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Palladium Nanoparticles Supported on a Porous Organic Polymer: An Efficient Catalyst for Suzuki-Miyaura and Sonogashira Coupling Reactions

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A new porous organic polymer (POP) with high thermal stability and large surface area has been synthesized and applied in the preparation of Pd/POP catalyst. Pd/POP was characterized by XRD, TGA, SEM and TEM. The catalyst consists of highly dispersed palladium nanoparticles of 0.9—4 nm size on POP with a large surface area of 650 m^2/g. It presents high catalytic activity for Suzuki-Miyaura and Sonogashira reactions. The catalyst was reusable for three to five times without significant loss of activity.

Keywords heterogeneous catalysis, palladium, porous organic polymers, Suzuki-Miyaura reaction, Sonogashira coupling reaction

Introduction

The palladium-catalyzed Suzuki-Miyaura[1] and Sonogashira[2] coupling reactions are very important and powerful methods for the construction of carbon-carbon bonds. Significant progress has been achieved with various homogeneous palladium catalysts.[3-5] However, it is difficult to separate and reuse the expensive palladium catalysts and palladium species may also be a toxic contamination in the product in the homogeneous catalysis system. To overcome these problems, considerable efforts have been made to the development of the heterogeneous palladium catalysts.[6,7] A successful example is that palladium nanoparticles (PdNPs) have been used for the formation of C—C bonds. It is a well-known fact that PdNPs without stabilization are prone to aggregate and lose their catalytic activity. Therefore, looking for suitable support materials is still an attractive challenge in the field of heterogeneous catalysis. So far various solid materials, such as mesoporous silica,[8-14] ionic liquids,[15-17] polymers,[18-23] metal oxides,[24-28] inorganic and organic hybrid materials,[29,30] and metal organic frameworks (MOFs)[31-34] have been successfully applied as catalyst supports, but less attention has been paid to the porous organic polymers (POPs).[35-37]

Porous organic polymers (POPs), including covalent organic frameworks (COFs), porous aromatic frameworks (PAFs), porous polymer networks (PPNs) and microporous organic networks (MONs) are constructed from well-designed organic groups by coupling or condensation reactions.[36-45] POPs, just like the metal-organic framework (MOF) counterparts,[46,47] are the promising solid platforms for heterogeneous catalysis due to their large surface area, low skeleton density and high thermal and chemical stability. Furthermore, POPs have the advantages of synthetic diversity and tunability of the pore size and surface area, and can easily be prepared by conventional methods. Therefore, they are attractive materials for heterogeneous catalyst supports. Great efforts have led to the rapid development of various POPs with interesting structures and properties, but there is still a pressing requirement to improve their application in heterogeneous catalysis.

This work describes the preparation of the PdNPs which were supported on a porous organic polymer (Pd/POP) and their application in Suzuki-Miyaura and Sonogashira coupling reactions.

Experimental

Materials and instruments

The FTIR spectra were taken at Perkin-Elmer Paragon 1000 spectrometer with KBr tablet at the ratio of 1∶100, wavelength range from 400—4000 cm^{-1}. The nitrogen adsorption-desorption isotherms were measured at 77 K with a Quantachrome Nova 4200E Porosimeter. Powder X-ray diffraction patterns were recorded using a Rigaku D/MAX-2200/PC equipped with Cu Kα radiation (40 kV, 20 mA) at the rate of 5.0 (°)/min over the range of 3°—60° (2θ). Thermogravimetric analysis (TGA) was performed from 20—800 ℃

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in nitrogen atmosphere with a Pyris 1 TGA instrument at a heating rate of 10 ℃/min. The scanning electron microscopy (SEM) patterns were observed by JSM-7401F instrument. High-resolution transmission electron microscopy (HRTEM) was performed by JEOL-JEM-3010 microscope operating at 200 kV (C_s=0.6 mm, resolution 1.7 Å). Images were recorded by means of a CCD camera (MultiScan model 794, Gatan, 1024×1024 pixels, pixel size 24 μm×24 μm) at 5—80 k magnification under low-dose conditions. The concentration of palladium supported on POP was determined by using inductively coupled plasma-atomic emission spectrometry (ICP-AES, iCAP 6000 Radial). ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury plus-400 spectrometer in $CDCl_3$ with TMS as the internal standard unless otherwise specified. Column chromatography was run on silica gel (200—300 mesh). All chemicals were purchased from Energy Chemical China, they were AR grade and used as received.

Preparation of the catalyst

Preparation of POP A mixture of tetra(4-azidophenyl)methane (484 mg, 1 mmol), 1,4-dialkynyl-benzene (252 mg, 2 mmol), $CuSO_4\cdot5H_2O$ (100 mg, 0.4 mmol) and sodium ascorbate (80 mg, 0.4 mmol) was stirred in DMF (100 mL) under nitrogen at 70 ℃ for 12 h, then stirred at 100 ℃ for 72 h.[48] The isolated solid was suspended in water (100 mL), to which EDTA-2Na (745 mg, 2 mmol) was added, the mixture was stirred for 12 h at room temperature. The solid was isolated by filtration and treated with EDTA-2Na solution for another 12 h. The solid was isolated by filtration, washed with water several times, followed by ethanol and ether. The material was further purified by Soxhlet extraction in a mixture of THF, chloroform and acetone for 24 h to eliminate the traces of unreacted starting materials, and dried under vacuum. POP was obtained as dark yellow powder (700 mg, yield 95%).

Preparation of Pd/POP The catalyst Pd/POP was prepared following the reported procedure.[31] $PdCl_2$ (0.14 g, 0.79 mmol) and NaCl (0.16 g, 2.63 mmol) were stirred in DMF (80 mL), and a clear orange solution was obtained. The freshly prepared POP (2.8 g) was added to the solution. After stirring for 10 min, 85% hydrazine hydrate (1 mL) was added dropwise to the suspension under vigorous stirring, the mixture changed to dark gray immediately. The resulted solid was isolated by filtration, washed with DMF (20 mL×2), followed by ether (10 mL×2), and dried under vacuum. Pd/POP was obtained as a black powder and kept under nitrogen atmosphere. The concentration of palladium supported on POP was 3 wt%, determined by ICP-AES.

Preparation of model compound tetrakis[4-(4-phenyl-1*H*-1,2,3-triazo-1-yl)phenyl]methane

A mixture of tetrakis(4-azidophenyl)methane (200 mg, 0.4 mmol), $CuSO_4\cdot5H_2O$ (119.8 mg, 0.48 mmol), sodium ascorbate (221.9 mg, 1.12 mmol) and phenylacetylene (818 mg, 8 mmol) in DMF (25 mL) was stirred at 90 ℃ for 48 h. The precipitate was collected by filtration, washed with excessive water, followed by methanol and dichloromethane, dried under vacuum. The model compound was obtained as a yellow solid. ^{1}H NMR (400 MHz, DMSO) δ: 9.27 (s, 4H), 7.97 (d, J=8.8 Hz, 8H), 7.91 (d, J=7.2 Hz, 8H), 7.60 (d, J=8.8 Hz, 8H), 7.6 (d, J=8.8 Hz, 8H), 7.46 (t, J=7.7 Hz, 8H), 7.35 (t, J=7.4 Hz, 4H); ^{13}C NMR (100 MHz, DMSO) δ: 148.00, 146.71, 135.52, 132.40, 130.87, 129.69, 128.98, 126.03, 120.74, 120.32, 59.98.

General procedure for the Pd/POP-catalyzed Suzuki-Miyaura coupling reaction

Bromobenzene (0.314 g, 2.0 mmol), phenylboronic acid (0.366 g 3.0 mmol), a certain base and Pd/POP (10.0 mg, 0.14 mol%) and solvent (10 mL) were added to a 50 mL flask, stirred at 70 ℃ for appropriate time. The mixture was cooled to room temperature, the solid was isolated by filtration and washed with MeOH (10 mL×2) and CH_2Cl_2 (10 mL×2), the solution was collected and the solvents were removed under vacuum. The residue was extracted with CH_2Cl_2 (20 mL×2), washed with brine (20 mL), dried over sodium sulfate, and the solvent was removed under reduced pressure. The obtained crude product was purified by silica gel chromatography using hexane as the eluent.

Reuse of the catalyst in Suzuki-Miyaura coupling reaction

After the first run of the coupling reaction between bromobenzene and phenylboronic acid, the catalyst was isolated by centrifuge, and washed with MeOH (10 mL×2), transferred to a 50 mL Schlenk flask, then KOH (0.224 g, 4.0 mmol), bromobenzene (0.314 g, 2.0 mmol) and phenylboronic acid (0.366 g, 3.0 mmol) were added. The mixture was heated for a certain time while stirring. The product was isolated following the procedure as the first run and the catalyst was collected and reused for the next cycle.

General procedure for the Pd/POP-catalyzed Sonogashira coupling reaction

A 50 mL Schlenk flask was charged with Pd/POP (15 mg, 0.14 mol% of Pd) and a certain base, and purged with nitrogen, solvent (10 mL) and phenylacetylene (0.337 g, 3.3 mmol) were added, followed by iodobenzene (0.612 g, 3.0 mmol). The flask was maintained at 80 ℃ in an oil bath and stirred for the appropriate reaction time under nitrogen. The isolation and purification procedures of the product were similar to those in Suzuki-Miyaura coupling reaction.

Reuse of the catalyst in Sonogashira coupling reaction

After the first run of the coupling reaction between phenylacetylene and iodobenzene, the catalyst was isolated by centrifuge, and washed with methanol (10 mL×2). The catalyst was transferred to a 50 mL Schlenk flask, then NaOH (0.3 g, 7.5 mmol), phenylacetylene (0.337 g, 3.3 mmol) and iodobenzene (0.612 g, 3 mmol) were added, and the mixture was heated while stirring for a certain time. The product was isolated following the procedure as the first run and the catalyst was collected and reused for the next cycle.

Results and Discussion

Characterizations of POP and Pd/POP

As shown in Scheme 1, POP was obtained in an excellent yield by copper catalyzed Huisgen 1,3-dipolar cycloaddition, the so-called click reaction[49,50] between 1,4-dialkynylbenzene and 4-tetra(azidophenyl)methane [Caution: tetra(azidophenyl)methane is a potential explosive)]. The FTIR spectrum of POP (Figure 1) matches with that of the model compound. A broad N=N stretch can be observed at 1610 cm^{-1}, together with a weak C=CH band at 3030 cm^{-1}, which are consistent with the formation of the expected triazole ring. IR stretches from unreacted azide could not be observed at 2120 cm^{-1}, implying that the azide-alkyne coupling is complete. A strong and broad stretch at 3400 cm^{-1} is also observed, elucidating the presence of adsorbed water. The solid state ^{13}C NMR spectrum of POP (Figure 2) matches well with that of the model compound, further confirming the formation of POP.

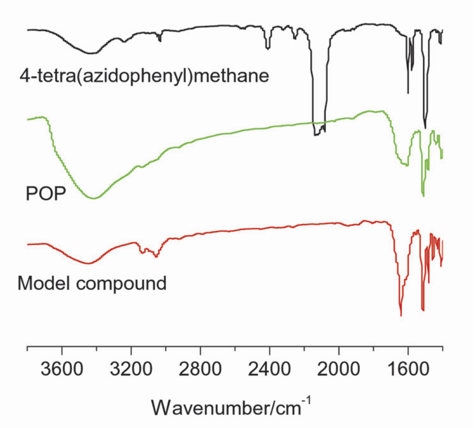


Figure 1 The FTIR spectra of POP and the model compound.

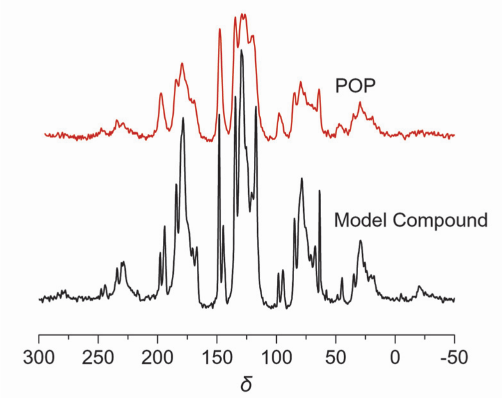
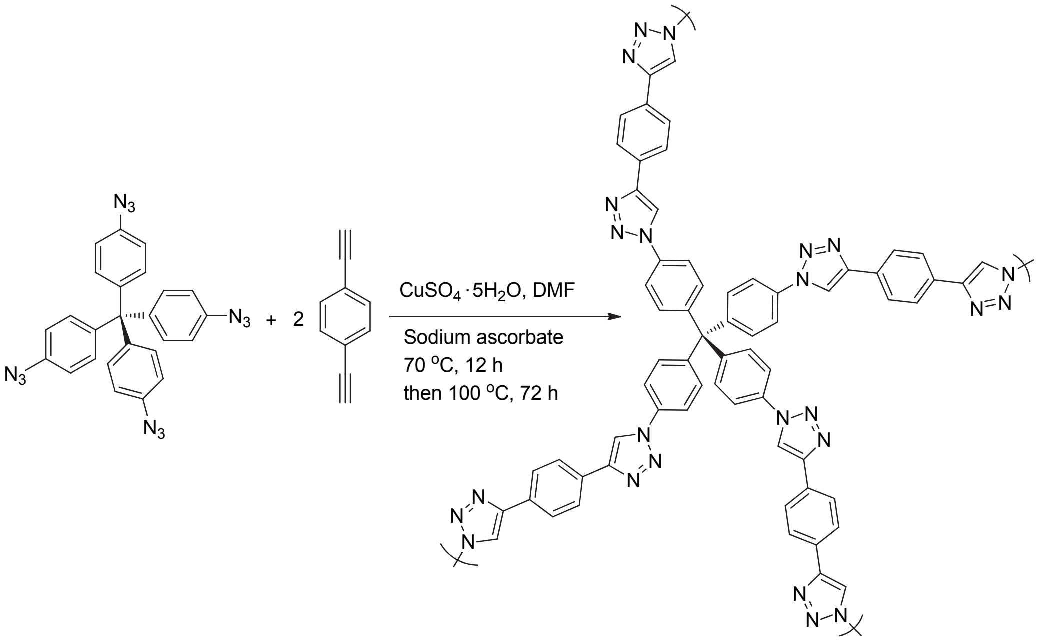


Figure 2 The solid ^{13}C NMR of POP and the model compound.

The N_2 sorption isotherms (Figure 3) were measured at 77 K. POP gave a Brunauer-Emmett-Teller (BET) surface area of 651 m^2/g, including micropore area of 596 m^2/g and external surface area of 55 m^2/g. Pd/POP exhibited a BET surface area of 573 m^2/g, including micropore area of 494 m^2/g and external surface area of 79 m^2/g. The obvious abrupt on the desorption curve at $p/p_0=0.4$ proves the existence of the microporous and mesoporous pores. The pore size (Figure 4) distributions of POP range from 0.4 to 1.2 nm and the maximum pores are at 0.45 nm calculated by density functional

Scheme 1 Synthesis of POP



theory (DFT). The sizes of Pd nanoparticles range from 0.9 to 4 nm estimated by TEM image (Figure 5).

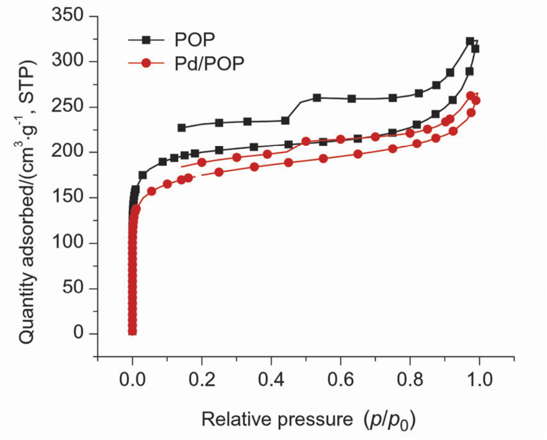


Figure 3 Nitrogen adsorption-desorption isotherms of POP and Pd/POP.

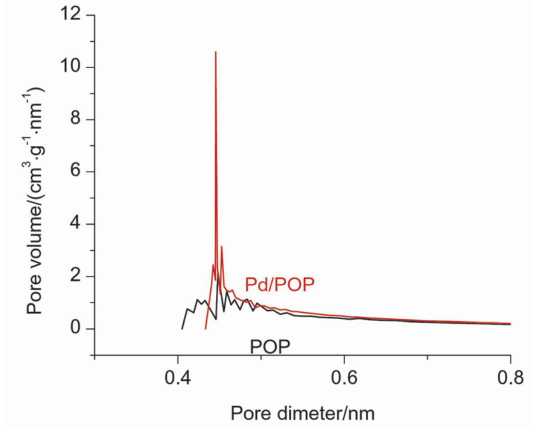


Figure 4 Pore size distribution curves of POP and Pd/POP.

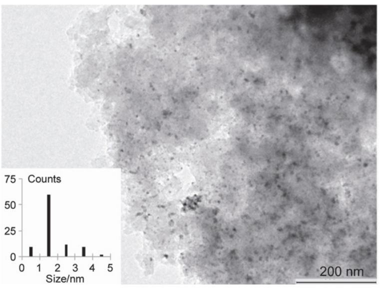


Figure 5 The TEM image of Pd/POP and the histogram illustrating the particle size distribution of Pd(0) nanoparticles.

The powder X-ray diffraction of POP and Pd/POP (Figure 6) showed that the materials were amorphous, and the characteristic peak of Pd(111) at $2\theta=40.1°$ confirms the existence of palladium nanoparticles. Thermogravimetric analysis (TGA) showed that POP and Pd/POP were stable up to 200 ℃, and decomposed above 250 ℃ (Figure 7). Weight loss up to 100 ℃ was about 10% for both POP and Pd/POP, resulting from loss of the absorbed solvent DMF. The second weight loss between 240 and 350 ℃ is related to the decomposition of small molecular fragments of low polymerization. The last zone of weight loss from 350 to 800 ℃ corresponds to the decomposition of molecular fragments of higher molecular weight polymer.

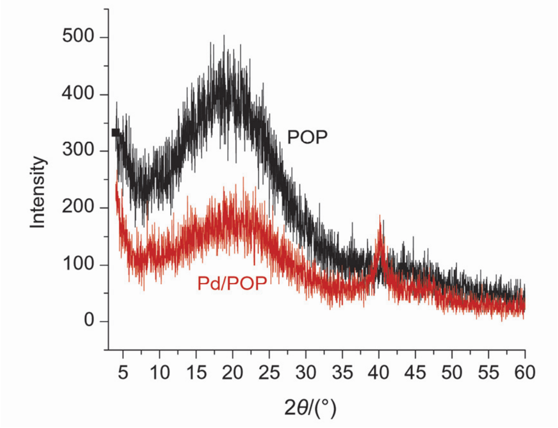


Figure 6 Powder X-ray diffraction patterns of POP and Pd/POP.

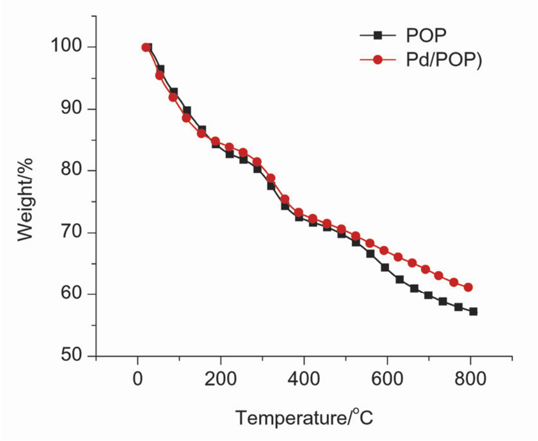


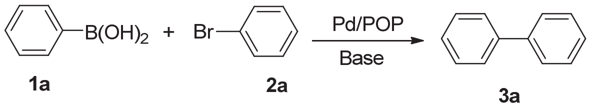
Figure 7 TGA of POP and Pd/ POP under nitrogen atmosphere.

Application in Suzuki-Miyaura reaction

Bromobenzene and phenylboronic acid were used as the substrates to investigate the reaction conditions. The influence of different bases (Table 1) on the reaction was studied using CH_3OH as solvent. No product was obtained (Entry 1) in the absence of base, lower yields were observed in case of Na_2CO_3 (Entry 2), K_2CO_3 (Entry 5), and Cs_2CO_3 (Entry 9). The reactions using $Na_3PO_4 \cdot 12H_2O$, $K_3PO_4 \cdot 3H_2O$ or KOH as the base gave the yield nearly 60%. The yield is related to the molar ratio of these bases (Entries 3, 4, 6—8, 11—14). It gave the highest yield of 68% when 2 equiv. of KOH was used (Entry 11).

A significant effect of the reaction temperature was observed (Table 1). Raising the temperature of oil bath from 20 to 70 ℃ improved the yields (Entries 15—17, 20), 70 ℃ gave the highest yield of 92% (Entry 20), but the yield was reduced at 80 ℃ (Entry 11).

Table 1 The optimization of reaction conditions for Suzuki-Miyaura reaction[a]



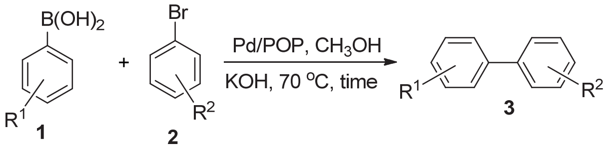
Entry	Base (Dosage/equiv.)	Solvent (V ∶ V)	T/℃	Yield[b]/%
1[c]	None	MeOH	80	0
2	Na$_2$CO$_3$ (2.0)	MeOH	80	19
3	Na$_3$PO$_4$•12H$_2$O (2.0)	MeOH	80	57
4	Na$_3$PO$_4$•12H$_2$O (2.5)	MeOH	80	22
5	K$_2$CO$_3$ (2.0)	MeOH	80	32
6	K$_3$PO$_4$•3H$_2$O (1.5)	MeOH	80	60
7	K$_3$PO$_4$•3H$_2$O (2.0)	MeOH	80	36
8	K$_3$PO$_4$•3H$_2$O (2.5)	MeOH	80	31
9	Cs$_2$CO$_3$ (2.0)	MeOH	80	18
10	NaOH (2.0)	MeOH	80	35
11	KOH (2.0)	MeOH	80	68
12	KOH (1.0)	MeOH	80	57
13	KOH (1.5)	MeOH	80	64
14	KOH (2.5)	MeOH	80	48
15	KOH (2.0)	MeOH	20	38
16	KOH (2.0)	MeOH	40	50
17	KOH (2.0)	MeOH	60	72
18[d]	KOH (2.0)	THF	70	13
19[d]	KOH (2.0)	Dioxane	70	4
20	KOH (2.0)	MeOH	70	92
21[d]	KOH (2.0)	MeOH/H$_2$O (2 ∶ 1)	70	66
22[d]	KOH (2.0)	MeOH/H$_2$O (1 ∶ 1)	70	45
23	KOH (2.0)	EtOH	70	83
24	KOH (2.0)	*i*-PrOH	70	69

[a] Reaction conditions: bromobenzene (0.314 g, 2.0 mmol), phenylbronic acid (0.366 g, 3.0 mmol), Pd/POP (10.0 mg, 0.14 mol%), 10 mL of solvent, oil bath, 3 h. [b] Isolated yield. [c] 24 h. [d] 6 h.

The solvent is also an important factor, both aprotic and protic solvents were tested (Table 1). Aprotic solvents such as THF and dioxane (Entries 18, 19) gave low yields. Protic solvents like pure alcohol and mixed alcohol aqueous solvents were tested, the mixed alcohol aqueous solvents gave moderate yield (Entries 21, 22), which may be due to the reduced solubility of reactants in mixed solvents. Among alcohol solvents, *i*-PrOH gave 69% yield (Entry 24), and 83% yield for EtOH (Entry 23), however MeOH resulted in full conversion and 92% yield in 3 h (Entry 20).

It was found that the best system for the reaction was 2.0 mmol of bromobenzene, 3.0 mmol of phenylboronic acid, 10 mg (3 wt%) Pd/POP, 4.0 mmol of KOH, 70 ℃ (oil bath) and 10 mL of methanol as solvent. These conditions were applied for various aryl bromides and phenylboronic acid to assess the scope towards a wide range of aryl bromides bearing either electron-withdrawing or electron-donating functional groups, the results are summarized in Table 2.

Table 2 Suzuki-Miyaura reaction with various substituents[a]



Entry	R^1	R^2	Product	Time/h	Yield[b]/%
1	H	H	**3a**	3	92
2	H	4-CF$_3$	**3b**	3	97
3	H	3,5-CF$_3$	**3c**	3	91
4	H	4-Me	**3d**	3	91
5	H	2-MeO	**3e**	12	77
6	H	2-Me	**3f**	3	76
7	H	4-MeO	**3g**	12	32
8	H	2-CF$_3$	**3h**	12	18
9	4-Me	H	**3d**	3	95
10	4-MeO	H	**3g**	3	96
11	2-MeO	H	**3e**	3	90
12	2-Me	H	**3f**	3	72
13	4-CF$_3$	H	**3b**	3	32
14	3,5-CF$_3$	H	**3c**	3	18
15	2-CF$_3$	H	**3h**	3	11
16	4-Me	4-Me	**3i**	3	73
17	4-CF$_3$	4-CF$_3$	**3j**	3	69
18	2-MeO	2-MeO	**3k**	12	49
19	4-MeO	4-MeO	**3l**	12	14
20	2-Me	2-Me	**3m**	12	14

[a] Reaction conditions: bromobenzene derivatives (2.0 mmol), derivatives of phenylboronic acid (3.0 mmol), Pd/POP (10.0 mg, 0.14 mol%), KOH (0.224 g, 4.0 mmol), CH$_3$OH (10 mL), 70 ℃ (oil bath). [b] Isolated yield.

Phenylboronic acid reacts with various bromobenzene with electron-rich and electron-deficient groups (Table 2, Entries 2—6), giving the corresponding products **3b**—**3h** with good yields. Electron-deficient *para*-substituted aryl bromides (Entry 2) showed higher activity compared to electron-rich aryl bromides (Entry 7), in the process of coupling with phenylboronic acid. *ortho*-Bromobenzotrifluoride gave the lowest yield of 18% (Entry 8), another two *ortho*-substituted aryl bromides gave the yield of no more than 80% (Entries 5, 6), this implies that their steric effect is lower than that of *ortho*-bromobenzotrifluoride. The electron-donating function group on aryl bromides is unfavorable to the coupling reaction, this can also be clearly seen from the reaction between 4-methoxybromobenzene and phenylboronic acid (Entries 7). Electronic-rich *para*-substituted arylboronic acids (Entries 9, 10) process better than electron-deficient ones (Entries 13—15). Cross couplings of both substituted substrates with various electron-withdrawing or electron-donating functional groups were also investigated and all gave yields less than 75% (Entries 16—20).

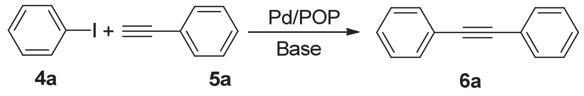
The catalytic system was applied for the coupling rection bewteen chlorobenzene and phenylboronic acid, however poor yield was obtained.

Application in Sonogashira coupling reactions

Pd/POP catalyst was also applied to the Sonogashira reaction. The coupling of iodobenzene (0.612 g, 3.0 mmol) with phenylacetylene (0.337 g, 3.3 mmol) was initially studied as a model reaction. The reaction conditions were systematically optimized. MeOH, EtOH, and *i*-PrOH were used in the presence of $K_3PO_4•3H_2O$ as the base to optimize the solvent which resulted in 82%, 4% and 71% yields, respectively (Table 3, Entries 1—3). So MeOH was chosen as the appropriate solvent.

No product was found without base (Table 3, Entry 4). Low yield was observed in case of Na_2CO_3 (Entry 14). The reactions using KOH, K_2CO_3, NaOH, $K_3PO_4•3H_2O$ as the base gave better yields, the molar ratio of these bases were changed to further increase the yields (Entries 5—13). Finally 2.5 equiv. of NaOH gave the highest yield of 99% (Entry 10).

Table 3 Optimization of reaction conditions for Sonogashira reaction[a]

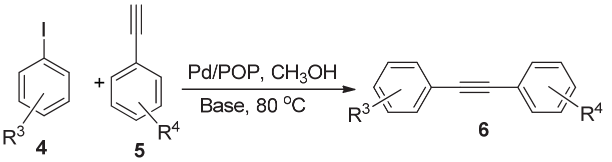


Entry	Base (Dosage/equiv.)	Solvent	Yield[b]/%
1	$K_3PO_4•3H_2O$ (1.5)	CH_3OH	82
2	$K_3PO_4•3H_2O$ (1.5)	C_2H_5OH	4
3	$K_3PO_4•3H_2O$ (1.5)	i-PrOH	71
4	None	CH_3OH	0
5	KOH (1.5)	CH_3OH	77
6	KOH (2.0)	CH_3OH	94
7	K_2CO_3 (1.5)	CH_3OH	91
8	NaOH (1.5)	CH_3OH	94
9	NaOH (2.0)	CH_3OH	98
10	NaOH (2.5)	CH_3OH	99
11	NaOH (1.0)	CH_3OH	61
12	$K_3PO_4•3H_2O$ (1.5)	CH_3OH	82
13	$K_3PO_4•3H_2O$ (2.0)	CH_3OH	75
14	Na_2CO_3 (1.5)	CH_3OH	28

[a] Reaction conditions: iodobenzene (0.612 g, 3.0 mmol), phenylacetylene (0.337 g, 3.3 mmol), Pd/POP (15.0 mg, 0.14 mol%), CH_3OH (10 mL), 80 ℃ (oil bath), 12 h. [b] Isolated yield.

The best system for Sonogashira reaction was 3.0 mmol of aryl iodide, 3.3 mmol of phenylacetylene, 15 mg (0.14 mol%) Pd/POP, 7.5 mmol of NaOH, 80 ℃ (oil bath) and 10 mL of methanol. The conditions tolerated the presence of a wide variety of functional groups, affording excellent yields of corresponding products. As shown in Table 4, coupling reactions between the arynes and iodobenzene with electron-withdrawing groups at *para*-position enhanced the yields (Entries 6, 8, 12—14). Phenylacetylene with electron-donating group gave the lower yield (Entry 9). When iodobenzene bearing electron-donating groups or phenylacetylene with electron-withdrawing groups were used as substrates, the yield was low (Entry 15). However, the catalyst is not active enough for bromobenzene.

Table 4 Study of the Sonogashira reaction with various substituents[a]

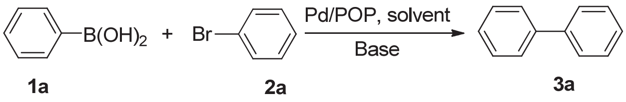


Entry	R^3	R^4	Product	Time/h	Yield[b]/%
1	H	H	**6a**	12	99
2	4-Me	H	**6b**	12	93
3	2-MeO	H	**6c**	12	93
4	4-MeO	H	**6d**	12	97
5	2-CF_3	H	**6e**	12	49
6	4-CF_3	H	**6f**	12	>99
7	3,5-CF_3	H	**6g**	12	92
8	4-NO_2	H	**6h**	12	>99
9	H	4-Me	**6b**	12	57
10	H	4-F	**6i**	12	94
11	H	4-C_5H_{11}	**6j**	12	93
12	4-NO_2	4-MeO	**6k**	12	99
13	4-CF_3	4-MeO	**6l**	12	99
14	4-CF_3	4-Me	**6m**	12	99
15	4-Me	4-F	**6n**	12	51
16	4-MeO	4-F	**6o**	12	92
17	4-Me	4-Me	**6p**	12	83
18	4-MeO	4-MeO	**6q**	12	41

[a] Reaction conditions: iodobenzene derivatives (3.0 mmol), derivatives of phenylacetylene (3.3 mmol), Pd/POP (15.0 mg, 0.14 mol%), NaOH (0.3 g, 7.5 mmol), CH_3OH (10 mL), 80 ℃ (oil bath). [b] Isolated yield.

Activity of recycled Pd/POP catalyst was also examined. No significant change was found in the second run (Table 5, Entry 2), but the activity decreased from the third run (Entries 3—5) in Suzuki reaction, however, it did not change significantly up to the fifth run in Sonogashira reaction (Table 6). The reduction of the catalyst reactivity may result from dissolution of palladium particles from the surface of the solid support or formation of Pd clusters in solution, and the palladium may redeposite onto the support.[51-55] Leaching of Pd in filtrate may lead to lowering its concentration in the Pd/POP catalyst. In order to find out the reasons for deactivation of catalyst, the ICP-AES analysis was performed to the cold filtrations after the first, third and fifth runs, Pd leaching amount was less than 0.3 and 0.5 mg•L^{-1} in Suzuki, and Sonogashira reactions, respectively. Negligible Pd leaching confirmed the heterogeneous process similar to the Pd/C system.[56] The catalyst is not active enough for aryl chlorides in Suzuki coupling reactions compared with the Pd/C[56] and Poly-NHC-2-Pd^{2+}[43] catalysts, but it is more stable than Pd/MOF-5, which has the similar reactivity in catalyzing Sonogashira reaction.[31] XPS survey scans of both fresh and used catalyst showed characteristic peaks of Pd3d along with C1s peak (Figure 8). High resolution narrow scans for Pd3d level show peaks at 336.6, 341.8 eV (fresh); 335.3, 340.5 eV (used in Suzuki reaction) and 335.5, 340.7 eV (used in Sonogashira reaction) for Pd 3d$_{5/2}$ and Pd 3d$_{3/2}$, which clearly indicates that the palladium is in the zero oxidation state even after five catalytic cycles. The slight negative XPS shift in the used catalyst comparing to the fresh one may be caused by the size changes of the PdNPs before and after use.[57]

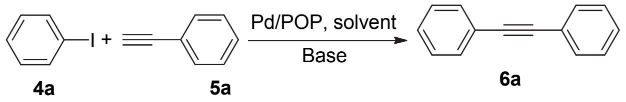
Table 5 Reusability of Pd/POP in Suzuki-Miyaura reaction[a]



Entry	Run	Time/h	Yield[b]/%
1	1	3	92
2	2	3	90
3	3	3	63
4	4	5	52
5	5	5	47

[a] Reaction conditions: bromobenzene (0.314 g, 2.0 mmol), phenylboronic acid (0.366 g, 3.0 mmol), Pd/POP (10.0 mg, 0.14 mmol%), KOH (0.224 g, 4.0 mmol), CH_3OH (10 mL), 70 ℃ (oil bath), 3 h. [b] Isolated yield.

Table 6 Reusability of Pd/POP in Sonogashira reaction[a]



Entry	Run	Time/h	Yield[b]/%
1	1	12	99
2	2	12	94
3	3	12	91
4	4	12	88
5	5	12	72

[a] Reaction conditions: iodobenzene (0.612 g, 3.0 mmol), phenylacetylene (0.337 g, 3.3 mmol), Pd/POP (15.0 mg, 0.14 mol%), CH_3OH (10 mL), NaOH (0.3 g, 7.5mmol). 80 ℃ (oil bath). [b] Isolated yield.

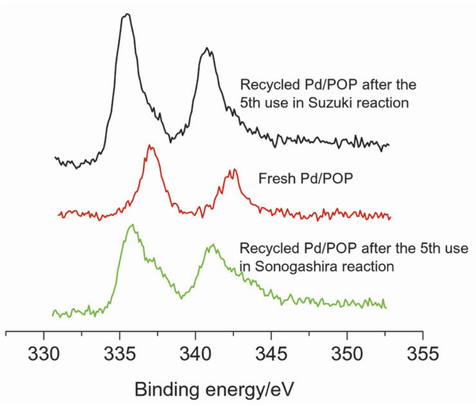


Figure 8 The XPS scan of fresh Pd/POP, Pd/POP in Suzuki reaction and Pd/POP in Sonogashira reaction after the 5th run.

The TEM images of the Pd/POP after fifth run (Figure 9) elucidate that the PdNPs aggregated at certain places. Therefore, the deactivation of the catalyst is mainly due to the aggregation of PdNPs.

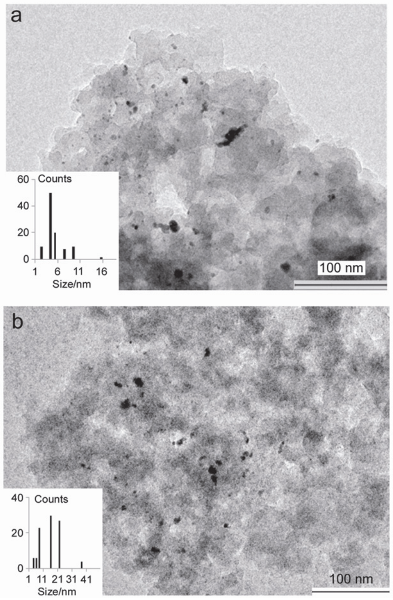


Figure 9 The TEM images of Pd/POP and the histograms illustrating the particle size distribution of Pd (0) nanoparticles in Suzuki-Miyaura reaction (a) and Sonogashira reaction (b) after the 5th run.

Conclusions

In summary, a porous organic polymer has been prepared from tetra(4-azidophenyl)methane and 1,4-dialkynylbenzene. Subsequent modification with palladium nanoparticles yielded a Pd/POP catalyst. Gas adsorption showed that Pd/POP had a BET specific surface area of 573 m^2•g^{-1} and a pore volume of 0.23 cm^3•g^{-1}. Although Pd nanoparticles are not in the pores, Pd/POP showed good catalytic activity in the Suzuki-Miyaura coupling reaction of arylboronic acids and aryl halides and Sonogashira reaction between halobenzenes and phenylacetylene. Both the reactions are applicable to a wide range of substrates with good electronic and steric tolerance. Additionally, the catalyst could be used for at least three times without significant loss of activity. The results represent a strategy to prepare a heterogeneous catalyst.

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