

A strategy to facilitate reuse of palladium catalyst stabilized by block copolymer micelles

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Received 15 May 2007; received in revised form 4 July 2007; accepted 6 July 2007
Available online 19 July 2007

Abstract

A strategy to facilitate reuse of palladium catalyst stabilized by block copolymer micelles is proposed. Following this strategy, the polystyrene-*b*-poly(4-vinyl pyridine) micelles were firstly anchored on the surface of polystyrene-*co*-poly(methyl acrylic acid) core-shell microspheres to form raspberry-like colloid. Then the raspberry-like colloid was used as scaffold to support colloidal palladium catalyst. The resultant raspberry-like colloid supported palladium catalyst, which showed similar activity to the catalyst stabilized by block copolymer micelles and much improved recoverability, was demonstrated to be a good alternative for Suzuki reaction either performed in water or in DMF/water.

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Keywords: Block copolymers; Microspheres; Micelles; Palladium; Raspberry-like colloid; Suzuki reaction

1. Introduction

Highly efficient and easily reusable catalyst combining the advantages of both homogeneous and heterogeneous catalysts has been one of the most important topics in scientific literatures, which strongly stimulates the development of new catalysts [1–4]. Therein, the catalyst of noble metal nanoparticles stabilized by amphiphilic block copolymer micelles is expected to be promising [5]. Up to date, monometallic catalysts and bimetallic catalysts such as Pd catalyst stabilized by micelles of polystyrene-*co*-poly(ethylene oxide) [6], poly(ethylene oxide)-*b*-poly(2-vinylpyridine) [7,8], polystyrene-*b*-poly(4-vinylpyridine) (PS-*b*-P4VP) [5,9], polyisoprene-*b*-poly(2-cinnamoyloxyethyl methacrylate)-*b*-poly(*tert*-butyl acrylate) [10] and Au catalyst stabilized by micelles of polystyrene-*b*-poly(2-vinylpyridine) [11], and bimetallic Au/Pd catalyst stabilized by micelles of PS-*b*-P4VP [9,12], have been studied. The advantages of the catalysts stabilized by

block copolymer micelles include high activity similar to that of the homogeneous system, absence of toxic and expensive phosphine ligands. However, compared with traditional heterogeneous catalysts, which can be easily separated and reused by simple filtration [13], the separation of the catalyst stabilized by block copolymer micelles is much more difficult, since the block copolymer micelles keep suspending in solvent and their size is usually smaller than 100 nm [5–12]. To fulfill reuse of the catalysts stabilized by block copolymer micelles, they are usually deposited on porous Al₂O₃ and used as hydrogenation catalysts [14–16]. However, this method sacrifices part of the catalytic efficiency since the porous Al₂O₃ cannot be dispersed in solution.

Recently, we have found that PS-*b*-P4VP micelles can be anchored onto the core-shell microspheres of polystyrene-*co*-poly(methyl acrylic acid) (PS-*co*-PMAA) to form raspberry-like colloid containing the secondary structure of micelles [17]. Herein, raspberry-like colloid supported Pd catalyst is synthesized following the strategy as shown in Fig. 1 and the catalysis in Suzuki reaction [18,19] is studied. It is found that the raspberry-like colloid supported catalyst has two superiorities in high efficiency and convenient reuse.

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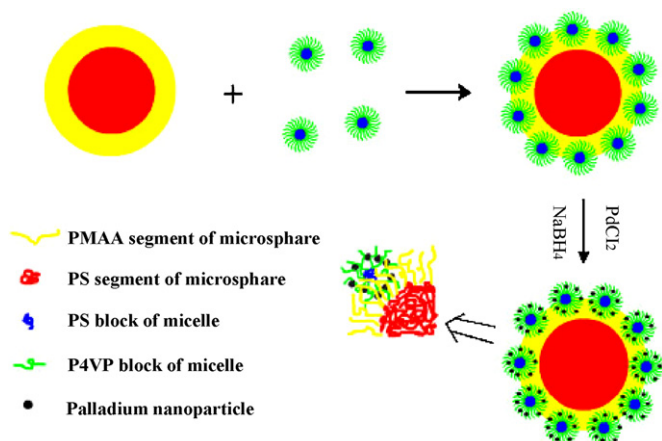


Fig. 1. Synthesis of the raspberry-like colloid supported Pd catalyst.

2. Experimental

2.1. Materials

The polystyrene-*b*-poly(4-vinyl pyridine) (PS-*b*-P4VP) micelles and the polystyrene-*co*-poly(methyl acrylic acid) (PS-*co*-PMAA) core-shell microspheres were prepared according to Ref. [17]. PdCl₂·2H₂O (>99.99%), NaBH₄ (>98.9%), *p*-bromobenzene (>99%), *p*-bromoanisole (>99%), *p*-bromophenol (>99%), and *p*-chloronitrobenzene (>99%) were purchased from Tianjin Chemical Company and used as received. Other reagents such as benzenboronic acid (>99%, Beijing Wisdom Chemicals Company), iodobenzene (>98%, Alfa Aesar), *p*-bromoacetophenone (>99%, Alfa Aesar), and *p*-chloroacetophenone (>99%, Merck-Schuchardt) were used as received.

2.2. Preparation of the palladium catalyst stabilized by block copolymer micelles (catalyst 1)

The PS-*b*-P4VP micelle solution with the block copolymer concentration at 11.0 mg/mL was firstly prepared according to Ref. [20]. Subsequently, a given volume of 10.0 mmol/L PdCl₂ aqueous solution was added into the micelle solution with vigorously stirring and then kept at room temperature overnight, wherein the molar ratio of the chelating pyridine group in the block copolymer to Pd²⁺ was 6:1. Then, 20-fold excess of 0.40 mol/L NaBH₄ aqueous solution was added. The solution was dialyzed against the mixture of DMF and water (1:1 by volume) for 4 days to remove the residual NaBH₄. Finally, the resultant dispersion of the palladium catalyst stabilized by block copolymer micelles (catalyst 1) was diluted to make the Pd catalyst at 2.30 mmol/mL.

2.3. Preparation of the raspberry-like colloid supported palladium catalyst (catalyst 2)

The raspberry-like colloid containing the secondary structure of micelles was firstly prepared by adding the dispersion of the PS-*co*-PMAA core-shell microspheres into the PS-*b*-

P4VP micelle solution according to Ref. [17]. Then the resultant raspberry-like colloid was used as scaffold to prepare the raspberry-like colloid supported palladium catalyst (catalyst 2) with the similar method to the synthesis of catalyst 1 and the Pd content in the dispersion of catalyst 2, which was 2.30 mmol/mL, was equal to that of catalyst 1.

2.4. Transmission electron microscope (TEM) measurement

TEM measurement was conducted by using a Philips T20ST electron microscopy at an acceleration voltage of 200 kV, whereby a small drop of the sample was deposited onto a carbon-coated copper grid and dried at room temperature under atmospheric pressure.

2.5. Typical procedures for Suzuki reaction

To a screw-capped vial with a side tube, 2.0 mmol of aryl halide, 6.0 mmol of K₂CO₃, 3.0 mmol (50% excess) of benzenboronic acid and 9.0 mL of dispersion containing 0.20 mol% catalyst 1 or catalyst 2 were added. The mixture was degassed under nitrogen purge for 10 min at room temperature and then the vial was placed in a preheated oil bath at a given temperature and magnetically stirred under nitrogen. After the reaction was completed, the screw-capped vial was firstly cooled by immersing in water at room temperature and then 4-fold excess volume of diethyl ether was added to extract the organic compound for 3 times. The precipitate of the palladium catalyst was separated by filtration. The collected organic phase was washed with water and concentrated. Lastly, the resultant product was dried under vacuum at 40 °C, weighted and analyzed by ¹H NMR.

2.6. Recovery and reuse of the catalyst

The precipitated catalyst was reused in another run, with proportional amounts of reactants and solvent of DMF/water or water added to keep the same solvent-catalyst ratios and the same concentration as demonstrated above.

3. Results and discussion

The PS-*b*-P4VP core-corona micelles (40 nm, Fig. 2A) are used as scaffold to stabilize Pd nanoparticles since the corona-forming block of P4VP is a coordination polymer [5,9]. The palladium catalyst stabilized by PS-*b*-P4VP micelles (catalyst 1, Fig. 2B) is synthesized by being adding PdCl₂ aqueous solution into the PS-*b*-P4VP micelle solution and then being reduced by NaBH₄. As shown in Fig. 2B, the micelles stick to each other since Pd²⁺ can be coordinated with multi-pyridine rings in the intra- or inter-micelles just as a cross-linker. The raspberry-like colloid containing the secondary structure of micelles (Fig. 2C) is synthesized according to Ref. [17]. The driven force to anchor the micelles onto the core-shell microspheres is ascribed to the affinity between the PMAA segment and P4VP block. The raspberry-like colloid supported palladium catalyst (catalyst 2, Fig. 2D) is synthesized similar to catalyst 1 and the size of the resultant Pd nanoparticles (3 nm) immobilized in the matrix

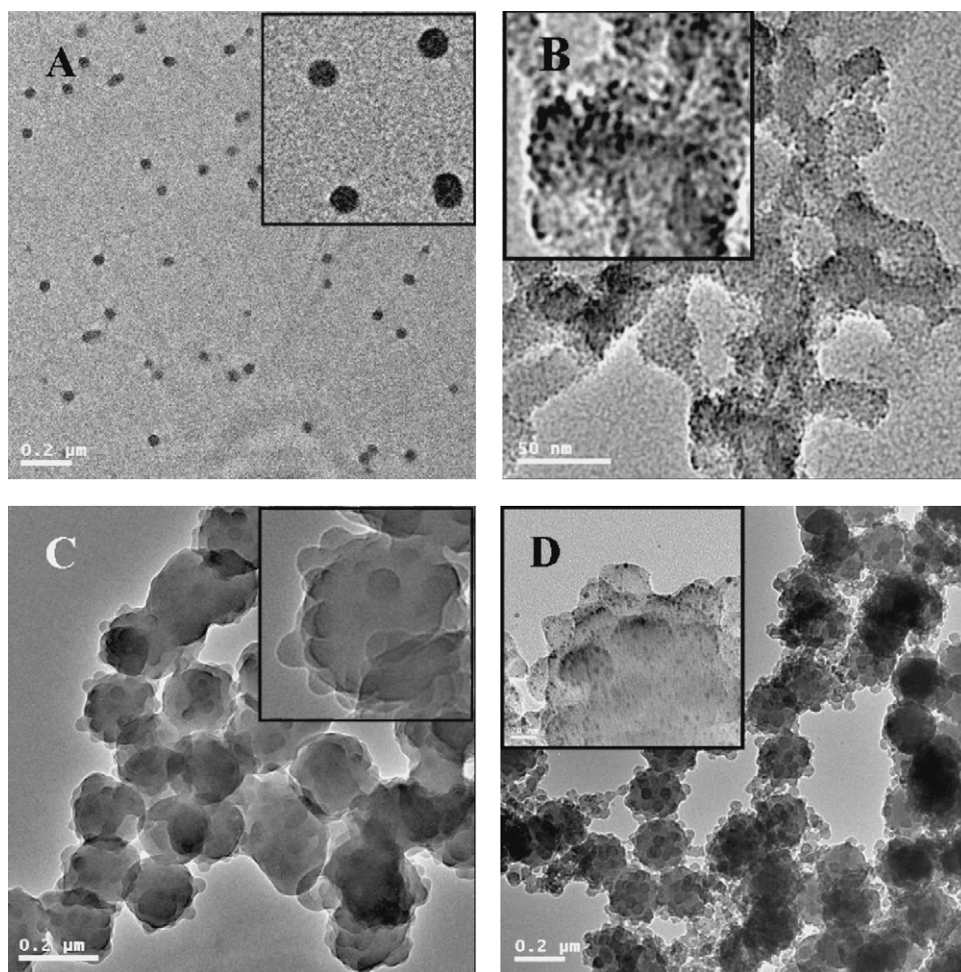


Fig. 2. The TEM images of micelles (A), Pd catalyst stabilized with micelle (B), raspberry-like colloids (C), and raspberry-like colloid supported Pd catalyst (D).

of catalyst 2 is almost equal to that of catalyst 1. The PS-*b*-P4VP micelles and the raspberry-like colloid exist as colloidal dispersion in DMF/water. Whereas, when Pd nanoparticles are immobilized, the resultant catalysts 1 and 2 exist as fine floccule-like aggregates, which can be dispersed in water or DMF/water when the solution is slightly stirred.

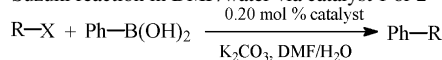
The Suzuki reaction via catalyst 1 or 2 was firstly performed in DMF/water (1:1 by volume). To cover a wide range, the Suzuki coupling reactions of benzenboronic acid with iodobenzene, brominated and chlorinated aromatic compounds are tested. The catalysis results are summarized in Table 1. For the substrate of iodobenzene, catalyst 2 affords 99% yield of biphenyl (entry 1). Whereas, catalyst 1 just affords 90% yield at the same reaction conditions. For the electron-deficient and therefore reactive aryl bromide of *p*-bromoacetophenone, both catalysts 2 and 1 are efficient and the Suzuki coupling with benzenboronic acid is quantitative (entry 2). For the non-activated *p*-bromobenzene (entry 3) and the electron-rich aryl bromides of *p*-bromophenol (entry 4) and *p*-bromoanisole (entry 5), catalysts 2 and 1 afford satisfactory yield of biphenyl, *p*-hydroxybiphenyl and *p*-methoxybiphenyl, respectively. For the aryl chloride, neither catalyst 2 nor 1 is efficient for the Suzuki coupling with benzenboronic acid. Even for the electron-deficient acryl chloride of *p*-chloroacetophenone, the coupling is also unsatisfactory


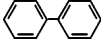
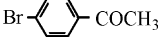
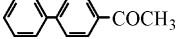

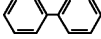
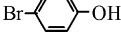
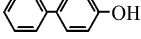
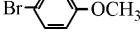
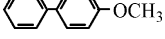
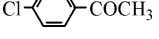
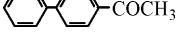
and the yield of *p*-acetylbiphenyl is only 70% (entry 6). These results demonstrate that catalyst 2 is as efficient as catalyst 1 when the Suzuki reaction is performed in DMF/water.

Suzuki reaction via catalyst 2 was also performed in water. Compared with the conditions as shown in Table 1, the Suzuki reactions were performed at a lower temperature with a longer time due to the limit of the lower boiling temperature of water. The catalysis results are summarized in Table 2. For the reactive iodobenzene, *p*-bromoacetophenone and the non-activated *p*-bromobenzene (entries 1–3), the catalysis in water is almost as efficient as those in DMF/water. Whereas for the electron-rich aryl bromide of *p*-bromoanisole, the yield of *p*-methoxybiphenyl is much lower (62%, entry 4). Interestingly, the hydrophilic electron-rich aryl bromide of *p*-bromophenol, which is as active as *p*-bromoanisole when the Suzuki reaction is performed in DMF/water, shows to be much more active and its coupling with benzenboronic acid in water is almost quantitative (entry 5). For the electron-deficient acryl chloride of *p*-chloroacetophenone, the Suzuki reaction performed in water is very inefficient and the yield of *p*-acetylbiphenyl is only 4% (entry 6). These results demonstrate that catalyst 2 is a suitable catalyst for the substrate of iodobenzene or aryl bromides, especially for the hydrophilic aryl bromides and the catalysis in water is almost as efficient as those in DMF/water.

Table 1

Suzuki reaction in DMF/water via catalyst 1 or 2



Entry	R-X	T (°C) ^a	Product	Yield (%) ^b	
				Catalyst 2	Catalyst 1
1		80		>99	90
2		120		>99 ^c	>99 ^c
3		120		98	98
4		120		>99	97
5		120		>99	>99
6		150		71 ^d	70 ^d

Reaction conditions: aryl halide (2.0 mmol) and benzenboronic acid (3.0 mmol, 1.5 eq.), K₂CO₃ (6.0 mmol, 3 eq.), 9.0 mL of colloidal dispersion in DMF/water containing 0.20 mol% Pd catalyst, reaction time 6 h except specially pointed out.

^a Oil bath temperature.

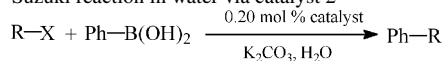
^b Isolated yield and the purity of the product was confirmed by ¹H NMR.


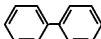
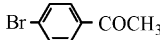
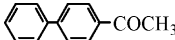

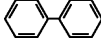
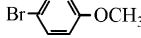
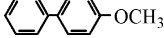

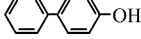
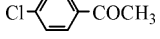
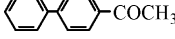
^c Reaction time was 4 h.

^d Reaction time was 10 h.

Table 2

Suzuki reaction in water via catalyst 2



Entry	R-X	T (°C)	t (h)	Product	Yield (%) ^a
1		80	8		>99
2		90	4		>99
3		90	10		92
4		90	10		62
5		90	10		>99
6		90	20		4

Reaction conditions: aryl halide (2.0 mmol) and benzenboronic acid (3.0 mmol, 1.5 eq.), K₂CO₃ (6.0 mmol, 3 eq.), 9.0 mL of colloidal dispersion in water containing 0.20 mol% catalyst 2.

^a Isolated yield and the purity of the product was confirmed by ¹H NMR.

The reuse of catalysts 1 and 2 in the Suzuki reaction of *p*-bromoacetophenone with benzenboronic acid in water is further studied and the results are summarized in Table 3. Compared with catalyst 1, the separation and reuse of catalyst 2 is much more convenient partly to the larger size of the raspberry-like colloid. Thus, as shown in Table 3, the reuse of catalyst 2 is highly improved with the recycling procedure demonstrated in Section 2. Atomic absorption spectrometer (AAS, Hitachi 180–80) analysis of Pd catalyst in the water phase in the first recycling suggests that 77% Pd for catalyst 1 and 92% Pd for catalyst 2 is preserved in the water phase. This suggests that the cross-linking or complexation between the P4VP block and the PMAA segment in catalyst 2 decelerates leaching of the Pd catalyst. These

Table 3

Recycling of catalysts 1 and 2, respectively

Yield ^a	Fresh use	1st reuse	2nd reuse	3rd reuse	4th reuse	5th reuse
Catalyst 1	>99	67	60	49	28	16
Catalyst 2	>99	89	81	66	63	69

Reaction conditions: *p*-bromoacetophenone (2.0 mmol) and benzenboronic acid (3.0 mmol, 1.5 eq.), K₂CO₃ (6.0 mmol, 3 eq.), 9.0 mL of dispersion initially containing 0.20 mol% Pd catalyst in fresh use, reaction temperature at 90 °C, reaction time being 4 h.

^a Isolated yield and the purity of the product was confirmed by ¹H NMR.

results demonstrate that anchoring the micelle supported Pd catalyst onto the PS-co-PMAA core-shell microspheres is a good alternative to keep its efficiency and enhance its durability.

In summary, we provide a strategy to facilitate reuse of palladium catalyst stabilized by block copolymer micelles firstly by being anchored the micelles on the surface of core-shell microspheres and following by being using the resultant raspberry-like colloid as scaffold of Pd catalyst. The resultant raspberry-like colloid supported Pd catalyst, which shows similar activity to the palladium catalyst stabilized by block copolymer micelles and much improved recoverability, is demonstrated to be a good alternative for Suzuki reaction either performed in water or in DMF/water. We anticipate the proposed strategy is helpful to improve the potential application of catalyst stabilized with block copolymer micelle in chemical synthesis.

Acknowledgements

The financial support by National Science Foundation of China (No 20504016) and the Program for New Century Excellent Talents in University was acknowledged.

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