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ORIGINAL PAPER

Synthesis of immobilized nanopalladium on polymer-supported Schiff base, and study of its catalytic activity in the Suzuki–Miyaura reaction

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Abstract Nanopalladium particles immobilized on a matrix of poly(vinyl chloride) (PVC)-supported Schiff base were prepared from PVC with sequential attachment of ethylenediamine and salicylaldehyde, followed by treatment with an ethanolic solution of palladium chloride. The as-prepared catalyst was found to be air and moisture-stable and to have significant catalytic activity in Suzuki–Miyaura reactions under mild operating conditions. Various phenyl halides were coupled with phenylboronic acid in aqueous ethanol, under air, to afford the corresponding cross-coupled products in good yields. Furthermore, the catalyst can be easily recovered by simple filtration and reused for up to five cycles without losing its activity.

Keywords Poly(vinyl chloride) · Schiff base · Nanopalladium · Heterogeneous catalysis · Suzuki–Miyaura reaction · Biaryls

Introduction

Transition metal-catalyzed cross-coupling is a versatile and highly useful transformation, which yields a variety of organic compounds. In particular, the Suzuki–Miyaura cross-coupling reaction, which is the palladium-catalyzed cross-coupling of organic halides with organoboron compounds, is one of the most important methods of forming sp^2–sp^2 carbon–carbon bonds in synthetic chemistry, and in industrial applications [1–6]. In the past few years, many attempts have been made to develop effective palladium complexes, which can act as highly active catalysts for this homogeneous reaction. Among these, various ligands for example phosphorus ligands [7–10], N-heterocyclic carbenes [11–13], P,O-based ligands [14], bis(thiourea) ligands [15], and thiosemicarbazone [16], etc., have been used to stabilize the catalytic palladium species. Although homogeneous catalysts often have greater activity in such transformations, most are expensive, not easily available, and require air-free handling to prevent oxidation; the main drawback of these catalysts is, however, the need to separate them from the reaction mixture at the end of the reaction. The heterogenization of these catalysts on polymeric supports therefore constitutes a logical approach to combining their homogeneous catalytic properties with the advantages of heterogeneous catalysts, for example facile separation from the reaction mixture and recyclability. Therefore, the development of an insoluble polymer-supported palladium catalyst has attracted much attention in organic synthesis. Palladium complexes immobilized on solid supports, for example organic polymeric matrices (e.g. PS–PEG resin [17], cellulose [18], and polymer-supported phosphine [19, 20], etc.) and inorganic microspheres (e.g. carbon [21], metal oxides [22], and zeolites [23], etc.), have been reported as catalysts in Suzuki–Miyaura reactions. Nevertheless, there is still a need for an efficient heterogeneous catalyst that is air and moisture stable and applicable to a wide range of Suzuki–Miyaura reactions.

It is well known that poly(vinyl chloride) (PVC) is widely used, inexpensive, and easily modified by functional groups via displacement reaction directly without chloromethylation, which makes it a suitable polymeric support for heterogeneous catalysts. Palladium is well known to form stable complexes with a wide variety of organic ligands with P, N, O, and S atoms, because of its

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pronounced coordination properties [7–17]. In a continuation of our work on the development of simple and reliable procedures for immobilization of catalytically active palladium nanoparticles on functionalized PVC, we have attempted to prepare and characterize the functionalized polymer of PVC-supported Schiff base and, further, to use it as carrier to immobilize palladium nanoparticles. In this paper, we report that the as-prepared catalyst had high activity as a recyclable heterogeneous catalyst for the Suzuki–Miyaura type carbon–carbon bond formation in ambient atmosphere, with excellent yields.

Results and discussion

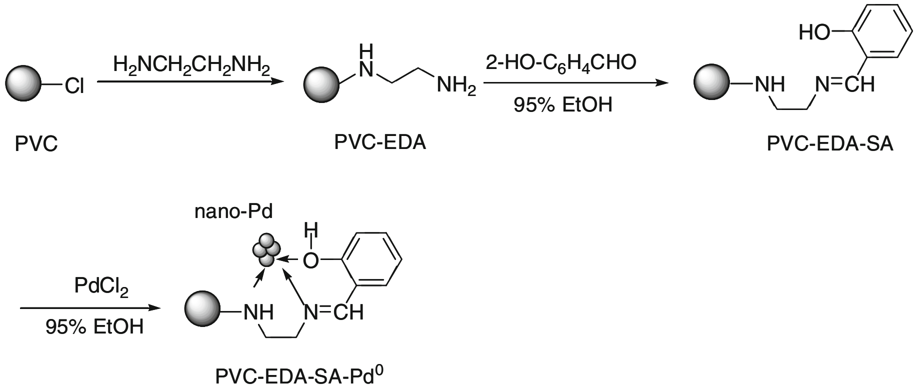
Preparation and characterization of PVC–EDA, PVC–EDA–SA, and PVC–EDA–SA–Pd^0

The preparation of the PVC–EDA involved addition of excess ethylenediamine to commercially available PVC resin at 80 °C for a specific time to afford the corresponding functionalized resin. The synthesized PVC–EDA resin was then treated with salicylaldehyde in ethanol solution to produce the PVC-supported Schiff base resin (PVC–EDA–SA). The catalyst PVC–EDA–SA–Pd^0 was directly prepared by simple in-situ reduction of of palladium chloride, in ethanolic solution, with heterogenized ligands of PVC–EDA–SA. The synthesis of nanopalladium immobilized on PVC-supported Schiff base is shown in Scheme 1.

The IR spectra of PVC–EDA–SA and PVC–EDA–SA–Pd^0 catalysts were recorded. The IR spectrum of PVC–EDA–SA contained absorption bands at 1,640.7 and 1,278.6 cm^{-1} for (C=N azomethine) and C–O (phenolic) bonds. These bands are negatively shifted to 1,630.5 cm^{-1} (C=N) and to 1,261.3 cm^{-1} (C–O) in the PVC–EDA–SA–Pd^0, indicating coordination of the nitrogen and oxygen atoms with the palladium in the complexes. Additionally, the IR spectrum of the PVC–EDA–SA–Pd^0 contains absorption at 551.0 cm^{-1}, which was assigned to the Pd–N bond, confirming the formation of a palladium complex on the surface of the polymer.

The morphology of PVC–EDA–SA–Pd^0 and the polymer support PVC–EDA–SA was studied by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). A clear change in morphology is observed after anchoring palladium on the polymer support (Fig. 1). TEM images showed the presence of palladium nanoparticles of about 40 nm size distributed on the surface of the polymer matrix (Fig. 2, left).

Scheme 1



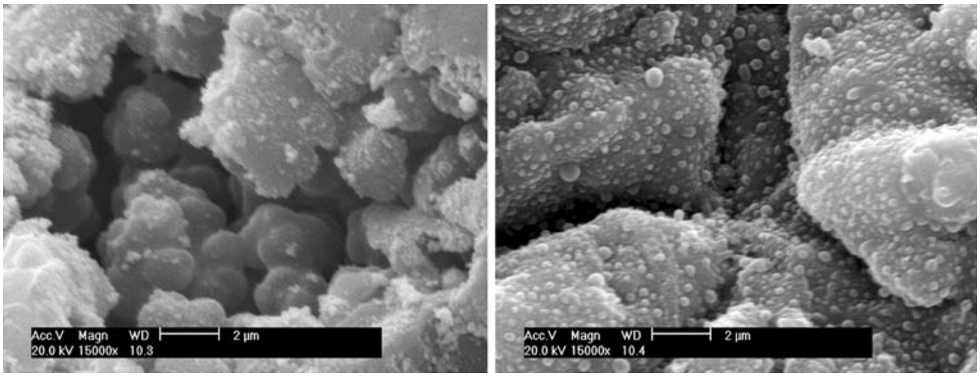


Fig. 1 SEM images of the polymer-supported PVC–EDA–SA (*left*) and the fresh catalyst PVC–EDA–SA–Pd^0 (*right*)

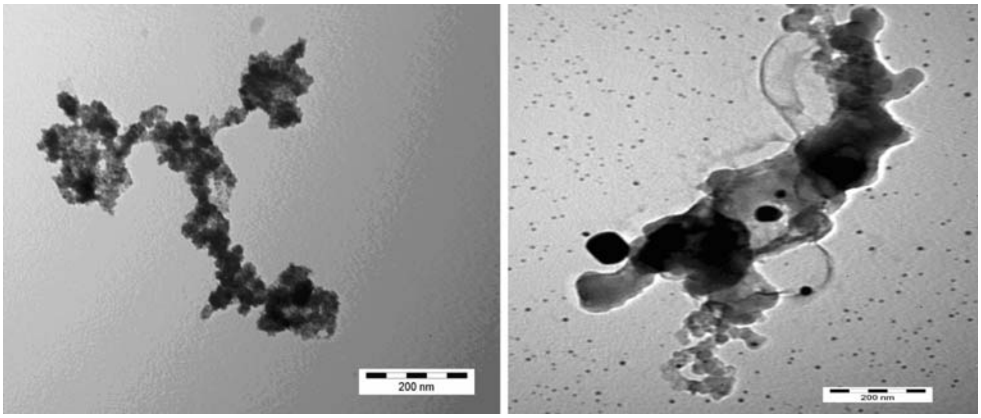


Fig. 2 TEM images of the fresh catalyst (*left*) and the reused catalyst (*right*) at the same magnification

Table 1 Effect of the base on catalyst performance

Entry	Base	Time (h)	Yield[a] (%)	TON[b]	TOF[c] (h^{-1})
1	No base	12	0	0	0
2	Cs_2CO_3	2	99	198	99
3	K_2CO_3	0.5	95	190	380
4	Na_2CO_3	4	99	198	50
5	$NaHCO_3$	1.25	99	198	158
6	Na_3PO_4	4.5	93	186	42
7	NaOH	1.25	65	130	104
8	KOH	1.5	72	144	96

Reaction conditions: 4-nitrophenyl iodide (1.0 mmol), phenylboronic acid (1.0 mmol), base (2.0 mmol), PVC–EDA–SA–Pd^0 (0.05 g, 0.01 mmol of Pd), and 10.0 cm^3 95% EtOH at reflux under air

[a] Isolated yield based on 4-nitrophenyl iodide

[b] TON (turnover number) = product (mol)/catalyst (mol)

[c] TOF (turnover frequency) = TON/reaction time (h)

Effect of the base on catalytic performance

For practical purpose, ethanol was used as the solvent of choice because it had better properties for both swelling of the catalyst and dissolution of the substrate. We first screened several different bases in the model reaction of *p*-nitrophenyl iodide with phenylboronic acid in the presence of 1.0 mol% Pd loading in 95% aqueous ethanol under air. The results are listed in Table 1.

It was shown that the base was required for Suzuki–Miyaura cross-coupling reaction (Table 1, entry 1). Among the bases screened, although Cs_2CO_3 worked best, it was not chosen owing to its high price (Table 1, entry 2). Using $NaHCO_3$ and Na_2CO_3 the reaction time is much longer than with K_2CO_3, with comparable yields (Table 1, entries 4 and 5). K_2CO_3 was thus chosen as base in the Suzuki–Miyaura reaction. Yields of up to 95% were obtained in reaction times less than 30 min. Turnover numbers (TON) and turnover frequencies (TOF) of up to 190 and 380 h^{-1}, respectively, were observed (Table 1, entry 3).

Suzuki–Miyaura reaction of aryl halides with aryl boronic acids catalyzed by PVC–EDA–SA–Pd^0

To explore the scope of the Suzuki–Miyaura reaction catalyzed by PVC–EDA–SA–Pd^0, a variety of substituted aryl halides and substituted aryl boronic acids were further evaluated (Scheme 2). The results are listed in Table 2.

Better results were obtained with the relatively reactive aryl iodides than with the aryl bromides. In particular, aryl iodides with electron-withdrawing groups, for example *p*-NO_2 and *p*-Cl, were more smoothly converted to the products in high yields with higher TON and TOF values (Table 2, entries 2, 3, and 6–9). Aryl bromides with electron-withdrawing groups, for example *p*-NO_2, *p*-CO_2Me, and *m*-NO_2, also resulted in moderate yields with slightly higher TON and TOF values (entries 14–17). In addition, the electronic nature of substituted arylboronic acids has no obvious effect on yields (entries 6–13, 15, and 17).

Reusability of the PVC–EDA–SA–Pd^0 catalyst

One of the main objectives of our study was to investigate the recycling and reuse of the catalyst. We explored the reusability of the PVC–EDA–SA–Pd^0 catalyst using the reaction of *p*-nitrophenyl iodide with phenylboronic acid as

Scheme 2

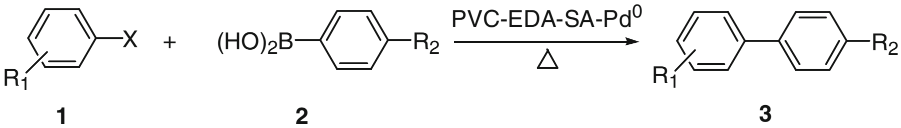


Table 2 The Suzuki–Miyaura coupling reactions catalyzed by PVC–EDA–SA–Pd^0

Entry	Aryl halides **1**	Arylboronic acid **2**	Time (min)	Product **3**	Yields[a] (%)	TON[b]	TOF[c] (h^{-1})
1	C_6H_5I	$C_6H_5B(OH)_2$	240	**3a**	84	168	42
2	4-NO_2–C_6H_4I	$C_6H_5B(OH)_2$	30	**3b**	95	190	380
3	4-Cl–C_6H_4I	$C_6H_5B(OH)_2$	30	**3c**	88	176	352
4	4-Me–C_6H_4I	$C_6H_5B(OH)_2$	60	**3d**	54	108	108
5	4-MeO–C_6H_4I	$C_6H_5B(OH)_2$	40	**3e**	76	152	228
6	4-NO_2–C_6H_4I	4-MeO–$C_6H_4B(OH)_2$	20	**3f**	99	198	594
7	4-NO_2–C_6H_4I	4-Me–$C_6H_4B(OH)_2$	20	**3g**	99	198	594
8	4-NO_2–C_6H_4I	4-Cl–$C_6H_4B(OH)_2$	20	**3h**	98	182	546
9	4-NO_2–C_6H_4I	4-F–$C_6H_4B(OH)_2$	20	**3i**	91	196	588
10	4-MeO–C_6H_4I	4-Me–$C_6H_4B(OH)_2$	60	**3j**	74	148	148
11	4-MeO–C_6H_4I	4-MeCO–$C_6H_4B(OH)_2$	60	**3k**	58	116	116
12	4-MeO–C_6H_4I	4-F–$C_6H_4B(OH)_2$	60	**3l**	40	80	40
13	4-MeO–C_6H_4I	4-MeO–$C_6H_4B(OH)_2$	30	**3m**	61	122	244
14	4-NO_2–C_6H_4Br	$C_6H_5B(OH)_2$	180	**3b**	53	106	35
15	4-NO_2–C_6H_4Br	4-Cl–$C_6H_4B(OH)_2$	240	**3h**	82	164	41
16	4-MeO_2C–C_6H_4Br	$C_6H_5B(OH)_2$	270	**3n**	51	102	23
17	3-NO_2–C_6H_4Br	4-Cl–$C_6H_4B(OH)_2$	180	**3o**	84	168	56
18	4-Br–C_6H_5Br	$C_6H_5B(OH)_2$	260	**3p**	10	20	4
19	4-NO_2–C_6H_4Cl	$C_6H_5B(OH)_2$	24 h	**3b**	Trace	–	–

Reactions were carried out with aryl halide (1.0 mmol), aryl boronic acid (2.0 mmol), PVC–EDA–SA–Pd^0 (0.1 g, 0.01 mmol of palladium), and K_2CO_3 (1.0 mmol) in 2 cm^{-3} 95% ethanol

[a] Yield of isolated product **3** based on the aryl halide

[b] TON (turnover number) = product (mol)/catalyst (mol)

[c] TOF (turnover frequency) = TON/reaction time (h)

model reaction. After the first run, the catalyst (1.0 mol% Pd) was filtered and extensively washed with EtOH and Et_2O and dried in vacuo. It was then directly reused under similar conditions. The product was obtained in 95, 95, 95, 98, 95, and 80% yields in consecutive runs, with the TOF decreasing from 380 to 46 h^{-1}. It can be seen that the catalyst could be reused up to five times while retaining its catalytic activity. Characterization of the fresh and the reused catalysts by transmission electron microscopy (TEM) showed that the deactivation could be correlated with an increase in the average size of the crystallites from 40 nm to >200 nm (Fig. 2).

Conclusion

Nanopalladium immobilized on the surface of PVC-supported Schiff base had high catalytic activity in Suzuki–Miyaura cross coupling reactions in 95% aqueous ethanol under atmospheric conditions. The catalyst can be easily separated and recovered from the reaction mixture by filtration and reused up to five times without noticeable lose of activity. The procedure has several advantages, for example mild reaction conditions, simple isolation procedure, cleaner reaction profiles, high yields of products, and a novel efficient catalyst for the Suzuki–Miyaura reaction.

Experimental

Melting points were measured on an Electrothermal X6 microscopic digital melting-point apparatus. IR spectra were recorded on a Bruker Equinox-55 spectrometer using KBr pellets. ^1H NMR spectra were obtained with a 300 MHz Bruker Avance instrument using $CDCl_3$ as solvent and TMS as internal standard. Elemental analyses were performed on a Perkin–Elmer EA2400II elemental analyzer. The elemental palladium content of the polymeric catalysts was determined by Perkin–Elmer Optima 2000DV inductively coupled plasma (ICP) spectroscopy. Scanning electron microscopy (SEM) was performed with a Philips XL 30ESEM instrument. Transmission electron microscopy (TEM) was performed with a Philips Tecnai instrument operating at 40–100 kV. The chemicals were obtained from commercial sources and used as received.

Preparation of PVC supported ethylenediamine (PVC–EDA)

Poly(vinyl chloride) (20.0 g) was added to 80 cm^3 ethylenediamine in a round-bottomed flask and the mixture was stirred at 80 °C, in air, for 48 h. After being cooled to room temperature, the reaction mixture was filtered and the solid was washed with a large volume of deionized water, ethanol (3 × 20 cm^3), and diethyl ether (3 × 20 cm^3), and dried at 60 °C in vacuo for 12 h to give brown PVC–EDA. The amino group content was found to be 8.95 mmol g^{-1} by elemental microanalysis.

Preparation of ethylenediamine functionalized PVC-supported Schiff base (PVC–EDA–SA)

The ethylenediamine-functionalized PVC (10.0 g) was allowed to swell in 50 cm^3 ethanol for 2 h. Salicylaldehyde (89.5 mmol) was then added and the solution and stirred at 60 °C for 8 h. After being cooled to room temperature, the brown colored polymer was isolated by filtration, washed thoroughly with water, ethanol (3 × 20 cm^3), and diethyl ether (3 × 20 cm^3), and dried in vacuo at 60 °C for 12 h. The IR spectrum showed the characteristic absorption of an azomethine (C=N) group at 1,640.5 cm^{-1}.

Preparation of nano-Pd immobilized on PVC-supported Schiff base (PVC–EDA–SA–Pd^0)

PVC–EDA–SA (2.0 g) was swollen in 15 cm^3 ethanol for 2 h, with magnetic stirring, then 0.3 g $PdCl_2$ (1.69 mmol) was added and the mixture was heated at reflux for 48 h. 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 isolated by filtration and washed with ethanol (3 × 20 cm^3), acetone (3 × 20 cm^3), and diethyl ether (3 × 20 cm^3). After drying, 2.02 g dry polymer immobilized nano-Pd^0 particles (PVC–EDA–SA–Pd^0) were obtained. The IR spectrum showed the characteristic absorption of an azomethine (C=N) group at 1,630.5 cm^{-1}. Metal content was found to be 0.107 mmol g^{-1} by ICP.

General procedure for the Suzuki–Miyaura cross-coupling reaction

In a typical experiment, 0.05 g PVC–EDA–SA–Pd^0 catalyst (0.01 mmol Pd) was added to a mixture of aryl halide (1.0 mmol), phenylboronic acid (2.0 mmol), and K_2CO_3 (2.0 mmol) in 2 cm^3 95% ethanol and the reaction mixture was stirred under reflux. After the reaction was judged to be complete, by TLC analysis, the solution was cooled to room temperature and the liquid was filtered through a Büchner funnel to remove the resin, which was washed with 95% ethanol (3 × 2 cm^3). The combined organic fractions were then concentrated on a rotary evaporator to obtain the desired biaryls in excellent yield. These were further purified by recrystallization. All the products were known and were characterized by melting point, and IR and ^1H NMR spectroscopy; the data were found to be identical with those reported in the literature [24–30].

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