

Catalytic Performance of PVC-Triethylene-Tetramine Supported Palladium Complex for Heck Reaction

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ABSTRACT: Polyvinyl chloride-triethylene-tetramine supported palladium complex (PVC-TETA-Pd) was prepared from polyvinyl chloride via simple method and the production cost of the complex was remarkably low. The complex was an efficient catalyst for Heck reaction. It was active for low activity substrates such as aryl bromides and aryl chlorides. The coupling of bromobenzene with styrene catalyzed by PVC-TETA-Pd afforded 99.8% yield of stilbene under the optimized

reaction conditions. PVC-TETA-Pd could catalyze the Heck reactions in the presence of several different kinds of acid-binding agents. Furthermore, the good reusability of PVC-DTA-Pd was also found for Heck reaction. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 2523–2527, 2010

Key words: metal-polymer complexes; catalysts; poly(vinyl chloride) (PVC); Heck reaction; palladium

INTRODUCTION

The palladium catalyzed coupling of alkene with aryl halide was well known as the Heck reaction and has proved to be one of the most important methods for carbon-carbon bond formation.^{1,2} It has been found widespread use in the synthesis of derivatives of cinnamate or *trans*-stilbene. The Heck reaction also holds much promise in the synthesis of intermediates for pharmaceuticals and in preparation of conjugated polymers.^{3,4} In view of these, much attention has been paid for the field in recent years.^{5–7} The commonly used homogeneous catalysts of palladium complexes (PdCl₂ or Pd(OAc)₂) with phosphine ligands have high activity in such transformations. However the drawbacks of these systems hampered the large-scale applications of Heck reaction, stemming from the precipitation of palladium black from reaction solution, the difficult in product separation and reusability of the catalysts. These problems can be overcome by the use of heterogeneous catalysts, made up of supported palladium complex. Palladium supported on various supports such as carbon,^{8,9} metal oxides,^{10,11} clays,¹²

zeolites,^{13,14} and molecular sieves^{15,16} have been shown to be efficient catalysts for the Heck arylation. Polymer supported palladium complexes attracted many scholars' attention because of their fine performance. Recently, a new catalytic system based on the palladium supported on poly(*N*-vinylimidazole) or poly(*N*-vinylimidazole-co-vinylcaprolactam) was prepared and high efficiency along with recycling ability of the catalyst was found.¹⁷ Luis and coworkers¹⁸ studied the catalytic performance of methyl imidazolium-modified polystyrene supported palladium complex for Heck reaction. The excellent yield and selectivity was obtained. Mahdavi et al.¹⁹ prepared poly[*N*-(2-aminoethyl)acrylamido]-imino-3-pyridine carbaldehyde supported palladium salts and summarized that the catalyst has excellent activity and stability in the Heck reaction. In addition, organosilicon-polymer supported palladium complexes also showed high activities for Heck reaction.^{20,21} But it has been found that the preparations of these polymer carriers involved long technological process. Together with the noble palladium compounds, the costs of these catalysts were very high and the applications of them were limited.

In recent years, several kinds of natural polymers supported palladium complexes were synthesized in our lab, and their catalytic activities for Heck reactions were studied.^{22–24} Here, a new synthetic polymer supported palladium catalyst, PVC-TETA-Pd, was synthesized from polyvinyl chloride by simple method. Compared with other supported palladium catalysts, the production cost of the complex was

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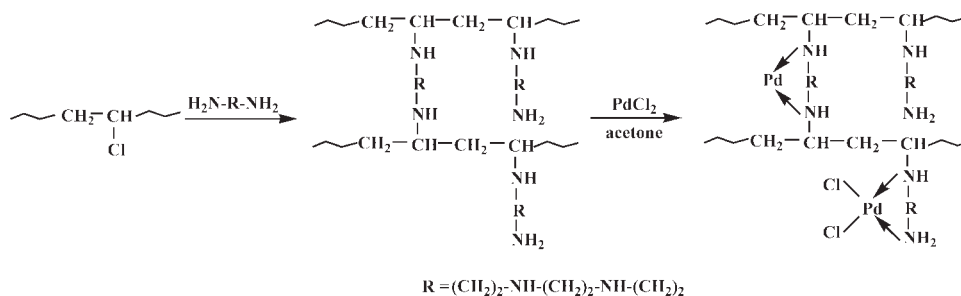


Figure 1 Synthesis route of PVC-TETA-Pd.

remarkably low because the method has advantages in easily obtaining material, simple synthetic route, and easy operation. How about the performance of the easily obtained catalyst? The effect of reaction temperature, reaction time, and tie-acid agent on catalytic activity of the complex was investigated in detail. The results showed that the complex is an efficient catalyst for Heck reactions of aryl bromides or aryl chlorides with alkenes at 120°C in tetrabutylammonium bromide.

EXPERIMENTAL

X-ray photoelectron spectra (XPS) were measured on an AXISULTRA spectrometer (Kratos Company, 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. The thermal analysis was performed on an EXSTAR6000 (Seiko Company, 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 Company, American). ¹H-NMR spectra were recorded on a Bruker AV400 (400 MHz) spectrometer with TMS as an internal standard in CDCl₃ or DMSO-*d*₆ as solvent. Pd content was measured on a Z-2000 atomic absorption spectrometry. N content was measured on a PE-2400 elemental analyzer.

Polyvinyl chloride powder was industrial grade. Triethylene-tetramine, tributylamine, and *p*-dibromobenzene were chemical pure. 4-Bromotoluene (98%), 4-bromo-nitrobenzene (98%) and 4-chloro-nitrobenzene (98%) were purchased from Lancaster and used as received. Palladium chloride, bromobenzene, 2,4-dinitro-bromobenzene, chlorobenzene, styrene, methyl acrylate, *n*-butyl acrylate, tetrabutylammonium bromide (TBAB) were analytical reagent. All other reagents were analytical reagents and used as received without further purification.

Preparation of the catalyst (Fig. 1)

The powder of polyvinyl chloride (1.0 g) was dispersed in 10 mL triethylene-tetramine. The mixture

was stirred at 80°C for 3 h in the air. The reaction mixture was filtered after it was cooled to room temperature. The brown powder was washed with plenty of water until the filtrate was colorless and pH value was neutral. Then the powder was dried at 100°C in vacuum for 12 h to give 1.12 g of polyvinyl chloride-triethylene-tetramine (abbreviated as PVC-TETA).

To a solution of PVC-TETA (1.0 g) in acetone (50 mL), PdCl₂ (0.1 g) was added. 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) and then dried at 100°C in vacuum for 6 h to give 1.02 g of puce PVC-TETA-Pd. N content in PVC-TETA-Pd is 5 mmol/g by element analysis and Pd content is 0.32 mmol/g. The molar ratio of N to Pd is about 1:15

Typical procedure for the Heck arylation of aryl bromides with styrene

PVC-TETA-Pd (0.02 g), styrene (2.25 mmol), bromobenzene or chlorobenzene (1.5 mmol), (*n*-Bu)₃N (3.0 mmol) and TBAB (0.8 g) were added in a 50 mL round-bottomed three necked flask. The reaction mixture was magnetically stirred 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 recrystallized to give the final product. The products were characterized by ¹H-NMR and IR.

RESULTS AND DISCUSSION

Characterization of PVC-TETA-Pd

To study the chemical state of palladium in the supported catalyst and the coordination of the polymer carrier with metal ion, the binding energies of Pd, PdCl₂, PVC-TETA and PVC-TETA-Pd were obtained through the XPS analysis. The results were summarized in Table I. The binding energy of Pd_{3d5/2} in PVC-TETA-Pd is 338.2 eV, which indicates that the chemical valence of palladium in the catalyst is

TABLE I
XPS Data for Pd, PdCl₂, PVC-TETA, and
PVC-TETA-Pd (eV*)^a

Sample	Binding energy of N _{1s}	Binding energy of Pd _{3d5/2}
Pd		335.4
PdCl ₂		338.3
PVC-TETA	399.3 401.1	
PVC-TETA-Pd	400.3 402.3	338.2

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

divalent. The binding energies of N_{1s} in PVC-TETA-Pd are 400.3 eV and 402.3 eV and they are higher than that in PVC-TETA, which indicates that electron transfer occurs and the electron density at nitrogen atom decreases. These results show that the coordination bonds are formed between N and Pd²⁺.

Thermal stability of the catalyst has great effect on its catalytic activity and recyclability because Heck reaction is usually carried out under high temperature condition. Figure 2 shows the TG and DTA curves of PVC-TETA-Pd under air atmosphere. TG analysis indicates that PVC-TETA-Pd is stable up to 250°C. Subsequently, the weight loss was occurred due to the oxidative decomposition of the polymer carrier. The thermal stability of PVC-TETA-Pd can satisfy the high temperature condition in Heck reaction.

Catalytic performance of PVC-TETA-Pd

Generally, the reaction activities of aryl iodides are very high in Heck reaction, but the prices of these substrates are also high and the applications of them are limited. Searching for effective catalyst systems used for cheap substrates such as aryl bromides or aryl chlorides is always an important research direc-

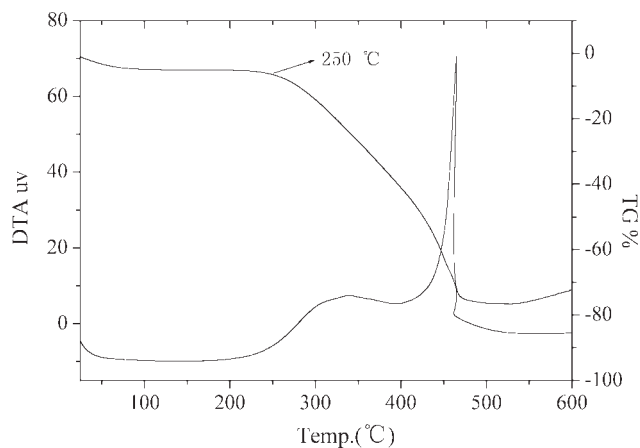


Figure 2 TG and DTA curves of PVC-TETA-Pd.

TABLE II
Effect of Reaction Temperature and Reaction
Temperature on Catalytic Performance^a

Entry	Temperature (°C)	Time (h)	Yield ^b (%)
1	100	8	42.4
2	110	8	74.1
3	120	8	99.8
4	130	8	97.1
5	120	1	9.8
6	120	2	87.3
7	120	3	90.9
8	120	4	96.7
9	120	6	99.7

^a Reaction conditions: PVC-TETA-Pd (0.02 g), bromobenzene (1.5 mmol), styrene (2.25 mmol), (n-Bu)₃N (3.0 mmol) and TBAB (0.8 g) in nitrogen atmosphere for 8 h.

^b Isolated yield was based on the bromobenzene.

tion. The catalytic performance of PVC-TETA-Pd for Heck reaction was evaluated by choosing the arylation of bromobenzene with styrene as model reaction. The reaction was typically carried out using TBAB as solvent and tributylamine as base under nitrogen atmosphere. The results showed that the reaction of bromobenzene with styrene catalyzed by PVC-TETA-Pd could be carried out smoothly and moderate to high yields of the *trans*-stilbene were obtained. To optimize the reaction conditions, the effects of reaction temperature, reaction time, and tie-acid agent were examined. Table II (Entry 1–4) showed the results of the model reaction at different temperature. It was initially performed at 100°C in N₂ and (n-Bu)₃N as a base. Only 42% yield of the product was obtained after the reaction was performed for 8 h. When the reaction temperature was increased to 110°C, the improved yield of 74% was obtained. A quantitative transformation was achieved with the temperature increased to 120°C (Entry 3). The yield of the product decreased slightly when the model reaction was processed at 130°C probably due to the side reactions increased at high temperature.

Table II (Entry 5–9) also showed the yield versus reaction time for the reaction of bromobenzene with styrene catalyzed by PVC-TETA-Pd at 120°C in TBAB using (n-Bu)₃N as the base. The cross-coupling reaction proceeded slowly within 1 h and the yield was only 9.8%. Subsequently, the reaction rate increased rapidly and yield of the *trans*-stilbene reached 87.3% after 2 h. With the reaction time increased continuously, the yield of the product increased slowly. The reaction was basically complete after 6 h. Compared with the catalytic performance of recently reported catalyst, MCM-41-supported poly(γ -mercaptopropylsiloxane palladium (0) complex,¹⁵ PVC-TETA-Pd showed higher activity for Heck reaction.

TABLE III
Effect of Tie-Acid Agents on Catalytic Performance of PVC-TETA-Pd^a

Entry	Base	Temperature (°C)	Yield ^b (%)
1	Et ₃ N	110	80.9
2	Et ₃ N	120	80.1
3	(n-Bu) ₃ N	110	74.1
4	(n-Bu) ₃ N	120	99.8
5	Na ₂ CO ₃	110	42.6
6	Na ₂ CO ₃	120	74.4
7	NaHCO ₃	110	71.3
8	NaHCO ₃	120	95.2
9	NaOAc	110	91.7
10	NaOAc	120	99.7
11	—	110	15.7

^a Reaction conditions: PVC-TETA-Pd (0.02 g), bromobenzene (1.5 mmol), styrene (2.25 mmol), tie-cid agent (3.0 mmol), and TBAB (0.8 g) in nitrogen atmosphere.

^b Isolated yield was based on the bromobenzene.

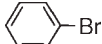

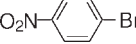

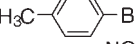

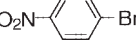

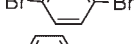

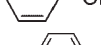

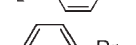

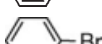

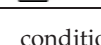

Tie-acid agent plays an important role in Heck reaction because it is necessary to recover Pd(0) in each catalytic cycle. Both organic tie-acid agents and inorganic tie-acid agents were applied for Heck arylation. Tributylamine, triethylamine, sodium carbonate, sodium acetate are the commonly used tie-acid agents in Heck reaction. In our studies, several tie-acid agents were screened for the reaction of bromobenzene with styrene, and the results were presented in Table III. With either organic or inorganic bases, the arylation products were obtained in moderate to high yields, which showed the high catalytic activity of PVC-TETA-Pd for Heck reaction in TBAB. It was also seen from the Table III that the yield of the model reaction at 120°C was higher than 110°C. The result was consistent with the effect of temperature that reported in the former part. However, when triethylamine was adopted as tie-acid agent, the yield almost unchanged no matter the reaction was carried out at 110°C or 120°C. It is probably due to the low boiling point of triethylamine. Inspired by researches on Heck reaction without tie-acid agent,²⁵ we investigated the catalytic activity of PVC-TETA-Pd for Heck reaction without tie-acid agent (Entry 11). Only 15.7% of the yield was obtained after the model reaction was processed for 8 h.

Table IV summarized the results of reactions using various aryl bromides or chlorides with varieties of olefins under the optimized reaction conditions. In the presence of the catalyst system, PVC-TETA-Pd, both the electron-rich and electron-deficient aryl halides reacted with the alkenes to give the corresponding *trans*-products in moderate to high yields. For example, treatment of 4-bromotoluene with styrene afforded 90.9% yield of the corresponding cross-coupled product. For the coupling of 4-bromo-nitrobenzene with styrene, the corresponding coupled product was obtained in 99.8% yield. The results

indicated that the PVC-TETA-Pd catalytic system is remarkably active and tolerant of a range of functionalities. The sterically challenging aryl bromide such as 2,4-dinitro-bromobenzene was also reacted with styrene to give the yield of 81.4%. Interestingly, the reaction of *p*-dibromobenzene with styrene produced 86% yield of di-coupling product. Similar result was also found in the studies of Heck reaction catalyzed by triaryl phosphine-functionalized *N*-heterocyclic carbene palladium complex.²⁶ Moderate to good yields were obtained when bromobenzene coupled with methyl acrylate or butyl acrylate, respectively. Chlorobenzene also reacted with styrene to give the moderate yield of 67%. Substituted the chlorobenzene with 4-nitro-chlorobenzene, the yield of the product was increased to 89.3%.

In Heck reaction, the recovery and reuse of the catalyst is highly important from an economic point of view, due to the high cost of the palladium compounds. So we investigated the possibility of reusability of the catalyst. When the reaction of bromobenzene with styrene was finished, 30 mL ether was added to the 50 mL round-bottomed three necked flask. The mixture was stirred for 5 min, and then placed statically for 10 min. The ether layer was separated, concentrated, and recrystallized to give the pure product. Then, bromobenzene, styrene, and tributylamine were added to the residual mixture in the round bottomed flask. The coupling of

TABLE IV
Heck Reactions of Aryl Bromides or Aryl Chlorides Catalyzed by PVC-TETA-Pd^a

Entry	Aryl haloid	Alkene	Yield ^b (%)
1			99.8
2			99.8
3			90.9
4			81.4
5			86.0
6			67.0
7			89.3
8			65.1
9			97.2

^a Reaction conditions: PVC-TETA-Pd (0.02 g), aryl bromide or aryl chloride (1.5 mmol), alkene (2.25 mmol), (n-Bu)₃N (3.0 mmol), and TBAB (0.8 g) in nitrogen atmosphere at 120°C for 8 h.

^b Isolated yield was based on aryl bromides or chlorides.

bromobenzene with styrene was occurred as before and the yield was up to 92.5%. With the catalyst system used repeatedly for the third and fourth time, the yield of the cross-coupled product was 84.8% and 72.5%, respectively. After the catalyst was reused for 4 times, Pd content in PVC-TETA-Pd was 0.26 mmol/g. The declining yields with the reused catalyst in successive cycles were probably due to that Pd leached from PVC-TETA-Pd and then Pd black was formed. So the catalytic activity of PVC-TETA-Pd decreased. However, the results showed that PVC-TETA-Pd was a reusable catalyst for Heck reaction all the same. In addition, the coupling product was easily separated, which indicated the practicability of the catalyst system. Because of the high price of the palladium complex, the reusability of PVC-TETA-Pd can reduce the cost of the Heck reaction greatly.

CONCLUSIONS

In conclusion, we have utilized the cheap and available material, polyvinyl chloride, to prepare a supported palladium catalyst with simple method. The catalyst was successfully applied for the Heck reactions of aryl bromides or aryl chlorides with alkenes to afford corresponding coupled products in moderate to good yields. The catalyst can be reused for several times to reduce the cost of the Heck reaction. Compared with other polymer supported palladium catalysts, PVC-TETA-Pd has the advantages of simple preparation process, low price of the raw material, good stability, and reusability. Currently, further efforts to extend the applications of the catalyst are underway in our laboratory.

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