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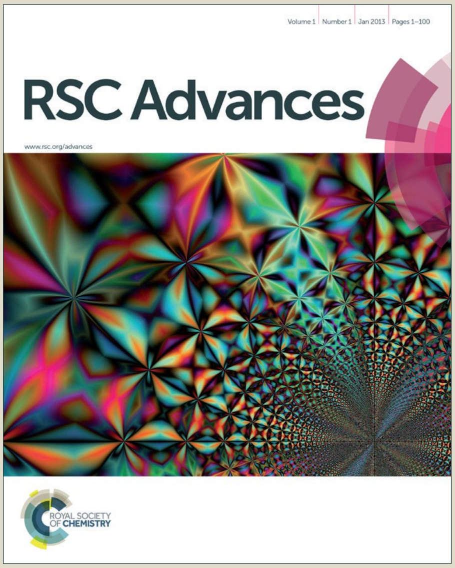

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Palladium Nanoparticle Embedded in Metal Organic Framework Derived Porous Carbon: Synthesis and Application for Efficient Suzuki-Miyaura Coupling Reaction

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A nanoporous carbon (NPC) material was prepared by one-step direct carbonization of metal organic framework, MOF-5, without additional carbon precursors. Pd nanoparticles were immobilized on MOF-5-derived NPC by an impregnation method coupled with subsequent reduction with $NaBH_4$. The prepared catalyst was in-depth characterized by X-ray photoelectron spectroscopy, transmission electron microscopy, scanning electron microscope, and N_2 adsorption. The catalyst was used to catalyze the Suzuki-Miyaura coupling reactions and exhibited high catalytic efficiency with the yields ranging from 90% to 99% under mild conditions. The results demonstrated the great application potential of the MOF precursor based metal nanoparticles composite in catalysis.

Introduction

Palladium-catalyzed Suzuki-Miyaura cross-coupling reaction plays a key role in the synthesis of pharmaceuticals, herbicides, polymers and so on[1-3]. Palladium organic complexes containing ligands such as phosphine, dibenzylideneacetone, and carbenes have been widely used as homogeneous catalysts for the Suzuki-Miyaura cross-coupling reaction[4,5]. Although homogeneous catalytic systems are known to exhibit high activity, problems associated with the separation and recovery of the expensive catalysts limit their large scale application in industry[6,7]. On the contrary, heterogeneous catalysts can be easily recovered from the reaction system and readily reused. Recently, as a new generation of heterogeneous catalysts, Pd nanoparticles supported on solid supports has gained much attention due to their ease of separation and satisfactory reusability, superior catalytic performance, good stability in comparison to the traditional homogeneous catalysts[8]. The supports for metal nanoparticles also play an important role to prevent the aggregation of metal nanoparticles, which would result in loss of their catalytic activity. Therefore, suitable supports for Pd nanoparticle catalysts are highly desirable.

Several solid materials, such as active carbon[9], zeolites[10], mesoporous silica[11] and polymers[12,13], have been used as heterogeneous catalyst supports for C-C coupling reactions. However, some of the supported catalysts involve disadvantages such as, uneven distribution of the active sites, tedious preparation of the catalyst, lower catalytic activity and so on. Therefore, the development of highly active and selective heterogeneous catalysts for catalyzing C-C coupling reactions under mild conditions is required for practical use.

Recently, nanoporous carbons (NPCs) materials, have been touted as ideal catalyst support for heterogeneous catalyst because of their high specific surface area and porosity[14] in combination with high chemical (acid and base resistant), thermal (>1000K) and excellent mechanical stability[15,16]. Highly porous carbons can be prepared via a variety of methods, including direct pyrolysis of organic precursors, activation (physical or chemical) of carbon[17], hard-template or soft-template route[18], and nanocast method[19]. However, these methods often encounter one or more shortcomings, such as the obtained carbon materials often contain disordered structures, the templates need to be removed after carbonization, the preparation process is tedious and so on. Therefore, the development of novel synthesis strategy based on facile, versatile, and reproducible method is highly desirable.

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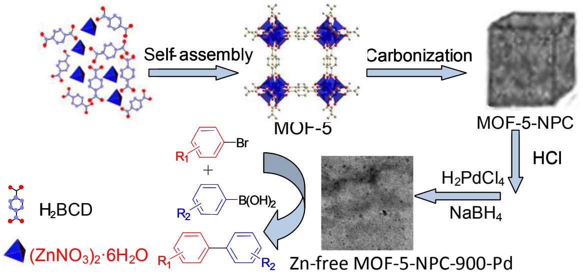
As an emerging class of highly porous material, metal-organic frameworks (MOFs) have gained particular attention in recent years mainly due to their ease of preparation, designable framework structures and multifunctional nature[20]. MOFs with fascinating diverse structures, topologies, permanent nanoscale porosity, high surface area and uniform structured cavities, have been demonstrated to be ideal templates for fabricating nanoporous carbon. Highly nanoporous carbon can be fabricated by direct carbonization of different MOFs without the need of additional carbon precursors because MOFs was taken as both a sacrificial template and a secondary carbon precursor. Several MOFs, such as UiO-66[21], MIL-100[22], and Al-PCP[23], have recently been demonstrated as promising templates to construct porous carbons. Compared with the conventional nanocasting technique with several steps, the merit of this approach lies in that it is a facile, controllable, and single-step procedure method. NPCs derived from MOFs have found a wide range of applications in different fields, such as water treatment, contamination removal[24], separation, electrode materials[18], gas storage[25] and carriers for drug delivery systems [26], due to their high specific surface area, large pore volume, high thermal stability and excellent electrochemical performance.

In continuation of our efforts in the development of a sustainable and active catalyst system[27-29], in this paper, porous carbon was fabricated by one–step direct carbonization of MOF-5 ($Zn_4O(H\text{-}BDC)_3$, BDC = 1,4-benzenedicarboxylate) without using any additional carbon precursors. The obtained MOF-5-derived NPC exhibited a high specific surface area and large pore volume. Pd nanoparticles were immobilized on MOF-5-derived NPC by an impregnation method coupled with subsequent reduction with $NaBH_4$. To evaluate the performance the MOF-5-NPC-Pd, Suzuki–Miyaura reaction was selected as the model reaction. The results indicated that the MOF-5-NPC-Pd can catalyzed the Suzuki–Miyaura reaction efficiently under mild conditions.



Scheme 1 The preparation process of the catalyst and the Suzuki coupling reaction.

Experimental

Materials and methods

Zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$), terephthalic acid (H_2BCD), sodium borohydride, potassium carbonate, chloroform, and N-N dimethylformamide (DMF) were all obtained from Chengxin Chemical Reagents Company (Baoding, China). Aryl boronic acids, aryl halides, and palladium chloride ($PdCl_2$) were purchased from Aladdin Reagent Limited Company and used as received.

X-ray photoelectron spectroscopy (XPS) was performed with a PHI 1600 spectroscope using Mg $K\alpha$ X-ray source for excitation. Scanning electron microscopy (SEM) studies were conducted on a Hitachi (Model S4800) instrument. The size and morphology of the nanoparticles were observed by transmission electron microscopy (TEM) using a JEOL model JEM-2011(HR) at 200 kV. The Brunauer–Emmett–Teller (BET) surface areas were determined from the N_2 adsorption at 300 K using V-Sorb 2800P (China). The amount of Pd and Zn was determined by means of inductively coupled plasma atomic emission spectroscopy (ICP-AES) on Thermo Elemental IRIS Intrepid II.

Synthesis of MOF-5-NPC

MOF-5 nanocrystals were prepared according to the reported synthesis protocol[30]. Typically, MOF-5 was prepared by mixing $ZnNO_3{\cdot}6H_2O$ (10.4 g) and H_2BCD (2 g) in DMF (140 mL) until complete dissolution of the solids. Then, the mixture was transferred into a round-bottom flask connected to a condenser and heated at 120 °C for 24 h. After cooling, the supernatant was removed and crystals deposited on the bottom of the flask were collected, washed with DMF, and then immersed in fresh chloroform overnight. The chloroform was changed twice during two days. Finally, crystals were collected and dried in a vacuum at 50 °C for 3 h. For the synthesis of MOF-5-NPC, MOF-5 was directly carbonized at various temperatures (from 700 to 1000 °C) under a flow of nitrogen gas. After the carbonization, the obtained black samples were denoted as MOF-5-NPC-700, MOF-5-NPC-800, MOF-5-NPC-900, and MOF-5-NPC-1000, respectively.

Synthesis of MOF-5-NPC-Pd

Pd nanoparticles were supported on the MOF-5-NPC by an impregnation method. 50 mg of MOF-5-NPC was dispersed in 5 mL (1 mg/mL) chlorine palladium acid solution. Then the resulting mixture was magnetically stirred in ambient tempreture. After 5 hours later, the obtained solution was filtered off and washed three times with distilled water, then dried under vacuum at 60 °C. The resultant was dispersed in 5 mL of water, and 5.5 mg $NaBH_4$ (0.027 mmol) was added slowly to the resulting mixture. Subsequently, the pH of the mixture was adjusted to 10 with 10% sodium hydroxide solutions and the reaction was stirred for 2 h at 98 °C. Finally, the isolated product was washed with distilled water and dried at 60 °C for 5 hours in vacuum.

To preparation of the Zn-free MOF-5-NPC-900-Pd, 50 mg of MOF-5-NPC-900 powder was dispersed in 20 mL of 10 % HCl and standed for 6 h. And then the mixture was filtered and washed with distilled water. Finally, the MOF-5-NPC-900 without Zn or ZnO was obtained by vacuum drying at 60 °C for 2 hours.

The Zn-free MOF-5-NPC-900-Pd was prepared according to the same procedure mentioned above except that 50 mg MOF-5-NPC-900 was replaced by 50 mg Zn-free MOF-5-NPC-900.

General procedure for Suzuki–Miyaura reactions

Phenylboronic acid (0.6 mmol), aryl halide (0.5 mmol), base (1.5 mmol), solvents (EtOH/H_2O = 1: 1, v/v, 4 mL) and a certain amount of the catalyst was placed in a 25 mL round-bottom flask, then the reaction mixture was shaken in an air atmosphere for an appropriate time at room temperature. After completing of the reaction, the reactor was diluted with 10mL of H_2O and the organic products were extracted with ethyl acetate (3 × 10 mL). Then the combined organic solution dried over anhydrous $MgSO_4$ and filtered. The pure products were obtained by flash chromatography using petroleum ether: ethyl acetate as the eluent. The preparation process of the catalyst and the Suzuki coupling reaction were illustrated in Scheme 1.

Results and discussion

Characterization of the catalyst

Table 1 The nitrogen adsorption-desorption isotherm and pore size distributions of the MOF-5-NPC.

Catalysts	S_{BET} /$m^2 \cdot g^{-1}$	Pore width ^{a} /nm	V ^{b} /$cm^3 \cdot g^{-1}$
MOF-5-NPC-700	222	9.10	0.51
MOF-5-NPC-800	400	6.60	0.56
MOF-5-NPC-900	2478	4.8	2.96
MOF-5-NPC-1000	1778	5.47	2.93
Zn-freeMOF-5-NPC-900	2700	4.35	2.88
Zn-freeMOF-5-NPC-900-Pd	2200	4.83	2.65

a. total adsorption average pore width; b. total pore volume.

In order to explore the pore structure of MOF-5-NPC samples, the nitrogen adsorption and desorption isotherms were recorded at 77 K. As we can see from Table 1, the sample carbonized at 700 °C and 800 °C, the BET surface area is just 222 and 400 $m^2 \cdot g^{-1}$ and the total adsorption average pore width is 9.1 nm to 5.47 nm, respectively. These results indicate that the heat treatment at 700 °C and 800 °C is insufficient to carbonize MOF-5 into porous carbon. When the temperature increased to 900 °C, the BET surface area is 2478 $m^2 \cdot g^{-1}$ and the total adsorption average pore width is 4.8 nm. As displayed in Fig. S1 (see ESI†), the sample MOF-5-NPC-900 showed typical Type IV isotherm with sharp uptakes at low relative pressure ($P/P^0 < 0.1$) and slight uptakes at high relative pressure ($P/P^0 > 0.9$), indicating that they are totally microporous materials with some macropores probably forming between particles. However, when the carbonization temperature was raise to 1000 °C, the BET surface area decreased to 1778 $m^2 \cdot g^{-1}$ and the total adsorption average pore width rise to 5.47 nm. The reason may be ascribed to that the carbon framework of MOF-5 has already graphitization at high temperature. In addition, it also worth mentioned that the surface area of Zn-free MOF-5-NPC-900 raised to 2700 $m^2 \cdot g^{-1}$ after the removal of Zn or ZnO impurities through washing with HCl solution. After embedded Pd NPs in the Zn-free MOF-5-NPC-900, the BET surface area of the sample deceased to 2200 $m^2 \cdot g^{-1}$, the result indicated that Pd NPs were embedded in the Zn-free MOF-5-NPC-900 successfully. The amount of Zn in Zn-freeMOF-5-NPC- 900 was determined by means of ICP-AES and the amount is < 0.001 wt %.

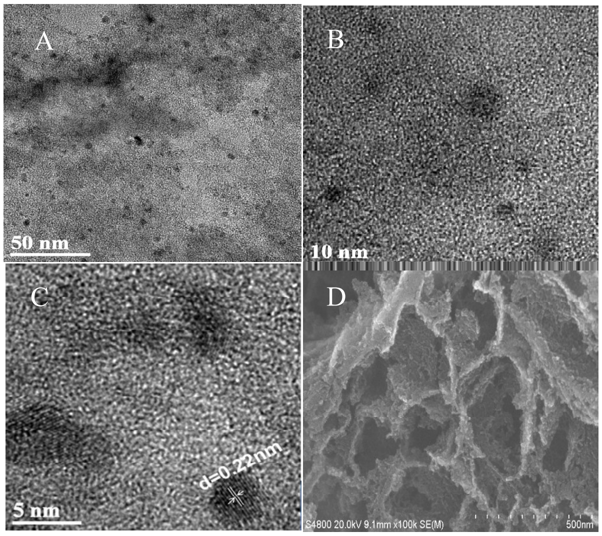


Fig. 1 TEM (A), HRTEM (B,C) and SEM (D) images of Zn-free MOF-5-NPC-900-Pd.

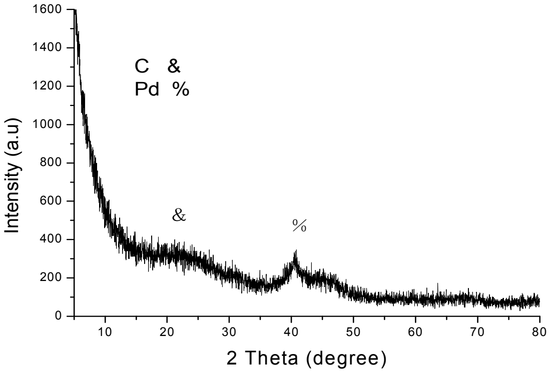


Fig. 2 The XRD image of Zn-free MOF-5-NPC-900-Pd.

The TEM investigations are carried out to observe the size, and the distribution of Pd nanoparticles embedded in Zn-free MOF-5-NPC-900-Pd. The highly existence of Pd nanoparticles, which embedded in Zn-free MOF-5-NPC-900 was clearly observed in Fig. 1A and 1B. The density of Pd nanoparticles in Zn-free MOF-5-NPC-900-Pd nanocatalyst is abundant and these nanoparticles did not form clusters. Fig. 1B and 1C showed the high-resolution TEM (HRTEM) image of the as-prepared catalyst, wherein the lattice spacing is 0.22 nm, which is just the lattice spacing of face centered cubic (fcc) Pd (0.22 nm), further indicating that is Pd nanoparticles. Besides, the mean diameter of the particles was just 2.7 nm and was almost

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similar to the pore diameter of the nanoporous carbon support. It also can be clearly seen from the SEM image (Fig. 1D) that some of the Pd NPs supported on the surface of the Zn-free MOF-5-NPC-900, and the most of them inserted into the cavities of Zn-free MOF-5-NPC-900. The element mapping images (Fig. S2, †) clearly showed the uniform distribution of fine Pd nanoparticles throughout the Zn-free MOF-5-NPC-900-Pd composite.

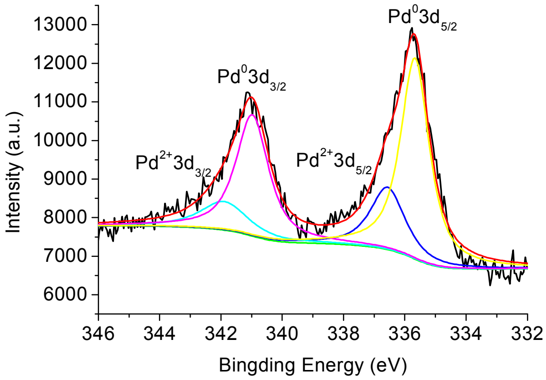

Fig. 3 The XPS image of Zn-free MOF-5-NPC-900-Pd.

The X-ray diffraction (XRD) pattern in Fig. 2 showed the crystalline structure of the Zn-free MOF-5-NPC-900-Pd samples. The wide diffraction peak at $2\theta = 25°$ can be indexed to porous carbon[19]. Besides, we characterized the XRD of the catalyst, the broadly peak appear at 40°, and the peaks at 47° and 68° were very poor, which suggests the well dispersion of Pd nanoparticles[31,32]. The three peaks appear at 40°, 47° and 68° can be assigned to (111), (200) and (220) crystal planes of Pd^0, respectively.

Entry	Catalysts	Yields / %
1	MOF-5-NPC-700-Pd	68
2	MOF-5-NPC-800-Pd	73
3	MOF-5-NPC-900-Pd	92.1
4	MOF-5-NPC-1000-Pd	90.3
5	Zn-free MOF-5-NPC-900-Pd	98.6

Table 2 Suzuki-Miyaura coupling reactions catalyzed by different catalysts

n (K$_2$CO$_3$): n (Aryl iodide): n (Phenylboronic acid) = 4: 1: 1.3; solvent: 2 mL ethanol + 2 mL H$_2$O; the dosage of catalyst was 0.1 mol %; room temperature.

Table 3 Suzuki coupling reactions of aryl halide with phenylboronic acid catalyzed by different catalysts.

Aryl halide	Catalyst	Reaction conditions: solvent/temp./time/Pd loading	Yield/ %	Ref.
Bromobenzene	MOF-5-NPC-900-Pd	EtOH–H$_2$O/25 ^{o}C/1h /0.1mol%	98.6	This work
Bromobenzene	Pd/MIL-53-NH$_2$	EtOH–H$_2$O/40^{o}C /0.5h/0.5mol%	94	35
Bromobenzene	Pd-MCM-41	EtOH–H$_2$O/80^{o}C /12h/0.05mol%	90	36
Iodobenzene	Pd/G	EtOH–H$_2$O/60^{o}C /02-24h/0.3 mol%	74	37
Iodobenzene	Pd/SBA-15	EtOH–H$_2$O/60^{o}C /2-24h/0.3mol%	42	37
4-Bromophenyl acetaldehyde	Pd@p-SiO$_2$	DMF–H$_2$O/200^{o}C /3h/0.003 mol %	65	38
Iodobenzene	Pd/CMK-3	DMF-H$_2$O/150^{o}C/10min/0.02 mol %	99	39

The XPS spectra (Fig. 3) demonstrated that the Pd species embedded in the sample Zn-free MOF-5-NPC-900 was present in metallic state rather than in oxidation state with the bond energies of 335.4 and 341.0 eV in the Pd 3d$_{5/2}$ and 3d$_{3/2}$ levels. As displayed in Fig. 3, the Pd 3d binding energy region was deconvoluted into four peaks with binding energies of 335.6, 337.1, 340.9 and 342.0 eV. The two minor peaks in the Pd 3d spectrum centered at 342.0 and 337.1 eV were ssigned to Pd^{2+} 3d$_{3/2}$ and Pd^{2+} 3d$_{5/2}$, and the other two peaks centered at 340.9 and 335.6 eV are very sharp with a huge intensity. These peaks are assigned to Pd^0 3d$_{3/2}$ and Pd^0 3d$_{5/2}$, respectively[33,34].

Suzuki–Miyaura reactions catalyzed by the prepared catalyst

In order to investigate the catalytic activity of the different catalysts for Suzuki–Miyaura coupling reaction, the coupling of phenyl boronic acid and phenyl bromide was chosen as model reaction. As we can see in Table 2, among all the catalysts tested, Zn-free MOF-5-NPC-900-Pd was found to be the efficient catalyst for it gave the highest yield of product. Besides, as the data in Table 3, comparing with the other reported Pd nanoparticles catalysts in terms of the reaction temperature, the dosage of catalyst and the yield of the product, the catalyst of Zn-free MOF-5-NPC-900-Pd can efficiently catalyze the Suzuki–Miyaura coupling reaction with comparable or higher yield, especially the coupling reaction which catalyzed by the MOF-5-NPC-900-Pd can be performed efficiently at room temperature. Good dispersion of the Pd NPs on the Zn-free MOF-5-NPC-900 is the key factor for the high catalytic activity of the catalyst. This is mainly owing to the high surface area of Zn-free MOF-5-NPC-900, which leads to high dispersion of Pd on the surface of support.

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To standardize the reaction conditions, a series of reactions were performed using several bases, solvents, and different catalyst dosage to obtain the best possible combination. Initially, the experiment was performed using Suzuki-Miyaura cross-coupling reaction of bromobenzene with phenyl boronic acid. As we can see from Table 2, when the reaction was carried out in MeOH, EtOH, DMF and H_2O under the same reaction conditions, the products were obtained in poor yields of 38% - 70% (Table 4, entries 1–4). However, when we adopted the organic/aqueous co-solvent, high yields of 78–98% were obtained (Table 4, entries 5–7). The merit of the co-solvent can be attributed to the good solubility of the organic reactants and the inorganic base, which can accelerate the transmetalation and contributed to fast overall coupling[40]. The reaction conditions were also optimized with respect to the base. The reactions were carried out under similar conditions using different bases such as Na_2CO_3, KOH, NaOH and K_2CO_3 (Table 4, entries 7–12), it clearly indicated that K_2CO_3 was the optimal base for the reaction. No product was obtained without base (Table 4, Entry13). We can also found that the amount of the catalyst has a great influence on the transformation (Table 4 Entries 14–16). When the dosage of the catalyst was above 0.1 mol%, the yield of the product was nearly quantitative (Table 4 Entry 14–15). And yield of the product was decreased to 77% (Table 3, Entry 16) with 0.05 mol% Pd. No product was obtained in the absence of Pd NPs (Table 4, Entry 17).

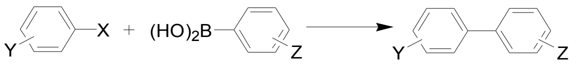
Table 4 Optimization of the reaction conditions for the Suzuki reaction of bromobenzene with phenylboronic acid[a].

Entry	Solvents	Bases	Pd /mol%	Yield /%
Solvents effect				
1	MeOH	K_2CO_3	0.1	53
2	EtOH	K_2CO_3	0.1	70.2
3	DMF	K_2CO_3	0.1	68.1
4	H2O	K_2CO_3	0.1	38
5	EtOH/ H_2O (1 : 3)	K_2CO_3	0.1	78.1
6	EtOH/ H_2O (1: 1)	K_2CO_3	0.1	98.6
7	EtOH/ H2O (3 : 1)	K_2CO_3	0.1	82.3
Bases effect				
8	EtOH/ H_2O (1: 1)	NaOH	0.1	72.1
9	EtOH/ H_2O (1: 1)	KOH	0.1	78.4
10	EtOH/ H_2O (1: 1)	Et_3N	0.1	65
11	EtOH/ H_2O (1: 1)	Na_2CO_3	0.1	89.7
12	EtOH/ H_2O (1: 1)	K2CO3	0.1	98.6
13	EtOH/ H_2O (1: 1)	no base	0.1	trace
Pd mol%				
14	EtOH/ H_2O (1: 1)	K_2CO_3	0.15	99.5
15	EtOH/ H_2O (1: 1)	K_2CO_3	0.1	98.6
16	EtOH/ H_2O (1: 1)	K_2CO_3	0.05	77
17	EtOH/ H_2O (1: 1)	K_2CO_3	0	trace

a. Reaction conditions: bromobenzene (0.5 mmol), phenylboronic acid (0.75 mmol), base (1.5 mmol), solvents (4 mL), room temperature.

To generalize the application of the Zn-free MOF-5-NPC-900-Pd catalyst, the reaction with a diverse range of arylboronic acids and aryl halides were carried out using 0.1 mol% Zn-free MOF-5-NPC-900-Pd as catalyst at room temperature (Table 5). It was seen that the catalytic system was applicable to various aryl bromides and tolerant to a broad range of functional groups and for most of the substrates, the reaction could be completed in 0.75–1.5 h with high yields, with the substrates having either electron-withdrawing groups (-OH, $-COCH_3$, -CHO) or electron-donating groups ($-OCH_3$, -H, $-CH_3$). It was also found that the yield of reaction para- or meta-substituted aryl bromide is higher than those of ortho-position aryl bromides. To test the feasibility of the aforementioned protocol for challenging substrates, several aryl chlorides with phenylboronic acid were employed and the reaction time was extended to 5 h. And the desired products were obtained in moderate yields (Table 5, entries 13, 14, 15), this just owning to the strength of the C-Cl bond, whose bond dissociation energy was 96 kcal/mol[41].

Table 5 Suzuki–Miyaura coupling of arylboronic acids and aryl halides catalyzed by Zn-free MOF-5-NPC-900-Pd[a].



Entry	X	Y	Z	t/ min	Yield[c]/%
1	Br	H	H	60	98.6
2	Br	$4-OCH_3$	H	45	93.1
3	Br	4-OH	H	45	95.4
4	Br	4-OH	$2-CH_3$	60	94.6
5	Br	$2-CH_3$	H	90	91.3
6	Br	$4-CH_3$	$4-NO_2$	90	93.8
7	Br	$4-OCH_3$	$4-NO_2$	50	91
8	Br	$4-COCH_3$	H	45	96.3
9	Br	4-OH	$3-CH_3$	60	96.2
10	Br	4-CHO	H	45	96.1
11	Br	4-CHO	$4-NO_2$	50	93.8
12	Br	$4-COCH_3$	$4-NO_2$	50	95.3
13[b]	Cl	H	H	300	74.2
14[b]	Cl	$4-OCH_3$	H	300	30.7
15[b]	Cl	$2-CH_3$	H	330	25.2

a. Reaction conditions: bromobenzene (0.5 mmol), phenyl boronic acid (0.6 mmol), K_2CO_3 (1.5 mmol), solvent: 2 mL ethanol + 2 mL H_2O, catalyst: Zn-free MOF-5-NPC-900-Pd (0.1 mol%), room temperature; b. aryl chlorides (0.5 mmol), phenyl boronic acid (0.6 mmol), K_2CO_3 (1.5 mmol), solvent: 2 mL ethanol + 2 mL H_2O, catalyst: Zn-free MOF-5-NPC-900-Pd (0.5 mol%), 78 °C, c. yield based on column chromatography.

The recovery and reusability of the catalyst were performed, using the reaction of bromobenzene with benzeneboronic acid as the representative reactants, which catalyzed by 0.1 mol % of Zn-free MOF-5-NPC-900-Pd. The results demonstrated that Zn-free MOF-5-NPC-900-Pd can be reused 5 times without significant loss of catalytic activity (Fig. 4). The catalyst after 5 cycles was characterized by TEM (Fig. S3, †) and XPS (Fig. S4, †), which was similar with that of the fresh prepared catalyst. The amount of Pd in the catalyst after five cycles decreased

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from 4.85% to 4.4%, which might be the reason for the disability of the catalyst.

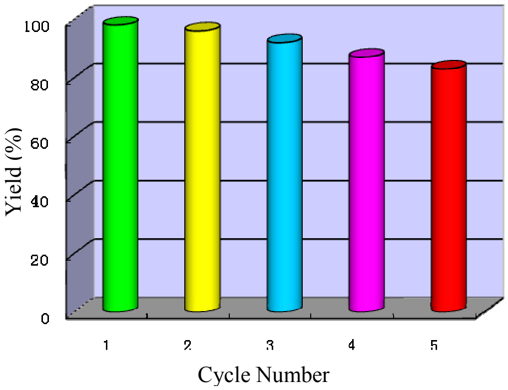

Fig. 4 Recyclability of the Zn-free MOF-5-NPC-900-Pd for the Suzuki-Miyaura reaction.

Conclusions

In summary, we have demonstrated that the fabrication of nanoporous carbon drived from a low-cost, facile and readily reproducible MOF and served as the carrier material for palladium nanoparticles. The resultant Zn-free MOF-5-NPC-900-Pd possessing large pore volumes and high surface area, the catalyst is highly efficient in the Suzuki-Miyaura coupling reaction between aryl boronic acid and aryl halide even the reaction was carried out at ambient temperature. Besides, good yield was obtained after the catalyst reused five cycles. The present research might highlight the development of high catalytic activity heterogeneous catalysts by using MOF-derived porous carbon as hosts for ultrafine metal nanoparticles.

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Graphical abstract

An efficient Pd catalyst supported on novel nanoporous carbon was developed for the Suzuki-Miyaura coupling reaction for the first time. The prepared catalyst can be readily recovered and reused 5 times without significant loss of catalytic activity.