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Porous Organic Polytriphenylimidazole Decorated with Palladium Nanoparticles for Cyanation of Aryl Iodides

Haiwen Yu,^[a] Siqi Xu,^[a] Yijiang Liu,^{*[a]} Hongbiao Chen,^{*[a]} and Huaming Li^{[a][b]}

Abstract: A novel porous organic polytriphenylimidazole (PTPI-Me) was prepared by Yamamoto self-coupling of 2,4,5-tris-(4-bromophenyl)-1-methyl-1H-imidazole (TPI-Me) in the presence of bis(1,5-cyclooctadiene)nickel(0), which was subsequently decorated with Pd nanoparticles (NPs) to afford a heterogeneous cyanation catalyst (Pd@PTPI-Me). Pd NPs with an average diameter of 2.7 nm were well-grown in the PTPI-Me frameworks due to the coordination of imidazole ring to Pd species. The resultant Pd@PTPI-Me catalyst with a Pd loading of 0.13 mmol g⁻¹ exhibited superior catalytic activity towards cyanation of aryl iodides. More importantly, the heterogeneous catalyst was readily recycled and displayed negligible deactivation after five cycles.

Introduction

In recent years, porous organic materials (POMs) including hyper-crosslinked polymers (HCPs), polymers of intrinsic microporosity (PIMs), covalent organic frameworks (COFs), and porous organic polymers (POPs), are gained considerable interest in gas adsorption/separation, luminescent materials, sensing, and catalysis.^[1-10] Among them, POPs are of special concern in the field of heterogeneous catalysis due to their high stability, high surface area, designable porosity and flexible synthetic approaches. Up to now, various functionalized POPs with N- or P-containing moieties have been successfully used to prepare heterogeneous catalysts through loading precious metal nanoparticles (NPs) in their frameworks, which showed superior catalytic performance with excellent recyclability and reusability. For example, Ding and co-workers^[11] reported the preparation of Ph₃P-containing POP for Pd NPs loading. The as-synthesized heterogeneous catalyst exhibited high chemoselectivity and efficiency towards hydrogenation of nitroarenes and olefins under gentle conditions. Li et al.^[12] synthesized N-heterocyclic carbene gold(I) complex-incorporated POPs and investigated their catalytic performance in hydration of phenylacetylenes. Wang et al.[13-14] have synthesized a series of imidazoliumcontaining POPs for loading Pd NPs and explored the catalytic activities in the reduction of nitroarenes. However, all the above-

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mentioned POPs have been synthesized via Pd-catalyzed Heck, Sonogashira, or Suzuki-Miyaura coupling reactions. Considering that ligand-complexed Pd catalysts were used in these coupling processes, the complete removal of Pd residues from the POPs was bound to be difficult because of the ionic or coordinative interactions between the synthesized POPs and Pd species. Undoubtedly, the residual Pd species can significantly interfere with the catalytic performance of POP-supported metal NPs in heterogeneous catalysis. In this regard, it is important to employ other strategies to synthesize POPs that metal residues can be thoroughly removed or without using any metal catalysts.

As an alternative strategy for POPs synthesis, Ni(0)-induced Yamamoto coupling is more attractive as compared with Pdcatalyzed coupling reactions due to the mild reaction conditions together with the easy removal of metal residues. Indeed, Ni species in Yamamoto coupling systems can be readily removed by washing with a mineral acid in the work-up procedure as proved by inductively coupled plasma atomic emission spectrometry (ICP-AES) analysis.[15] In this manner, the interference of metal residues can be excluded. At present, a (metal)porphyrin^[16-18], POPs variety of based on triphenylamine^[19], tetraphenylphosphonium^[20], tetraphenylmethane^[21], triphenylbenzene^[22], spriobifluorene^[23], triptycene^[24], pyrene^[25], imidazolium^[26], and triazole^[27] skeletons have been successfully synthesized by Yamamoto self-coupling or cross-coupling reactions. Among them, imidazolium- and triazole-containing POPs are considered as the most promising catalyst supports. For example, ultrafine Pd NPs with an average diameter of 1.39 ± 0.31 nm had been effectively loaded in the cavities of 1,2,3-triazole-containing POP.^[27] Such supported catalyst exhibited high activity and recyclability in the hydrogenation of olefins. In addition, Au NPs with an average diameter of 3.42 nm were also immobilized in imidazoliumcontaining POP that fabricated by Yamamoto cross-coupling reaction, which showed high activity, selectivity, and recyclability in the reduction of nitrobenzene.^[15] Notably, the catalytic activity of metal NPs is closely related to their particle size, and the smaller particulate is usually thought to have higher catalytic activity due to the larger reactive area.[28-29] On the other hand, it is also very important to lower the metal NPs loading while maintaining the high catalytic activity considering that precious metals are much expensive. In this context, it is highly desirable to design and synthesize POP supports at a molecular level that can achieve these goals mentioned above.

Herein, we demonstrated a novel polytriphenylimidazolecontaining POP (PTPI-Me) that fabricated by Yamamoto selfcoupling of 2,4,5-tris-(4-bromophenyl)-1-methyl-1H-imidazole (TPI-Me), which was then employed as the support for Pd NPs loading (Pd@PTPI-Me). The choice of triphenylimidazole as the building block is based on the fact that it has a rigid molecular structure on the one hand, and on the other hand, imidazole ring can complex with metal ions, which facilitates to load metal NPs. In addition, previous investigations have demonstrated that triphenylimidazole-containing linear polymers possess high thermal and chemical stabilities.^[30-31] Due to the coordinative FULL PAPER

interaction between imidazole ring and Pd precursor, Pd NPs with an average diameter of 2.7 nm were well-grown in the PTPI-Me frameworks. The resultant Pd@PTPI-Me catalyst with a Pd loading of 0.13 mmol g^{-1} exhibited superior catalytic activity

towards cyanation of aryl iodides. More importantly, the heterogeneous catalyst was readily recycled and displayed negligible deactivation after five cycles.



Scheme 1. Schematic representation of the synthesis of Pd@PTPI-Me.

Results and Discussion

The synthetic route of the porous organic polymer PTPI-Me was shown in Scheme 1. The monomer TPI-Me was synthesized by a one-step condensation reaction between 4,4'-dibromobenzil, 4-bromobenzaldehyde and ammonium acetate, and followed by a substitution reaction with methyl iodide (Scheme S1). The structure of TPI-Me was fully characterized by ¹H NMR (Figure S1), ¹³C NMR (Figure S2) and FT-IR (Figure S3, black line). The Yamamoto self-coupling of TPI-Me in the presence of bis(1,5-cyclooctadiene)nickel(0) (Ni(COD)₂) generated a light yellow powder PTPI-Me. The as-synthesized PTPI-Me was then dispersed in DMF followed by incubation with an H₂PdCl₄ aqueous solution. After reduction with NaBH₄, the brown power of Pd@PTPI-Me was obtained (Scheme 1).

The structure of PTPI-Me was initially characterized by solid state ¹³C NMR spectrum. As illustrated in Figure 2a, the signal at δ = 139.2 ppm confirmed the success of Yamamoto phenylphenyl coupling among TPI-Me monomers. The signals at δ = 137.5-151.1 ppm were ascribed to carbon atoms of imidazolyl ring, and the broad signals at 118.2-137.6 ppm were attributed to the carbon atoms of phenyl ring, In addition, the methyl carbon also appeared at δ = 35.4 ppm. The FT-IR spectra of PTPI-Me and Pd@PTPI-Me are shown in Figure S3. As seen, the strong C-Br stretching vibration band at 513 cm⁻¹ that corresponded to TPI-Me building block almost disappeared in the FT-IR spectrum of PTPI-Me, indicating that homocoupling of TPI-Me occurred (Figure S3, black and blue line). After Pd NPs was immobilized onto the PTPI-Me skeleton, the symmetric stretching vibration of C=N-C=C bond in imidazolyl ring shifted from 1450 cm⁻¹ to 1445 cm⁻¹, indicating the strong coordination interaction between Pd and imidazolyl ring (Figure S3, red line). Thermogravimetric analyses showed that both PTPI-Me and Pd@PTPI-Me are stable below 300 °C, and the thermal stability of Pd@PTPI-Me is somewhat higher than that of PTPI-Me (Figure S4). The morphologies of PTPI-Me and Pd@PTPI-Me were then investigated by scanning electron microscopy (SEM) and transmission electron microscope (TEM). As shown in Figure 1, PTPI-Me is composed of spherical particles (Figure 1a), and no morphological change is observed after Pd NPs loading (Figure 1b). TEM images demonstrate that ultrafine Pd NPs are uniformly distributed in the polymeric frameworks due to the coordination effect between Pd NPs and the imidazole moieties in PTPI-Me scaffold (Figure 1c, d). The average size of Pd NPs is evaluated through statistical analysis of TEM image and is found to be 2.7 nm (Figure 1c, inset). However, some Pd aggregates are still observed (Figure 1d).



Figure 1. (a) TEM image of PTPI-Me; (b-e) SEM (b), TEM (c, d), and HRTEM (e) images of Pd@PTPI-Me, inset of c shows Pd NPs size distribution; (f) EDX mapping image of Pd@PTPI-Me.

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The HRTEM image of Pd@PTPI-Me revealed that the lattice-fringe spacing of Pd NPs was found to be 0.21 nm (Figure 1e), which corresponded to the Pd (111) plane. In addition, energy-dispersive X-ray (EDX) mapping clearly confirmed that Pd NPs were homogeneously distributed in the PTPI-Me frameworks (Figure 1f).

Powder X-Ray diffraction (PXRD) showed almost no peak for PTPI-Me support, while weak peaks at $2\theta = 40.0^{\circ}$, 46.1° and 67.5° were observed for Pd@PTPI-Me, indicating the successful immobilization of Pd(0) NPs (Figure 2b). The Pd content in Pd@PTPI-Me was 0.13 mmol g⁻¹ as determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The chemical composition of Pd@PTPI-Me was further confirmed by X-ray photoelectron spectroscopy (XPS). As shown in Figure 2c, the binding energies at around 285 eV, 339 eV, 398 eV and 532 eV corresponded to C 1s, Pd 3d, N 1s and O 1s, respectively. The Pd 3d spectrum was split into double peaks. The peaks at around 340.1 eV (Pd 3d_{3/2}) and 334.2 eV (Pd 3d_{5/2}) are assigned to Pd(0) species, while the peaks at around 341.3 eV (Pd $3d_{3/2}$) and 335.2 eV (Pd 3d_{5/2}) are attributed to Pd(II) species that may be resulted from the reoxidation of Pd(0) owing to air contact (Figure 2d). The ratio of Pd(0) to Pd(II) in Pd@PTPI-Me is calculated to be 1.71 according to their relative peak area, indicating that Pd(0) is predominant, which is consistent with PXRD analysis.



Figure 2. (a) Solid-state ¹³C NMR spectrum of PTPI-Me; (b) PXRD patterns of PTPI-Me, Pd@PTPI-Me and Pd(0); (c, d) XPS survey (c) and Pd 3d (d) spectra of Pd@PTPI-Me; (e) N₂ adsorption/desorption isotherms of PTPI-Me and Pd@PTPI-Me; (f) Pore size distribution of PTPI-Me and Pd@PTPI-Me.

The porous properties of PTPI-Me and Pd@PTPI-Me were finally investigated by N_2 isotherms at 77 K. As shown in Figure

2e, the isotherms of PTPI-Me showed a type IV behavior. The rapid uptake of N_2 at low pressure (P/P₀ < 0.1) indicated the existence of micropores in PTPI-Me, and the obvious hysteresis between the adsorption/desorption branch confirmed the presence of mesopores. The coexistence of micropores and mesopores in PTPI-Me was further confirmed by the pore size distribution (Figure 2f). The Brunauer-Emmett-Teller (BET) surface area of PTPI-Me is 712 $m^2 g^{-1}$, and the total pore volume is 0.52 cm³ g⁻¹. After loading of Pd NPs, Pd@PTPI-Me exhibited a type IV isotherms, and the pore size distribution also suggested the existence of mesopores. The BET surface area and the total pore volume of Pd@PTPI-Me were decreased to 457 m² g⁻¹ and 0.33 cm³ g⁻¹, respectively, owing to the pore filling and mass increment of Pd NPs in the polymer scaffold. However, the Pd@PTPI-Me still remained mesoporous structure and could be applicable to heterogeneous catalysis.

Table 1. Optimization of reaction conditions in the cyanation of iodobenzene [a]

	\bigcirc	I + K₄[Fe	(CN) ₆]	Pd@PTPI-Me, 120 °C	DMF	CN
entry	Pd (mol %)	Temp. (°C)	Time (h)	solvent	alkali	yield (%) ^[b]
1		120	10	DMF	Na ₂ CO ₃	No reaction
2	0.2	120	10	DMF	Na ₂ CO ₃	90
3	0.3	120	10	DMF	Na ₂ CO ₃	99
4	0.3	80	10	DMF	Na ₂ CO ₃	No reaction
5	0.3	120	7	DMF	Na ₂ CO ₃	88
6	0.3	120	10	DMSO	Na ₂ CO ₃	95
7	0.3	120	10	DMAC	Na ₂ CO ₃	94
8	0.3	120	10	DMF		30
9	0.3	120	10	DMF	K ₂ CO ₃	98
10	0.3	120	10	DMF	NaOH	87
11	0.3	120	10	DMF	K ₃ PO ₄	90
12	0.3	120	10	DMF	CH₃COOK	95

[a] Reaction conditions: iodobenzene, 0.2 mmol; K₄[Fe(CN)₆], 0.05 mmol;
Pd@PTPI-Me, 4.5 mg, 0.3 mol % of Pd; solvent, 2 mL; alkali, 0.08 mmol. [b]
GC yield.

Aromatic nitriles are extensively used in agrochemical and pharmaceutical industries due to their flexible nature of nitrile moiety, which can be easily converted to versatile functionalities such as aldehyde, ketone, amine and so forth. Cyanation of aryl halides under the catalysis of transition metals is a general and powerful approach to achieve aromatic nitriles. Pd-catalyzed cyanation is of special interest because of its milder reaction conditions, economical cost and good recyclability.^[32] To evaluate the catalytic ability of Pd@PTPI-Me, the transformation of iodobenzene to benzonitrile has been selected as the model reaction. K₄[Fe(CN)₆] was used as cyanide source because it is nontoxic and inexpensive. After the reaction was completed, the mixture was extracted with ethyl acetate, and the yield was determined by GC-MS. When the reaction was carried out in the absence of Pd@PTPI-Me, no desired product was obtained (Table 1, entry 1). The yield of benzonitrile was improved with increasing the amount of Pd@PTPI-Me. For example, 0.2 mol%

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Pd gave nearly 90% of benzonitrile (Table 1, entry 2). When Pd was increased to 0.3 mol%, a yield of 99% was achieved, indicating that almost all iodobenzene has been converted to benzonitrile (Table 1, entry 3). The optimal reaction conditions were selected by a serial of experiments with varying reaction time, temperature, alkali and solvent. The reaction temperature was considered to be the most crucial factor for the cyanation of iodobenzene. No product was obtained when the reaction proceeded at 80 °C, while other reaction parameters kept unchanged (Table 1, entry 4). The possible reason is that the $K_4[Fe(CN)_6]$ has low solubility at low temperature. Meanwhile, the change of reaction time from 10 h to 7 h reduces the yield from 99% to 88% (Table 1, entry 5). The solvent has less influence on the yield of benzonitrile (Table 1, entry 6, 7). On the

contrary, obvious change of yield was observed with different alkalis. A quite low yield was obtained in the absence of alkali (Table 1, entry 8). We are glad to found that carbonates such as K₂CO₃ and Na₂CO₃ give rise to high yield of 98% and 99% (Table 1, entry 9, 3), while NaOH can lower the yield from 99% to 87% (Table 1, entry 10). In the case of K₃PO₄, the yield of the desired product is slightly reduced to 90% (Table 1, entry 11). Previous investigation indicated that alkalis such as carbonates can help to dissolve K₄[Fe(CN)₆] and to promote [Fe(CN)₆]⁴⁻ species to form intermediates.^[33] These results suggested that the highest yield (~ 99%) was achieved in DMF with 0.3 mol% Pd as the catalyst and Na₂CO₃ as the alkali after heating at 120 °C for 10 h.

Fable 2. Cyanation	reaction of substituted	aryl iodides cata	lyzed by Pd@PTPI-Me ^[a] .
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[a] Reaction conditions: substrate (0.40 mmol), K₄[Fe(CN)₆] (0.10 mmol), Na₂CO₃ (0.16 mmol), DMF (4 mL), temperature 120 °C, 9 mg Pd@PTPI-Me (0.3 mol% of Pd). [b] Isolated yield. [c] K₄[Fe(CN)₆] = 0.2 mmol.

As we all known, the catalytic properties of heterogeneous Pd catalysts supported on porous materials are closely related to the active Pd species, Pd particle size/morphology, specific surface area/pore volume, and the characteristics of the porous supports.^[34-39] By comparison with other reported heterogeneous Pd catalysts, for example, Pd-metalated porous polycarbazole (Pd-CNP-2) catalyst with 8.7 wt% Pd loading showed 99% yield in the cyanation of 1,4-dibromobenzene with K₄[Fe(CN)₆] in the presence of 0.41 mol% Pd.^[40] Another example is porous ZnO-supported Pd catalyst with only 0.11 mmol g⁻¹ Pd loading for the

same cyanation reaction, in which above 70% product yield was obtained for ligand-, base-, and additive-free cyanation of aryl bromides with K_4 [Fe(CN)₆] in the presence of 0.2 mol% Pd.^[41] In our case, it is not surprised that Pd@PTPI-Me catalyst shows a 99% product yield in the cyanation of highly active aryl iodides with 0.3 mol% Pd. The porous-structured Pd@PTPI-Me catalyst had a relatively high BET surface area and a small Pd particle size, which facilitated the accessibility to the catalytic site as well as effective mass transfer.^[34] Meanwhile, the electron-donating nature of TPI-Me also helped to improve catalytic efficiency and

stability.^[36] Last but not least, the Pd(0)/Pd(II) ratio in Pd@PTPI-Me was much higher than that of previous reported Pd catalysts, which also played an important role in cyanation reaction.^[27,29]

The excellent catalytic activity of Pd@PTPI-Me in cyanation of iodobenzene promoted us to investigate the generality of such catalytic system. A series of aryl iodides with different electronic groups and steric hindrances were explored. As shown in Table 2, a promising yield was observed at 10 h when para-position of iodobenzene was substituted by electron-withdrawing groups, such as -NO₂, -CN, -COCH₃ and -COOCH₃ (Table 2, entry 1, 2, 4, 5). However, the conversion of 2-iodobenzonitrile was slightly decreased compared with 4-iodobenzonitrile owing to the steric hindrance in the ortho-position (Table 2, entry 3). As expected, the electron-donating substrates including 4-iodoanisole and 4iodoaniline gave slightly low yields even at a longer reaction time (Table 2, entry 8, 9). Most importantly, p-diiodobenzene could be converted to 1,4-benzodinitrile at a relatively high yield with only increasing K₄[Fe(CN)₆] while keeping the same amount of Pd (Table 2, entry 6), which was promising for the application in cvanation reaction.



Figure 3. Recyclability of the Pd@PTPI-Me catalyst.

Recyclability is an important character for the heterogeneous catalysts, which is also an intrinsic advantage of such catalysts as compared to their homogeneous counterparts. With this in mind, the recyclability of Pd@PTPI-Me was further studied using the model reaction of iodobenzene transforming to benzonitrile. In this case, the used Pd@PTPI-Me was simply recovered by centrifugation, washing, followed by drying, and added to a new reaction. As shown in Figure 3, the recovered catalyst displayed a negligible decrease in catalytic activity after five cycles. The TEM image of the collected Pd catalyst after five consecutive cycles revealed no distinct aggregation of Pd NPs, indicating the good stability of Pd NPs in the PTPI-Me frameworks (Figure S5). These results demonstrated that the as-fabricated Pd@PTPI-Me was an efficient heterogeneous Pd catalyst for the cyanation reaction.

Conclusions

In summary, we have prepared a triphenylimidazole-based porous organic polymer (PTPI-Me) via Yamamoto homocoupling

reaction. Due to the well-incorporated imidazole moieties in the PTPI-Me frameworks, the Pd NPs were successfully grown and uniformly dispersed on the polymeric scaffold, affording a stably heterogeneous Pd@PTPI-Me catalyst. This Pd catalyst with only 0.13 mmol g⁻¹ Pd loading was highly active in the cyanation of aryl iodides. Notably, the heterogeneous Pd@PTPI-Me catalyst was recyclable without sacrificing the catalytic performance. This study provides an effective strategy for the construction of POPs supported Pd catalysts, which is general and applicable for other heterogeneous catalysts.

Experimental Section

Materials and Instruments

All chemicals were purchased from Aladdin Reagent (Shanghai) Co., Ltd. and used without further purification unless otherwise noted. ¹H NMR and ¹³C NMR spectra were recorded with a 400 MHz Bruker AV-400 NMR spectrometer. Solid-state ¹³C CP/MAS NMR was performed on a Bruker SB Avance III 500 MHz spectrometer with a 4 mm double-resonance MAS probe. FT-IR spectra were recorded on a Nicolet 6700 spectrometer. Inductively coupled plasma atomic emission spectrometry (ICP-AES) analyse was carried out on a Perkin Elmer Optima 5300 DV spectrometer. Thermogravimetric analysis (TGA) was carried out on a STA 449C instrument with a heating rate of 5 °C min⁻¹ under a N₂ flow rate of 60 mL min⁻¹. The powder X-ray diffraction (PXRD) patterns of the samples were collected on a Rigaku/Max-2500PC X-ray diffractometer with Cu Ka radiation, the operation voltage and current were maintained at 40 kV and 25 mA, respectively. The N₂ adsorption/desorption isotherms were characterized at 77 K using Micromeritics TriStar II 3020. The specific surface area was obtained by Brunauer-Emmett-Teller (BET) method. The pore size distribution was calculated from the adsorption branches of the isotherms using the DFT model. Scanning electron microscopy (SEM) images were recorded using S-4800 (JEOL) operated at an acceleration voltage of 10 kV. The transmission electron microscopy (TEM) images were recorded on a JEM-1011 (JEOL) transmission electron microscope operating at 100 kV. The X-ray photoelectron spectroscopy (XPS) was performed on a K-Alpha 1063 photoelectron spectrometer (Thermo Fisher Scientific, England) with AI-Ka X-ray radiation as the X-ray source for excitation. The conversion of the iodobenzene was calculated with an Agilent 5975 GC-MS instrument.

Synthesis of monomer (TPI-Me)

In a typical procedure, 4,4'-dibromobenzil (3.68 g, 100 mmol), 4bromobenzaldehyde (1.85 g, 100 mmol), ammonium acetate (2.31 g, 300 mmol) and 50 mL of acetic acid were added into round-bottom flask successively. The mixture was refluxed for 6 h and a light yellow solution was obtained. After cooling to ambient temperature, excessive deionized water was added to the mixture and white precipitates was formed. After filtration and recrystallized from ethyl acetate, the product TPI was collected. Subsequently, methyl iodide (0.85 g, 6.0 mmol) was added to the mixture of TPI (3.2 g, 6.0 mmol), K₂CO₃ (2.5 g, 18 mmol) and 20 mL of dry DMF at 0 °C for 0.5 h. Afterward, the reaction was heated to reflux for 6 h. After the reaction was complete, excessive water was added and a white solid was precipitated. The TPI-Me monomer was obtained by filtration, drying overnight and recrystallization from ethyl acetate (yield: 90.3%).

Synthesis of porous organic polymer (PTPI-Me)

The porous organic polymer (PTPI-Me) was synthesized by Yamamoto coupling reaction (Scheme 1). Typically, under the protection of nitrogen, TPI-Me (0.55 g, 1.0 mmol), bis(1,5-cyclooctadiene)nickel(0) (1.0 g, 3.6 mmol), 2,2'-bipyridyl (0.40 g, 3.6 mmol), 1,5-cyclooctadiene (0.60 g, 3.6 mmol) and dry DMF (38 mL) were added into a flask with a stirrer. The mixture was heated to 80 °C for 72 h, and a purple suspension was obtained. After cooling to ambient temperature, the mixture was treated with concentrated HCI, and the derived milky white suspension was filtered and successively washed with NaOH solution (10%), dichloromethane, methanol and petroleum ether. Finally, a light yellow PTPI-Me (yield: 90.7%) was obtained after drying under vacuum at 80 °C for 24 h.

Synthesis of Pd@PTIP-Me

PTPI-Me (100 mg) was first dispersed in 5 mL of DMF, and then 0.8 mL H_2PdCl_4 aqueous solution (0.2 mol mL⁻¹) was added. The mixture was refluxed at 100 °C for 5 h. After cooling to 0 °C, excessive NaBH₄ was added and stirred. The mixture was collected by centrifugation, and then washed with deionized water and ethanol. Finally, the targeted catalyst Pd@PTIP-Me was achieved by drying under vacuum at 80 °C for 24 h.

General procedure for the catalytic reaction

The catalytic performance of the Pd@PTIP-Me was evaluated by cyanation of aryl iodides. In a typical procedure, iodobenzene (0.4 mmol), K₄[Fe(CN)₆]·3H₂O (0.1 mmol), Na₂CO₃ (0.16 mmol), 9 mg of Pd@PTIP-Me and DMF (4 mL) were added into a Schlenk tube under N2 atmosphere, and the mixture was heated to 120 °C for 12 h. After the reaction was completed (monitored by TLC), the mixture was cooled to room temperature, and the solid catalyst was separated by centrifugation. The solution was extracted with ethyl acetate, and the combined organic layer was dried over anhydrous MgSO₄. After evaporating off the solvent, the crude product was further purified by column chromatography, and the structure was confirmed by ¹H NMR and ¹³C NMR spectra. The separated solid catalyst was washed with ethanol and water for several times, and the recovered catalyst was directly used for the next run with the addition of fresh substrates. Conversion was estimated by an Agilent 5975 GC-MS instrument (EI).

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Keywords: porous organic polymers • polytriphenylimidazole • Pd nanoparticles • heterogeneous catalyst • cyanation

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A novel porous organic polytriphenylimidazole (PTPI-Me) synthesized by Yamamoto coupling was utilized as a heterogeneous platform for loading of ultrafine Pd NPs (2.7 nm). The resultant Pd@PTPI-Me catalyst with a Pd loading of 0.13 mmol g^{-1} exhibited superior catalytic activity and recyclability towards cyanation of aryl iodides, which is one of the most efficient POP-supported Pd catalysts with such a low Pd loading.

Haiwen Yu, Siqi Xu, Yijiang Liu, * Hongbiao Chen* and Huaming Li

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Title: Porous Organic Polytriphenylimidazole Decorated with Palladium Nanoparticles for Cyanation of Aryl lodides