

# Novel Pd Nanocubes Supported on Activated Carbon as a Catalyst for the Suzuki-Miyaura Coupling Reaction

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**Abstract:** Palladium nanocubes with diameters of 6~10 nm have been successfully synthesized by a simple reduction route with the assistance of PVP as stabilizing agent and KBr as a capping agent. The palladium nanocubes supported on activated carbon (Pd/C) were prepared by a physical absorption method. The prepared Pd/C catalysts were characterized by X-ray diffraction (XRD), transmission electron microscopy technology (TEM), thermogravimetric analyzer (TGA) and X-ray photoelectron spectroscopy (XPS). The results demonstrated that the palladium nano particles with the face-centered-cubic structure were uniformly supported on the activated carbon. It was shown from experimental results that the product yield for the Suzuki-Miyaura reaction between aryl bromides with aryl boronic acid attains more than 90% and has no significant loss of catalytic activity after five reaction cycles.

**Keywords:** Palladium nanocubes, Pd/C catalyst, Suzuki-Miyaura coupling reaction.

## 1. INTRODUCTION

Undoubtedly, for the pharmaceutical and fine chemical industry, the Suzuki-Miyaura cross-coupling reaction represents probably the most widely used carbon-carbon bond forming process [1]. Such reactions are usually catalyzed by noble Pd metal in the presence of many solids as a support [2]. Like many other catalysts, the activity and selectivity of Pd nanoparticles (NPs) often have a strong dependence on the size and shape (or more appropriately the facets or surface structures) [3]. In principle, one could tailor these parameters to maximize the catalytic performance of a Pd catalyst in an effort to reduce the loading of this precious and rare metal [4]. Therefore, the development of high-performance palladium catalysts for Suzuki-Miyaura cross-coupling reactions has been an important area of research and consequently, the synthetic methods with a rigorous size and shape control of the NPs have become the leading research focus [5-8].

Some previous researchers have made great efforts to explain that catalysts with well-defined shapes of metal nanocrystals supported with exposed distinct crystal facets have different performances [9-11]. However, the Pd catalysts currently used in the aforementioned reactions are mainly based on polycrystalline nanoparticles of Pd with poorly controlled sizes and shapes [12, 13]. As such, they do not present a high catalytic performance. The catalytic selectivity for some reactions could be altered by adjusting the exposed facets of metal nanocrystals, while maximizing the catalytic performance and thus minimizing the loading, it is necessary to replace these nanoparticles with single-crystal

nanoparticles enclosed by a specific set of facets [14]. Recently, Xia *et al.* prepared Pd-Pt nanocrystals with different shapes such as cubes, tetrahedrons, and octahedrons, and then used them as catalysts for electrocatalytic activity to elucidate the dependence of catalytic activity on surface structure [15]. They found that the Pd-Pt concave nanocubes were four times more active for electrocatalytic activity and the (100)-facet-enclosed catalyst showed a higher activity, while the (111)-facet-enclosed held a better durability [16, 17]. They, then reported that Br<sup>-</sup> ions were found to adsorb onto Pd {100} facets selectively with a coverage density of ca. 0.8 ions per surface Pd atom and without Br<sup>-</sup>, the {100} facets could not be stabilized by the capping agent, leading to the formation of nanocubes with truncated corners [18, 19]. Dai and Wang have prepared the catalysts of Pd cuboctahedron and tetrapod nanocrystals with KBr and hydrogen and carbon monoxide mixture as capping agents, respectively [20, 21]. They found the Pd (111)-facet-enclosed showed a higher activity on selective hydrogenation of acetylene and electro-oxidations of formic acid [22].

On the basis of these observations, we reported a simple and efficient method for synthesizing activated carbon-supported Pd nanoparticles as a catalyst. As stabilizing agent, the PVP (Polyvinylpyrrolidone) was reported for preventing the agglomeration of NPs, the Pd nanocubes were prepared in the presence of KBr. Nanocube Pd supported on the activated carbon catalyst (Pd/C) was prepared by a mild and superior physical absorption method. In addition, the catalytic activities of Pd/C in the Suzuki-Miyaura coupling action were studied.

## 2. EXPERIMENTAL

### 2.1. Materials

Polyvinylpyrrolidone (PVP, K30, MW=50,000) and PdCl<sub>2</sub> (the metal salt used as precursors) were purchased from Sinopharm Chemical Reagent Co., Ltd. The citric acid

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(AR) and KBr (AR) were purchased from Tianjin Kernel. Benzenboronic acid and aryl bromides were obtained from Yurui Chemical Co., Ltd. (Shanghai, China). All of these reagents were used without further purification. The activated carbon made from Coconut shell was obtained from Activated Carbon Company (Henan, China). Before used as a supporter, the activated carbon was treated by the oxidation with  $\text{HNO}_3$  at 353 K.

## 2.2. Preparation of Nanocube Pd/C Catalyst

Solution A was prepared by dissolving 0.45 g of PVP and 0.13 g of KBr in 70.0 ml of deionized water with vigorous stirring at 358 K. Solution B was obtained by dissolving 0.05 g of  $\text{PdCl}_2$  and 0.03 g of NaCl in 10.0 ml of deionized water under ultrasonic. The citric acid solution was added to the mixed solution of Solutions A and B at 353 K and stirred until the yellow solution of  $\text{PdCl}_2/\text{PVP}$  changed to a brown color, which indicated the completion of chemical reduction. 1.0 g the above-treated activated carbon was added to the brown solution under constant stirring. Resulting catalyst was separated by centrifugation and washed three times with water and ethanol. The content of Pd from ICP analysis is 2.47% in the above-prepared Pd/C catalyst.

## 2.3. Characterization

Thermogravimetric analysis (TGA) was performed on a Netzsch STA449C instrument from 30 °C to 800 °C at a heating rate of 10 K/min in an air atmosphere. The X-ray diffraction (XRD) was measured on a Bruker D8 Advance X-ray diffractometer using  $\text{Cu K}\alpha$  irradiation ( $\lambda = 0.15418$  nm) with the scanning speed of 0.5°/s from 10° to 70° (2 $\theta$ ). Micro structural analyses were performed by transmission electron microscopy (JEOL JEM-2010 TEM, operating at 200 KV with a point resolution of 0.23 nm). X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Thermo S Structural characterization of Pd/C catalyst was recorded by scientific ESCALAB 250. The analysis of the reaction products were performed on a Waters e2695-HPLC system by using an external standard method.

## 2.4. General Procedure for Suzuki-Miyaura Coupling Reactions

Aryl bromide (1.0 mmol) and phenyl boronic acid (1.5 mmol) were added to a flask containing Pd/C and  $\text{K}_2\text{CO}_3$  (2 mmol) in a mixture of 12 ml  $\text{H}_2\text{O}:\text{EtOH}$  (1:1). The mixture was stirred in a water bath under 60 °C. After the completion of the reaction, the reaction mixture was cooled down to room temperature and mixed with NaOH (0.2 mol/l, 5 ml), and then extracted with ethyl to acetate (10 ml). The yield of product was determined by means of HPLC.

# 3. RESULTS AND DISCUSSION

## 3.1. Characterizations of the Activated Carbon-Supported Pd Nanocatalysts

Like other cubic noble metals, the thermodynamically favorable shapes of Pd nanocrystals are cuboctahedron and multiply twinned particles [23]. To obtain an anisotropic nanostructure and new shapes, impurities or capping agents

are generally employed to alter the surface free energies of nanoparticles. The capping agent bromide ions, has been widely employed in inducing new shapes. With bromide ions introduced into the reaction system, they may chemisorb onto the surface of Pd seed and alter the relative order of surface free energies [24]. Additionally PVP was employed as a stabilizing agent to prevent the aggregation of particles.

The Pd/C catalyst and its precursor-Pd nano particles were characterized by TEM (Fig. 1a-d). Fig. (1a, b) show Pd nano particles prepared under the conditions without or with the existence of the bromide ions respectively. It was confirmed from TEM micrographs that the shape of the Pd nano particles prepared is an imperfect sphere and the diameter of these particles distribution is somewhat broad without the bromide ions (Fig. 1a). Compared with Fig. (1a), Pd nanoparticles with a uniform cube shape were obtained after bromide ions were introduced into reaction system (Fig. 1b). The average edge length of Pd nanocube was  $7.3 \pm 2$  nm. A corresponding histogram of size distribution was shown in the inset of Fig. (1c). A small portion (<10%) of the nanocubes was slightly elongated along one of the axes to form rectangular bars with aspect ratios (length to width) somewhat larger than one, but they are still nanocubes. It can be assumed from the above results that bromide ions play an important role in terms of selecting the Pd particle shape. It was observed from Fig. (1d) that the loading ratio is estimated to be higher than ca. 60%.

The thermogravimetric analysis (TGA) curves (Fig. 2) reveal the superior thermal stability of both the activated carbon and Pd/C up to 450 °C. There is a 2.5% difference of the weight loss ( $\Delta W_1 + \Delta W_2$ ) between activated carbon and Pd/C was close to Pd content of 2.47% from ICP analysis.

Fig. (3) shows the XRD patterns of Pd nanoparticles, the activated carbon supporter and Pd/C catalyst. The diffraction peak at  $2\theta = 24.4^\circ$  and  $43.5^\circ$  in both active carbon and Pd/C catalyst is attributed to the carbon support. In addition to the peak of carbon, there were some other diffraction peaks in the Pd/C catalyst and Pd nanoparticles. The diffraction peaks at  $2\theta = 40.1^\circ$ ,  $46.7^\circ$  and  $68.1^\circ$  in both of Pd nanoparticles and Pd/C catalysts are characteristics of the face-centered-cubic (fcc) Pd, corresponding to the facets (111), (200) and (220), respectively. It was revealed that the Pd nanoparticles have been loaded onto carbon successfully. The average crystallite sizes of the Pd nanoparticles on the Pd/C catalyst can be estimated by using the Scherrer equation after background subtraction. In the XRD pattern of the Pd/C catalyst, the (220) diffraction peak at  $2\theta = 68.1^\circ$  of Pd was far from the background signal and thus it was chosen for the calculation. The average crystallite size was about 7.6 nm for the Pd/C. These values are the same as that observed by TEM.

Fig. (4) shows the XPS spectrum of the Pd/C catalyst for identifying the oxidation state of the surface-loaded Pd NPs. It was observed from Fig. (4) that there were two distinct peaks with binding energies of 335.6 and 341 eV, which can be assigned to the signals of  $3d_{5/2}$  and  $3d_{3/2}$  of  $\text{Pd}^0$ , respectively. The binding energy difference of the two peaks is 5.4 eV, which is in accordance with the theoretical value. Therefore, the XPS analysis indicates that the in situ formed  $\text{Pd}^0$  were thoroughly reduced to be neutral.

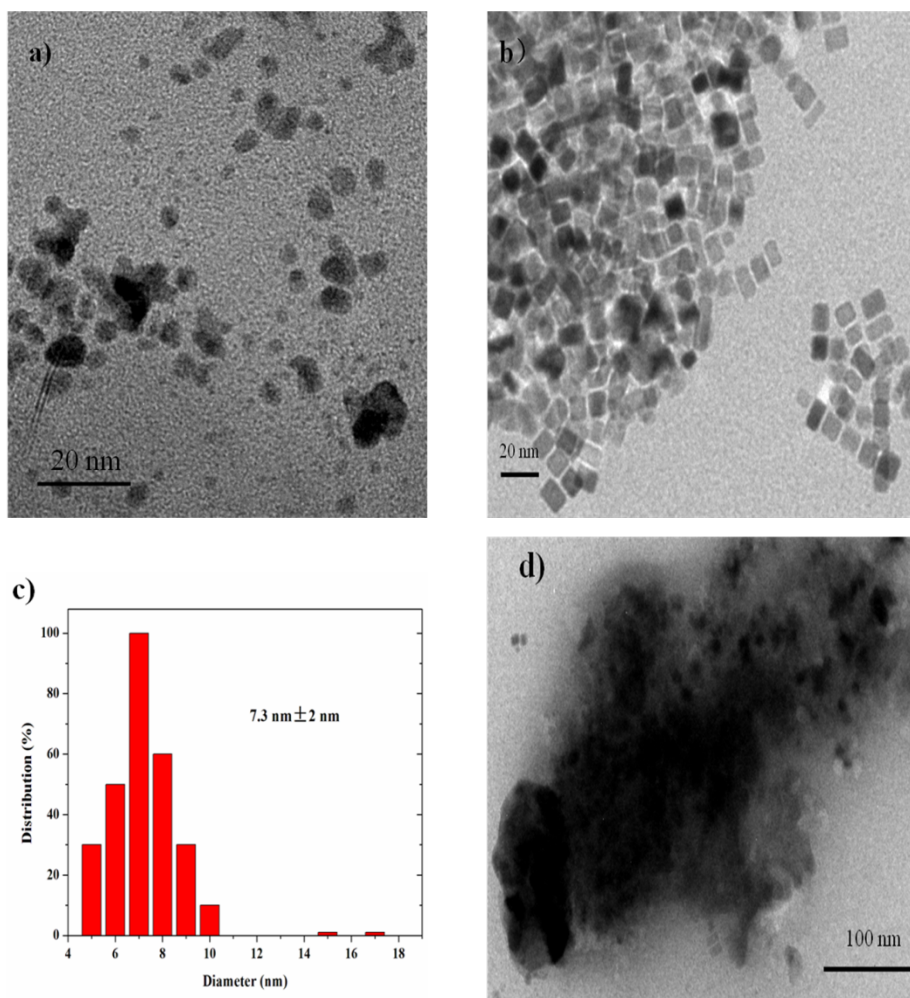


Fig. (1). TEM images of Pd/C catalyst and its precursor-Pd nano particles. (a) and (b) TEM images of Pd nanoparticles and Pd nanocube. (c) The diameter distribution histogram of Pd nanocubes. (d) TEM images of Pd/C catalyst.

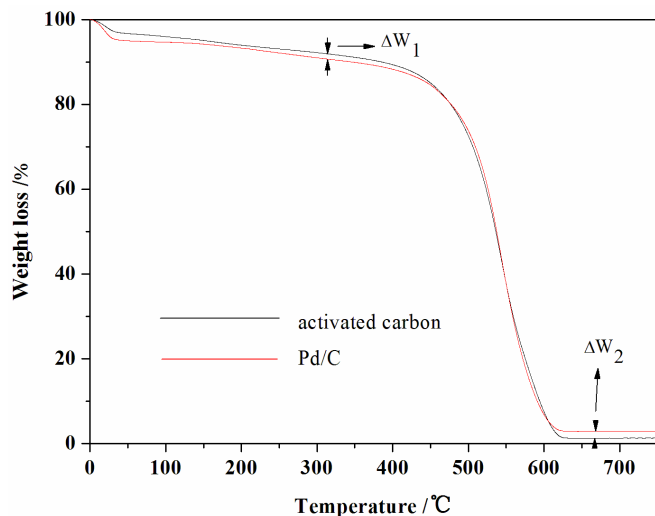


Fig. (2). TGA curve of activated carbon and Pd/C catalyst.

### 3.2. Catalytic Activity of the Nanocube Pd/C Catalyst

To evaluate the catalytic efficiency of the-above prepared nanocube Pd/C catalyst, a series of Suzuki-Miyaura cross-

coupling reactions were carried out and the results are presented in Table 1.

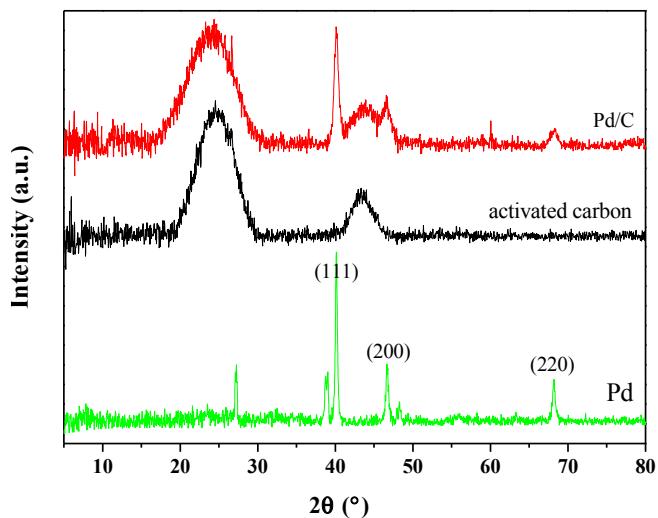


Fig. (3). XRD patterns of Pd nanocube, activated carbon and Pd/C.

High yields were easily obtained in a short time at room temperature when aryl iodides were used (>99% for HPLC

yield, entries 1-2 in Table 1). It is well known that electronic effects strongly affect the Suzuki-Miyaura cross-coupling reactions. Compared with electron-rich para-substituted aryl halides, electron-deficient para-substituted aryl halides show high activity in the process of coupling with arylboronic acids due to the activation of the benzene ring as well as the ease of the charge-transfer, while it is the opposite in the case of para-substituted arylboronic acids. However, high catalytic activities were observed for both electron-rich and electron-deficient para-substituted aryl bromides under a relatively mild condition (60 °C for 0.5-1.0 h in air), and good yields of different cross-coupling products were approached (>91% for HPLC yield, entries 3-8 in Table 1). When the less active aryl chloride was employed, a HPLC yield of 74% and 65% was observed (90 °C for 10 h in air, entry 9-10 in Table 1). The yield of chlorobenzene achieved 53% (90 °C for 20 h in air, entry 11 in Table 1). That is, the prepared *nanocube* Pd/C catalyst has very high activity for the coupling of aryl chloride and aryl boronic acids.

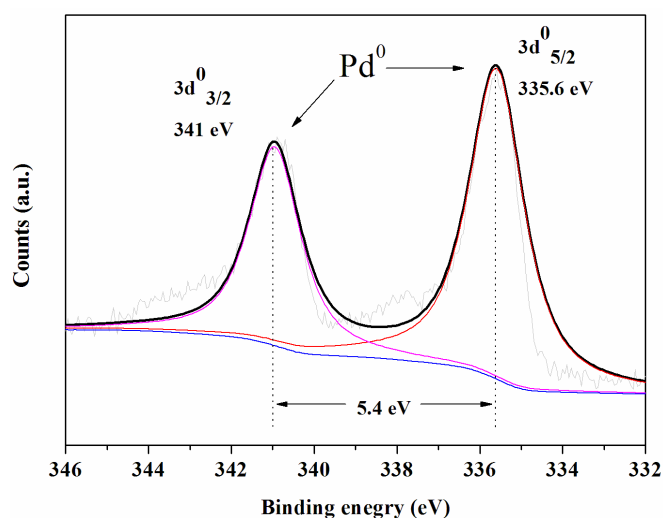


Fig. (4). XPS spectrum of Pd/C catalyst.

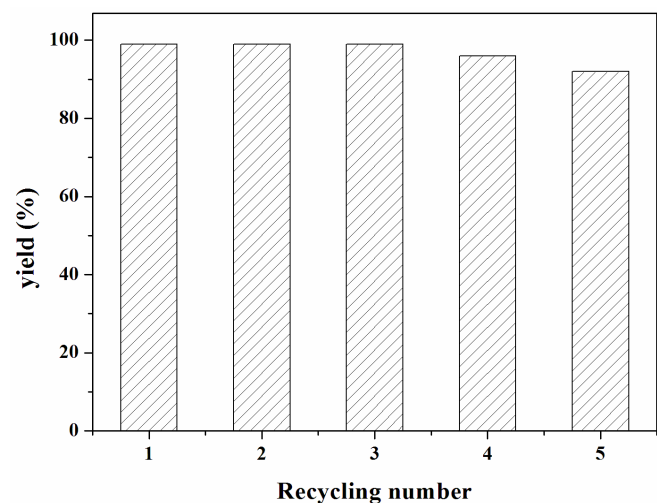
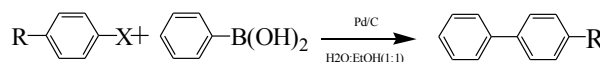


Fig. (5). Recycling test of nanocube Pd/C.

To evaluate the recycling efficiency, the Suzuki-Miyaura cross-coupling reactions with para-bromoacetophenone and phenylboronic acid over the prepared nanocube Pd/C were carried out under the same condition as entry 4 of Table 1

(except 1 h) for five times and the results are shown in Fig. (5). The catalyst could be separated from products by simple phase separation and recycled for five times without evident loss of activity.

Table 1. Representative Suzuki-Miyaura cross-coupling reactions over nanocube Pd/C catalyst<sup>a</sup>.



| Entry | X  | R                  | T/°C | Time/h | Yield <sup>b</sup> /% |
|-------|----|--------------------|------|--------|-----------------------|
| 1     | I  | -OCH <sub>3</sub>  | 40   | 0.5    | 99                    |
| 2     | I  | -H                 | 40   | 0.5    | 99                    |
| 3     | Br | -NO <sub>2</sub>   | 60   | 0.5    | 99                    |
| 4     | Br | -COCH <sub>3</sub> | 60   | 0.5    | 98                    |
| 5     | Br | -CN                | 60   | 0.5    | 96                    |
| 6     | Br | -OCH <sub>3</sub>  | 60   | 0.5    | 91                    |
| 7     | Br | -H                 | 60   | 1.0    | 98                    |
| 8     | Br | -CH <sub>3</sub>   | 60   | 1.0    | 92                    |
| 9     | Cl | -NO <sub>2</sub>   | 90   | 10     | 74                    |
| 10    | Cl | -COCH <sub>3</sub> | 90   | 10     | 65                    |
| 11    | Cl | -H                 | 90   | 20     | 53                    |

<sup>a</sup>Reaction condition: aryl halide (1.0 mmol), phenylboronic acid (1.2 mmol), EtOH:H<sub>2</sub>O (1:1, 12 mL), K<sub>2</sub>CO<sub>3</sub> (2.0 mmol), Pd/C catalyst (0.015 g, 0.37 mmol% Pd).  
<sup>b</sup>yields determined by HPLC with methyl alcohol as the external standard.

## CONCLUSION

Pd nanocubes with controllable size and shape have successfully been prepared with the assistance of PVP as a stabilizing agent and KBr as a capping agent. KBr and PVP were found to play an important role in the formation and size of Pd nanocubes, respectively. The nanocube Pd/C catalyst exhibits high catalytic activity and good stability in the Suzuki-Miyaura cross-coupling reaction. The catalytic activity of nanocube Pd/C catalyst was found to have no evident loss after five catalytic cycles. Therefore, this new nanocube Pd/C catalyst with the advantages of high efficiency and good recyclability will become a promising candidate for potential applications in industrial synthesis.

## CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

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