Recyclable Pd ionic catalyst coated on cordierite monolith for high TOF Heck coupling reaction

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Abstract. Pd²⁺ ionic catalyst, Ti_{0.97}Pd_{0.03}O_{1.97} was coated over cordierite monolith by solution combustion method. The catalyst coated on the cordierite is nano-crystalline as seen from XRD studies. Coated catalyst was used for Heck coupling reactions with different substrates of aryl halides and olefins. Thus handling nano-crystalline catalyst powder is avoided by fixing it on a solid catalyst cartridge. Heck coupled products were characterized using ¹H NMR, ¹³C NMR, Mass and FTIR spectroscopy. This catalyst showed high selectivity towards Heck coupling reaction. Turnover frequencies (TOF) for each of the reactions were found to be very high. The catalyst was recycled up to 7 times with total TOF 3017 h⁻¹, which is found to be a new green technique in the Heck coupling reaction.

Keywords. Noble metal ionic catalyst; cordierite monolith; solution combustion method; Heck coupling.

1. Introduction

The Heck coupling reaction has been considered as one of the most widely used a method for the formation of C–C bonds.^{1–4} Literature indicated the application of this coupling reaction in the synthesis of complex organic molecules such as drugs, natural products and advanced materials.^{5–11} For these reactions, Pd based catalysts were used extensively where they ensure enhanced reaction rates, high turnover frequencies and very good selectivity.^{12–14} Homogeneous palladium-based catalysts are extensively used in Heck coupling reaction as it provides high reaction rates and turnover number (TON) and often ends up with high selectivity and yields.^{15–17} In these cases, Palladium catalyst can be activated with the help of ligands such as phosphines, carbines, amines and dibenzylidene acetone(dba). On the other hand, homogeneous catalysis has a number of drawbacks such as reusing of the catalyst and impurities in the products which leads to loss of expensive

Palladium metal, ligands and the need to remove a metal particle from the products.¹⁸ Due to the high cost of Palladium and environmental issues, the development of heterogeneous catalysis is important for the industrial application to perform such coupling reactions. Therefore researchers are looking towards a heterogeneous catalyst which is highly stable and reusable.^{19–23} Recent studies show that PdO supported carbon nanomaterials²⁴ and palladium(0) on copper ferrite nanowires were designed for traditional Heck reaction as well as Heck reaction between iodoarenes and allylic alcohols.²⁵

Instead of Pd metal nanoparticles or PdO, Pd²⁺ ion substituted in reducible oxides showed high rates of redox catalytic reactions. A new class of catalysts called “Noble Metal Ionic Catalysts” (NMIC) were developed here.²⁹ Noble metal ions substituted in reducible oxide such as TiO₂ is a new class of catalyst which was synthesized by solution combustion method.^{26–29} Among different metals, Pd showed very good catalytic activity for CO oxidation reaction,

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hydrocarbon oxidation reaction and hydrogen–oxygen recombination reaction.^{27–30} When catalyst coated over cordierite monolith, it showed very good catalytic activity towards hydrogen–oxygen recombination reaction at room temperature.³¹ On Pd²⁺ ion substitution in TiO₂ lattice, a stable stoichiometric compound Ti_{1-x}Pd_xO_{2-x} (x = 0.03) is formed with one oxide ion vacancy per Pd²⁺ ion for charge compensation. When Pd²⁺ is substituted, an oxide ion vacancy is automatically created in the lattice. Pd²⁺ ion and oxide ion vacancy were next to each other as seen from the structure.³¹ Pd ion acted as an electrophile and oxide ion vacancy as a nucleophile. TiO₂ is cheaper reducible oxide support and non-toxic. 100% Pd ion dispersion is achieved so that all the Pd metal used becomes the active site.

Here we have attempted Heck coupling reaction with ionic palladium substituted TiO₂ having composition Ti_{0.97}Pd_{0.03}O_{1.97}. To avoid handling nano-material in the form of powder, and also to see if a catalyst cartridge can be developed, we coated the catalyst on cordierite monolith by solution combustion method.^{31,32} We have avoided the use of powder catalyst. The reaction was carried out with the solid monolith and removed it from the reaction flask, reused it and calculated overall TOF which was very high. The Heck coupling reaction was done in a specially designed reaction flask, which prevents breaking of cordierite monolith from fast rotating magnetic beads.

2. Experimental

2.1 General

X-ray diffraction patterns of catalysts were recorded on a Philips X'Pert Diffractometer. Reactions were monitored by using pre-coated silica TLC plates. Mass spectra were recorded on EI and ESI (TOF) modes. NMR spectra were recorded in at 400 MHz spectrometers in CDCl₃, tetramethylsilane (TMS; δ = 0.00 ppm) served as an internal standard for ¹H NMR. The corresponding residual non-deuterated solvent signal (CDCl₃; δ = 77.00 ppm) was used as internal standard for ¹³C NMR. Column chromatography was carried out on silica gel 230–400 mesh or 100–200 mesh (SDFCL) and thin-layer chromatography was carried out using SILICA GEL GF-254. Chemicals obtained from Sigma Aldrich and SD Fine chemicals were used without further purification.

2.2 Synthesis of Ti_{0.97}Pd_{0.03}O_{1.97} powder catalyst

The catalyst Ti_{0.97}Pd_{0.03}O_{1.97} was synthesized by solution combustion method. Titanium tetraisopropoxide (Ti(OC₃H₇)₄), palladium chloride and glycine were used as

starting materials. A solution of TiO(NO₃)₂ (9.89 mmol), which was prepared from titanium tetraisopropoxide, PdCl₂ (0.31 mmol), and glycine (10.99 mmol) were taken in a 300 mL crystallizing dish. The solution was kept in a 350 °C preheated muffled furnace and combustion of starting materials took place followed by dehydration. The dish was kept inside the furnace for more than 20 min to burn all the carbon contents. Then the dish was removed from the furnace, allowed to cool and collected the catalyst powder. The catalyst was ground in a pestle and mortar and characterized by PXRD. The combustion reaction is given by:

X-ray diffraction patterns were recorded on a Philips X'Pert Diffractometer at a scan rate of 0.1°/min with a step size in the 2 θ range between 10° and 90°. The diffraction profiles were refined by Rietveld refinement method.

2.3 Coating of γ -Al₂O₃ over cordierite monolith

Before coating the catalyst over monolith, γ -Al₂O₃ was coated over monolith to increase the surface area and adhesion to TiO₂. This process was done by solution combustion method by taking 15 mmol of Al(NO₃)₃ and 9 mmol of glycine. A solution of starting materials was made and pre-weighed monolith was dipped in the solution and kept inside the furnace for combustion. After 15 min, monolith was removed from the furnace and allowed to cool. The weight of the monolith was taken. This procedure was repeated until the weight of the coated γ -Al₂O₃ was 2 to 2.5% of cordierite monolith weight.

2.4 Coating Ti_{0.97}Pd_{0.03}O_{1.97} catalyst over cordierite monolith

The solution was prepared in a beaker using starting materials such as TiO(NO₃)₂, palladium chloride and glycine. A piece of the pre-weighed monolith was dipped in the solution and kept inside the preheated muffled furnace for combustion. After 20–30 min the hot monolith was taken out and allowed to cool to room temperature. Then the cooled monolith was kept for sonication process to remove loosely held particles. The monolith was dried again to remove the moisture and allowed to cool down. This procedure was repeated to get the desired weight of catalyst to be coated. About 50 mg of catalyst was coated on the monolith of 2.5 cm diameter, 2 cm height with 400 cells/inch. Alumina coated monolith and catalyst coated monolith are shown in Figure 1. We observed that catalyst becomes black during the reaction due to adsorption of olefins on palladium. After the reaction, catalyst is regenerated by heating at 200 °C in the air for about 2 h. Then it

Figure 1. Photographs of (a) Alumina coated honeycomb monolith, (b) and (c) top view and side view of catalyst coated monolith respectively, (d) catalyst coated honeycomb after several cycles of reactions.

can be reused for many cycles consecutively. This Pd catalyst showed excellent catalytic activity towards Heck coupling reaction.

2.5 Procedure for the Heck coupling reaction

Screening reactions were carried out in 25 mL round bottom flask. Iodobenzene (200 mg, 1 equivalent), methyl acrylate (1.1 equivalents), catalyst (10 mg) and K_2CO_3 (1.5 equivalent) were taken into a 25 mL round bottom flask. 3 mL of DMF was added. The reaction was kept under an argon atmosphere at $110^\circ C$. Reaction was monitored by TLC. Extracted the product with diethyl ether and 3 times water work up. Percentage of yield was determined by using gas chromatography.

Heck coupling reactions were done in the specially designed reaction flask. Aryl halides (2 g, 1 equivalent), olefins (1.1 equivalents) and base (1.5 equivalents) were taken into the reaction flask. Catalyst coated cordierite monolith was put inside the flask. The reaction was kept under an argon atmosphere at $110^\circ C$. The reaction was monitored by TLC. After completion of the reaction, the coupled product was extracted by diethyl ether and washed 3 times with water to remove the solvents and base. Catalyst coated monolith was removed from the flask, washed with water to remove solvent and base. Then washed with n-hexane to remove organic impurities and dried in a hot air oven for 2 h at $200^\circ C$. Dried catalyst cartridge was reused for two more substrates of Heck coupling reactions.

The product was isolated using column chromatography. The eluents used were pet ether and ethyl acetate. The ratio was standardised by using TLC according to the polarity of the products. Coupled products were characterized by 1H NMR, ^{13}C NMR, IR spectra and mass spectra.

3. Results and Discussion

Catalyst $Ti_{0.97}Pd_{0.03}O_{1.97}$ was prepared by solution combustion method from the starting materials $TiO(NO_3)_2$, palladium chloride and glycine at $350^\circ C$. Pd substituted TiO_2 crystalizes in anatase structure. Rietveld refined XRD pattern for 3 atoms % Pd in TiO_2 is given in Figure 2. There are no peaks either of PdO or Pd metal in the difference profile. Lattice parameters are: $a=3.796 \text{ \AA}$ and $c=9.534 \text{ \AA}$ which are close to pure TiO_2 values, $a=3.796 \text{ \AA}$ and $c=9.533 \text{ \AA}$. This is to be expected because the ionic radius of Pd^{2+} is $0.64 \text{ \AA}$ which is close to that of Ti^{4+} ($0.605 \text{ \AA}$). A detailed study of the structure of $Ti_{0.97}Pd_{0.03}O_{1.97}$ has been reported earlier.³¹ The XRD patterns of cordierite monolith and catalyst coated cordierite monolith is shown in Figure 3. Cordierite monoliths are in cylindrical shape with 2.5 cm diameter and 2 cm height and are made up of $Mg_2Al_4Si_5O_{18}$. One can see the (101) diffraction line of the catalyst in the XRD pattern at angle 25.3° in the difference plot between coated and uncoated cordierite monolith

Figure 2. Rietveld refined XRD pattern of $\text{Ti}_{0.97}\text{Pd}_{0.03}\text{O}_{1.97}$ catalyst. There is no peak of Pd metal or TiO_2 rutile phase, which confirms the formation of single phase Pd substituted catalyst.

Figure 3. Powder XRD patterns of (a) cordierite monolith, (b) catalyst coated over cordierite monolith and inset figure showing a broad peak of (101) line of the catalyst. * (101) line of $\text{Ti}_{0.97}\text{Pd}_{0.03}\text{O}_{1.97}$.

shown inset of Figure 3. Each monolith is having parallel channels of a square shape. Thus high surface area is exposed to the reactants. The color of the catalyst is

brown. Average crystallite size is 8 ± 2 nm which was calculated from half-width of (101) line of coated catalyst (inset of Figure 3) using Scherrer formula ($d = 0.9$

$\lambda/\beta \cos\theta$) in the powder and on the surface also a similar size is expected because half width of the (101) peak is of the same order.

Figure 4. Specially designed reaction flask for Heck coupling reaction with the reaction mixture and coated honeycomb catalyst.

3.1 Heck coupling reaction flask

Figure 4 shows the two-necked cylindrical flask with diameter 3.5 cm and height 12 cm. Above 1.5 cm from the bottom, the diameter of the flask is reduced to make two separate compartments with a small passage between them. The bottom space contained magnetic bead and reaction mixture. Above the passage, the catalyst coated honeycomb (HC) catalyst was placed. The sufficient solvent was taken such that the HC catalyst was submerged in the solvent. Condenser and argon-filled balloon were fitted above the flask. The flask was kept on preheated oil bath at temperature 110 °C. The rotation speed of stirrer was high enough to circulate reaction mixture with solvent through the HC catalyst.

3.2 Screening studies

Screening of the Heck coupling reaction was started with the reaction of iodobenzene and methyl acrylate as starting materials. Powder catalyst was used in each of the screening reaction. 0.98 mmol (200 mg) of Iodobenzene and 1.1 equivalent of methyl acrylate were taken.

Table 1. Screening of the reaction.

Entry	Base	Solvent	Time (h)	Temp. (°C)	Yield (%)
1.	K ₂ CO ₃	Acetonitrile	4	110	Nil
2.	K ₂ CO ₃	DMSO	4	110	20
3.	K ₂ CO ₃	DMF	1.5	110	> 99(95^b)
4.	K ₂ CO ₃	1,4-Dioxane	4	110	Nil
5.	K ₂ CO ₃	THF	4	110	Trace
6.	K ₂ CO ₃	NMP	4	110	35
7.	K ₂ CO ₃	Toluene	4	110	Nil
8.	—	DMF	2	110	Trace
9.	Cs ₂ CO ₃	DMF	2	110	34
10.	NEt ₃	DMF	2	110	97
11.	CH ₃ COONa	DMF	2	110	30
12.	t-BuONa	DMF	2	110	Nil
13.	KOH	DMF	2	110	93
14.	K ₂ CO ₃	DMF	2	80	16
15.	K ₂ CO ₃	DMF	2	60	Trace
16.	K ₂ CO ₃	DMF	8	RT	Trace
17.	K ₂ CO ₃	DMF	1	110	> 99^c(92^b)
18.	K ₂ CO ₃	DMF	1	110	> 99^d(94^b)
19.	K ₂ CO ₃	DMF	2	110	93 ^e
20.	K ₂ CO ₃	DMF	2	110	92 ^f

Reaction conditions: 1 equivalent (200 mg) of Iodobenzene, 1.1 equivalent of Methyl acrylate, 1.5 equivalent of base, 3 mL of solvent, 5 weight % of powder catalyst, temperature at 110 °C, under Ar atmosphere. All are GC yield. ^b Isolated yield, ^c50 mg of catalyst coated over monolith, ^d100 mg of catalyst coated over catalyst, ^e0.5 equivalent of base, ^f1 equivalent of base. The converted reactions that are complete are given in bold.

Table 2. Substrate scope of the reaction.

$ \begin{array}{c} \text{R} \text{---} \text{C}_6\text{H}_4 \text{---} \text{X} \\ \text{x = I, Br} \end{array} + \text{CH}_2=\text{CH}-\text{R}_1 \xrightarrow[\text{DMF / 110}^\circ\text{C / Ar}]{\text{Ti}_{0.97}\text{Pd}_{0.03}\text{O}_{1.97} / \text{K}_2\text{CO}_3} \text{R} \text{---} \text{C}_6\text{H}_4 \text{---} \text{CH}=\text{CH}-\text{R}_1 $						
Entry	Aryl halide	Olefins	Product	Time (h)	Yield (%)	TOF (h ⁻¹)
1.				4	98	159
2.				5	99	129
3.				6	80	81
4.				5	91	110
5.				6	80	81
6.				2	92	299
7.				3	70	141
8.				1	95	660
9.				2	85	296
10.				1.5	98	454
11.				6	70	105
12.				6	73	150
13.				7	69	89

Table 2. (contd.)

Entry	Aryl halide	Olefins	Product	Time (h)	Yield (%)	TOF (h ⁻¹)
14.				7	90	91
15.				8	50	45
16.				3	91	211
17.				1.5	100	463
18.				2	100	348
19.				2	56	195
20.				3	83	165
21.				3	88	175
22.				4	75	112

Reaction condition: 1 equivalent (2g) of aryl halide, 1.1 equivalent of olefins, 1.5 equivalent of K₂CO₃ as base, 20 mL of DMF as solvent, 50 mg catalyst coated over honeycomb monolith, temperature at 110 °C, under Ar atmosphere. All are isolated yield.

TOF = [(No. of moles of product/ No. of moles of active site of catalyst)]/time in hours.

10 mg of catalyst was used which contains 3.7 μmol of Pd²⁺ ion. Initially, solvent study was carried where different solvents were used for the reaction. Except for the reaction in *N, N*-dimethyl formamide (DMF) as a solvent, all other reactions with different solvents have given almost negligible yield. Time of the reaction with solvent DMF was 90 min at temperature 110 °C using K₂CO₃ (1.5 equivalent) as a base. We tried the reaction without base and resulted with a trace amount of yield. Then we investigated the reaction with 1.5 equivalent of different bases such as Cs₂CO₃, NEt₃, CH₃COONa, *t*-BuONa and KOH, the reaction with NEt₃ and KOH have ended up with very good yield same as that of K₂CO₃. Next step of screening was temperature; reactions were

done at 80 °C, 60 °C and at room temperature, the yields were very low. So we have decided to keep DMF as a solvent, 1.5 equivalent of K₂CO₃ as base and temperature at 110 °C as standard reaction condition for the Heck coupling reaction. We have also tried the reaction with 1 and 0.5 equivalent of K₂CO₃ and observed slightly lesser yield compared to 1.5 equivalent of base. We have done two more reactions using honeycomb monolith catalyst where, one monolith was coated with 100 mg catalyst, another with 50 mg of catalyst. 2 g of iodobenzene was used as starting material. Both the reactions were ended up with yield more than 99%. Interestingly, the time taken for these two reactions was just one hour. Compared to the reactions with powder catalyst, honeycomb

Figure 5. Flowchart of recycling of HC monolith catalyst in the Heck coupling reaction.

monolith catalyst shown faster rate. Finally, we decided to coat 50 mg of catalyst over cordierite monolith for the remaining reactions. The screening of Heck coupling reactions is summarised in Table 1.

3.3 Substrate scopes

22 substrates of aryl halides and olefins were used for substrate scope of the Heck coupling reaction listed in Table 2. We have used optimized condition that is 1 equivalent of aryl halide (2 g), 1.1 equivalent of olefins, 1.5 equivalent of K_2CO_3 as a base and 20 mL of DMF as a solvent. About 50 mg of catalyst was coated on cordierite monolith and every reaction was done with the coated catalyst. Substituted aryl iodide compounds showed very good reactivity towards olefins despite having electron-withdrawing and electron-donating groups (Table 2, entry 1–7); the time taken for the reaction was about 5 h. The reaction between un-substituted iodobenzene showed very high reactivity (Table 2, entry 8–10, 16–18) towards different olefins with very high TOF. The TOF of the reaction between iodobenzene and methyl acrylate was found to be 660 h^{-1} which

is highest among all other substrates. Substrate scope of aryl bromides were also done, yields were above 50% in case of aryl bromides, but the time taken for the reactions were about 6 to 8 h. Because of less reactivity of bromides, the TOF were low compared to iodo substrates (Table 2, entry 11–15). Finally 1 – chloro – 4 – iodobenzene reacted with different olefins (Table 2, entry 20–22), reaction were ended up with more than 75% yield by substitution at iodo position and chlorides remained as it is in the product which is confirmed by mass spectra. All products were isolated and found to be trans from 1H NMR. The catalyst was well-tolerated to different varieties of aryl halides and olefins. Reaction with aryl iodide ended up with very good yield compared to aryl bromide.

3.4 Recycling of the catalyst

We have carried out the recycling of the catalyst for several cycles. Iodobenzene (2 g) and methyl acrylate (1.1 equiv.) were taken as starting materials by employing standard conditions. The whole process of recycling the HC monolith catalyst is depicted in Figure 5. After each

Figure 6. Recycling of the catalyst by employing standard reaction condition.

Figure 7. The mechanism for Heck coupling reaction with $\text{Ti}_{0.97}\text{Pd}_{0.03}\text{O}_{1.97}$ catalyst.

cycle, the used monolith was taken out from the reaction flask and washed with distilled water to remove base and solvent, then washed with hexane to remove organic impurities. Washed monolith was dried in a hot air oven at a temperature 200°C for 2 h. Dried monolith was reused for another reaction. We obtained 100% yield up to 6th cycle and in the 7th cycle, we observed a drop in the yield to 85%. The recycling chart of the catalyst is given in Figure 6. The reaction time up to 6th cycle was 1 to 3 h and in 7th cycle, reaction time was 14 h. Total TOF after 7 cycles of the reaction was 3017 h^{-1} .

3.5 Mechanism for the Heck coupling reaction

A mechanism is proposed for the Heck coupling reaction with $\text{Ti}_{0.97}\text{Pd}_{0.03}\text{O}_{1.97}$ catalyst is given in Figure 7. The catalyst is $\text{Ti}_{0.97}\text{Pd}_{0.03}\text{O}_{1.97}$ where for every Pd^{2+} ion there is an oxide ion vacancy. Pd ion is electron deficient

and the oxide ion vacancy is electro rich. The active site in the catalyst is Pd^{2+} ion. There was no Heck reaction on pure TiO_2 which means that neither Ti^{4+} nor O^{2-} is the active sites in the catalyst. Olefins bind with Pd^{2+} ions because olefins can donate π electrons and thus becomes a normal site for the adsorption of olefin. $-\text{I}$ or $-\text{Br}$ of aryl halides that are accommodated on oxide ion vacancy of the catalyst. Here oxide ion vacancy acts as a nucleophile. HI is eliminated with the help of base, which leads to C–C coupling.

4. Conclusions

In summary, we have developed a new class of catalyst for the C–C coupling reaction. This method is environmentally friendly without using any toxic catalyst or reagents. This reaction tolerates a variety of functional groups. Reactions were done using catalyst coated over cordierite monolith by a unique method, which is also helpful for recovering the catalyst.

Supplementary Information (SI)

Supplementary information is available at www.ias.ac.in/chemsci.

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