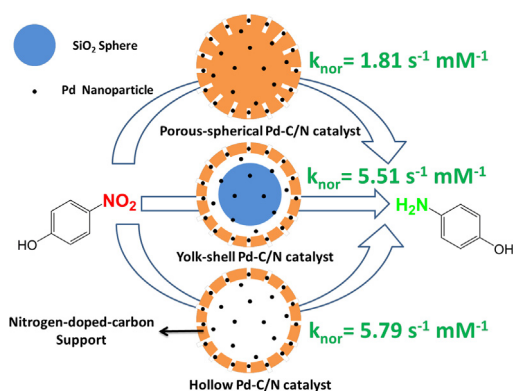Regular Article

Distinctive morphology effects of porous-spherical/yolk-shell/hollow Pd-nitrogen-doped-carbon spheres catalyst for catalytic reduction of 4-nitrophenol

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GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

Pd-nitrogen-doped-carbon nanocatalysts (Pd-C/N) with different morphologies, such as porous spheres, yolk-shell and hollow structures, had been synthesized and compared. The yolk-shell Pd-nitrogen-doped-carbon nanocatalysts (YS-Pd-C/N) and hollow Pd-nitrogen-doped-carbon nanocatalysts (H-Pd-C/N) were prepared through different etch time using SiO_2 spheres as hard-templates. The as-prepared catalysts were characterized thoroughly by TEM, BET, XRD, FT-IR, and XPS. Importantly, the catalysts have moderate BET specific surface area in the range from 200 to 300 $m^2\,g^{-1}$ and pore volume between 0.2 and 0.3 $cm^3\,g^{-1}$. The reduction of 4-nitrophenol is chosen as a model reaction to research the morphology effects of these prepared Pd-C/N catalysts with the same chemical compositions. Interestingly, H-Pd-C/N exhibited the best catalytic performance, which could be attributed to its high nitrogen content, the uniform distribution of abundant active sites, as well as the synergistic effect of graphitic C/N shell and Pd species for the catalytic reaction. Especially, the unique hollow morphology and porous shell of H-Pd-C/N made it to be a nanoreactor, which was beneficial to improve the catalytic activities. In addition, H-Pd-C/N nanocatalysts exhibited favorable stability in the recycling reactions.

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1. Introduction

Porous carbon materials have attracted great attention due to their remarkable performance in various applications including adsorption, separation, catalysis, energy devices and chromatography [1–3]. Compared with carbon materials, nitrogen-doped carbon seems to be more attractive [4]. Carbon nitride and its precursors were firstly described by Liebig [5]. As a well-known and fascinating material, carbon nitride has attracted increasing attention because incorporating nitrogen atom into the carbon nanostructure would efficiently enhance the mechanical, field emission, and energy-storage properties [6–13]. Nitrogen-doped carbons as interesting functional materials have been proposed as metal-free catalysts for oxygen reduction [14] and metal-catalyst supports for hydrogen evolution reactions [15]. Importantly, they were also regarded as supports for transition metal catalysts [16–27]. It has already been confirmed the introduction of nitrogen atoms can improve the electron-donor properties and surface polarity of the carbon matrix [28]. One reason is that nitrogen introduced into carbon supports can modify nucleation during the active nanoparticle deposition, which results in smaller active nanoparticle size and increased dispersity. In addition, nitrogen functional groups can enhance the interaction between active site and support, especially for those active sites which can coordinate with nitrogen. Thus, the introduction of nitrogen could improve intrinsic catalytic activity [4,29]. Because of these advantages, nitrogen doping has been used to tune the properties of carbon nanotubes [30–32], graphene nanosheets [33–36], nano-bulk [37] and nanoribbons in recent years [38,39]. Both in situ doping and post synthesis doping methods are used to prepare nitrogen doping materials [40,41].

Besides the chemical compositions of catalysts and the existence form of active sites, the morphologies of catalysts have significant impact on their catalytic performances [42–44]. A large accessible surface area with pores of adequate size would allow more active sites to be exposed to the surrounding media, facilitating efficient transportations of reactants and products [45,46]. On the other hand, one-dimensional supports, two-dimensional supports, three-dimensional supports have exhibited different support effects in heterogeneous catalysis. Among the three-dimensional materials supported catalysts, porous spherical structure, core-shell structure, yolk-shell structure, and hollow structure are classical morphologies. Therefore, in heterogeneous catalysis, it has a far-reaching significance to explore morphology effects of supported catalysts with the same chemical compositions. In order to give a rigorous experimental comparison and convincing evidence, it is essential to control both the morphologies and structures of the catalysts.

In this work, the processor can combine with Pd and directly generate porous spherical Pd-nitrogen-doped-carbon nanocatalysts (PS-Pd-C/N) catalyst through a polymerization process [46]. On the other hand, solid SiO_2 spheres are used to synthesis other nitrogen-doped-carbon (C/N) materials with yolk-shell and hollow structures. During the polymerization process, the Pd nanoparticles were facilely embedded in the C/N material, and the shedding of Pd nanoparticles was efficiently reduced. In addition, the morphologies of these catalysts seemed to be well controlled. Importantly, the preparation of porous spherical, yolk-shell and hollow Pd-nitrogen-doped carbon nanostructures are prepared via facile simultaneous doping of nitrogen and metal-containing species, especially one-pot synthesis of catalysts precursor which contain both precious metals and nitrogen. The reduction of 4-nitrophenol is chosen as a model reaction to research the morphology effects of these prepared Pd-C/N catalysts with the same chemical compositions.

2. Materials and methods

2.1. Materials

Tetraethoxysilane (TOES), Pd(II) acetate is purchased from Aladdin Chemical Co., Ltd. Concentrated ammonia aqueous solution and 4-nitrophenol (4-NP) is purchased from Lanzhou Aihua Chemical Company. $NaBH_4$ and dopamine (DA) is supplied by Sinophrm Chemical Reagent Co., Ltd. Organic solvents used in this work are of analytical grade and do not require further purification.

2.2. Preparation of catalysts

2.2.1. Preparation of SiO_2 microsphere

The silica spheres are synthesized according to Stöber method with modification [47,48]. Typically, TEOS (2.7 mL) is added dropwise into a mixture solution of ethanol (180 mL), concentrated ammonia aqueous solution (30 mL) and distilled water (9 mL) with magnetic stirring at room temperature. After additional stirring for 5 h, the SiO_2 microspheres are collected by centrifugation (8000 rpm, 3 min) and washed with distilled water and ethanol for 3 times. Then the collected microspheres are dried at 40 °C in a vacuum drying oven over night for further use.

2.2.2. Preparation of porous spherical nitrogen-doped-carbon material (PS-C/N) and porous spherical Pd-nitrogen-doped-carbon nanocatalysts (PS-Pd-C/N) sphere

Dopamine (200 mg) is dissolved in deionized water (200 mL) before the addition of palladium acetate acetonitrile solution (2 mg Pd/mL, 10 mL) with magnetic stirring in 10 min. Then Tris (500 mg) is added into the mixture and the solution is stirred for 24 h to generate PS-Pd-C/N. The product is collected by filtration and dried in oven at 80 °C for 30 min. Then the solid is put into the tube furnace and annealed under N_2 atmosphere at 650 °C. The synthesis process of PS-C/N microsphere is similar to PS-Pd-C/N, but without the addition of Pd solution.

2.2.3. Preparation of yolk-shell Pd-C/N (YS-Pd-C/N) and hollow Pd-C/N (H-Pd-C/N)

The silica spheres covered with Pd^{2+}-polydopamine (Pd^{2+}-PDA) complexes (Pd^{2+}-PDA@SiO_2) are synthesized by polymerization of dopamine on SiO_2 templates in Tris buffer (pH = 8.5) in the presence of $Pd(C_2H_3O_2)_2$. In a typical procedure, SiO_2 (500 mg) is dispersed in deionized water (1000 ml) under sonication, and dopamine (500 mg) and palladium acetate acetonitrile solution (2 mg Pd/mL, 10 mL) are added in turn into the solution to form the complex. Tris (1.2 g) is added into the solution to initiate the polymerization of dopamine. Then, the mixture is stirred at room temperature for 20 h. The suspension is filtrated and washed with deionized water for 3 times. The solid is dried in oven at 80 °C for 30 min before transferred into the tube furnace and annealed under N_2 atmosphere at 650 °C for 2 h. The YS-Pd-C/N microspheres are obtained by removing a portion of SiO_2 template using 3 M KOH solution at room temperature for 8 h. The H-Pd-C/N microspheres are obtained by removing the SiO_2 template using 10 M hydrofluoric acid solution at room temperature for 24 h [46].

2.3. Characterizations of catalysts

These magnetic micro-materials were characterized by transmission electron microscopy (TEM), inductively coupled plasma (ICP), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Fourier transform-infrared (FT-IR) and vibrating sample magnetometry (VSM). XRD measurements were performed on a Rigaku D/max-2400 diffractometer using Cu–Ka radiation as the