

Article

Application of “Boomerang” Linear Polystyrene-Stabilized Pd Nanoparticles to a Series of C-C Coupling Reactions in Water

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Academic Editors: Masahiko Arai and Fengyu Zhao

Received: 19 December 2014 / Accepted: 3 February 2015 / Published: 9 February 2015

Abstract: The application of a catch-and-release system for soluble Pd species between water (reaction medium) and polystyrene (polymer support) was examined in the Suzuki coupling reaction with 2-bromothiophene and the Heck reaction with styrene or bromobenzene. Although a slight increase in particle size was observed by TEM after re-stabilization of the Pd species on linear polystyrene, no agglomeration was observed.

Keywords: nanoparticles; boomerang catalyst; C-C coupling; water

1. Introduction

Recently, homogeneous-heterogeneous switching catalysts have become of great interest to chemists, because they have the advantages of both homogeneous (high activity) and heterogeneous (recovery and recyclability) catalysts [1–4]. For example, Ikegami and Aoshima have developed homogeneous-heterogeneous switching catalysts by using thermosensitive polymers, such as poly(*N*-isopropylacrylamide) and poly[2-(2-ethoxy)ethoxyethyl vinyl ethers]. We have also reported a switching catalyst using a pH-sensitive polyion complex. A polymer supported “boomerang” catalyst that operates through the reversible release of a homogeneous catalyst into the solution phase from the polymer support is another example of a homogeneous-heterogeneous switching catalyst [5–10]. For instance, Reiser *et al.* have developed a method for the reversible immobilization of pyrene-tagged palladium *N*-heterocyclic carbene (NHC) complexes on highly magnetic, graphene-coated cobalt nanoparticles through π - π stacking interactions.

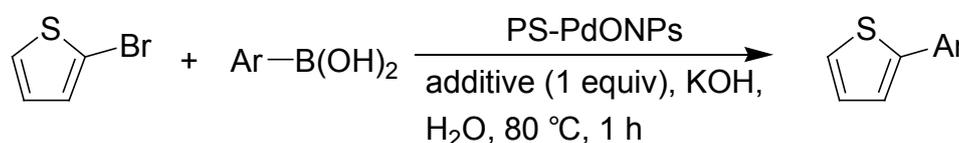
On the other hand, metal nanoparticles possess high catalytic activity in water [11–19] and have been used not only as semi-heterogeneous catalysts, but also as semi-heterogeneous supports [20–23]. Unfortunately, heterogenization of metal nanoparticles decreases catalytic activity. Additionally, the recovery and reuse of metal nanoparticles have been difficult to achieve due to a significant loss and/or morphology changes of the metal nanoparticles during reaction and workup [13–15]. Since leaching of soluble metal species from the support is a major cause of catalyst deactivation, efforts have been reported to develop an effective support that prevents leaching of metal species [16–19]. In contrast, leaching of Pd species has been observed directly and shows high catalytic activity in some systems [24–26]. Recently, palladium nanoparticles generated *in situ* for the Suzuki coupling reaction and aerobic alcohol oxidation in water were recovered using linear polystyrene, even in the presence of organic compounds [27]. These reports prompted efforts to develop recyclable “boomerang” nanoparticles that are able to overcome the problems mentioned above. Previously, we developed a catch-and-release system for soluble Pd species in water using linear polystyrene as an efficient reservoir [28]. This report describes the application of this system to a series of coupling reactions.

2. Results and Discussion

In the previous report, we confirmed that a recyclable homogeneous-heterogeneous switching system was constructed using polystyrene-stabilized PdO nanoparticles (PS-PdONPs) and aryl halide and that tetrabutylammonium bromide (TBAB) would act as a stabilizer for leached palladium species [28]. To evaluate the applicability of the homogeneous-heterogeneous catalytic system, the Suzuki coupling reaction of 2-bromothiophene with arylboronic acid was investigated (Table 1). When the coupling reaction of 2-bromothiophene with 4-methylphenylboronic acid was performed in the absence of TBAB, only 14% of the product was obtained (Entry 1). In contrast, the same reaction took place smoothly in water at 80 °C for 1 h in the presence of TBAB to afford 2-(4-methylphenyl)thiophene in a 78% yield (Entry 2). After washing with water and diethyl ether and subsequent drying, the recovered catalyst was used for the next run under the same conditions. The yield of the reaction did not decrease markedly, even after five consecutive runs (Entries 3–6). When the reaction solution was analyzed by ICP-AES to determine the extent of palladium leaching after the reaction, palladium was not detectable (<0.1 ppm)

after any of the runs. However, 0.4% of palladium leached after heating the mixture of PS-PdONPs and 2-bromothiophene under reaction conditions. A slight increase in the size of palladium was observed by TEM after the recycling experiments (Figure 1). The 1s peak of N was not observed by XPS analysis, indicating the absence of tetrabutylammonium species in the recovered catalyst (Figure 2). These results suggest that leached palladium species are participating in the catalytic process and are redeposited onto linear polystyrene after the reaction is complete. Indeed, similar processes have been observed in organic solvent [29,30]. After the reaction, leached palladium species were re-stabilized onto linear polystyrene, probably due to the chelate effect [31]. The reaction in the presence of SDS gave a low yield (Entry 7) and no corresponding product was obtained in the case of 5-bromo-2-thiophenecarboxylic acid, suggesting that TBAB did not simply act as a phase-transfer catalyst (Entry 8). Both electron-rich and electron-deficient arylboronic acids were reactive, affording the desired coupling products in good yields (Entries 9 and 10). The Suzuki coupling reaction with 1-naphthylboronic acid and 2-thienylboronic acid gave the corresponding coupling products in 87 and 99% yields, respectively (Entries 11 and 12).

Table 1. Suzuki coupling reaction of thienyl halides with arylboronic acids ^a.



Entry	Ar	Additive	Yield (%) ^b
1	4-methylphenyl	-	14
2	4-methylphenyl	TBAB	78
3 ^c	4-methylphenyl	TBAB	74
4 ^d	4-methylphenyl	TBAB	72
5 ^e	4-methylphenyl	TBAB	74
6 ^f	4-methylphenyl	TBAB	74
7	4-methylphenyl	SDS	24
8 ^g	4-methylphenyl	-	<1
9	4-methoxyphenyl	TBAB	81
10	4-acetylphenyl	TBAB	56
11	1-naphthyl	TBAB	87
12	2-thienyl	TBAB	99

^a All reactions were performed with 2-bromothiophene (0.5 mmol), arylboronic acid (0.75 mmol), PS-PdONPs (1.5 mol% of Pd), 1.5 mol/L KOH aqueous solution (1 mL). ^b NMR yields. ^c 2nd use. ^d 3rd use. ^e 4th use. ^f 5th use. ^g 5-Bromo-2-thiophenecarboxylic acid was used as a substrate.

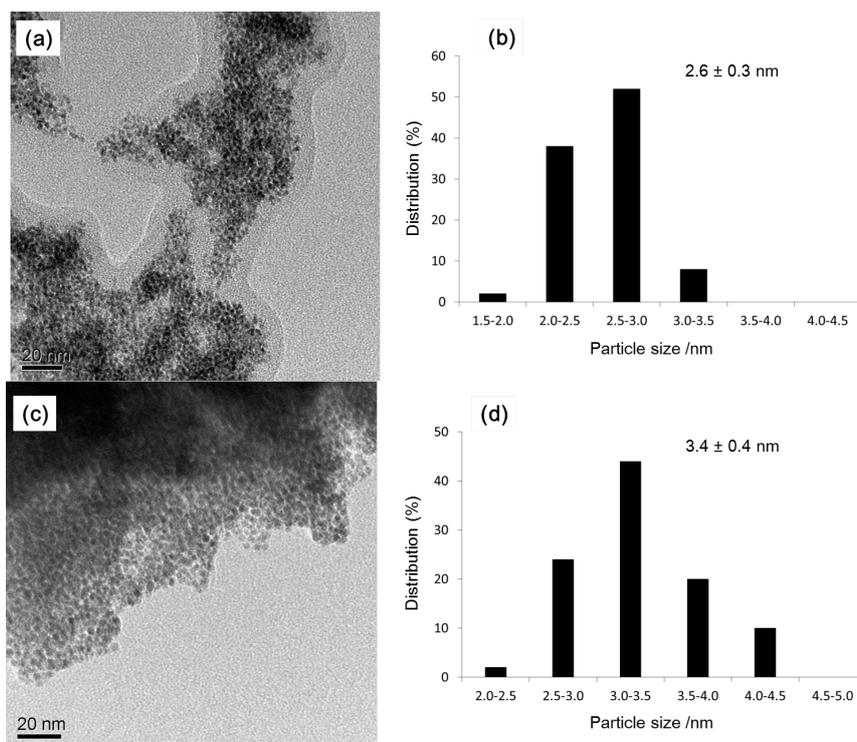


Figure 1. (a) TEM micrograph of PS-PdONPs (scale bar = 20 nm); (b) size distribution of PS-PdONPs; (c) TEM micrograph of recovered catalyst after fifth run (scale bar = 20 nm); (d) size distribution of recovered catalyst after fifth run.

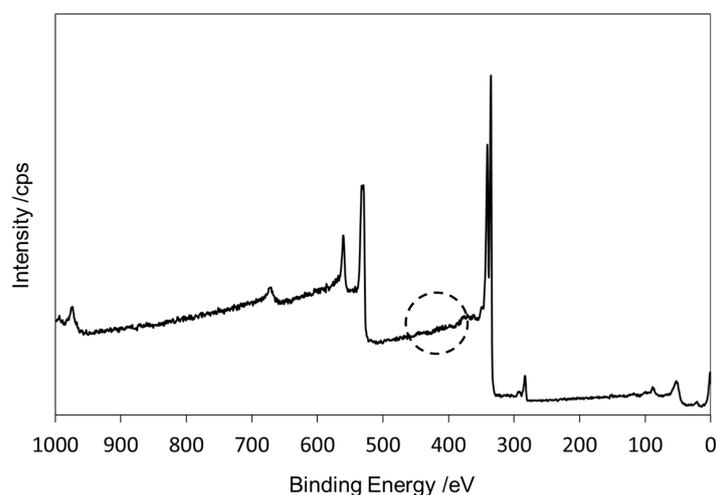
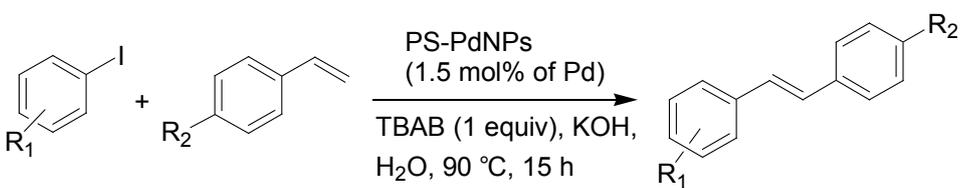


Figure 2. XPS spectrum of the recovered catalyst.

As we reported earlier [32], PS-PdONPs showed low catalytic activity for the Heck reaction with styrene or bromobenzene. Therefore, we also examined the applicability of our boomerang system in the Heck reaction. When the Heck reaction of iodobenzene with styrene was performed in $1.5 \text{ mol} \cdot \text{L}^{-1}$ KOH aqueous solution at $90 \text{ }^\circ\text{C}$ in the absence or presence of TBAB, only 14% or 17% of the product was obtained, respectively (Table 2, Entries 1 and 2). However, on using polystyrene-stabilized Pd nanoparticles (PS-PdNPs) as a catalyst, the coupling reaction proceeded efficiently (Entry 4). Based on the mechanism of the Heck reaction using Pd(II) species as the catalyst, the first step is the reduction of

Pd(II) to Pd(0) with alkene. The difference in activity is thought to be caused by the rate of the reduction step (insertion of alkene). Indeed, the reduction of palladium was observed by XPS after treatment of PS-PdONPs with acrylic acid in 1.5 mol·L⁻¹ KOH aqueous solution at 90 °C for 5 h. In contrast, no formation of Pd(0) was observed after treatment of PS-PdONPs with styrene (Figure 3). When the recyclability of the catalyst was examined under the same conditions, catalytic deactivation was observed in the second and third runs. However, similar yields of products were obtained after the third run as in the Suzuki coupling reaction of aryl chloride with arylboronic acid [28]. When the reaction solution was checked by ICP-AES, no palladium species was observed in any runs. In addition, the size of palladium nanoparticles in the recovered catalyst was slightly larger than that of PS-PdNPs (fresh catalyst, Figure 4). The Heck reaction using both electron-rich and electron-deficient aryl iodides also occurred to produce the desired product in good yields. On the other hand, coupling products were obtained in moderate yields from the reaction with 4-methoxystyrene (Entries 18–20).

Table 2. Heck reaction of aryl iodide with styrene ^a.



Entry	R ₁	R ₂	Yield (%) ^b
1 ^{c,d}	H	H	14
2 ^c	H	H	17
3 ^d	H	H	35
4	H	H	95
5 ^e	H	H	88
6 ^f	H	H	56
7 ^g	H	H	52
8 ^h	H	H	53
9 ⁱ	H	H	20
10 ^j	H	H	11
11	4-CH ₃ -	H	95
12	4-CH ₃ O-	H	95
13	4-CF ₃ -	H	83
14	2-CH ₃ -	H	98
15	H	Cl	99
16	4-CH ₃ -	Cl	99
17	4-CH ₃ O-	Cl	96
18	H	OMe	74
19	4-CH ₃ -	OMe	77
20	4-CH ₃ O-	OMe	41

^a All reactions were performed with aryl iodide (0.5 mmol), styrene (0.75 mmol), catalyst (1.5 mol% of Pd), 1.5 mol/L KOH aqueous solution (1 mL). ^b NMR yield. ^c PS-PdONPs was used as a catalyst. ^d Reaction was performed in the absence of TBAB for 20 h. ^e 2nd run. ^f 3rd run. ^g 4th run. ^h 5th run. ⁱ SDS was used as an additive. ^j 2-Iodophenol was used as a substrate.

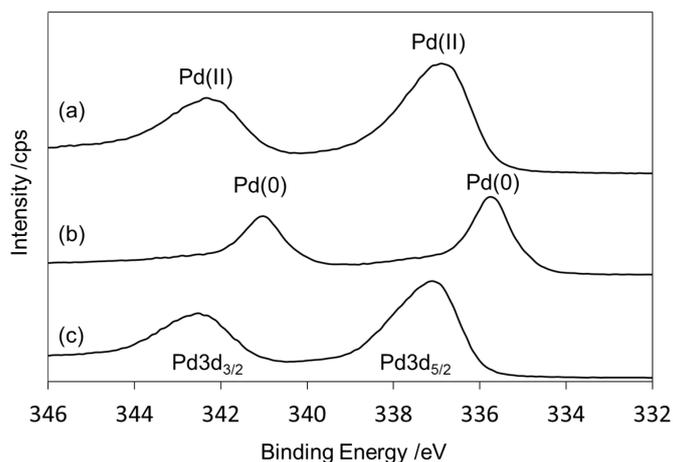


Figure 3. XPS spectrum of the Pd 3d region of the catalyst: (a) PS-PdONPs; (b) after treatment with acrylic acid; (c) after treatment with styrene.

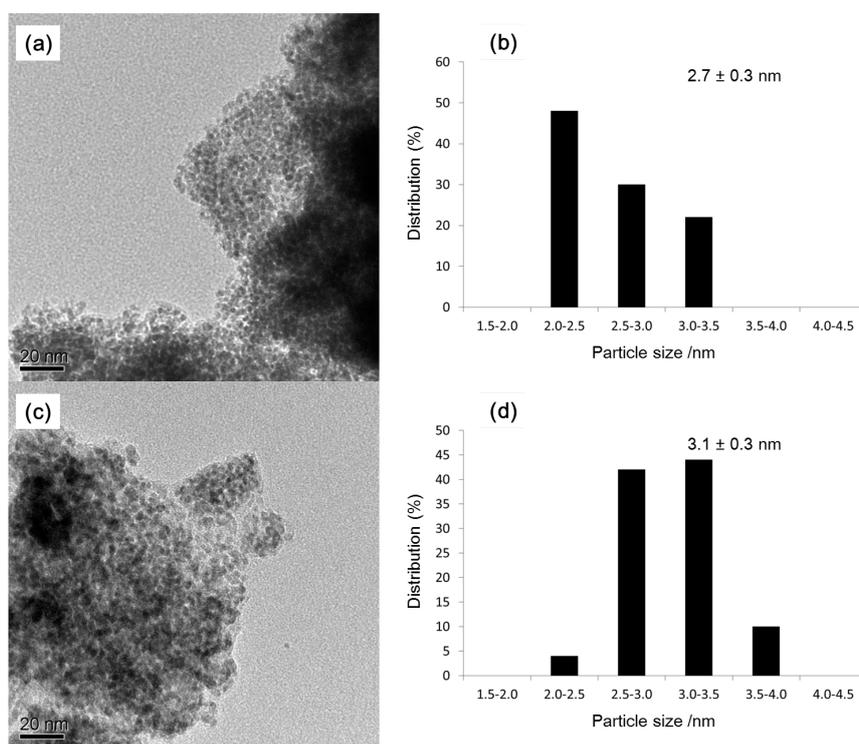


Figure 4. (a) TEM micrograph of PS-PdNPs (scale bar = 20 nm); (b) size distribution of PS-PdNPs; (c) TEM micrograph of recovered catalyst after fifth run (scale bar = 20 nm); (d) size distribution of recovered catalyst after fifth run.

When the Heck reaction of bromobenzene with acrylic acid was performed in $1.5 \text{ mol}\cdot\text{L}^{-1}$ KOH aqueous solution at $90 \text{ }^\circ\text{C}$ for 5 h, only 5% of the product was obtained in the absence of additive (Table 3, Entry 1). In contrast, in the presence of TBAB, as expected, an increased product yield was observed (Entry 2). Although a similar yield was obtained with the recovered catalyst, a broader size distribution was observed by TEM in the recovered catalyst (Figure 5). Both electron-rich and electron-deficient aryl bromides were reactive, affording the desired coupling products in high yields (Entries 3–6). 2-Bromotoluene and 1-bromonaphthalene also underwent the Heck reaction with acrylic

acid under similar conditions to afford 2-methylcinnamic acid and 3-(1-naphthyl)propanoic acid in 78% and 96% yields, respectively (Entries 7 and 8).

Table 3. Heck reaction of aryl bromide with acrylic acid ^a.

Entry	R	Additive	Yield (%) ^b
1	H	-	5
2	H	TBAB	84
3	4-CH ₃ -	TBAB	97
4 ^c	4-CH ₃ -	TBAB	94
5	4-CH ₃ O-	TBAB	96
6	4-CF ₃ -	TBAB	88
7	4-NO ₂ -	TBAB	71
8	2-CH ₃ -	TBAB	78
9	2-naphthyl	TBAB	96

^a All reactions were performed with aryl bromide (0.5 mmol), acrylic acid (0.75 mmol), PS-PdONPs (1.5 mol% of Pd), 1.5 mol/L KOH aqueous solution (1 mL). ^b NMR yield. ^c 2nd run.

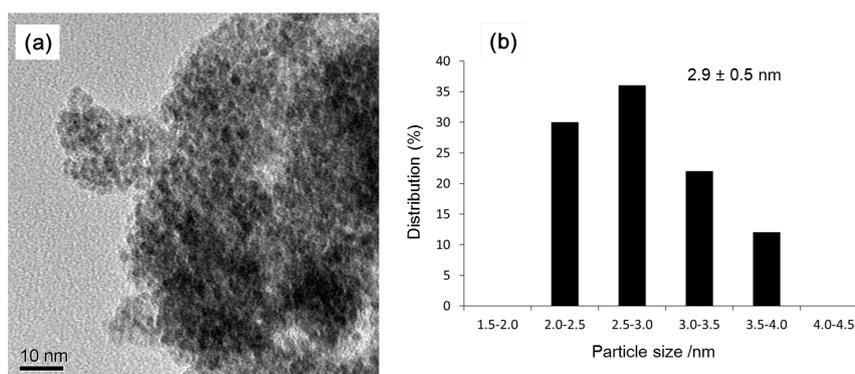


Figure 5. (a) TEM micrograph of the recovered catalyst (scale bar = 10 nm); (b) size distribution of the recovered catalyst.

3. Experimental Section

3.1. Preparation of PS-PdONPs

To a screw-capped vial with a stirring bar were added 9.0 mg of polystyrene (85 μmol of styrene unit), $\text{Pd}(\text{OAc})_2$ 5.5 mg (25 μmol) and 1.5 M aqueous K_2CO_3 solution (3 mL). After stirring at 90 °C for 1 h, the reaction mixture was filtered with hot water. Subsequently, the polystyrene-stabilized PdO nanoparticles were washed with water (5×1.0 mL) and acetone (5×1.0 mL).

3.2. Preparation of PS-PdNPs

To a screw-capped vial with a stirring bar were added 1.8 mg of polystyrene (17 μmol of styrene unit), $\text{Pd}(\text{OAc})_2$ 1.0 mg (5 μmol), phenylboronic acid 9.1 mg (0.75 mmol) and water (1 mL). After stirring at 90 °C for 1 h, the aqueous solution was decanted. Subsequently, the polystyrene-stabilized Pd nanoparticles were washed with water (5×1.0 mL) and acetone (5×1.0 mL).

3.3. Determination of Loading of the Palladium

PS-PdONPs (2.9 mg) was placed in a screw-capped vial and then 13 M nitric acid (5 mL) was added. The mixture was heated at 80 °C to dissolve completely. After cooling to room temperature, the solution was adjusted to 50 mL by water, and then, the amount of Pd metal was measured by ICP-AES analysis (15.3 ppm). The amount of Pd in PS-PdNPs was 15.5 ppm.

After the catalytic reaction, the aqueous phase was adjusted to 10 g by nitric acid, and then, the amount of Pd metal was measured by ICP-AES analysis.

3.4. Typical Procedures for the Suzuki Coupling Reaction

To a screw-capped vial with a stirring bar were added 2-bromothiophene (81.5 mg, 0.5 mmol), 4-methylphenylboronic acid (110 mg, 0.75 mmol), PS-PdONPs (2.9 mg, 1.5 mol% of Pd), TBAB (161 mg, 0.5 mmol) and 1.5 mol·L⁻¹ aqueous KOH solution (1 mL). After stirring at 80 °C for 1 h, the reaction mixture was cooled to room temperature by immediately immersing the vial in water (~20 °C) for about 10 min. After separating the catalyst and the aqueous phase by centrifugation, the aqueous phase was decanted. Recovered catalyst was washed with H₂O (5×3.0 mL) and diethyl ether (5×3.0 mL), which were then added to the aqueous phase. The aqueous phase was extracted eight times with diethyl ether. The combined organic extracts were dried over MgSO_4 and concentrated under reduced pressure. The product was analyzed by ¹H NMR. The recovered catalyst was dried *in vacuo* and reused. Furthermore, the amount of Pd metal in the aqueous phase determined by ICP-AES analysis was <0.1 ppm.

2-(*p*-Tolyl)thiophene: ¹H NMR (CDCl_3) δ 7.48 (d, $J = 8.2$ Hz, 2 H), 7.23 (d, $J = 3.6$ Hz, 1 H), 7.19 (d, $J = 5.0$ Hz, 1 H), 7.15 (d, $J = 8.2$ Hz, 2 H), 7.06 (dd, $J = 5.0$ Hz, 3.6 Hz, 1 H), 2.32 (s, 3 H): ¹³C NMR (CDCl_3) δ 144.6, 137.0, 131.7, 129.5, 127.9, 125.8, 124.2, 122.6, 21.2. CAS registry number: 16939-04-1.

2-(4-Methoxyphenyl)thiophene: ¹H NMR (CDCl_3) δ 7.55 (d, $J = 8.8$ Hz, 2 H), 7.20 (m, 2 H), 7.05 (dd, $J = 3.5$ Hz, $J = 5.0$ Hz, 1 H), 6.92 (d, $J = 8.8$ Hz, 2 H), 3.83 (s, 3 H): ¹³C NMR (CDCl_3) δ 159.1, 144.2, 127.9, 127.2, 127.1, 123.8, 122.0, 114.2, 55.3. CAS registry number: 42545-43-7.

2-(4-Acetylphenyl)thiophene: ^1H NMR (CDCl_3) δ 8.02–7.90 (m, 2 H), 7.73–7.60 (m, 2 H), 7.42 (d, $J=3.6$ Hz, 1 H), 7.35 (d, $J=5.1$ Hz, 1 H), 7.10 (dd, $J=5.1$ Hz, $J=3.6$ Hz, 1 H), 2.60 (s, 3 H): ^{13}C NMR (CDCl_3) δ 197.2, 143.0, 138.7, 135.5, 129.1, 128.3, 126.5, 125.5, 124.6, 26.7. CAS registry number: 35294-37-2.

2-(*o*-Tolyl)thiophene: ^1H NMR (CDCl_3) δ 7.42 (d, $J=7.2$ Hz, 1 H), 7.35 (d, $J=5.0$ Hz, 1 H), 7.20–7.30 (m, 3 H), 7.10 (dd, $J=5.0$ Hz, $J=3.5$ Hz, 1 H), 7.07 (d, $J=3.5$ Hz, 1 H), 2.44 (s, 3 H): ^{13}C NMR (CDCl_3) δ 143.0, 136.1, 134.1, 130.7, 130.4, 127.8, 127.0, 126.5, 125.9, 125.0, 21.5. CAS registry number: 99846-56-7.

2-(1-Naphthyl)thiophene: ^1H NMR (CDCl_3) δ 8.20 (m, 1 H), 7.88 (m, 1 H), 7.85 (d, $J=8.4$ Hz, 1 H), 7.56 (d, $J=7.2$ Hz, 1 H), 7.55–7.48 (m, 3 H), 7.40 (d, $J=5.2$ Hz, 1 H), 7.23 (d, $J=3.3$ Hz, 1 H), 7.18 (dd, $J=5.2$ Hz, $J=3.3$ Hz, 1 H): ^{13}C NMR (CDCl_3) δ 141.7, 133.8, 132.4, 131.8, 128.4, 128.3, 128.2, 127.3, 127.2, 126.4, 126.0, 125.7, 125.6, 125.2. CAS registry number: 4632-51-3.

2,2'-Bithiophene: ^1H NMR (CDCl_3) δ 7.22–7.15 (m, 4 H), 7.05–7.00 (m, 2 H): ^{13}C NMR (CDCl_3) δ 137.4, 127.5, 124.3, 123.5. CAS registry number: 492-97-7.

3.5. Typical Procedures for the Heck Reaction

To a screw-capped vial with a stirring bar were added iodobenzene (102 mg, 0.5 mmol), styrene (78.1 mg, 0.75 mmol), PS-PdNPs (3.0 mg, 1.5 mol% of Pd), TBAB (161 mg, 0.5 mmol) and $1.5 \text{ mol}\cdot\text{L}^{-1}$ aqueous KOH solution (1 mL). After stirring at 90°C for 15 h, the reaction mixture was cooled to room temperature by immediately immersing the vial in water ($\sim 20^\circ\text{C}$) for about 10 min. After separating the catalyst and the aqueous phase by centrifugation, the aqueous phase was decanted. Recovered catalyst was washed with H_2O ($5 \times 3.0 \text{ mL}$) and diethyl ether ($5 \times 3.0 \text{ mL}$), which were then added to the aqueous phase. The aqueous phase was extracted eight times with diethyl ether. The combined organic extracts were dried over MgSO_4 and concentrated under reduced pressure. The product was analyzed by ^1H NMR. The recovered catalyst was dried *in vacuo* and reused. Furthermore, the amount of Pd metal in the aqueous phase determined by ICP-AES analysis was <0.1 ppm.

Cinnamic acid: ^1H NMR (CDCl_3) δ 7.81 (d, $J=16.0$ Hz, 1 H), 7.62–7.50 (m, 2 H), 7.42 (m, 3 H), 6.47 (d, $J=16.0$ Hz, 1 H): ^{13}C NMR (CDCl_3) δ 172.7, 147.0, 134.0, 130.7, 128.9, 128.3, 117.3. CAS registry number: 140-10-3.

4-Methylcinnamic acid: ^1H NMR (CDCl_3) δ 7.78 (d, $J=15.9$ Hz, 1 H), 7.46 (d, $J=8.1$ Hz, 2 H), 7.20 (d, $J=8.1$ Hz, 2 H), 6.40 (d, $J=15.9$ Hz, 1 H), 2.38 (s, 3 H): ^{13}C NMR (CDCl_3) δ 172.6, 147.0, 141.0, 131.5, 129.8, 128.4, 116.2, 21.4. CAS registry number: 940-61-4.

4-Methoxycinnamic acid: ^1H NMR (CDCl_3) δ 7.75 (d, $J=15.9$ Hz, 1 H), 7.52 (d, $J=8.7$ Hz, 2 H), 6.92 (d, $J=8.7$ Hz, 2 H), 6.32 (d, $J=15.9$ Hz, 1 H), 3.85 (s, 3 H): ^{13}C NMR (CDCl_3) δ 172.2, 161.8, 146.5, 130.5, 126.8, 114.4, 114.2, 55.4. CAS registry number: 943-89-5.

4-Trifluoromethylcinnamic acid: ^1H NMR ($\text{DMSO}-d_6$) δ 7.90 (d, $J=8.1$ Hz, 2 H), 7.74 (d, $J=8.1$ Hz, 2 H), 7.65 (d, $J=15.9$ Hz, 1 H), 6.67 (d, $J=15.9$ Hz, 1 H): ^{13}C NMR ($\text{DMSO}-d_6$) δ 167.8, 142.2, 138.2, 130.7 (q, $J=25.4$ Hz), 129.7, 126.6 (q, $J=3.1$ Hz), 126.0, 125.8, 122.1. CAS registry number: 16642-92-5.

4-Nitrocinnamic acid: ^1H NMR (DMSO- d_6) δ 8.22 (d, $J = 8.1$ Hz, 2 H), 7.97 (d, $J = 8.1$ Hz, 2 H), 7.68 (d, $J = 15.9$ Hz, 1 H), 6.74 (d, $J = 15.9$ Hz, 1 H): ^{13}C NMR (CDCl₃) δ 167.7, 148.4, 141.8, 141.3, 129.7, 124.4, 123.8. CAS registry number: 619-89-6.

2-Methylcinnamic acid: ^1H NMR (CDCl₃) δ 8.00 (d, $J = 15.6$ Hz, 1 H), 7.60 (d, $J = 7.8$ Hz, 1 H), 7.30–7.20 (m, 3 H), 6.36 (d, $J = 15.6$ Hz, 1 H), 2.40 (s, 3 H): ^{13}C NMR (CDCl₃) δ 170.4, 144.2, 138.0, 133.8, 131.8, 131.2, 126.8, 118.8, 19.7. CAS registry number: 2373-76-4.

Stilbene: ^1H NMR (CDCl₃) δ 7.60 (dd, $J = 8.4$ Hz, $J = 1.5$ Hz, 4 H), 7.45 (tt, $J = 7.5$ Hz, $J = 1.5$ Hz, 4 H), 7.34 (tt, $J = 7.2$ Hz, $J = 1.5$ Hz, 2 H), 7.20 (s, 2 H): ^{13}C NMR (CDCl₃) δ 137.4, 128.8, 128.7, 127.7, 126.6. CAS registry number: 103-30-0.

4-Methylstilbene: ^1H NMR (CDCl₃) δ 7.52 (d, $J = 7.2$ Hz, 2 H), 7.43 (d, $J = 8.1$ Hz, 2 H), 7.35 (t, $J = 7.5$ Hz, 2 H), 7.26 (t, $J = 7.2$ Hz, 1 H), 7.18 (d, $J = 8.1$ Hz, 2 H), 7.10 (s, 2 H), 2.38 (s, 3 H): ^{13}C NMR (CDCl₃) δ 137.7, 137.5, 134.8, 129.4, 128.7, 127.7, 127.4, 126.5, 126.4, 21.4. CAS registry number: 1860-17-9.

4-Methoxystilbene: ^1H NMR (CDCl₃) δ 7.53–7.46 (m, 4 H), 7.37 (t, $J = 7.5$ Hz, 2 H), 7.25 (t, $J = 7.2$ Hz, 1 H), 7.10 (d, $J = 16.2$ Hz, 1 H), 6.94 (d, $J = 8.7$ Hz, 2 H), 3.85 (s, 3 H): ^{13}C NMR (CDCl₃) δ 159.4, 137.7, 130.2, 128.5, 127.8, 127.2, 126.4, 126.1, 114.2, 55.3. CAS registry number: 1694-19-5.

4-Trifluoromethylstilbene: ^1H NMR (CDCl₃) δ 7.62–7.56 (m, 4 H), 7.54 (d, $J = 7.5$ Hz, 2 H), 7.4–7.36 (m, 2 H), 7.32–7.28 (m, 1 H), 7.19 (d, $J = 16.5$ Hz, 1 H), 7.12 (d, $J = 16.5$ Hz, 1 H): ^{13}C NMR (CDCl₃) δ 140.8, 136.6, 131.2, 129.2 (q, $J = 32.3$ Hz), 128.8, 128.3, 127.1, 126.8, 126.5, 125.6 (q, $J = 3.8$ Hz), 124.2. CAS registry number: 1149-56-0.

2-Methylstilbene: ^1H NMR (CDCl₃) δ 7.66 (d, $J = 7.2$ Hz, 1 H), 7.58 (d, $J = 7.5$ Hz, 2 H), 7.45–7.35 (m, 3 H), 7.30–7.25 (m, 4 H), 7.05 (d, $J = 16.2$ Hz, 1 H), 2.48 (s, 3 H): ^{13}C NMR (CDCl₃) δ 137.7, 136.5, 135.8, 130.5, 130.0, 128.7, 127.5, 127.5, 126.6, 126.3, 125.3, 20.1. CAS registry number: 22257-16-5.

4-Chlorostilbene: ^1H NMR (CDCl₃) δ 7.52 (d, $J = 7.2$ Hz, 2 H), 7.43 (d, $J = 8.4$ Hz, 2 H), 7.40–7.20 (m, 5 H), 7.07 (s, 2 H): ^{13}C NMR (CDCl₃) δ 137.0, 135.9, 133.2, 129.3, 128.8, 128.7, 127.9, 127.7, 127.4, 126.6. CAS registry number: 1657-50-7.

4-Chloro-4'-methylstilbene: ^1H NMR (CDCl₃) δ 7.43 (d, $J = 8.1$ Hz, 2 H), 7.41 (d, $J = 8.4$ Hz, 2 H), 7.31 (d, $J = 8.4$ Hz, 2 H), 7.17 (d, $J = 8.1$ Hz, 2 H), 7.07 (d, $J = 15.9$ Hz, 1 H), 7.00 (d, $J = 15.9$ Hz, 1 H), 2.36 (s, 3 H): ^{13}C NMR (CDCl₃) δ 137.8, 136.0, 134.1, 132.9, 129.4, 129.2, 128.8, 127.5, 126.4, 126.3, 21.3. CAS registry number: 3041-83-6.

4-Chloro-4'-methoxystilbene: ^1H NMR (CDCl₃) δ 7.49–7.35 (m, 4 H), 7.33–7.20 (m, 2 H), 7.02 (d, $J = 16.2$ Hz, 1 H), 6.95–6.88 (m, 3 H), 3.83 (s, 3 H): ^{13}C NMR (CDCl₃) δ 159.6, 136.2, 132.5, 129.7, 128.9, 128.8, 127.8, 127.4, 125.3, 114.2, 55.4. CAS registry number: 18878-89-2.

4-Methoxy-4'-methylstilbene: ^1H NMR (CDCl₃) δ 7.45 (d, $J = 8.7$ Hz, 2 H), 7.40 (d, $J = 8.1$ Hz, 2 H), 7.16 (d, $J = 7.8$ Hz, 2 H), 7.04 (d, $J = 16.2$ Hz, 1 H), 6.96 (d, $J = 16.2$ Hz, 1 H), 6.90 (d, $J = 8.7$ Hz, 2 H), 3.83 (s, 3 H), 2.36 (s, 3 H): ^{13}C NMR (CDCl₃) δ 159.3, 137.2, 135.0, 130.5, 129.5, 127.7, 127.4, 126.7, 126.3, 114.3, 55.5, 21.4. CAS registry number: 37163-68-1.

4,4'-Dimethoxystilbene: ^1H NMR (CDCl_3) δ 7.44–7.41 (m, 4 H), 6.94–6.86 (m, 6 H), 3.83 (s, 6 H); ^{13}C NMR (CDCl_3) δ 159.3, 130.7, 127.7, 126.4, 114.4, 55.6. CAS registry number: 15638-14-9.

4. Conclusions

In summary, a “boomerang” catalytic system, which allows one to combine the benefits of homogeneous (high catalytic activity) and heterogeneous (easy separation and recycling) catalysts, was constructed by using PS-PdONPs and TBAB. The results with water-soluble substrates or another stabilizer suggested that TBAB did not simply act as a phase-transfer catalyst. A slight increase in the size of palladium was observed by TEM after re-stabilization of the Pd species on linear polystyrene. This system is applicable to the Suzuki coupling reaction of 2-bromothiophene with arylboronic acid and the Heck reaction with aryl styrene or bromide.

Acknowledgements

The authors are grateful to the Nanomaterials and Microdevices Research Center (NMRC) of OIT for financial and instrumental support.

Author Contributions

Atsushi Ohtaka and Toshiyuki Okagaki contributed to the experimental design and the article writing and revising. Go Hamasaka, Yasuhiro Uozumi, and Tsutomu Shinagawa contributed to the catalyst characterization. Osamu Shimomura and Ryoki Nomura contributed to a helpful discussion.

Conflicts of Interest

The authors declare no conflict of interest.

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