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Detailed Mechanism for Hiyama Coupling Reaction in Water Catalyzed by Linear Polystyrene-Stabilized PdO Nanoparticles

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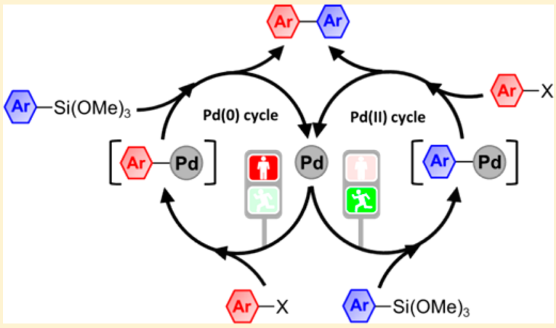
ABSTRACT: The catalytic cycle of the Hiyama coupling reaction in water catalyzed by linear polystyrene-stabilized PdO nanoparticles (PS-PdONPs) was investigated. The formation of 4-methylbiphenyl was confirmed from the reaction of 4-bromotoluene with the catalyst recovered from the reaction of PS-PdONPs with trimethoxyphenylsilane. The catalytic activity of PS-PdONPs significantly diminished upon addition of NaI or poly(4-vinylpyridine). The Hiyama coupling reaction using PS-PdONPs as a catalyst proceeds through a different mechanism from the commonly accepted one that starts from the oxidative addition of an aryl halide to a $Pd^{(0)}$ species.



INTRODUCTION

Carbon−carbon bond formation is an important research topic in organic synthesis. From the viewpoint of green sustainable chemistry, it is preferable to carry out reactions in water rather than in flammable organic solvents. An enormous number of metal nanoparticles catalysts, which have high catalytic activity for carbon−carbon coupling reactions such as Suzuki,[1] Heck,[2] Sonogashira,[3] Stille,[4] and Hiyama[5] coupling in water, have been developed in recent years. Research on the mechanism of the reactions using metal nanoparticle as a catalyst has been focused on whether the reaction proceeds in solution or on the surface of the nanoparticles.[6] Unfortunately, there are few studies of the actual mechanism, and in most cases, those studies concluded that the detailed mechanism is similar to that in the case of a metal complex.

Recently, we developed linear polystyrene-stabilized PdO nanoparticles (PS-PdONPs) that showed high catalytic activity for several carbon−carbon coupling reactions in water.[7] In the course of our research on the Hiyama coupling reaction catalyzed by PS-PdONPs,[8] we determined that the reaction must occur through a different mechanism than that of $Pd^{(0)}$−$Pd^{(II)}$−$Pd^{(0)}$ cycle by metal complex catalysts because of the following: (1) The Hiyama coupling reaction did not take place with polystyrene-stabilized Pd nanoparticles (PS-PdNPs, $Pd^{(0)}$ species), but it proceeded smoothly with PS-PdONPs ($Pd^{(II)}$ species). (2) No formation of $Pd^{(0)}$ species was confirmed by XPS analysis of the recovered catalyst after the reaction. These data prompted us to examine the detailed mechanism of the Hiyama coupling reaction in water using PS-PdONPs as a catalyst.

RESULTS AND DISCUSSION

PS-PdONPs were prepared by heating the mixture of $Pd(OAc)_2$ and TSKgel standard polystyrene (M_W = 5.06 × 10^3) in 1.5 $mol \cdot L^{-1}$ K_2CO_3 aqueous solution at 90 °C for 5 h. The composition (PdO) was confirmed by X-ray diffraction (XRD) measurement (Figure 1). A transmission electron microscopy (TEM) image of PS-PdONPs showed a fairly uniform particle size of 2.1 ± 0.4 nm (Figure 2). Inductively

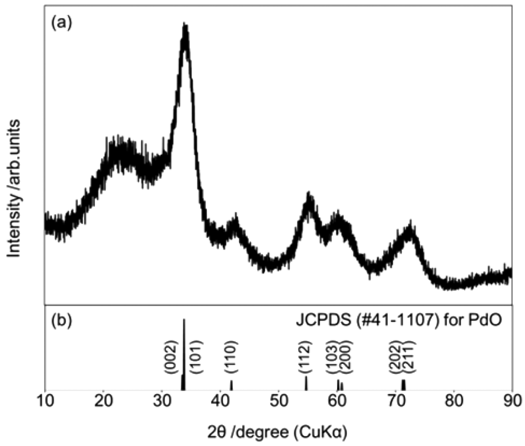


Figure 1. (a) XRD patterns of PS-PdONPs; (b) Powder Diffraction File #41-1107 (Joint Committee on Powder Diffraction Standards) for PdO.

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coupled plasma-atomic emission spectroscopy (ICP-AES) revealed that PS-PdONPs contained an average of 2.5 mmol·g^{-1} of Pd.

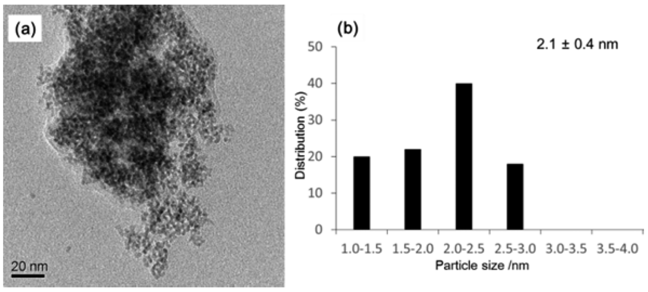


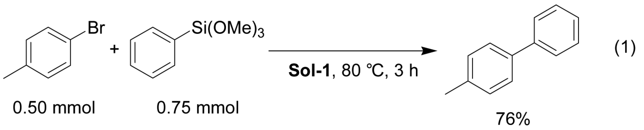
Figure 2. (a) TEM micrograph of PS-PdONPs (scale bar = 20 nm); (b) size distribution of PS-PdONPs.

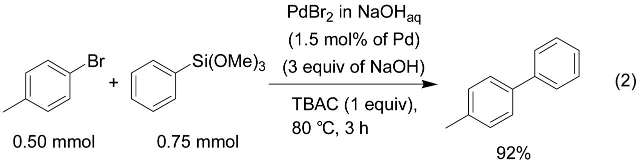
First, stepwise reactions were performed in order to confirm whether the Hiyama coupling reaction catalyzed by PS-PdONPs takes place on the surface of the catalyst or in solution, and whether aryl halide or aryltrimethoxysilane is first involved in the reaction (Scheme 1). After heating the mixture of PS-PdONPs and 4-bromotoluene in 1.5 mol·L^{-1} NaOH aqueous solution at 80 °C for 3 h in the presence of TBAC, the catalyst and the aqueous phase were separated. When the reaction of the recovered catalyst (**ReCat-1**) with trimethoxyphenylsilane was performed at 80 °C for 3 h, no formation of 4-methylbiphenyl was confirmed. Additionally, no coupling product was obtained after heating of trimethoxyphenylsilane in the solution phase (**Sol-1**). Based on the hypothesis that coupling product was not obtained because 4-bromotoluene would be filtered out with the catalyst, **Sol-1** was heated in the presence of both 4-bromotoluene and trimethoxyphenylsilane to give 4-methylbiphenyl in 76% yield (eq 1). This result is consistent with the fact that leaching of palladium was observed when PS-PdONPs was heated in the presence of 4-bromotoluene (entry 3 in Table 1). Indeed, 92% of 4-methylbiphenyl was obtained from the reaction of 4-bromotoluene with trimethoxyphenylsilane in the presence of a water-soluble palladium species, which was prepared by dissolving $PdBr_2$ in 1.5 mol·L^{-1} NaOH aqueous solution (eq 2). Considering that the yield of 4-methylbiphenyl was low (34%) in the case of 4-iodotoluene using water-soluble palladium species as a catalyst (eq 3) and that no increase in the yield of coupling product was observed in the hot filtration test (eq 4), the reaction would not proceed only in solution if leached palladium species was involved in the reaction cycle.

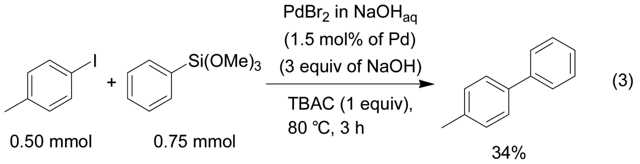
Table 1. Leaching Test

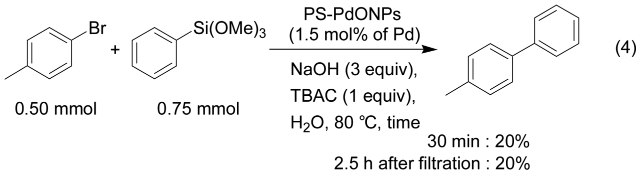
entry	reagent	amount of Pd leached (%)[a]
1	none	2.8
2	TBAC	2.9
3	*p*-tolyl-Br + TBAC	3.3
4	$PhSi(OMe)_3$ + TBAC	<0.1
5	*p*-tolyl-Br + $PhSi(OMe)_3$ + TBAC	<0.1
6	NaI	<0.1
7	TBAI	<0.1

[a] Average weight of Pd atoms detected by ICP-AES in the supernatant liquid after exposure of PS-PdONPs to different reagents in NaOH aqueous solution at 80 °C for 3 h.



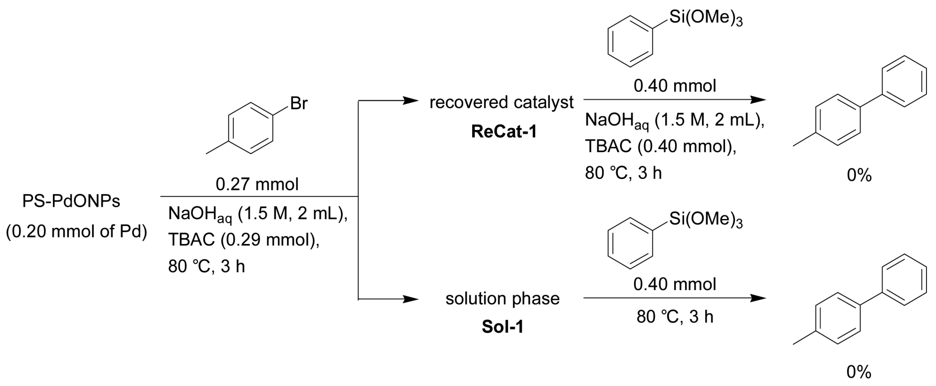




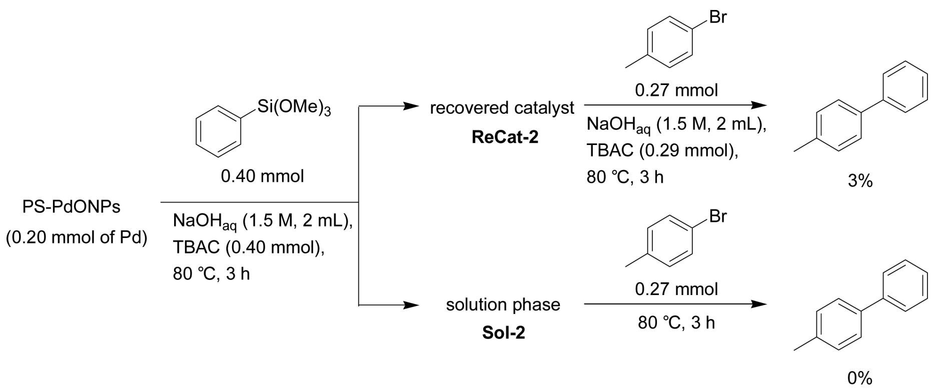


A similar stepwise experiment was conducted with the order of 4-bromotoluene and trimethoxyphenylsilane reversed (Scheme 2). No coupling product was obtained from the reaction of 4-bromotoluene with the solution phase (**Sol-2**), which was separated after heating the mixture of PS-PdONPs and trimethoxyphenylsilane in 1.5 mol·L^{-1} NaOH aqueous

Scheme 1. Stepwise Experiment of Reacting from 4-Bromotoluene

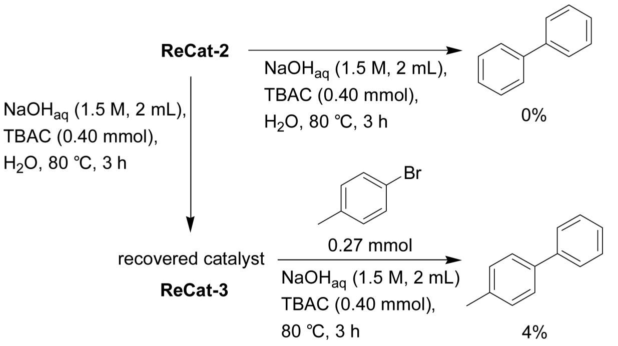


Scheme 2. Stepwise Experiment of Reacting from Trimethoxyphenylsilane

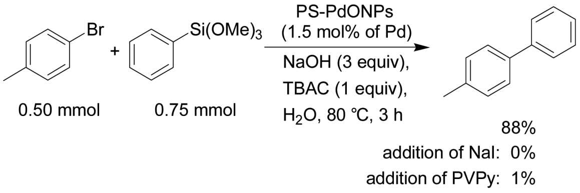


solution at 80 °C for 3 h. This result is consistent with the fact no palladium species was detected in the solution phase after heating of PS-PdONPs in the presence of trimethoxyphenylsilane (entry 4 in Table 1). In contrast, the formation of 4-methylbiphenyl was confirmed, although the yield was low (3%) from the reaction of the recovered catalyst (**ReCat-2**) with 4-bromotoluene. In order to confirm that the desired coupling product was not obtained from the reaction with physically absorbed trimethoxyphenylsilane, the following experiment was performed. When **ReCat-2** was heated in the absence of 4-bromotoluene in 1.5 mol·L^{-1} NaOH aqueous solution at 80 °C for 3 h, no biphenyl was obtained (Scheme 3). However, 4% 4-methylbiphenyl was confirmed after heating of the recovered catalyst (**ReCat-3**) and 4-bromotoluene, indicating that the phenyl group derived from trimethoxyphenylsilane was present on the surface of the catalyst.

Scheme 3. Formation of Coupling Product from the Recovered Catalyst



When the Hiyama coupling reaction of 4-bromotoluene with trimethoxyphenylsilane was performed in the presence of NaI, no coupling product was obtained (eq 5). To elucidate the effect of NaI, the amount of leached palladium species in the aqueous solution was checked by ICP-AES. After heating of PS-PdONPs in 1.5 mol·L^{-1} aqueous NaOH solution at 80 °C for 3 h, 2.8% palladium was detected in the aqueous solution (entry 1 in Table 1), and the peak at 360 nm corresponding to Pd$^{(II)}$ was observed by UV–vis spectra (Figure 3).[9] In contrast, no palladium species was observed in the presence of NaI (entry 6). The activation effect of trimethoxyphenylsilane by TBAC would also decrease because TBAI was generated by addition of NaI into the reaction mixture,[10,11] and no leaching of palladium was confirmed in the presence of TBAI (entry 7). These results suggest that iodide ion retards the leaching of palladium. To further investigate the correlation between leaching of palladium species and progress of the reaction, a catalyst-poisoning experiment was performed. Poly(4-vinylpyridine) (PVPy: addition of 0.5 mmol of 4-vinylpyridine unit, M_W = 16 000) was employed as the catalyst poison,[12] resulting in inhibition of the catalytic reaction. This result is consistent with the idea that leaching of palladium species is involved in the catalytic cycle.



(5)

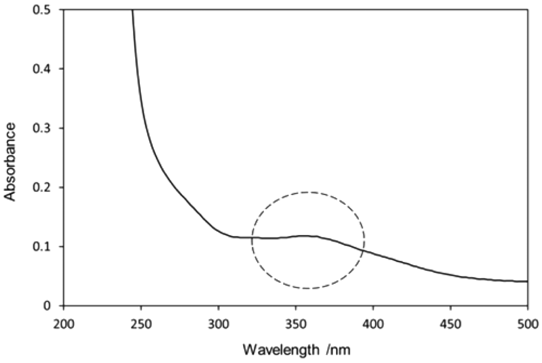
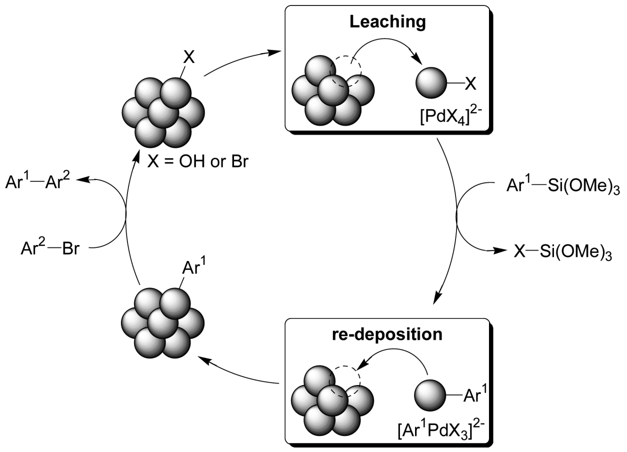


Figure 3. UV–vis spectra of the filtrate after heating of PS-PdONPs in 1.5 mol·L^{-1} aqueous NaOH solution at 80 °C for 3 h.

All of the above results strongly suggested that the Hiyama coupling reaction using PS-PdONPs as a catalyst proceeds through a different mechanism from the commonly accepted one that starts from the oxidative addition of an aryl halide to a Pd$^{(0)}$ species. A more plausible mechanism is a Pd$^{(II)}$ catalytic cycle (Scheme 4), where aryltrimethoxysilane reacts with the catalyst rather than aryl halide.[13] Although leaching of palladium into reaction medium occur, the leached palladium species is immediately restabilized on the catalyst surface. Subsequently, the reaction with aryl halide takes place on the catalyst surface to give desired coupling product. If the reaction proceeds via this mechanism, then the valence of palladium remains divalent, which is consistent with the results of XPS, in which no Pd$^{(0)}$ species was observed even after the reaction.[8]

Scheme 4. Plausible Reaction Mechanism



Results of leaching and hot filtration tests also support this mechanism. Furthermore, the size of nanoparticles was maintained even after the recycle experiment, and no detectable Pd species was observed from the filtrate in the hot filtration test.[8] These data suggest that the leaching of Pd species in this system is "local leaching".[6a]

■ CONCLUSION

The mechanism of the Hiyama coupling reaction in water catalyzed by PS-PdONPs was investigated. Stepwise reactions showed that the catalyst reacted first with aryltrimethoxysilane and that the reaction of the catalyst with aryl halide took place on the surface of the catalyst. The existence of NaI retarded the progress of the reaction and prevented leaching of palladium species. The leaching of palladium species into the reaction medium was supported by the results of a poisoning test. This result indicates that the mechanism of the reaction using metal nanoparticles as a catalyst may be different from that in the case of a complex catalyst.

■ EXPERIMENTAL SECTION

^{1}H NMR spectra in $CDCl_3$ were recorded with a 300 MHz NMR spectrometer (UNITY 300, Varian, Palo Alto, CA) using tetramethylsilane ($\delta = 0$) as an internal standard. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) was performed using ICPS-8100 (Shimadzu Co., Kyoto, Japan). X-ray photoelectron spectroscopy (XPS) analysis was carried out using a PHI 5700MC (ULVAC-PHI, Inc., Kanagawa, Japan).

Preparation of Polystyrene-Stabilized PdO Nanoparticles (PS-PdONPs). To a screw-capped vial with a stirring bar were added polystyrene (9.0 mg , 85 μmol of styrene unit), $Pd(OAc)_2$ (5.5 mg, 25 μmol), and 1.5 mol·L^{-1} aqueous K_2CO_3 solution (3 mL). After stirring at 90 °C for 5 h, the reaction mixture was cooled to room temperature by immediately immersing the vial in water for approximately 10 min. After separating the catalyst and the aqueous phase through centrifugation, the aqueous phase was decanted. The catalyst was washed with water (5 × 1.0 mL) and MeOH (5 × 1.0 mL).

Typical Procedures for Stepwise Experiments. To a screw-capped vial with a stirring bar were added PS-PdONPs (80 mg, 0.20 mmol of Pd), 4-bromotoluene (48 mg, 0.27 mmol), TBAC (81 mg, 0.29 mmol), and 1.5 mol·L^{-1} aqueous NaOH solution (2 mL). After stirring at 80 °C for 3 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 (**ReCat-1**) was washed with H_2O (3 × 3.0 mL) and diethyl ether (3 × 3.0 mL). To a screw-capped vial including the recovered catalyst were added trimethoxyphenylsilane (80 mg, 0.40 mmol), TBAC (111 mg, 0.40 mmol), and 1.5 mol·L^{-1} aqueous NaOH solution (2 mL). After stirring at 80 °C for 3 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 H_2O (3 × 3.0 mL) and diethyl ether (3 × 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 ^{1}H NMR. However, the aqueous phase (**Sol-1**) which was filtered with a membrane filter was stirred at 80 °C for 3 h after addition of trimethoxyphenylsilane (80 mg, 0.40 mmol). The mixture was cooled to room temperature by immediately immersing the vial in water (~20 °C) for about 10 min and extracted eight times with diethyl ether. The organic extracts were dried over $MgSO_4$ and concentrated under reduced pressure. The product was analyzed by ^{1}H NMR.

Typical Procedures for Leaching Tests. To a screw-capped vial with a stirring bar were added PS-PdONPs (3.0 mg, 7.5 μmol of Pd), 4-bromotoluene (86 mg, 0.5 mmol), TBAC (142 mg, 0.5 mmol), and 1.5 mol·L^{-1} aqueous NaOH solution (1 mL). After stirring at 80 °C for 3 h, the aqueous phase was filtered with a membrane filter and adjusted to 10 mL by hydrochloric acid (1.0 mol·L^{-1}). The amount of Pd metal was measured by ICP-AES analysis (2.1 ppm).

General Procedure for Hiyama Coupling Reaction. To a screw-capped vial with a stirring bar were added 4-bromotoluene (86.4 mg, 0.5 mmol), trimethoxyphenylsilane (152 mg, 0.75 mmol), PS-PdONPs (2.9 mg, 1.5 mol % of Pd), TBAC (142 mg, 0.5 mmol), and 1.5 mol·L^{-1} aqueous NaOH solution (1 mL). After stirring at 80 °C for 3 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. 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 ^{1}H NMR.

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Notes

The authors declare no competing financial interest.

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(9) When $PdBr_2$ was dissolved in 1.5 $mol \cdot L^{-1}$ aqueous NaOH solution, the peak at 368 nm was observed by UV–vis spectra.

(10) No coupling product was obtained from the reaction of 4-bromotoluene with trimethoxyphenylsilane using PS-PdONPs as a catalyst in the presence of TBAI.

(11) When the reaction of 4-iodotoluene with trimethoxyphenylsilane was performed at 80 °C for 3 h in the presence of TBAC using PS-PdONPs as a catalyst, 4-methylbiphenyl was obtained in 13% yield, and a white precipitate of TBAI was confirmed.

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