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# Palladium Nanoparticles Stabilized by an Ionic Polymer and Its Application in Heck Reaction

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The palladium nanoparticles immobilized on the surface of poly(vinyl chloride)-supported pyridinium (PVC-Py-$Pd^0$) were prepared by using the corresponding functionalized polymer and palladium chloride in ethanol solution. The palladium nanoparticles catalyst (PVC-Py-$Pd^0$) was stable in the air and exhibited significant catalytic activity for Mizoroki-Heck coupling reaction of bromobenzene or iodobenzene with styrene under milder operating conditions. The catalytic system presented here showed several merits such as short reaction time, excellent yields of products, simple experimental and isolated procedure. Furthermore, the catalyst can be easily recycled and reused for at least five times with consistent activities.

**Keywords: Palladium nanoparticle, Immobilized, Heck reaction, Poly(vinyl chloride).**

## INTRODUCTION

Carbon-carbon cross-coupling reactions are among the most useful and most widely studied synthetic transformations[1]. One of the most important C-C coupling reactions is the Mizoroki-Heck reaction, such as the arylation or vinylation of olefins by aryl or vinyl halides[2], which has been abundantly applied in many areas, including the syntheses of natural product and fine chemicals[3-5]. In the past decades, numerous efforts have been made to develop efficient catalyst systems for Mizoroki-Heck cross-coupling reaction. The Heck reaction is usually carried out in the presence of phosphine ligands[6-9]. The main role of phosphine ligands is to stabilize the palladium(0) as the $PdL_4$ species, which can enter the catalytic cycle and consequently prevent the formation of inactive palladium black. However, phosphine ligands are expensive, poisonous, difficult to recover, air sensitive and subject to P-C bond degradation at elevated temperatures. In such cases, catalyst reuse can be difficult. From an economic and environmental standpoint[10-12], it is desirable to use solid catalyst without the use of hazardous phosphine additives as an greener alternative to conventional homogeneous processes. Recently, the preparation and application of polymer-supported catalysts has drawn dramatic attention during the past years[13-19], serious interest in these catalysts originated with efforts to develop catalytic systems displaying the high activity, convenient work-up, easy separability and recovery, low toxicity[20].

In this paper, we wish report the Heck reaction using palladium nanoparticles catalyst immobilized on the surface of functionalized poly(vinyl chloride) (PVC) without adding phosphine ligands. This catalyst could be easily isolated from the reaction mixture by simple procedure and it could be reused without significant degradation in activity.

## EXPERIMENTAL

All chemicals were analytical grade and used without further purification.

### General procedure

**General procedure for the synthesis PVC-Py-$Pd^0$ catalyst:** To a 250 mL three-necked flask was added pyridine (30 mL, 0.375 mol), sodium hydroxide (24 g, 0.6 mol) and water (45 mL). Poly(vinyl chloride) (15 g) was added to the solution. The reaction mixture stirred below 60 °C for 3 h and then stirred at 95-100 °C for another 16 h. After cooling to the room temperature, the reaction mixture was poured into 500 mL water, filtered and washed with water (3 × 20 mL) and 95 % ethanol (3 × 20 mL), respectively. The as-prepared resin was then treated with $PdCl_2$ (2 g, 9.4 mmol) in 100 mL 95 % ethanol for 48 h. After the completion of the reaction, the black solid particles were obtained by being filtered, washed with ethanol and dried. The characterization of palladium nanoparticles catalyst could be found in our previous research[21].

**General procedure for the PVC-Py-$Pd^0$ catalyzed the Heck reaction:** The palladium nanoparticles catalyst (4.8 mol % Pd), styrene (0.14 mL, 1.2 mmol), triethlamine (0.28 mL, 2 mmol) and aryl halides (1 mmol) were added to a 25 mL reaction flask containing dimethyl formamide (10 mL). The reaction was initiated at a certain temperature controlled by silicon oil bath. The progress of the reaction was monitored by TLC. After the completion of the reaction, the catalyst was filtered off and washed with 95 % ethanol (3 × 10 mL). The filtrate was poured into 50 mL distilled water and the solid materials were filtered and treated with 95 % ethanol. The products were further purified with recrystallization.

$^1$H NMR spectra were recorded on a Bruker AVANCE 300 instrument at 300 MHz in DMSO-$d_6$ using TMS as the internal standard. Melting points were measured by X6 micro-melting point apparatus and uncorrected. The contents of elemental palladium in the polymeric catalyst were determined by Perkin Elmer Optima 2000DV inductive coupled plasma (ICP) spectroscopy. The elemental analyses were performed on a Perkin Elmer EA2400II elemental analyzer. Transmission electron microscopy (TEM) was performed with a Philips Tecnai instrument operating at 40-100 kV. Scanning electron microscopy (SEM) was performed with Philips XL 30ESEM instrument.

## RESULTS AND DISCUSSION

**Effect of the base on the catalytic performance:** In order to study the efficiency of this catalyst for the Mizoroki-Heck reaction, the coupling of iodobenzene and styrene was chosen as the model reaction to investigate the effect of base. The results were shown in Table-1. According to the Table-1, it could conclude that the palladium nanoparticles catalyst had a highly efficient for the model reaction in the existence of tributylamine. Therefore, tributylamine was ultimately chosen as the base for this system.

TABLE-1
EFFECT OF THE BASE[a]

| Entry | Base | Reaction time (h) | Yield (%)[b] |
|---|---|---|---|
| 1 | $K_2CO_3$ | 7 | 25.1 |
| 2 | $Na_2CO_3$ | 7 | 31.5 |
| 3 | NaOH | 7 | 42.7 |
| 4 | $Et_3N$ | 5 | 72.3 |
| 5 | $Bu_3N$ | 3.5 | 91 |
| 6 | $Na_3PO_4$ | 7.5 | 20.8 |

[a]Reaction condition: iodobenzene (1 mmol); styrene (1.2 mmol); base (2 mmol); DMF (10 mL); PVC-Py-Pd$^0$ (4 mol %); All the reactions were carried out in air
[b]Isolated yield of pure product based on iodobenzene

**Effect of the solvent:** The solvent can play an important effect in the reaction sometomes. Some can improve the catalytic activity and promote the reaction obviously. So in this paper, the effect of solvent on the coupling reaction was studied. The results were shown in Table-2. Compared with other solvents, the DMF was found to be most efficient for present catalytic system.

**Effect of the temperature:** The reaction temperature has a great influence on the Mizoroki-Heck coupling reaction. The results were shown in the Table-3. At room temperature, a very low yield of cross-coupling product was obtained. As the temperature increased from 30 to 150 °C, the yield of product was increased. When the temperature was above 120 °C, the conversion was increased unobviously. So the temperature of 120 °C was selected as the best condition for coupling reaction.

TABLE-2
EFFECT OF THE SOLVENT[a]

| Entry | Solvent | Reaction time (h) | Yield (%)[b] |
|---|---|---|---|
| 1 | Dimethyl formamide | 3 | 90.5 |
| 2 | EtOH | 5 | 75.6 |
| 3 | Toluene | 24 | No reaction |
| 4 | $H_2O$ | 9 | 17.2 |
| 5 | Dichloromethane | 7 | 26.4 |
| 6 | Tetrahydrofuran | 7.5 | 30.7 |
| 7 | Acetonitrile | 8 | 27.2 |

[a]Reaction condition: iodobenzene (1 mmol); styrene (1.2 mmol); $Bu_3N$ (2 mmol); Solvent (10 mL); PVC-Py-Pd$^0$ (4 mol %); All the reactions were carried out in air
[b]Isolated yield of pure product based on iodobenzene

TABLE-3
EFFECT OF THE TEMPERATURE[a]

| Entry | Temp. (°C) | Reaction time (h) | Yield (%)[b] |
|---|---|---|---|
| 1 | 25 | 24 | 23.6 |
| 2 | 60 | 15 | 45.3 |
| 3 | 90 | 7 | 76.8 |
| 4 | 120 | 3 | 91.3 |
| 5 | 150 | 3 | 92.2 |

[a]Reaction condition: iodobenzene (1 mmol); styrene (1.2 mmol); $Bu_3N$ (2 mmol); DMF (10 mL); PVC-Py-Pd$^0$ (4.8 mol %); All the reactions were carried out in air
[b]Isolated yield of pure product based on iodobenzene

**Effect of the amount of catalyst:** The amount of palladium nanoparticles catalyst plays the critical factor on the coupling reaction. The effects of the amount of catalyst were shown in the Table-4. It was found that the Heck reaction could be carried out efficiently even with low amount of catalyst. No product was obtained if there was no catalyst in the reactor. The conversion was increased as the amount of catalyst was increased. When the amount of palladium in catalyst exceeded 4.8 mol %, the yield of product would not increase obviously.

TABLE-4
EFFECT OF THE AMOUNT OF CATALYST[a]

| Entry | Amount of catalyst, mol % Pd | Reaction time (h) | Yield (%)[b] |
|---|---|---|---|
| 1 | 0 | 24 | No reaction |
| 2 | 1.2 | 8 | 82.4 |
| 3 | 2.4 | 6 | 86.3 |
| 4 | 3.6 | 4.5 | 88.7 |
| 5 | 4.8 | 3 | 93.1 |
| 6 | 6.0 | 3 | 92.6 |

[a]Reaction condition: iodobenzene (1 mmol); styrene (1.2 mmol); $Bu_3N$ (2 mmol); DMF (10 mL); All the reactions were carried out in air
[b]Isolated yield of pure product based on iodobenzene

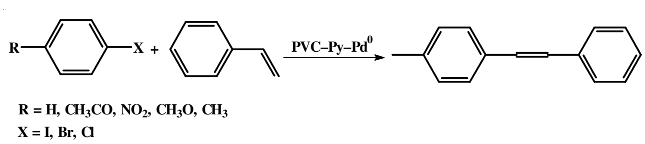
**Mizoroki-Heck reaction of benzene halide with styrene catalyzed by PVC-Py-Pd$^0$:** Based on the optimized reaction conditions, the Mizoroki-Heck coupling reactions between a variety of benzene halides and styrene were carried out to study the general effectiveness of the PVC-Py-Pd$^0$ nanoparticles catalyst (**Scheme-I**).

The results were shown in Table-5. As depicted in Table-5, the PVC-Py-Pd$^0$ catalyst exhibited good activity for Heck reaction. It could be seen from the results that the catalyst had highly efficient for the coupling of iodobenzene or bromobenzene with styrene. The catalyst had no catalytic activity

TABLE-5
PVC-PY-PD0 CATALYZED HECK REACTION OF DIFFERENT ARYL HALIDES AND STYRENE[a]

| Entry | R | X | Product | Time (h) | Yield (%)[b] |
|---|---|---|---|---|---|
| 1 | H | I | Stilbene | 3 | 86.3 |
| 2 | $CH_3CO$ | I | 4-Acetylstilbene | 4.5 | 91.5 |
| 3 | $CH_3$ | I | 4-Methylstilbene | 3.5 | 88.6 |
| 4 | $CH_3O$ | I | 4-Methoxystilbene | 3.5 | 86.4 |
| 5 | $NO_2$ | I | 4-Nitrostilbene | 4.5 | 93.1 |
| 6 | H | Br | Stilbene | 5 | 87.3 |
| 7 | $CH_3CO$ | Br | 4-Acetylstilbene | 5.5 | 90.6 |
| 8 | $CH_3$ | Br | 4-Methylstilbene | 7.5 | 86.4 |
| 9 | $CH_3O$ | Br | 4-Methoxystilbene | 6 | 85.6 |
| 10 | $NO_2$ | Br | 4-Nitrostilbene | 5.5 | 92.2 |
| 11 | H | Cl | Stilbene | 24 | No reaction |
| 12 | $CH_3CO$ | Cl | 4-Acetylstilbene | 24 | No reaction |
| 13 | $CH_3$ | Cl | 4-Methylstilbene | 24 | No reaction |
| 14 | $CH_3O$ | Cl | 4-Methoxystilbene | 24 | No reaction |
| 15 | $NO_2$ | Cl | 4-Nitrostilbene | 24 | No reaction |

[a]Reaction condition: aryl halide (1 mmol); styrene (1.2 mmol); $Bu_3N$ (2 mmol); DMF (10 mL); PVC-Py-$Pd^0$ (4.8 mol%); All the reactions were carried out at 120 °C in air, [b]Isolated yield was based on the aryl halide




**Scheme-I:** Heck reaction catalyzed by PVC-Py-$Pd^0$

for the coupling of chlorobenzene with styrene under the same conditions.

**Recycling of the PVC-Py-$Pd^0$ catalyst:** To investigate the reuse and recycling the catalyst was one of the main aims of our study. In each iteration, the catalyst in the reaction mixture was filtered off, washed and reused. The results were shown in Table-6. It could be concluded that the catalytic activities of PVC-Py-$Pd^0$ were nearly unchanged after reused for 5 runs. The results declared that this kind of palladium nanoparticles catalyst was relatively stable in this catalytic system.

TABLE-6
RECYCLING AND REUSE OF PVC-Py-$Pd^0$ IN HECK REACTION[a]

| Run | Reaction time (h) | Yield (%)[b] |
|---|---|---|
| 1 | 3 | 86.3 |
| 2 | 3 | 85.7 |
| 3 | 4 | 86.8 |
| 4 | 4.5 | 83.5 |
| 5 | 4 | 84.3 |

[a]Reaction condition: iodobenzene (1 mmol); styrene (1.2 mmol); $Bu_3N$ (2 mmol); DMF (10 mL); PVC-Py-$Pd^0$ (4.8 mol%); All the reactions were carried out at 120 °C in air
[b]Isolated yield of pure product based on iodobenzene

## Conclusion

In conclusion, PVC-Py-$Pd^0$ has been synthesized easily by simple procedure. This kind of catalyst has highly efficient for the Mizoroki-Heck coupling reaction of iodobenzene or bromobenzene with styrene in the air. This catalytic system has several advantages, such as simple experimental and isolated procedure, satisfactory yields of products, as well as excellent catalytic activity and reusability. Further application of the catalytic system to other transformations is on progress.

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