Polymer-Supported Palladium (II) Containing N_2O_2: An Efficient and Robust Heterogeneous Catalyst for C–C Coupling Reactions

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ABSTRACT: A new polymer was prepared from 1,3,5-triformylphloroglucinol (noted as TDTB) and *o*-phenylenediamine through Schiff base condensation reaction, and palladium (II) was immobilized on the polymer (noted as TbPo-Pd(II)). This process was easy to work-up and cost-effective. The structure and composition of TbPo-Pd(II) were fully characterized by FTIR, TGA, XPS, AAS, SEM, and TEM analyses. Meanwhile, this catalyst showed desired thermal stability and excellent performance in water/methanol system for Suzuki and Sonogashira coupling reactions. In addition, this heterogeneous catalyst can be readily recovered by simple filtration with no appreciable Pd leaching in the reaction. This work provides a powerful protocol for rapid access to asymmetrical biphenyls and aryl alkynes. © 2018 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2018**

KEYWORDS: heterogeneous catalyst; palladium; Sonogashira reaction; Suzuki reaction

INTRODUCTION The C–C coupling reactions have attracted considerable attention due to its significant role in a series of chemical syntheses,[1–4] such as the famous Sonogashira–Hagihara, Mizoroki–Heck, and Suzuki–Miyaura coupling reactions.[5–8] Palladium-catalyzed Suzuki–Miyaura coupling reaction has become one of the most popular reactions since it was recognized by awarding the 2010 Nobel Prize in Chemistry to Professor Suzuki,[1] which has been extensively used in the syntheses of pharmaceuticals, herbicides, natural products, and advanced functional materials in the recent decades.[9–13] The great attention of Suzuki–Miyaura coupling reaction in both academic and industrial laboratories can be explained for several reasons: (1) numerous functional groups are tolerated because of the mild reaction conditions, (2) the reaction is achievable with various aryl halides, and (3) boron compounds (especially boronic acids) are readily available and stable. Although numerous efficient homogeneous catalysts have been developed for the palladium-catalyzed Suzuki–Miyaura coupling reaction,[10,14,15] the homogeneous reaction is not suitable for industrial application due to the difficulty in the separation of catalysts from products. Alternatively, the growing interest has been shifted to the development of heterogeneous Pd catalysts for the Suzuki–Miyaura coupling reaction.[3] The Pd heterogeneous catalysts were frequently reported for the Suzuki–Miyaura coupling reaction in the last decade, such as metal organic frameworks (MOFs),[16,17] activated carbons (ACs),[18,19] covalent organic frameworks (COFs),[20,21] and so forth. The heterogeneous Pd catalyzed C–C bond formation via Suzuki–Miyaura coupling reaction represents a cost-efficient protocol with excellent recyclability of catalyst and lower metal pollution of production.

Porous organic polymers are recognized in a broader sense as a new alternative class material after introduction of COF. These porous organic polymers are usually synthesized from one or two components via coupling or condensation reaction and obtained great attention because of their ease of synthesis, chemical and water stabilities, high specific surface areas, high thermal stability, and light weight.[22] The catalysts (containing N_2O_2 active center) synthesized via Schiff base reaction from the monomers of 1,3,5-triformylphloroglucinol and amines have witnessed impressive progress for their applications in catalytic supports,[23] electronic devices and energy storage,[24] gas storage,[25] anticancer agent,[26] and water purification.[27] In particular, several polymers (N_2O_2 active center) were proved that they have promising performance in heterogeneous catalysis. For example, Rahul Banerjee has synthesized crystalline and porous COF, Pd(0)@TpPa-1, providing perfect stability without significant metal leaching for the C–C coupling reaction.[23] Ekambaram Balaramanhas and Rahul Banerjee have reported Pd@TpBpy catalyst, which showed

Additional supporting information may be found in the online version of this article.

excellent recyclability and superior reactivity for the synthesis of biologically and pharmaceutically important 2-substituted benzofurans via a tandem process.[28] To date, these catalysts containing N_2O_2 active center have attracted great attention in catalytic fields because of good catalytic capacity and extensive application. Therefore, it is desirable to design an efficient catalyst (N_2O_2 active center) with the monomers of 1,3,5-triformylphloroglucinol and amines via Schiff base condensation reaction under mild condition for Suzuki–Miyaura coupling reaction.

On the basis of the above consideration and in connection with our ongoing research, our primary goal is to design an excellent metal-N_2O_2 heterogeneous catalyst with simple operation. Here, we report a new catalyst containing N_2O_2 active center via Schiff base condensation reaction, including the reagents of 1,3,5-triformylphloroglucinol (TDTB) and *o*-phenylene diamine. Then palladium ion was anchored onto the polymer networks by postsynthesis modification, and the resulting catalyst was noted as TbPo-Pd(II) (Sch. 1). The TbPo-Pd(II) was investigated by various characterization techniques and successfully applied as an efficient catalyst for Suzuki and Sonogashira coupling reactions in aqueous media. The TbPo-Pd(II) showed superior catalytic performance of high selectivity, excellent activity, easy work-up, and multiple cycles of recovery and reuse. Meanwhile, the activity of TbPo-Pd(II) was further discussed by comparison with other catalysts.

EXPERIMENTAL

Materials

All chemical reagents were purchased and used without further purification unless otherwise stated. Anhydrous ethanol (≥99.7%), dichloromethane (DCM) (≥99.5%), hexamethylene tetramine (≥99.5%), Na_2SO_4 (≥99.0%), *o*-phenylene diamine (≥98.5%), and tetrahydrofuran (≥99.0%) were obtained from Sinopharm Chemical Reagent Co., Ltd. Phloroglucinol anhydrous was provided by Aladdin Industrial Corporation and used as received. CF_3COOH (99.0%) was purchased from Energy Chemical. Deionized water was adopted in the present experiments.

Instrumentation

Fourier transform infrared spectra (FTIR) were recorded on a Bruker VERTEX70 FTIR Spectrometer. Transmission electron microscope (TEM) (FEI Corp) was used to investigate morphology operated at an accelerating voltage of 200 kV. The content of Pd ion was determined by atomic absorption spectroscopy (AAS) analysis with an Analyst 300 Perkin Elmer. The polymer samples were analyzed on a FEI Sirion 200 scanning electron microscope at 10.0 kV. XPS was obtained in a VG multilab 2000 spectrometer, using a Mg–Al Ka X-ray source with the passing energy flow of 100 eV. The degassed condition is a chamber at 5×10^{-10} mbar at room temperature. GC analyses were obtained in a Fuli GC9790, equipped with a FFAP (30 m × 0.25 mm × 0.25 μm) capillary column and a flame ionization detector (FID). Field emission transmission electron microscope (FTEM) (Tecnai G2 F30) was used to investigate the morphology of sample. The melting point measure was performed on the SGW X-4B melting point instrument. ^{13}C CP MAS NMR measurement was performed on Agilent-NMR-vnmrs600 spectrometer, and Powder X-ray diffraction pattern was collected on x'pert pro MPD. N_2 adsorption isotherm was measured using V-Sorb 2800P surface area and porosity analyzer.

Catalyst Preparation

Synthesis of 1,3,5-Triformylphloroglucinol (TDTB)

The monomer was synthesized according to the previous literatures.[26,29,30] A solution of CF_3COOH (180 mL) containing hexamethylene tetramine (30.20 g, 215 mmol) and phloroglucinol anhydrous (12.06 g, 96 mmol) was magnetically stirred at 100 °C under inert atmosphere for 2.5 h. Then, HCl aqueous solution (3 mol/L, 300 mL) was added to this solution and the mixture was stirred for another 1 h. After the reaction, the solution was hot filtered and the filtrate was cooled to room temperature. Then the filtrate was extracted with DCM and the combined organic phases were dried with Na_2SO_4 and concentrated *in vacuo.* The compound was obtained and denoted as TDTB (yield: 22%; mp: 196–199 °C).

Synthesis of Polymer (TbPo)

The polymer was synthesized according to previous literatures.[24,26,31] The TDTB (1.94 g, 9 mmol) and *o*-phenylene diamine (1.02 g, 9 mmol) were added into redistilled DMF (30 mL), and the solution was magnetically stirred at 150 °C for 72 h under air. The resulting precipitate was filtered and washed three times with ethanol (3 × 100 mL), and the powder was dried. The crude product was refluxing in a Soxhlet with ethanol, tetrahydrofuran, and dichloromethane, respectively, and the process under each solvent required 24 h. The brownish red powder was obtained and dried in a vacuum oven at 60 °C for 24 h (denoted as TbPo, yield: 88%). Elemental analysis (%): C, 61.28; H, 4.22; N, 11.44.

Preparation of TbPo-Pd(II) Catalyst

Then palladium ion was anchored onto the polymer networks by postsynthesis modification (denoted as TbPo-Pd(II)). Palladium acetate (0.51 g, 2 mmol) was added to the solution, which included TbPo (1.50 g) and dichloromethane (30 mL), and the mixture was stirred at 50 °C for 24 h. The resulting solid was isolated by filtration and washed with dichloromethane for three times, and then dried under vacuum at 60 °C for 24 h. The powder was denoted as TbPo-Pd(II).

General Procedure for Suzuki–Miyaura Coupling Reaction

All the reagents were adopted without any further treatments. In a typical experiment, reactions were conducted in 10 mL glass bottles equipping with magnetic stirrer, which contained 5 mL solvent ($MeOH:H_2O$ = 3:2 vol/vol), 1 mmol bromobenzene, 1.5 mmol phenylboronic acid, 0.35 mmol% Pd(II) based on bromobenzene, and 2 mmol NaOH. Then the mixture was stirred at 80 °C for certain time. After the reaction, the quantitative analysis was conducted by GC. Reaction was performed at least in duplicate, and average data were adopted in Section 3.

General Procedure for Sonogashira–Hagihara Coupling Reaction

All the reagents were adopted without further treatments. In a typical procedure, 1 mmol iodobenzene, 1.5 mmol phenylacetylene, 0.35 mmol% Pd(II) based on iodobenzene, and 2 mmol NaOH were added into 5 mL solvent (MeOH: H_2O = 3:2 vol/vol) in a glass tube, then the reaction mixture was stirred at 80 °C. After the reaction, the quantitative analysis was conducted by GC. Reaction was performed at least in duplicate, and average data were adopted in Section 3.

General Procedure for the Recycling of the Catalyst

The reactions were carried out under the similar reaction conditions as described above except that the recovered catalyst was used. For each cycle, the catalyst was recovered by centrifugation, and the yield of the product was analyzed by GC. Catalyst was washed thoroughly with water and dichloromethane, respectively. The recovered catalyst was dried under vacuum at 60 °C overnight for the next run.

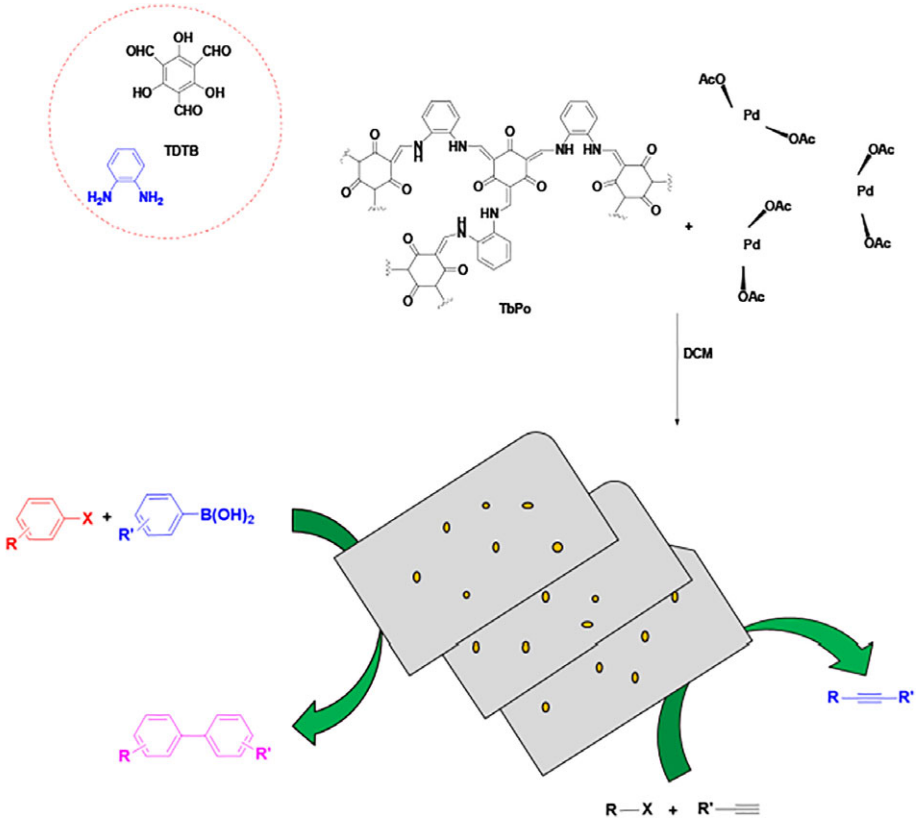
General Procedure for the Hot Filtration Experiment

In a typical procedure, 1 mmol bromobenzene, 1.5 mmol phenylboronic acid, 0.35 mmol % Pd(II) based on bromobenzene, and 2 mmol NaOH were added into 5 mL solvent (MeOH: H_2O = 3:2 vol/vol) in a glass tube. The reaction was stopped in 7 min, and the catalyst was filtrated via organic filter membrane. The negligible liquid was injected to GC, and the remaining liquid was allowed to continue to react at the same condition, and the yield was analyzed by GC.

RESULTS AND DISCUSSION

Characterization

FTIR characterization was used to detect the structures of the intermediates in the synthetic process. As displayed in Figure 1, the spectrum of TDTB demonstrated a typical stretching band at 1643 cm^{-1}, which could be assigned to the –CHO stretching vibrations. The results confirmed that the structure of TDTB is consistent with the previous report.[27,32] The FTIR spectrum of TbPo showed the disappearance of carbonyl stretching band at 1643 cm^{-1} and the generation of the stretching band at 1620 cm^{-1}, which was assigned to the α,β-unsaturated ketone of the enol tautomer in the polymer moiety.[26,33] The peak at 1254 cm^{-1} is attributed to the –C–N stretching, and the –N–H weak adsorption bands was observed at around 3421 cm^{-1}.[26,27,34] The results from FTIR spectra clearly indicated that the TbPo can be obtained successfully by the condensation reaction.[25] The solid-state ^{13}C CP MAS NMR spectrum has been recorded to elucidate the structure of the catalyst (Tbpo-Pd(II)). The resonance signal at 147 ppm was attributed to the formation of enamine carbon. The signal appeared at 181 ppm for the carbonyl carbon atom, and the peak at 108 ppm corresponded to α-carbon of the keto-enamine isomer (Supporting Information, Fig. S7).[20,26] Powder X-ray diffraction (PXRD) analysis was



SCHEME 1 Preparation of TbPo-Pd(II) and application of catalyst. [Color figure can be viewed at wileyonlinelibrary.com]

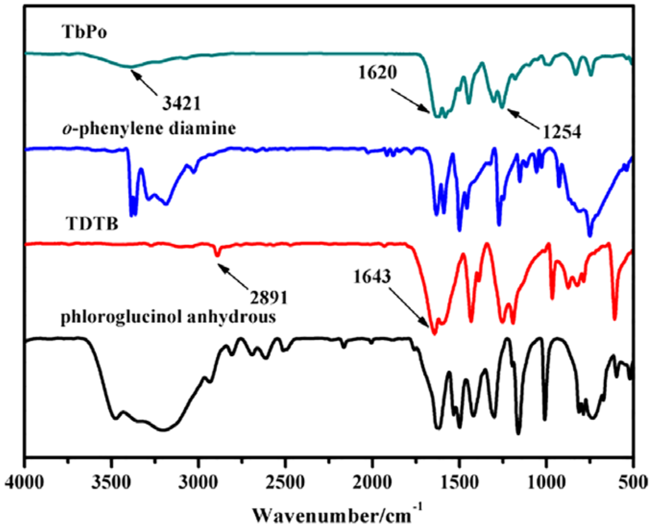


FIGURE 1 FTIR spectra of (a) phloroglucinol anhydrous, (b) TDTB, (c) *o*-phenylene diamine, and (d) TbPo. [Color figure can be viewed at wileyonlinelibrary.com]

carried out to investigate the structural features of the catalyst (Tbpo-Pd(II)), and a broad reflection at ~25 2θ degrees confirmed the synthesis of π–π stacked form (Supporting Information, Fig. S8).

The FTEM analyses of TbPo gave the direct evidence that the polymer contains abundant nanosheets in micro dimensions. Figure 2(a) showed that polymer is accumulation of nanosheets. Meanwhile, the folds can be observed clearly in 10 nm [Fig. 2(b)]. The SEM image showed that the surface of sample (Tbpo) was rough [Fig. 2(d)]. To obtain the pore size of the polymer support, the sample (Tbpo) was also analyzed by BET (Supporting Information, Fig. S5). At relative high-pressure regions (P/P_0 = 0.4–1.0), a slight hysteresis loop and a sharp rise were clearly observed, indicating the existence of mesoporous and macroporous in the sample. The results of FTEM, SEM, and BET support the conclusion that the morphology of catalyst was the porous nanosheets.

Thermal gravimetric analysis (TGA) was performed by using powdered sample. As illustrated in Figure 3, the first slow weight loss below 300 °C was caused by the removal of residual solvent and coordinated DMF. The polymer was stable up to 300 °C. The slightly lower decomposition temperature of the solid polymer may be origin from the high content of organic functional groups.[35–38] The TGA curve vividly demonstrated that the TbPo was stable with meeting the demands for potential application in heterogeneous catalysis.

X-ray photoelectron spectroscopy (XPS) characterization was employed to investigate the elemental compositions of the catalyst and coordination states of Pd species. The full spectrum of XPS shows that the catalyst contains C, N, O, and Pd elements (Supporting Information, Fig. S1). As displayed in Figure 4, Pd species in the catalyst were mostly of present in the Pd(II) oxidation state, corresponding to the binding energies (B.E.) of 338.5 and 343.7 eV in the Pd $3d_{5/2}$ and $3d_{3/2}$ levels, respectively. Compared to $PdCl_2$ (337.9 and 343.1 eV), the Pd(II) binding energy in the TbPo-Pd(II) shifted negatively by 0.6 eV, suggesting that the Pd(II) was coordinated successfully to the N_2O_2.[39,40] A small amount of Pd was present in the metallic state. Oxygen (1s) XPS peaks at 532.9 eV and a shoulder peak at 531.2 eV may be due to the influences of (C═O) and (Pd–O), respectively (Supporting Information,

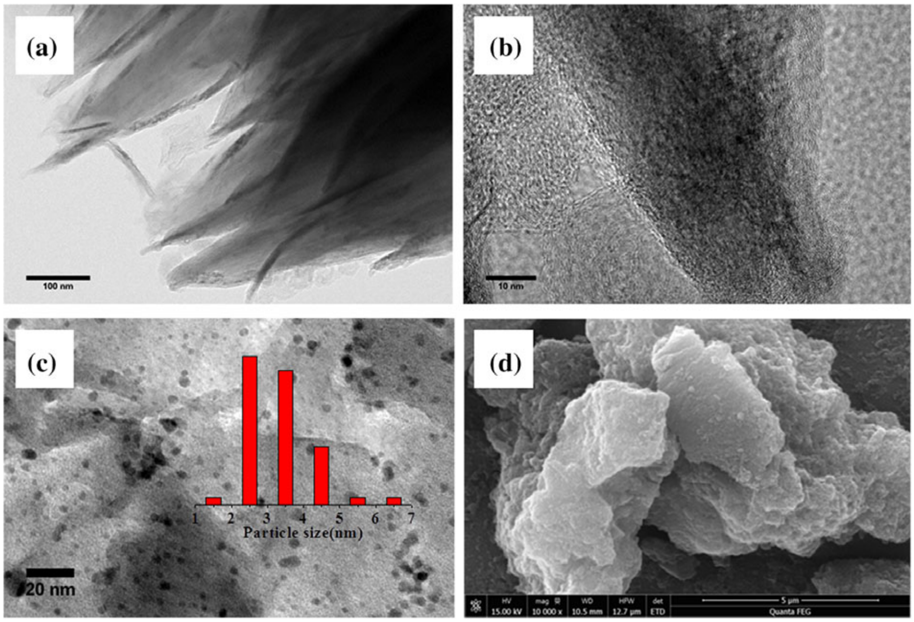


FIGURE 2 (a,b) FTEM images of fresh TbPo (a: 100 nm, b: 10 nm). (c) TEM image and particles size distribution of TbPo-Pd(II) after fourth recycle (c: 20 nm). (d) SEM image of TbPo (d: 5 μm). [Color figure can be viewed at wileyonlinelibrary.com]

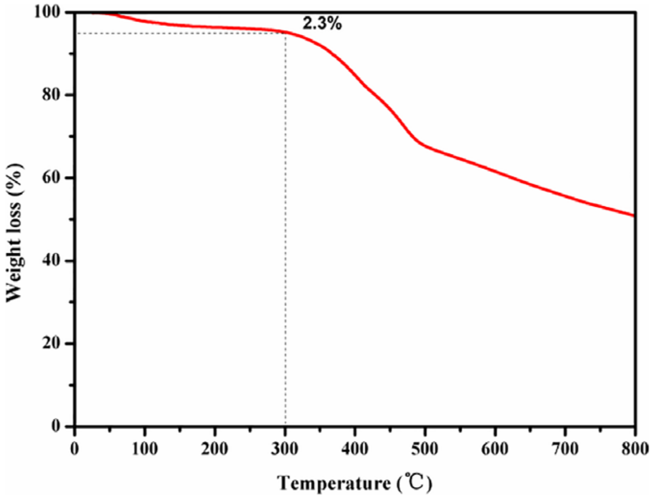


FIGURE 3 Thermal gravimetric analysis of TbPo. [Color figure can be viewed at wileyonlinelibrary.com]

Fig. S2).[41,42] The nitrogen (1s) XPS peak at binding energy of 400.4 eV was observed (Supporting Information, Fig. S3).[43] These results ensure that palladium could be immobilized successfully on TbPo by coordination to N_2O_2 functional groups rather than by physical adsorption of Pd(II) on the surface.

We have also investigated the UV–vis absorption spectra of $Pd(OAc)_2$ and the TbPo-Pd(II). The TbPo-Pd(II) has absorption from 200 to 800 nm (Supporting Information, Fig. S4).

Application of TbPo-Pd(II) in Suzuki–Miyaura Coupling Reaction

The products of Suzuki–Miyaura coupling reaction were extensively applied in the syntheses of natural products, herbicides, pharmaceuticals, and advanced functional materials in the recent decades. Thus TbPo-Pd(II) was attempted as catalyst in the Suzuki–Miyaura coupling reaction, and amazing effect was observed. First, the previous studies reported that the influences of solvents and bases were significant for the Suzuki–Miyaura coupling reaction.[9,44] So, the promotional effect between solvents and TbPo-Pd(II) was initially investigated with bromobenzene as the typical substrate, during which $K_3PO_4{\cdot}3H_2O$ was applied as the base, and the results are summarized in Table 1 (entries 1–10). When dioxane was used as the solvent in the reaction, no product was detected by the GC (Table 1, entry 5). Tetrahydrofuran, DMF, and ethyl acetate were used as solvent, accompanying 10.4%, 30.9%, and 5.6% yields of biphenyl, respectively (Table 1, entries 1–2 and 4). The continuously remarkable promotion was observed when the solvent was replaced by alcohol. Anhydrous methanol and ethanol played the positive role in the Suzuki–Miyaura coupling reaction, and the yields of the biphenyl were 78.9% and 73.4%, respectively (Table 1, entries 3 and 6). Methanol is the better solvent comparing with other single solvents. Furthermore, we also adopted different mixed solvents between methanol and water in the reaction due to the advantages of environmental friendly property, economy, and the perfect solubility for the inorganic base (Table 1, entries 7–10). The solvent (MeOH: H_2O = 3:2) was the best choice of the mixed solvents, and the yield of biphenyl was 96.3% (Table 1, entry 9).

Next, the bases were also investigated under the same condition, including $NaHCO_3$, NaOH, Na_2CO_3, CH_3COOK, $HCOONa{\cdot}2H_2O$, and $K_3PO_4{\cdot}3H_2O$. Remarkably, the yield of biphenyl was 98.5% with the base of NaOH (Table 1, entry 15). It reduced to 84.3% when NaOH was replaced by Na_2CO_3 (Table 1, entry 13). The weaker bases, such as $NaHCO_3$, $HCOONa{\cdot}2H_2O$, and CH_3COOK, played poor promotion in the Suzuki–Miyaura coupling reaction, accompanying the yields of 31.4%, 10.8%, 36.3%, respectively (Table 1, entries 11–12 and 14). The results vividly showed the synergistic effect between base and TbPo-Pd(II).

Consequently, the optimum reaction conditions of Suzuki–Miyaura coupling reaction were obtained in 5 mL of solvent (MeOH:H_2O = 3:2) using 0.35 mmol% Pd(II) and 2 mmol of NaOH as base in the reaction of bromobenzene (1.0 mmol) and phenylboronic acid (1.5 mmol).

To investigate whether the active intermediate can be generated in situ by the interaction of solvent (MeOH:H_2O = 3:2) and catalyst in the absence of base, the Suzuki–Miyaura coupling reactions were conducted in the presence/absence of NaOH and the results were listed in the Table 1 (entries 15–16). The process of reaction can hardly be proceeded in the absence of base in 1 h (Table 1, entry 16). However, the Suzuki–Miyaura coupling reaction was rapidly accomplished in the addition of NaOH with 98.5% yield of coupling product within 30 min. Meanwhile, the blank experiment without catalyst only provided 0.5% yield of biphenyl in 1 h as displayed in Table 1 (entry 17). The control experiments clearly indicated that the presence of base and catalyst was necessary to trigger the reaction and generate the coupling product.

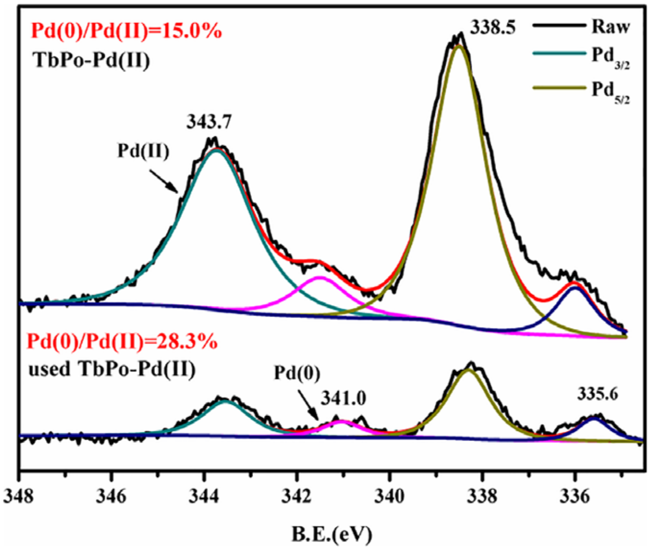


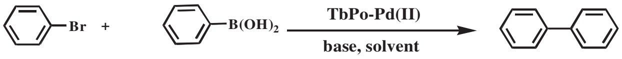
FIGURE 4 The XPS for the Pd species of fresh TbPo-Pd(II) and TbPo-Pd(II) after fourth recycle. [Color figure can be viewed at wileyonlinelibrary.com]

Furthermore, we have also explored whether the inert gas is necessary for the catalytic system. As shown in Table 1, the yield of biphenyl was 98.5% under the protection of the inert atmosphere, and the control experiments provided 98.3% yield of coupling product in air (entries 15 and 18). The supplementary experiments clearly disclosed that the performance under inert atmosphere was identical to that in the open-flask procedure. Therefore, reactions for expanding the scope of substrates were carried out in air.

To expand the scope of substrates, we examined the TbPo-Pd (II) catalyst in the Suzuki–Miyaura coupling reaction of various substrates, and the results were summarized in Table 2. First of all, the derivatives of bromobenzene were explored. The lower temperature displayed sluggish influence for the catalyst in the tested substrates. For example, 2-bromotoluene was greatly promoted by the catalyst with 3 h at 80 °C, and the yield of 2-methyl-1,1′-biphenyl was 91.5% (Table 2, entry 3). However, under the similar condition, the reaction displayed poor conversion with 15.5 h at 30 °C, the yield can only reach 53.1% (Table 2, entry 2). Compared with 2-bromotoluene, 4-bromotoluene can be easily converted to the coupling product with the yield of 86.2% at 30 °C (Table 2, entry 5), because *ortho*-methyl group has stronger steric hindrance than *para*-methyl group during the Suzuki–Miyaura coupling reaction procedure. Under the identical conditions, the different yields of the entries 8 and 9 were also caused by the steric hindrance (Table 2). As mentioned above, $-OCH_3$ and $-CH_3$ groups can promote the reaction due to electron donative groups. However, the time of reaction was longer than the case of bromobenzene (Table 2, entries 1–5 and 8–9). The TbPo-Pd(II) catalyst also afford superior performance to 4-bromoacetophenone, corresponding to the yield of 96.5% with 7.5 h (Table 2, entry 7). Furthermore, we found that the catalyst has also good advantage of promoting the Suzuki–Miyaura coupling reaction with iodobenzene as substrate, and the yield was 99.2% with 0.3 h (Table 2, entry 10). The trend in the activation of aryl halides in the Suzuki–Miyaura coupling reactions follows the order of R–I > R–Br > R–Cl. In addition, the yields of coupling products in the cases of 4-iodotoluene and 4-*tert*-butyliodobenzene were 98.6% and 91.0%, which needed longer time than iodobenzene because of the steric hindrance (Table 2, entries 11 and 12). Methyl 4-iodobenzoate was converted to the corresponding product with the yield of 94.6% (Table 2, entry 13). The data clearly indicated that TbPo-Pd(II) catalyst showed desired performance for derivatives of bromobenzene and iodobenzene in the Suzuki–Miyaura coupling reaction.

In addition to the derivatives of aryl halide, we have also evaluated the derivatives of phenylboronic acid. When 4-acetylphenylboronic acid was tested as substrate, the yield only was 59.3% with 11.5 h at 80 °C (Table 2, entry 15). The conversion of 4-(methoxycarbonyl) phenylboronic acid was higher than the case of 4-acetylphenylboronic acid under the identical conditions (Table 2, entry 14), because the electron-withdrawing capacity of $-COCH_3$ was stronger than $-COOCH_3$. The yield was 94.4% when 4-methoxyphenylboronic acid was used as substrate (Table 2, entry 16). In summary, the data in Table 2 clearly disclosed that the TbPo-Pd(II) catalyst was effective for Suzuki–Miyaura coupling reaction.

TABLE 1 Influences of Base and Solvent in Suzuki–Miyaura Coupling Reaction Catalyzed by TbPo-Pd(II) Catalyst[a]



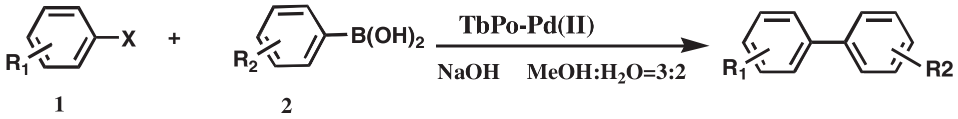
Entry	Base	Solvent	Yield[b] (%)
1	$K_3PO_4·3H_2O$	THF	10.4
2	$K_3PO_4·3H_2O$	DMF	30.9
3	$K_3PO_4·3H_2O$	MeOH	78.9
4	$K_3PO_4·3H_2O$	Ethyl acetate	5.6
5	$K_3PO_4·3H_2O$	Dioxane	Trace
6	$K_3PO_4·3H_2O$	EtOH	73.4
7	$K_3PO_4·3H_2O$	$MeOH/H_2O$ (1:4)	71.6
8	$K_3PO_4·3H_2O$	$MeOH/H_2O$ (2:3)	86.9
9	$K_3PO_4·3H_2O$	$MeOH/H_2O$ (3:2)	96.3
10	$K_3PO_4·3H_2O$	$MeOH/H_2O$ (4:1)	91.6
11	$NaHCO_3$	$MeOH/H_2O$(3:2)	31.4
12	$HCOONa·2H_2O$	$MeOH/H_2O$ (3:2)	10.8
13	Na_2CO_3	$MeOH/H_2O$ (3:2)	84.3
14	CH_3COOK	$MeOH/H_2O$ (3:2)	36.3
15	NaOH	$MeOH/H_2O$ (3:2)	98.5
16[c]	/	$MeOH/H_2O$ (3:2)	Trace
17[c,d]	NaOH	$MeOH/H_2O$ (3:2)	0.5
18[e]	NaOH	$MeOH/H_2O$ (3:2)	98.3
19[f]	NaOH	$MeOH/H_2O$ (3:2)	98.9
20[g]	NaOH	$MeOH/H_2O$ (3:2)	99.8
21[h]	NaOH	$MeOH/H_2O$ (3:2)	71.0

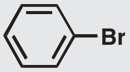
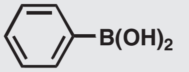
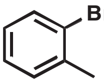
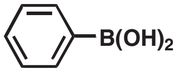
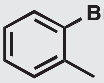
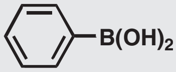
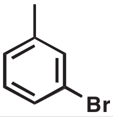
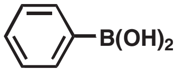
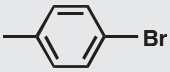
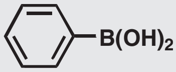
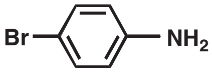
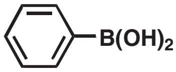
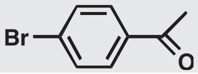
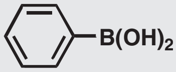
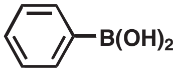
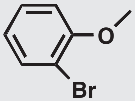
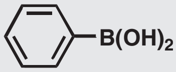
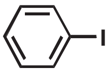
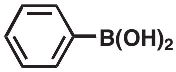
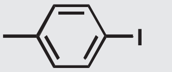
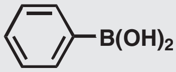
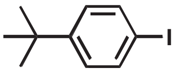
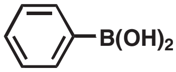
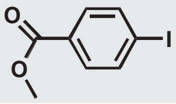
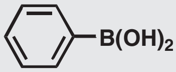
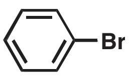
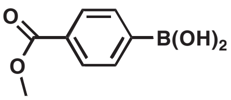
[a] Conditions: bromobenzene (1.0 mmol), phenylboronic acid (1.5 mmol), base (2.0 mmol), solvent (5 mL), 80 °C, 0.35 mmol % Pd(II), under inert atmosphere, 30 min.
[b] Determined by GC.
[c] 1 h.
[d] No catalyst.
[e] In air.
[f] The second run.
[g] The third run.
[h] The fourth run.

The Leaching Studies and Recyclability Test

To determine if the heterogeneous Pd species were the real catalysts responsible for the reaction, we have carried out the hot filtration experiment. In a typical experiment, bromobenzene and phenylboronic acid were adopted as the model substrates. The TbPo-Pd(II) catalyst was removed when the Suzuki–Miyaura coupling reaction was performed at 7 min, the yield of biphenyl was 19.4%. Then the mother liquid was allowed to react for another 14.5 h under the similar conditions. The yield had no significant increase, which indicated

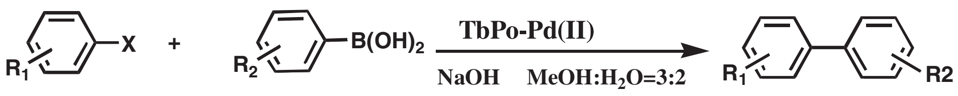
TABLE 2 Suzuki–Miyaura Coupling Reaction of Various Substrates Catalyzed by TbPo-Pd(II)[a]



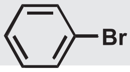
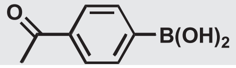
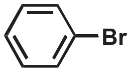
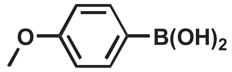
Entry	Substrate 1	Substrate 2	Temperature (°C)	Time (h)	Yield[b] (%)
1			80	0.5	97.0
2			30	15.5	53.1
3			80	3	91.5
4			80	9	96.1
5			30	3	86.2
6			80	21	41.8
7			80	7.5	96.5
8			30	7	98.3
9			30	7	83.2
10			80	0.3	99.2
11			80	0.5	98.6
12			80	2	91.0
13			80	3	94.6
14			80	11.5	98.4

(Continues)

TABLE 2 Continued



1 2

Entry	Substrate 1	Substrate 2	Temperature (°C)	Time (h)	Yield[b] (%)
15			80	11.5	59.3
16			80	10	94.4

[a] Reaction conditions: aryl halide (1.0 mmol), phenylboronic acid (1.5 mmol), NaOH (2.0 mmol), 5 mL of MeOH/H_2O (3:2 v/v), 0.35 mmol % Pd(II), in air.

[b] Determined by GC.

that almost no Pd species was leached into the liquid from the TbPo-Pd(II) catalyst. The Pd content of the mother liquid was also analyzed by the AAS, and the content of Pd(II) was only 0.01 ppm in the mother liquid. The AAS result also indicated that only little Pd leaching during the reaction. Undoubtedly, these results are very promising and encouraging, manifesting that the TbPo-Pd(II) is stable heterogeneous catalyst in nature.[45]

Additionally, the recycling results showed that the yield of coupling product can achieve >95% on the third recycle (Table 1, entry 20). However, the yield decreased on the fourth run. We have analyzed the TbPo-Pd(II) after 4th recycle by TEM. Despite Pd nanoparticles uniformly dispersing on the nanosheets and ranging from 1 to 7 nm, the TEM images exhibited slight aggregation as seen in Figure 2(c).[16,39,46,47] Combined with the AAS results, these observations indicated that the aggregation of Pd could be account for the decrease of catalyst activity.

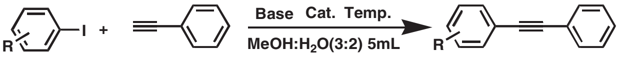
Furthermore, we have characterized the status of Pd species in the heterogeneous TbPo-Pd(II) catalyst after fourth recycle by XPS (Fig. 4). The presence of Pd(0) in the polymer was confirmed by the peaks at 335.6 eV (Pd $3d_{5/2}$) and 341.0 eV (Pd $3d_{3/2}$).[23,38] The spectra of XPS disclosed that most of Pd species were present in Pd(II) and a little amount of Pd species were present in the metallic state. The amount of Pd in the metallic state has increased slightly after the recycle experiment compared with the fresh catalyst. The XPS spectrum of catalyst after first recycle also proved above conclusion (Supporting Information, Fig. S6). Together with the XPS spectra, the results of TEM and AAS confirmed that the slight decrease of activity was caused by the aggregation of Pd nanoparticles.

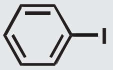
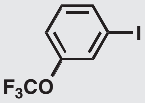
To further exhibit the catalysis capacity of TbPo-Pd(II), this catalytic system was compared with other supported palladium catalysts. As shown in Table 3, TbPo-Pd(II) catalyst exhibits extensive progress in reaction time and temperature. For example, SMNPs-salen Pd(II)[49] needed longer time for the model reaction, and the temperature was high. Furthermore, a higher yield (97%) was obtained than that of PS-tsu-Pd(II)[48]

TABLE 3 Performance of TbPo-Pd(II) and Other Pd Catalysts for the Reaction of Bromobenzene with Phenylboronic Acid

Entry	Catalyst	Temperature (°C)	Time (h)	Yield (%)	Ref.
1	PS-tsu-Pd(II)	80	6	92	48
2	SMNPs-salen Pd(II)	100	3	100	49
3	PS-btsu-Pd(II)	Room temperature	8	94	50
4	Pd(salen)-POM	50	5	95	51
5	PS-Pd-salen	Room temperature	20	89	52
6	Fe_3O_4/P(GMA-AA-MMA)-Schiff base-Pd	80	1	98	53
7	TbPo-Pd(II)	80	0.5	97	This work

TABLE 4 Sonogashira–Hagihara Coupling Reaction Catalyzed by TbPo-Pd(II)[a]



Entry	Substrate	Time (h)	Conversion (%)[b]
1[c]		12	93.9
2		14	95.2
3		14	99.9

[a] Reaction conditions: aryl halide (1.0 mmol), phenylacetylene (1.5 mmol), 5 mL of MeOH/H_2O (3:2 vol/vol), 0.35 mmol % Pd(II), 80 °C, in air.

[b] Determined by GC.

[c] 100 °C.

(92%), and the time was shorter than the case of Fe_3O_4/P (GMA-AA-MMA)-Schiff base-Pd.[53] The TbPo-Pd(II) is a promising candidate showing excellent catalytic activity in short time and low temperature.

Application of TbPo-Pd(II) in Sonogashira–Hagihara Reaction

Here we report a short study of the Sonogashira–Hagihara reaction with TbPo-Pd(II) catalyst. The Sonogashira–Hagihara coupling reaction was conducted following the optimal condition of the Suzuki–Miyaura coupling reaction. The results of these reactions are shown in Table 4. In all cases, the yields of coupling products were higher than 90%. As can be deduced from Table 4, the presence of electron-donors or electron-withdrawing groups in the aryl bromide does not affect yields (entries 1–3). The data in Tables 2 and 4 indicated that TbPo-Pd(II) showed excellent performance for the Suzuki–Miyaura and Sonogashira–Hagihara coupling reactions. It is certain that the TbPo-Pd(II) has great potential application for the C–C coupling reactions.

CONCLUSIONS

In this study, we reported a novel strategy that polymer-supported palladium (II) containing N_2O_2 active center was an efficient and robust heterogeneous catalyst for C–C coupling reactions, and the polymer could be synthesized via Schiff base condensation reaction with facile and cost-effective synthesis approach. The Suzuki–Miyaura and Sonogashira–Hagihara coupling reactions catalyzed by TbPo-Pd(II) could be proceeded smoothly in the aqueous solution with excellent activity and selectivity. Meanwhile, the structure and composition of TbPo-Pd(II) and Tbpo were fully characterized by FTIR, TGA, XPS, AAS, SEM, and TEM analyses. Furthermore, the stability at relatively high temperatures, insensitivity to oxygen, total separation from the reaction products, and reusability may be helpful to use TbPo-Pd(II) on an industrial scale. This work also highlights that the TbPo can not only display strong metal binding capacity as support materials but also positively affect the catalytic activity. Finally, we expect that the N_2O_2 type polymers will find extensive application, via the advantage of coordinating various transition metals, in other fields of research and in catalytic applications.

ACKNOWLEDGMENTS

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