

Polyvinyl chloride–polyethylene–polyamine supported palladium complexes as high efficient and recyclable catalysts for Heck reaction

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Abstract

Two kinds of polyvinyl chloride–polyethylene–polyamine supported palladium complexes were synthesized and characterized by XPS, TG, DTA, TEM, etc. These complexes are efficient catalysts for Heck reaction of acrylic acid with aryl iodides in air at the low temperature (50 °C) using 0.125 mol% of the catalysts. Effect of amount of the catalyst indicates that the Heck reaction acrylic acid with iodobenzene can be carried out with tiny amount of the catalyst (0.02%) at 90 °C. The complexes have high thermal stability and can be easily recovered and reused. Yields of making cinnamic acid were even high as 68.3 and 78.0% respectively for Heck reaction of acrylic acid with iodobenzene by using the two complexes that were recovered for 12 times.

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Keywords: Polyvinyl chloride; Polyethylene–polyamine; Palladium; Supported catalyst; Heck reaction

1. Introduction

The palladium-catalyzed Heck reaction [1] has received considerable attention in recent years [2], as it offers a versatile method for the generation of new C–C bonds in organic synthesis. The reaction is normally carried out with a palladium catalyst (PdCl₂) about 1 mol% of reactant, a phosphine ligand, and a base in homogeneous mode of operation. However, the reaction suffers from severe problems related with the separation, recovery and the instability of the homogeneous catalysts at high temperatures, which have so far precluded its widespread industrial application.

These problems can be overcome, however, by the use of heterogeneous catalysts, made up of supported palladium complex. These complexes include polymer supported palladium catalysts, palladium on carbon [3], palladium-supported metal oxides [4], clays [5], zeolites [6], and molecular sieves [7]. Polymer-supported metal complexes having

high activity and selectivity are currently attracting great interest because they can be easily separated and recovered. Andersson et al. [8] reported that polystyrene-supported phosphine palladium complex with a Pd/P of 1/1 showed very high activity in the arylation of methyl acrylate and styrene with iodobenzene. They found that the catalyst was more efficient than Pd/C, Pd(OAc)₂, PdCl₂, Pd(OAc)₂/2PPh₃, or Pd(PPh₃)₄, but noticeable deactivation of catalyst during repeated use was detected. Schwarz et al. [9] found that polymer-supported carbene palladium complexes were air stable and recyclable catalysts for Heck reaction. Uozumi and Kimura [10] studied Heck reaction of various aryl halides with alkenes proceeding in water in the presence of a palladium complex of a PS-PEG resin supported triarylphosphine ligand. Organosilicon polymer supported palladium catalysts for Heck reactions have also been reported recently [11]. Buchmeiser and Wurst [12] have made efforts in the same field as polymer supported catalysts for Heck reactions. All these catalysts show good catalytic activity for the Heck reaction, but the preparations of the catalyst supports involve many steps. Polyvinyl chloride modified by

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functional group can be prepared via displacement reaction directly without chloromethylation and makes its inexpensive and practical support for heterogeneous catalyst. Herein we report the synthesis and characterization of these two kinds of polyvinyl chloride–polyethylene–polyamine supported palladium complexes and the application of these complexes in Heck arylation of alkenes that can afford excellent yield and high *trans*-selectivity.

2. Experimental

2.1. Materials

Acrylic acid, styrene and DMF were distilled before use. 4-Iodoanisole (98%), 1-iodo-4-nitrobenzene (98%), 4-iodotoluene (98%), and 1-iodo-4-chlorobenzene (98%) were obtained from Lancaster company and were used as received. All other reagents were obtained from commercial sources and were used as received.

2.2. Measurements

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, and in air atmosphere. TEM images were obtained on a JEM100-CXIITEM instrument (JEOL Company, Japan) operated at an accelerating voltage of 100 kV.

2.3. Preparation of the catalysts

Polyvinyl chloride–ethylenediamine (abbreviated as PVC–EN) and polyvinyl chloride–diethylenetriamine (abbreviated as PVC–DTA) were prepared according to the procedure in literature [13]. Polyvinyl chloride (2.0 g) was added to ethylenediamine (20 mL) in a round-bottomed flask, then, 4 mL of H₂O was added, the mixture was

stirred at 60 °C in the air for 8 h. After being cooled to room temperature, and the reaction mixture was filtered and washed with plenty of H₂O and then dried at 80 °C in the air for 12 h to give 2.2 g of brown PVC–EN. PVC–DTA (2.3 g) was prepared according to the same procedure.

To a solution of PVC–EN (2.0 g) in acetone (50 mL), PdCl₂ (0.3 g) was added. The mixture was stirred at 60 °C in the air for 72 h. 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 2.2 g of puce polyvinyl chloride–ethylenediamine supported palladium complex (abbreviated as PVC–EN–Pd). Another puce complex, polyvinyl chloride–diethylenetriamine supported palladium complex (abbreviated as PVC–DTA–Pd) (2.2 g) was prepared according to the same procedure (Scheme 1).

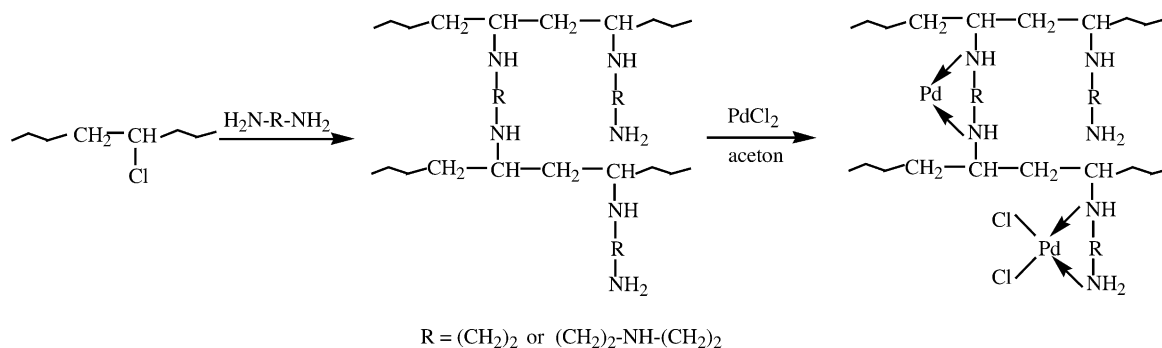
2.4. Catalytic reactions

2.4.1. Typical procedure for the Heck arylation of aryl halides with acrylic acid

PVC–EN–Pd or PVC–DTA–Pd complex (0.1 mol%), acrylic acid (6.0 mmol), aryl halides (5 mmol), tributylamine (12.0 mmol) and DMF (1 mL) were taken in a round-bottomed flask and stirred at 90 °C in the air for 3 h. After the reaction mixture was cooled to room temperature, H₂O (25 mL) and Na₂CO₃ (1.0 g) were added. After stirring for 10 min, PVC–EN–Pd or PVC–DTA–Pd complex was separated by filtration. The filtrate was treated with 3N HCl (5 mL). The precipitate was filtered, washed with H₂O (2 × 15 mL) and dried in the air to give *trans*-cinnamic acid.

2.4.2. Typical procedure for the Heck arylation of aryl halides with styrene

PVC–EN–Pd or PVC–DTA–Pd complex (0.1 mol%), styrene (6.0 mmol), aryl halides (5 mmol), tributylamine (6.0 mmol) and DMF (1 mL) were taken in a round-bottomed flask and stirred at 90 °C in the air for 3 h. The mixture was cooled to room temperature and dissolved in Et₂O (30 mL). PVC–EN–Pd or PVC–DTA–Pd complex was recovered from the mixture by filtration, and was washed with distilled H₂O (2 × 15 mL), EtOH (2 × 15 mL) and Et₂O (2 × 15 mL). The fil-



Scheme 1.

trate was treated with 3N HCl (2×15 mL), brine (3×15 mL) and dried over MgSO_4 . The solid product was obtained by recrystallization from Et_2O to give *trans*-stilbene.

3. Results and discussion

3.1. Characterization of the catalysts

XPS is used to study not only the coordination of macromolecular ligands and metal ions but also the chemical state of palladium presenting in the supported catalysts. The binding energies of Pd, PdCl_2 , PVC-EN, PVC-DTA, PVC-EN-Pd and PVC-DTA-Pd obtained in the XPS analysis are summarized in Table 1. The binding energies of Pd $3d_{5/2}$ of PVC-EN-Pd are 335.5 and 337.7, which suggests the existence of two different chemical state of Palladium, Pd^0 and Pd^{2+} . It can be seen that the binding energies of N 1s of PVC-EN-Pd also have two different data (339.4, 401.5) and the data are higher than those of PVC-DTA, which indicates the lone-pair electrons on the nitrogen transfers and the electron cloud density at nitrogen atom decreases. These results are probably due to the coordination of N with Pd^0 or Pd^{2+} . The same outcomes almost can be obtained by analyzing the binding energies of PVC-DTA and PVC-DTA-Pd.

Thermal stability of the catalyst has great effect on its catalytic activity and recyclability because Heck reaction is usually carried out under high temperature conditions. Figs. 1 and 2 show the TG and DTA curves of PVC-EN-Pd and PVC-DTA-Pd respectively at atmospheric conditions.

Table 1

XPS data for Pd, PdCl_2 , PVC-EN, PVC-DTA, PVC-EN-Pd and PVC-DTA-Pd (in eV)^a

Samples	N 1s	Pd $3d_{5/2}$
Pd		335.4
PdCl_2		338.3
PVC-EN	339.4, 401.5	
PVC-TEA	398.6, 400.1	
PVC-EN-Pd	399.8, 401.9	335.5, 337.7
PVC-TEA-Pd	339.3, 400.6	335.4, 337.5

^a All relative to C 1s = 284.8 eV.

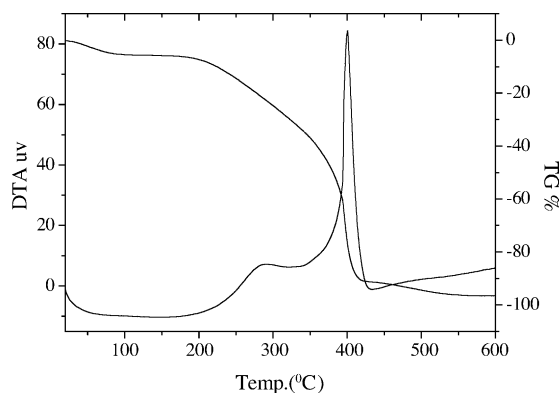


Fig. 1. TG and DTA curves of PVC-EN-Pd.

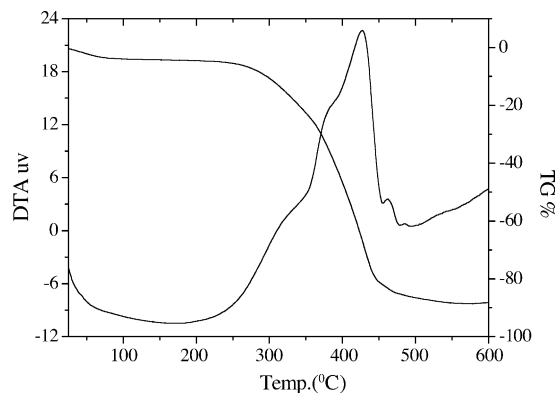


Fig. 2. TG and DTA curves of PVC-DTA-Pd.

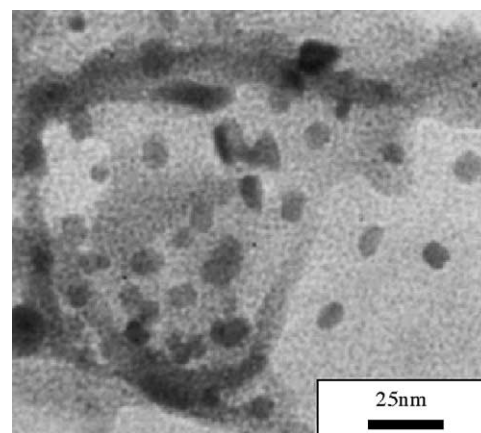


Fig. 3. TEM image of PVC-EN-Pd.

TG analysis show that PVC-EN-Pd and PVC-DTA-Pd are stable up to 200 and 250 °C respectively. DTA analysis of PVC-EN-Pd shows a strong exothermic peak at 400 °C, corresponding to the oxidation of the polymer carrier, and a similar strong exothermic peak is found at 425 °C for PVC-DTA-Pd. Figs. 3 and 4 show TEM images of PVC-EN-Pd and PVC-DTA-Pd. TEM confirms that Pd particles have uniform distribution in both of the catalysts. The

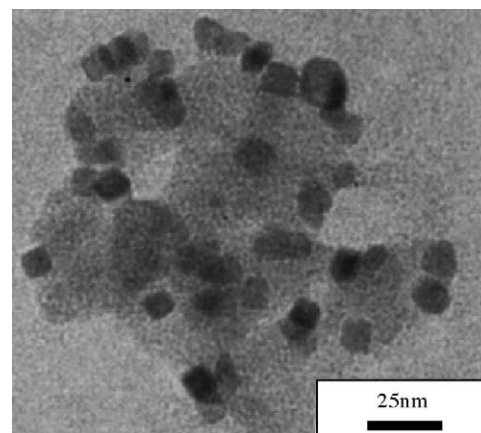


Fig. 4. TEM image of PVC-DTA-Pd.

Table 2
Effect of the reaction temperature on catalytic performance^a

Entry	Temperature (°C)	Time (h)	Yield (%) ^b	
			PVC-EN-Pd	PVC-DTA-Pd
1	100	3	95.0	95.2
2 ^c	100	3	95.2	95.0
3	90	3	94.8	95.2
4 ^c	90	3	95.0	95.3
5	80	5	84.6	83.5
6	70	5	81.4	80.1
7	60	5	76.6	78.3
8	50	12	70.8	70.6

^a Reactions were carried out with PVC-EN-Pd or PVC-DTA-Pd (0.125 mol% Pd), iodobenzene (5.0 mmol), acrylic acid (6.0 mmol), tributylamine (11.0 mmol), DMF (1.0 mL) in the air.

^b Isolated yield was based on the iodobenzene.

^c The reaction were carried out in nitrogen atmosphere.

average size of the Pd particles is 10 nm (PVC-EN-Pd) and 15 nm (PVC-DTA-Pd) respectively. Thermal analysis and TEM analysis indicate that both PVC-EN-Pd and PVC-DTA-Pd meet the basic qualifications as an efficient supported catalyst.

3.2. Heck arylation

Most homogeneously and heterogeneously catalyzed Heck reactions were studied under inert conditions. However if PVC-EN-Pd or PVC-DTA-Pd catalyst is used in Heck reaction, almost no catalytic activity difference was observed no matter they are carried out in the inert atmosphere or in the air (Table 2, entry 1–4). Such nature of the catalysts makes them convenient in industrial applications. The temperature that was required for Heck reaction is correlated with the catalyst adopted. The Heck reaction catalyzed by supported palladium complex is usually carried out at 100 °C [8,11 e.g.,14]. However, high temperature is one of the important problems to restrict its widespread application. The influence of temperature on catalytic property of PVC-EN-Pd and PVC-DTA-Pd was investigated by using Heck arylation of acrylic acid with iodobenzene. It can be seen from Table 2 that the reaction temperature has the same effect on the catalytic performance of these two catalysts. In the presence of PVC-EN-Pd or PVC-DTA-Pd, the Heck reaction can be carried out efficiently at low temperature (50 °C) but the yield is not very high. The yield of the product increases while reaction time is reduced to 3 h and the temperature arises from 50 to 90 °C. As result, excellent yields could be obtained at 90–100 °C with short reaction time (3 h) in the air.

It is a key issue to note that the amount of palladium catalyst plays an important role in the product yields. The arylation of acrylic acid with iodobenzene was studied with the amount of catalyst ranging from 0.02 to 0.5% (Table 3). It was found that the arylation could be carried out efficiently even with tiny amount of the catalyst (0.02%) at 90 °C, the yield of the cinnamic acid was 75.7% (PVC-EN-Pd) and 76.0% (PVC-DTA-Pd). Increasing the amount of palladium

Table 3
Effect of amount of catalyst on catalytic performance^a

Entry	Amount of catalyst (mol% Pd)	Time (h)	Yield ^b (%)	
			PVC-EN-Pd	PVC-DTA-Pd
1	0.5	3	95.2	95.5
2	0.25	3	95.0	95.3
3	0.125	3	95.0	95.2
4	0.1	3	94.6	95.2
5	0.08	5	89.5	90.6
6	0.06	5	85.2	84.8
7	0.04	12	80.6	80.6
8	0.02	12	75.7	76.0

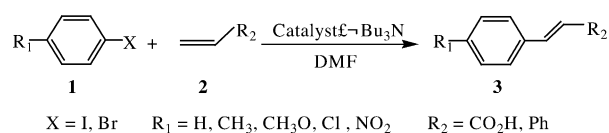
^a Reactions were carried out with proper amount of PVC-EN-Pd or PVC-DTA-Pd, iodobenzene (5.0 mmol), acrylic acid (6.0 mmol), tributylamine (11.0 mmol), DMF (1.0 mL) at 90 °C in the air.

^b Isolated yield was based on the iodobenzene.

catalyst gave higher yield and shorter reaction time until the amount of the catalyst increased to 0.1%. In order to reduce the cost, several groups [15] had focused on using low Pd-loading catalyst in Heck reaction. Reetz et al. [15b] reported the reaction of styrene with bromobenzene using only 0.0009 mol% of Pd(OAc)₂ (130 °C), and the conversion turned out to be 85% after 96 h. The low palladium concentration usually led to a long period of reaction, which was consistent with our experimental result. de Vries et al. [15c] concluded that the appropriate palladium concentration is between 0.01 and 0.1 mol%. However, most of these catalytic systems are homogeneous and suffer from the problems related with the separation and recovery of the catalysts.

PVC-EN-Pd and PVC-DTA-Pd were evaluated in Heck arylation (Scheme 2) of aryl halide with acrylic acid or styrene using DMF as a solvent and tributylamine as base under atmospheric conditions. The aryl olefins were obtained with yields ranging from good to excellence (Table 4). IR and ¹H NMR spectra of all products were conformed. It can be seen from the table that the Heck arylations of acrylic acid or styrene with aryl iodides can be efficiently carried out at 90 °C to afford the *trans*-product in high yield, and *cis*-product was not observed. Neither electron-donating group nor electron-withdrawing group on aryl iodides has much effect on the yield of products. In presence of a catalytic amount of PPh₃, the arylations of aryl bromides with acrylic acid or styrene can also be carried out at higher temperature (120 °C) for longer time (5 h). The results are similar to Cai's researches [11g], but the amount of the catalyst of 0.1 mol% is much less than those of 0.6 mol% reported by Cai et al.

The catalysts were recovered from the reaction mixture by simple filtration after the arylation, washed with H₂O, CH₃CH₂OH and CH₃CH₂OCH₂CH₃, then dried in



Scheme 2.

Table 4
Heck arylation of aryl halides with alkenes catalyzed by PVC–EN–Pd or PVC–DTA–Pd^a

Entry	Aryl halide	R ₂	Temperature (°C)	Time (h)	Products	Yield (%) ^b	
						PVC–EN–Pd	PVC–DTA–Pd
1	C ₆ H ₅ I	CO ₂ H	90	3	3a	94.5	95.2
2	C ₆ H ₅ Br	CO ₂ H	120	5	3a	85.5	85.0
3	4-CH ₃ C ₆ H ₄ I	CO ₂ H	90	3	3b	92.6	92.0
4	4-CH ₃ C ₆ H ₄ Br	CO ₂ H	120	5	3b	81.6	82.8
5	4-CH ₃ OC ₆ H ₄ I	CO ₂ H	90	3	3c	89.5	89.5
6	4-ClC ₆ H ₄ I	CO ₂ H	90	3	3d	88.9	89.5
7	4-O ₂ NC ₆ H ₄ I	CO ₂ H	90	3	3e	87.8	90.0
8	C ₆ H ₅ I	Ph	90	3	3f	92.6	92.0
9	C ₆ H ₅ Br	Ph	120	5	3f	83.5	84.5
10	4-CH ₃ C ₆ H ₄ I	Ph	90	3	3g	89.3	89.7
11	4-CH ₃ C ₆ H ₄ Br	Ph	120	5	3g	81.2	80.0
12	4-CH ₃ OC ₆ H ₄ I	Ph	90	3	3h	94.1	92.6
13	4-ClC ₆ H ₄ I	Ph	90	3	3i	91.6	93.3
14	4-O ₂ NC ₆ H ₄ I	Ph	90	3	3j	93.0	94.8

^a Reactions were carried out with PVC–EN–Pd or PVC–DTA–Pd (0.1 mol% Pd), aryl halides (5.0 mmol), alkene (6.0 mmol), tributylamine (6.0 mmol), DMF (1.0 mL) in the air. When alkene was used as acrylic acid, 11.0 mmol tributylamine was added. As for Heck arylations of aryl bromides with acrylic acid or styrene, 0.0005 mmol of PPh₃ was added.

^b Isolated yield was based on the aryl halides.

Table 5
Recycling and reuse of the catalysts in the Heck reaction^a

Cycle	Time (h)	Yield (%) ^b	
		PVC–EN–Pd	PVC–DTA–Pd
1	3	94.5	94.8
2	3	94.2	94.6
3	3	94.5	93.5
4	3	94.0	94.1
5	3	94.2	94.1
6	3	93.8	94.2
7	3	93.5	94.0
8	3	86.0	88.7
9	3	83.3	86.9
10	5	78.7	84.9
11	5	74.2	80.6
12	5	68.3	78.0

^a Reactions were carried out with PVC–EN–Pd or PVC–DTA–Pd (0.125 mol% Pd), iodobenzene (5.0 mmol), acrylic acid (6.0 mmol), tributylamine (11.0 mmol), DMF (1.0 mL) at 90 °C in the air.

^b Isolated yield was based on the iodobenzene.

air. Recyclabilities of the PVC–EN–Pd and PVC–DTA–Pd were examined for the reaction of iodobenzene with acrylic acid. It can be seen from Table 5 that the catalytic activities of PVC–EN–Pd and PVC–DTA–Pd are almost unchanged after seven times of recovery, and the difference between the catalytic activities of these two catalysts is not obvious. In the subsequent cycles, the catalytic activity of these two catalysts decrease observably, with PVC–EN–Pd decreasing faster than PVC–DTA–Pd, which probably attributed to the fact that PVC–EN–Pd has higher thermal stability than PVC–DTA–Pd.

4. Conclusions

In summary, PVC–EN–Pd and PVC–DTA–Pd have been prepared easily by using inexpensive supports and exhibit

high activity toward the Heck reaction of aryl iodides with olefins without inert atmosphere. Small amounts of catalysts (0.1%) and low temperature are required to perform the Heck reaction on aryl iodides. These catalysts can be easily separated and recovered from the reaction mixture by filtration and reused many times. The results show that these new supported palladium catalysts are very effective for Heck reaction under gentle conditions, such as low temperature without inert atmosphere, and should be considered as effective heterogeneous catalysts for Heck reaction.

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