



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



Yong Li^{a,*}, Yu Dai^a, Zhengyin Yang^b, Tianrong Li^b

^a Faculty of Materials Science and Chemistry, China University of Geosciences, Wuhan 430074, PR China

^b College of Chemistry and Chemical Engineering and State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, PR China

ARTICLE INFO

Article history:

Received 7 October 2013

Received in revised form 13 January 2014

Accepted 22 January 2014

Available online 8 February 2014

Keywords:

Palladium nanoparticles

Transmission electron microscope

Catalytic ability

Heck reaction

Suzuki reaction

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.

© 2014 Elsevier B.V. All rights reserved.

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

* Corresponding author. Tel.: +86 027 67883739.

E-mail address: liyong07@126.com (Y. Li).

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-

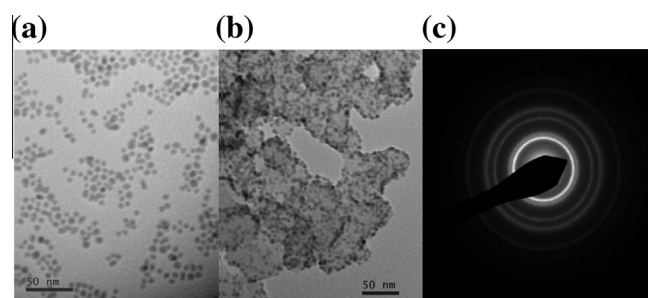


Fig. 1. TEM images of Pd NPs (a), Pd/C NPs (b) and SAED pattern of polycrystalline Pd NPs (c).

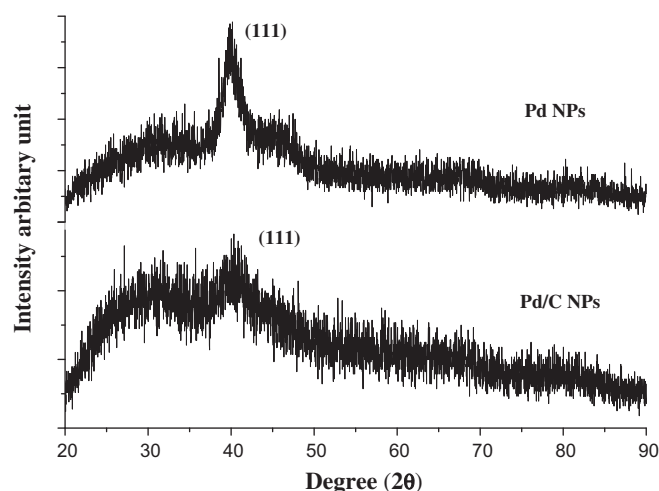


Fig. 2. XRD patterns of Pd NPs and Pd/C NPs.

Download English Version:

<https://daneshyari.com/en/article/1305664>

Download Persian Version:

<https://daneshyari.com/article/1305664>

[Daneshyari.com](https://daneshyari.com)