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Short communication

Highly efficient palladium catalysts supported on nitrogen contained polymers for Suzuki-Miyaura reaction

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ABSTRACT

Through Pd catalyzed C—N coupling reaction, Pd nanoparticles and diadamantylphosphine ligand were immobilized in situ into the formed N contained polymers as heterogeneous Pd catalysts for Suzuki-Miyaura reaction. The Pd@NPad$_2$-1.0 catalyst was found to be highly efficient and only 4 ppm of Pd (Pd@NPad$_2$-1.0) was required for the coupling of aryl bromides with phenylboronic acid, and the corresponding products were obtained in good to excellent yields with high TON and TOF as 250,000 and 41,666 h^{-1} respectively. Moreover, the coupling of various aryl chlorides with phenylboronic acids gave the corresponding products in high yields also. And the Pd@NPad$_2$-1.0 catalyst is reusable at least 5 times with only slight deactivation.

1. Introduction

Pd catalyzed Suzuki-Miyaura reaction had received more and more attention over the past few decades [1], as it was used widely in the synthesis of agrochemicals, pharmaceuticals, natural products and other materials [2–10]. Traditionally, homogeneous catalysts were developed rapidly, and lots of efficient ligands were designed and applied for Suzuki-Miyaura reaction [11–13]. But separation of homogeneous Pd catalysts from the reaction mixtures is difficult in industrial applications. It is highly desirable to develop efficient heterogeneous Pd catalysts for Suzuki-Miyaura reaction. Some heterogeneous Pd catalysts had been developed by immobilizing Pd particles on supports, such as on oxides [14], polymers [15–21], carbon nanotubes [22], magnetic nanomaterials [23], and silica [24]. Unfortunately, heterogeneous Pd catalysts are generally less active than homogeneous Pd catalysts for Suzuki-Miyaura reaction.

In order to combine high activity with good reusability, some highly active heterogeneous Pd catalysts were developed for Suzuki-Miyaura reaction of aryl bromides with phenylboronic acids [25–26]. But the activation of aryl chlorides is much more difficult than that of aryl bromides, so the development of heterogeneous Pd catalysts that can activate aryl chlorides with high efficiency is highly desirable.

We have reported the C—O coupling and C–CN coupling of aryl chlorides and bromides with heterogeneous or homogeneous catalyst systems recently [27–29]. Moreover, we have developed a highly active heterogeneous Pd catalyst for Suzuki-Miyaura reaction of aryl halides with phenylboronic acid [30]. Pd nanoparticles were formed and immobilized in situ in the ionic polymers, and only 10 ppm Pd catalyst was needed for the Suzuki-Miyaura reaction of aryl bromides with phenylboronic acid [30]. Additionally, Pd nanoparticles trapped by Pd catalyzed Suzuki-Miyaura reaction were also reported as highly heterogeneous Pd catalysts, and the Pd catalysts were found to be highly active, recyclable and clean for Suzuki-Miyaura reaction [31]. We are still interested in the development of highly active Pd catalysts through Pd catalyzed cross-coupling reactions. Based on homogeneous Pd catalyst systems, good ligands for cross-coupling reactions combine both electronic and steric properties. On one hand, electron-rich ligands can help the oxidative addition into the Pd center to activate aryl halides. On the other hand, sterically demanding ligands can improve the reductive elimination from the Pd center to form products. Here, using Pd catalyzed C—N coupling reaction, Pd nanoparticles were immobilized in situ in the N contained polymers as highly efficient heterogeneous Pd catalysts for Suzuki-Miyaura reaction (see Scheme 1). Along with Pd nanoparticles, the electron rich and bulky P ligands were immobilized in situ into the N contained polymers. The heterogeneous Pd@NPad$_2$ catalysts were found to be highly efficient for Suzuki-Miyaura reaction of the aryl bromides and chlorides with arylboronic acids. Only 4 ppm Pd (Pd@NPad$_2$-1.0) was required for Suzuki-Miyaura reaction of 4-bromoanisole with phenylboronic acid. And the TON and TOF are as high as 250,000 and 41,666 h^{-1} respectively.

2. Experimental

Reagents were purchased from Sigma-Aldrich Company, Alfa-Aesar Company and Aladdin Reagent Company and used without further

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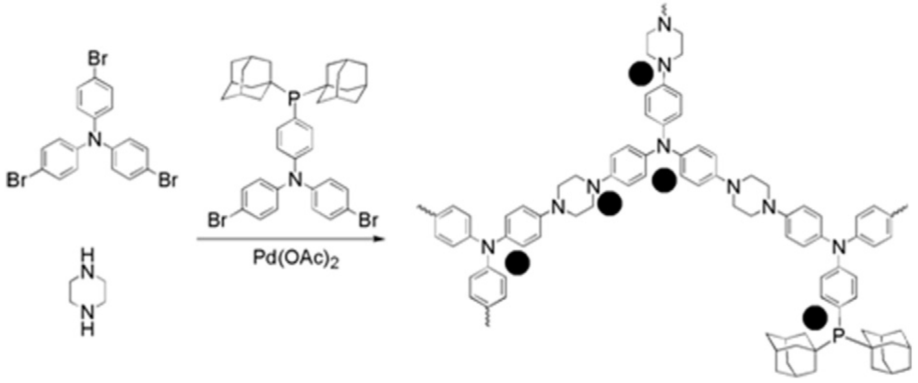


Scheme 1. The preparation of the Pd@$NPad_2$ catalyst.

purification. Thermal gravimetric(TG) analysis was performed on a STA409 apparatus under dry nitrogen at a heating rate of 20 °C/min. ^{1}H NMR spectra were measured with a Bruker AVANCE 400D spectrometer in $CDCl_3$ using tetramethylsilane (TMS) as internal reference. The solid-state NMR spectra were recorded on a Bruker AVANCE III 400 MHz spectrometer using a double-bearing standard MAS probe for ^{31}P NMR. TEM images were obtained using a JEOL JEM-2010 (200 kV) TEM apparatus and SEM images were obtained with a HITACHI S-4800 field-emission scanning electron microscope. X-ray photoelectron spectroscopy data (XPS) were gained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W AlKa radiation. The polymer surface area was measured using a Micromeritics ASAP2010 analyzer before samples degassed at 150 °C for 8 h under vacuum. The FT-IR spectra were recorded in the 4000–400 cm^{-1} region using a Nicolet 360 FT-IR instrument. The amount of palladium was measured using a Jarrell-Ash 1100 ICP-AES spectrometer. The dispersion of Pd nanoparticles was also measured using Catalyst Analyzer BELCAT-B, BEL JAPAN, INC.

3. The preparation of catalysts

3.1. The preparation of Pd@$NPad_2$-1.0

The C—P coupling was synthesized according to reference [32]. Pd $(OAc)_2$ (10.3 mg, 0.046 mmol), 1.1′-bis(diisopropylphosphino)-ferrocene (DIPPF, 3.2 mg, 0.0075 mmol), tris(4-bromophenyl)amine (602.5 mg, 1.25 mmol), di-1-adamantylphosphine (75.6 mg, 0.25 mmol) and NaO*t*Bu (36.0 mg, 0.375 mmol) were added in a Schlenk tube with 2.0 mL of toluene. And then the tube was heated to 105 °C. After stirring for 20 h under argon, the mixture was cooled down to room temperature. Toluene (30 mL), 1,4-diazacyclohexane (150.7 mg, 1.75 mmol) and NaO*t*Bu (672.7 mg, 7.0 mmol) were added into the reaction mixture under argon. The reaction mixture was stirred for another 24 h under 120 °C. After the reaction mixture was cooled down to room temperature, a green solid was obtained via centrifugated and washed with water and ethanol three times respectively. The obtained green solid was dried in a vacuum oven at 40 °C for 24 h and stored in argon atmosphere as Pd@$NPad_2$-1.0 catalyst. The amount of Pd in the Pd@$NPad_2$-1.0 catalyst was found to be 0.79 wt% (determined by ICP).

The Pd@$NPad_2$-0.5 was prepared similarly and less $Pd(OAc)_2$ (5.2 mg, 0.023 mmol) was used. The amount of Pd in the Pd@$NPad_2$-0.5 was found to be 0.38 wt% (determined by ICP).

The Pd@$NPad_2$-2.0 was prepared similarly and more $Pd(OAc)_2$ (20.7 mg,0.092 mmol) was used. The amount of Pd in the Pd@$NPad_2$–2.0 was found to be 1.7 wt% (determined by ICP).

3.2. The Pd@$NPad_2$–1.0 catalyzed Suzuki-Miyaura coupling of aryl chlorides with phenyboronic acid

Typically, an aryl chloride (2.0 mmol), phenylboronic acid (3.0 mmol), Pd@$NPad_2$-1.0 catalyst (5.4 mg, 0.02 mol% Pd), K_2CO_3 (552.8 mg, 4.0 mmol) and 4.0 mL of *i*-PrOH/water (1:1) were added into a 25 mL pressure tube under Ar. The reaction mixture was stirred at 100 °C for 18 h in an oil bath. After the reaction mixture cooled down to room temperature, the product was isolated by column with silica gel and analyzed by ^{1}H NMR. The yield was calculated based on the obtained product against the consumed aryl chloride. Yield = obtained product/theoretical product from the consumed aryl chloride. The TON and TOF were calculated based on Pd added (suppose that all Pd atom are accessible for the reaction). TON = the number of product/the number of Pd added (mol product/mol Pd). TOF = the number of product/the number Pd added in 1 h (mol product/mol Pd $*$ h^{-1}).

3.3. The Pd@$NPad_2$–1.0 catalyzed Suzuki-Miyaura coupling of aryl bromides with phenylboronic acid

In a typical reaction, an aryl bromide (25.0 mmol), phenylboronic acid (37.5 mmol), Pd@$NPad_2$-1.0 catalyst (1.35 mg, 4.0 ppm Pd), K_2CO_3 (6.9105 g, 50.0 mmol) and 20.0 mL of *i*-PrOH-water (1:1) were added into a 50 mL pressure tube under Ar. The reaction was performed at 100 °C for 6 h in an oil bath. After the reaction mixture cooled to room temperature, the organic layer was extracted with ethyl acetate (4 × 10.0 mL). The product was isolated by column with silica gel (hexane/ethyl acetate) and analyzed by ^{1}H NMR. The yeild was calculated based on the obtained product against the comsumed aryl bromide. Yield = obtained product/theoretical product from the consumed aryl bromide. The TON and TOF were calculated based on Pd added (suppose that all Pd atom are accessible for the reaction). TON = the number of product/the number of Pd added (mol product/mol Pd). TOF = the number of product/the number Pd added in 1 h (mol product/mol Pd $*$ h^{-1}).

3.4. The Pd@$NPad_2$–1.0 catalyzed Suzuki-Miyaura coupling of 2-nitrochlorobenzene with 4-chlorophenylboronic acid

2-Nitrochlorobenzene (1.5755 g, 10.0 mmol), 4-chlorophenylboronic acid (1.8764 g, 12.0 mmol), Pd@$NPad_2$-1.0 catalyst (27.0 mg, 0.02 mol% Pd), K_2CO_3 (2.7642 g, 20.0 mmol) and 10.0 mL of *i*-PrOH-water (1:1) were added into a 25 mL pressure tube under Ar. The reaction mixture was stirred for 10 h at 100 °C in an oil bath. After the reaction mixture cooled down to room temperature, the organic layer was extracted with ethyl acetate (10.0 mL). The product was isolated by column with silica gel (hexane/ethyl acetate).

3.5. Recycling procedure

After centrifugation and washed with water and ethanol, the catalyst Pd@NPad$_2$-1.0 was reused for the next time reaction under the same conditions.

4. Results and Discussion

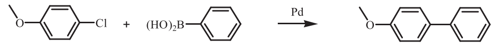
The Pd@NPad$_2$-1.0 catalyst was prepared by the Pd catalyzed C—P coupling reaction of tris(4-bromophenyl)amine and di-1-adamantylphosphine firstly, followed with the Pd catalyzed C—N coupling reaction of tris(4-bromophenyl)amine with 1,4-piperazine. Along the formation of C—N bonds, the di-1-adamantylphosphine ligand was anchored into the N contained polymers, and the Pd nanoparticles were immobilized and supported on the polymers to form the heterogeneous catalysts Pd@NPad$_2$.

The Pd@NPad$_2$-1.0 catalyst was characterized by TEM and SEM. The TEM images showed that Pd nanoparticles were dispersed well in the polymer (Fig. 1, left), and the average diameter of the Pd nanoparticles is about 2–5 nm. The SEM images showed (Fig. S1) that the catalyst was composed of irregular snowflake structure with irregular pores. The Pd@NPad$_2$-1.0 catalyst was characterized also by EDX elemental spectra, and Pd, P and N chemical elements were found in the Pd@NPad$_2$-1.0 catalyst, which indicated that the di-1-adamantylphosphine P ligand was anchored in the polymer (Fig. S2).

Thermogravimetric (TG) analysis showed that the Pd@NPad$_2$-1.0 catalyst was stable up to 350 °C (Fig. S3). The weight loss before 150 °C was due to the loss of the adsorbed water and solvent, and the further weight loss above 350 °C was attributed to the decomposition of the catalyst. And the BET surface area was about 60.9 $m^2\ g^{-1}$ with average pore diameter of 8.9 nm calculated by nitrogen adsorption–desorption analysis (Fig. S4). As the BET surface of the polymeric catalyst was low, we can predict low Pd dispersion and some Pd species are inaccessible (Table 1S). Interestingly, the recovered Pd@NPad$_2$-1.0 was slightly inactive but with much higher Pd dispersion than the fresh Pd@NPad$_2$-1.0 based on CO gas adsorption analysis. Since the polymer was not a hard support, Pd species inaccessible may be used again as active Pd reservoir. Thus, the TON (turn over number) was calculated based on all Pd species (suppose every Pd is accessible in the Suzuki-Miyaura reaction.

The Pd@NPad$_2$-1.0 was studied by X-ray photoelectron spectroscopy (XPS) (Fig. S5 in SI). As shown in Fig. S5, the binding energy peaks at 341.6 (Pd $3d_{3/2}$) and 336.8 eV (Pd $3d_{5/2}$) are corresponding to Pd(II) species. The binding energy peaks at 339.5 (Pd $3d_{3/2}$) and 335.7 eV (Pd $3d_{5/2}$) are assigned to Pd(0) species. The molar ratio of Pd(II)/Pd(0) is about 2:1 in the Pd@NPad$_2$-1.0, but changed to about 1:2 in the recovered Pd@NPad$_2$-1.0 (Fig. S6 in SI). Generally, the active Pd species for Suzuki reaction is Pd(0) species, as Pd(0) is ready for the oxidative addition of aryl halides. But Pd(II) species was also exist as the Pd(0) outside (outside of Pd nanoparticles) can be oxidized easily in air. And in the Suzuki-Miyaura reaction, Pd(II) species can be reduced as active center by phenylboronic acid.

Table 1
The optimization of reaction conditions for the Pd@NPad$_2$ catalyzed Suzuki-Miyaura coupling of 4-chloroanisole with phenylboronic acid.[a]



Entry	Base	Solvent	Pd (mol%)	Yield (%)[e]
1	K_2CO_3	*i*-PrOH/H_2O	0.1	94
2	K_2CO_3	*i*-PrOH	0.1	64
3	K_2CO_3	H_2O	0.1	80
4	K_2CO_3	1,4-Dioxane/H_2O	0.1	52
5	K_2CO_3	1,4-Dioxane	0.1	20
6	K_2CO_3	Ethanol/H_2O	0.1	91
7	K_2CO_3	Ethanol	0.1	70
8	K_2CO_3	DMSO	0.1	1
9	K_2CO_3	Acetonitrile/H_2O	0.1	79
10	K_2CO_3	Acetonitrile	0.1	8
11	K_2CO_3	Toluene	0.1	5
12	K_2CO_3	DMF/H_2O	0.1	35
13	K_2CO_3	DMF	0.1	17
14	K_3PO_4	*i*-PrOH/H_2O	0.1	76
15	Cs_2CO_3	*i*-PrOH/H_2O	0.1	97
16	Na_2CO_3	*i*-PrOH/H_2O	0.1	90
17	NaOH	*i*-PrOH/H_2O	0.1	11
18	K_2CO_3	*i*-PrOH/H_2O	0.05	85
19	K_2CO_3	*i*-PrOH/H_2O	0.02	75
20[b]	K_2CO_3	*i*-PrOH/H_2O	0.02	92
21[c]	K_2CO_3	*i*-PrOH/H_2O	0.02	88
22[c]	K_2CO_3	*i*-PrOH/H_2O	0.02	90
23[d]	K_2CO_3	*i*-PrOH/H_2O	0.02	1

[a] Reaction conditions: 4-chloroanisole, 2.0 mmol; phenylboronic acid, 3.0 mmol; catalyst Pd@NPad$_2$-1.0 (Pd contained 0.79 wt%); K_2CO_3, Na_2CO_3 and Cs_2CO_3, 4.0 mmol; K_3PO_4, 2.6 mmol; NaOH, 8.0 mmol; solvents, 4.0 mL; at 100 °C; for 11 h; under argon.

[b] For 18 h.

[c] catalyst Pd@NPad$_2$-0.5 (Pd contained 0.38 wt%); catalyst Pd@NPad$_2$-2.0 (Pd contained 1.7 wt%).

[d] Catalyst Pd/C (Pd contained 5 wt%).

[e] Yields were determined by GC using dodecane as an internal standard.

The FT-IR spectra of Pd@NPad$_2$–1.0 catalyst are presented as Fig. S7. The IR bands from 1500 cm^{-1} to 500 cm^{-1} were appeared for the phenyl rings from tris(4-bromophenyl)amine. Bands from 1496 cm^{-1} to 1280 cm^{-1} and the band at 3130 cm^{-1} were assigned to the C—N bonds, including C—N bond in tris(4-bromophenyl)amine and the new formed C—N bonds. The IR bands from 3000 cm^{-1} to 2750 cm^{-1} and the band at 1500 cm^{-1} were assigned to the adamantly groups, which indicated that the -P(Ad)$_2$ group was anchored into the N contained polymer catalyst Pd@NPad$_2$-1.0. Moreover, the P in the

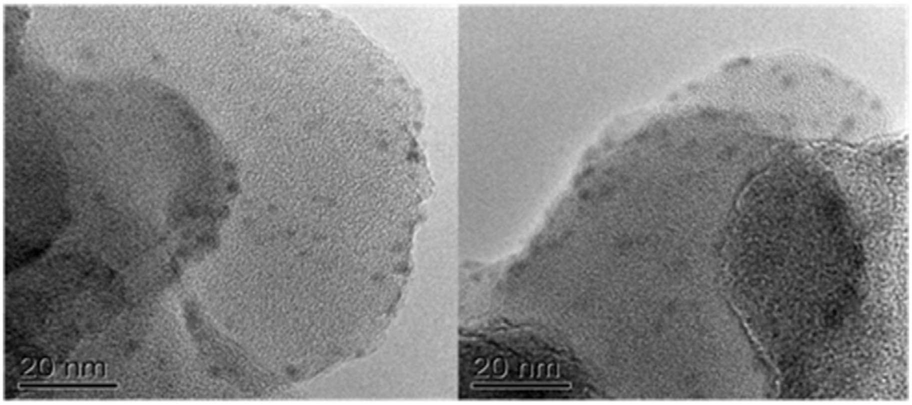


Fig. 1. TEM images of the fresh Pd@NPad$_2$-1.0 catalyst (left); recycled Pd@NPad$_2$-1.0 catalyst after fourth reaction run (right).

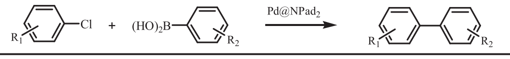
catalyst Pd@NPad$_2$-1.0 can be detected by ^{31}P NMR at 42 ppm, which is in agreement with the -P(Ad)$_2$ group on phenyl group (see Fig. S8).

The Pd@NPad$_2$-1.0 was studied for the Suzuki-Miyaura reaction of 4-chloroanisole with phenylboronic acid and the results are listed in Table 1. Solvents and bases were optimized for the reaction of 4-chloroanisole with phenylboronic acid. Several solvents were tested, and *i*-PrOH with water (*i*-PrOH/water, 1/1) was found to be the best solvent, and 4-methoxybiphenyl was obtained in 94% yield (Table 1, entries 1–13). Carbonate bases, such as K_2CO_3, Na_2CO_3 and Cs_2CO_3 are suitable bases, and K_3PO_4 and NaOH were less effective for the transformation (Table 1, entries 1 and 14–17). The loading of catalyst Pd@NPad$_2$-1.0 was also tested and only 0.02% of Pd (Pd@NPad$_2$-1.0) was required for the transformation, and 4-methoxybiphenyl was obtained in 92% yield within 18 h (Table 1, entries 18–20). The catalysts Pd@NPad$_2$-0.5 and Pd@NPad$_2$-2.0 (contained 0.38 wt% and 1.7 wt% of Pd respectively) were found to be similarly active and selective for the coupling reaction of 4-chloroanisole with phenylboronic acid (Table 1, entries 21, 22). For comparison, the commercial Pd/C was found to be not active under the same reaction conditions (Table 1, entry 23).

Using the optimized reaction conditions, we tested the application scope of the Pd@NPad$_2$-1.0 for the coupling of aryl chlorides with aryl boronic acids, and various aryl chlorides were used for the Pd@NPad$_2$–1.0 catalyzed Suzuki-Miyaura reaction. The results are listed in Table 2. The coupling reaction of aryl chlorides with phenylboronic acid gave the corresponding biphenyl compounds in excellent yields with 0.02 mol% Pd loading of Pd@NPad$_2$-1.0 under mild conditions (Table 2, entries 1–9). Electron-donating and electron-withdrawing groups, such as methyl, methoxyl, nitro, nitrile, acyl and formyl groups were well tolerated, and the corresponding products were obtained in high yields (Table 2, entries 1–9). Moreover, substituted phenylboronic acids such as 4-methylphenylboronic acid and 4-methoxylphenylboronic acid, can also be used for the coupling reaction with high yields of the corresponding products (Table 2, entries 10–12). Interestingly, the coupling of 2-chlorobenzonitrile with 4-methylphenylboronic acid gave sartanbiphenyl in 100% yield, as sartanbiphenyl is a significant intermediate for the production of sartans, which are used widely as hypertension drugs.

As some aryl bromides are also cheap and available widely, we investigated the coupling of aryl bromides and phenylboronic acid with the Pd@NPad$_2$-1.0 catalyst, and the results are listed in Table 3. The Pd@NPad$_2$-1.0 catalyst showed ultimate activity for the coupling of aryl bromides and phenylboronic acid, and only 4 ppm Pd loading was required under mild conditions (Table 3, entries 1–6). 4-Bromoanisole was coupled smoothly with phenylboronic acid at 100 °C in 6 h. The *para*-substituents, including methoxyl, nitrile, methyl, nitro, *tert*-butyl, formyl and acyl groups were well tolerated under the reaction conditions. The corresponding biphenyls were obtained in good to excellent yields, and the maximum of TON was up to 250,000 (Table 3, entries 1–6). The coupling of *ortho*-substituted aryl bromides with phenylboronic acid also afforded the corresponding biphenyls in excellent yields with increased Pd loading (Table 3, entries 7–11).

Table 2
Suzuki-Miyaura coupling reactions of aryl chlorides and phenylboronic acids.[a]



Entry	R$_1$	R$_2$	Yield(%)[b]	TON[c]
1	4-MeCO	H	99	4950
2	4-CH_3	H	99	4950
3	4-CHO	H	99	4950
4	4-NO_2	H	99	4950
5	4-CN	H	99	4950
6	2-CN	H	99	4950
7	2-NO_2	H	99	4950
8	2-Me	H	92	4600
9	2-MeO	H	92	4600
10	H	4-Me	90	4500
11	H	4-MeO	90	4500
12[d]	2-CN	4-Me	100	5000

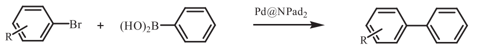
[a] Reaction conditions: aryl chlorides, 2.0 mmol; phenylboronic acids, 3.0 mmol; Pd@NPad$_2$-1.0 catalyst, 5.4 mg; Pd, 0.02 mol%; K_2CO_3, 4.0 mmol; *i*-PrOH/H_2O, 4.0 mL; at 100 °C; 18 h; under argon.

[b] Isolated yield, yield based on aryl chloride.

[c] turn over number, suppose every Pd atom is accessible for the reaction.

[d] For 7 h.

Table 3
Suzuki-Miyaura coupling of aryl bromides and phenylboronic acid.[a]



Entry	R	Yield(%)[b]	TON[c]
1	4-MeO	100	250,000
2	4-NO_2	100	250,000
3	4-Me	90	225,000
4	4-CHO	100	250,000
5	4-MeCO	100	250,000
6	4-CN	100	250,000
7[d]	4-*tert*-Butyl	100	25,000
8[d]	2-MeO	99	24,750
9[d]	2-Me	99	24,750
10[d]	2-CN	99	24,750
11[d]	2-NO_2	99	24,750

[a] Reaction conditions: aryl bromides, 25.0 mmol; phenylboronic acid, 37.5 mmol; Pd@NPad$_2$–1.0 catalyst, 1.35 mg; Pd, 4.0 ppm; K_2CO_3, 50.0 mmol; *i*-PrOH/H_2O, 20 mL; at 100 °C; 6 h; under argon.

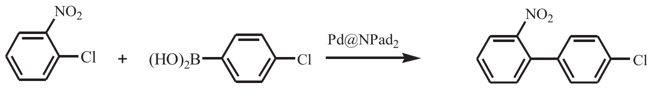
[b] Isolated yield, based on aryl bromide.

[c] Turn over number, suppose every Pd atom is accessible for the reaction.

[d] Pd@NPad$_2$-1.0 catalyst, 14.0 mg; Pd, 40 ppm; 10 h.

To explore the Pd@NPad$_2$-1.0 catalyst in industrial application, we studied the coupling of 2-nitrochlorobenzene with 4-chlorophenylboronic acid (see Scheme 2), as the corresponding product 4′-chloro-2-nitro-1,1′-biphenyl is a key intermediate for the production of Boscalid (Bactericide). The coupling of 2-nitrochlorobenzene and 4-chlorophenylboronic acid proceeded smoothly to the corresponding product in 98% yield. Moreover, the Pd@NPad$_2$-1.0 catalyst can be recovered easily by centrifugation and reused several times. And the reusability of Pd@NPad$_2$-1.0 catalyst was studied for the coupling of 2-nitrochlorobenzene with 4-chloro- phenylboronic acid. As shown in Fig. 2, the yield of the product was decreased slightly, and the deactivation may be due to oxidation of P ligand and the slightly aggregation of the Pd nanoparticles. In order to examine the leaching of Pd from Pd@NPad$_2$-1.0 catalyst, Pd in the reaction solution was measured by ICP-AES after removal of the Pd@NPad$_2$-1.0 catalyst (stopped after 3 h), and no Pd was detected in the solution (below detect limit, <7 ppb). The solution was not active any more for the cross-coupling reaction. It is indicated that the catalyst Pd@NPad$_2$-1.0 is heterogeneous for Suzuki-Miyaura reaction, and no contamination (ligand or Pd) was found from the catalyst system, which is important for pharmaceutical chemistry.

In the one-pot process, both Pd nanoparticles and diadamantylphosphine ligand were immobilized and supported on the polymers as heterogeneous catalysts. Evidently, more active Pd nanoparticles were immobilized preferentially into the N contained polymers, as the polymerization was catalyzed by the active Pd nanoparticles. Thus, we can obtain the highly active Pd@NPad$_2$-1.0 catalyst. As the surface of the Pd@NPad$_2$-1.0 was low, the reaction solvent was important for the Pd@NPad$_2$-1.0 catalyzed Suzuki-Miyaura reaction. Suitable solvent (*i*-PrOH with water) can enhance the movement of aryl halides and aryl boronic acids into active nanoparticles.



Scheme 2. Suzuki-Miyaura catalyzed coupling of 2-nitrochlorobenzene and 4-chlorophenylboronic acid.

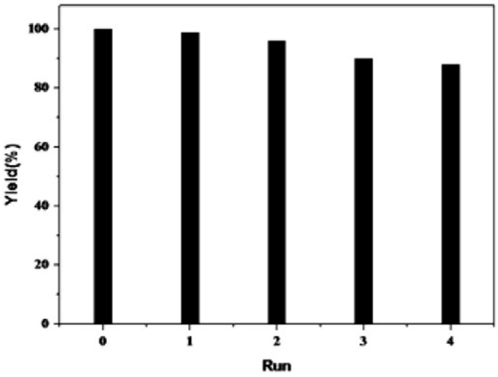


Fig. 2. Recycling of the Pd@NPad$_2$–1.0 catalyst.

Moreover, N contained groups are electron rich, and can improve the activity of the P ligand (diadamantylphosphine). Based on homogeneous Pd catalysts, electron rich and sterically demanding ligands can enhance Pd catalysts for cross coupling reactions. Electron-rich ligands can help the oxidative addition into the Pd center to activate aryl halides, and increasing catalyst activity. Sterically demanding ligands can improve the reductive elimination from the Pd center to form products to improve selectivity to the corresponding product. The formation of the N contained polymer not only improved the electron property of the bulky ligand diadamantylphosphine, but also immobilized the active Pd nanoparticles, thus Pd@NPad$_2$-1.0 catalyst was highly active, selective and reusable for the cross-coupling reaction.

5. Conclusions

Using Pd catalyzed C–N coupling reaction, both Pd nanoparticles and diadamantylphosphine ligand were immobilized in situ in the N contained polymers as heterogeneous Pd catalysts, and the Pd@NPad$_2$-1.0 catalyst was found to be highly efficient for the Suzuki-Miyaura reaction. Only 4 ppm of Pd (Pd@NPad$_2$-1.0) was required for the coupling of aryl bromides with phenyl boronic acid, and the corresponding products were obtained in good to excellent yields. The coupling of various aryl chlorides with phenylboronic acids gave the corresponding products in high yields also with 0.02 mol% of Pd loading under mild conditions. The Pd@NPad$_2$-1.0 catalyst can be reusable at least 5 times with only slight deactivation. The formation of the N contained polymer improved the electron property of the bulky ligand diadamantylphosphine and immobilized the active Pd nanoparticles, thus enhanced the efficiency of the Pd catalyst.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.catcom.2016.04.011.

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