

## Full Length Article

# Nitrogen-doped hierarchically porous carbon derived from cherry stone as a catalyst support for purification of terephthalic acid



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## ABSTRACT

Development of efficient functionalized carbon support holds great importance in catalysis especially for those reactions under harsh reaction conditions. Herein, we use cherry stone as the precursor to produce porous carbon via a nitrogen doping and simultaneously chemical activation process. The obtained N-AcCS material showed high surface area of 1155 m<sup>2</sup>/g and a unique hierarchically pore structures with interconnected macro and micro pores. Meanwhile, 6% N was doped in the carbon framework with predominantly pyrrolic and pyridinic N. It showed superior activity and stability as catalyst support for terephthalic acid purification reaction, even better than the commercially used activated carbon. This may be due to the nitrogen doped surface benefiting for the catalyst dispersion and the hierarchical structure could facilitate the mass transfer. In addition, the high mechanical strength and the shaped morphology of the cherry stone derived carbon making itself a potential candidate for the industrial application.

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## 1. Introduction

Polyethylene terephthalate (PET) is an important raw material to make fibers, resins, films, bottles, etc., which is commonly polymerized using terephthalic acid (TA) as the monomer. The industrial crude terephthalic acid (CTA) contains ppm level of 4-carboxybenzaldehyde (4-CBA) as impurity leading to poor quality of the final products. To get purified terephthalic acid (PTA), 4-CBA should be hydrogenated to p-toluic acid (Fig. 1), which is more soluble and will remain in liquid after crystallization [1–4]. In the hydrogenation process, palladium (Pd) is commonly used as catalyst [3,5–7] and activated carbon is employed as catalyst support making use of its unique properties, e.g. high surface area, tunable pore structure, surface functionalization, chemical inertness, etc. [8–10]. It is estimated that the annual worldwide demand for PTA exceeds 42 million tons, along with the huge amount consumption of Pd/C catalyst [11]. Nevertheless, the activity of Pd/C still needs to be improved and the lifetime of the catalyst is not satisfactory since the commercially used AC tends to be

crushed under the harsh reaction conditions e.g. high pressure and temperature, which leads to catalyst deactivation as well as product contamination [12,13].

To improve the performance of Pd/C, there are many works devoted to a rational design of the carbon support to replace AC. Tourani et al. [15] reported that functionalized CNTs could better anchor Pd particles leading to improved performance. 3D RGO-CNT composite was found to further improve the 4-CBA hydrogenation performance for its ultrahigh density of the active graphene edges and the porous CNT structure [16]. However, the novel nano carbon materials are powders which are not suited for the industrial application. In our earlier work, we synthesized nitrogen doped C-SiC core-shell structured composite to combine the superiority of the shaped morphology and the high mechanical strength of SiC as well as the nitrogen doped carbon surface [17], which demonstrated its potential application in CTA hydro-purification reaction [13,18]. Nevertheless, the cost for the C-SiC is not competitive due to the complexed preparation procedure. Hence the development of a robust porous carbon material with high mechanical strength, molding shape and low cost is still desirable. To this end, biomass as sustainable, renewable, cheap, wide available material could serve as an efficient precursor for the porous carbon production [19–24]. Especially, the transformation of

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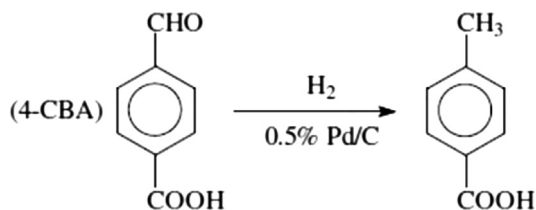


Fig. 1. Illustration of catalytic hydrogenation of 4-CBA to *p*-toluic acid [14].

natural waste attracts wide attention since it turns trash to treasure [25–27]. Yang et al. [28], transformed pomelo peel into a nanoporous N/C catalyst for highly selective and energy saving  $H_2O_2$  production. By a catalytic steam reforming process, wood was processed into a novel 3D carbon monolith and exhibited excellent catalytic performance as catalyst support as well as a reactor [29]. Shrimp shell derived carbon could well complex with cobalt precursor, which showed a promising application in hydrogenation of nitroarenes [30]. Although the above progress, as far as we know there is still no report on the application of biomass derived carbon as catalyst support for 4-CBA hydrogenation reaction. Cherry stone is one of the biochar wastes, most of which are abandoned or incinerated all over the world. Considering that cherry stone has advantages of wide availability, ultrahigh mechanical strength, formed granula, etc., here we use cherry stone as raw material to manufacture porous carbons. Different from the traditional treatment procedure, in this study, we adapted a novel all-in-one process to chemical activate and simultaneously dope nitrogen in the cherry stone derived carbon material. A multifunctional porous carbon could be achieved by this synthesis procedure with features of hierarchical porosity containing both macro-pores and micro-pores, oxygen functionalization and high amount of nitrogen doped in the carbon framework. When used as catalyst support in 4-CBA hydrogenation reaction, it showed superior activity and stability than the commercial used activated carbon.

## 2. Experimental

### 2.1. Preparation of CS materials

Cherry stones were firstly washed thoroughly with distilled water and then dried at 60 °C. 1 g of cherry stones were calcined at 800 °C at Ar atmosphere for 3 h. After removal of the inner seed, the obtained sample was labeled as CS. Then, CS was seized to 20–40 mesh and incipient wetness impregnated with KOH (Shanghai Macklin Biochemical Co., Ltd) solution with the mass ratio of KOH to CS at 2:1. After dried at 60 °C overnight, the sample was calcined at 800 °C at an Ar atmosphere or  $NH_3$  atmosphere which was named as Ac-CS or N-Ac-CS correspondingly. CS was treated with  $NH_3$  directly at 800 °C to prepare the sample of N-CS. 0.5 wt % Pd was loaded to the above carbon supports by incipient method to get Pd/CS, Pd/Ac-CS and Pd/N-Ac-CS. As comparison, commercial used activated carbon (AC) (Shanghai Macklin Biochemical Co., Ltd) was also adapted as support to prepare 0.5 wt% Pd/AC using the same preparation method described above.

### 2.2. Sample characterizations

The morphology was carried out by a JEOL JSM-7800F scanning electron microscope (SEM) and JEOL JEM-2100 transmission electron microscope (TEM). The crystallographic information was investigated with Rigaku Ultima IV X-ray diffractometer (XRD, Cu  $K\alpha$  radiation  $\lambda = 0.15418$  nm). Nitrogen adsorption-desorption was measured at Quantachrome Autosorb iQ3. Prior to the analy-

sis, the samples were degassed at 200 °C for 6 h. The specific surface area was calculated according to the Brunauer-Emmet-Teller (BET) method, and pore size distribution was determined by Non-Localized DFT (NL-DFT) method. Raman spectra were recorded on a Bruker Optic Senterra Raman spectrometer with laser wavelength of 532 nm. X-ray photoelectron spectrometer (XPS) was recorded in a Thermo Fisher ESCALAB 250Xi spectrometer with Al  $K\alpha$  X-ray source (1486.6 eV, operated at 15 kV and 10.8 mA). Scanning transmission electron microscopy (STEM) images were obtained by using a FEI Tecnai G2 F30 S-Twin electron microscope with an accelerating voltage of 300 kV. The aged catalysts after reaction was washed with a large amount of ethanol absolute (Damao Chemical Reagent Co., Ltd, Tianjin, China) before they were characterized by STEM.

### 2.3. Catalyst testing

The hydrogenation of 4-carboxybenzaldehyde (4-CBA) (TCI (Shanghai) Development Co., Ltd.) was carried out with a 100 mL Parr stirred reactor. In a typical run, the catalysts were firstly reduced by  $H_2$  at 250 °C for 2 h and then 50 mg catalyst, 200 mg 4-CBA and 70 mL deionized water were mixed together in the reactor. The agitator speed was set at 300 rpm. Prior to the reaction, the reactor was purged three times by Ar and filled with 4 atm Ar, and then the reaction mixture was heated to 120 °C. The reaction was started with inlet of 5 atm  $H_2$ . The samples were analyzed at every 10 min with an Agilent 1260 Infinity liquid chromatography. In an aging procedure, the catalysts were kept in the reactor at 200 °C for 24 h with 1.5 MPa  $H_2$  and 70 mL deionized water.

## 3. Results and discussion

As depicted in Fig. 2, after calcination at temperature of 800 °C, cherry stones turn to black while the initial sphere morphology as well as the high mechanical strength is maintained. It is interesting to find from SEM characterization (Fig. 3(a) and (b)) that CS is stacked by flakes with abundant cavities all-over the surface. The cavities are in macro scale and some are not straight through but interconnected in the bulk. This unique texture is also evidenced by TEM characterization in Fig. 3(c) and (d), from which we can still detect that the holes are perplexing with different pointing directions (highlighted in the red dashed box). We deduce that the macro-pores may be inherited from the initial structure of cherry stone, since there are always channels contained in the cellulose materials [29,31]. Considering that there is seed encapsulated in the hard shells of the cherry stone. We further calcine the shells alone so as to exclude the influence of the seed on the pore structure. From the SEM image in Fig. S1, we can still detect the existence of macro-pores, suggesting that the creation of macro-pores could be intrinsically derived from the cherry stone shell. HRTEM in Fig. 3(e) shows that CS is mainly composed of amorphous carbon with less graphitization. The low crystalline degree is also proved by broad diffraction peaks at  $2\theta$  of 24° and 44° in the XRD patterns (Fig. 4(a)), which are attributed to (0 0 2) planes of the graphite structure and (1 0 0) plane of the interlayer condensation. The pore structure is further characterized by  $N_2$  adsorption-desorption experiment, as shown in Fig. 4(b) and Table 1, CS shows porous structure with specific surface area of 366.7  $m^2/g$ , pore volume of 0.29  $cc/g$  and the average pore size is mainly centered at 0.5 nm and 1.7 nm as calculated by NL-DFT method (Fig. 4(c)). The porous structure could be derived from the release of the volatile gases such as  $CO_2$ ,  $H_2O$ , and  $CH_x$  during the decomposition of cherry stone.

To increase the specific surface area, we further chemical activate CS by KOH which is a widely used agent to create micro

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