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Nanopalladium immobilized on aminoethanol-functionalized poly(vinyl chloride): an easily prepared, air and moisture stable catalyst for *Heck* reactions

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Abstract The Pd nanoparticles with narrow size distribution immobilized on the polymer surface of poly(vinyl chloride) supported 2-aminoethanol (*PVC-AE*) were achieved by a simple procedure applying the corresponding functionalized polymer and $PdCl_2$ in ethanol. The as-prepared catalyst (*PVC-AE*-Pd^0) was found to be air and moisture stable and exhibits significant catalytic activity for *Heck* reactions under mild operating conditions. Furthermore, the catalyst can be easily recovered by simple filtration and reused for at least 6 cycles without losing its activity.

Keywords Nanopalladium; Poly(vinyl chloride); Supported catalyst; *Heck* reaction.

Introduction

The Pd-catalyzed arylation or vinylation of olefins, universally referred to as the *Heck* reaction [1], is one of the most important C–C coupling reactions which provide a direct route to produce functionalized olefin. They may be used for the synthesis of multifunctional derivatives [2] including bioactive compounds, natural products, pharmaceuticals, and high-performance materials. The *Heck* reaction is generally catalyzed by soluble Pd^{2+} or Pd^0 complexes in the presence of phosphane ligands [3], which play the role of stabilizers of *in situ* formed soluble Pd^0 in homogeneous solution in the presence of base under an inert atmosphere. However, the relatively high price of the palladium complex has greatly limited the industrial application of homogeneous *Heck* reaction, and some of the palladium phosphine complexes are sensitive to air and moisture. On the other hand, phosphane-free catalysts have received great interest recently as a less complicated, environmentally friendly alternative to phosphane-containing systems [4]. Significant advances have been made in the past few years in developing such catalysts. These include the use of N- [5] or S-based palladacycles [6], N,S-based carbenes [7], and N-heterocyclic carbenes (NHC) [8] as ligands in palladium-catalyzed *Heck* reactions. However, all of these catalyst systems suffer from drawbacks of one kind or another, such as the high sensitivity of ligands towards air and moisture, the problems of tedious separation, recycling, and deactivation *via* the aggregation of Pd^0 nanoparticles formed *in situ* during the *Heck* reaction process. To overcome these problems, many approaches to separate and recycle metal nanoparticles are to immobilize them on solid supports such as organic polymer matrix [9] and inorganic microsphere [10] (*e.g.*, carbon, metal oxides, sol-gel, clays, and zeolites), making them more stable and really easy and simple to separate from the reaction products mixture. Among

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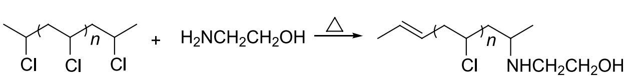
the preparations of nano-Pd^0 particles, the chemical reduction of palladium salt in an aqueous or organic solution by suitable reducing agents such as hydrazine [11], hydrogen [12], and sodium borohydride [13] have been widely adopted in most cases, even though there are questions regarding the toxicity of some of these reducing agents. The employment of polymers in these systems was mainly involved with the protection of the nanosized palladium from aggregation. The report of other properties about the polymer such as reducing properties was extremely rare. It would still be desirable to develop a more robust, simple, and cost-effective non-phosphane ligands catalyst system for use in nano-Pd^0 catalyzed *Heck* reactions.

It is well known that poly(vinyl chloride) (*PVC*) is widely used, inexpensive, and easily modified by functional groups *via* a displacement reaction directly without chloromethylation which makes it a suitable polymeric support for the heterogeneous catalyst. Recently, it has been discovered that amino alcohols such as prolinol, *trans*-2-aminocyclohexanol, and triethanolamine are effective ligands (O,N-ligands) in the nickel-catalyzed *Suzuki* [14] and in the palladium-catalyzed *Heck* reaction [15]. To develop simple and reliable protocols for the immobilization of catalytically active palladium nanoparticles on functionalized *PVC* we attempted to prepare and characterize the functionalized polymer of *PVC* supported 2-aminoethanol (*e.g.*, *PVC*–$NHCH_2CH_2OH$, abbreviated as *PVC-AE*) and further use it as support to immobilize palladium nanoparticles. Herein, we demonstrate that the as-prepared catalyst provides an active and recyclable heterogeneous catalyst for the *Heck* type carbon-carbon bond formation reaction in the absence of phosphine ligands under air and moisture with excellent yields.

Results and discussion

The preparation of the *PVC-AE* involved the addition of an excess of 2-aminoethanol to commercially available *PVC* resin at 80°C for the specific time to afford the corresponding functionalized resin (Scheme 1).

The IR spectrum of the *PVC-AE* showed the characteristic absorption of an amino (N–H) group at $3438\,cm^{-1}$ and the absorption of a double bond (C=C) at $1637\,cm^{-1}$. The amino group content was found to be 2.87 mmol/g. The catalyst *PVC-AE*-Pd^0 is directly prepared by simple *in situ* reduction of an ethanolic solution of palladium chloride in the presence of *PVC-AE* support. Metal content in *PVC-AE*-Pd^0 catalyst was found to be 0.52 mmol/g by atomic absorption spectroscopy. The TEM image shows the formation of palladium nanoparticles in the range of 20–40 nm (Fig. 1).



Scheme 1

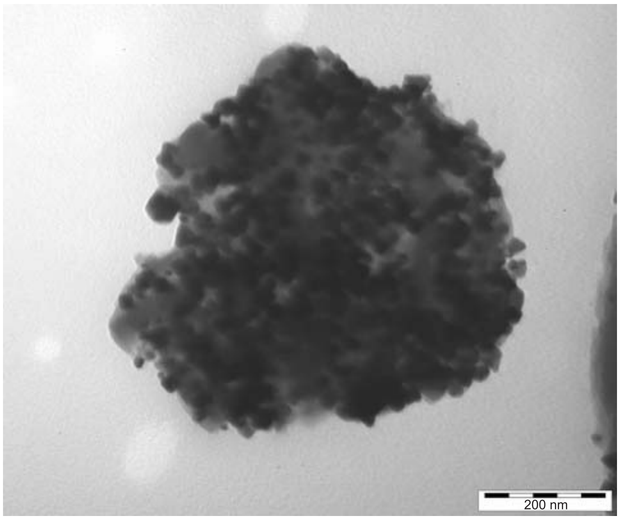


Fig. 1 TEM image of *PVC-AE*-Pd^0

The thermal stability of the *PVC-AE* has a great effect on its catalytic activity and recyclability because the *Heck* reaction is usually carried out under heat conditions. Figure 2 displays the TG curve of *PVC-AE*-Pd^0 at atmospheric conditions. TG analysis shows that *PVC-AE*-Pd^0 is stable up to 200°C.

Preliminary testing for *Heck* reaction was carried out by treating 4-iodoanisole with styrene in ethanol catalyzed by *PVC-AE*-Pd^0 with a yield of 90%. Encouraged by this result, we studied other aryl halides and olefins under the same nonoptimized conditions. All reactions were performed at reflux conditions by using 1.0 mol% of catalyst loading (Scheme 2). The results are as shown in Table 1.

PVC-AE-Pd^0 was used in *Heck* arylation of aryl halide with styrene or acrylic acid using ethanol as a solvent and triethylamine as base under atmospheric conditions. The aryl olefins were obtained with yields ranging from good to excellent and the structures of the products were confirmed by IR and ^1H NMR spectra. It can be seen that the *Heck* arylations

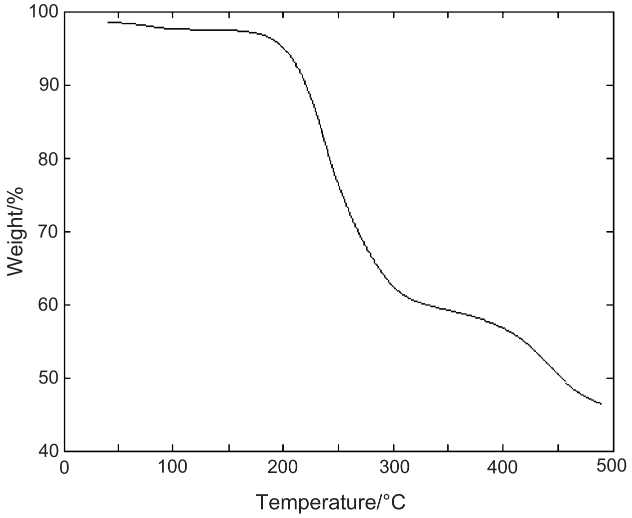
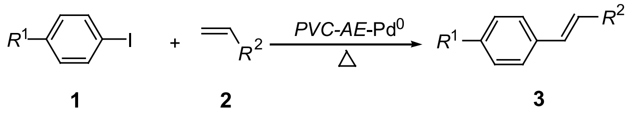


Fig. 2 TG curves of *PVC-AE*-Pd^0



Scheme 2

of acrylic acid or styrene with aryl halides can be efficiently carried out at 78°C to afford the (*E*)-products in high yield, and the (*Z*)-products were not observed. The electronic effects and the nature of substituents on aryl halides ring did show obvious effects on the yield of products. When an aromatic cycle containing electron-donating groups (such as a methoxy group) were employed (Table 1, entries 1 and 6), higher yields were obtained than for those with electron-withdrawing groups (such as a nitro group) on the aromatic ring (Table 1, entries 5 and 10).

One of the main aims of our study was to investigate the reuse and recycling of the *PVC-AE*-Pd^0 catalyst. The catalyst was easily recovered from the reaction mixture by simple filtration after the arylation, washed with 95% ethanol and diethyl ether, and then dried in air. Reusabilities of the *PVC-AE*-Pd^0 were examined by using the reaction of 4-chloro-1-iodobenzene with acrylic acid as model. It can be seen from Fig. 3 that the catalyst could be reused for 6 runs while retaining the same activity and selectivity as well as without loss of the activity.

The TEM analysis shows the presence of smaller palladium nanoparticles along with some slight agglomeration of the particles in the used catalyst (Fig. 4). However, the consistent activity of the catalyst from the recycling experiments reveals that slight particle agglomeration has less influence on the reactivity.

In conclusion, *PVC-AE*-Pd^0 was prepared easily by using an inexpensive support and exhibited high activity in the *Heck* reaction of aryl iodides with olefins in air. The catalyst can be easily separated and recovered from the reaction mixture by filtration and reused at least for 6 times. The protocol offers several advantages, such as mild reaction condition, simple isolation procedure, cleaner reaction profiles, high yields of products, as well as ease of recovery and reuse of the novel supported nano-Pd^0 catalyst.

Table 1 *PVC-AE*-Pd^0 catalyzed *Heck* reactions

Entry	R^1	R^2	Time/h	Yields[a]/%	Mp/°C	
					Found	Ref. [16]
1	CH_3O	*Ph*	5	90	134–136	134–135
2	CH_3	*Ph*	5	81	118–120	118–119
3	H	*Ph*	5	77	123–125	124
4	Cl	*Ph*	5	83	126–128	127–128
5	NO_2	*Ph*	5	66	156–158	156–157
6	CH_3O	COOH	4	80	171–173	173–174
7	CH_3	COOH	4	68	198–200	200–201
8	H	COOH	4	71	130–132	131–132
9	Cl	COOH	4	82	247–249	249–250
10	NO_2	COOH	4	62	285–287	286–287

[a] Isolated yields

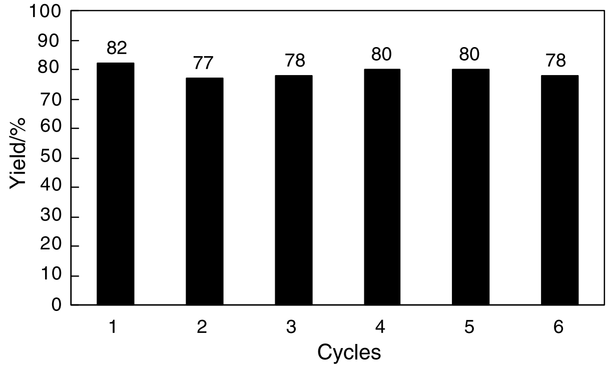


Fig. 3 Reuse of the *PVC-AE*-Pd^0 catalyst

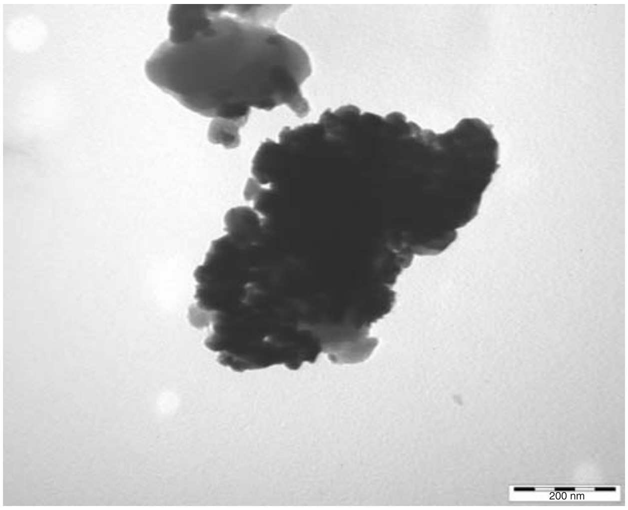


Fig. 4 TEM image of *PVC-AE*-Pd^0 after six reaction cycles

Experimental

The chemicals were obtained from commercial sources and used as received. Melting points were measured on an Electrothermal X_6 microscopy digital melting point appratus. IR spectra were recorded on a Bruke Equinox-55 spectrometer using KBr pellets. ^1H NMR spectra were performed with a 300 MHz Bruker Advance instrument using $CDCl_3$ as a solvent and *TMS* as an internal standard. The contents of elemental palladium in the polymeric catalyst were determined by TAS-990 atomic absorption spectroscopy (AAS). The thermal analysis was performed on a Perkin Elmer TGS-2 thermal analysis system at a heating rate of 10°C/min under air atmosphere. Transmission electron microscopy (TEM) was performed with a Philips Tecnai instrument operating at 40–100 kV.

Preparation of the PVC-AE

Poly(vinyl chloride) (10.0 g) was added to 30 cm^3 2-aminoethanol in a round-bottomed flask, then, the mixture was stirred at 100°C in the air for 48 h. After being cooled to room temperature, the reaction mixture was filtered and washed with plenty of H_2O until the filtrate reached neutral and then dried in air to give brown *PVC-AE*. The amino group content was found to be 2.87 mmol/g by elemental microanalysis.

Preparation of nano-Pd immobilized on PVC-AE (PVC-AE-Pd⁰)

The nano-Pd^0 preparation process is "green" and very straightforward. Specifically, 1 g *PVC-AE* was swollen in 20 cm^3 ethanol for 2 h by magnetic stirring, then 0.3 g $PdCl_2$ (1.69 mmol) were added to the mixture and it was heated to reflux. The resulting light yellow solution was further stirred for 24 h at the same temperature. During this process the color of the solution turned from light yellow to colorless, indicating the formation of nano-Pd^0. The supported Pd^0 nanoparticles were filtered off and washed with ethanol, acetone, and diethyl ether. After drying, 2.2 g of dry *PVC-AE* immobilized nano-Pd^0 particles (abbreviated as *PVC-AE*-Pd^0) were obtained. The pallladium content was found to be 0.52 mmol/g of dry resin by AAS. The as-prepared nano-Pd^0 can be preserved for months under air without changes of properties.

General procedure for Heck reaction of aryl iodides with olefins

To a mixture of 5.0 mmol aryl iodide, 12.0 mmol triethylamine, and 6.0 mmol olefin in 1.0 cm^3 95% ethanol, 0.1 g *PVC-AE*-Pd^0 catalyst (0.05 mmol) were added and stirred under reflux. After a specified period, the reaction mixture was filtered and the residue was washed with 95% ethanol. When a styrene was used as substrate, the solvent was evaporated under vacuum, diethyl ether was added, and it was washed with distilled water. The organic layer was separated, dried over Na_2SO_4, and the solvent was removed under vacuum. The resultant mixture was purified by preparative TLC to get the desired product; when acrylic acid was used as substrate, the filtrate was poured into water, then neutralized with diluted HCl to precipitate the product, which was further purified by recrystallization. All of the products are known and the data were found to be identical with those reported in literature.

Acknowledgements

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