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N-doped mesoporous carbons supported palladium catalysts prepared from chitosan/silica/palladium gel beads

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ABSTRACT

In this study, a heterogeneous catalyst including palladium nanoparticles supported on nitrogen-doped mesoporous carbon (Pd@N-C) is synthesized from palladium salts as palladium precursor, colloidal silica as template, and chitosan as carbon source. N_2 sorption isotherm results show that the prepared Pd@N-C had a high BET surface area (640 $m^2 g^{-1}$) with large porosity. The prepared Pd@N-C is high nitrogen-rich as characterized with element analysis. X-ray photoelectron spectroscopy (XPS), high-resolution transmission electron microscopy (HR-TEM), and Raman spectroscopy characterization of the catalyst shows that the palladium species with different chemical states are well dispersed on the nitrogen-containing mesoporous carbon. The Pd@N-C is high active and shows excellent stability as applied in Heck coupling reactions. This work supplies a successful method to prepare Pd heterogeneous catalysts with high performance from bulk biopolymer/Pd to high porous nitrogen-doped carbon supported palladium catalytic materials.

1. Introduction

Chitosan (CS) is a deacetylation product of chitin, the second most abundant natural biopolymer next to cellulose. It has strong chelating property with transition metals for its plenty of —NH_2 and/or —OH groups within its molecule backbone. Therefore, it is seemed as one of the most ideal polymeric support materials for transition metals in heterogeneous catalyst preparing [1–4]. Currently, palladium nanoparticles supported on chitosan (Pd/CS) are high attractive catalysts for a variety of organic reactions, such as Heck, Ullmann, Suzuki, Sonogashira reactions, and so on [5–10]. According to the reported results [11–17], the CS supported Pd catalysts have been fabricated into various form such as membranes, microspheres, gel beads and fibers. Only a few methods, like supercritical CO_2 technique drying method [12,13], have been demonstrated to be effective in preparing the CS/Pd catalyst having a specific surface area >100 m^2/g. In addition, the polymeric support material CS has other drawbacks [18,19], such as limited thermal stability (decomposition starts from 180 °C), mechanical properties (chemical crosslinking and/or physical modification for further improvements in mechanical strength are often needed), and organic solvent-resistances properties (having high affinity with polar solvents) in high temperature and so on. Therefore, the prepared CS supported Pd heterogeneous catalyst has limited resistance to harsh organic reaction conditions, such as high reaction temperature, continuous high speed stirring processing, swelling and even dissolving effects of the polar solvents. And it could be recycled limited times (often below 10 times) [11,16,17,20,21].

Porous active carbon supported Pd catalyst (Pd/C) is another common and commercial available heterogeneous Pd catalyst applied widely in both experimental and industrial scale [22]. It certainly has much higher physical properties than general Pd/CS catalysts, including high porosity, specific surface area, thermal stability, and solvent-resistances properties. However, the interaction between Pd species and carbon support is often poor due to the lack of polar groups within carbon supports.

One way to enhance the interactions between Pd species and porous carbon support is to dope with heteroatom, like nitrogen (N) [23,24]. As demonstrated in the recently available literature [25–28], directly pyrolyzing nitrogen-containing polymers (like chitosan) to obtain N-doped carbons has been considered as a more applicable method. CS can be used as a carbon precursor to prepare porous carbons with a high nitrogen content (up to 7 or even 11 wt%). For example [29,30], Lukaszewicz et al. successfully prepared N-containing porous carbons with high specific area (above 400 m^2/g) using Na_2CO_3 or silica as porogens. Such nitrogen-rich carbons have been demonstrated as novel materials having obviously improved electrocatalytic activity [31], CO_2

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capture performance [32], supercapacitor performance [33], etc. Reasonably, it should be also an ideal support material for Pd for its distinctive properties, including large specific area (far bigger than general Pd/CS catalyst), much improved interactions between Pd species with porous carbon (resulting from electron donor properties of the surface after N doped). Recently, Xiao et al. [34] prepared a composite catalyst including Pd nanoparticles on TiO_2 and on N-modified porous carbon from palladium salts, tetrabutyl titanate and chitosan. It showed excellent activity and stability towards hydrogenation of vaillion to 2 methoxy-4-methylphenol using formic acid as hydrogen source. However, no more studies have been done to make use of CS/Pd in preparing porous N-doped C supported Pd heterogeneous catalysts.

In the present study, it was aimed to synthesis novel nitrogen-doped mesoporous carbons supported Pd heterogeneous catalysts (Pd@N-C), with the use of CS as carbon precursor, colloidal silica as a template, and $PdCl_2$ as palladium precursor. Our main idea was to eliminate the above-mentioned drawbacks of CS and active carbon as supports respectively in order to prepare Pd heterogeneous catalysts with much better comprehensive performances. The reported preparation procedure in this study is simple and effective. It began with the carbonizing CS/Pd gel beads in the presence of silica under N_2 atmosphere. And then washing the silicas with a 10% HF solution allowed one to obtain nitrogen-doped mesoporous carbons supported Pd heterogeneous catalysts with high specific surface area. The catalytic performances of the prepared novel heterogeneous catalyst were carefully evaluated by typical Heck coupling reactions.

2. Experimental

2.1. Material

Chitosan (95% deacetylated, molecular weight 1.2×10^5) was purchased from Zhejiang Aoxing Biotechnology Co., Ltd., China. A colloidal silica solution (Ludox AS-40, 40 wt%) was purchased from Shanghai sigma-aldrich trade Co., Ltd., China. $PdCl_2$ was supplied by Zhejiang Metallurgical Research Institute Co., Ltd., China. All the other chemical reagents and solvents used in this study were in analytical grade. They were used without further purification.

2.2. Preparation of the Pd@N-C

In a typical procedure, a certain amount (0, 1, 2 g, respectively) of colloidal silica solution (40 wt%) was dropped into a 60 ml of a 1.33% (w/v) CS solution in 2% aqueous acetic acid under continuous magnetic stirring for about half an hour to form homogeneous mixture. The mass ration of CS/silica was set as 1:0, 1:0.5, and 1:1. Then, about 1.2 ml Na_2PdCl_4 solution (0.3% (w/v) g $PdCl_2$ in 2% (w/v) NaCl aqueous solution) was dropped into the resultant mixture under magnetic stirring for half an hour. The flowable viscous mixing solution was dropped into 200 ml of NH_3/H_2O (v/v: 1/1) solution through a needle of 0.7 mm interior diameter. CS/silica/Pd gel beads were then precipitated from the solution and filtered out. The resultant gel beads was washed by deionized water to pH = 7 and dried in an oven at 80 °C. The dried gel beads were heated from the room temperature to 900 °C and held for 4 h under N_2 atmosphere in a Beiyike heater. Removing of the silica template was done by washing with 10 wt% HF solution for 0.5 h. The obtained nitrogen doped carbon supported palladium materials (Pd@N-C) were washed thoroughly with deionized water to eliminate the residue HF. And they were reduced by ethylene glycol for 1 h at 100 °C before catalysis use. Finally, the Pd@N-C materials were naturally dried. Pd@N-C samples prepared from CS/silica/Pd with different CS/silica mass ration (1/0, 1/0.5, 1/1) were recorded as Pd@N-C(1-0), Pd@N-C(1-0.5), and Pd@N-C(1-1), respectively. Details in studies of catalytic performances for Heck reactions of the Pd@N-C catalysts were similar with our recent publication [14]. In addition, CS/Pd gel beads (Pd@CSGB) were prepared by the similar method without addition of silica and high-temperature carbonization for comparing in catalytic performances.

2.3. Characterizations of the Pd@N-C

Nitrogen adsorption-desorption isotherms (at 77 K) were measured with a Micromeritics TriStar II series surface area and porosity analyzer (US). Raman spectra were recorded with a Renishaw in Via Raman Microscope. Thermal gravimetric analysis (TGA) curves were recorded by a TG/DTA 6300 Seiko instrument (Japan) (condition: air atmosphere, from 50 °C to 750 °C, rate 20 °C/min). X-ray photoelectron spectroscopy (XPS) analysis was performed with a Thermo Scientific ESCALAB 250Xi X-ray photoelectron spectrometer (US). High-resolution transmission electron microscopy (HR-TEM) observation was performed with a JEM-2100F (Japan) high resolution transmission electron microscope. (Scanning electron microscopy) SEM observation was performed with a JEM-6360 (Japan) scanning electron microscope equipped with energy dispersive X-ray spectroscopy (EDX, Oxford EDX System). The palladium loading was determined by a Leemann ICP-AES Prodigy XP inductively coupled plasma-atomic emission spectrometer (US). Element analysis was determined with an Organic analyzer (E3000. Italy).

3. Results and discussion

3.1. Porous structure characterization of the Pd@N-C

The HR-TEM images of the prepared Pd@N-C samples are depicted in Fig. 1. As expected, thermal carbonization and silica template removing techniques enabled successful high porous carbon material. As shown in Fig. 1**a**, with no addition of silica, the pores induced by the high-temperature thermal carbonization of CS itself were random. After using silica as template, as shown in Fig. 1**b**, majority of pores were regular spherical (as marked with red circle) with an internal diameter 20–30 nm reflecting the size of the incorporation SiO_2 nanoparticles. During the Pd@N-C preparation, the added colloidal silica could transform to regular SiO_2 spherical nanoparticles, which was dispersed uniformly in the matrix of both CS beads before carbonization and N-doped carbon after carbonization. And they were effectively etched by HF to form mesopores. At high silica-to-CS ratios, as shown in Fig. 1**c**, some pores connected to form a few big defects (as marked with red circle), indicating some SiO_2 aggregates formed in CS matrix during gel beads preparation with high silica porogen used. As shown in Fig. 1**a**, there were many black spots visible in HR-TEM images reflecting Pd nanoparticles distributed in such porous carbon materials. The size of the Pd nanoparticles decreased obviously after using silica as template. As shown in Fig. 1**d**, the Pd loading on the prepared N-doped carbon was confirmed with the element mapping of the SEM-EDX analysis results.

The porous structure of Pd@N-C was also studied by N_2 adsorption/desorption measurements. As shown in Fig. 2, for all the samples, the shapes of the N_2 adsorption/desorption isotherms were of the type II with H_4 hysteresis loops at P/P_0 higher than 0.4, indicating the presence of the developed mesopores. Compared with Pd@N-C(1-0), the hysteresis loops of Pd@N-C(1-0.5, 1-1) are significantly larger, indicating the total volume of the pores increased significantly. The maximum pore volume value of Pd@N-C(1-0) was found at the pore size of 1.95 nm. Meanwhile, a wide weak peak (peak at 70.87 nm) was found in the pore size range