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Polyion complex stabilized palladium nanoparticles for Suzuki and Heck reaction in water

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ABSTRACT

Palladium nanoparticles stabilized by a polyion complex composed of poly{4-chloromethylstyrene-*co*-(4-vinylbenzyl) tributylammonium chloride} and poly(acrylic acid) were easily recovered by filtration after pH treatment. The polyion complex stabilized palladium nanoparticles have high catalytic activity for the Suzuki and Heck reactions in water.

1. Introduction

The palladium catalyzed coupling of aryl halides by Suzuki-[1] and Heck-type reactions[2] is a well-established methodology in modern organic synthesis. The coupling products find good applications as intermediates in the preparation of materials, natural products, and bioactive compounds.[3] The current trend is to conduct organic reactions in water because it is an eco-friendly, nontoxic, and economic solvent.[4] Jeffery and Bandone discovered that the use of quaternary ammonium salts considerably enhances the rates of both the Heck[5] and Suzuki coupling reactions[6] in water. Reetz et al. demonstrated that $Pd(OAc)_2$ in combination with tetrabutylammonium bromide (TBAB) gave rise to nanometric Pd-colloids, which were the actual catalysts under the so-called Jeffery conditions.[7] Recently, it was found that surfactant-stabilized palladium nanoparticles (PdNPs) have high catalytic activity for the Suzuki and Heck reactions in water.[8] However, it was difficult to reuse the catalyst because the PdNPs were dispersed in water. Zhang synthesized pH-responsive core-shell microspheres of poly[styrene-*co*-2-(acetoacetoxy)ethyl methacrylate-*co*-methyl acrylic acid] (PS-*co*-PAEMA-*co*-PMAA) supported PdNPs[9] and thermoresponsive poly(*N*-isopropylacrylamide)-grafted PdNPs.[10] These catalysts have high catalytic activity toward Suzuki and Heck reactions in water, and were recovered by filtration after pH or thermal treatment. However, a significant decrease in the catalytic activity was observed in the recycling of the catalyst, due to loss of the catalyst during the collection process.

A polyion complex (PIC) can easily be formed when oppositely charged polyelectrolytes are mixed in aqueous solution and interact via electrostatic (Coulombic) interactions.[11] Hirai has reported that a colloidal palladium supported on PIC composed of poly(acrylic acid) and poly(ethylene imine) catalyzes the selective hydrogenation of conjugated diolefins to monoolefins.[12] We report herein our results demonstrating that both the Suzuki and Heck reactions proceed in water in the presence of PdNPs stabilized by PIC composed of poly{4-chloromethylstyrene-*co*-(4-vinylbenzyl) tributylammonium chloride} and poly(acrylic acid).

2. Results and discussion

2.1. Synthesis of polyion complex stabilized palladium nanoparticles (PIC-PdNPs)

A polystyrene derivative was chosen because the stability of PICs is dependent on the hydrophobicity of the polymer.[11b] The synthesis of poly{4-chloromethylstyrene-*co*-(4-vinylbenzyl) tributylammonium chloride} (**2**) is shown in Scheme 1. A homopolymer of 4-chloromethylstyrene was prepared by conventional radical polymerization using AIBN as the initiator. The molecular weight (M_n) of poly(4-chloromethylstyrene) (**1**) estimated by gel permeation chromatography (GPC) was low (5.6×10^3) and the molecular weight distribution (M_w/M_n) was slightly broad (1.8). The reaction of **1** with tributylamine was performed in THF at 70 °C for 20 h to

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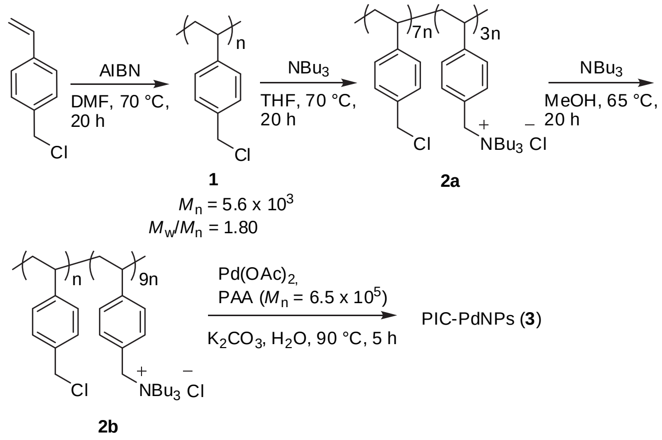


Scheme 1.

give a partially quaternarized polymer **2a**, which is insoluble in water. In the ^{1}H NMR spectrum of **2a**, new signals at δ 3.02, 1.67, 1.27, and 0.91 are observed, which are assigned to the butyl protons of the (4-vinylbenzyl)tributylammonium chloride unit (30% of the 4-chloromethylstyrenes converted to ammonium units). A water-soluble polymer **2b** (90% of the 4-chloromethylstyrenes converted to ammonium units) was obtained from the reaction of the partially quaternarized polymer **2a** with tributylamine in MeOH.

For the preparation of PIC stabilized PdNPs (**3**), the mixture of Pd$(OAc)_2$, polymer **2b** [12 equiv of ammonium unit for Pd$(OAc)_2$], and PAA (M_n=6.5×10^5, 3 equiv of AA unit for each ammonium unit in **2b**) was added to a 1.5 mol L^{-1} K_2CO_3 aqueous solution and stirred for 5 h at 90 °C.[7] Aggregation of PIC-PdNPs was observed when the pH of the solution was changed (pH $<$6). ^{1}H NMR of the aqueous phase confirmed the absence of polymer, indicating that all polymers were recovered completely by formation of PIC.[13] Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) revealed that **3** contained an average of 0.13 mmol/g of Pd. Figure 1 shows a TEM image of **3**, where a fairly uniform particle size of 2.6±0.5 nm is evident. In addition, PIC-PdNPs **3** were easily re-dispersed in water by changing the pH, due to the stability of the PIC (Fig. 2, Scheme 2).

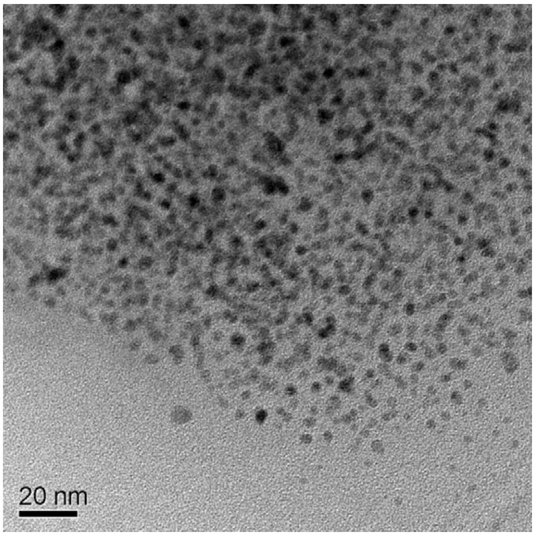


Figure 1. TEM images of PIC-PdNPs (**3**).

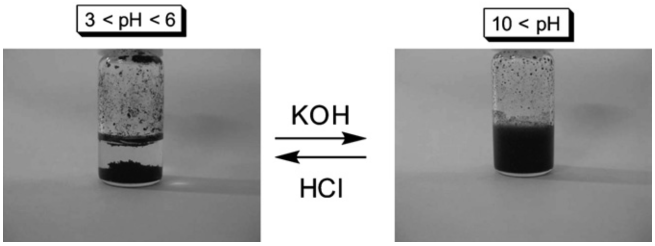
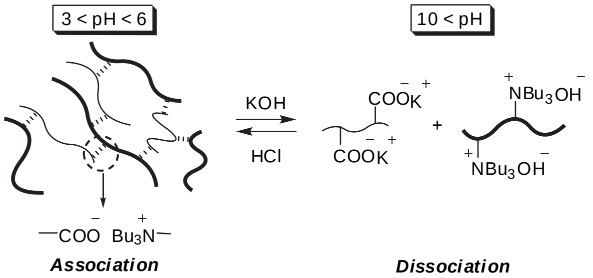


Figure 2.



Scheme 2. The stability of polyion complex.

2.2. Suzuki coupling reaction in water

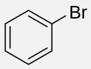
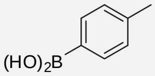
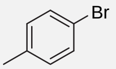
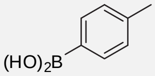
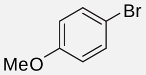
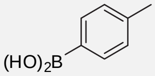
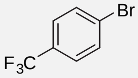
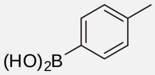
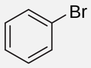
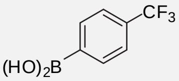
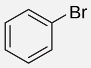
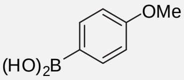
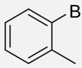
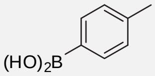
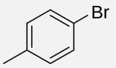
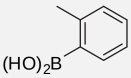
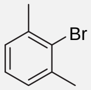
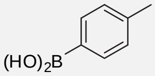
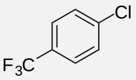
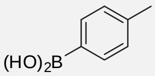
To test the potency of **3** as a catalyst, we examined the Suzuki coupling reaction of various aryl halides with arylboronic acids in 1.5 mol L^{-1} aqueous KOH solution as a test reaction (Table 1). The coupling of bromobenzene with 4-methylphenylboronic acid took place smoothly in water at 60 °C to give 4-methylbiphenyl in 99% yield (entry 1). The Suzuki coupling reaction of 4-bromotoluene and 4-bromoanisole bearing electron donating groups at their *para* positions gave the corresponding coupling products in 99% and 87% yields, respectively (entries 2 and 3). 4-Bromobenzotrifluoride with an electron deficient aromatic ring also underwent the Suzuki coupling reaction with 4-methylphenylboronic acid under similar conditions to afford 4-methyl-4′-trifluoromethylbiphenyl in 93% yield (entry 4). The coupling of 4-trifluoromethylphenylboronic acid and 4-methoxyphenylboronic acid took place with bromobenzene to give the corresponding product in 99% and 98% yields, respectively (entries 5 and 6). Sterically hindered substrates were also examined. The formation of 2,4′-dimethylbiphenyl could be achieved by the coupling of 2-bromotoluene with 4-methylphenylboronic acid or 4-bromotoluene with 2-methylphenylboronic acid in 74% and 77% yields, respectively (entries 7 and 8). However, 2-bromo-*m*-xylene and 4-chlorobenzotrifluoride gave the low yields (entries 9 and 10).

2.3. Heck reaction in water

Heck reactions of aryl halides with styrene using **3** as a catalyst were also studied. Heck reactions are generally performed at relatively high temperatures, thus we conducted our reactions at 80 °C. Representative results are summarized in Table 2. The coupling of iodobenzene with styrene took place smoothly in water in the presence of 3 equiv of KOH and 1 mol % palladium of PIC-PdNPs **3** to give a quantitative yield of (*E*)-stilbene (Table 2, entry 1). The Heck reaction of 4-iodotoluene and 4-iodoanisole bearing electron donating groups at their *para* positions gave the corresponding coupling products in 99% and 88% yields, respectively (entries 2 and 3). 4-Iodobenzotrifluoride with an electron deficient aromatic ring

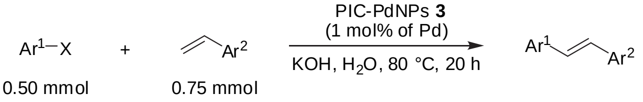
Table 1
PIC-PdNPs catalyzed Suzuki coupling reaction in water

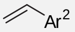
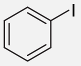
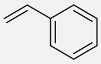
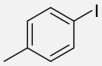
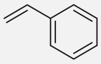
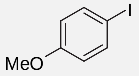
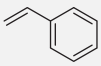
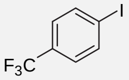
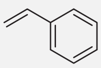
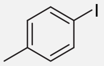
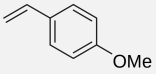
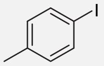
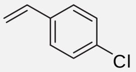
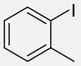
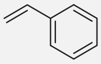
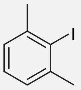
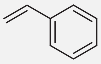
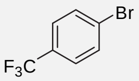
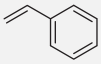
$$\underset{0.50\ \text{mmol}}{Ar^1{-}X} + \underset{0.75\ \text{mmol}}{Ar^2{-}B(OH)_2} \xrightarrow[\text{KOH, H}_2\text{O, 60 °C, 3 h}]{\text{PIC-PdNPs } \mathbf{3}\ \text{(1 mol\% of Pd)}} Ar^1{-}Ar^2$$

Entry	Ar^1–X	Ar^2–B(OH)$_2$	Yield (%)
1			99
2			99
3			87
4			93
5			99
6			98
7			74
8			77
9			37
10			2[a]

[a] The reaction was carried out for 12 h.

Table 2
PIC-PdNPs catalyzed Heck reaction in water

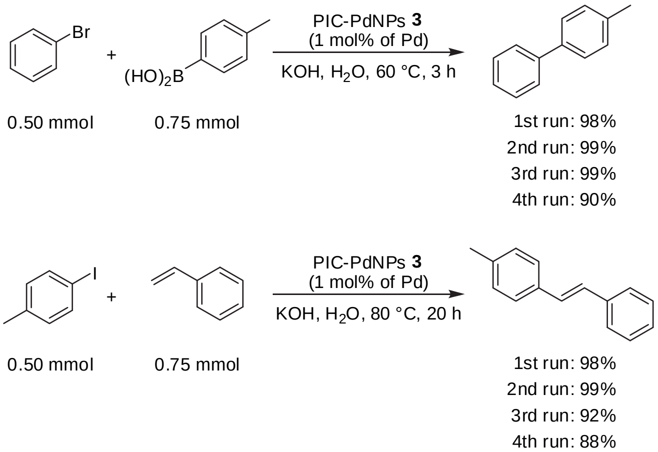


Entry	Ar^1–X		Yield (%)
1			99
2			99
3			88
4			90
5			98
6			75
7			97
8			29
9			5

also underwent the Heck reaction with styrene under similar conditions to afford 4-trifluoromethylstilbene in 90% yield (entry 4). The coupling of 4-methoxystyrene and 4-chlorostyrene took place with 4-iodotoluene to give the corresponding products in 98% and 75% yields, respectively (entries 5 and 6). 2-Iodotoluene was easily converted to the corresponding product (entry 7). However, 2-iodo-*m*-xylene and bromobenzene gave the low yields (entries 8 and 9).

2.4. Recycling of the catalyst

Lastly, the recycling of the catalyst was evaluated by both the Suzuki coupling reaction of bromobenzene with 4-methylphenylboronic acid and the Heck reaction of 4-iodotoluene with styrene (Scheme 3). The Suzuki coupling reaction proceeded efficiently to give 4-methylbiphenyl in 99% yield. When the reaction was completed, PIC-PdNPs were recovered by filtration after pH treatment.[14] The catalyst **3** was recycled at least two times without any loss of activity. However, a slight decrease in the yield was observed in the fourth run in the Suzuki and the Heck reaction. TEM images of the recovered catalyst revealed a similar size of palladium was observed in the Suzuki reaction (2.4±0.6 nm), probably due to the stabilization by arylboronic acid (Fig. 3).[15,16] Indeed, B 1s peak was observed in the recovered catalyst by XPS analysis. On the contrary, the palladium size increased to 6.0±1.3 nm in the Heck reaction.[17,18] The reaction solutions were analyzed by ICP-AES after every run to determine the amount of palladium leaching during the reaction. The total amount of palladium leaching after the fourth run was <1.5% in both reactions.



1st run: 98%
2nd run: 99%
3rd run: 99%
4th run: 90%

1st run: 98%
2nd run: 99%
3rd run: 92%
4th run: 88%

Scheme 3.

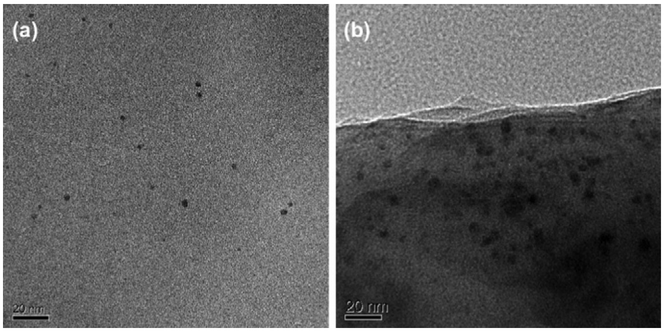


Figure 3. TEM images of recovered PIC-PdNPs. (a) After Suzuki coupling reaction. (b) After Heck reaction.

3. Conclusions

In summary, highly efficient polyion complex supported palladium nanoparticles for Suzuki and Heck reactions in water were prepared. The PIC-supported PdNPs were easily re-dispersed in water by changing the pH.

4. Experimental

4.1. General remarks

^{1}H NMR spectra in DMSO-d_6 or $CDCl_3$ were recorded with a 300 MHz NMR spectrometer (UNITY 300, Varian, Palo Alto, CA) using tetramethylsilane (δ=0) as an internal standard. Gel permeation chromatographic (GPC) analysis in DMF was carried out with a HPLC-8020 instrument (Tosoh Co., Tokyo, Japan) (column: Tosoh TSKgel α-3000 and α-5000). The columns were calibrated with polystyrene of narrow molecular weight distribution standards. Lyophilization was carried out with a freeze dryer (FDU-830, Tokyo Rikakikai Co., Ltd., Tokyo, Japan). CHN elemental microanalyses were carried out using a CHN-Corder MT-5 (Yanaco, Japan). Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) was performed using ICPS-8100 (Shimadzu Co., Kyoto, Japan). Pd nanoparticles were investigated by transmission electron microscopy (TEM) on a JEM 2100F transmission electron microscope (JEOL Ltd., Tokyo, Japan). The samples were prepared by placing a drop of the solution on carbon coated copper grids and allowed to dry in air. X-ray photoelectron spectroscopy (XPS) analysis was carried out using a PHI 5700MC (ULVAC-PHI, Inc., Kanagawa, Japan). Polystyrene of narrow molecular weight distribution standards was purchased from Tosoh Co., Ltd. (Tokyo, Japan). $Pd(OAc)_2$ was obtained from Sigma/Aldrich Co. (Missouri, USA).

4.2. Preparation of poly(4-chloromethylstyrene) (1)

Into a two-necked reaction vessel were added 4-chloromethylstyrene (2.07 g, 13.6×10^{-3} mol), AIBN (0.11 g, 6.2×10^{-4} mol), and DMF (8 mL). After stirring at 70 °C for 20 h under N_2 atmosphere, the solvent was removed in vacuo to give a crude product. Reprecipitation was carried out at least three times in a THF/MeOH system. The last precipitate was dried under reduced pressure and lyophilized with a freeze dryer to give **1** (1.7 g, 82% yield) as a white powder. The number-average molecular weight (M_n) and the molecular weight distribution (M_w/M_n) determined by GPC analysis were ca. 5.6×10^3 and 1.8, respectively. ^{1}H NMR (DMSO-d_6, 300 MHz): δ 7.40 (br, 2H), 6.78 (br, 2H), 4.93 (br, 2H), 2.04–1.62 (br, 3H).

4.3. Preparation of poly{4-chloromethylstyrene-*co*-(4-vinylbenzyl) tributylammonium chloride} (2)

Synthesis of polymer (**2**) was performed in two stages. To a screw-capped vial with a stirring bar were added **1** (0.795 g, 5.2×10^{-3} mol of 4-chloromethylstyrene unit), tributylamine (2.4 mL, 10.3×10^{-3} mol), and THF (8 mL). After stirring at 70 °C for 20 h, the solvent was removed in vacuo to give a partially quaternarized polymer (**2a**, 0.996 g). Subsequently, to a screw-capped vial with a stirring bar were added a partially quaternarized polymer (0.503 g, 1.3×10^{-3} mol of 4-chloromethylstyrene unit), tributylamine (1.2 mL, 5.1×10^{-3} mol), and MeOH (4 mL). After stirring at 65 °C for 20 h, the solvent was removed in vacuo to give a crude product. The residual tributylamine was extracted ten times with hexane. The aqueous phase was lyophilized with a freeze dryer to give **2b** (0.63 g) as a white powder. The ammonium unit content in **2b** (90%) was determined by ^{1}H NMR spectra. ^{1}H NMR (D_2O, 300 MHz): δ 6.52–7.10 (br, 4H), 4.23 (br, 2H), 2.80–3.15 (br, 6H), 1.53–0.72 (br, 21H). Nitrogen content (3.95 wt %) was determined by elemental analysis.

4.4. Preparation of PIC-PdNPs (3)

To a screw-capped vial with a stirring bar were added **2b** (22 mg, 60 μmol of ammonium unit), PAA (13 mg, 180 μmol of monomer unit), $Pd(OAc)_2$ (1.1 mg, 5 μmol), and 1.5 M aqueous K_2CO_3 solution (1 mL). After stirring at 90 °C for 5 h, the reaction mixture was cooled to room temperature by immediately immersing the vial in water (~20 °C), and then 6.0 mol L^{-1} HCl aqueous solution (0.22 mL) was added to the reaction mixture. Subsequently, the aqueous phases were removed, and recovered catalyst was washed with acetone (3×1.0 mL).

4.5. Determination of the amount of palladium

Compound **3** (36 mg) was placed in a screw-capped vial and then added aqua regia (5 mL). The mixture was heated at 80 °C to dissolve completely. After cooled to room temperature, the solution was adjusted to 50 g by nitric acid and then measured the amount of Pd metal by ICP-AES analysis (9.5 ppm).

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

4.6. Typical procedures for Suzuki coupling reaction

To a screw-capped vial with a stirring bar were added bromobenzene (78.5 mg, 0.5 mmol), *p*-methylphenylboronic acid (102 mg, 0.75 mmol), **3** (36 mg, 0.9 mol % of Pd), and 1.5 M aqueous KOH solution (1 mL). After stirring at 60 °C for 3 h, the reaction mixture was cooled to room temperature by immediately immersing the vial in water (~20 °C), and then 6.0 mol L^{-1} HCl aqueous solution (0.22 mL) was added to the reaction mixture. Subsequently, the aqueous phases were removed, and recovered catalyst was washed with 1.5 M aqueous KCl solution (5×1.5 mL) and diethyl ether (5×1.5 mL), which were then added to the aqueous phase. The aqueous phase was extracted five times with diethyl ether. The combined organic extracts were dried over $MgSO_4$ and concentrated under reduced pressure. The resulting product was analyzed by ^{1}H NMR. The recovered **3** 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.

4.7. Typical procedures for Heck reaction

To a screw-capped vial with a stirring bar were added 4-iodotoluene (109 mg, 0.5 mmol), styrene (79 mg, 0.75 mmol), **3** (36 mg, 1 mol % of Pd), and 1.5 M aqueous KOH solution (1 mL). After stirring at 60 °C for 3 h, the reaction mixture was cooled to room temperature by immediately immersing the vial in water (~20 °C), and then 6.0 mol L^{-1} HCl aqueous solution (0.22 mL) was added to the reaction mixture. Subsequently, the aqueous phases were removed, and recovered catalyst was washed with 1.5 M aqueous KCl solution (5×1.5 mL) and diethyl ether (5×1.5 mL), which were then added to the aqueous phase. The aqueous phase was extracted five times with diethyl ether. The combined organic extracts were dried over $MgSO_4$ and concentrated under reduced pressure. The resulting product was analyzed by ^{1}H NMR. The recovered **3** 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.

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Supplementary data

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.tet.2010.05.076.

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