2144 *Chem. Mater.* **2008,** *20,* 2144–2150

Synthesis of Noble Metal Nanoparticles Embedded in the Shell Layer of Core−Shell Poly(styrene-*co*-4-vinylpyridine) Micospheres and Their Application in Catalysis

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Received November 28, 2007. Revised Manuscript Received January 14, 2008

The noble metal nanoparticles of Pd, Au, and Ag embedded in the shell layer of core−shell poly(styrene-*co*-4-vinylpyridine) micospheres were synthesized, and the catalytic activity of the shell-embedded Pd nanoparticles was investigated. To increase the accessible active site and therefore increase the catalytic activity of noble metal nanoparticles, the in situ synthesized noble metal nanoparticles are selectively immobilized in the outer shell layer of the core−shell poly(styrene-*co*-4-vinylpyridine) microspheres, which are synthesized by one-stage soap-free emulsion polymerization in water and contain a core of polystyrene and a coordinative shell of poly(4-vinylpyridine). It is found the Pd nanoparticles embedded in the shell layer of the core−shell micospheres are an efficient and easily reusable catalyst for Suzuki reactions performed in water.

Introduction

The well-defined noble metal nanoparticles have a characteristic high surface to-volume ratio and consequently large fraction of metal atoms that are exposed to reactant molecules, which makes them a promising catalyst in chemical synthesis.[1–5] However, the direct application of noble metal nanoparticles in catalysis is often difficult as a result of their ultrasmall size and high tendency toward agglomeration because of van der Waals forces.[6] Consequently, various methods have been developed to synthesize noble metal nanoparticles in the presence of various stabilizers such as surfactants,[7,8] dendrimers,[9] functioned polymers,[10] polymeric gel,[11] nano- or microspheres,[12] and polymeric micelles[13] through cation complexation followed by gentle reduction. The catalyst of noble metal nanoparticles stabilized by polymeric microspheres has advantages including: (1) it can be easily isolated by precipitation, ultracentrifugation, or ultrafiltration and then recycled; (2) the high dispersion of the polymeric microspheres in the reaction medium allows the reactant molecules to easily access to the active site of noble metal nanoparticles, therefore accelerating the chemical conversion. Up to now, various polymeric microspheres have been synthesized and used to immobilize noble metal nanoparticles. For examples, Thompson and co-workers used non-cross-linked carboxylic acid- and amino-functionalized polystyrene microspheres to load Pt, Pd, and Au nanoparticles, and they found that the noble metal nanoparticles were bound very strongly to the surface of the microspheres and could not be removed by either extensive stirring or sonication.[14] Akashi et al. synthesized Pd nanoparticles using the microspheres of poly(*N*-isopropylacrylamide)-*co*-polystyrene as scaffold and then studied their catalytic properties in hydrogenation.[15] Kumachev et al. used poly(*N*-isopropylacrylamide-acrylic acid-2-hydroxyethyl acrylate) microgel

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10.1021/cm703378c CCC: $40.75

particles as template to prepare various noble metal nanoparticles and deemed that they were a promising catalyst.[16]

Generally, immobilization of noble metal nanoparticles on a solid support can facilitate the separation process but may simultaneously lead to a decrease in activity, most probably as a result of the restriction of the geometry of noble metal nanoparticles or leaching of the active species.[17] Therefore, it is necessary to develop a suitable scaffold to immobilize these noble metal nanoparticles without destroying their activity. To solve this problem, the general method is to load noble metal nanoparticles onto the surface of the catalyst scaffold instead of incorporation of them into the polymer matrix, which increases the amount of accessible active site of noble metal nanoparticles and therefore increases the activity of the catalyst. Besides, immobilization of noble metal nanoparticles on a porous or thin film scaffold is also helpful to increase the accessible site of the catalyst.[18] Clearly, these strategies increase the potential of catalyst leaching, although they facilitate access of the reactants to noble metal nanoparticles. Herein, we propose a compromise strategy to load noble metal nanoparticles into the outer shell layer of core−shell microspheres. This selective immobilization of noble metal nanoparticles in the shell layer makes the noble metal nanoparticles easily accessible, and meanwhile the shell layer prevents leaching of the active species by steric repulsion. Furthermore, the catalyst of noble metal nanoparticles embedded into the outer shell layer of core−shell microspheres has the general advantage of a heterogeneous catalyst to be easily recycled as a result of the relatively large size of the core−shell microspheres. Recently, we proposed a strategy of one-stage soap-free emulsion polymerization to easily synthesize various core−shell microspheres,[19] which makes the present strategy a promising alternative.

The palladium-catalyzed cross-coupling of aryl halide with arylboronic acid, the Suzuki reaction,[20] represents a straightforward and highly effective method for carbon−carbon bond formation in synthesis of biaryl compounds. The general conditions for performing Suzuki reaction include the use of a palladium catalyst and a base such as K_3PO_4, K_2CO_3, KOH, triethylamine, and so forth.[21] In the present study, the core−shell microspheres of poly(styrene-*co*-4-vinylpyridine) (PS-*co*-P4VP), which contain a PS core and a coordinative shell of P4VP, were first synthesized by one-stage soap-free emulsion polymerization, and then the resultant core−shell microspheres were used as scaffold to prepare shell-embedded noble metal nanoparticles, and last the catalyst of Pd nanoparticles embedded in the shell layer of the core−shell PS-*co*-P4VP micospheres (PS-*co*-P4VP-Pd) was evaluated using Suzuki reaction as the model reaction. The catalysis demonstrates that the PS-*co*-P4VP-Pd catalyst has advantages including: (1) high efficiency possibly because of the easily accessible Pd nanoparticles immobilized in the outer shell of core−shell microspheres; (2) low or nonleachability; and (3) ease of catalyst recovery and reuse at least six times without loss of catalytic activity.

Experimental Section

Materials. The monomers of styrene (>98%, Tianjin Chemical Company) and 4-vinylpyridine (4VP, >95%, Aldrich) were distilled under vacuum before being used. $PdCl_2$ (>99.99%, Alfa Aesar) and triethylamine (NEt_3, >99%, Tianjin Chemical Company) were used as received. Benzeneboronic acid (>99%, Beijing Wisdom Chemicals Co., Ltd.), 4-bromophenol (>99%, Tianjin Guangfu Fine Chemical Research Institute), 4-bromoacetophenone (>99%, Alfa Aesar), iodobenzene (>98%, Alfa Aesar), 4-iodophenol (>99%, Shanghai Haiqu Chemical Co., Ltd.), 4-iodobenzoic acid (>99%, Shanghai Bangcheng Chemical Co., Ltd.), 4-iodobenzaldehyde (>99%, Shanghai Bangcheng Chemical Co., Ltd.), 4-iodoanisole (>99%, Shanghai Bangcheng Chemical Co., Ltd.), 4-bromobenzoic acid (>99%, Beijing Henye Fine chemical Co., LTD), 3-bromotoluene (>95%, Shanghai Chemical Reagent Company), 4-chlorobenzoic acid (>99%, Tianjin Chemical Company), 4-chloroacetophenone (>98%, Merck Chemicals Ltd.), 4-nitrochlorobenzene (>95%, China Chemical Company), and 4-bromoanisole (>99%, Tianjin Chemical Company) were used as received. Double-distilled water was employed in the present experiments. Other reagents were analytical reagents and used as received.

Synthesis of Core−Shell PS-*co*-P4VP Microspheres. The core−shell PS-*co*-P4VP microspheres were synthesized by one-stage soap-free emulsion polymerization as described in our recent manuscript.[19] The typical synthesis procedure was introduced as follows. To a flask, 80 mmol of 4VP and 360 mL of water were added at room temperature. Then 160 mmol of styrene was added to the homogeneous aqueous solution of 4VP. The mixture was vigorously stirred at about 300 rpm for about 30 min at room temperature, and then 1.30 g of $K_2S_2O_8$ initiator was added into the mixture. The pH of the dispersion was adjusted to 7 with 0.1 mol/L HCl aqueous solution. Finally, the mixture was degassed under nitrogen purge, and then polymerization was performed with vigorously stirring at 80 °C for 24 h under nitrogen atmosphere. Lastly, the resultant colloidal dispersion was first precipitated in excessive volume of 0.1 mol/L NaOH aqueous solution, and then the precipitate was washed with neutral water and dried under vacuum at 50 °C.

Synthesis of Pd Nanoparticles Embedded in the Shell Layer of Core−Shell PS-*co*-P4VP Microspheres (PS-*co*-P4VP-Pd) in Water. First, a given volume of 5.0 mmol/L $PdCl_2$ aqueous solution was added into the colloidal dispersion of the core−shell PS-*co*-P4VP microspheres, where the molar ratio of 4VP to $PdCl_2$ was 6/1. The mixture was kept overnight at room temperature, and then a 10-fold excess volume of 0.40 mol/L $NaBH_4$ aqueous solution was added dropwise with vigorously stirring. The mixture turned

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immediately into brown and was kept at room temperature with vigorously stirring for 4 h. The resultant colloidal dispersion was purified by dialyzing against water at room temperature for 4 days. Lastly, the dispersion of the PS-*co*-P4VP-Pd catalyst was held in a volumetric flask, where the Pd concentration was calculated to be 2.50 mmol/L.

Synthesis of Au and Ag Nanoparticles Embedded in the Shell Layer of Core–Shell PS-*co*-P4VP Microspheres (PS-*co*-P4VP-Au and PS-*co*-P4VP-Ag) in Water. The noble metal nanoparticles of PS-*co*-P4VP-Au or PS-*co*-P4VP-Ag were prepared by reduction of $HAuCl_4$ or $AgNO_3$ with $NaBH_4$ aqueous solution in the colloidal dispersion of the core–shell PS-*co*-P4VP microspheres with a method similar to that of the PS-*co*-P4VP-Pd catalyst as described above. The molar ratio of P4VP/$HAuCl_4$ or P4VP/$AgNO_3$ was also kept at 6.

Typical Procedures for Suzuki Reaction. To a screw-capped vial with a side tube, 1.0 mmol of aryl halide, 2.0 mmol of benzenboronic acid, 3.0 mmol of base, 1.0 mL of colloid dispersion of the PS-*co*-P4VP-Pd catalyst (containing 0.25 mol % Pd catalyst to the aryl halide), and 3.5 mL of double-distilled water were added. The mixture was degassed under nitrogen purge for 10 min at room temperature, and then the vial content was placed in a preheated oil bath at a given temperature and magnetically stirred under nitrogen. After the reaction was completed, the product was extracted from the reaction mixture with diethyl ether (3 × 30 mL), and then the organic phase was collected, washed with water, and concentrated. The resultant product was dried under vacuum at 40 °C, weighed, and analyzed by ^1H NMR. The catalyst of PS-*co*-P4VP-Pd remaining in the water phase was collected by filtration.

Reuse of the PS-*co*-P4VP-Pd Catalyst. The collected catalyst of PS-*co*-P4VP-Pd was reused in another run of the Suzuki reaction of 4-bromoacetophenone with benzenboronic acid, with the same amounts of reactants and solvent being added as those in the fresh run.

Characterization. Transmission electron microscopy (TEM) measurement was conducted by using a Philips T20ST electron microscope at an acceleration voltage of 200 kV, whereby a small drop of the colloidal dispersion was deposited onto a piece of copper EM grid and dried at room temperature under atmospheric pressure. Powder X-ray diffraction (XRD) measurement was performed on a Rigaku D/max 2500 X-ray diffractometer, where the powder sample was prepared by freeze drying of the colloidal dispersion. The XRD patterns were recorded by using Cu Kα irradiation ($\lambda = 1.54178$ Å). The ^1H NMR measurement was carried out on a UNITY PLUS-400 NMR spectrometer, where $DCCl_3$ or dimethyl sulfoxide-d_6 (DMSO) was used as solvent. Atomic absorption spectrum (AAS) analysis was performed on a Solaar AAS 2 atomic absorption spectrometer.

Results and Discussion

The core–shell PS-*co*-P4VP microspheres are synthesized by one-stage soap-free emulsion polymerization in water using $K_2S_2O_8$ as initiator as described elsewhere.[19] The polymerization runs steadily, and the mixture becomes a little milky just after 20 min, which indicates formation of microspheres. The total conversion of the two monomers, which is defined by the weight ratio of the dried powder of the core–shell PS-*co*-P4VP microspheres to the sum weight of the two monomers, in 24 h is about 96%. Figure 1 shows the TEM image of the core–shell PS-*co*-P4VP microspheres. Clearly, the core–shell structure of the microspheres can be clearly distinguished, which is indicated with arrows in the inset TEM image. The core–shell PS-*co*-P4VP microspheres contain a PS core and a P4VP shell.[19] The size of the core–shell microspheres is narrowly dispersed. The average diameter of the core–shell PS-*co*-P4VP microspheres, the PS core diameter, and the P4VP shell thickness are 458, 272, and 93 nm, respectively.

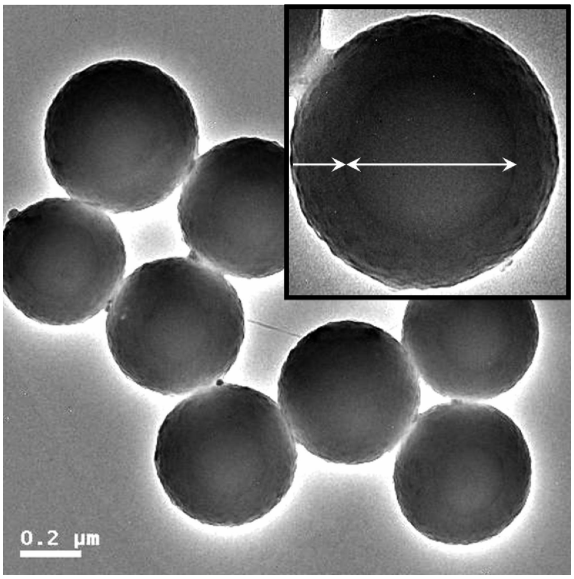


Figure 1. TEM image of the core–shell PS-*co*-P4VP microspheres.

It is known that P4VP is a typical coordinative polymer, which contains tethered ligands of the pyridine group and can coordinate with various transition metal ions such as Au^{3+}, Ag^+, Cu^{2+}, and Pd^{2+}.[13] The convenient synthesis of the core–shell microspheres containing a P4VP shell provides the potentially extensive application of the microspheres as a catalyst scaffold. Actually, the catalyst of Pd nanoparticles was easily synthesized by reduction of Pd^{2+} with $NaBH_4$ aqueous solution in the colloidal dispersion of the core–shell PS-*co*-P4VP microspheres. As shown in Figure 2A, the synthesized Pd nanoparticles are uniformly embedded in the P4VP shell layer of the core–shell microspheres. Figure 2B shows the Pd nanoparticle size distribution in the resultant PS-*co*-P4VP-Pd catalyst. Analysis of more than 100 Pd nanoparticles indicates that the average size of the Pd nanoparticles is 4.4 nm and the deviation is 1.5 nm. Herein, it should be pointed out, the molar ratio of 4VP/Pd^{2+} is set at 6/1 to ensure full coordination of the P4VP segment with all Pd^{2+} ions. At this condition, almost all the resultant Pd nanoparticles are embedded in the shell layer of the core–shell PS-*co*-P4VP microspheres, and no free Pd aggregates are found by TEM observation. Furthermore, the present catalyst of PS-*co*-P4VP-Pd is very stable. No Pd black can be optically observed, and TEM observation also shows that no conglomeration of the Pd nanoparticles occurs in 6 months in the PS-*co*-P4VP-Pd dispersion. Furthermore, when the ratio of 4VP/Pd^{2+} decreases to 1/1, no black Pd is optically observed during the synthesis and purification of the PS-*co*-P4VP-Pd catalyst, which suggests that the core–shell PS-*co*-P4VP microspheres are suitable scaffold for Pd nanoparticles.

The XRD patterns of the PS-*co*-P4VP-Pd catalyst are shown in Figure 3. Three peaks at 2θ of 39.4°, 44.8°, and 65.8° (curve a) corresponding to the diffraction of the (111),

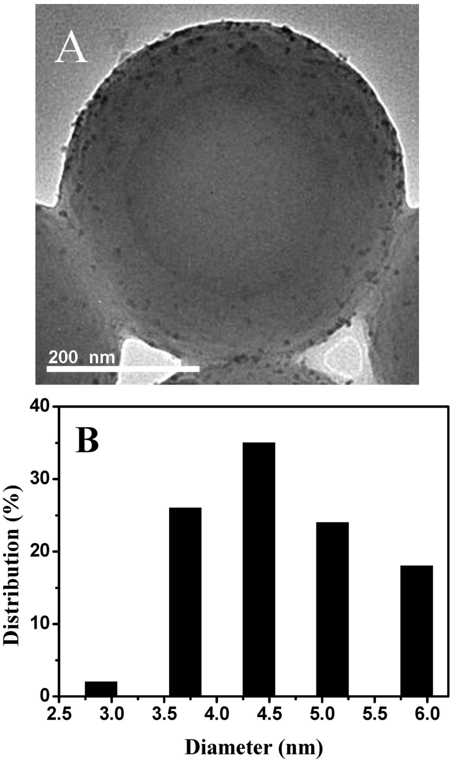


Figure 2. TEM images of the PS-*co*-P4VP-Pd catalyst (A) and the size distribution of Pd nanoparticles in the PS-*co*-P4VP-Pd catalyst (B).

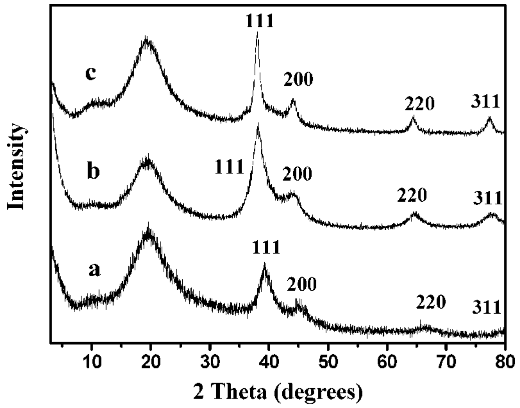
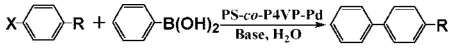
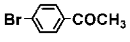
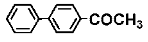
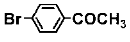
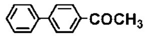
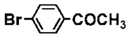
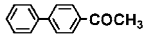
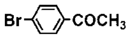
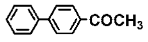
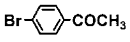
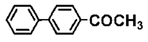
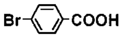
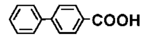
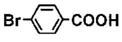
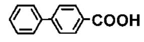


Figure 3. XRD patterns of the catalysts of PS-*co*-P4VP-Pd (a), PS-*co*-P4VP-Au (b), and PS-*co*-P4VP-Ag (c), respectively.

Table 1. Study of the Reaction Conditions in the Suzuki Reaction Performed in Water via the PS-*co*-P4VP-Pd Catalyst[a]



Entry	R-X	Base	T (°C)	Time (h)	Biaryl	Yield (%)[b]
1		NaOH	90	6		12
2		K_2CO_3	90	6		68
3		NEt_3	90	4		99
4		NEt_3	50	4		16
5		NEt_3	25	4		6
6		K_2CO_3	90	2		99
7		NEt_3	90	6		68

[a] General conditions: aryl halide (1.0 mmol), benzenboronic acid (1.5 mmol, 1.5 equiv), base (3.0 mmol, 3 equiv), 4.5 mL of dispersion containing 0.25 mol % Pd catalyst. [b] Isolated yield and the purity of isolated product being confirmed by ^{1}H NMR.

(200), and (220) lattice planes of Pd crystals can be clearly seen. The results reveal that Pd crystals are cubic phase with cell constants of $a = 0.3974$ nm. In terms of the Scherrer equation[22] utilizing the diffraction peak of the (111) lattice plane, the average size of the Pd nanoparticles is calculated to be 3.9 nm, which is almost consistent with those observed by TEM.

The palladium-catalyzed Suzuki cross-coupling reaction of aryl halide with arylboronic acid is an effective synthetic route for biaryls.[20] The Suzuki reaction is usually performed in organic solvent or in the solvent mixture of water and polar organic solvent such as *N*,*N*-dimethylformamide (DMF), which helps with solvation of the organic substrates and the inorganic base,[23] although a few successful examples have been achieved in the sole solvent of water.[24] Herein, Suzuki cross-coupling reaction is adopted as a model reaction to test the catalytic ability and the recycle of the PS-*co*-P4VP-Pd catalyst. Considering that the shell-forming P4VP segment is not fully hydrophobic and it can swell somewhat in water, we perform the Suzuki reaction in the sole solvent of water.

In preliminary catalysis study, the Suzuki reactions of two typical halides, the hydrophobic 4-bromoacetophenone and the hydrophilic 4-bromobenzoic acid, are chosen to optimize the reaction conditions. As shown in Table 1, base has great effect on the yields of the biaryls. Of all the bases tested, NEt_3 affords the highest yield of 4-acetylbiphenyl at 90 °C for the hydrophobic 4-bromoacetophenone (entries 1−3). When the temperature decreases from 90 to 25 °C, the yield dramatically decreases from 99% to 6% (entries 3−5). Whereas for the hydrophilic substrate of 4-bromobenzoic acid, K_2CO_3 is the suitable base for the Suzuki reaction at 90 °C and 99% yield of 4-biphenylcarboxylic acid is achieved in 2 h (entries 6 and 7). In the following study, the Suzuki reactions are performed in water at 90 °C in the presence of 0.25 mol % PS-*co*-P4VP-Pd catalyst and 3 equiv of NEt_3 for hydrophobic substrates or 3 equiv of K_2CO_3 for hydrophilic substrates.

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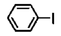
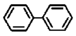
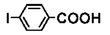
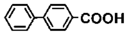
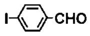
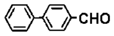
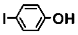
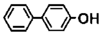
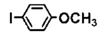
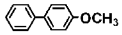
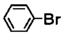
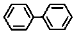
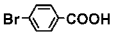
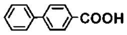
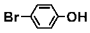
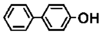
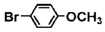
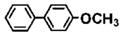
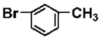
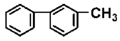
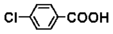
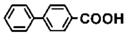
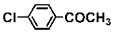
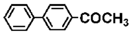
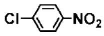
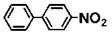
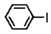
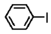
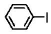
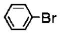
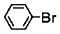
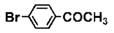
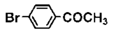
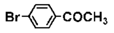
Table 2. Suzuki Reactions of Aryl Halides with Benzeneboronic Acid via the PS-*co*-P4VP-Pd Catalyst in Water[a]

Entry	Aryl halide	Base	Biaryl	Time (h)	Yield (%)[b]
1		NEt_3		3	99
2		K_2CO_3		1/6	99
3		NEt_3		1	99
4		NEt_3		2 10	27 94
5		NEt_3		4	97
6		NEt_3		6	99
7		K_2CO_3		2	99
8		NEt_3		1	6
9		NEt_3		10	90
10		NEt_3		3	94
11		K_2CO_3		24	17
12		NEt_3		24	6
13		NEt_3		24	8

[a] Reaction conditions: aryl halide (1.0 mmol) and benzenboronic acid (1.5 mmol, 1.5 equiv), K_2CO_3 or NEt_3 (3.0 mmol, 3 equiv), 4.5 mL of aqueous dispersion containing 0.25 mol % PS-*co*-P4VP-Pd catalyst, temperature at 90 °C. [b] Isolated yield and the purity of isolated product being confirmed by ^{1}H NMR.

Table 3. Suzuki Reactions of Aryl Halides with Benzeneboronic Acid via Different Pd Catalysts

Entry	Substrate	Pd catalyst (mol%)/reference	Temp/time	Solvent	Yield (%)/ TOF (h^{-1})
1		PS-*co*-P4VP-Pd (0.1)/-	78 °C/5 h	H_2O	51/102
2		Pd/PE-MCM-41 (0.1)/25d	78 °C/5 h	H_2O	93/186
3		Pd-PVP (0.3)/27	~80 °C/12 h	C_2H_5OH/H_2O	95/26
4		PS-*co*-P4VP-Pd (0.25)/-	90 °C/6 h	H_2O	99/66
5		Pd/PE-MCM-41 (1)/25d	90 °C/15 h	H_2O	100/6.6
6		PS-*co*-P4VP-Pd (0.25)/-	90 °C/4 h	H_2O	99/99
7		Pd/cyclodextrin (1)/25b	88 °C/7 h	H_2O/CH_3CN	88/13
8		GnDenP-Pd (0.06)/28	101 °C/20 h	dioxane	99/82

With the optimized conditions in hand, Suzuki reactions of a wide range of substrates such as iodinated, brominated, and chlorinated aromatic compounds are tested. The catalysis results are summarized in Table 2. The experimental results indicate that the catalytic system is active for both the aryl bromides and the aryl iodides except for 4-bromophenol. The yields of the corresponding biaryls are higher than 90% in 1−10 h (entries 1−10). Similar to general Pd nanoparticle catalyst,[24] the PS-*co*-P4VP-Pd catalyst is also unsuitable for the Suzuki reaction of aryl chlorides in the sole solvent of water. Even for the electron-deficient aryl chlorides, the yield of biaryl is unsatisfactory though the reaction time is prolonged to 24 h (entries 11−13). Generally, the activity of aryl halides decreases in the I > Br > Cl order, and the electron-deficient aryl halide is generally more active than the electron-rich one.[25] However, the substrates of 4-bromophenol and 4-iodophenol seem abnormal in activity (entries 4 and 8). It is found that the present PS-*co*-P4VP-Pd catalyst exist as floccule-like suspension in the reaction mixture during the Suzuki reaction, whereas conglomeration of the PS-*co*-P4VP-Pd catalyst occurs when 4-bromophenol or 4-iodophenol is used. Thus, we think the abnormal activity of 4-bromophenol and 4-iodophenol is ascribed to the conglomeration of the PS-*co*-P4VP-Pd catalyst. Summarily, considering that Suzuki reactions are performed in the sole solvent of water, we think the present PS-*co*-P4VP-Pd catalyst is a promising alternative, although the coupling reaction is not as efficient as those performed in organic solvent.[26]

To further evaluate the activity of the PS-*co*-P4VP-Pd catalyst, the PS-*co*-P4VP-Pd catalyst is compared with four kinds of Pd nanoparticles under other similar conditions. The first Pd/PE-MCM-41 catalyst is the Pd nanoparticles supported on pore-expanded mesoporous silica by Sayari et al.[25d] The second Pd-PVP is the Pd nanoparticles stabilized with poly(*N*-vinyl-2-pyrrolidone) (PVP) by Das and El-Sayed.[27] The third Pd/cyclodextrin is the Pd nanoparticles stabilized with surface-attached perthiolated cyclodextrin by Kaifer et al.[25b] The last GnDenP-Pd is the Pd nanoparticles stabilized with phosphine dendrimer by Fan et al.[28] As shown in Table 3, compared with the Pd/PE-MCM-41 and Pd-PVP catalysts, the PS-*co*-P4VP-Pd catalyst is moderately efficient for the Suzuki reaction of iodobenzene, and it gives a middle turnover frequencies (TOF) of 102 h^{-1} (Table 3, entries 1−3). For the Suzuki reactions of electron-neutral bromobenzene and the electron-deficient 4-bromoacetophenone with benzeneboronic acid, the PS-*co*-P4VP-Pd catalyst is the most efficient in all five of the Pd catalysts (Table 3, entries 4−8), and it gives a TOF of 66 h^{-1} for the Suzuki reaction of bromobenzene and a TOF of 99 h^{-1} for the Suzuki reaction of 4-bromoacetophenone, respectively. Considering its easy synthesis, high efficiency, nonleachability, and good durability discussed subsequently, the present PS-*co*-P4VP-Pd catalyst is believed to be a promising alternative.

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(25) (a) Artok, L.; Bulut, H. *Tetrahedron Lett.* **2004**, *45*, 3881. (b) Strimbu, L.; Liu, J.; Kaifer, A. E. *Langmuir* **2003**, *19*, 483. (c) Yamada, Y. M. A.; Takeda, K.; Takahashi, H.; Ikegami, S. *J. Org. Chem.* **2003**, *68*, 7733. (d) Das, D. D.; Sayari, A. *J. Catal.* **2007**, *246*, 60.

(26) (a) Barder, T. E.; Walker, S. D.; Martinelli, J. R.; Buchwald, S. L. *J. Am. Chem. Soc.* **2005**, *127*, 4685. (b) Kirchhoff, J. H.; Dai, C.; Fu, G. C. *Angew. Chem., Int. Ed.* **2002**, *41*, 1945. (c) Navarro, O.; Nolan, S. P. *J. Am. Chem. Soc.* **2003**, *125*, 16194. (d) Baleizao, C.; Corma, A.; Garcia, H.; Leyva, A. *J. Org. Chem.* **2004**, *69*, 439.

(27) Li, Y.; Hong, X. M.; Collard, D. M.; El-Sayed, M. A. *Org. Lett.* **2000**, *2*, 2385.

(28) Wu, L.; Li, B.-L.; Huang, Y.-Y.; Zhou, H.-F.; He, Y.-M.; Fan, Q.-H. *Org. Lett.* **2006**, *8*, 3605.

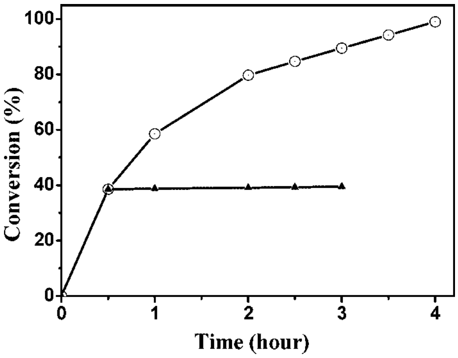

Figure 4. Time conversion plot for the Suzuki reaction of *p*-bromoacetophenone with benzenboronic acid in water at 90 °C in the presence of 0.25 mol % PS-*co*-P4VP-Pd catalyst (○) and after removal of the catalyst by filtration (▲).

When using an immobilized catalyst two points become crucial issues. The first is the catalyst leaching from the solid scaffold into liquid phase, where the leached catalyst will become responsible for a significant extent of the catalytic activity. To explore the possible catalyst leaching, the Suzuki reaction of 4-bromoacetophenone with benzenboronic acid was carried out in water in the presence of 0.25 mol % PS-*co*-P4VP-Pd until the conversion reached 38%, and at that point the catalyst of PS-*co*-P4VP-Pd was filtered off at the reaction temperature.[29] The liquid phase was then allowed to react; however, no further conversion was observed as shown in Figure 4, whereas the conversion gradually increased with time to 100% in 4 h in the presence of 0.25 mol % PS-*co*-P4VP-Pd catalyst. The liquid phase after filtration of the PS-*co*-P4VP-Pd catalyst was analyzed, and no Pd was detected by AAS analysis (detection limit is 0.03 ppm). These indicate that less than 0.1% Pd catalyst is leached into the liquid phase of water. The nature of the active palladium species (homogeneous vs heterogeneous) in C−C coupling reactions has been a matter of much debate.[30] It is generally deemed that the homogeneous Pd species are, at least partially, responsible for such coupling reactions.[30] Meanwhile, some authors[31] have also argued that their catalysts are truly heterogeneous. In the current case, the leaching of Pd species from the PS-*co*-P4VP-Pd catalyst is extremely limited. Nonetheless, based solely on this observation, it is difficult to claim that the reaction occurs in a truly heterogeneous medium, because the mobile active homogeneous species may redeposit onto the scaffold of the PS-*co*-P4VP microspheres support surface during the filtration as a result of an unavoidable minor temperature decrease during the filtration workup.[32] The second point is the reusability of the immobilized catalyst. To test this, a series of six consecutive runs were carried out in water at 90 °C. At the end of the 4-h reaction, the catalyst of PS-*co*-P4VP-Pd was filtered, washed consecutively with water, ethyl ether, and water, and reused for a new batch. As shown in Table 4, the yield of 4-acetylbiphenyl does not decrease at all even after six cycles. Furthermore, analysis of the recycled catalyst by XRD shows that the average size of the Pd nanoparticles, 3.8 nm, is almost as same as those in the fresh catalyst of PS-*co*-P4VP-Pd. These results confirm the good durability of the PS-*co*-P4VP-Pd catalyst.

Table 4. Recycling of the PS-*Co*-P4VP-Pd Catalyst in the Suzuki Coupling of 4-Bromoacetophenone with Benzeneboronic Acid in Water[a]

		cycle				
	fresh	1st	2nd	3rd	4th	5th
yield[b] (%)	99	99	99	99	99	99

[a] Reaction conditions: 4-bromoacetophenone (2.0 mmol) and benzenboronic acid (3.0 mmol, 1.5 equiv), potassium carbonate (6.0 mmol, 3 eqiuv), 9.0 mL of dispersion containing 0.25 mol % PS-*co*-P4VP-Pd catalyst, 90 °C, 4 h. [b] Isolated yield and the purity of isolated product was confirmed by ^{1}H NMR.

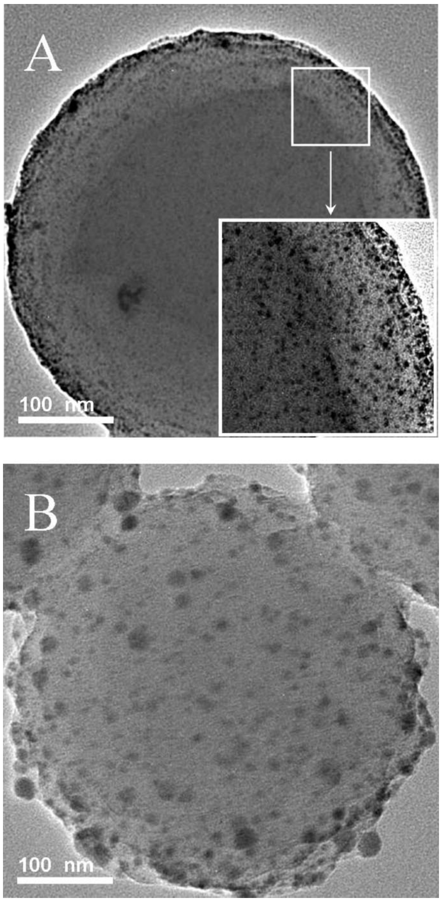

Figure 5. TEM images of PS-*co*-P4VP-Au (A) and PS-*co*-P4VP-Ag (B).

Besides Pd nanoparticles, Au and Ag nanoparticles embedded in the shell layer of the core−shell PS-*co*-P4VP microspheres (PS-*co*-P4VP-Au and PS-*co*-P4VP-Ag) were synthesized. As shown in Figure 5A,B, the in situ synthesized Au and Ag nanoparticles, the average sizes of which are 3.7 and 10.6 nm, are uniformly embedded in the P4VP shell layer of the core−shell PS-*co*-P4VP microspheres and no conglomeration of noble metal nanoparticles is observed. The XRD patterns of PS-*co*-P4VP-Au and PS-*co*-P4VP-Ag are

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(29) Lempers, H. E. B.; Sheldon, R. A. *J. Catal.* **1998**, *175*, 62.

(30) (a) Astruc, D.; Lu, F.; Aranzaes, J. R. *Angew. Chem., Int. Ed.* **2005**, *44*, 7852. (b) Phan, N. T. S.; Sluys, M. V. D.; Jones, C. W. *Adv. Synth. Catal.* **2006**, *348*, 609.

(31) (a) Molnar, A.; Paap, A.; Miklos, K.; Forgo, P. *Chem. Commun.* **2003**, 2626. (b) Mandal, S.; Roy, D.; Chaudhari, R. V.; Sastry, M. *Chem. Mater.* **2004**, *16*, 3714. (c) Shimizu, K.; Maruyama, R.; Komai, S.; Kodama, T.; Kitayama, Y. *J. Catal.* **2004**, *227*, 202.

(32) (a) Lipshutz, B. H.; Tasler, S.; Chrisman, W.; Spliethoff, B.; Tesche, B. *J. Org. Chem.* **2003**, *68*, 1177. (b) Davies, I. W.; Matty, L.; Hughes, D. L.; Reider, P. J. *J. Am. Chem. Soc.* **2001**, *123*, 10139.

also shown in Figure 2. Three diffraction peaks at 2θ of 38.2°, 44.2°, and 64.5° (curve b) and 38.1°, 44.1°, and 64.4° (curve c), corresponding to the diffraction of (111), (200), and (220) lattice planes of Au and Ag crystals, reveal that Au and Ag crystals are cubic phase with cell constants of $a = 0.4072$ and 0.4092 nm, respectively. On the basis of XRD patterns, the average sizes of the Au and Ag nanoparticles embedded in the shell layer of the core−shell PS-*co*-P4VP microspheres are calculated to be 3.4 nm and 10.0 nm, which are well consistent with those observed by TEM.

Conclusions

The core−shell microspheres of poly(styrene-*co*-4-vinylpyridine) containing a core of polystyrene and a coordinative shell of poly(4-vinylpyridine) are synthesized by one-stage soap-free emulsion polymerization in water. The core−shell microspheres, of which the average size, the core diameter, and the shell thickness are about 458, 272, and 93 nm, respectively, are used as scaffold to synthesize shell-embedded noble metal nanoparticles. That the resultant 4.4-nm Pd, 3.7-nm Au, and 10.6-nm Ag nanoparticles are uniformly embedded in the shell layer of the core−shell microspheres is found, which is useful to increase the amount of accessible active site and therefore increase the catalytic activity of the noble metal nanoparticles. The Suzuki reaction performed in the sole solvent of water demonstrates that the Pd nanoparticles embedded in the shell layer of the core−shell poly(styrene-*co*-4-vinylpyridine) microspheres are an efficient and easily reusable catalyst.

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

CM703378C