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Synthesis of polyphenol microsphere-supported palladium complex and evaluation of its catalytic performance for Heck reaction

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Polyphenol microspheres were prepared by template polymerization of phenol in the presence of horseradish peroxidase as bio-enzyme catalyst and aqueous 1,4-dioxane as solvent. The morphology of polyphenol microspheres thus obtained was observed with a scanning electron microscope. Further, polyphenol microspheres as obtained were loaded with palladium to generate polyphenol microsphere-supported Pd complex. Resultant Pd complex catalyst supported by polyphenol microspheres was characterized by means of Fourier transformation infrared spectrometry, X-ray diffraction, X-ray photoelectron spectroscopy and scanning electron microscopy, and its thermal stability was examined. Moreover, the catalytic activity of polyphenol microsphere-supported Pd catalyst as synthesized for the Heck reactions of acrylic acid with aryl iodides was evaluated. Results indicate that the polyphenol microsphere as obtained has a diameter of about 500 nm. Polyphenol microsphere-supported Pd catalyst, as synthesized, at a dosage of 0.37 mol% Pd, possesses good catalytic activity for the Heck reactions of acrylic acid with aryl iodides in air at a low temperature of 50°C, and it also exhibits catalytic activity for bromide and activated chlorobenzene. The polyphenol microsphere-supported Pd complex has good thermal stability, and it can be readily separated and reused; the yield of the reaction of iodobenzene with acrylic acid remains at 82% after five recycle runs, showing promising potential as a catalyst for Heck reactions. Copyright © 2012 John Wiley & Sons, Ltd.

Keywords: horseradish peroxidase; polyphenol microsphere; supported Pd catalyst; heck reaction; catalytic activity

Introduction

As a powerful tool for the construction of C-C bonds in organic synthesis, the palladium-catalyzed Heck reaction[1] has received increasing attention in recent decades.[2–5] For example, the palladium-catalyzed Heck reaction can be used to synthesize a variety of compounds, including cinnamic acid ester derivatives and pharmaceutical intermediates,[6] in which palladium compounds such as $PdCl_2$ and $Pd(OAc)_2$ (palladium acetate) are widely used as homogeneous catalysts.[7,8] However, these traditional homogeneous catalysts are expensive and hard to separate and recycle, which significantly limits their widespread application in industry.[9,10] These drawbacks, fortunately, can be overcome by adopting polymer-supported palladium catalysts that can be easily separated and recovered in synthetic and industrial chemistry. In this respect, studies on polymer-supported palladium complexes for the Heck reaction are of particular significance.[11–14]

We are particularly interested in enzyme-catalyzed polymerization,[15–17] since it can be well adapted to synthesize polymers as a support for palladium complexes for the Heck reaction. For example, a new class of useful and high-performance polymeric materials can be prepared in the presence of peroxidase as catalyst, which is usually infeasible using conventional methods.[18–20] Specifically, the enzymatic oxidative polymerization of a variety of phenol derivatives produce phenolic polymers without the use of toxic formaldehyde,[21,22] providing an alternative route for preparing phenolic resins. By making use of the enzymatic polymerization of phenol in water, many researchers have successfully prepared phenolic polymers in the presence of cyclodextrin derivatives[23,24] and carbon nanotubes[25] as templates. We also obtained desired phenolic polymers in high yield by enzymatic polymerization of phenol in an aqueous micelle system.[26]

Noting that strict control of the structure and morphology plays a key role in adjusting the function of polymers, and polymer-supported noble metal catalysts of homogeneous micrometer size can be readily recycled,[27,28], we pay special attention to palladium complexes supported by microsphere materials exhibiting unique high volume-to-surface ratio properties relative to their larger counterparts.[29–31] Here we report the synthesis and characterization of a polyphenol microsphere-supported palladium complex and its application as a catalyst with excellent yield and high trans-selectivity for Heck reactions.

Experimental

Materials and Methods

Horseradish peroxidase (HRP; RZ = 2.5, activity ≥ 200 U mg^{-1}) was purchased from Shanghai Guoyuan Biotechnology Co. and used

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without further purification. Acrylic acid, styrene and DMF were distilled before use. Aryl halides were obtained from Lancaster Co. and used as received. All other reagents were obtained from commercial sources and were used as received.

An Avatar360 FT-IR spectrometer (Nicolet Co., USA) was performed to record IR spectra. X-ray diffraction (XRD) patterns were measured with a Philips X'Pert Pro X-ray diffractometer (Philips Co., Holland; Cu-K_α radiation, 2θ range 10–80°, scan step size 0.04°, time per step 0.5 s, generator voltage 40 kV, tube current 40 mA). Polymer molecular weight was estimated by gel permeation chromatography (GPC) using a Waters 515 apparatus with THF as the eluent at a flow rate of 1.0 mL min^{-1}. The calibration curves for the GPC analysis were obtained using polystyrene as the standard. X-ray photoelectron spectra were measured with an AXISULTRA spectrometer (Kratos Co., UK; monochromatized Al-K_α radiation). The binding energy of contaminant carbon (C1s, 284.8 eV) was used for binding energy calibration. An EXSTAR6000 (Seiko Co., Japan) thermal analysis system was performed at a heating rate of 10°C min^{-1} for thermogravimetric analysis (TGA) and scanning differential thermal analysis (SDTA). A JSM-7001F scanning electron microscope (JEOL Co., Japan; accelerating voltage 30 kV) was performed to observe the morphology and microstructure of the product as synthesized. The elemental composition of the product was analyzed with an Oxford Link ISIS energy dispersive spectrometer attached to the scanning electron microscope.

Preparation of Catalyst

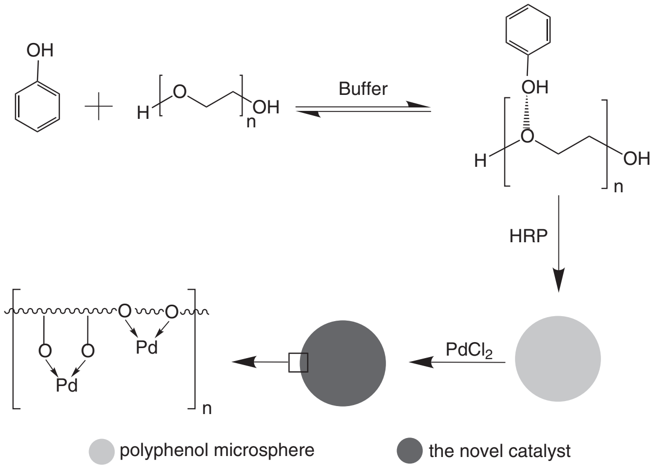
Phenol (0.47 g, 5 mmol) and polyethylene glycol-400 (PEG-400, 0.24 g) were dissolved in a mixed solution of 5 mL of 0.1 M phosphate buffer (pH 7) and 15 mL of 1,4-dioxane, followed by addition of the enzyme solution of HRP (2 mg) in 0.1 M phosphate buffer (5 mL, pH 7). To the resultant mixed solution was added hydrogen peroxide (5%, 0.25 mL) every 5 min for 14 times with mild stirring at room temperature. The mixture was stirred for an additional 30 min. After that, the black mixture obtained was vacuum filtered and washed with water thoroughly to remove HRP, phenol, residual PEG-400 and hydrogen peroxide. The dark-brown filtered solid was dried at 60°C under vacuum to give polyphenol microspheres.

Ethanol (60 mL) followed by 0.04 g $PdCl_2$ were added to a 100 mL round-bottomed flask and stirred for 20 min. To the resultant mixed solution was added polyphenol microspheres (0.2 g), followed by stirring at 60°C for 72 h. The mixture obtained was filtered, washed with ethanol and water, and dried at 60°C under vacuum for 12 h to give about 0.2 g palladium complex supported by polyphenol microspheres. The Pd content of the polymer-supported complex, determined by inductively coupled plasma mass spectrometry, was 0.466 mmol g^{-1}.

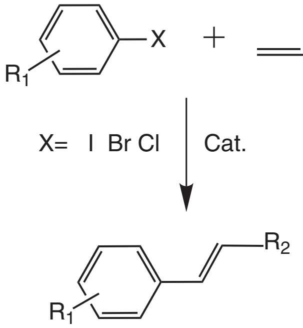
The synthesis of polyphenol microspheres and loading of palladium are outlined in Scheme 1.

General Procedure for Heck Arylation of Aryl Halides with Acrylic Acid (Scheme 2)

Aryl halide (1 mmol), acrylic acid (1.5 mmol), tri-*n*-butylamine (3 mmol) and polyphenol microsphere-supported Pd complex (0.37 mol% Pd, mixed with 1.0 mL DMF) were introduced into a three-necked flask (50 mL) equipped with a reflux condenser. The charged flask was heated at a pre-set temperature in an oil bath and stirred for 7 h. At the end of the reaction, the reactant mixture was cooled to room temperature. To the cooled mixture were added 25 mL H_2O and 0.6 g Na_2CO_3, followed by stirring at room temperature for 20 min. The catalyst was then separated from the reagent by filtration, while the pH of the filtrate was adjusted to 1–2 with a diluted aqueous solution of HCl. The white precipitate obtained was filtered, washed with H_2O several times and dried in air to give the desired product, whose yield was calculated based on the aryl halide.



Scheme 1. Schematic procedure for preparation of the novel catalyst



Scheme 2. Heck coupling reaction

General Procedure for Heck Arylation of Aryl Halides with Styrene (Scheme 2)

Aryl halide (1 mmol), styrene (1.5 mmol), tri-*n*-butylamine (1.5 mmol) and polyphenol microsphere-supported Pd complex (0.37 mol% Pd, mixed with 1.0 mL DMF) were introduced into a three-necked flask (50 mL) equipped with a reflux condenser. The charged flask was heated at a pre-set temperature in an oil bath and stirred for 7 h. The reactant mixture was then cooled to room temperature and dissolved in diethyl ether (30 mL), followed by stirring at room temperature for 20 min and filtration. The filtrate was treated with 3 N HCl (2 × 15 mL) and brine (3 × 15 mL) and dried over $MgSO_4$. The desired solid product was obtained by recrystallization from ethyl ether (Et_2O).

General Procedure for Catalyst Recycling

After the Heck arylation reactions of aryl halide with acrylic acid and styrene were completed, the polyphenol microsphere-supported Pd catalyst was recovered from the reaction system by filtration and washed with distilled H_2O (2×15 mL), ethanol (EtOH, 2×15 mL) and Et_2O (2×15 mL). The washed catalyst was then dried at 60°C under vacuum for 24 h and was ready for further runs in the Heck reaction.

Results and Discussion

Characterization of the Catalyst

The molecular weight of the THF-soluble part was evaluated by gel permeation chromatography (GPC) with refractive index (RI)-light-scattering (LS) detectors. The weight-average molecular weight of the polyphenol microsphere was 4.3×10^4. Figure 1 shows the FT-IR spectra of polyphenol microspheres and polyphenol microsphere-supported Pd catalyst. As seen in Fig. 1(a), the broad peak at 3427 cm^{-1} is ascribed to phenolic O-H bond, which has coordination ability with palladium chloride. The peaks at 1588, 1489, 833, 753 and 693 cm^{-1} arise from the polyphenol microspheres and can be assigned to various vibration modes of the C-H and C-C bonds of aromatic nuclei/rings. The strong peak at 1207 cm^{-1} is due to the asymmetric stretching vibration of C-OH and/or C-O-C, while the peak at 1103 cm^{-1} corresponds to the symmetric vibration of the ether bond. These FT-IR data are very similar to those of phenol polymers obtained in an aqueous micelle system.[26] Polyphenol microsphere-supported Pd catalyst displays all the characteristic absorption bands of polyphenol microspheres, but the FT-IR bands shift to some extent as compared with those of the phenolic polymer (Fig. 1b), which is due to the interaction between polyphenol microspheres and Pd.

Figure 2 shows the XRD patterns of polyphenol microspheres and polyphenol microsphere-supported Pd catalyst. Polyphenol microspheres exhibit a broad scattering peak at 19.1°, corresponding to their homogeneous amorphous phase (Fig. 2a). Also, the polyphenol microsphere-supported Pd catalyst shows major diffraction peaks at 2θ of 40.1°, 46.7° and 68.1° (Fig. 2b), which can be indexed to the diffraction of (1 1 1), (2 0 0) and (2 2 0) crystallographic planes of face-centered cubic palladium (JCPDS file no. 89-4897).[32] Moreover, the additional peak at 19.1° in Fig. 2(b) is attributed to the polyphenol microspheres, which indicates that Pd is readily deposited on the polyphenol microspheres.

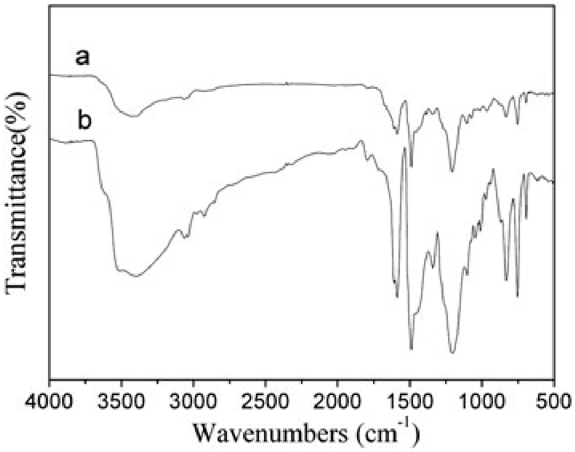


Figure 1. FT-IR spectra of polyphenol microsphere (a) and polyphenol microsphere-supported Pd catalyst (b)

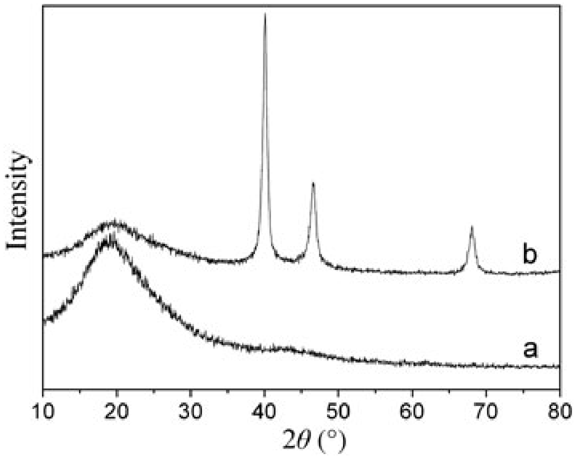


Figure 2. XRD patterns of polyphenol microsphere (a) and polyphenol microsphere-supported Pd catalyst (b)

Figure 3 shows the X-ray photoelectron survey spectrum as well as Pd3d and O1s spectra of polyphenol microsphere-supported Pd catalyst, where the O1s spectrum of the polyphenol microspheres is also provided for comparison. The polyphenol microsphere-supported Pd catalyst as synthesized shows a Pd3d peak together with C1s and O1s peaks derived from the polyphenol microspheres (Fig. 3a); the two characteristic peaks of $Pd3d_{5/2}$ appear at 336.0 and 338.3 eV (Fig. 3b), which suggests that Pd in the catalyst coexists as Pd^0 and Pd^{2+}, as reported elsewhere.[30] In the meantime, the O1s binding energy of the novel catalyst (533.25 eV) is higher than that of the polyphenol microspheres (531.85 eV), which is attributed to the coordination of O with Pd^0 or Pd^{2+}.

Figure 4 shows SEM images of polyphenol microspheres and polyphenol microsphere-supported Pd catalyst. It is seen that polyphenol microspheres as prepared are nearly monodispersed and have an average diameter of about 500 nm (Fig. 4a). This differs from what is reported by Young-Jin in that the aggregates of irregular-shaped products are formed by the enzymatic oxidative polymerization of phenol in the presence of PEG template in water,[33] which is possibly attributed to the adoption of different reaction systems and different modes to add hydrogen peroxide as well. Besides, polyphenol microsphere maintains their configuration after coordination with palladium chloride (Fig. 4b), while a large number of fine Pd particulates are uniformly adsorbed on polyphenol microspheres (Fig. 4c), as evidenced by relevant energy-dispersive spectrometric analysis (Fig. 5).

Figure 6 presents the TGA and SDTA curves of polyphenol microsphere-supported Pd catalyst. Polymer-supported Pd catalyst as synthesized is stable up to 250°C, and it experiences continuous weight loss within 250–350°C (Fig. 6a). The novel catalyst shows a strong exothermic peak at 330°C (Fig. 6b), corresponding to oxidation of the polymer support. These thermal analysis results indicate that the novel catalyst possesses good thermal stability.

Catalytic Activity

The ideal substrates for Heck reactions are aryl chlorides, since they are cheaper and more widely available than their bromide or iodide counterparts, but so far few polymer-supported Pd catalysts have been found to convert aryl chlorides effectively at high temperatures.[34–36] In the present research we adopt

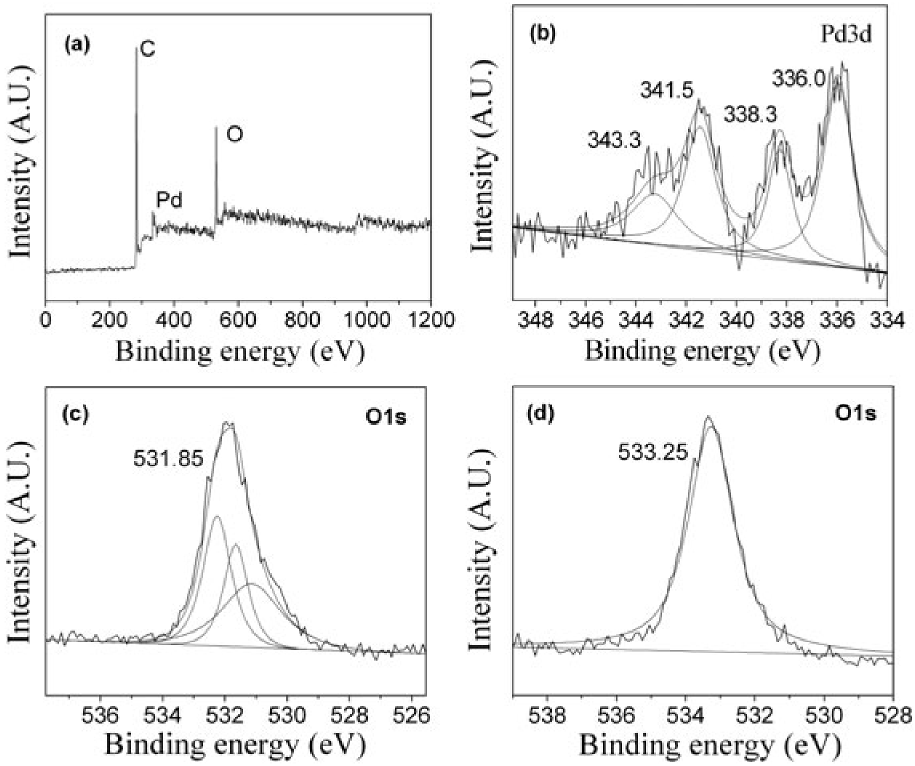


Figure 3. X-ray photoelectron spectrum (a) and Pd3d spectrum (b) of polyphenol microsphere-supported Pd catalyst as well as O1s spectra of polyphenol microsphere (c) and polyphenol microsphere-supported Pd catalyst (d)

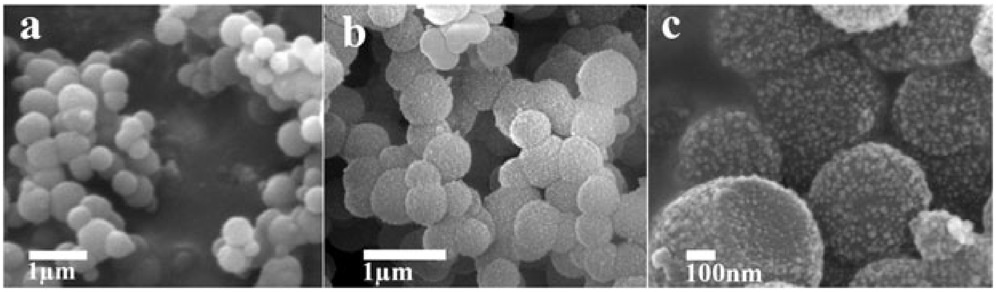


Figure 4. Scanning electron microscopy images of polyphenol microsphere (a) and polyphenol microsphere-supported Pd catalyst (b, c)

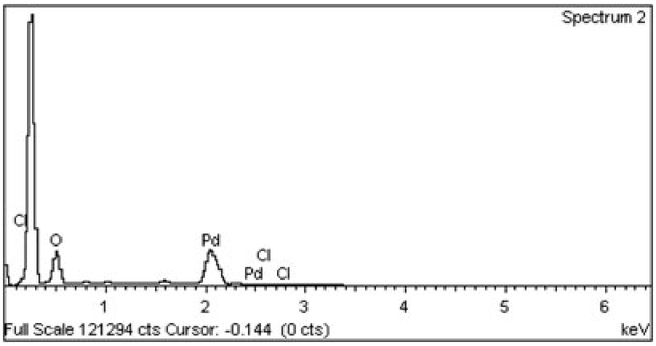


Figure 5. EDS pattern of the region containing fine Pd particulates on the surface of polyphenol microsphere-supported Pd catalyst as synthesized

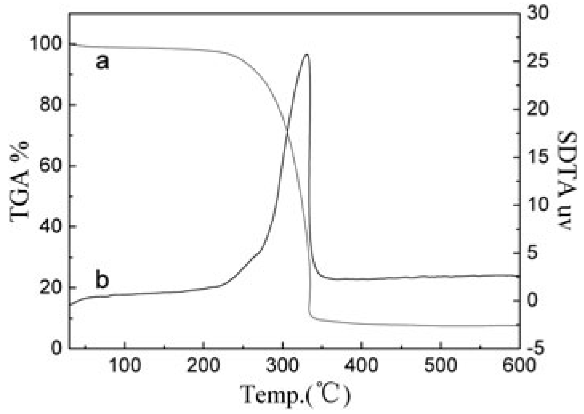


Figure 6. TGA (a) and SDTA (b) curves of polyphenol microsphere-supported Pd catalyst

the polyphenol microsphere-supported palladium complex as synthesized as a catalyst for Heck reactions of various aryl halides with olefins. The influences of amount of catalyst, reaction temperature and reaction time on catalytic activity have been systematically investigated using the coupling of iodobenzene and acrylic acid as a model reaction. Relevant results are presented in Tables 1 and 2. It is seen that the optimum amount of polymer-supported Pd catalyst is 0.37 mol% Pd (Table 1). However, a decrease in the Heck reaction yield was observed for concentrations over 0.37 mol%. This result is probably due to the aggregation of palladium particulates to 'palladium black' at higher concentrations.[37,38] Therefore, increase of palladium catalyst concentration was accompanied by a decrease in the reaction yield. As the reaction temperature increases from 50 to 90°C, the yield increases (Table 2; entries 3, 4, 5, 6, and 7), but the yield remains almost unchanged above 90°C (Table 2, entry 8). To our surprise, the novel catalyst remains active at a low temperature of 50°C, giving an acceptable yield of 61%. It also gives excellent yields at a fixed reaction time of 7 h (Table 2, entry 7).

In order to prove the efficiency of the novel catalyst, we studied the Heck reactions of different types of aryl halides with acrylic acid and styrene under optimized reaction conditions. As shown in Table 3, aryl iodide with either electron-withdrawing or electron-donating substituents reacts with acrylic acid or styrene at 90°C, generating corresponding coupled products in excellent yield after 7 h reaction (entries 1–8).

The coupling reactions of aryl bromides with alkenes require higher temperatures and a nitrogen atmosphere because of the relatively high bond energy of the C-Br bond. As summarized in Table 4, bromobenzene and 4-nitrobromobenzene in association with acrylic acid or styrene also perform effectively when the reactions are carried out in tetrabutyl ammonium bromide under nitrogen atmosphere (Table 4, entries 1, 3, 4 and 6). When *p*-bromoanisole is allowed to react with acrylic acid or styrene at 135°C for 7 h, the coupled product is produced in low yields (Table 4, entries 2 and 5).

Moreover, more challenging couplings of olefins with aryl chloride were also investigated, but no coupled product was obtained from the coupling reaction between chlorobenzene with acrylic acid or styrene in the presence of the polyphenol

Table 1. Influence of amount of catalyst on model reaction[a]

X (Pd) (mol%)	0.19	0.28	0.37	0.47	0.93
Yield (%)	58	80	91	87	86

[a]Reaction conditions: 1 mmol iodobenzene; 1.5 mmol acrylic acid; 3 mmol tributylamine; 1.0 mL DMF; 90°C, 7 h.

Table 2. Influence of reaction temperature and reaction time on model reaction[a]

Entry	Time (h)	Temp (°C)	Yield (%)
1	3	90	76
2	5	90	82
3	7	50	61
4	7	60	68
5	7	70	70
6	7	80	78
7	7	90	91
8	7	100	90
9	9	90	87

[a]Reaction conditions: 1 mmol iodobenzene; 1.5 mmol acrylic acid; 3 mmol tributylamine; 1.0 mL DMF; 0.37 mol% Pd.

Table 3. Heck reactions of acrylic acid and styrene with different aryl iodide.[a]

Entry	R_1	R_2	X	Time (h)	T(°C)	Yield (%)
1	H	CO_2H	I	7	90	91
2	p-Me	CO_2H	I	7	90	95
3	p-OCH_3	CO_2H	I	7	90	97
4	p-NO_2	CO_2H	I	7	90	97
5	H	Ph	I	7	90	94
6	p-Me	Ph	I	7	90	80
7	p-OCH_3	Ph	I	7	90	90
8	p-NO_2	Ph	I	7	90	90

[a]Reaction conditions: 1 mmol aryl iodide, 1.5 mmol alkene, tributylamine, 1.0 mL DMF, 90 °C, 0.37 mol% Pd.

Table 4. Heck reactions of acrylic acid and styrene with different aryl halides.[a]

Entry	R_1	R_2	X	Time (h)	T (°C)	Yield (%)
1	H	CO_2H	Br	7	120	77
2	p-OCH_3	CO_2H	Br	7	135	44
3	p-NO_2	CO_2H	Br	7	120	94
4	H	Ph	Br	7	120	87
5	p-OCH_3	Ph	Br	7	135	50
6	p-NO_2	Ph	Br	7	120	95
7	H	CO_2H	Cl	10	120	0
8	H	Ph	Cl	10	120	0
9	p-NO_2	CO_2H	Cl	10	120	53
10	p-NO_2	Ph	Cl	10	120	86

[a]Reaction conditions: 1 mmol aryl halide, 1.5 mmol alkene, 2.5 mmol tetrabutyl ammonium bromide (TBAB), 0.37 mol% Pd.

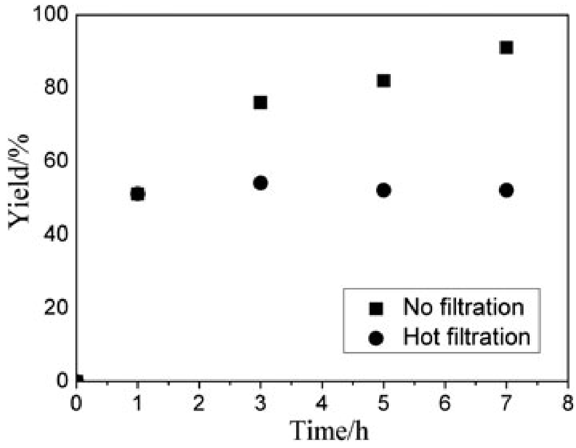


Figure 7. Application of hot filtration to the novel catalyst-catalyzed Heck reaction

microsphere-supported Pd catalyst. Nevertheless, the novel catalyst can catalyze aryl chlorides with an electron-withdrawing group (Table 4, entries 9 and 10).

Furthermore, the reusability of the catalyst was tested by carrying out repeated runs of the model reaction and the reaction of bromobenzene with styrene separately. It has been found that, when the catalyst is repeatedly used for up to five times, the target product of the model reaction is obtained in a yield of 91%, 90%, 88%, 83% and 82%, respectively. Meanwhile, the catalyst was reused for the Heck reaction of bromobenzene with styrene. Repeatedly using the catalyst for four times, the yield of the product was 87%, 82%, 74% and 50%, respectively. The results indicate that polyphenol microsphere-supported Pd catalyst, as synthesized, possesses practical utility.

A hot filtration technique is preferred to check whether the leached metal species are responsible for the catalytic activity.[39] As shown in Fig. 7, when the novel catalyst was hot filtered after 1 h of reaction and the filtrate placed back into the flask, the yield was highly dependent on whether the solid catalyst was removed or not. Thus the yield with hot filtration remained at nearly 52% after reaction for up to 7 h, which is similar to the yield observed immediately after filtration and is much lower than that without filtration (91%). This may imply that the supported Pd is the active site of the reaction.

Further, the performance of the polyphenol microsphere-supported palladium catalyst was compared with aggregates of irregular-shaped polyphenol-supported palladium catalyst by Heck reaction between iodobenzene and acrylic acid. Aggregates of irregular-shaped polyphenol was obtained in an aqueous micelle system.[26] Both the control experiment using irregular-shaped polyphenol-supported palladium catalyst and the typical experiment with polyphenol microsphere-supported palladium catalyst were conducted under identical conditions. The yield of target product in the presence of polyphenol microsphere-supported palladium catalyst was found to be 91%, while the yield of the same target product using irregular-shaped polyphenol-supported palladium catalyst was found to be 72%. This results are probably due to the unique high volume-to-surface ratio properties of the polyphenol microsphere relative to irregular-shaped polyphenol. On the whole, the polyphenol microspheres are ideal platforms for better immobilization of Pd and to gain their enhanced performance.

Conclusions

Polyphenol microsphere has been prepared via template polymerization of phenol catalyzed by the bio-enzyme catalyst HRP in aqueous 1,4-dioxane. Polyphenol microspheres as obtained were effectively employed as a substrate to load Pd particles. The catalytic activity of the resultant polyphenol microsphere-supported Pd catalyst for Heck reactions of iodide, bromide and activated aryl chloride under phosphine-free conditions was evaluated. It was found that the novel catalyst possesses good activity for the above-mentioned Heck reactions. Besides, as-synthesized polyphenol microsphere-supported Pd catalyst can be easily separated and recycled, showing potential as a promising catalyst for Heck reactions.

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