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In-situ preparation of Pd nanoparticles in the pore channel of CMK-3 for Suzuki coupling reaction

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ABSTRACT

Palladium nanoparticles (PdNPs) supported on ordered mesoporous carbon (CMK-3) were prepared by Ar glow discharge plasma technology (P-PdNPs/CMK-3) without the use of any chemical additives or surfactants and chemical method using ascorbic acid as reducing agent (AA-PdNPs/CMK-3), respectively. The PdNPs/CMK-3 catalysts were characterized by XRD, N_2 absorption-desorption and TEM analysis. The results showed that the as-prepared PdNPs were of the face-centered cubic structure, P-PdNPs/CMK-3 had an average particle size of 3.4 nm (lower than CMK-3 pore diameter of 3.7 nm), which corresponded to an average diameter of 11.1 nm for AA-PdNPs/CMK-3. The *in-situ* preparation of P-PdNPs/CMK-3 had a higher dispersion of Pd species and mainly formed inside the pore channels of CMK-3, but distributed on the outer surface of support for AA-PdNPs/CMK-3. The yield reached 95% in the presence of 0.1 mmol% P-PdNPs/CMK-3 at 40 °C for 30 min towards the reaction of 4-bromonitrobenzene and phenylboronic acid, which corresponded to 86% for AA-PdNPs/CMK-3. The better stability and recyclability for P-PdNPs/CMK-3 were confirmed by the hot filtration and recycling test.

1. Introduction

Transition metal palladium has been immensely used for catalyzing coupling reactions such as Suzuki, Heck, Negishi reactions [1–3] to construct carbon-carbon bond. The Suzuki coupling reactions of aryl halides with organic boric acid has wide applications for the synthesis of biaryl unit that exists in numerous compounds including natural product, agrochemicals, pharmaceuticals and other materials [4–7] owing to its mild reaction conditions and broad functional group tolerance.

The Suzuki coupling reactions catalyzed by palladium (0) complex with ligands under homogeneous systems have been widely adopted in the past decades [8,9]. The high catalytic activity is one of the most important advantages for homogenous catalyst. However, the homogenous systems suffer from the problems of economy and environment such as high price, poisonous ligands and difficulty in separation, which cannot be ignored in industrial scale applications [10,11]. The heterogeneous catalytic systems without any ligands have gained much attention due to their low cost, easy preparation process and good recycling performance. There are many kinds of carriers such as mesoporous silica [12–16], metal oxides [17,18], polymer [19], particularly carbonaceous materials have been greatly used to prepare supported metal catalyst [20–24]. Ordered mesoporous carbon (OMC) as a kind of carbon-based material has aroused great interest due to its high surface area, large pore size and volume, and superior thermal stability. CMK-3 mesoporous carbon, one of the most common and widely used OMC materials, owning the excellent properties of OMC materials has been a suitable support for the immobilization of metal nanoparticles [25–27].

The supported Palladium nanocatalysts have attracted much attention due to their high catalytic performance, stability and reusability. A traditional method for preparing supported metal nanocatalysts mainly involves metals salt, support materials and reducing agent. A protective agent such as polymers, surfactants and ligands [28,29] is also necessary to the reduction process for preparing small-size metal nanoparticles. Glow discharge plasma, a new reduction technology, has been applied in nanocatalysts preparation without any chemical reduction and protective agents [30–32]. The preparation process is similar to the *in-situ* reduction of palladium ions so that greatly avoid agglomeration of the nanoparticles. The small and highly dispersed PdNPs are much easier to be prepared by glow discharge plasma technology.

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In this work, we present a facile method for preparing supported PdNPs/CMK-3 catalysts using ordered mesoporous carbon materials (CMK-3) as support material by Ar glow discharge plasma (P-PdNPs/CMK-3). The AA-PdNPs/CMK-3 was prepared by a traditional chemical method using ascorbic acid as reducing agent in the presence of Polyvinylpyrrolidone (PVP) for a comparison. Catalytic performances of PdNPs/CMK-3 in Suzuki coupling reaction were examined.

2. Experimental

2.1. Materials

Mesoporous carbon materials (CMK-3) were purchased from Nanjing Jcnano Co. Ltd. All chemicals were of reagent grade and were purchased from Sinopharm Chemical Reagent Co., Ltd.

2.2. Characterization

The N_2 absorption and desorption isotherms at 77 K were measured using Micrometrics ASAP2020 system. The specific surface area and the pore size distribution were calculated using the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods. X-ray diffraction (XRD) patterns were measured on the Shimadzu XRD-7000 X-ray diffractometer with a Cu Ka radiation ($\lambda = 0.154$ nm). The scanning range 2θ of the wide-angle is from 10° to 80° with a scanning speed of 4°/min. The structure and morphology of samples were performed on a JEM-2100FX transmission electron microscopy at an accelerating voltage of 200 kV. H_2-TPR experiments were carried out by a Micromeritics AutoChem II 2920 absorption instrument.

2.3. Preparation of Pd/CMK-3 catalysts

$PdCl_2$ (0.0834 g) and NaCl (0.0550 g) were added into 10 mL deionized water to prepare the solution of sodium tetrachloropalladate (Na_2PdCl_4) under ultrasonic treatment for 40 min. Then CMK-3 (1 g) was immersed in the obtained Na_2PdCl_4 solution and stirred for 12 h at room temperature. The resultant sample was then reduced by glow discharge plasma using argon as the plasma forming gas in the discharge tube of plasma reactor under the system pressure of 100 Pa. The reduction process was performed for 60 min to prepare the P-PdNPs/CMK-3 catalyst with Pd amount of 5 wt.%.

The 5 wt.% AA-PdNPs/CMK-3 catalyst reduced by ascorbic acid was prepared by the following steps: Na_2PdCl_4 solution was first prepared and impregnated in Na_2PdCl_4 solution as the same procedure mentioned above. Then AA-PdNPs/CMK-3 was prepared with molar radio Pd/PVP/AA = 1:8:1.2 at 60 °C under vigorous stirring for 2 h.

2.4. Catalytic tests

A mixture of aryl bromides (1.0 mmol), phenylboronic acid (1.5 mmol), K_2CO_3 (2 mmol), PdNPs/CMK-3 catalyst (0.1 mmol%), EtOH/H_2O (6 mL/6 mL) was stirred at 40 °C for 30 min. After completion of the reaction, the mixture was extracted with ethyl acetate. The organic layers were collected, and dried at room temperature to obtain the product. Evaluation results of products were identified by the HPLC.

2.5. Recycle test

The recycle test was examined by the Suzuki coupling reaction of 4-bromonitrobenzene and phenylboronic acid. After the coupling was completed, PdNPs/CMK-3 catalysts were washed several times, dried and reused for the next run.

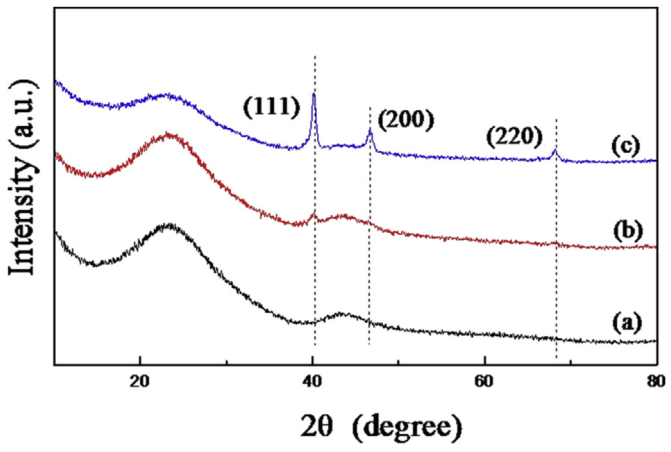

Fig. 1. XRD patterns of (a) CMK-3; (b) P-PdNPs/CMK-3; (c) AA-PdNPs/CMK-3.

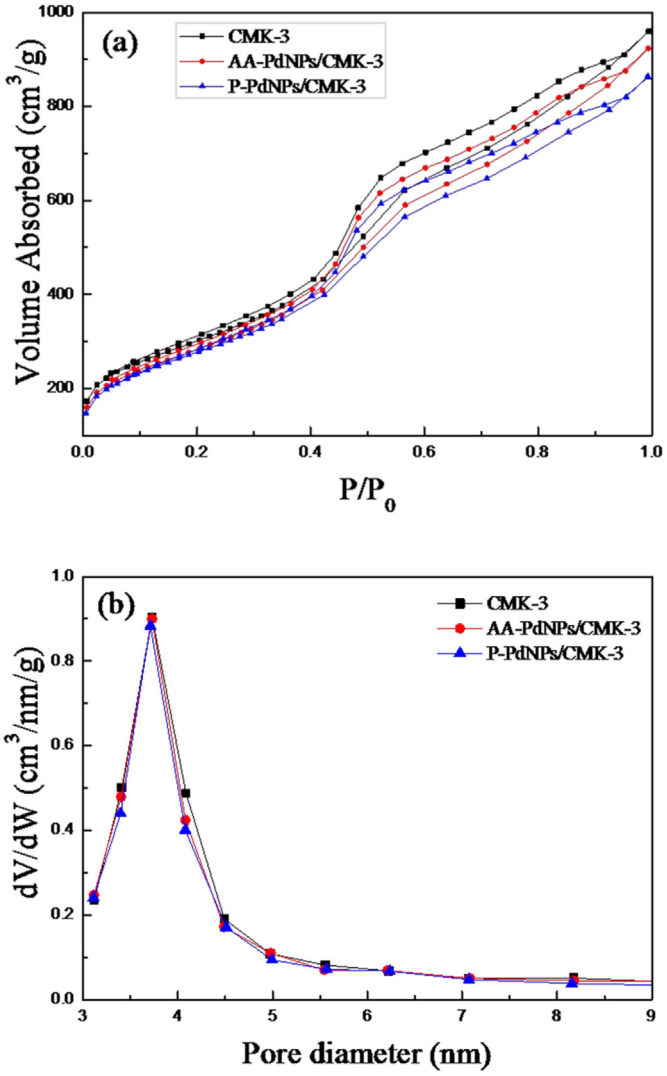

Fig. 2. N_2 adsorption-desorption isotherms (a) and pore size distribution (b) of CMK-3, P-PdNPs/CMK-3 and AA-PdNPs/CMK-3.