



Controllable synthesis of palladium nanoparticles and their catalytic abilities in Heck and Suzuki reactions



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ABSTRACT

The monodisperse palladium nanoparticles with the size of about 5.0 nm were prepared by the thermal decomposition of palladium acetylacetonate in the presence of oleylamine and borane tributylamine complex. The palladium nanoparticles were loaded on the active carbon black by the sonication followed by the acetic acid cleaning, and then they are used as the nanocatalysts for carbon coupling reactions, such as Heck reactions and Suzuki reactions. The nanocatalysts can promote Heck reactions and Suzuki reactions efficiently with the high catalytic activity and stability. The nanocatalysts can be recycled for at least six times and their morphologies almost have no great changes. In addition, the catalytic performances of nanocatalysts would decrease with the repeated usages due to the increasing sizes of the palladium nanoparticles.

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1. Introduction

Carbon–carbon bonds are found in many compounds that exhibit very important biological, pharmaceutical and materials properties [1–3]. Classically, the synthesis of carbon–carbon bonds always involved the nucleophilic aromatic substitution reactions, which required the use of electron-deficient aryl halides or N₂ as a leaving group [4–8]. The synthetic procedure is fussy and rigorous, so new mild and general methods should be developed. The discovery of transition-metal mediated reactions was important for the synthesis. Palladium (Pd) catalysts are usually used in cross-coupling reaction which can generate carbon–carbon bonds efficiently and simply [9]. While homogeneous Pd catalysts are not used in industrial application due to the difficulty in separating and recycling, low catalytic efficiency, and the high leaching of metal species [10,11]. In order to solve the problem, new strategies should be developed.

Metallic nanoparticles (NPs) are of wide interest since they lead to many interesting size-dependent electrical, chemical, and optical properties. Pd related NPs, such as Pd NPs, PdM (M = Cu, Ag, Ni, Co, Pt) alloy NPs and Pd core/shell (Au/Pd, Ag/Pd, Pd/Pt) NPs on various supports were most widely applied to many important reactions, such as carbon coupling reactions, small molecule electro-oxidation/reduction reactions, hydrocarbon hydrogenations, isomeriza-

tion, alkylation, hydrodealkylation, polymerization so on [12–14]. Recently, the investigations of NPs with precisely controlled shape and size have attracted great interest due to their great surface areas, and their wide applications, such as medicine industry, catalysis, energy, pollution controlling and so on [15–17]. Among the NPs, Pd NPs have gained considerable interest in the last few decades [18,19]. Furthermore, Pd NPs loaded on the inorganic supports can increase the stability of NPs, and thus the catalytic efficiency would increase greatly [20].

Herein, we described a simple method for preparing Pd NPs and carbon loaded Pd NPs (denoted as Pd/C NPs) by high-temperature decomposition method. Furthermore, the catalytic efficiencies of Pd/C catalysts were evaluated by Heck and Suzuki reactions.

2. Experimental

2.1. Materials and instrumentation

All the reagents, such as palladium acetylacetonate (Pd(acac)₂), oleylamine (OAm, technical grade, 70%), carbon black (Kejen EC 300J), acetic acid, borane tributylamine complex (BTB), Et₃N, aryl halides, styrene, phenylboronic acid were purchased and used without further purification. Water used in the experiments was deionized (DI) and doubly distilled prior to use. Unless otherwise stated, all the experiments were performed under air atmosphere.

Transmission electron microscope (TEM) images and selected area electron diffraction (SAED) patterns were acquired on a Philips

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CM 20 (200 kV) transmission electron microscope. X-ray powder diffraction (XRD) patterns of the samples were recorded on a Bruker AXS D8-Advanced diffractometer with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). The yields of Heck and Suzuki reactions were determined by GC analysis.

2.2. Synthesis of Pd NPs

Under a nitrogen flow, 75 mg of Pd(acac)₂ was mixed with 15 mL OAm. The formed solution was heated to 60 °C in 10 min, resulting in a near colorless solution. 60 °C is the injection temperature, at this temperature, and 300 mg of BTB was solvated in minimum amount of OAm (about 3–4 mL) and quickly injected into the Pd–OAm solution. A visible color change from colorless to a brown-black was observed. The temperature was raised to 90 °C (3 °C/min) and kept at this temperature for 60 min. The solution was cooled down to room temperature. 30 mL of ethanol was added and the product was separated by centrifugation. The product was then dispersed in hexane for next step.

2.3. Synthesis of Pd/C NPs

10 mg of Pd NPs were dissolved in hexane in a 20 mL vial and an equal amount of carbon support was added to it. This colloidal mixture was sonicated for 2 h to ensure complete adherence of Pd NPs onto the carbon support. After evaporation of hexane, 20 mL of acetic acid was added to the Pd/C dispersion and heated for 10 h at 70 °C. The reaction mixture was cooled down to room temperature. 30 mL of ethanol was added and the mixture was centrifuged at 8000 rpm for 8 min. This procedure was repeated for three times. The Pd/C NPs were recovered by adding acetone. Acetone was vaporated and the resultant Pd/C NPs were weighed. A measured amount of de-ionized water was added, resulting in a 2 mg/mL solution. This mixture was sonicated for 1 h to ensure uniform distribution. The Heck and Suzuki reactions were carried out using 4 mg of this catalyst.

2.4. General procedure for Heck reaction

Typically, the as-prepared 4 mg catalyst was added into the mixture solution of 10 mmol aryl halide, 20 mmol Et₃N and 5 mL DMF. The mixture solution was preheated for 1 h, and then 12 mmol styrene was added. Then the solution was heated and stirred at 140 °C for 6 h. After cooling down to the room temperature, the catalyst was recycled for next reaction cycle by acetone precipitation and centrifugation. The organic phase was collected, dried and used for GC analysis. The experiments were repeated with the catalyst recycled from previous reaction.

2.5. General procedure for Suzuki reaction

Typically, the as-prepared 4 mg catalysts was dispersed in 5 mL DMF, and then 10 mmol aryl halide, 15 mmol phenylboronic acid and 20 mmol Et₃N were added into a 100 mL round-bottom flask. The flask was sealed, stirred, and heated at 140 °C for 2 h. After cooling down to the room temperature, the catalyst was recycled for next reaction cycle by acetone precipitation and centrifugation. And the filtrated solution was collected and dried. The presence of the product was determined by GC analysis. The experiments were repeated with the catalyst recycled from previous reaction.

3. Results and discussion

The Pd NPs were prepared by the high-temperature decomposition of palladium acetylacetonate in the presence of OAm and BTB.

In this reaction, OAm is acted as the reaction solvent, surfactant and reductant. And BTB served as a coreductant. The NPs became monodisperse during the 1 h growth at 90 °C due to Ostwald ripening. In the synthetic procedure, the use of OAm is very important. If another alkylamine, such as hexadecylamine, octadecylamine, or dodecylamine was used, no high quality Pd NPs can be obtained, showing that the double bond present in oleylamine plays a critical role in Pd NP stabilization and growth with a narrow size distribution. However, oleylamine alone cannot be used to prepare monodisperse Pd NPs. The weak reducing power offered by oleylamine prolongs the reduction process, causing multinucleation and an uneven growth rate over differently sized Pd nuclei. BTB fared better than other borane reductants we tested, such as borane–morpholine complex and NaBH₄. It offers an ideal combination with oleylamine for the facile synthesis of monodisperse Pd NPs. As shown in Fig. 1a, the size of Pd NPs is about 5.0 nm, and Pd NPs show a narrow size distribution with a standard deviation of about 8% with respect to the diameter of the Pd NPs. XRD patterns of Pd NPs have been determined by X-ray diffraction apparatus. As shown in Fig. 2, the obvious peak (111) has been found, and the peak is corresponding to the characteristic peak of Pd NPs. The polycrystalline structure of the NPs can be confirmed by the X-ray diffraction pattern of the Pd NP assembly, from which the average NP size was estimated to be about 4.0 nm, which is smaller than the value of 5.0 nm measured from the TEM images in Fig. 1a. [21] In addition, in order to differentiate the crystalline model of Pd nanoparticles, its selected area electron diffraction (SAED) image was performed (Fig. 1c). Its SAED pattern exhibited several diffused rings, which confirms the polycrystalline nature of Pd nanoparti-

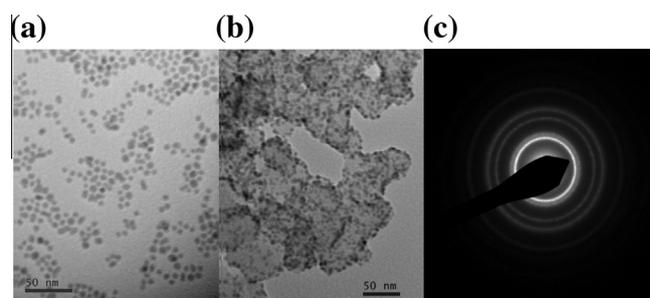


Fig. 1. TEM images of Pd NPs (a), Pd/C NPs (b) and SAED pattern of polycrystalline Pd NPs (c).

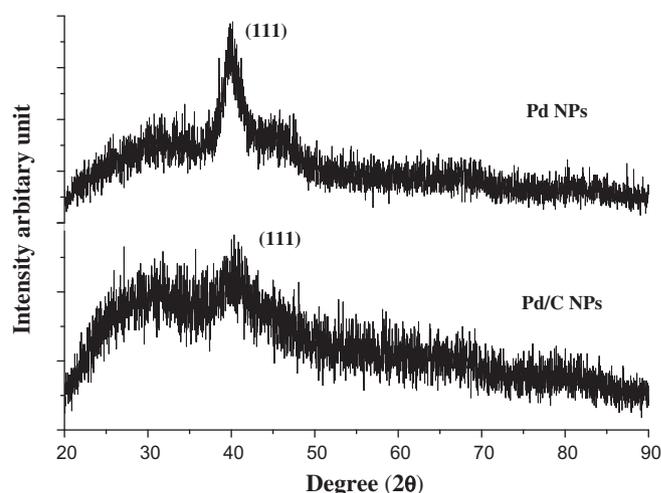
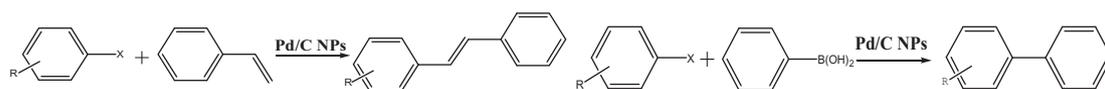


Fig. 2. XRD patterns of Pd NPs and Pd/C NPs.

Table 1

Heck and Suzuki reactions of aryl halides and styrene or phenylboronic acid catalyzed by Pd/C NPs.



Entry	R	X	Yield (%) ^a	Yield (%) ^a
1	H	Cl	61	41
2	H	Br	91	92
3	H	I	95	98
4	<i>m</i> -Me	Br	75	69
5	<i>m</i> -Me	I	82	87

^a Yields were determined by GC analyses.**Table 2**

Repeated uses of Pd/C NPs for catalyzing Heck and Suzuki reactions, respectively.

Entry	Reagent 1	Reagent 2	Yield of each round (%) ^a					
			1	2	3	4	5	6
1			91	88	84	82	78	72
2			92	86	82	80	71	69

^a Yields were determined by GC analyses.

cles. In order to prepare nanocatalysts for Heck and Suzuki reactions, Pd NPs were loaded on the Ketjen carbon black by the sonication followed by the acetic acid cleaning. As shown in Fig. 1b, the Pd NPs are well dispersed on the carbon support. The size and morphology of Pd NPs on carbon black have no great changes. In addition, the XRD patterns of Pd/C NPs have been obtained. As shown in Fig. 2, the peak (1 1 1) of Pd/C NPs is corresponding to the characteristic peak of Pd NPs, which indicated that Pd NPs were well-dispersed onto the carbon black.

The Pd/C NPs were tested for catalyzing carbon–carbon coupling reactions–Heck and Suzuki reactions. The reaction variables such as the temperature, reaction time, and base were optimized. For Heck reactions catalyzed by Pd/C NPs, Et₃N as the base and DMF as the reaction solvent were used. Furthermore, we investigated that the reaction time for 6 h and reaction temperature for 140 °C are the optimal reaction conditions. For Suzuki reactions, the base is Et₃N and the reaction solvent is DMF. When the reactions were terminated, the reaction solutions were removed from the flask and then subjected to GC analyses. Pd/C NPs were washed and dried for next recycle reactions, and more than 95% of Pd/C NPs could be recovered based on the calculations of weights of Pd/C NPs.

The yields of Heck reactions for aryl halides and styrene were showed in Table 1. The yields of chlorobenzene, bromobenzene and iodobenzene with styrene increase with the stronger of electron donating ability. For the reaction of 2-bromotoluene and styrene, the yield is 75%. While when the substituted group is iodide, the yield increases greatly. All these indicated that the electron donating ability of the substituted groups has a great importance on the reaction yields [22–24]. The yields of Suzuki reactions for aryl halides and phenylboronic acid were shown in Table 1. For Suzuki reactions, the yield of reaction for chlorobenzene and phenylboronic acid is the worst, while the yield of reaction for iodobenzene

and phenylboronic acid is best. When the substituted group, such as methyl group exists, the reaction yield would decrease accordingly due to its hindrance ability.

We also investigated the feasibility of repeated use of Pd/C NPs on Heck and Suzuki reactions. In Table 2, we present the experimental results from the investigations of recycling of Pd/C NPs for six consecutive rounds under the same experimental conditions. After each round, the Pd/C NPs were centrifugated, dried and used directly for the next round without any further purifications. The yields of Heck and Suzuki reaction decrease slowly. For Heck reaction of bromobenzene and styrene, TEM images of Pd/C NPs after each round were exhibited in Fig. 3. As seem, the morphology of Pd/C NPs after every round has no great changes. But the size of Pd NPs loaded on carbon black is increasing subtly with the increasing cycles, and that is why the reaction yield is decreasing [25,26]. Similarly, the yield of Suzuki reaction also decreases due to the same reason. We have compared the activities of prepared Pd/C nanoparticles with other similar catalysts according to your suggestion. Pd nanoparticles immobilized on amine-functionalized zeolite can promote Heck reaction greatly, but we found the morphologies of the nanoparticles have changed a lot with its repeated use [27]. Pd–Fe₃O₄ heterodimer nanocrystals exhibited good activities for various Suzuki coupling reactions. The yield is only 81%, which is lower than that of our nanocatalysts [28]. Pd catalyst on amorphous silica for Suzuki couplings was prepared, which was efficient in coupling of aryl iodides and aryl bromides but not active enough toward aryl chlorides. The catalyst could be reused only three times without losing activity [29]. Compared with these similar catalysts, we found our nanocatalysts are easy to prepare, and they can promote Heck and Suzuki reactions greatly with its repeated uses without losing its activity.

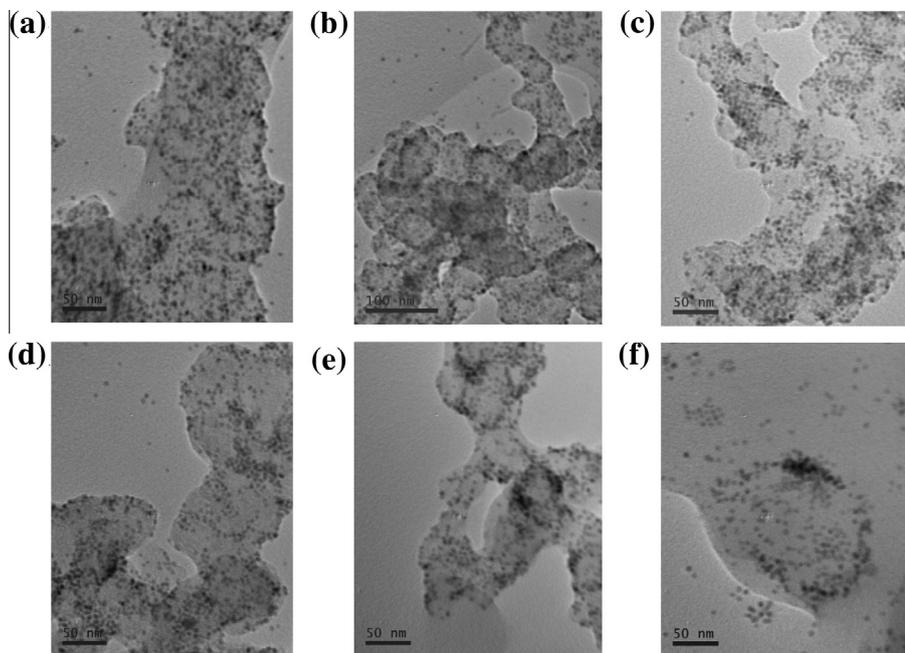


Fig. 3. TEM images of Pd/C NPs after catalyzing Heck reaction of bromobenzene and styrene for the first cycle (a), second cycle (b), third cycle (c), fourth cycle (d), fifth cycle (e) and sixth cycle (f).

4. Conclusions

In summary, the monodisperse Pd NPs were synthesized via the high-temperature decomposition of Pd(acac)₂ in the presence of OAm and BTB with the size of about 5.0 nm. Pd NPs were loaded on carbon black to be used as nanocatalysts for carbon coupling reactions, such as Heck and Suzuki reactions. Pd/C NPs showed great catalytic ability on Heck and Suzuki reactions. In addition, Pd/C NPs can be recycled in Heck and Suzuki reactions for at least six cycles without any changes of their morphologies. Pd/C NPs are good and efficient nanocatalysts for carbon coupling reactions such as Heck reaction and Suzuki reactions.

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