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ARTICLE

Immobilized Palladium Nanoparticles within polymers as active catalysts for Suzuki-Miyaura reaction

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A highly active and reusable catalyst Pd@PNP was developed for Suzuki-Miyaura reaction of aryl chlorides and bromides with aryl boronic acids, and the corresponding biphenyl compounds were obtained in good to excellent yields. Triphenylphosphine and palladium nanoparticles were immobilized in situ in the polymer formed from Pd catalyzed coupling of tris(4-bromophenyl)amine and benzene-1,4-diboronic acid. The immobilized triphenylphosphine enhanced the activity and the stability of the catalyst Pd@PNP, and the catalyst Pd@PNP can be reused at least 5 times with good activity. Functional groups, such as methoxyl, nitriles, *tert*-butyl, nitro, acyl and formyl groups, were well tolerated under the reaction conditions, and the corresponding products were obtained in high yields.

Introduction

Palladium catalyzed cross-coupling reactions are applied widely for synthesis of pharmaceuticals,^[1] agricultural chemicals and natural products.^[2] Although some highly active ligand/palladium systems were designed and used for Pd catalyzed Suzuki-Miyaura reaction,^[3] Heck reaction,^[4] Sonogashira reaction and Negishi reactions,^[5] heterogeneous Pd catalyst systems are more convenient for the cross-coupling reactions in practical applications, as Pd/ligand systems are difficult to be recycled, and the Pd/ligand may be leaked into the products. The recovery of the active Pd/Ligand catalyst systems is highly valuable not only for the economic reasons but also for avoiding product contamination. Therefore, active heterogeneous Pd catalysts were designed and applied for cross-coupling reactions, including Pd supported on carbon,^[6] graphite,^[7] metal oxides,^[8] hybrid materials and polymers.^[9] But heterogeneous Pd catalysts are usually less active than that of Pd/ligand systems, especially for activation of aryl chlorides. Aryl chlorides are cheaper than aryl bromides and iodides and commercial available widely, but the activation of aryl chlorides is difficult as the C-Cl bond is much stronger than C-Br and C-I bonds. Thus, it is highly desirable to develop highly active heterogeneous catalysts for the cross coupling reactions.

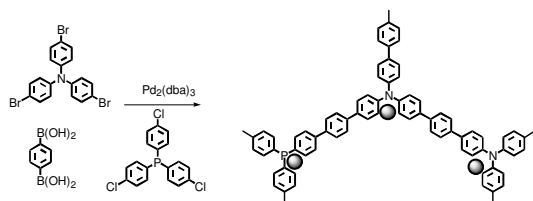
Recently, we reported highly active Pd heterogeneous catalysts for Suzuki-Miyaura reaction, and the catalysts can be reused several times and no P/Pd contamination was found in

the products.^[10] The electron rich and bulky P ligands were anchored into the Pd catalyzed polyphenylene polymers, and the active Pd nanoparticles were in situ formed and trapped into the polymers as highly active Pd heterogeneous catalysts. Moreover, Pd nanoparticles supported in ionic solid polymers were reported as highly active heterogeneous catalysts for Suzuki-Miyaura reaction, and only 10 ppm Pd catalysts were required for Suzuki-Miyaura reaction of aryl bromides.^[11] In addition, we also reported the C-O coupling and C-CN coupling of aryl chlorides and bromides with heterogeneous or homogeneous catalyst systems.^[12]

Here, the in situ formed Pd nanoparticles were trapped and immobilized into the polymers with triphenylphosphine ligand as highly active Pd heterogeneous catalysts for Suzuki-Miyaura reaction. The Pd@PNP catalysts were found to be highly active for the Suzuki-Miyaura coupling of the aryl bromides and chlorides with aryl boronic acids. As the P ligands and Pd were both immobilized into the polymers, the biphenyl products can be separated easily without contamination from P and Pd. Additionally, the Pd@PNP catalysts are stable in air since the TPP ligand is not sensitive to air.

The Pd@PNP catalysts were synthesized by palladium catalyzed Suzuki-Miyaura reaction of tris(4-bromophenyl)amine with benzene-1,4-diboronic acid. Tris(dibenzylideneacetone)-dipalladium with tris(4-chlorophenyl)phosphine was selected as the Pd catalyst, and then the ligand tris(4-chlorophenyl)phosphine can participate into the Suzuki-Miyaura reaction of tris(4-bromophenyl)amine with benzene-1,4-diboronic acid to form the polymers. Moreover, Pd nanoparticles were trapped and immobilized into polymers to form the Pd@PNP catalysts (see Scheme 1).

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Scheme 1 The preparation of the Pd nanocatalysts

Experimental section

Preparation of catalysts Pd@PNP

The procedure for the synthesis of Pd@PNP catalyst was as followed. Tris(4-bromophenyl)amine 0.482 g (1.0 mmol), benzene-1,4-diboronic acid 0.348 g (2.1 mmol), $\text{Pd}_2(\text{dba})_3$ 0.0458 g (0.05 mmol), tris(4-chlorophenyl)phosphine 0.146 g (0.4 mmol) and K_2CO_3 0.4119 g (3.0 mmol) were added into a Schlenk tube with 30 mL DMF under argon. And then the tube was heated to 150 °C in an oil bath with stirring for 24 h. After the reaction mixture cooled to room temperature, the precipitated yellow powder was collected by centrifugation. After washed with water and DMF 3 times, the powder was dried by vacuum and stored in argon atmosphere as the Pd@PNP catalyst. The amount of Pd in the Pd@PNP catalyst was found to be 1.81 wt% (determined by ICP-AES).

The Pd@PNP-1 was prepared similarly with $\text{Pd}_2(\text{dba})_3$ 0.0229 g (0.025 mmol), tris(4-chlorophenyl)phosphine 0.073 g (0.2 mmol) added. The amount of Pd in the Pd@PNP-1 catalyst was found to be 0.92 wt% (determined by ICP-AES).

The Pd@PNP-2 was synthesized with similar procedures using $\text{Pd}(\text{OAc})_2$ 0.0224 g (0.1 mmol) instead of $\text{Pd}_2(\text{dba})_3$. The amount of Pd in the Pd@PNP-2 catalyst was found to be 1.91 wt% (determined by ICP-AES).

The Pd@PN was synthesized using similar procedures using tetrakis(triphenylphosphine)palladium instead of $\text{Pd}_2(\text{dba})_3$ without ligand tris(4-chlorophenyl)phosphine. Tris(4-bromophenyl)amine 0.482 g (1.0 mmol), benzene-1,4-diboronic acid 0.2486 g (1.5 mmol), tetrakis(triphenylphosphine)palladium 0.1156 g (0.1 mmol) and K_2CO_3 0.2746 g (2.0 mmol) were added into a schlenk tube with 30 mL DMF under argon. The amount of Pd in the Pd@PN catalyst was found to be 1.92 wt% (determined by ICP-AES).

Typical procedure for Pd catalyzed Suzuki-Miyaura coupling reaction of aryl halides with aryl boronic acid

Aryl chlorides (1.0 mmol), phenylboronic acid (1.2 mmol), Pd@PNP catalyst (0.2%-0.3% Pd), K_2CO_3 (2 mmol) and methanol (2.0 mL) were added into a pressure tube under Ar. The pressure tube was placed in an oil bath for 14 h at 80 °C. The reaction mixture was cooled to room temperature and the crude products were purified by column with silica gel (eluting with ethyl acetate/hexane).

The coupling reaction of aryl bromides with aryl boronic acids was performed similarly, except the adding of less amount of catalyst Pd@PNP. The crude products were purified by column with silica gel (eluting with ethyl acetate/hexane).

Reusability of catalyst Pd@PNP

The coupling of 4-chlorotoluene with phenylboronic acid was used to test the reusability of catalyst Pd@PNP. After centrifugation and washed with ethyl acetate, the catalyst Pd@PNP was added to the reaction mixture again for the coupling of 4-chlorotoluene with phenylboronic acid, and the yield of methyl biphenyl was determined by GC.

Results and discussions

Catalyst characterization

To study the structure of the catalyst, the Pd@PNP was characterized by TEM (transmission electron microscope) and SEM (scanning electron microscopy) presented as Fig. 1 and Fig. S1, respectively. From Fig. 1, we can see that Pd nanoparticles were dispersed on the polymers PNP, and the diameter size of the Pd particles is about 1-5 nm (Fig. 1, left). The Pd nanoparticles were kept well and the average diameter of the Pd particle was about 1-5 nm too, and nearly no evident aggregation was found in the recycled Pd@PNP catalyst after 5 reaction runs (Fig. 1, right). The SEM image of the Pd@PNP showed that the catalyst Pd@PNP was irregular shaped particles with irregular pores (Fig. S1). From nitrogen adsorption-desorption analysis, the BET surface area of the catalyst Pd@PNP was about 48 $\text{m}^2 \text{g}^{-1}$ (Fig. S2). The average pore diameter the catalyst Pd@PNP was about 6.7 nm. The thermogravimetric analysis (TGA) showed that the Pd@PNP was thermally stable up to 500 °C. As shown in TG curve (Fig. S3), a sharp weight loss from room temperature to 150 °C was due to the loss of moisture and solvent (DMF). There is no evident mass loss between 150 °C to 500 °C, which showed good thermo stability of the catalyst Pd@PNP. The catalyst Pd@PNP decomposed slowly after 500 °C.

The X-ray diffraction patterns of Pd@PNP (Fig. S4) exhibited broad peaks at $2\theta=40.016^\circ$, 46.664° , 68.378° and 82.199° corresponding to Pd metal diffraction lines (111), (200), (220), (311) respectively. The diffraction peaks in this pattern confirm that Pd was supported on solid N contained polymer. The EDX elemental analyses of the Pd@PNP revealed the presence of the C, N, P, Br and Pd (Fig. S5). No Cl peak was found, which may be due to the amount of tris(4-chlorophenyl)phosphine added was low, and most of the Cl was removed via the reaction with benzene-1,4-diboronic acid. The existence of P was in agreement with the deduction. The FT-IR spectra of Pd@PNP catalyst was shown in Fig. S6. The IR band between 1500 cm^{-1} and 500 cm^{-1} are for the phenyl rings.

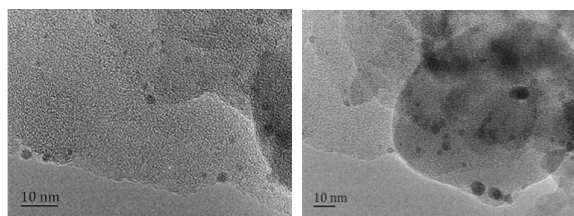
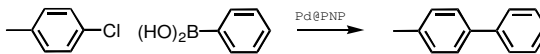


Fig.1 TEM images of Pd@PNP catalyst (left); the catalyst after fifth runs reaction (right); scale bar, 10nm.

Suzuki-Miyaura coupling of 4-chlorotoluene with phenylboronic acid

The catalyst Pd@PNP was studied for the Suzuki-Miyaura coupling of 4-chlorotoluene with phenylboronic acid, and reaction conditions were optimized. The catalyst Pd@PNP, Pd@PNP-1, Pd@PNP-2 and the Pd@PN were tested for comparison, and the catalyst Pd@PNP was found to be more active than the other catalysts for the coupling reaction (Table 1, entries 1-4). The formation of the polymers was affected by the amount of Pd added and the Pd source, as the polymerization was catalyzed by the active Pd nanoparticles. Comparing of Pd@PNP with Pd@PNP-1, the decreasing of added Pd₂(dba)₃ may slow down the formation of polymers, and simultaneously lead to the aggregation of Pd nanoparticles. In addition, Pd(Ac)₂ added was required to be reduced to active Pd(0) by benzene-1,4-diboronic acid firstly, which slowed down the formation of the polymers and led to the aggregation of Pd nanoparticles. In Pd@PN, Pd[P(C₆H₅)₃]₄ was used as catalyst and Pd source. As the P(C₆H₅)₃ cannot couple with benzene-1,4-diboronic acid, and Pd nanoparticles in the polymers were not stable enough, and the aggregated Pd particles were not quite active for the coupling reaction. Solvents DMF, DMSO, toluene, ethanol, 1,4-dioxane and methanol were used, and methanol was found to be best solvent for the coupling reaction (Table 1, entries 5-10). Bases Na₂CO₃, K₃PO₄, K₂CO₃, KOH and NaOH were tested, and K₂CO₃ was the suitable base for the coupling reaction (Table 1, entries 11-13). And then, the added Pd amount and reaction time were optimized, and 4-phenyltoluene was obtained in 99% yield with 0.2 mol% of Pd in 14 hours (Table 1, entries 14-17). The Pd@PNP stored in air for 1 week was used for the coupling of 4-chlorotoluene with phenylboronic acid, and 4-phenyltoluene was obtained in 99% yield also, which showed the Pd@PNP was not sensitive to air (Table 1, entry 18).

Table 1 Pd catalyzed Suzuki-Miyaura coupling of 4-chlorotoluene with phenylboronic acid



Entry	Catalyst	Base	Solvent	Pd (mol%)	Yield (%)
1 ^[a]	Pd@PNP	K ₂ CO ₃	Methanol	0.1	63
2 ^[a]	Pd@PNP-1	K ₂ CO ₃	Methanol	0.1	29
3 ^[a]	Pd@PNP-2	K ₂ CO ₃	Methanol	0.1	4
4 ^[a]	Pd@PN	K ₂ CO ₃	Methanol	0.1	5
5 ^[b]	Pd@PNP	K ₃ PO ₄	DMF	0.1	36
6 ^[b]	Pd@PNP	K ₃ PO ₄	DMSO	0.1	<1
7 ^[b]	Pd@PNP	K ₃ PO ₄	Ethanol	0.1	15
8 ^[b]	Pd@PNP	K ₃ PO ₄	Toluene	0.1	2
9 ^[b]	Pd@PNP	K ₃ PO ₄	1,4-Dioxane	0.1	28

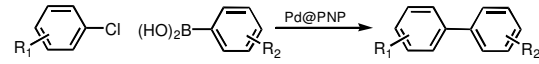
10	Pd@PNP	K ₃ PO ₄	Methanol	0.1	38
11 ^[c]	Pd@PNP	Na ₂ CO ₃	Methanol	0.1	61
12 ^[c]	Pd@PNP	KOH	Methanol	0.1	15
13 ^[c]	Pd@PNP	NaOH	Methanol	0.1	11
14	Pd@PNP	K ₂ CO ₃	Methanol	0.2	99
15 ^[d]	Pd@PNP	K ₂ CO ₃	Methanol	0.2	86
16 ^[e]	Pd@PNP	K ₂ CO ₃	Methanol	0.2	99
17 ^[f]	Pd@PNP	K ₂ CO ₃	Methanol	0.2	95
18 ^[g]	Pd@PNP	K ₂ CO ₃	Methanol	0.2	99

^[a] Reaction conditions: 4-chlorotoluene, 1.0 mmol; phenylboronic acid, 1.2 mmol; base, K₂CO₃, 2 mmol; at 80 °C; for 16 h; under argon. ^[b] K₃PO₄, 1.3 mmol; at 100 °C. ^[c] Na₂CO₃, 2.0 mmol; NaOH and KOH, 4.0 mmol. ^[d] at 70 °C. ^[e] 14 h. ^[f] 12 h. ^[g] the catalyst Pd@PNP was exposed to the air for a week.

Suzuki-Miyaura coupling of aryl chlorides with aryl boronic acids

With optimized reaction conditions, the catalyst Pd@PNP was tested for Suzuki-Miyaura coupling reaction of aryl chlorides with aryl boronic acids, and the results are presented in table 2. The cross coupling of aryl chlorides with both electron withdrawing substituents and electron donating substituents afforded the corresponding biphenyl compounds in good to excellent yields (Table 2, entries 1-8). The acyl, formyl, nitro and nitriles groups were tolerated well in the reaction conditions, and high yields of the corresponding products were obtained (Table 2, entries 1-6). The coupling of deactivated aryl chlorides, such as 4-chlorotoluene and 2-chloroanisole, gave the corresponding products in high yields also (Table 2, entries 7-8). Moreover, phenylboronic acid with functional groups, including methy, methoxyl and nitriles groups, were coupled well with chlorobenzene, and the corresponding biphenyl products were obtained in 83% to 96% yields (Table 2, entries 9-11).

Table 2 Suzuki-Miyaura coupling of aryl chlorides and arylboronic acids^[a]



Entry	R ₁	R ₂	Yield (%) ^[b]
1 ^[c]	4-MeO	H	96
2	4-MeCO	H	96
3	4-CHO	H	94
4	4-NO ₂	H	93
5	2-CN	H	70
6 ^[c]	2-NO ₂	H	94
7 ^[c]	2-Me	H	95
8 ^[c]	2-MeO	H	95
9 ^[c]	H	4-CN	83
10 ^[c]	H	4-CH ₃	95
11 ^[c]	H	4-MeO	96

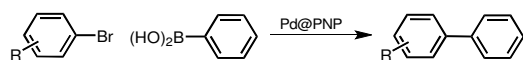
^[a] Reaction conditions: aryl chlorides, 1.0 mmol; phenylboronic acid, 1.2 mmol; Pd catalyst Pd@PNP, Pd, 0.2 mol%; K₂CO₃, 2 mmol;

Methanol, 2 mL; at 80 °C; 14 h; under argon. ^[b] Isolated yield. ^[c] Pd, 0.3 mol%.

Suzuki-Miyaura coupling of aryl bromides with phenylboronic acid

Aryl bromides were also examined for the Suzuki-Miyaura coupling with phenylboronic acid, and the results are listed in table 3. As C-Br bond (in aryl bromides) is weaker than C-Cl bond, Suzuki-Miyaura coupling of aryl bromides with phenylboronic acid were performed with lower catalyst loading (catalyst Pd@PNP, 0.02-0.05 mol% of Pd added). The Pd catalyst Pd@PNP showed high efficiency for the cross coupling reaction of aryl bromides with phenylboronic acid. The coupling of aryl bromides with electron withdrawing or electron donating groups gave the corresponding products in good to excellent yields. The 4-substituted of aryl bromides, including substituents methoxyl, nitriles, *tert*-butyl, acyl and formyl groups, were well tolerated under the reaction conditions, and the corresponding products were obtained in high yields (Table 3, entries 1-5). The coupling reaction of *ortho*-substituted and 2,6-dimethyl substituted bromobenzene afforded the corresponding products in good yields also (Table 3, entries 6-10).

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



Entry	R	Yield (%) ^[b]
1	4-MeO	99
2	4-CN	98
3	4- <i>tert</i> -Butyl	80
4	4-CHO	99
5	4-MeCO	99
6 ^[c]	2-MeO	86
7 ^[c]	2-Me	94
8 ^[c]	2-NO ₂	95
9 ^[c]	2-CN	98
10 ^[c]	2,6-Di-Me	93

^[a] Reaction conditions: aryl bromides, 5.0 mmol; phenylboronic acid, 6.0 mmol; Pd@PNP Pd catalyst, Pd, 0.02 mol%; K₂CO₃, 10.0 mmol; Methanol, 3 mL; at 70 °C; 11 h; under argon. ^[b] Isolated yield. ^[c] Pd, 0.05 mol%.

Catalyst reusability and discussion

The reusability of the catalyst Pd@PNP was tested for the cross-coupling of 4-chlorotoluene with phenylboronic acid, and the yields with recycled catalyst Pd@PNP are presented in Fig. 2. The catalyst Pd@PNP can be reused 5 times at least, but slightly deactivation of the Pd@PNP catalyst was observed. The deactivation may be due to the loss of the catalyst in the recycle processes and the slightly

aggregation of the Pd nanoparticles. And 4-phenyltoluene can be obtained in high yield also.

To test the leak of Pd@PNP catalyst, the content of Pd was measured by ICP-AES in the 5th run reaction solution, and no Pd was detected in the solution (below detect limit, <7 ppb). Moreover, no P (from the P ligand) was detected leaked into the solution. The solution was not active for the cross-coupling of 4-chlorotoluene with phenylboronic acid after removal of the catalyst Pd@PNP, which indicated that the catalyst Pd@PNP is a heterogeneous catalyst for Suzuki-Miyaura reaction. There was no contamination (ligand or Pd) found from the catalyst system, which is important for pharmaceutical chemistry.

In the one-pot process, Pd with tris(4-chlorophenyl)phosphine catalysed the coupling of tris(4-bromophenyl)amine with benzene-1,4-diboronic acid to form the polymer, and the tris(4-chlorophenyl) phosphine can also participate the coupling reaction with benzene-1,4-diboronic acid. And then the triphenylphosphine (from tris(4-chlorophenyl)phosphine) was anchored into the polymer. Furthermore, active Pd nanoparticles were trapped and immobilized into the polymer. Evidently, active Pd nanoparticles were trapped and immobilized into the polymer preferentially, as the polymerization was catalyzed by the active Pd nanoparticles. Thus, highly active Pd@PNP catalyst can be obtained in the one-pot process.

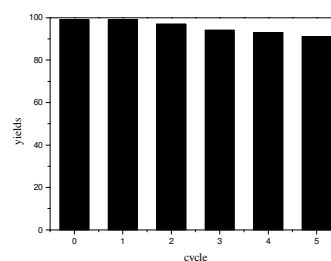


Fig. 2 Recycling of the Pd@PNP catalyst

Reaction conditions: ^[a] 4-chlorotoluene, 1.0 mmol; phenylboronic acid, 1.2 mmol; Pd@PNP Pd catalyst, Pd, 0.4 mol%; K₂CO₃, 2.0 mmol; Methanol, 2 mL; at 80 °C; within 14 h; under argon.

Conclusions

In summary, we demonstrated a highly active and reusable Pd catalyst Pd@PNP for Suzuki-Miyaura reaction of aryl chlorides and bromides with aryl boronic acids, and the corresponding biphenyl compounds were obtained in good to excellent yields. The in situ immobilized triphenylphosphine in the polymer support enhanced the activity and the stability of the catalyst Pd@PNP, and the catalyst Pd@PNP can be reused several times with good activity. Moreover, the Pd@PNP catalyzed Suzuki-Miyaura reaction was applicable widely, and various aryl chlorides and bromides can be coupled with aryl boronic acids in high yields. Functional groups, such as

methoxyl, nitriles, *tert*-butyl, nitro, acyl and formyl groups, were well tolerated under the reaction conditions, and the corresponding products were obtained in high yields.

Acknowledgements

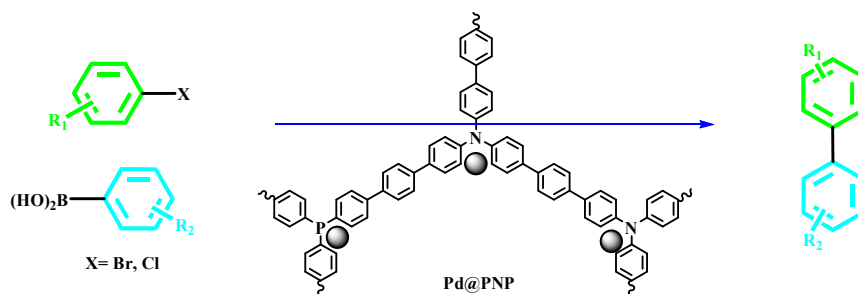
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Immobilized Palladium Nanoparticles within polymers as active catalysts for Suzuki-Miyaura reaction

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A highly active and reusable catalyst Pd@PNP was developed for Suzuki-Miyaura reaction of aryl chlorides and bromides with aryl boronic acids, and the corresponding biphenyl compounds were obtained in good to excellent yields. Triphenylphosphine and palladium nanoparticles were immobilized in situ in the polymer formed from Pd catalyzed coupling of tris(4-bromophenyl)amine and benzene-1,4-diboronic acid. The immobilized triphenylphosphine enhanced the activity and the stability of the catalyst Pd@PNP, and the catalyst Pd@PNP can be reused at least 5 times with good activity. Functional groups, such as methoxyl, nitriles, *tert*-butyl, nitro, acyl and formyl groups, were well tolerated under the reaction conditions, and the corresponding products were obtained in high yields.