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Facile One-Pot Ultrasound-Assisted Reduction Synthesis of Pd/C Nanocatalyst for Green Suzuki-Miyaura Coupling

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***Abstract*—Palladium nanoparticles (Pd NPs) supported on active carbon was prepared via ultrasonically treating Pd precursors in ethylene glycol without any protective agents. The Pd/C nanocatalysts were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), N2-adsorption analysis, and X-ray photoelectron spectrometry (XPS). The results suggested that Pd NPs with an average particle size of 7.54 nm are formed in Pd/C-600W. Pd NPs of Pd/C-600 W nanocatalysts were highly distributed on the surface of active carbon. Even under mild conditions, Pd/C-600 W catalyst exhibited a better catalytic performance than that of Pd/C-T catalysts in Suzuki-Miyaura coupling reactions. The yield of 4-bromonitrobenzene reached 94.28% with only 0.1 mmol% Pd/C-600 W catalyst. Pd/C-600 W catalyst could be easily separated by filtration. It could be recycled four times with limited activity decrease. The catalytic activity and recyclability of Pd/C-600 W is higher than Pd/C-T. This ascribed to smaller size and more uniform dispersion of Pd/C-600 W.**

Keywords—ultrasonic reduction, pd/c nanocatalyst, heterogeneous catalysts, green suzuki-miyaura coupling reaction.

I. INTRODUCTION

Palladium (Pd)-based nanometerials have get great attention as catalyst due to its high activity in various catalysis systems including the well-known Suzuki [1, 2], Sonogashira and Heck, which are the vital way to construct carbon-carbon bond.

To achieve the high activity of the Pd nanocatalyst, controlling the size and increasing the active sites are important. A large amount of attempts have been made to synthesize Pd NPs using complicated procedures, such as adding protective agents to prevent Pd NPs from reuniting. However, these methods lead to the reduction of active sites resulted from absorbing on the surface of nanocatalyst by protective agents.

Various approaches have been used to prepared Pd nanocatalsyst, such as impregnation, chemical reduction [3], electrochemical deposition [4], microwave assisted chemical reduction and ultrasonic reduction. Among various methods for preparing nanocatalysts, the ultrasonic reduction is more promising because of its facile process, low cost, mild reaction conditions and potential for large-scale production. The mechanism of ultrasonic reduction arise from acoustic cavitation, which is the formation, growth and implosive collapse of bubbles in liquid. The extreme transient conditions introduced by ultrasound produced hot spots with temperature up 5000 K, pressure above 1000 atmospheres, heating and colling rates exceeding 1010 $K\cdot s^{-1}$, permitting the preparation of catalysts in mild conditions instead of high temperature and strong reductants [5].

Therefore, in this research, the supported Pd/C nanocatalyst is synthesized from Na_2PdCl_4 as Pd precursor by one-pot ultrasonic reduction, employed ethylene glycol as reductant and solvent without any protective agent in reaction system. The catalytic properties and recyclability of Pd/C-600W for the Suzuki-Miyaura coupling reaction of 4-bromotoluene and phenylboronic acid were examined.

II. PREPARATION OF PD/C NANOCATALYST

Firstly, a commercially available coconut shell activated carbon was crushed and sieved. In a typical ultrasonic synthesis, 0.5 g active carbon (200-300 mesh) was dispersed in 30 mL of ethylene glycol at an ultrasonic power of 100 W for 30 min. Then, a required amount (5 wt% Pd) of the precursor solution (Na_2PdCl_4, 0.5 mol/L) was sonicated at ultrasonic power of 600 W for another 30 min. The final black solid was centrifuged and washed, dried at 40 °C in an oven for 12 h, and ground into a fine powder. During the reaction process, the reaction temperature was kept at about 30°C using the water surrounding the reactor. The obtained catalysts were denoted as “Pd/C-600 W”. As a comparison, Pd/C nanocatalyst was prepared by conventional water-bath and magnetic stirring without ultrasound, denoted as “Pd/C-T”.

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III. GENERAL PROCEDURES OF SUZUKI COUPLING REACTION

The required amount of the Pd/C nanocatalysts (0.1 mmol%, 0.25 μmol) was added to the stirring mixture of 4-bromotoluene (2.5 mmol), K_2CO_3 (691.0 mg, 5.0 mmol), 30 mL of EtOH/H_2O (1:1) and phenylboronic acid (365.8 mg, 3.0 mmol) followed. The mixture was then stirred at 60°C for 60 min. in a water bath and extracted with ethyl acetate (3 × 10 mL). The organic layer was combined and then analyzed by HPLC. In order to check the recycling and stability of Pd/C nanocatalyst, Pd/C nanocatalyst was collected by centrifugation and then washed thoroughly with NaOH to remove the redundant phenylboronic acid, followed by water and ethanol to remove the impurity present in the used catalysts.

IV. RESULTS AND DISCUSSIONS

Fig. 1 showed the XRD patterns of the activated carbon, Pd/C-600 W, and Pd/C-T. Two broad peaks at about 24.6° and 43.8° appeared at all samples are assigned to the planes typical for graphite carbons. In the patterns of Fig. 1a and b, the peaks appearing at 40.1°, 46.6° and 68.1° were due to the presence of face-centered cubic Pd planes (111), (200), (220) [6]. This suggests that Pd was successfully loaded on the surface of active carbon through two different reduction methods. The peak intensity of Pd/C-T nanocatalyst was significantly sharper in shape and higher in intensity. This indicates that Pd/C-600 W nanocatalyst prepared by ultrasonic method had smaller size.

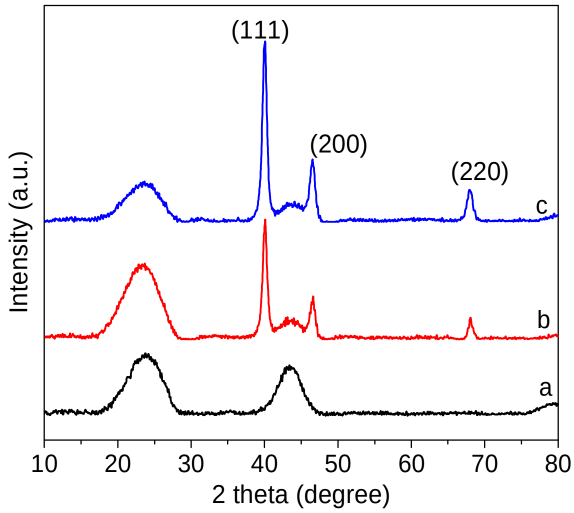


Fig. 1. XRD patterns of (a) activated carbon, (b) Pd/C-600 W and (c) Pd/C-T.

The N_2 adsorption-desorption isotherms and the corresponding pore size distribution of activated carbon, Pd/C-T and Pd/C-600 W are depicted in Fig. 2. All the samples present a type I isotherm according to the IUPAC classification and exhibited a H4 hysteresis loop indicating the typical micropore structure [7]. The overall form of the N_2 adsorption-desorption isotherms of Pd/C nanocatalysts were similar to that of active carbon, suggesting that they retained ordered structure.

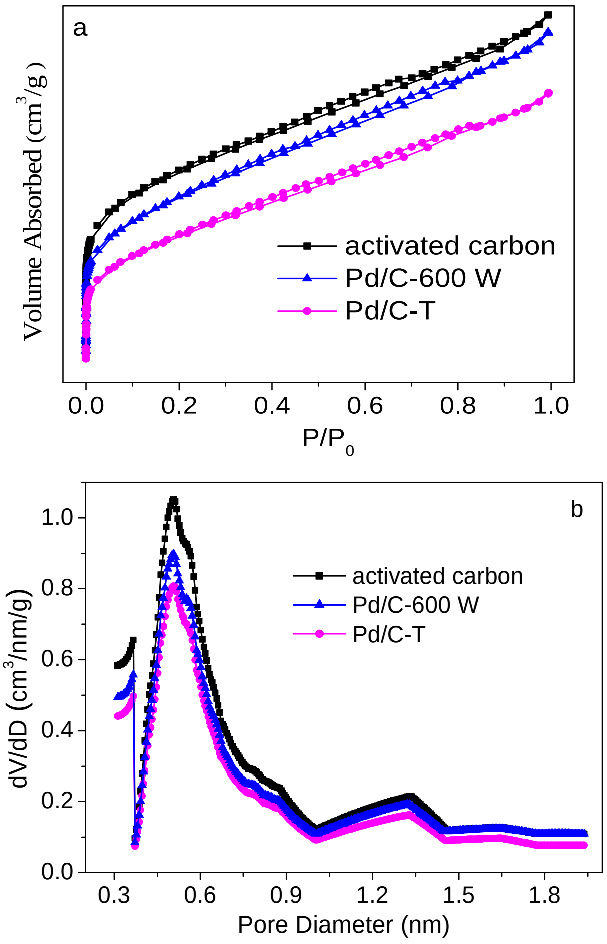


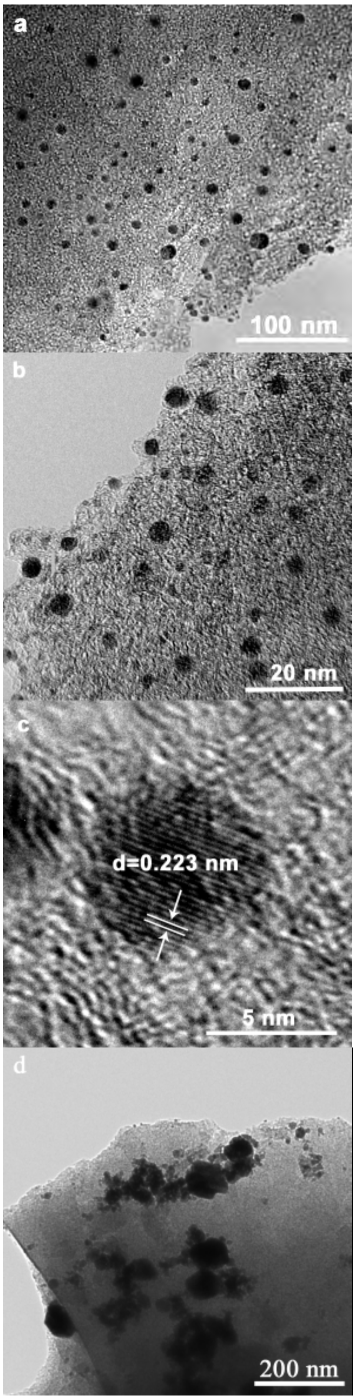
Fig. 2. (a) N2 adsorption-desorption isotherms and (b) Pore size distributions curves of activated carbon, Pd/C-T and Pd/C-600 W

The main textual properties of the samples are shown in Table 1. Compared with the support active carbon, BET surfaces and pore volume of Pd/C-600W and Pd/C-T nanocatalysts are decreased. The decrease suggests that Pd at least partially located inside the channels of support. The reduction of BET surfaces and pore volume are more remarkable for Pd/C-600W, which may be due to the Pd NPs of Pd/C-T prepared by conventional method have increased size resulted in moving from the channel to surface or edge of support. This result will be evidenced by TEM. According to the adsorption branches using the HK method, the pore distribution of active carbon reveals uniform micropores distribution with pore diameter 0.508 nm, with no significant differences for Pd/C catalysts. This demonstrates that the pore structure of active carbon is not destroyed.

TABLE 1. TEXTURAL PROPERTIES OF ACTIVATED CARBON, PD/C-600 W AND PD/C-T.

Samples	S_{BET} [m^2/g]	D_{HK} [nm]	V_{HK} [cm^3/g]
Activated carbon	1200.0	0.508	0.9208
Pd/C-600 W	910.7	0.502	0.6774
Pd/C-T	1048.7	0.508	0.8770

The TEM images and the particle size distribution of Pd/C-600W are displayed in Fig. 3. After introduction of Pd, uniform Pd distribution can be observed. The high-resolution transmission electron microscopy (HRTEM) image further demonstrated the lattice fringe was 0.223 nm, which was attributed to the lattice spacing of the Pd (111) plane [8] (Fig. 3c). The Pd NPs size of Pd/C-600W catalyst ranges from 3.77 nm-17.87 nm and the mean size is about 7.54 nm (Fig. 3e). For the Pd/C-T catalyst, the Pd NPs tended to aggregate remarkably. This further validates that the ultrasound provides the sufficient volatility and diffusion leading to the formation of highly disperse Pd NPs.



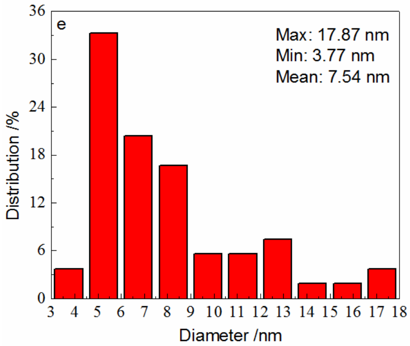


Fig. 3. (a, b) TEM images and (c) HRTEM image of Pd/C-600 W, (d) TEM image of Pd/C-T and (e) particle size distribution of Pd/C-600 W.

The XPS spectrum of the Pd 3d region consists of four peaks (Fig. 4). The peaks at lower binding energy (335.05 and 340.45 eV) belong to Pd^0, and the other peaks at 337.1 and 342.5 eV are assigned to Pd^{2+} [8]. The presence of Pd^{2+} may arise from an incomplete reduction of Pd^{2+} ions and the oxidation of naked metal Pd atoms under ambient conditions. According to the peak area of zerovalent palladium and bivalent palladium, the similar reduction degrees are determined, about 68% and 65% for Pd/C-600W and Pd/C-T.

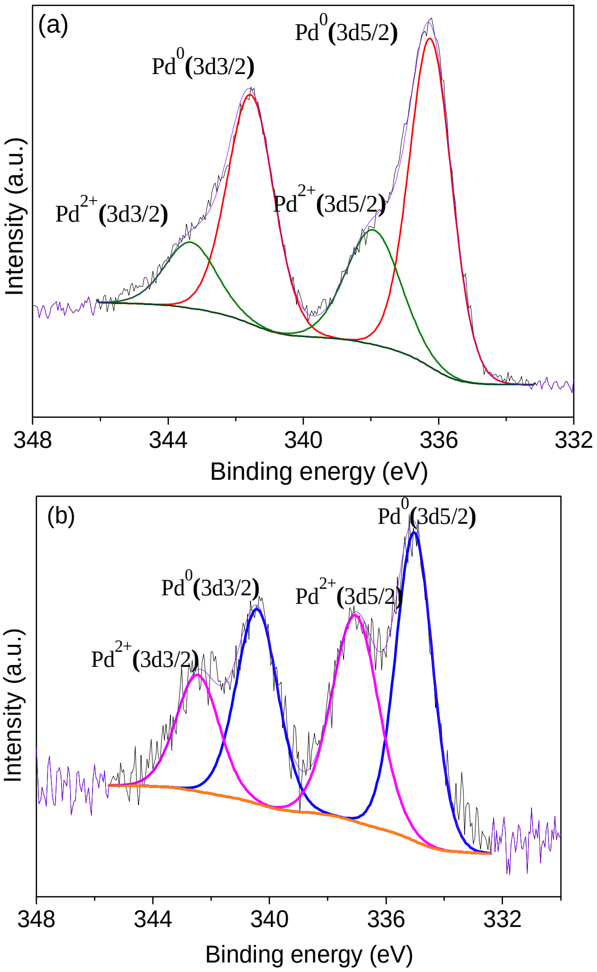


Fig. 4. Pd 3d XPS spectrum: (a) Pd/C-600 W and (b) Pd/C-T

V. SUZUKI-MIYAURA COUPLING REACTION

As shown in Fig. 5a, the yield increase gradually along with the increase of reaction time in catalytic processes of two kinds of catalysts, and the catalytic activity of Pd/C-600W prepared by ultrasonic reduction method is superior to the traditional preparation of Pd/C-T catalyst. The conversion of 4-bromotoluene reached to 94.28% at 60 min, up to 96.09% at 90 min with only 0.1 mmol% catalyst. Combined with TEM analysis, it indicates that the dispersion of Pd NPs on the surface of support plays a decisive role to the catalytic activity of catalysts. The high dispersion of Pd NPs is advantageous to expose more active sites and contact more sufficiently with reactants, resulted in increasing the catalytic activity. And the preparation of supported Pd NPs by ultrasonic method in the absence of protective agent can effectively improve its dispersion, obtaining the high catalytic efficiency. Pd/C-600 W nanocatalyst was tested in terms of durability of five cyclic run. Fig. 5b shows that Pd/C-600 W nanocatalyst still exhibits over 90% after three cycles, and retains 80% in the fifth cycle. As for the Pd/C-T catalyst, the activity decreased to 50% after using three cycles. It can be explained that the Pd NPs in the case of Pd/C-600W has smaller size and more uniform dispersion, determining more strong interaction between Pd species and support, and further obtained the better recyclability and stability for Pd/C-600W than Pd/C-T.

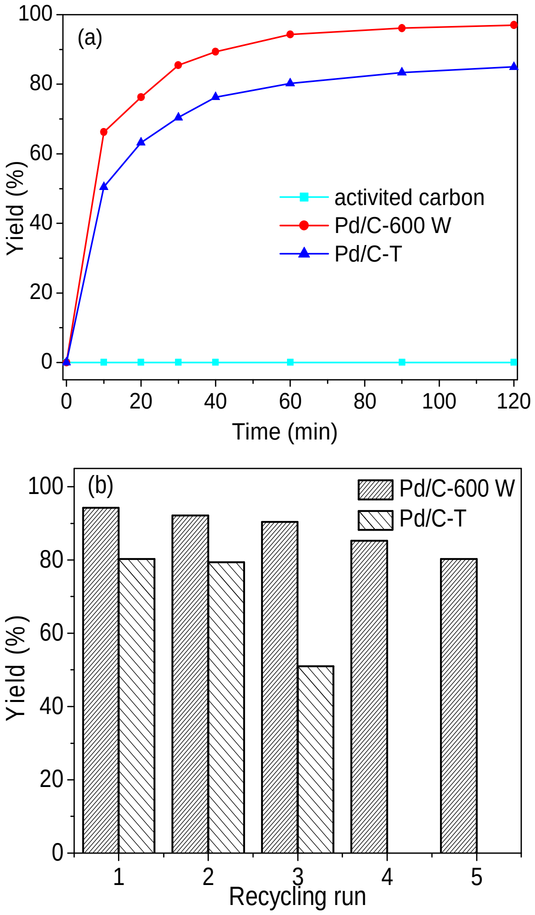


Fig. 5. (a) Yield of 4-bromotoluene at different intervals with various catalyst and (b) The recyclability of the Pd/C catalysts for the Suzuki-Miyaura coupling reaction

VI. SUMMARY

In conclusion, we have succeeded in synthetizing Pd/C-600W catalyst for green Suzuki-Miyaura coupling reaction by facile one-pot ultrasonic reduction. The Pd NPs with an average particle size of 7.54 nm were uniformly dispersed on the active carbon surface in Pd/C-600W catalyst without any protective agent. The catalyst shows high activity toward Suzuki-Miyaura coupling reaction under mild conditions employed only 0.1 mmol% amount of catalyst. In addition, the yield of d/C-600W catalyst retained 80% after recycling five times.

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