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Original article

N-Doped porous carbon supported palladium nanoparticles as a highly efficient and recyclable catalyst for the Suzuki coupling reaction

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ABSTRACT

A new catalyst, Pd particles supported on the *N*-doped porous carbon (PC) derived from Zn-based metal–organic frameworks (zeolitic imidazolate framework: ZIF-8), was successfully prepared for the first time. The as-prepared catalyst was designated as *N*-doped PC-Pd, and characterized by X-ray diffraction, X-ray photoelectron spectroscopy, transmission electron microscopy, scanning electron microscope, N_2 adsorption and inductively coupled plasma atomic emission spectroscopy. The *N*-doped PC-Pd composite exhibited high catalytic activity toward the Suzuki–Miyaura cross-coupling reactions. The yields of the products were in the range of 90–99%. The catalyst could be readily recycled and reused at least 6 consecutive cycles without a significant loss of its catalytic activity.

1. Introduction

Palladium-catalyzed Suzuki–Miyaura cross-coupling reactions of aryl halides with aryl boronic acids have been accredited as one of the most powerful and convenient synthetic tools to synthesize unsymmetrical bi-aryl compounds [1]. Recently, as a new generation of heterogeneous catalysts for the Suzuki coupling reaction, immobilization of Pd nanoparticles on solid supports has received considerable attention because of their superior catalytic performance, good stability, ease of separation and satisfactory reusability in comparison to the traditional homogeneous catalysts, such as $Pd(OAc)_2$ and $PdCl_2$ [2–6]. Generally, the solid supports, especially carbon nanomaterials such as activated carbon [7], carbon molecular sieve [8], fullerene [9], carbon nanotube [10], nanofiber and graphene [11], have been used as the support for heterogeneous palladium catalysts [12,13]. However, noble metals (*e.g.*, Pt, Pd, and Ru) deposited on these carbon nanomaterials can easily leach during the catalytic processes because the interaction between the metal nanoparticles and the carbon support is weak, and also the chemical or catalytic properties of the traditional carbon supports do not always satisfy the sharply increasing demands of catalysis [9,14].

Currently, nitrogen-doped porous carbon (*N*-doped PC), as a kind of novel material, has attracted considerable attention. *N*-Doped PC promises a wide range of applications in many fields because the incorporation of nitrogen atoms in the carbon architecture can enhance chemical, electrical, and functional properties. Furthermore, thanks to the activation of neighboring carbon atoms caused by the electron affinity of nitrogen, the presence of doped nitrogen heteroatoms on carbon support could stabilize the noble metal (*e.g.*, Pd, Pt) nanoparticles, which is rather beneficial for heterogeneous catalysts [15,16]. In general, *N*-doped PC has conventionally been synthesized *via* chemical vapor deposition, arc-discharge/vaporization approach and plasma treatment under an NH_3 atmosphere or in the presence of other nitrogen sources such as pyridine and acetonitrile [17]. However, these methods often encounter one or more shortcomings, such as rigorous, tedious and multistep preparative processes, and the resulting *N*-doped PC materials often have poor control to the loading amount of nitrogen, and tend to have low chemical homogeneity and disordered structures [18].

Recently, metal–organic frameworks (MOFs) resulting from periodically arranged organometallic complexes have emerged as a new family of solid matrices for use as hard templates for the casting of porous carbons owing to their high specific surface area and porosity, chemical tunability, and well-defined pore structure [14,19–25]. Moreover, since the organic ligands contain various types of atoms (N, O, P or S, *etc.*) other than carbon, MOFs might be a kind of promising candidate for the fabrication of heteroatom-doped

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nanoporous carbon materials with uniformly distributed catalytic centers and a highly active site density. So for, several MOFs containing nitrogen have been demonstrated as promising self-sacrificial templates to afford capacitance [17,24,30] and sensing [28,31]. Zhao et al. synthesized an *N*-doped PC material by direct carbonization of an amine to highly *N*-doped PC materials [20,26,27]. The *N*-doped PC materials have found many applications in gas adsorption [28,29], electrochemical functionalized aluminum-based MOF (amino-MIL-53). The obtained material was used as metal-free, electro-catalysts for oxygen reduction reactions [19]. *N*-doped PC derived from zeolitic imidazolate framework 8 (ZIF-8) nanocrystals has also been used as efficient electro-catalysts for oxygen reduction reactions [18]. However, the application of MOF-derived *N*-doped PC in heterogeneous catalysis is still very limited.

In continuation of our interest in exploring efficient catalysts for organic transformations [2,32,33], in this paper, *N*-doped PC was fabricated by a one-step, direct, carbonization of ZIF-8, which serves as the nitrogen source, the carbon source, as well as the hard template. After that, Pd nanoparticles were supported on the as-prepared *N*-doped PC. In order to evaluate the catalytic activity of the catalyst, the Suzuki–Miyaura coupling reaction was chosen as the model reaction.

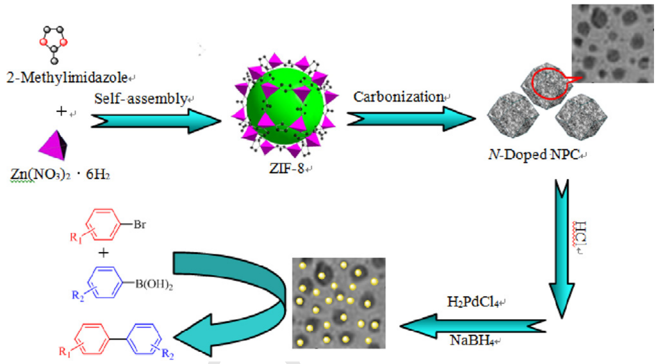
2. Experimental

2-Methylimidazole (99%, MIm), aryl boronic acids, aryl halides, and palladium chloride ($PdCl_2$) were purchased from Aladdin Reagent Limited Company and used as received. Sodium hydroxide, $Zn(NO_3)_2·6H_2O$ (99%) and sodium borohydride were obtained from Chengxin Chemical Reagents Company (Baoding, China) and used without further purification. Methanol and ethanol were provided by the Boaixin Co., Ltd. (Baoding, China).

The size and morphology of the catalyst was observed by scanning electron microscopy (SEM) using a FEI Quanta 200F field emission electron microscope operated at 30 kV. The transmission electron microscopy (TEM) was acquired using a JEOL model JEM-2011(HR) at 200 kV. The X-ray diffraction (XRD) patterns of the samples were recorded with a Rigaku D/max 2500 X-ray diffractometer using Cu Kα radiation (40 kV, 150 mA) in the range 2θ = 10–80°. The Brunauer–Emmett–Teller (BET) surface area and porous structure were measured using V-Sorb 2800P. After the samples were degassed in vacuum at 120 °C for 6 h, the nitrogen adsorption and desorption isotherms were measured at 77 K. X-ray photoelectron spectroscopy (XPS) was performed with a PHI 1600 spectroscope using Mg Kα X-ray source for excitation. The Pd content of the catalyst was determined by means of inductively coupled plasma atomic emission spectroscopy (ICP-AES) on Thermo Elemental IRIS Intrepid II.

The ZIF-8 nanocrystals were prepared according to the reported synthesis protocol [18]. Typically, a solution of $Zn(NO_3)_2·6H_2O$ (2.348 g, 7.89 mmol) in 160 mL of methanol is rapidly poured into a solution of 2-methylimidazole (5.192 g, 63.24 mmol) in 160 mL of methanol under magnetic stirring. The mixture was stirred at room temperature for 1 h. The solid product was separated from the milky colloidal dispersion by centrifugation. After washing with methanol three times, the white ZIF-8 product was dried in a vacuum at 60 °C for 2 h. For the synthesis of *N*-doped PC, the carbonization of the ZIF-8 was performed at 700, 800, 900, 1000 °C for 8 h with an Ar flow, respectively. The resulting products were denoted as *N*-doped PC-700, *N*-doped PC-800, *N*-doped PC-900, and *N*-doped PC-1000, respectively.

Pd nanoparticles were immobilized on the *N*-doped PC by an impregnation method. A 100 mg *N*-doped PC sample was dispersed in 10 mL (1 mg/mL) chlorine palladium acid solution, and then the solution was stirred overnight. After filtration, the solid was washed with water and dried under vacuum at 70 °C. The resultant was dispersed in 10 mL water, then 11 mg sodium borohyride ($NaBH_4$, 0.027 mmol) was added to the solution. The pH of the mixture was adjusted to 10 with a 10% sodium hydroxide solution and the reaction was carried out at 98 °C for 2 h. The obtained solid, *N*-doped PC-Pd, was washed with water and dried in vacuum at 50 °C.



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

For the preparation of Zn-free *N*-doped PC-900-Pd, 100 mg of *N*-doped PC-900 powder was suspended in 35 mL of 10% HCl solution and held for 5 h, and then the mixture was filtered and washed with distilled water. Finally, the *N*-doped PC-900 without ZnO or Zn was obtained by vacuum drying at 80 °C overnight.

The Zn-free *N*-doped PC-900-Pd was fabricated according to the same procedure mentioned above except that 50 mg *N*-doped PC was replaced by 50 mg Zn-free *N*-doped-900-PC.

To a 25 mL round-bottom flask, aryl halide (0.5 mmol), phenylboronic acid (0.6 mmol), base (1.5 mmol), solvents (EtOH/H_2O = 1:1, v/v, 4 mL) and a certain amount of the catalyst *N*-doped PC-Pd were added and stirred at r.t. After a desired reaction time, the mixture was diluted with 10 mL of H_2O and extracted with diethyl ether (3× 10 mL). The organic layers were combined, dried over anhydrous $MgSO_4$ and filtered. Then the filtrate was concentrated by vacuum. The pure products were obtained by flash chromatography using petroleum ether:ethyl acetate (9:1) as the eluent. The preparation process of the catalyst and the Suzuki coupling reaction were illustrated in Scheme 1.

3. Results and discussion

In order to explore the pore structure of *N*-doped PC samples, the nitrogen adsorption and desorption isotherms were recorded at 77 K. As detailed in Table 1, with increasing the carbonization temperature from 700 °C to 900 °C, the experimental multipoint BET surface area of the *N*-doped PC increased from 416 to 740 $cm^3\,g^{-1}$ and the total adsorption average pore width also increased to 5.0 nm. However, the BET then slightly decreased to 720 $cm^3\,g^{-1}$ and the total adsorption average pore width increased to 7.0 nm when the carbonization temperature was 1000 °C. The reason may probably be due to the cleavage of C-N and escape of nitrogen as well as the further graphitization of the carbon framework at high temperature [18,34]. Additionally, it is also worth noting that the BET surface area of *N*-doped PC-900 increased from 740 to 850 $cm^3\,g^{-1}$ after the removal of Zn impurities by washing with HCl. Since the *N*-doped PC was fabricated from the ZIF-8 precursor originating from a carbonization process, the morphology and pore texture of the parent MOF may well be inherited and even enhanced [18].

The TEM and SEM images of Zn-free *N*-doped PC-900 and Zn-free *N*-doped PC-900-Pd samples are shown in Fig. 1. Comparing with Fig. 1A and B, it can be clearly seen that the Pd nanoparticles were highly dispersed on the surface of Zn-free *N*-doped PC-900.

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Table 1
The nitrogen adsorption–desorption isotherm and pore size distributions of the *N*-doped PC.

Catalyst	Surface area ($m^2 g^{-1}$)		Total adsorption average pore width (nm)	SF median pore width (nm)	Total pore volume ($cm^3 g^{-1}$)
	BET method	Langmuir method			
N-doped PC-700	416	560	3.8	0.74	0.7
N-doped PC-800	572	770	3.9	0.77	0.7
N-doped PC-900	740	1010	5.0	0.78	0.65
N-doped PC-1000	722	970	7.0	0.75	1.2
Zn-free *N*-doped PC-900	850	1150	6.7	0.79	0.76
Zn-free *N*-doped PC-900-Pd	600	850	3.5	0.76	0.6

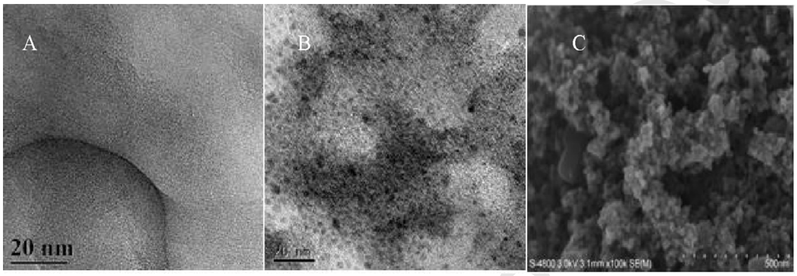

Fig. 1. TEM images of (A) Zn-free *N*-doped PC-900, (B) Zn-free *N*-doped PC-900-Pd and SEM image (C) of Zn-free *N*-doped PC-900-Pd.

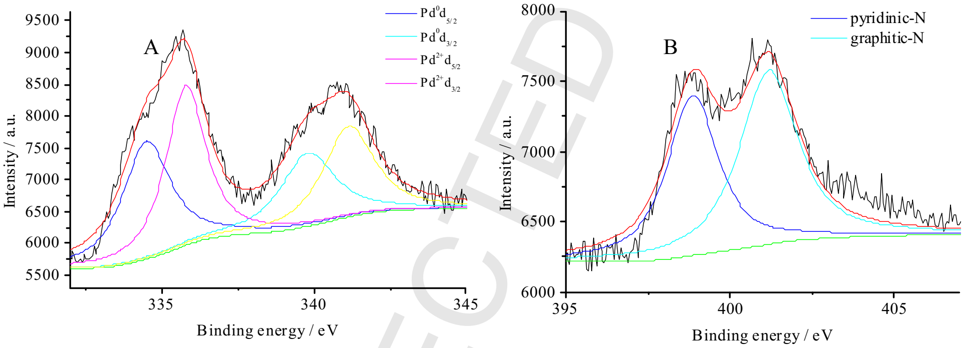

Fig. 2. The XPS image of Zn-free *N*-doped PC-900.

The average size of the Pd nanoparticles is 3.6 nm. The results indicated that the high BET and the pore volume of Zn-free *N*-doped PC-900 promote the dispersion of Pd. Besides, nitrogen in the composite also plays an important role to improve the dispersability of Pd nanoparticles. It also can be clearly seen from the SEM image (Fig. 1C) that some of the Pd NPs were supported on the surface of the Zn-free *N*-doped PC-900, and part of them inserted into the cavities of Zn-free *N*-doped PC-900. The palladium content in Zn-free *N*-doped PC-900-Pd was determined by means of ICP-AES and amounted to 4.03 wt%.

The XPS spectra (Fig. 2A) demonstrated that the Pd species in the Zn-free *N*-doped PC-900-Pd sample are present in the metallic state with the bond energy about 335.5 and 340.98 eV in the Pd $3d_{5/2}$ and $3d_{3/2}$ core level, and Pd 3d spectrum can be deconvoluted to four sub-peaks, containing Pd^0 $3d_{3/2}$ (334.7 eV), Pd^0 $3d_{5/2}$ (340.1 eV), Pd^{2+} $3d_{3/2}$ (341.2 eV) and Pd^{2+} $3d_{5/2}$ (336.1 eV) [35,36]. Moreover, the high resolution nitrogen (N) 1s spectrum can be deconvoluted to two sub-peaks due to the spin orbit coupling, including pyridinic-N (398.51 eV) and graphitic-N (400.98 eV) [37,38], which is a common characteristic for nitrogen-doped carbon materials. In general, nitrogen in a carbon texture is suitable for stabilizing highly dispersed metal nanoparticles. The nitrogen content in Zn-free *N*-doped PC-900-Pd was determined by means of XPS and amounted to 10 wt%.

Fig. 3 displays the XRD pattern of Zn-free *N*-doped PC-900-Pd composite. The wide diffraction peak at $2\theta = 25°$ can be indexed to porous carbon [39]. The well-defined peaks around 40°, 47°, 68° and 83° can be assigned to (1 1 1), (2 0 0), (2 2 0) and (3 1 1) crystal planes of Pd^0 in the composite.

In order to investigate the catalytic activity of different catalysts for the C–C coupling reaction, the coupling of phenylbromide and phenylboronic acid was selected as a model reaction. As shown in Table 2, among the catalysts tested at room temperature, Zn-free *N*-doped PC-900-Pd was found to be the most effective catalyst since it gave the highest yield of product. Good dispersion of the active species (Pd) on the support is a key factor for the catalytic

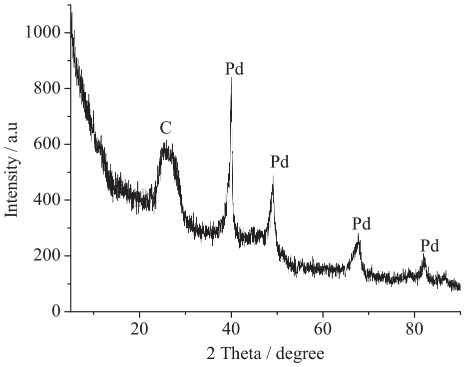

Fig. 3. XRD patterns of Zn-free *N*-doped PC-900-Pd. C: porous carbon.

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Table 2
Suzuki–Miyaura coupling reactions catalyzed by different catalysts.

Entry	Catalyst	Yield (%)
1	*N*-doped PC-700-Pd	54
2	*N*-doped PC-800-Pd	73
3	*N*-doped PC-900-Pd	91
4	*N*-doped PC-1000-Pd	77
5	Zn-free *N*-doped PC-900-Pd	95

n (K_2CO_3): n (aryl iodide): n (phenylboronic acid) = 4:1:1.3; solvent: 2 mL ethanol + 2 mL H_2O; the quantity of catalyst was 0.15 mol%; room temperature.

activity of the catalyst. This is mainly due to the high surface area of Zn-free *N*-doped PC-900, which leads to high dispersion of Pd on the surface of support. Additionally, the presence of nitrogen element in the carbon texture was also helpful to increase the dispersion of the active species.

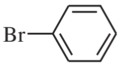
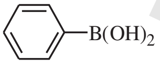
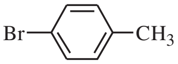
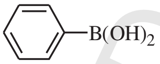
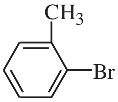
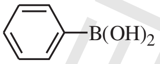
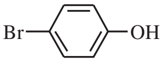
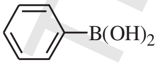
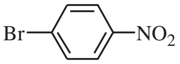
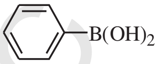
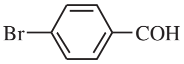
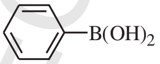
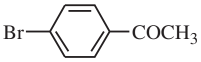
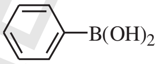
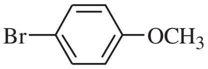
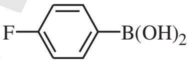
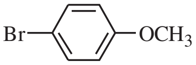
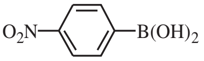
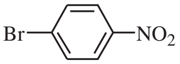
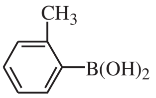
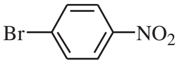
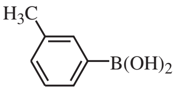
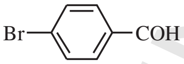
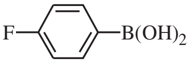
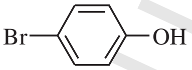
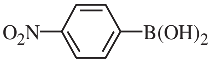
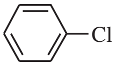
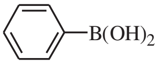
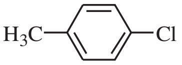
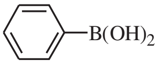
To evaluate the catalytic performance of the as-obtained catalyst and optimize the reaction conditions of the Suzuki

Table 3
Optimization of the reaction conditions for the Suzuki reaction of bromobenzene with phenylboronic acid.[a]

Entry	Solvents	Base	Pd (mol%)	Yield (%)
1	EtOH	K_2CO_3	0.15	63
2	MeOH	K_2CO_3	0.15	53
3	H_2O	K_2CO_3	0.15	17
4	EtOH:H_2O = (3:1)	K_2CO_3	0.15	81
5	EtOH:H_2O = (1:3)	K_2CO_3	0.15	72
6	EtOH:H_2O = (1:1)	K_2CO_3	0.15	95
7	EtOH:H_2O = (1:1)	KOH	0.15	55
8	EtOH:H_2O = (1:1)	NaOH	0.15	43
9	EtOH:H_2O = (1:1)	Na_2CO_3	0.15	85
10	EtOH:H_2O = (1:1)	$NaHCO_3$	0.15	68
11	EtOH:H_2O = (1:1)	Triethylamine	0.15	37
12	EtOH:H_2O = (1:1)	K_2CO_3	–	0
13	EtOH:H_2O = (1:1)	K_2CO_3	0.10	68
14	EtOH:H_2O = (1:1)	K_2CO_3	0.20	97

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

Table 4
Suzuki–Miyaura coupling of aryl boronic acids and aryl halides catalyzed by *N*-doped PC-900-Pd.[a]

Entry	Aryl halides	Aryl boronic acids	*T* (h)	Yield (%)[b]
1			1	95
2			1.5	91
3			2	92
4			1	95
5[c]			0.5	99
6			1	94
7			1	96
8			1	90
9			1	92
10			1	91
11[c]			1	92
12			1	94
13			1	95
14[d]			8	17
15[d]			8	Trace

[a] Reaction conditions: bromobenzene (0.5 mmol), phenylboronic acid (0.6 mmol), K_2CO_3 (1.5 mmol), solvent: 2 mL ethanol + 2 mL H_2O, catalyst: Zn- free *N*-doped PC-900-Pd (0.2 mol%), room temperature.
[b] Isolated yield based on column chromatography.
[c] The reaction temperature is 50 °C.
[d] The reaction temperature is 75 °C.

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coupling reaction, the reaction between phenylbromide and phenylboronic acid was chosen as model reaction. Initially, single solvents, such as EtOH, MeOH, and H_2O, were studied. As documented in Table 3, the single solvents gave low yields for the reaction (Table 3, entries 1–3). However, when we adopted the organic/aqueous co-solvent, high yields of 72–95% were obtained (Table 3, entries 4–6). The beneficial effect of the co-solvent may be attributed to the good solubility of the organic reactants and the inorganic base, so EtOH:H_2O (1:1, v/v) was chosen as the reaction solvent for the subsequent reactions. As is well known, a base has a strong influence on Suzuki reactions. When the organic and inorganic bases, such as Et_3N, K_2CO_3, Na_2CO_3, NaOH, KOH, $NaHCO_3$, were taken into consideration for the Suzuki coupling reaction (Table 3, entries 7–11), the experiments showed that K_2CO_3, as a base, afforded the product in the highest yield. It was also determined that the amount of the catalyst has a great influence on the transformation (Table 3, entries 6, 12–14), and the best results were obtained with 0.15 mol% of catalyst. When the amount of the catalyst was increase to 0.20 mol%, the product was obtained in a nearly quantitative yield (Table 3, entry 14). However, the yield of the reaction decreased to 68% (Table 3, entry 13) in 0.10 mol% Pd, and the coupling reaction does not proceed at all in the absence of Pd nanoparticles (Table 3, entry 12).

After optimizing the reaction conditions, the catalytic activity of Zn-free *N*-doped PC-900-Pd for the Suzuki–Miyaura reaction was explored with respect to various aryl halides and phenylboronic acids. It was found that the catalyst showed a high reactivity and selectivity for aryl bromides with an electron-withdrawing group and electron-donating group. As shown in Table 4, the coupling reactions could be proceeded well and the reactions could be completed in 0.5–2 h at room temperature with good to excellent yields. Typically, compared with the electron-donating groups on aryl bromides, such as $-CH_3$, $-OCH_3$ (Table 4, entries 2–3, 8–9), the electron-withdrawing groups, such as $-COCH_3$, –OH (Table 4, entries 4–7, 11–13), have higher reaction activity. To test the feasibility of the aforementioned protocol for challenging substrates, several aryl chlorides with aryl boronic acids were employed and the reaction time was increased to 8 h. Unfortunately, the catalytic system was less effective for the reaction of aryl chlorides (Table 4, entries 14 and 15) because of the strong strength of the C–Cl bond, whose bond dissociation energy was 96 kcal/mol [40].

The recycling and reusability of a catalyst is very important for industrial uses. Thus, the reusability of Zn-free *N*-doped PC-900-Pd was studied in the Suzuki–Miyaura cross-coupling of bromobenzene with phenylboronic acid under the optimal reaction conditions. As can be seen in Fig. 4, after being recycled for six successive runs, the catalyst still exhibits an excellent activity. Good reusability is mainly attributed to the high specific surface area and pore volume of Zn-free *N*-doped PC-900. Additionally, the nitrogen element in carbon texture also plays an important role for stabilizing highly dispersed Pd nanoparticles. Therefore, the Zn-free *N*-doped PC-900 catalyst exhibits both excellent catalytic activity and good reusability.

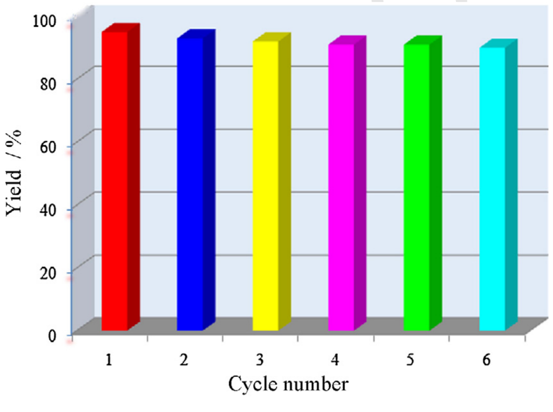

Fig. 4. Recyclability of the *N*-doped PC-Pd for the Suzuki–Miyaura reaction.

4. Conclusion

In summary, we have demonstrated the fabrication of nitrogen-doped carbon by a facile, low-cost and readily reproducible approach using ZIF-8 as precursor, and the prepared *N*-doped PC was used as the carrier material for palladium nanoparticle. The resultant Zn-free *N*-doped PC-900-Pd offers high surface area and exhibits a significant activity toward the Suzuki coupling reaction between aryl halide and aryl boronic acid, even when the reaction was carried out at room temperature for a relatively short time. Moreover, good yields were obtained even after the Zn-free *N*-doped PC-900-Pd catalyst was reused six times. 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.

Acknowledgments

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