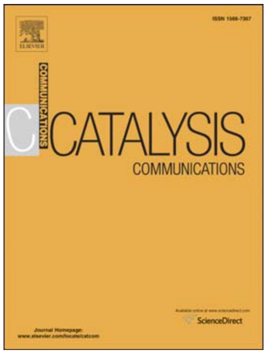

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Palladium nanoparticle supported on metal organic framework derived *N*-decorated nanoporous carbon as an efficient catalyst for the Suzuki coupling reaction

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Abstract:

A novel catalyst made of Pd nanoparticles supported on the *N*-doped nanoporous carbon, which was derived from Al-based metal-organic frameworks, was successfully fabricated for the first time. The prepared catalyst was characterized by transmission electron microscopy, scanning electron microscope, X-ray diffraction, X-ray photoelectron spectroscopy and N_2 adsorption. The as-obtained catalyst showed high catalytic activity for the Suzuki-Miyaura coupling reactions. The coupling reactions can be conducted at room temperature. The yields of the products were in the range from 90% to 99%. The catalyst can be recycled and reused at least 6 consecutive cycles without any significant loss in catalytic activity.

Keywords: Suzuki-Miyaura coupling reaction; Pd catalyst; *N*-doped nanoporous carbon; metal-organic frameworks

1. Introduction

Palladium-catalyzed Suzuki-Miyaura reaction of aryl halides with arylboronic acids is one of the most powerful methods for constructing biaryl structures [1]. Usually, the cross-coupling reactions were performed under homogeneous condition employing soluble palladium complex or organomentallic complexes as catalysts [2]. However, homogeneous palladium catalysts suffer from the problems including the difficulty to separate and recycle the expensive metal catalysts from reaction mixture, and the contamination of the ligand residue in the final products [3]. To overcome the problems mentioned above, heterogeneous palladium catalysts have been employed in recent years [1]. Pd supported on different materials, such as polymers [4], glass polymer composites [5], silica [6], clays and zinc ferrite [1], have been used as catalysts for C-C coupling reactions. However, these materials have one or more limitations in terms of stability, catalytic efficiency, and recyclability. Therefore, it is still attractive to explore efficient heterogeneous Pd catalyst for the coupling reactions.

Carbons, especially nanoporous carbon (NPC) materials, have been the most important and traditionally support for heterogeneous catalyst due to their high specific surface area and large pore volume in combination with excellent thermal, chemical and mechanical stability [7,8]. Recently, the utilization of metal-organic-frameworks (MOFs) as templates or precursors for the preparation of porous carbon materials has been received considerable attention. Due to the highly ordered porous structures with significant amount of carbon source, MOFs might be the promising candidates to give highly porous carbon materials under proper thermolysis conditions [9-10]. So far, several MOFs, such as MOF-5 [11], IRMOF [12], ZIF-63 [13], and ZIF-8 [14], have been demonstrated as promising templates to construct nanoporous carbons. The MOF-derived porous carbon materials have found a wide range of applications [15], such as contamination removal [16, 17], energy storage [18], electrode materials [14] and carriers for drug delivery systems [16]. However, to the best of our knowledge, there has been no report on the application of MOF-derived nanoporous carbon as catalyst carriers till now.

It has been demonstrated that the coupling of nitrogen into the carbon materials could enhance the mechanical, energy-storage properties, and showed more stability for the noble metals (e.g., Pt, Pd) nanoparticles due to the activation of neighboring carbon atoms caused by the electron affinity of nitrogen, which is rather beneficial for heterogeneous catalysts [19, 20]. These *N*-decorated carbon materials are thermally/chemically stable and have good regeneration ability. In general, *N*-decorated porous carbons could be synthesized via amine grafting on the carbon matrix. However, the postsynthetic incorporation method not only blocks pores but also suffers from leaching and instability in any subsequent regeneration step. Another synthesis strategy of *N*-decorated porous carbons is high temperature pyrolysis of *N*-containing precursors.

In this report, nitrogen-doped nanoporous carbon was fabricated by direct carbonization of the nitrogen containing Al-based MOF [21]. The MOF itself acts as the carbon source, the nitrogen source, as well as the template, thus reducing a number of steps required to modify porous carbon with nitrogen. In continuation of our interest in exploring efficient catalysts for organic transformations [3, 22-25], Pd nanoparticle was immobilized onto the as-prepared *N*-doped NPC for the first time. To evaluate the catalytic activity of the prepared catalyst, the Suzuki–Miyaura coupling reaction was employed as the model reaction.

2. Experimental

2.1. Materials and methods

Aluminium chloride hexahydrate, 2-amino-1,4-benzene-dicarboxylic acid (H_2N-H_2bda), sodium borohydride, potassium carbonate and methanol 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.

The size and morphology of the nanoparticles were observed by transmission electron microscopy (TEM) using a JEOL model JEM-2011(HR) at 200 kV. Scanning electron microscopy (SEM) studies were conducted on a Hitachi (Model S4800) instrument. The XRD patterns of the samples were recorded with a Rigaku D/max 2500 X-ray diffractometer using Cu $K\alpha$ radiation (40 kV, 150 mA) in the range $2\theta = 10^{o}$ - 90^{o}. X-ray photoelectron spectroscopy (XPS) was performed with a PHI 1600 spectroscope using Mg $K\alpha$ X-ray source for excitation. The Brunauer–Emmett–Teller (BET) surface areas were determined from the N_2 adsorption at 300 K using V-Sorb 2800P. The Pd and Al content of the catalyst was determined by means of inductively coupled plasma atomic emission spectroscopy (ICP-AES) on Thermo Elemental IRIS Intrepid II.

2.2 Synthesis of *N*-doped NPC-Pd

Al-MOF was prepared according to the procedure reported by Tim Ahnfeldt [19]. $AlCl_3 \cdot 6H_2O$ (0.927g, 3.84 mmol), $H_2N\text{-}H_2bda$ (0.233 g, 1.29 mmol) and methanol (12.35 mL) was transferred into a 50 mL Teflon-lined stainless steel autoclave and heated to 125 ^{o}C for 5 h under autogenous pressure. After the reaction mixture was cooled down to room temperature, the precipitate was filtered and a yellow microcrystalline product was obtained. The microcrystalline product was washed with water for three times and dried at 80 °C under vacuum. The carbonization of the Al-MOF was performed at 800 °C for 10 h with an N_2 flow. The resulting product was denoted as *N*-doped NPC.

Pd nanoparticles were immobilized on the *N*-doped NPC by an impregnation method. 50 mg of *N*-doped NPC were dispersed in 5 mL water. 6 mg $PdCl_2$ (0.034 mmol) was added and the mixture was sonicated (200 W, 40 kHz) for 5 min. Then the solution was stirred overnight. After filtration, the solid was washed with water and dried under vacuum at 80 °C. The obtained solid was dispersed in 5 mL of water, and then 5.5 mg sodium borohydride (0.0135 mmol) was added. The pH of the mixture was adjusted to 10 with 25% ammonium hydroxide and the reaction was carried out at 98 °C for 2 h. The final product, *N*-doped NPC-Pd, was washed with water and dried in vacuum at 50 °C. As the preparation process was illustrated in Scheme 1.

For the preparation of aluminium-free *N*-doped NPC, 100 mg of *N*-doped NPC powder was suspended in 35 mL of 10 % HCl and stirred for 5 h. Then the mixture was filtered and the obtained solid was washed with distilled water. Finally, the *N*-doped NPC without aluminium oxide or aluminum was obtained by vacuum drying at 80 ^{o}C overnight. The aluminium-free *N*-doped NPC-Pd was fabricated according to the same procedure for *N*-doped NPC-Pd except that 50 mg *N*-doped NPC was replaced by 50 mg aluminium-free *N*-doped NPC.

2.3. General procedure for Suzuki–Miyaura reactions

In a round-bottomed flask, a solution of aryl halide (0.5 mmol), phenylboronic acid (0.6 mmol), the catalyst (2.2 mg, 0.2 mol%), and K_2CO_3 (1.45 mmol) were dissolved in a mixture of 4 mL H_2O:EtOH (1:1, v/v). The mixture was stirred at room temperature for a desired reaction time. Upon the completion of the reaction, the reaction mixture was diluted with 10 mL H_2O and extracted with ethyl acetate (3 × 10 mL). The organic layer was combined, dried with $MgSO_4$, and filtered. The filtrate was concentrated by vacuum. The residue was subjected to column chromatography with petroleum ether/ethyl acetate as the eluent to afford the desired biphenyl product.

3. Results and discussion

3.1. Characterization of the catalyst

The typical TEM and SEM images of *N*-doped NPC-Pd were shown in Fig. 1. As can be seen from Fig. 1a, the Pd was well dispersed on the surface of *N*-doped NPC. The particle size of Pd nanoparticles was about 5 nm. It can be clearly seen from the SEM image (Fig. 1b) that the crumpled silk waves-like carbon sheets exist.

Fig. 2 displays the XRD pattern of *N*-doped NPC-Pd composite. The wide diffraction peak at $2\theta = 26°$ can be indexed to porous carbon [26]. The well-defined peaks around 40°, 47°, 68° and 83° can be assigned to (111), (200), (220) and (311) crystal planes of Pd^0 in the composite [3]. The characteristic peaks of aluminum at 39^o, 45^o, and 65^o can be assigned to (111), (200), and (220) crystal planes of aluminum. Besides, the peak of β-aluminium oxide can also be observed at 16°, and 20°.

The XPS of *N*-doped NPC before and after Pd deposition was measured and the images were shown in Fig. 3. From which we can see that the Al's binding energy was 74.17 eV in the *N*-doped NPC sample (Fig. 3a). However, the Al's binding energy increased to 75.01 eV after Pd deposition on the *N*-doped NPC sample (Fig. 3b), which indicated that there is a strong interaction between Pd and Al. The electron transfer between Pd and Al might lead to the change of Al's binding energy. The XPS of Pd $3d_{5/2}$ and $3d_{3/2}$ (Fig. 3c) showed that the fitted peaks at 335.5 and 340.98 eV corresponded to Pd(0), which demonstrated that the Pd species in the *N*-doped NPC-Pd was present in the metallic state. The N1s peaks appear at 399.2 eV (Fig. 3d) obviously confirm the presence of nitrogen in the Al-MOF derived NPC. Nitrogen element in the carbon texture is favorable for the stabilization of highly dispersed Pd nanoparticles.

The pore properties of the *N*-doped NPC-Pd composite were investigated by nitrogen adsorption-desorption isotherms. The general shape of the N_2 sorption isotherms for the *N*-doped NPC-Pd (Fig. 4A) could confirm the existence of different pore sizes spanning from micro- to macropores. The steep increase in the adsorbed volume at low relative pressures reveals the presence of the micropores in the catalyst, and the following small slope observed at medium relative pressures as well as the desorption hysteresis denotes the existence of the mesopores while the final almost vertical increase at the relative pressures near 1.0 points to the presence of macropores. The pore size distributions of the *N*-doped NPC-Pd calculated from the nitrogen adsorption branches were shown in Fig. 4B. The BET surface area, total pore volume, total adsorption average pore width and SF median pore width are 600 m^2 g^{-1}, 0.55 cm^3 g^{-1}, 7.98 nm and 0.72 nm, respectively.

In older to check the actual loading of Pd and the amount of Al in the *N*-doped NPC-Pd, the ICP-AES analysis was performed. The results indicated that the palladium content in *N*-doped

NPC-Pd and aluminium-free *N*-doped NPC-Pd was 4.3 wt% and 1.5 wt%, respectively. The results clearly demonstrated that the presence of aluminum oxide and aluminum in *N*-doped NPC may be helpful to stabilize the Pd nanoparticles in the nanoporous carbon. After treatment of the *N*-doped NPC with 10% HCl solution, no aluminium element can be detected in the *N*-doped NPC.

3.2. Suzuki–Miyaura reactions catalyzed by the prepared catalyst

To evaluate the catalytic performance of the as-obtained catalyst and optimize the reaction conditions of the Suzuki coupling reaction, the coupling of phenyl bromide and phenyl boronic acid was selected as a model reaction. The results indicated that *N*-doped NPC-Pd could catalyze the reaction efficiently even at room temperature. When the amount of the catalyst was 0.2 mol%, the coupling reaction can be completed within 1 h to afford the corresponding biphenyl in 97% yield with $EtOH/H_2O$ (1:1, v/v) as the solvent. The reaction does not take place in the absence of catalyst or using *N*-doped NPC as a catalyst, which indicated that aluminium oxide containing in the *N*-doped NPC has not catalytic activity for the coupling reaction. However, when the *N*-doped NPC was treated by 10 % HCl for 5 h to remove the aluminium oxide or aluminum, only 69% yield of biphenyl was obtained with the corresponding aluminium–free NPC-Pd as a catalyst. The results clearly demonstrated that the presence of aluminum oxide and aluminum in *N*-doped NPC may be helpful to improve the dispersion of the Pd nanoparticles. In general, regardless of the exact mechanism of the reaction, the catalytic activity of nanocatalyst is determined by the size of nanoparticles. The smaller the nanoparticle is, the more effective the catalytic activity become. *N*-doped NPC-Pd exhibited high activities due to the good dispersion and small size of the Pd nanoparticles. With the commercially available Pd supported on activated carbon (5% Pd/C, the most often used catalyst in heterogeneous Pd catalyzed coupling reactions) as the catalyst, only

78% yield of biphenyl was obtained under the same conditions.

The influence of the amount of catalyst was also investigated. The results indicated that 0.2 mol% amount of *N*-doped NPC-Pd was sufficient to guarantee a clean and complete conversion. When the amount of *N*-doped NPC-Pd increased from 0.02 mol% to 0.20 mol%, the yield of biphenyl increased from 80% to 97%. When the amount of catalyst was higher than 0.20 mol%, the yield of biphenyl almost remained constant.

To generalize the application of the *N*-doped NPC-Pd catalyst, the coupling reactions of various substituted aryl halides and phenylboronic acids were carried out in the presence of K_2CO_3 using H_2O:EtOH (1:1) as environmentally benign solvents. The results are summarized in Table 1. For all the substrates, the reactions could be completed in 0.5-3 h with the substrates having either electron-donating groups (Entries 2-4, 10), such as $–CH_3$, $-OCH_3$, or electron-withdrawing groups (Entries 5-9), such as $-COCH_3$, -OH. The yields of the corresponding coupled products were in the range from 90% to 99%. Additionally, aryl chlorides was chosen as the challenging substrates (Table 1 entry 14), however, the catalytic system was less effective even prolonged reaction time, which might be ascribed to the strong strength of the C-Cl bond, whose bond dissociation energy was 96 kcal/mol [27].

The recyclability of the catalyst was further investigated because the recycling of the heterogeneous catalysts is desirable in practical applications. The Suzuki-Miyaura cross-coupling reaction between bromobenzene and phenyl boronic acid catalyzed by 0.2 mol% of *N*-doped NPC-Pd was chosen as a model reaction. The results indicated that *N*-doped NPC-Pd can be reused 6 times without significant loss of its catalytic activity (Fig. 5). Good reusability mainly attributed to the high specific surface area *N*-doped NPC. Moreover, nitrogen element in carbon texture is also playing an important role for stabilizing highly dispersed Pd nanoparticles. Therefore, the Pd NPs deposited on *N*-doped NPC are not easily leached during catalytic processes.

4. Conclusions

In this paper, *N*-doped nanoporous carbon was fabricated by direct carbonization of the nitrogen containing Al-based MOF and which was used as the carrier material for palladium nanoparticle. The as-obtained heterogeneous catalyst, *N*-doped NPC-Pd, exhibited excellent catalytic activity for the Suzuki cross-coupling reaction even when the reaction was carried out at room temperature for a relative short time. The catalyst can be readily recovered and reused at least 6 times without significant loss of its catalytic activity. 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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Table 1 Suzuki–Miyaura coupling of arylboronic acids and aryl halides catalyzed by *N*-doped NPC-Pd[a]

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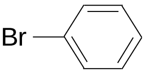
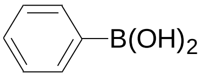
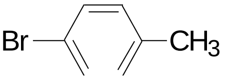
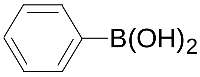
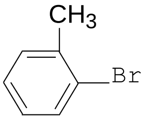
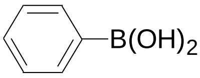
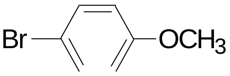
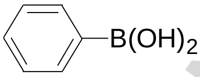
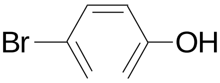
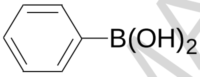
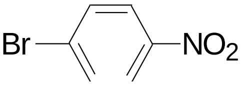
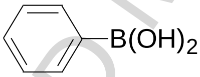
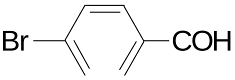
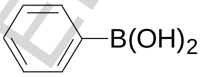
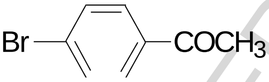
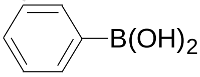
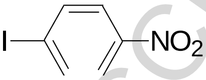
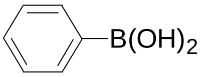
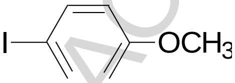
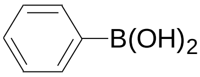
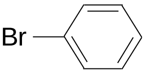
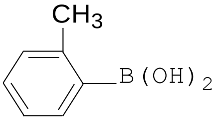
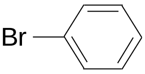
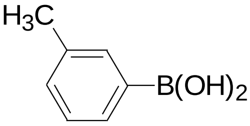
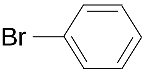
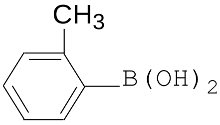
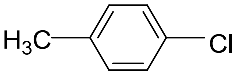
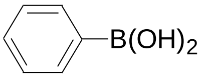
1			1	97
2			1	95
3			1	90
4			1	94
5			1	94
6[c]			0.5	98
7			1	96
8			1	95
9[c]			0.5	99
10			1	97
11			1.5	90
12			1	92
13			1	94
14[d]			3	14

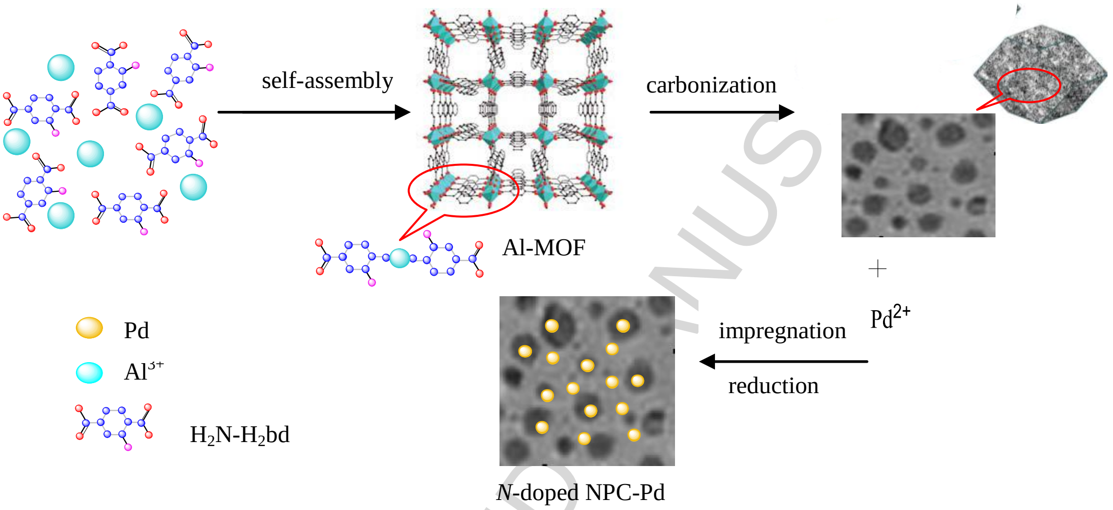
[a] Reaction conditions: bromobenzene (0.5 mmol), phenyl boronic acid (0.6 mmol), K_2CO_3 (1.5 mmol), solvent: 2

mL ethanol + 2 mL H_2O, catalyst: *N*-doped NPC-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 60 °C.



Scheme 1. Schematic illustration of the synthetic processes of *N*-doped NPC-Pd

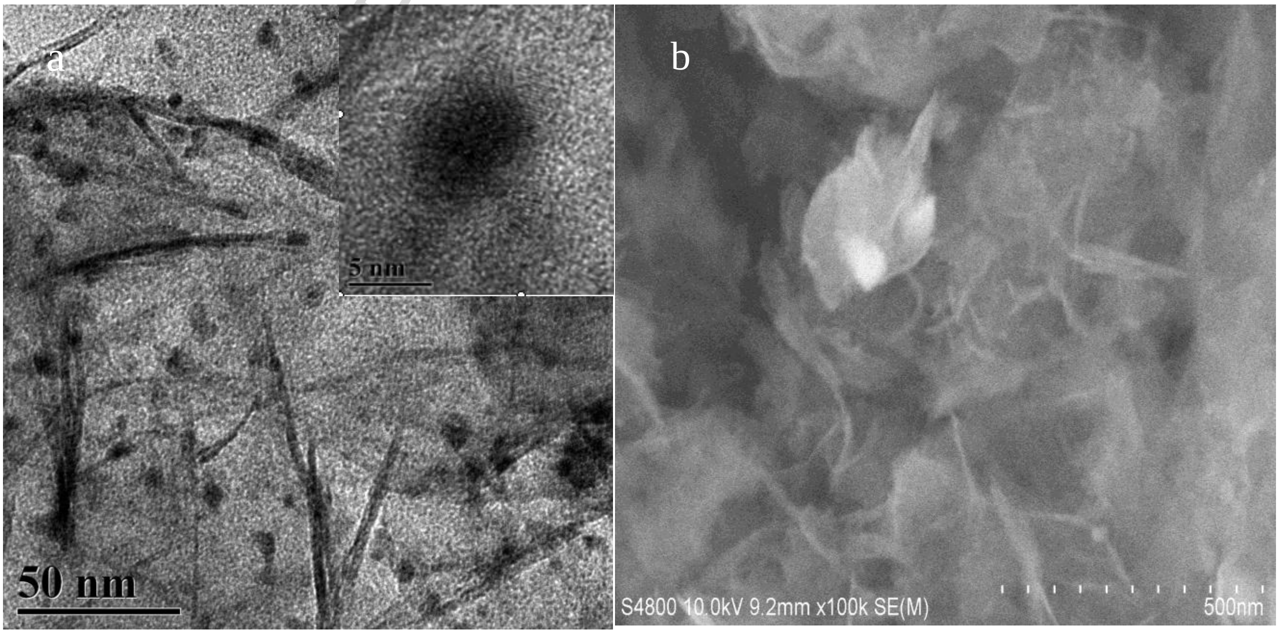


Fig. 1. TEM (a) and SEM (b) images of *N*-doped NPC-Pd. The inset in (a) is the HRTEM image.

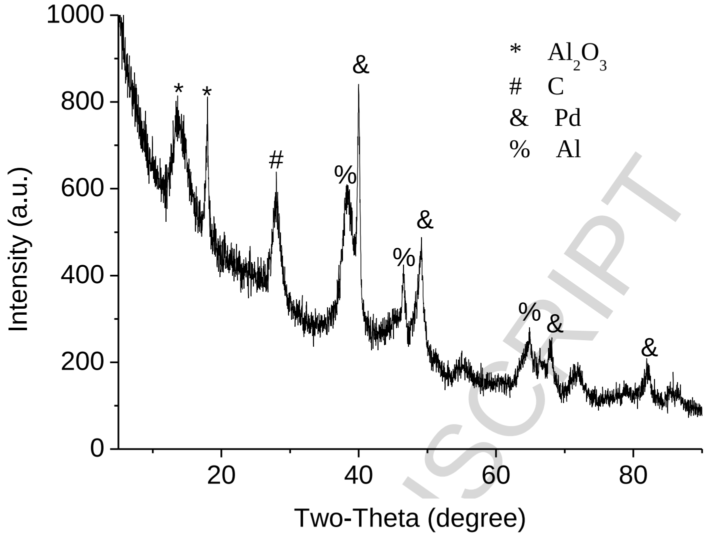


Fig. 2. XRD patterns of *N*-doped NPC-Pd

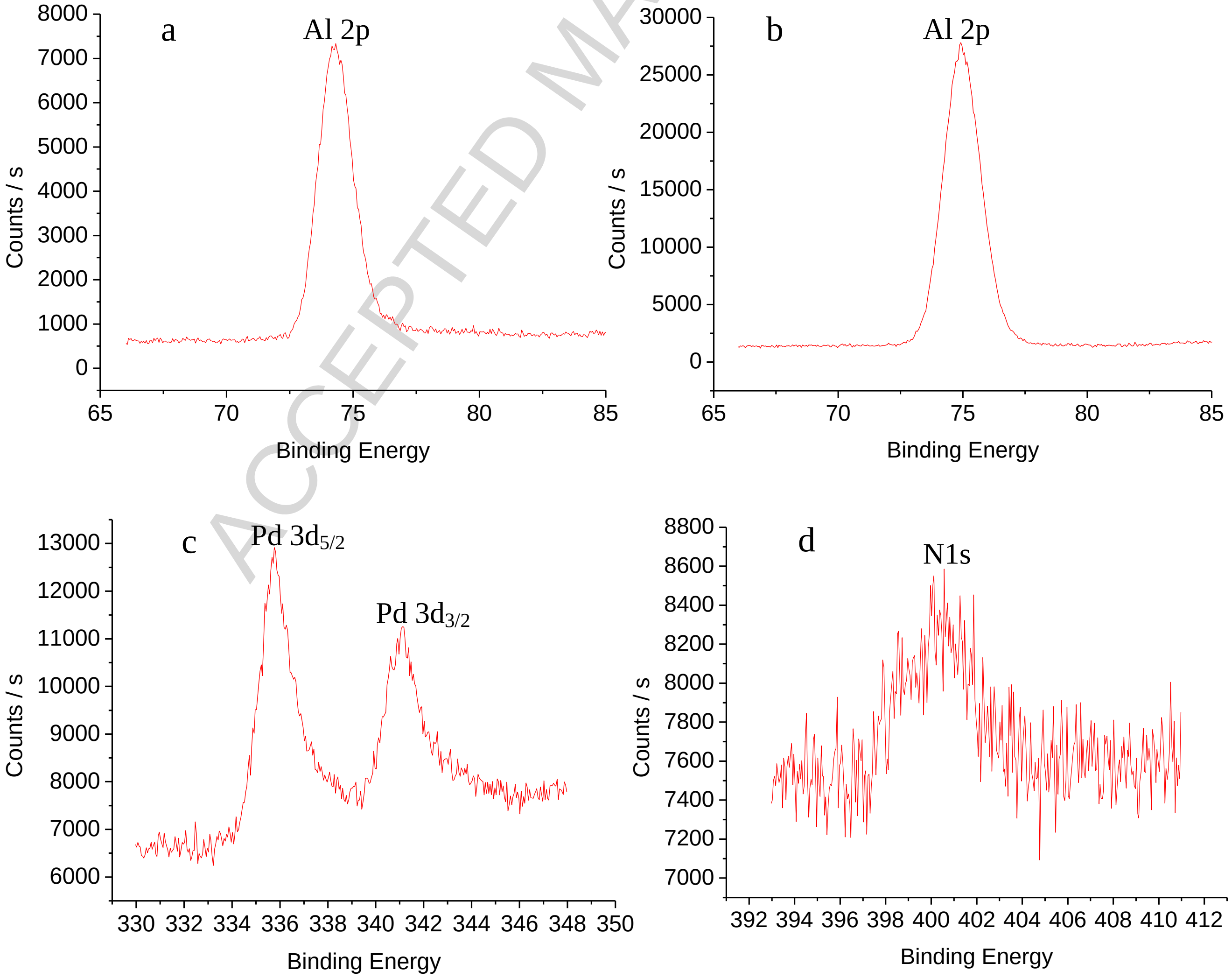


Fig. 3. The XPS image of *N*-doped NPC (a) and *N*-doped NPC-Pd (b, c and d).

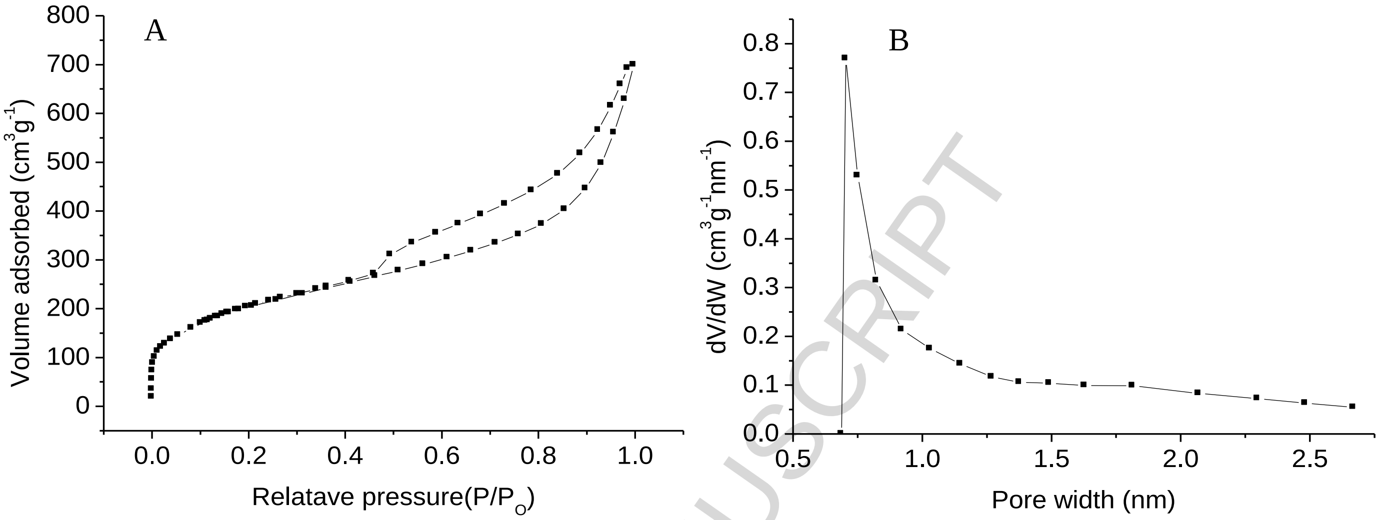


Fig. 4. The nitrogen adsorption-desorption isotherm (A) and pore size distributions (B) of the *N*-doped NPC-Pd

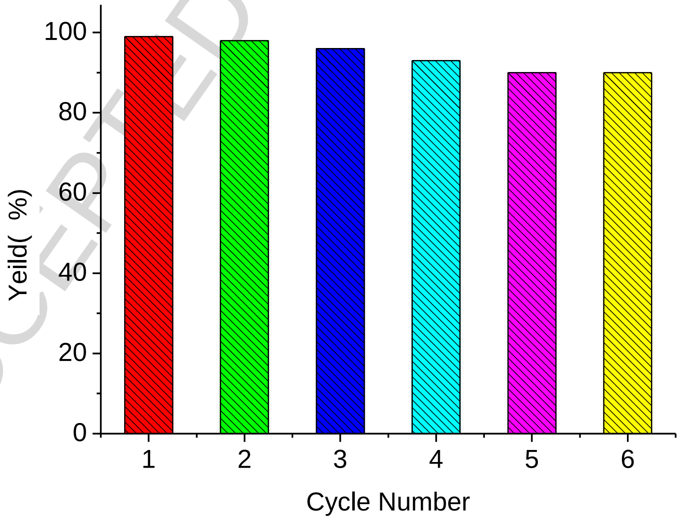
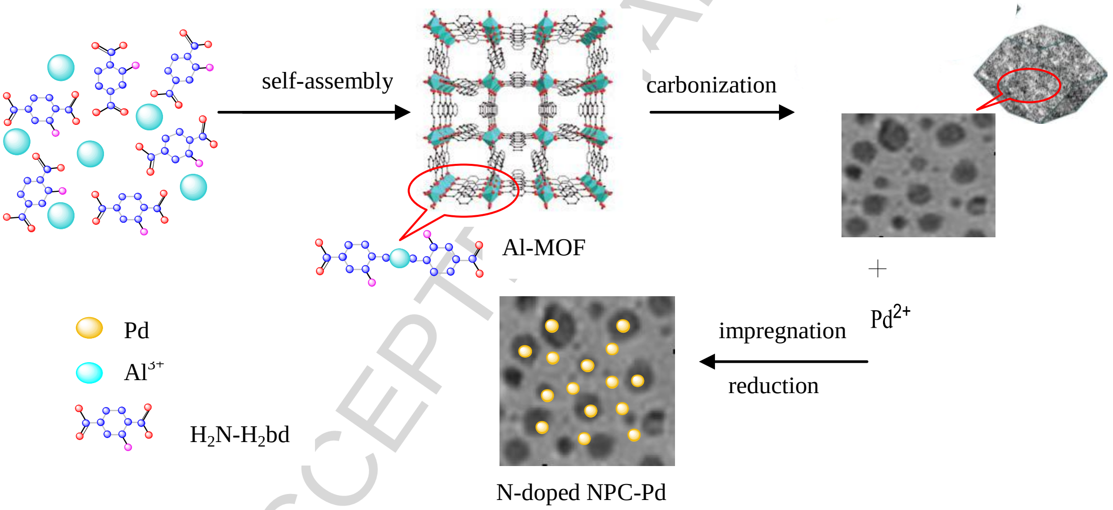


Fig. 5. Recyclability of the *N*-doped NPC-Pd for the Suzuki-Miyaura reaction

Graphical abstract

N-doped nanoporous carbon was fabricated by direct carbonization of the nitrogen containing Al-based MOF and which was used as the carrier material for palladium nanoparticle for the first time. The as-obtained heterogeneous catalyst, *N*-doped NPC-Pd, exhibited excellent catalytic activity for the Suzuki cross-coupling reaction.



Highlights

► *N*-doped porous carbon (NPC) was synthesized by direct carbonization of Al-based MOF. ► Heterogeneous catalyst, NPC-Pd, was prepared for the first time. ► NPC-Pd exhibited excellent catalytic activity for the Suzuki coupling reaction.