



Poly(vinylidene dichloride)-diethylene Triamine Supported Palladium as a New Re-cyclable Catalyst for Heck Reaction

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ABSTRACT

Poly(vinylidene dichloride)-diethylene triamine supported palladium complex (PVDC-DTA-Pd) was prepared from poly(vinylidene dichloride) by a simple method. In contrast with other polymer-supported catalysts, the greatest advantage of the catalyst system was that the cost of the catalyst was remarkably low due to the easily obtained materials and the simple synthetic route. Heck reactions of aryl iodides with acrylic acid catalyzed by PVDC-DTA-Pd could be performed efficiently in water. Yield of cinnamic acid was 99.6% as the coupling of iodobenzene with acrylic acid was carried out in water at 90°C for 3 h in the air. Both electron-rich and electron-deficient aryl iodides reacted with the alkenes to give the corresponding *trans*-products. When styrene was adopted as alkene, high yields were obtained in DMF rather than in water because the hydrophilicity of styrene was poor. High activities for aryl bromides and activated aryl chlorides were also found when the reactions were carried out in tetrabutylammonium bromide to afford the coupled products in moderate to good yields. However, high temperature (120°C) and inert atmosphere were required. The catalyst can be recovered easily by filtration and re-used for Heck reaction. Yield of the cinnamic acid was up to 78.5% at the cycle of five, which indicated the high stability and good re-usability of PVDC-DTA-Pd.

Key Words:

poly(vinylidene dichloride);
Heck reaction;
palladium;
aryl halide;
polymer-supported catalyst.

INTRODUCTION

The C-C coupling reaction plays an important role in modern organic synthesis. Richard Heck, Ei-ichi Negishi and Akira Suzuki won the 2010 Nobel Prize in Chemistry for the development of new ways to synthesize complex organic molecules using palladium-catalyzed cross-couplings which were known as Heck reaction, Negishi reaction and Suzuki reaction, respectively. Heck reaction is the coupling of aryl halide with olefin and has

received considerable attentions due to its wide use in the synthesis of various chemicals [1-4]. The reaction is usually catalyzed by palladium compound [PdCl₂ or Pd(Ac)₂] in homogeneous solution in the presence of phosphorus ligand. However, these expensive catalysts are hardly separated for re-use because of the precipitation of palladium black from reaction media. In view of these, the use of heterogeneous catalysts is

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favourable. Palladium supported on carbon [5], metal oxide [6,7], zeolite [8,9], and molecular sieves [10,11] were found to be efficient catalysts for Heck reactions. Polymer-supported palladium complexes were also used in Heck reaction. Recently, a re-usable polymer-anchored palladium(II) Schiff-base complex catalyst for Heck reaction was reported. The catalyst showed high activity and could be recovered by filtration [12]. Another paper summarized the performance of palladium supported on poly(*N*-vinylimidazole) or poly(*N*-vinylimidazole-*co*-vinylcaprolactam) for Heck reaction. High efficiency along with recycling ability of the catalyst was also found [13]. Natural polymers supported palladium complexes have been prepared in our laboratory and their catalytic activities for Heck reaction were studied [14,15]. Nonetheless, we found that the preparations of these catalysts were rather complicated. Therefore, study on new types of polymer-support palladium catalysts which can be prepared easily has theoretical and practical significance. We have reported the catalytic performance of poly(vinyl chloride)-diethylene triamine supported palladium complex which was obtained via a simple synthetic route [16]. In this work, we utilized another easily obtained polymer material, poly(vinylidene dichloride), as carrier to prepare the supported palladium catalyst. The cost of the catalyst was also very low due to the easily obtained materials and the simple synthetic route. This novel polymer-supported palladium catalyst showed high performance for Heck reactions of aryl halides with alkenes.

EXPERIMENTAL

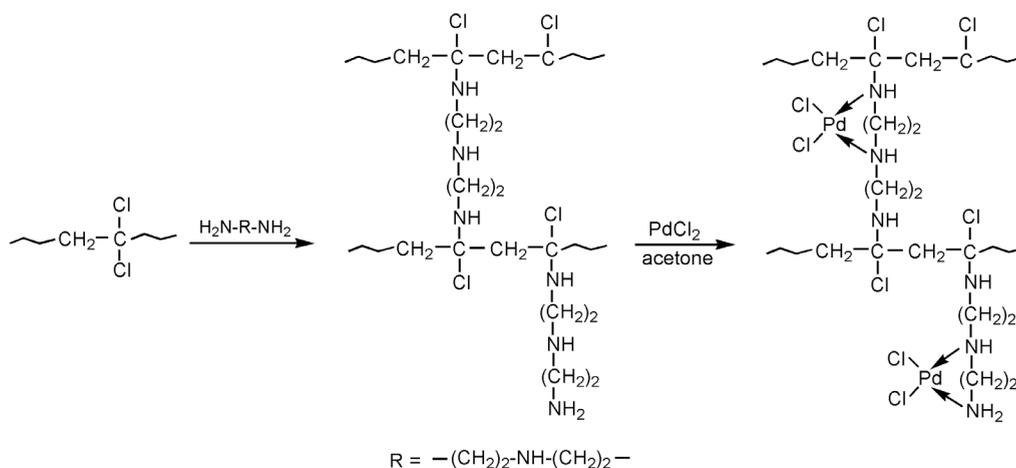
Materials and Equipment

Poly(vinylidene dichloride) powder was obtained from Kureha Co. (Japan), $\overline{M}_w = 1.7 \times 10^5$ and $d = 3.4$. Diethylene triamine, tributylamine and iodobenzene were chemical pure (China). *p*-Iodoanisole, *p*-chloriodobenzene, *p*-iodotoluene, *p*-iodonitrobenzene, *p*-bromo-nitrobenzene, *p*-chloronitrobenzene and *p*-bromotoluene were purchased from Lancaster (England) and used as received. All other reagents were analytical reagents and used as received without further purification.

X-Ray photoelectron spectra (XPS) were measured on an Axisultra Spectrometer (Kratos Co., England) using mono-Al K α radiation. The C_{1s} photoelectron line was used for energy calibration and the C_{1s} binding energy was taken to be 284.8 eV. Thermal analysis was performed on an EXSTAR6000 (Seiko Co., Japan) thermal analysis system at a heating rate of 10°C/min in the air. IR Spectra were performed on an Avatar360 Fourier Transform Infrared FTIR spectroscopy (Nicolet Co., USA). ¹H NMR Spectra were recorded on a Bruker AV400 (400 MHz) spectrometer (Germany) with TMS as an internal standard in CDCl₃ or DMSO-d₆ as solvent. Palladium content in PVDC-DTA-Pd was measured on a Z-2000 atomic absorption spectrometry (Hitachi, Japan).

Preparation of the Catalyst

The powder of poly(vinylidene dichloride) (1.5 g)



Scheme 1. Synthetic route of PVDC-DTA-Pd.

was dispersed in diethylene triamine (10 mL). The mixture was stirred at room temperature for 6 h in the air. The reaction mixture was filtered and washed with plenty of water until the filtrate was colourless and pH value was neutral. Then the powder was dried at 80°C in vacuum for 12 h to give 1.4 g of poly(vinylidene dichloride)-diethylene triamine (PVDC-DTA). PVDC-DTA (0.5 g) was added to the solution of PdCl₂ (0.05 g) in acetone (20 mL). The mixture was stirred at 60°C for 72 h in the air. After being cooled to room temperature, the reaction mixture was filtered and washed with acetone (3×20 mL) and H₂O (3×20 mL). Then, the powder was dried at 80°C in vacuum for 6 h to give 0.51 g of black poly(vinylidene dichloride)-diethylene triamine supported palladium complex (PVDC-DTA-Pd) (Scheme 1). Palladium content in PVDC-DTA-Pd was 0.23 mmol/g.

Typical Procedure for the Heck Reaction of Aryl Iodides with Acrylic Acid

In a 50 mL round-bottomed flask, PVDC-DTA-Pd (0.015 g), acrylic acid (2.25 mmol), iodobenzene (1.5 mmol), base (3.0 mmol) and solvent (0.6 mL) were added. The mixture was stirred and heated to 90°C in the air for 3 h. The reaction mixture was cooled to room temperature, and H₂O (25 mL) and Na₂CO₃ (1.0 g) were added. After the mixture was stirred for 10 min, PVDC-DTA-Pd was separated by filtration. The filtrate was treated with 3 M HCl (5 mL) and a precipitate was formed. The precipitate was filtered, washed with H₂O (2×15 mL) and dried in the air. The product was characterized by ¹H NMR and IR [17].

Typical Procedure for the Heck Arylation of Aryl Halides with Styrene

PVDC-DTA-Pd (0.015 g), styrene (2.25 mmol), aryl halides (1.5 mmol), (n-Bu)₃N (3.0 mmol) and DMF (0.6 mL) were added into a 50 mL round-bottomed three-necked flask. The reaction mixture was stirred at 90°C in the air for 3 h. When aryl bromides or aryl halides were used, the reactions were carried out in TBAB (0.8 g) under nitrogen atmosphere at 120°C for 8 h. Then, the mixture was cooled to room temperature and ether (30 mL) was added. The ether layer was separated, concentrated and re-crystallized

Table 1. XPS Data of Pd, PdCl₂, PVDC-DTA and PVDC-DTA-Pd^a.

Sample	Pd _{3d5/2}	N _{1s}
Pd	335.3	-
PdCl ₂	338.3	-
PVDC-DTA	-	401.4
PVDC-DTA-Pd	338.1	401.6

^(a) The binding energies refer to C_{1s} (284.8 eV).

to give the final product. The products were characterized by ¹H NMR and IR [17].

RESULTS AND DISCUSSION

Characterization of PVDC-DTA-Pd

To study the chemical state of palladium in the supported catalyst and the coordination of the macromolecular carrier with metal ion, the binding energies of Pd, PdCl₂, PVDC-DTA and PVDC-DTA-Pd were obtained by XPS analysis. The results are summarized in Table 1. The binding energy of Pd_{3d5/2} in PVDC-DTA-Pd is 338.1 eV, which indicates that the chemical valence of palladium in the catalyst is divalent. The binding energy of N_{1s} in PVDC-DTA-Pd is 401.6 eV and it is slightly higher than that in PVDC-DTA, which indicates that an electron-transfer takes place and the electron density at nitrogen atom is decreased. These results show that the coordination bonds are formed between N and Pd²⁺.

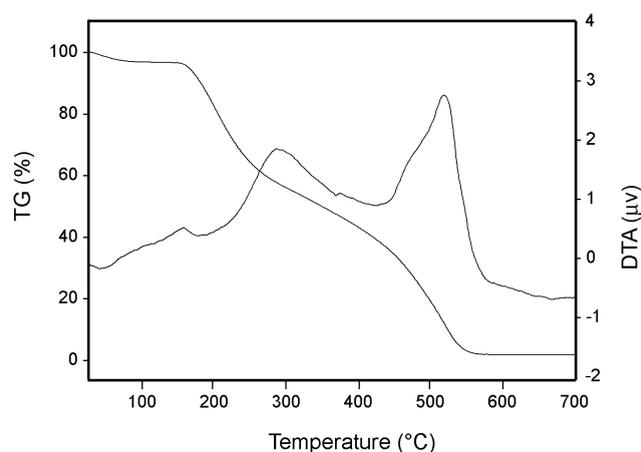


Figure 1. TG and DTA curves of PVDC-DTA-Pd.

Thermal stability of the catalyst influences the catalytic activity and re-cyclability greatly because Heck reaction is usually carried out at high temperature. Figure 1 shows the TG and DTA curves of PVDC-DTA-Pd in air atmosphere. PVDC-DTA-Pd is stable up to 160°C, and then the weight loss occurs due to the oxidative decomposition of the polymer carrier. The thermal stability of PVDC-DTA-Pd perfectly meets the high temperature condition which is required in Heck reactions.

Catalytic Performance of PVDC-DTA-Pd for Heck Reaction

The Heck reactions of aryl iodides catalyzed by the novel catalyst (PVDC-DTA-Pd) could be smoothly performed in the air, which makes it very convenient in practical application. Moreover, Heck reactions were usually carried out in organic solvent such as *N,N*-dimethyl formamide (DMF), *N*-methyl pyrrolidone (NMP), *N,N*-dimethyl acetamide (DMAc), toluene, acetonitrile, and etc. Generally, the catalytic performance varied with the solvent changes even though the reactions were catalyzed by the same catalyst. The catalytic activities of PVDC-DTA-Pd for Heck reaction of iodobenzene with acrylic acid in different solvents were evaluated. The results summarized in Table 2 show that the activity was low in solvents of low polarity. The activity was enhanced if the reaction was carried out in polar solvents (DMF, NMP), and the yield of the product increased. Interestingly, when substituted the organic solvent by water, the reaction of iodobenzene with acrylic acid

Table 2. Effect of solvent on catalytic performance of PVDC-DTA-Pd^a.

Entry	Solvent	Yield ^b (%)
1	Dioxane	84.8
2	<i>p</i> -Xylene	71.8
3	NMP	89.5
4	DMF	89.2
5	H ₂ O	99.6

^(a) Reaction conditions: PVDC-DTA-Pd (0.015 g), iodobenzene (1.5 mmol), acrylic acid (2.25 mmol), (n-Bu)₃N (3.0 mmol) and solvent (0.6 mL) in air at 90°C for 3 h; ^(b) isolated yield is based on iodobenzene.

could also be catalyzed perfectly by PVDC-DTA-Pd, and 99.6% of the cinnamic acid was obtained. We found that only a few papers were reported on Heck reactions in water. Bhattacharya et al. [18] reported Heck and Suzuki reactions catalyzed by PdCl₂ in water, but proper amount of cationic surfactant was required in the catalyst system. Dawood [19] and Leadbeater et al. [20] reported the Heck or Suzuki reactions promoted by microwave in water. Yokoyama et al. [21] and Weberskirch et al. [22] reported Heck reactions catalyzed by polymer supported palladium catalyst in water. However, the preparations of the polymer supports were complicated. Nonetheless, the lack of organic solvent in the reaction system is environmentally friendly and will be helpful to potential application.

Heck reactions catalyzed by supported palladium complexes were usually carried out at high temperature (160°C) [23]. High temperature is one of the important problems that restrict the widespread application of Heck reaction. The effect of reaction temperature on catalytic performance of PVDC-DTA-Pd was investigated by using Heck reaction of acrylic acid with iodobenzene in water. The results are summarized in Table 3. In the presence of PVDC-DTA-Pd, the model reaction could be carried out efficiently at very low temperature (50°C), though the yield was not high (Entry 1). Yield of the product increased when the temperature was raised from 50 to 90°C. Excellent yield (Entry 7) was obtained when

Table 3. Effect of reaction temperature and reaction time on catalytic performance^a.

Entry	Temperature (°C)	Time (h)	Yield ^b (%)
1	50	8	42.4
2	60	6	85.2
3	70	2	92.2
4	80	2	94.4
5	90	1	90.3
6	90	2	98.4
7	90	3	99.6

^(a) Reaction conditions: PVDC-DTA-Pd (0.015 g), iodobenzene (1.5 mmol), acrylic acid (2.25 mmol), (n-Bu)₃N (3.0 mmol) and H₂O (0.6 mL) in the air; ^(b) isolated yield is based on iodobenzene.

Table 4. Effect of catalyst content on catalytic performance^a.

Entry	Amount of catalyst (mol%)	Yield ^b (%)
1	0.015	75.9
2	0.075	86.7
3	0.150	92.7
4	0.230	99.6
5	0.310	99.6

(^a) Reaction conditions: iodobenzene (1.5 mmol), acrylic acid (2.25 mmol), (n-Bu)₃N (3.0 mmol) and H₂O (0.6 mL) in air at 90°C for 3 h; (^b) isolated yield is based on iodobenzene.

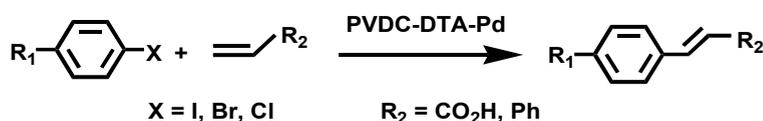
the reaction of acrylic acid with iodobenzene was performed at 90°C in water for 3 h. In contrast with other research works on Heck reaction catalyzed by polymer-supported palladium catalysts [24,25], PVDC-DTA-Pd should be considered as a novel and efficient heterogeneous catalyst.

The effect of the amount of catalyst on catalytic property is also one of the important factors to

estimate the performance of the catalyst because palladium is an expensive metal. The effect was studied by using the model Heck reaction and the results are listed in Table 4. The reaction was carried out efficiently even at low catalyst level (0.015 mol%), and the yield of the cinnamic acid was 75.9% (Entry 1). With increasing amount of catalyst, the yield of the Heck reaction increased gradually. When the amount of the catalyst reached 0.23 mol%, the yield of the product reached 99.6% (Entry 4).

Base plays an important role in Heck reaction because it is necessary to recover Pd(0) in each catalytic cycle. Both organic bases and inorganic bases were applied in Heck reaction. However, in our studies, when NaOAc was employed as a base, the reaction of iodobenzene with acrylic was very much limited in water. On the other hand, high yield was obtained by choosing (n-Bu)₃N as a base for the reaction of acrylic acid with iodobenzene catalyzed by PVDC-DTA-Pd in water.

The couplings of various aryl halides with acrylic acid or styrene catalyzed by PVDC-DTA-Pd were

Table 5. Heck reactions of aryl halides with alkenes catalyzed by PVDC-DTA-Pd^a.

Entry	Aryl iodide	Alkene	Temperature (°C)	Time (h)	Yield ^b (%)
1 ^c	4-CH ₃ OC ₆ H ₄ I	CO ₂ H	90	3	88.6
2 ^c	4-ClC ₆ H ₄ I	CO ₂ H	90	3	88.8
3 ^c	4-CH ₃ C ₆ H ₄ I	CO ₂ H	90	3	79.0
4 ^c	4-O ₂ NC ₆ H ₄ I	CO ₂ H	90	3	89.2
5 ^d	4-CH ₃ OC ₆ H ₄ I	Ph	90	3	84.2
6 ^d	4-ClC ₆ H ₄ I	Ph	90	3	98.7
7 ^d	4-CH ₃ C ₆ H ₄ I	Ph	90	3	87.3
8 ^d	4-O ₂ NC ₆ H ₄ I	Ph	90	3	94.2
9 ^e	PhBr	Ph	120	8	99.8
10 ^e	4-CH ₃ C ₆ H ₄ Br	Ph	120	8	88.0
11 ^e	4-O ₂ NC ₆ H ₄ Br	Ph	120	8	94.7
12 ^e	4-O ₂ NC ₆ H ₄ Cl	Ph	120	8	96.2

(^a) Reaction conditions: PVDC-DTA-Pd (0.015 g), aryl iodide (1.5 mmol), acrylic acid (2.25 mmol) and (n-Bu)₃N (3.0 mmol); (^b) isolated yield is based on aryl iodides; (^c) H₂O (0.6 mL) is used as solvent; (^d) DMF (0.6 mL) is used as solvent; (^e) tetrabutylammonium bromide (0.8 g) is used as solvent and the reaction is carried out in N₂ atmosphere.

Table 6. Re-usability of PVDC-DTA-Pd for Heck reaction^a.

Cycle	Time (h)	Yield ^b (%)
1	3	99.6
2	3	81.9
3	3	78.9
4	4	83.0
5	4	78.5
6	4	66.4

(^a) Reaction conditions: PVDC-DTA-Pd (0.015 g), iodobenzene (1.5 mmol), acrylic acid (2.25 mmol), (n-Bu)₃N (3.0 mmol) and H₂O (0.6 mL) in air at 90°C; (^b) isolated yield is based on iodobenzene.

also studied and the results are summarized in Table 5. It can be concluded that both electron-rich and electron-deficient aryl halides reacted with the alkenes to give the corresponding *trans*-products in moderate to high yields. The reactions of aryl iodides with acrylic acid were carried out smoothly at 90°C in water in the air (Entries 1-4). When acrylic acid was substituted for styrene (Entries 5-8), the moderate to high yields were obtained in DMF rather than in water because the hydrophilicity of styrene was poor. The possibility to use aryl bromides or aryl chlorides as substrates has also been examined. Unfortunately, the reactions were not effective either in water or in DMF, even at higher temperature. Inspired by Calo et al. [26], tetrabutylammonium bromide (TBAB) was adopted as solvent and the results (Entries 9-12) indicated that the coupling of aryl bromides or activated aryl chlorides with styrene could be carried out efficiently. The enhanced activity was ascribed to the phase transition of TBAB and the high stability of palladium active centre in TBAB.

The recovery and re-use of the catalyst is highly important because of the high price of the palladium compounds. So, we finally investigated the re-usability of the catalyst (Table 6). After completion of Heck reaction, the catalyst was re-cycled easily by filtration, then washed with CH₃CH₂OH and dried in the air. Palladium content in the re-cycled catalyst was 0.22 mmol/g, which was almost the same as the new catalyst. The result showed that the leaching of Pd in the reaction media was negligible. The recycled heterogeneous catalyst PVDC-DTA-Pd can be re-used for Heck reaction of iodobenzene with acrylic

acid. The yield of the cinnamic acid is up to 78.5% at the cycle of five, which indicated the high stability and good re-usability of PVDC-DTA-Pd. Because of the high price of the palladium complex, the re-usability of the PVDC-DTA-Pd reduced the cost of the Heck reaction considerably.

CONCLUSION

In conclusion, we first utilized the easily obtainable polymer material, poly(vinylidene dichloride), as carrier to prepare a new supported palladium catalyst by simple method. The catalyst was successfully applied for the Heck reactions to afford corresponding coupled products in moderate to good yields. When aryl iodides were chosen as substrates, Heck reactions could be carried out efficiently in water. Furthermore, the stability and re-usability of the catalyst in water was also good. Because of the high price of the palladium complex, the easily obtainable catalyst with good re-cyclability reduced the cost of the Heck reaction to a large extent.

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