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Linear polystyrene-stabilized Rh^(III) nanoparticles for oxidative coupling of arylboronic acids with alkenes in water



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1. Introduction

After the first report of the stoichiometric oxidative coupling reaction of alkenylboronic acids with olefins by Heck [1], various catalytic systems have been developed, with most performed with Pd catalysts [2–5]. When the reaction of an arylboronic acid with an α , β -unsaturated ester is performed in the presence of a homogeneous Rh catalyst, both products of oxidative coupling and conjugate addition are possible and the selectivity of the product is tunable by the reaction conditions. For example, Zou and coworkers influenced the selectivity for the oxidative coupling by adjusting the base and phosphine ligand [6]. Genet, Darses, and coworkers reported only the conjugate adduct was obtained when the reaction of potassium phenyltrifluoroborate with butyl acrylate was performed in the presence of water, although the oxidative coupling product was obtained from the reaction in 1,4-dioxane [7,8]. On the other hand, the oxidative coupling reaction of an arylboronic acid with an α,β -unsaturated ester proceeded with a heterogeneous Rh catalyst. Li and Nejat demonstrated that a Rh⁽¹⁾ catalyst supported by mesoporous silica or silica-coated iron oxide

ABSTRACT

Linear polystyrene-stabilized Rh^(III) nanoparticles (PS-Rh^(III)NPs) were obtained when an aqueous solution of RhCl₃ was stirred at 90 °C in the presence of KOH, 4-methylphenylboronic acid, and linear polystyrene, as indicated by X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM). PS-Rh^(III)NPs exhibited high catalytic activity for the oxidative coupling of arylboronic acids with alkenes. In contrast, PS-Rh⁽⁰⁾NPs prepared with NaBH₄ had little activity for the same reaction. © 2018 Elsevier B.V. All rights reserved.

exhibited high catalytic efficiency in the Heck-type oxidative coupling reaction [9-11]. Trivedi and co-workers developed a phosphine-free method for the olefination of arylboronic acids using a Rh⁽⁰⁾ catalyst [12,13]. However, the reported method required an organic co-solvent for the reaction to take place efficiently.

Water has gained much attention recently due to the appealing properties of organic reactions in aqueous media from both the economical and "green chemistry" points of view [14–18]. Metal nanoparticles have recently received considerable attention in organic synthesis because of their efficient catalytic activity in water [19–24]. We found that linear polystyrene was capable of stabilizing metal nanoparticles, and that the resultant polystyrene-stabilized metal nanoparticles had high catalytic activity for several reactions in water [25–30]. Our continuing interest in the scope and applicability of this methodology led us to investigate the preparation and application of polystyrene-stabilized Rh nanoparticles for the reaction of arylboronic acids with alkenes in water.

2. Experimental

2.1. Preparation of PS-Rh^(III)NPs

To a screw-capped vial with a stirring bar were added 13.5 mg of

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polystyrene (129 µmol of styrene unit). 4.0 M aqueous solution of RhCl₃ (9.4 µL, 37.6 µmol), 4-methylphenylboronic acid (51 mg, 0.375 mmol), and 1.5 M aqueous KOH solution (3 mL). After stirring at 90 °C for 24 h, the aqueous solution was decanted. Subsequently, the polystyrene stabilized Rh nanoparticles were washed with water (5 \times 3.0 mL), MeOH (1 \times 3.0 mL), and Et₂O (1 \times 3.0 mL).

2.2. Determination of loading of the rhodium

PS-Rh^(III)NPs (1.0 mg) was placed in a screw-capped vial and then added 36% hydrochloric acid (5 mL). After rhodium species dissolved completely, the solution was adjusted to 50 mL by water and then measured the amount of Rh metal by ICP-AES analysis (8.67 ppm).

After the catalytic reaction, the aqueous phase was adjusted to 20 mL by 1 M hydrochloric acid and then measured the amount of Rh metal by ICP-AES analysis.

2.3. Typical procedures for oxidative coupling reaction

To a screw-capped vial with a stirring bar were added PS-Rh^(III)NPs (3.0 mg, 2.5 mol% of Rh), 4-methylphenylboronic acid (68.0 mg, 0.5 mmol), butyl acrylate (153.8 mg, 1.2 mmol), and H₂O (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) 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 × 3.0 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 MgSO₄ 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 Rh metal in the aqueous phase determined by ICP-AES analysis was 1.6 ppm.

2.3.1. Butyl trans-4-methylcinnamate

¹H NMR (CDCl₃, 400 MHz): δ 7.66 (d, J = 16.0 Hz, 1H), 7.42 (d, J = 8.0 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H), 6.39 (d, J = 16.0 Hz, 1H), 4.20 (t, J = 7.2 Hz, 2H), 2.37 (s, 3H), 1.72–1.65 (m, 2H), 1.49–1.39 (m, 2H), 0.96 (t, J = 7.2 Hz, 3H).

¹³C NMR (CDCl₃, 400 MHz): δ 167.33, 144.54, 140.61, 131.68, 129.58, 128.02, 117.13, 64.34, 30.75, 21.45, 19.19, 13.75.

2.3.2. Methyl trans-4-methylcinnamate

¹H NMR (CDCl₃, 400 MHz): δ 7.67 (d, J = 16.0 Hz, 1H), 7.42 (d, J = 8.0 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H), 6.40 (d, J = 16.0 Hz, 1H), 3.80 (s, 3H), 2.37 (s, 3H).

 ^{13}C NMR (CDCl₃, 400 MHz): δ 167.65, 144.88, 140.73, 131.59, 129.60, 128.05, 116.63, 51.65, 21.46.

2.3.3. Phenyl trans-4-methylcinnamate

¹H NMR (CDCl₃, 400 MHz): δ 7.85 (d, J = 16.0 Hz, 1H), 7.49 (d, *I* = 7.6 Hz, 2H), 7.41 (t, *I* = 7.2 Hz, 2H), 7.27–7.22 (m, 3H), 7.17 (d, I = 8.8 Hz, 2H), 6.59 (d, I = 16.0 Hz, 1H), 2.40 (s, 3H).

¹³C NMR (CDCl₃, 400 MHz): δ 165.61, 150.80, 146.58, 141.22, 131.41, 129.72, 129.41, 128.30, 125.72, 121.65, 116.12, 21.54.

2.3.4. Methyl trans-4-methoxycinnamate

¹H NMR (CDCl₃, 400 MHz): δ 7.66 (d, J = 16.0 Hz, 1H), 7.48 (d, J = 8.4 Hz, 2H), 6.91 (d, J = 8.4 Hz, 2H), 6.32 (d, J = 16.0 Hz, 1H), 3.84 (s, 3H), 3.80 (s, 3H).

¹³C NMR (CDCl₃, 400 MHz): δ 167.79, 161.34, 144.52, 129.72, 127.06, 115.20, 114.29, 55.36, 51.60.

2.3.5. Methyl trans-4-trifluoromethylcinnamate

¹H NMR (CDCl₃, 400 MHz): δ 7.71 (d, I = 16.0 Hz, 1H), 7.60–7.66 (m, 4H), 6.52 (d, I = 16 Hz, 1H), 3.831 (s, 3H).

¹³C NMR (CDCl₃, 400 MHz): δ 166.86, 142.99, 137.70, 131.92, 128.17, 125.87, 125.83, 120.31, 51.93.

2.3.6. 4-(4-methylphenyl)-3-buten-2-one

¹H NMR (CDCl₃, 400 MHz): δ 7.50 (d, I = 16.4 Hz, 1H), 7.45 (d, *I* = 8.0 Hz, 2H), 7.21 (d, *I* = 8.0 Hz, 2H), 6.68 (d, *I* = 16.4 Hz, 1H), 2.38 (s, 3H), 2.37 (s, 3H).

¹³C NMR (CDCl₃, 400 MHz): δ 198.59, 143.56, 141.04, 131.60, 129.71, 128.25, 126.23, 27.43, 21.50.

2.3.7. 4-(4-methylphenyl)-2-butanone

¹H NMR (CDCl₃, 400 MHz): δ 7.06–7.11 (m, 4H), 2.86 (t, J = 7.6 Hz, 2H), 2.74 (t, J = 7.6 Hz, 2H), 2.31 (s, 3H), 2.18 (s, 3H).

¹³C NMR (CDCl₃, 400 MHz): δ 208.18, 137.82, 135.57, 129.14, 128.12, 45.32, 30.07, 29.27, 20.96.

2.3.8. 1-(4-methylphenyl)-1-penten-3-one

¹H NMR (CDCl₃, 400 MHz): δ 7.54 (d, I = 16.0 Hz, 1H), 7.45 (d, *I* = 8.0 Hz, 2H), 7.20 (d, *I* = 8.0 Hz, 2H), 6.71 (d, *I* = 16.0 Hz, 1H), 2.69 (q, J = 7.2, 2H), 2.38 (s, 3H), 1.17 (d, J = 7.2 Hz, 3H). ¹³C NMR (CDCl₃, 400 MHz): δ 201.16, 142.37, 140.93, 131.90,

129.76, 128.32, 125.19, 34.03, 21.58, 8.38.

2.3.9. 1-(4-methylphenyl)-3-pentanone

¹H NMR (CDCl₃, 400 MHz): δ 7.12–7.04 (m, 4H), 2.86 (t, J = 7.2 Hz, 2H), 2.71 (t, J = 7.2 Hz, 2H), 2.40 (q, J = 7.2 Hz, 2H), 2.31 (s, 3H), 1.04 (t, *I* = 7.2 Hz, 3H).

¹³C NMR (CDCl₃, 400 MHz): δ 210.96, 138.15, 135.65, 129.25, 128.27, 44.15, 36.22, 29.52, 21.09, 7.85.

3. Results and discussion

Linear polystyrene-stabilized Rh^(III) nanoparticles (PS-Rh^(III)NPs) were prepared according to the previous paper [25]. A mixture of rhodium chloride hydrate, linear polystyrene ($M_{\rm n} = 6.0 \times 10^3$), and 4-methylphenylboronic acid was added to a 1.5 moL/L aqueous KOH solution. After the mixture was stirred at 90 °C for 24 h, the color of the solution disappeared and a yellow precipitate formed. X-ray photoelectron spectroscopy curve-fitting showed binding energy at 308.6 eV and 307.3 eV, which assigned to Rh 3d_{5/2} for Rh₂O₃ and metallic Rh, respectively (Fig. 1). Broad diffraction peaks were observed in powder X-ray diffraction (XRD), suggesting the composition was Rh₂O₃ (Fig. 2). In contrast to the case of Pd [25], it is considered that Rh⁽⁰⁾ nanoparticles did not be obtained from the above procedure, probably due to the difficulty of the reductive



Fig. 1. XPS spectrum of PS-Rh^(III)NPs.



Fig. 2. (a) XRD pattern of PS-Rh^(III)NPs; (b) Powder Diffraction File #41–0541 (International Centre for Diffraction Data) for Rh₂O₃; (c) Powder Diffraction File #05–0685 (International Centre for Diffraction Data) for Rh.

elimination step. A transmission electron microscopy (TEM) image of the yellow precipitate revealed a fairly uniform particle size of 1.2 ± 0.3 nm (Fig. 3), which is consistent with the result broad peaks were observed in XRD. When the mixture of rhodium chloride hydrate, 4-methylphenylboronic acid, and a 1.5 moL/L aqueous KOH solution was stirred at 90 °C for 24 h, most of the Rh formed aggregates, suggesting polystyrene acted as the stabilizer for RhNPs (Figure S1). The loading of rhodium, confirmed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) was 4.26 mmoL/g.

The catalytic activity of PS-Rh^(III)NPs was investigated for the reaction of arylboronic acids with alkenes in water. 4-Methylphenylboronic acid and butyl acrylate were used as model substrates in order to optimize the reaction conditions (Table 1). The reaction of 4-methylphenylboronic acid (0.5 mmol) with butyl acrylate (0.75 mmol) was performed in water at 70 °C for 5 h under aerobic conditions in the presence of PS-Rh^(III)NPs (2.5 mol% of Rh) to give butyl trans-4-methylcinnamate in 28% yield, which was calculated based on 4-methylphenylboronic acid (entry 1). No product of 1,4-addition [butyl 3-(4-methylphenyl)propanoate] was obtained in this reaction. The yield of butyl trans-4methylcinnamate increased at higher temperatures (80 °C: 48%; 90 °C: 68%, entries 2 and 3). The oxidative coupling product formed in 80% yield using 1.2 mmol of butyl acrylate and a similar yield was obtained under N₂ atmosphere (entries 4 and 5). No reaction occurred on using Rh species prepared in the absence of PS, indicating the size of RhNPs is important to take place the reaction (entry 6). When PS-Rh⁽⁰⁾NPs prepared by NaBH₄ were used as the catalyst, no coupling product was obtained, suggesting the active catalytic species was Rh^(III) (entry 7). In addition, the reaction was retarded in the presence of base (entry 8). The use of lower catalyst loadings resulted in incomplete reactions (entry 9). Thus, the optimized reaction conditions were found to be 0.5 mmol of 4methylphenylboronic acid, 1.2 mmol of butyl acrylate, 2.5 mol% of PS-Rh^(III)NPs and water as solvent at 90 °C for 5 h under aerobic conditions.

With the optimized reaction conditions in hand, the scope of the protocol was extended to several arylboronic acids and alkenes (Table 2). Methyl acrylate afforded the corresponding coupling product in 73% yield (entry 1). In the case of phenyl acrylate, the formation of phenyl propanoate (37%) was also observed along with phenyl *trans*-4-methylcinnamate (43%), suggesting that bimolecular alkenes were involved in the catalytic cycle [6]. The



Fig. 3. (a) TEM image of PS-Rh^(III)NPs (scale bar = 10 nm); (b) TEM image of PS-Rh^(III)NPs (scale bar = 5 nm); (c) Size distribution of PS-Rh^(III)NPs.

Table 1

Optimization of reaction conditions.



entry	x	temp (°C)	yield (%) ^a
1	0.75	70	28
2	0.75	80	48
3	0.75	90	68
4	1.2	90	80
5 ^b	1.2	90	79
6 ^c	1.2	90	0
7^{d}	1.2	90	0
8 ^e	1.2	90	6
9 ^f	1.2	90	57

^a NMR yield.
 ^b Under N₂.
 ^c Rh^(III) species prepared in the absence of PS was used as a catalyst.
 ^d PS-Rh^(O)NPs was used as a catalyst.

^e In the presence of K_2CO_3 . ^f 1.0 mol% of PS-Rh^(III)NPs was used.

Table 2

Oxidative coupling of arylboronic acids with alkenes in water.

B(OH) ₂	+ alkana	PS-Rh ^(Ⅲ) NPs (2.5 mol% of Rh)	R^2
R ¹	- aikene	H ₂ O, 90 °C, time	\mathbb{R}^{1}
0.5 mmol	1.2 mmol		IX

entry	R ¹	alkene	time	yield (%) ^a
1	Me	OMe	5	73
2	Me	O CPh	5	43 ^b
3	OMe		5	77
4	CF ₃	O O O O O O	5	88
5	Ме	O OMe	24	32
6	Ме	O CMa	24	trace
7	Me		5	47 ^c
8	Me		5	46 ^d
9	Me	_`Ph	5	16
10	Me	C ₄ H ₉	5	0
11	Ме		24	0

^a NMR yield.

^a NMR yield.
 ^b Phenyl propanoate was obtained in 37% yield.
 ^c 4-(4-methylpheyl)-2-butanone was obtained in 52% yield.
 ^d 1-(4-methylphenyl)-3-pentanone was obtained in 54% yield.



Scheme 1. Recycling experiment.

substituent on the arylboronic acid did not influence the product yield, whereas the existence of a methyl group on the olefin retarded the reaction (entries 3–6). When methyl vinyl ketone and ethyl vinyl ketone were used as substrates, both products of oxidative coupling and conjugate addition were obtained (entries 7 and 8). Only 16% of the coupling product was obtained from the reaction of 4-methylphenylboronic acid with styrene (entry 9), and the reaction did not proceed at all when using 1-hexene or 2-cyclopenten-1-one as substrates (entries 10 and 11).

When the recyclability of PS-Rh^(III)NPs was investigated, a decrease in yield was observed (Scheme 1). TEM measurement of the recovered catalyst revealed that the Rh particle size did not change after the reaction (Figs. 3 and 4), suggesting that catalyst deactivation was not caused by aggregation of Rh. On the other hand, 2.5% of Rh species was detected by ICP-AES analysis in the solution phase after the reaction, suggesting catalyst deactivation was caused by a decrease in the amount of Rh in the nanoparticles.

In order to obtain insight into the reaction mechanism, a hot filtration test was conducted. When the reaction of 4methylphenylboronic acid with butyl acrylate was interrupted at 14% conversion (1 h) and continued after removal of the catalyst, no increase in the yield of coupling product was observed (eq 1). Although leaching of Rh species into the reaction medium was observed during the reaction, no Rh species was detected in the solution phase when heating only the catalyst in water at 90 °C for 20 h. In addition, 1.1% of Rh was observed in the aqueous phase after heating of PS-Rh $^{(\rm III)}$ NPs in KOH aqueous solution at 90 $^{\circ}C$ for 5 h, and the catalytic reaction was reduced dramatically under basic conditions (entry 7 in Table 1). These data indicated that the reaction did not occur with leached homogeneous Rh species. Butyl trans-4-methylcinnamate was obtained, although the yield was low (2%) from the reaction of PS-Rh^(III)NPs (0.1 mmol of Rh) with butyl acrylate (1.2 mmol). This result indicates that the aryl group derived from the arylboronic acid was present on the surface of the catalyst (eq 2). This data is consistent with the result Rh^(III) nanoparticles was obtained after heating the mixture of rhodium chloride hydrate and 4-methylphenylboronic acid. When the reaction of phenyl acrylate with phenylboronic acid pinacol ester was performed in D₂O, phenyl 2-deuteriopropanoate (>99% D) was obtained (eq 3).

A plausible mechanism for the reaction described herein is given in Scheme 2. After insertion of the alkene into Rh-Ar on the surface of the catalyst, β -hydride elimination occurs to form the coupling product along with a Rh-H species. The Rh-H species reacts with another alkene, followed by the reaction with water to give the reduction product and a Rh-OH species. Finally, transmetalation with the arylboronic acid takes place to regenerate the Rh-Ar species.



Scheme 2. A plausible reaction mechanism.

OR



Fig. 4. (a) TEM image of the recovered catalyst after 3rd run (scale bar = 10 nm); (b) Size distribution of the recovered catalyst.

Table 3

A comparison of the present catalyst with the other catalysts.



entry	Rh catalyst	Rh (mol%)	solvent	temp/°C	time/h	yield (%)	Ref.
1	[Rh(COD)Cl] ₂ + TPPDS	2.0	H ₂ O	80	15	77	[31]
2	RhCl ₃	3.0	toluene/H ₂ O (3/1)	100	20	83	[32]
3	$RhCl_3 + PPh_3$	3.0	toluene/H ₂ O (3/1)	120	5	85	[6]
4	SiO ₂ -Rh ⁽⁰⁾	1.1	toluene/H ₂ O (5/1)	100	10	82	[12]
5	LDH-Rh(0) + SDS	2.0	toluene/H ₂ O (5/1)	100	12	85	[13]
6	Rh(I)-PPh ₂ -PMO(Ph)	1.5	H ₂ O	100	5	78	[9]
7	Rh-PPh2-MCM-41@SiO2@Fe3O4	1.0	H ₂ O	100	22	97	[10]
8	Fe ₃ O ₄ @SiO ₂ @S-PPh ₂ -Rh	0.9	EtOH/H ₂ O (1/2)	100	12	90	[11]

A comparison of the present catalyst with others reported in the literature and the results are summarized in Table 3. Although various Rh catalysts have been developed to achieve the oxidative coupling reaction of alkenes with arylboronic acids, most reactions were performed in the presence of organic co-solvents such as toluene and ethanol (entries 2–5 and 8). In the case of the reaction in water, phosphine ligands were used to achieve the excellent catalytic performance (entries 1, 6, and 7). In contrast, neither the co-solvent nor the phosphine ligand was needed in our catalytic system.

4. Conclusion

It was confirmed that linear polystyrene acted as a stabilizer of RhNPs and that Rh^(III)NPs formed after heating an aqueous solution of RhCl₃ in the presence of 4-methylphenylboronic acid. PS-Rh^(III)NPs exhibited good catalytic activity for the oxidative coupling of arylboronic acids with alkenes, whereas no reaction was confirmed with PS-Rh⁽⁰⁾NPs as the catalyst. The catalyst could not be reused because the amount of Rh decreased by leaching during the reaction and the leached Rh species had little catalytic activity for the oxidative coupling. Currently, further efforts to reactivate the leached Rh species are under-way in our laboratory.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.jorganchem.2018.07.037.

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