolith was removed from the furnace and allowed to cool it to room temperature. Weight of the monolith was measured. This procedure was repeated until the weight of γ-Al_2O_3 become 2 to 2.5% of cordierite monolith weight.

Coating the catalyst as follows: The solution was prepared in a 100 mL capacity beaker using starting materials such as $TiO(NO_3)_2$, $PdCl_2$ and glycine. A piece of γ-Al_2O_3 coated monolith was dipped in the solution and kept inside the 350 °C pre-heated muffled furnace for combustion. After 20–30 min the monolith was removed from the furnace and allowed to cool to room temperature. The monolith was kept for sonication process in water to remove loosely held particles, which was dried again in the furnace to remove the water content. This procedure was repeated to get desired weight of catalyst to be coated. 25 mg of catalyst was coated on monolith of 2.5 cm diameter, 2 cm height with 400 cells/inch.

2.3 Procedure for C–C Coupling Reactions

Procedure for homocoupling reaction: Screening reactions were carried out in a 25 mL two necked round bottom flask. 1 equivalent of phenylboronic acid (1.64 mmol, 200 mg), 1.5 equivalent of base, 1.5 equivalent of oxidant and 5 weight percentage of catalyst (10 mg) were mixed with 4 mL of solvent in the flask and stirred at 100 °C on an oil bath. Substrate scope of the reactions were carried out in specially designed flask (figure is given in supporting information). 25 mg coated honeycomb cartridge catalyst was used in these reactions. 500 mg of arylboronic acid (1 equiv.), K_2CO_3 (1.5 equiv.), $K_2S_2O_8$ (1.5 equiv.), mixture of acetone and water as a solvent (3:1, 20 mL) were taken in the flask. The volume of solvent was taken in such way that the honeycomb cartridge catalyst was completely dipped in the solvent. Reactions were performed under open atmosphere at 100 °C temperature. Reactions were monitored by TLC.

Coupled products were extracted by diethyl ether (15 mL) and water (3 × 15 mL) work up to remove base, oxidant and solvents. The aqueous layer was discarded and organic layer was dried under vacuum. Desired coupled products were isolated by column chromatography using petroleum ether and ethyl acetate as eluents. The ratio of eluents was standardized by using TLC according to the polarity of the products. Coupled products were characterized by ^{1}H NMR and ^{13}C NMR. The honeycomb catalyst used in the reactions were taken out from the flask, washed with water (15 mL) to remove base and oxidant, and then washed with hexane (15 mL) to remove organic compounds. Washed honeycomb was dried in a furnace at 200 °C for 2 h and it was used for another reaction.

Procedure for oxidative Heck coupling reaction: Reactions were carried out in a 25 mL round bottom flask. 200 mg of phenylboronic acid (1 equiv.), 155.3 mg of methyl acrylate (1.1 equivalent), 65 mg of 1,10-phenanthroline (0.2 equivalent) and 10 mg of catalyst (5 weight percentage to the phenylboronic acid) were charged into the flask. 4 mL of toluene and 1 mL of water were added and kept on 110 °C pre-heated oil bath. Reaction was monitored by using TLC. After completion of the reaction, flask was allowed to cool to room temperature. Coupled product was extracted using diethyl ether and water workup. The aqueous layer was discarded and organic layer was collected. Organic layer was dried under vacuum and collected the crude product. Coupled product was isolated by column chromatography by using the petroleum ether and ethyl acetate as eluents. Isolated products were characterized by ^{1}H NMR and ^{13}C NMR.

In the recycling of the catalyst process, specially designed flask was used to accommodate honeycomb monolith catalyst. 500 mg of phenylboronic acid (4.1 mmol, 1 equiv.), 388.3 mg of methyl acrylate (4.51 mmol, 1.1 equiv.) and 162.4 mg of 1,10-phenanthroline (0.82 mmol, 0.2 equiv.) were charged into the flask, catalyst coated monolith was also placed in the flask. 16 mL toluene and 4 mL water were added (4:1, total 20 mL), condenser was fitted and kept on oil bath. Reaction was monitored by TLC. Crude product was extracted as explained earlier followed by isolation by column chromatography.

After each reaction, honeycomb monolith was taken out from the flask, washed with water to remove solvent and ligand, and then washed with hexane to remove any organic compounds. Washed monolith was kept in a hot air oven at 200 °C, for 2 h and used for another reaction.

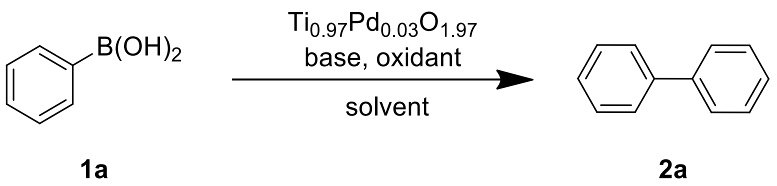
3 Results and Discussion

3.1 Optimization and Substrate Scope of Homocoupling Reaction

Synthesis, characterization and coating method of $Ti_{0.97}Pd_{0.03}O_{1.97}$ catalyst over cordierite monolith honeycomb were reported in earlier studies [65–67]. Phenylboronic acid (200 mg, 1 equiv.) was chosen as a model substrate for the optimization studies of homocoupling reaction, and the results are summarized in Table 1 where 10 mg of powder catalyst is used in each of the reactions. Initially, K_2CO_3 (1.5 equiv.) was used as base, $K_2S_2O_8$ (1.5 equiv.) as oxidant and toluene–water mixture (3:1 ratio, 4 mL) used as solvent in the reaction and the yield was 30% after 24 h (Table 1, entry1). In next reaction, only toluene has been used as a solvent, which led to 38% yield (Table 1, entry 2). Screening was continued at different temperature by using various solvents (Table 1, entry 2 to entry 12). Mixture of acetone and water turned out to be a better solvent for the reaction which gave **2a** in 91, 92, 98 and 100% (Table 1, entry 3–6) at room temperature, 50 °C, 90 °C and 100 °C, respectively. In every reaction 10 mg of $Ti_{0.97}Pd_{0.03}O_{1.97}$ powder catalyst was used whereas the reaction without catalyst was unsuccessful (Table 1, entry 7). Acetone and water mixture was a better solvent than neat acetone and neat water (Table 1, entry 8 and entry 9), Similarly, reactions with solvents such as 1,4-dioxane/water (3:1, 4 mL) and methanol at room temperature furnished low yields of biphenyl (trace amount and 20% respectively, Table 1, entry 10, entry 11) whereas, reaction in ethanol furnished 70% yield after 20 h of reaction (Table 1, entry 12). The reaction without oxidant in acetone/water mixture (3:1, 4 mL) (Table 1, entry 13) and reaction under oxygen as an oxidant furnished biphenyl in trace amount of yield (Table 1, entry 14). Optimization studies were continued for base screening. The reaction without base was unsuccessful (Table 1, entry 15), reaction with KOH and Cs_2CO_3 furnished biphenyl in 67% and 86% yield, respectively (Table 1, entry 16 and entry 17). Finally, we decided to keep K_2CO_3 (1.5 equiv.) as base, $K_2S_2O_8$ (1.5 equiv.) as oxidant at 100 °C for 1.5 h in acetone/water (3:1, 4 mL) with 10 mg of powder catalyst (5 weight percentage to phenylboronic acid) as standard reaction conditions (Table 1, entry 6) for the scope of substrates.

Core levels of Pd (3d), Ti (2p), O (2s) and C (1s) in XPS of Pd substituted TiO_2 before and after the catalytic reaction were recorded. XPS studies show that, Pd ($3d_{5/2}$) of $Ti_{0.97}Pd_{0.03}O_{1.97}$ showing a peak at 337.5 eV and thus Pd is in +2 state [65]. After the reaction also, Pd is in +2 state with Pd ($3d_{5/2}$) peak at 337.5 ± 0.2 eV and it has not reduced to Pd^0.Pd (3d) and Ti (2p) core level spectra are given in Fig. 1. Ti ($2p_{3/2}$) and O (1s) showing peaks at 459.0 ± 0.2 eV

Table 1 Optimization of reaction conditions



Entry	Base	Oxidant	Solvent	Temp (°C)	Time (h)	Yield (%)
1.	K_2CO_3	$K_2S_2O_8$	Toluene/Water (2:1)	110	24	30
2.	K_2CO_3	$K_2S_2O_8$	Toluene	110	24	38
3.	K_2CO_3	$K_2S_2O_8$	Acetone/water (3:1)	RT	20	91
4.	K_2CO_3	$K_2S_2O_8$	Acetone/water (3:1)	50	20	92
5.	K_2CO_3	$K_2S_2O_8$	Acetone/water (3:1)	90	3.5	98
6.	K_2CO_3	$K_2S_2O_8$	Acetone/Water (3:1)	100	1.5	100
7.	K_2CO_3	$K_2S_2O_8$	Acetone/water (3:1)	RT	20	NR[b]
8.	K_2CO_3	$K_2S_2O_8$	Acetone	RT	20	41
9.	K_2CO_3	$K_2S_2O_8$	Water	RT	20	30
10.	K_2CO_3	$K_2S_2O_8$	1,4-Dioxane/Water (3:1)	RT	20	trace
11.	K_2CO_3	$K_2S_2O_8$	Methanol	RT	20	20
12.	K_2CO_3	$K_2S_2O_8$	Ethanol	RT	20	70
13.	K_2CO_3	-	Acetone/water (3:1)	100	20	NR
14.	K_2CO_3	O_2	Acetone/water (3:1)	100	20	trace
15.	-	$K_2S_2O_8$	Acetone/water (3:1)	100	20	trace
16.	KOH	$K_2S_2O_8$	Acetone/water (3:1)	100	5	67
17.	Cs_2CO_3	$K_2S_2O_8$	Acetone/water (3:1)	100	5	86

Reaction conditions: 1 equivalent of **1a** (1.64 mmol, 200mg), 1.5 equivalent of base, 1.5 equivalent of oxidant, 5 weight percentage of $Ti_{0.97}Pd_{0.07}O_{1.97}$ catalyst (10 mg), 4 mL solvent. All are isolated yield. [b] Reaction without catalyst, NR – no reaction

and 530 ± 0.2 eV respectively, confirm that Ti is in +4 state as in TiO_2.

We explored the scope of the reaction for different substrates of arylboronic acid (Table 2). 500 mg of various arylboronic acids were taken for each of the reaction and 25 mg of $Ti_{0.97}Pd_{0.03}O_{1.97}$ coated honeycomb monolith catalyst was used in the substrate scope. As can be seen, the reaction proceeded well with variety of substituted arylboronic acids. The homocoupling reactions of phenylboronic acid, *p*-methylphenylboronic acid, *m*-methylphenylboronic acid and *o*-methylphenylboronic acid gave corresponding biaryl derivative **2a, 2b**, **2c** and **2d** in more than 99% yields, respectively. The reaction of halo-substituted arylboronic acids such as 3-chlorophenylboronic acid,

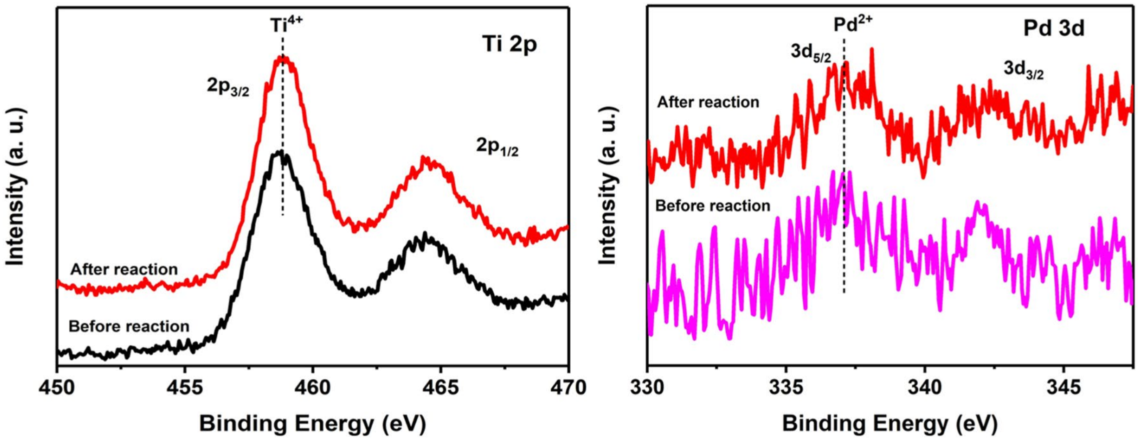


Fig. 1 Ti (2p) and Pd (3d) core level XPS of $Ti_{0.97}Pd_{0.03}O_{1.97}$ before catalytic reaction and after catalytic reaction

4-chlorophenylboronic acid, 3,4-dichlorophenylboronic acid and 4-fluorophenylboronic acid proceeded smoothly furnishing the products **2e**, **2f**, **2g** and **2h** in 99%, 99%, 87% and 92% yields, respectively. 4-methoxyphenylboronic acid, 4-cyanophenylboronic acid and 4-aminophenylboronic acid underwent homocoupling reaction forming the coupled products **2i**, **2j** and **2k** in 95%, 86% and 80% yields, respectively. These experiments reveal that the catalyst is well tolerated to electron—withdrawing or electron—donating groups which led to corresponding coupled products in good to excellent yields. In the substrate scope experiment, only 3 catalyst coated honeycomb monoliths have been used for all the homocoupling reactions of arylboronic acid where each of the honeycomb monoliths were recycled. Cumulative turnover numbers have been calculated for each of the honeycomb monolith catalysts which are 1637, 1298 and 971, respectively (Table 3).

We have performed cross coupling reactions between two different arylboronic acids under standard optimized conditions (Scheme 1). Firstly, 3-chlorophenylboronic acid and 4-methoxyphenylboronic acid were chosen for the cross coupling reaction, furnishing the products **2e**, **2i** and **2ei** in 22%, 25% and 46% yields, respectively. We observed that the percentage yields of each of the symmetrical biaryls such as **2e** and **2i** were almost half of the unsymmetrical biaryl, **2ei**. Cross coupling experiment was repeated by taking 3-chlorophenylboronic acid and phenylboronic acid, the reaction furnished the products **2e**, **2a** and **2ea** in 23%, 23% and 45% yields, respectively, which are of same trend as observed in previous cross coupling reaction.

3.2 Reaction Mechanism of Homocoupling Reaction

Plausible mechanism for the homocoupling reaction is depicted in Scheme 2. In the initial step, oxidative addition of aryl moiety to palladium catalyst takes place which leads to organopalladium complex **A**. In next step, another arylboronic acid activated by base interacts with complex **A** resulting in the formation of intermediate **B**. Finally, reductive elimination occurs to form desired homocoupled product and the catalyst recovers for next run. In cross coupling reaction both the arylboronic acids are almost equally capable to form complex **A**. Therefore, we observed homocoupled products along with cross coupled product.

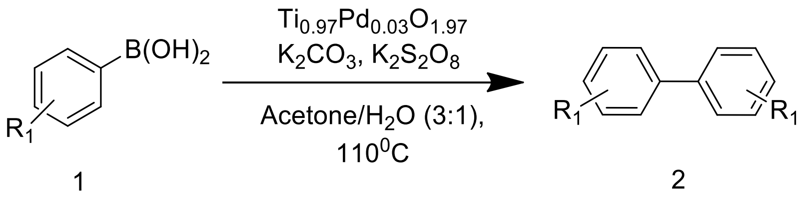
3.3 Comparison of $Ti_{0.97}Pd_{0.03}O_{1.97}$ Catalyst with Other Pd-Catalysts in Homocoupling Reaction

Activity of $Ti_{0.97}Pd_{0.03}O_{1.97}$ catalyst in Homocoupling reactions have been compared with two other catalysts such as $PdCl_2$ and 3% Pd/C. In both the cases, reaction furnished the biphenyl in 76% and 80% yields respectively, but we observed that the reaction also furnished phenol as a by-product in 20 to 25% yield. In case of $Ti_{0.97}Pd_{0.03}O_{1.97}$ catalyst, complete conversion with 100% yield of biphenyl has been achieved. Here $Ti_{0.97}Pd_{0.03}O_{1.97}$ gets advantage of selectivity, recoverability and recyclability over $PdCl_2$ and Pd/C catalysts. TON for $PdCl_2$ and Pd/C were nearly 250 to 400, whereas TON for $Ti_{0.97}Pd_{0.03}O_{1.97}$ was 443 and still the catalyst coated monolith was not deactivated after several cycles which can be used further for many more reactions.

3.4 Optimization and Substrate Scope of Oxidative Heck Reaction

Reactivity, recyclability and stability of the catalyst showed in homocoupling reaction, prompted us to investigate the catalytic activity in oxidative heck reaction between arylboronic acid and olefins. Screening of the reaction has been studied using phenylboronic acid and methyl acrylate as model substrates. Initially, reaction was performed using

Table 2 Substrate scope



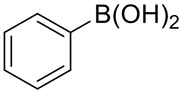
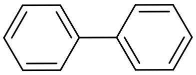
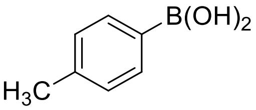
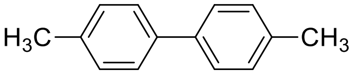
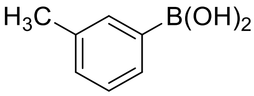
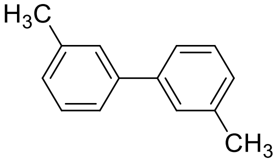
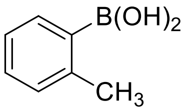
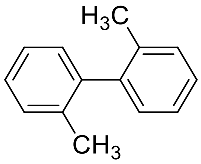
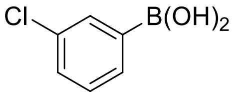
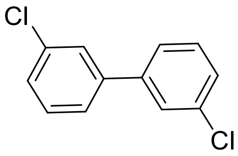
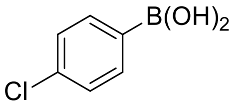
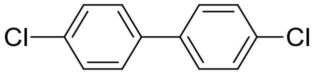
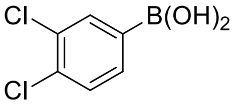
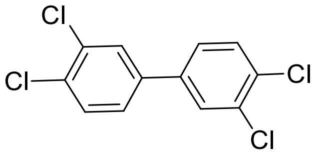
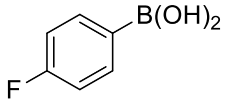
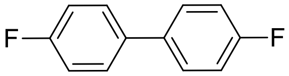
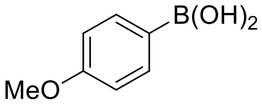
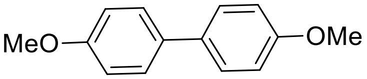
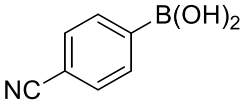
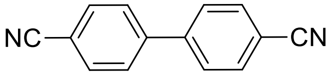
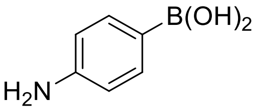
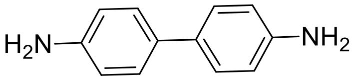
Entry	Substrates	Products	Time (h)	Yield (%)[b]
1	 **1a**	 **2a**	1.5	>99
2	 **1b**	 **2b**	4	>99
3	 **1c**	 **2c**	4	>99
4	 **1d**	 **2d**	4	>99
5	 **1e**	 **2e**	2	>99
6	 **1f**	 **2f**	3	>99

Table 2 (continued)

7	 **1g**	 **2g**	3	87
8	 **1h**	 **2h**	2	92
9	 **1i**	 **2i**	2	95
10	 **1j**	 **2j**	3.5	86
11	 **1k**	 **2k**	3	80

Reaction conditions: 1 equivalent of arylboronic acid (4.1 mmol, 500 mg), 1.5 equivalent of K_2CO_3 (6.15 mmol, 850 mg), 1.5 equivalent of $K_2S_2O_8$ (6.15 mmol, 1661 mg), 5 weight percentage of $Ti_{0.97}Pd_{0.03}O_{1.97}$ catalyst (25 mg coated over honeycomb monolith), 15 mL of acetone, 5 mL of water, 100 ^{0}C. All are isolated yields.

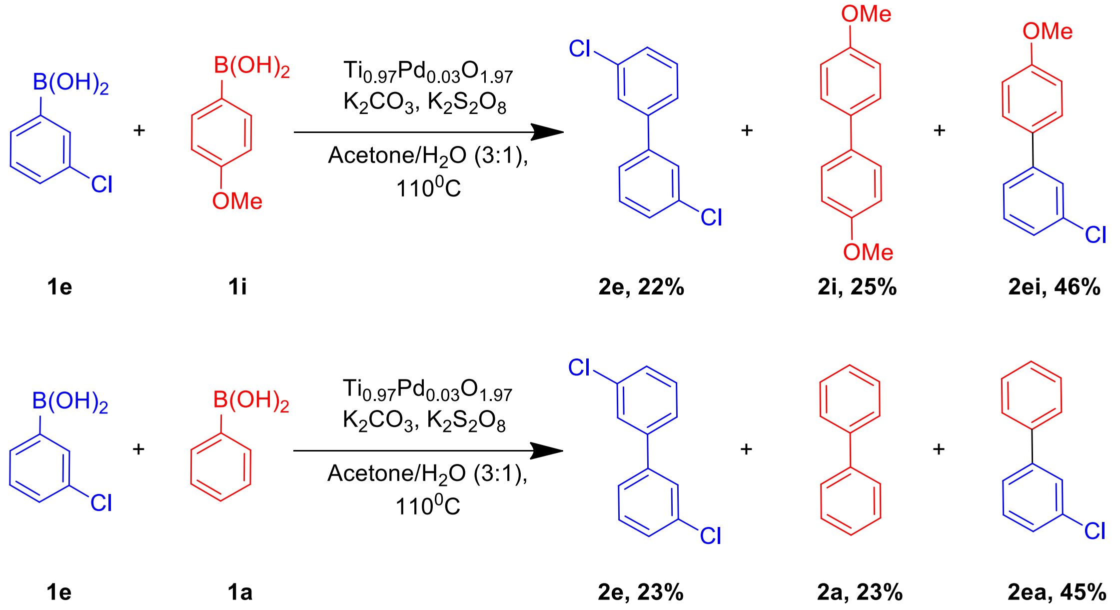
K_2CO_3 (1.5 equiv.) as base and O_2 as oxidant at 110 °C in *N*,*N*-dimethylformamide (DMF), reaction was unsuccessful (Table 4, entry 1) whereas, reaction without base was also unsuccessful (Table 4, entry 2). In next reaction, Na_2CO_3 has been used as base under oxygen atmosphere; no product has been observed (Table 4, entry 3). In next reaction, K_2CO_3 has been employed as base, with trifluoroacetic acid (TFA), no reaction was observed (Table 4, entry 4), similarly, reaction without oxidant also unsuccessful (Table 4, entry 5). When reaction was carried out with the oxidant, $K_2S_2O_8$ at 90 °C, furnished the product **5aa** in 10% (Table 4, entry 6). Interestingly, when oxidant, $K_2S_2O_8$ was employed without any base, furnished the yields **5aa** in 40% and 48% at 80 °C and 120 °C, respectively (Table 4, entry 7 and entry 8). In presence of base, NEt_3 and KOH, the yield decreased to 20% and 25%, respectively (Table 4, entry 9 and entry 10). In next reactions, solvent was changed to toluene, acetic acid and toluene/water mixture (4/1, 5 mL) by using K_2CO_3, $K_2S_2O_8$ at 90 °C, all three reactions were unsuccessful (Table 4, entry 11 to entry 13), even the reaction in mixture of acetic acid and 3 N of HCl, without base and oxidant at 90 °C was also unsuccessful (Table 4, entry 14). In next reactions, oxidant was changed to $Cu(OAc)_2$, furnished the product **5aa** in 25% and 36% at room temperature and 100 °C, respectively (Table 4, entry 15 and entry 16), whereas reaction without base was failed to furnish **5aa** (Table 4, entry 17). Till now,

Table 3 Turn over number (TON) for each of the honeycomb monolith (HCM)

HCM	Substrates (% yield)	TON	Cumulative TON
1	**2a** (> 99)	443	1637
	2b (> 99)	398	
	2c (> 99)	398	
	2d (> 99)	398	
2	**2e** (> 99)	347	1298
	2f (> 99)	347	
	2g (87)	248	
	2h (92)	356	
3	**2i** (95)	338	971
	2j (86)	317	
	2k (80)	316	

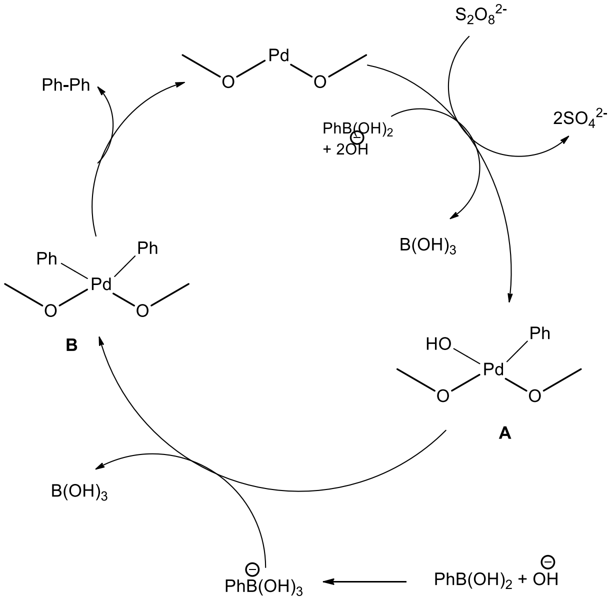
none of the reactions has furnished **5aa** quantitatively. Now onwards 1,10-phenanthroline ligand (0.2 equiv.) has been employed in the reaction. The reaction in toluene/water mixture (4/1, 5 mL), by using K_2CO_3 and 1,10-phenanthroline ligand, furnished **5aa** in 92% yield at 110 °C (Table 4, entry 18), whereas at room temperature reaction was unsuccessful (Table 4, entry 19). Reactions were unsuccessful too in DMF and H_2O (Table 4, entry 20 and entry 21). In next reaction, base was not used, interestingly in presence of ligand reaction furnished **5aa** in 96% at 110 °C after 2.5 h (Table 4, entry 23). It is confirmed that ligand has huge impact in the reaction along with palladium catalyst. In presence of oxidant $K_2S_2O_8$, reaction furnished only 45% yield at 110 °C (Table 4, entry 24). Solvent ratio has been changed to 3/2 (5 mL) instead of 4/1 ratio (5 mL) of toluene/water mixture, there was slight decrease in the yield up to 91% (Table 4, entry 25). Finally, we decided to keep entry 23 (Table 4) as the standard conditions for the substrate scope of oxidative Heck coupling reaction. In each of the screening reaction 10 mg catalyst (5 weight percentage to phenylboronic acid) has been used which accounts for 3.6 μmol of palladium ion (0.38 mg of Pd^{2+}).

We explored scope of the substrates in oxidative Heck coupling reaction by employing the standard conditions (Table 5). Phenylboronic acid, 4-methylboronic acid, 4-methoxyphenylboronic acid, 4-chlorophenylboronic acid and 4-acetylphenylboronic acid reacted very well with various acrylates affording Heck coupled products with a high



Reaction conditions: 0.5 equivalent arylboronic acids (250 mg), 1.5 equivalent of K_2CO_3 (6.15 mmol, 850 mg), 1.5 equivalent of $K_2S_2O_8$ (6.15 mmol, 1661 mg), 5 weight percentage of $Ti_{0.97}Pd_{0.03}O_{1.97}$ catalyst (25 mg coated over honeycomb monolith), 15 mL of acetone, 5 mL of water, 100 ^{0}C. All are isolated yields.

Scheme 1 Cross coupling reactions of arylboronic acid



Scheme 2 Proposed mechanism for homocoupling reaction

selectivity in quantitative yields. Reaction of phenylboronic acid (**3a**) with methyl acrylate (**4a**), ethyl acrylate (**4b**) and *n*-butyl acrylate (**4c**) furnished **5aa**, **5ab** and **5ac** in 96, 89 and 92% yields, respectively (Table 5, entry 1–3). The reaction of 4-methylphenylboronic acid (**3b**) with **4a**, **4b** and **4c** afforded coupled product **5ba**, **5bb** and **5bc** in 90, 92 and 89% yields, respectively (Table 5, entry 4–6). The reaction of 4-methoxyphenylboronic acid (**3c**) with **4a**, **4b** and **4c** furnished **5ca**, **5cb** and **5 cc** in 91, 74 and 83% yields, respectively (Table 5, entry 7–9). Reaction of **3a** with phenyl acrylate (**4d**) and benzyl acrylate (**4e**) furnished **5ad** and **5ae** in 95 and 96% yields, respectively (Table 5, entry 10 and entry 11). Reaction of 4-chlorophenylboronic acid (**3d**) with **4a** and **4b** afforded **5da** and **5db** in 80 and 82% yields, respectively (Table 5, entry 12 and entry 13). Finally, reaction of 4-acetylphenylboronic acid (**3e**) with **4a** produced **5ea** in 86% yield (Table 5, entry 14). Overall, the catalyst tolerated for various types of arylboronic acid and acrylates despite having electron withdrawing or electron donating groups.

3.5 Reaction Mechanism of Oxidative Heck Reaction

In the first step, ligand attacks to the palladium forms a complex which facilitates oxidative addition of phenylboronic acid along with air oxidant. In the next step, peroxo bond breaks easily with the elimination of boric acid. The mechanism moves further by the adsorption of methyl acrylate leads to the formation of palladacycle which eventually disintegrate with the elimination of water. In the final step, coupled product obtained by reductive elimination and catalyst recovers for next run with the help of ligand. The plausible mechanism is depicted in Scheme 3.

Scheme 3 Proposed mechanism for oxidative Heck coupling reaction

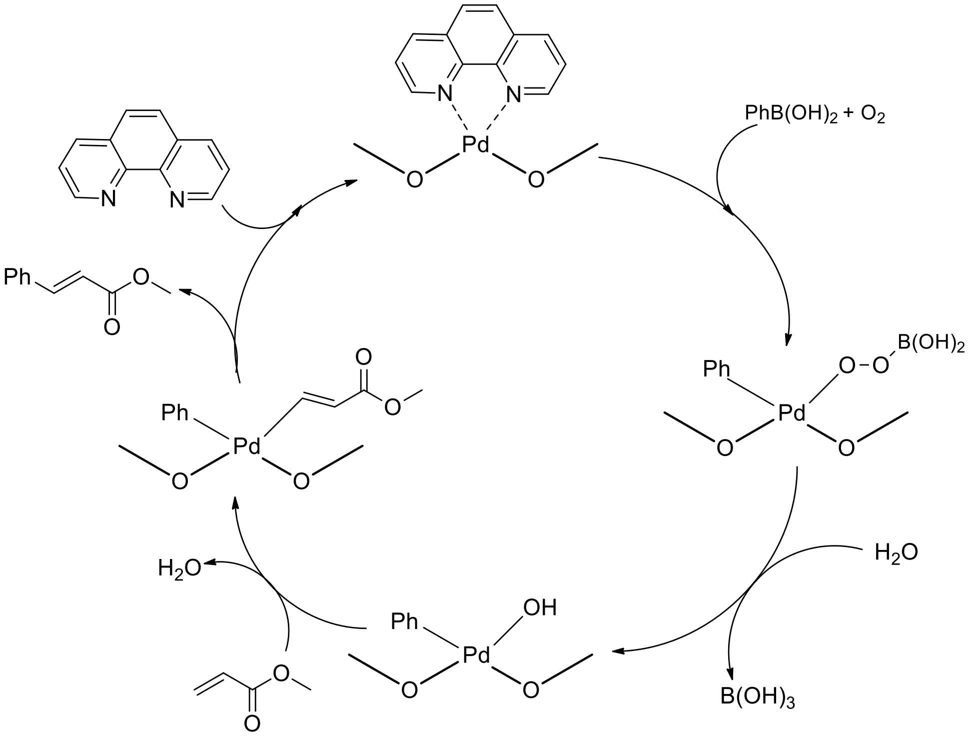
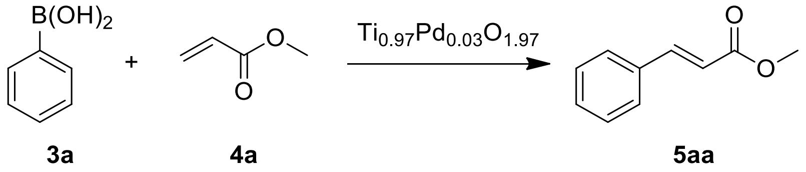


Table 4 Screening of oxidative Heck coupling reaction



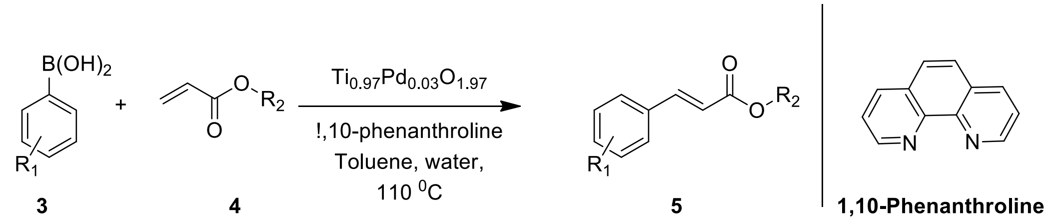
Entry	Base	Oxidant	Solvent	T (⁰C)	Time (h)	Yield (%)[b]
1.	K_2CO_3	O_2	DMF	110	24	NR
2.	-	O_2	DMF	80	24	Trace
3.	Na_2CO_3	O_2	DMF	RT	24	Trace
4.	K_2CO_3	TFA	DMF	110	24	NR
5.	K_2CO_3	-	DMF	110	24	NR
6.	K_2CO_3	$K_2S_2O_8$	DMF	90	24	10
7.	-	$K_2S_2O_8$	DMF	80	24	40
8.	-	$K_2S_2O_8$	DMF	120	24	48
9.	NEt_3	$K_2S_2O_8$	DMF	120	24	20
10.	KOH	$K_2S_2O_8$	DMF	120	24	25
11.	K_2CO_3	$K_2S_2O_8$	Toluene	90	24	Trace
12.	K_2CO_3	$K_2S_2O_8$	Acetic acid	90	24	Trace
13.	K_2CO_3	$K_2S_2O_8$	Toluene/H_2O (4/1)	90	24	NR
14.	-	-	Acetone/3N HCl (4/1)	RT	24	NR
15.	K_2CO_3	$Cu(OAc)_2$	Acetone	RT	24	25
16.	K_2CO_3	$Cu(OAc)_2$	Acetone	100	24	36
17.	-	$Cu(OAc)_2$	Acetone	RT	24	Trace
18.	K_2CO_3	-	Toluene/H_2O (4/1)	110	5	92[c]
19.	K_2CO_3	-	Toluene/H_2O (4/1)	RT	10	NR[c]
20.	K_2CO_3	-	DMF	110	10	Trace[c]
21.	K_2CO_3	-	H_2O	110	10	NR[c]
22.	K_2CO_3	-	Toluene/H_2O (4/1)	110	5	NR
23.	-	-	Toluene/H_2O (4/1)	110	2.5	96[c]
24.	-	$K_2S_2O_8$	Toluene/H_2O (4/1)	110	5	65[c]
25.	-	-	Toluene/H_2O (3/2)	110	3	91[c]

Reaction conditions: 1 equivalent of phenylboronic acid (1.64 mmol, 200 mg), 1.1 equivalent of methyl acrylate (1.8 mmol, 155.25 mg), base (1.5 equivalent), oxidant (1.5 equivalent), 5 weight percentage of catalyst (10 mg), 5 mL of solvent. [b]isolated yield, [c]0.2 equivalent of 1,10 – phenanthroline (0.33 mmol, 59.04 mg).

3.6 Comparison of $Ti_{0.97}Pd_{0.03}O_{1.97}$ Catalyst with Other Pd-Catalysts in Oxidative Heck Reaction

Activity of $Ti_{0.97}Pd_{0.03}O_{1.97}$ catalyst has been compared with other catalysts in oxidative Heck reaction between **3** and **4a** which is summarized in Table 6. Various catalysts

Table 5 Oxidative Heck coupling of various substrates



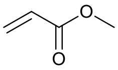
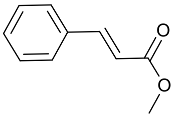
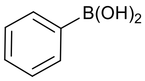
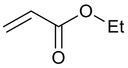
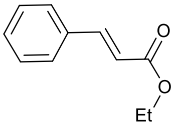
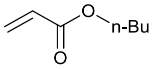
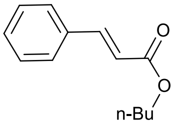
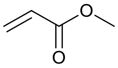
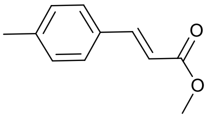
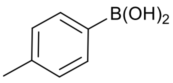
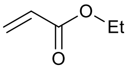
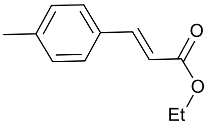
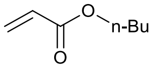
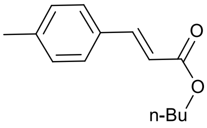
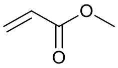
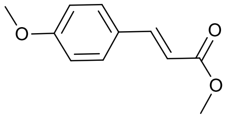
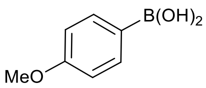
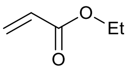
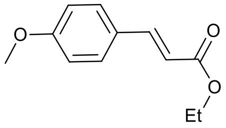
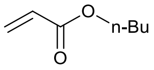
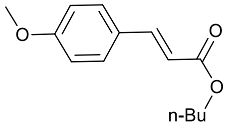
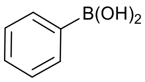
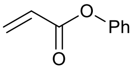
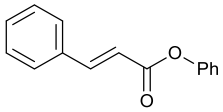
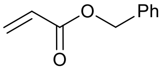
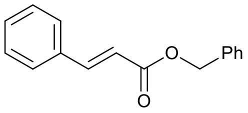
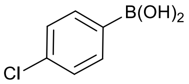
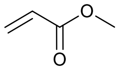
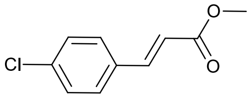
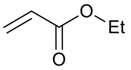
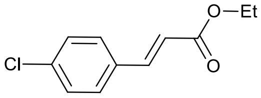
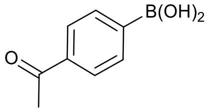
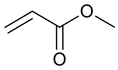
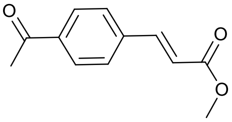
Entry	$R_1PhB(OH)_2$	Olefins	Product	Time (h)	Yield (%)
1.		 **4a**	 **5aa**	2.5	96
2.	 **3a**	 **4b**	 **5ab**	3	89
3.		 **4c**	 **5ac**	2.5	92
4.		 **4a**	 **5ba**	4	90
5.	 **3b**	 **4b**	 **5bb**	4	92
6.		 **4c**	 **5bc**	5	89
7.		 **4a**	 **5ca**	5	91
8.	 **3c**	 **4b**	 **5cb**	5	74
9.		 **4c**	 **5cc**	5	83

Table 5 (continued)

10.	 **3a**	 **4d**	 **5ad**	2	95
11.		 **4e**	 **5ae**	2	96
12.	 **3d**	 **4a**	 **5d** **a**	4	80
13.		 **4b**	 **5** **db**	3	82
14.	 **3e**	 **4a**	 **5ea**	5	86

Reaction conditions: 1 equivalent of phenylboronic acid (1.64 mmol, 200 mg), 1.1 equivalent of methyl acrylate (1.8 mmol, 155.25 mg), powder catalyst (10 mg), 0.2 equivalent of 1,10 – phenanthroline (0.33 mmol, 59.04 mg), 4 mL of toluene, 1 mL of water, 110 ^{0}C. All are isolated yield.

Table 6 Oxidative Heck reaction with different catalyst

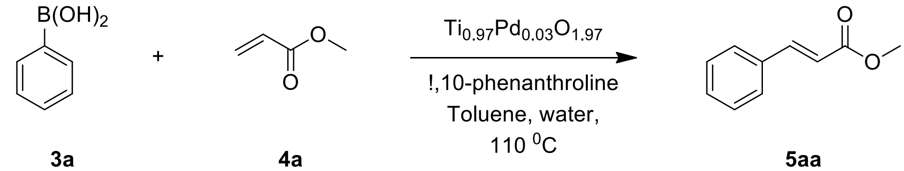
Entry	Catalyst	Weight of the catalyst (mg)	Time (h)	Yield (%)	TOF (h^{-1})
1	$Ti_{0.97}Pd_{0.03}O_{1.97}$	10	2.5	96	172
2	$Ti_{0.97}Pd_{0.03}O_{1.97}$[a]	25	2	95	212
3	$Ti_{0.98}Pd_{0.02}O_{1.98}$	10	5	71	63
4	$Ti_{0.99}Pd_{0.01}O_{1.99}$	10	10	45	20
5	TiO_2	40	20	NR	–

Reaction conditions: 1 equivalent of phenylboronic acid (1.64 mmol, 200 mg), 1.1 equivalent of methyl acrylate (1.8 mmol, 155.25 mg), powder catalyst (10 mg), 0.2 equivalent of 1,10-phenanthroline (0.33 mmol, 59.04 mg), 4 mL of toluene, 1 mL of water, 110 °C. All are isolated yield

[a] Coated honeycomb monolith catalyst

have been prepared by solution combustion method. Catalyst having 3% palladium has shown very good catalytic activity under standard conditions, furnishing **5aa** in 96% yield with TOF 172 h^{-1} (Table 6, entry 1). When $Ti_{0.97}Pd_{0.03}O_{1.97}$ coated honeycomb monolith was used in the reaction, reaction completed within 2 h, furnishing the product in 95% yield with TOF 212 h^{-1} (Table 6, entry 2). The reason being more catalysts are exposed to the reactant due to much higher surface area of honeycomb monolith. Reactions become slower when $Ti_{0.98}Pd_{0.02}O_{1.98}$ and $Ti_{0.99}Pd_{0.01}O_{1.99}$ were used in the reactions, furnished **5aa** in 71% and 40% yield with TOF 63 and 20 h^{-1}, respectively (Table 6, entry 3 and entry 4). No reaction has been observed when TiO_2 was used as a catalyst (Table 6, entry

Scheme 4 Scale up reaction



3a 3g, 24.6 mmol

4a 2.53g, 29.5 mmol

5aa 3.5g, 22.09 mmol

5). Reaction was scaled up to 3 g by using 100 mg coated honeycomb monolith catalyst and it furnished **5aa** in 90% yield in 4 h (Scheme 4).

3.7 Recycling of $Ti_{0.97}Pd_{0.03}O_{1.97}$ Catalyst

We have carried out the recycling of the catalyst for both homocoupling reaction and oxidative Heck coupling reactions. Starting materials were taken by employing standard conditions. Cordierite monolith honeycomb was used in the recycling process by coating 25 mg of the catalyst which accounts for 9.2 µmol (0.97 mg) of Pd^{2+} as an active site in the catalyst. The catalyst was recycled for 8 times in homocoupling reaction of phenylboronic acid. Reaction furnished 100% yield at 1st cycle and 90% yield at 8th cycle. The total turnover number (TON) has been calculated which is 3419 after 8 cycles. Similarly, catalyst was recycled for 8 times in oxidative Heck coupling reaction between phenylboronic acid and methyl acrylate. At first cycle, reaction furnished the product in 96% yield, whereas the reaction at 8th cycle, it was 82% yield. The turnover number after 8 cycles of the reaction is 2839. The reaction time in recycling process increased from 1.5 h to 5 h in homocoupling and 2 h to 4 h in oxidative Heck coupling reactions. A recent review tells that the general rule in the recycling process is that the decrease in percentage yield cannot be higher than the number of cycles [69]. Our catalyst showed decrease in catalytic activity in long run, but the method of using cordierite monolith in the organic synthesis made easy to separate the catalyst from the reaction mixture and recycle it for another reaction which is highly desirable for industrial application.

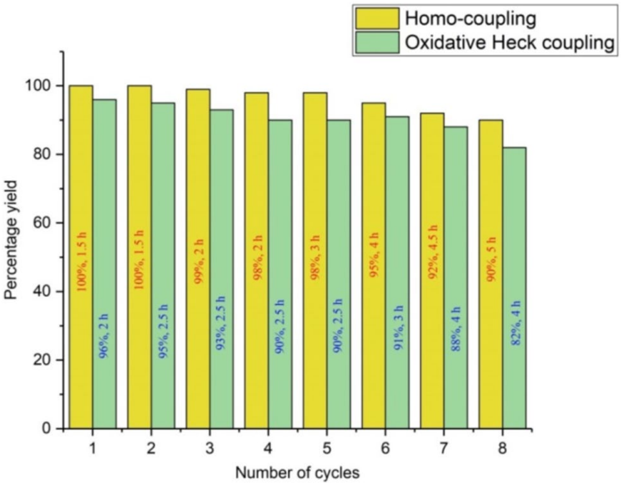


Fig. 2 Recycling of the catalyst in homocoupling and oxidative Heck coupling reactions. Reaction conditions for homocoupling reaction: 1 equivalent of phenylboronic acid (4.1 mmol, 500 mg), 1.5 equivalent of K_2CO_3 (6.15 mmol, 850.3 mg), 1.5 equivalent of $K_2S_2O_8$ (6.15 mmol, 1662.4 mg), $Ti_{0.97}Pd_{0.03}O_{1.97}$ (25 mg coated on cordierite monolith), acetone (15 mL), water (5 mL), 100 °C, all are isolated yield. Reaction conditions for oxidative Heck coupling reaction: 1 equivalent of Phenylboronic acid (4.1 mmol, 500 mg), 1.1 equivalent of methyl acrylate (4.51 mmol, 388 mg), 0.2 equivalent of 1,10-phenanthroline (0.82 mmol, 147.7 mg), toluene (16 mL), water (4 mL), 110 °C, all are isolated yield

To investigate the catalyst leaching, we have performed the following experiment. The cordierite monolith was taken in the reaction flask and solvent mixture (15 mL acetone, 5 mL water) was added to it; stirred the reaction flask at 100 °C. After 2 h, we removed cordierite monolith from the flask and added phenylboronic acid (500 mg), K_2CO_3 (850.3 mg) and $K_2S_2O_8$ (1662 mg). Reaction was allowed to run for 2 h at 100 °C. Trace amount ($<3\%$) of homocoupled product was observed in the reaction. It indicates, small amount of catalyst is getting leached from the monolith into the reaction mixture in present solvent system.

After each cycle, the coupled products were isolated by column chromatography and the used monolith was taken out from the reaction flask. Washed the monolith with distilled water to remove base and solvent, and then washed with hexane to remove organic impurities. Washed monolith was dried in a hot air oven at 200 °C for 2 h. Dried monolith was reused for another reaction. The recycling chart of the catalyst is given in Fig. 2.

4 Conclusion

In conclusion, we have developed reusable noble metal ionic catalyst $Ti_{0.97}Pd_{0.03}O_{1.97}$ coated over cordierite monolith for C–C coupling reactions, such as homocoupling reaction of arylboronic acids and oxidative Heck coupling reaction between arylboronic acids and olefins. The catalyst $Ti_{0.97}Pd_{0.03}O_{1.97}$, is very efficient and compatible with water and aerobic conditions. The salient features of using $Ti_{0.97}Pd_{0.03}O_{1.97}$ catalyst in these two reactions are, (a) readily available starting materials, (b) air- and moisture-stable, easily recoverable catalyst, (c) mild reagents, environmentally benign reaction conditions (d) good functional group tolerance and (e) high TON as compared to other Pd-catalysts.

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