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# Biowaste soybean curd residue-derived Pd/nitrogen-doped porous carbon with excellent catalytic performance for phenol hydrogenation

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## GRAPHICAL ABSTRACT

A *N*-doped porous carbon material PNCM was prepared using the biomass waste soybean curd residue as the precursor material and modified with small Pd NPs to fabricate the Pd/PNCM catalyst for the catalytic hydrogenation of phenol to cyclohexanone with excellent catalytic performance.
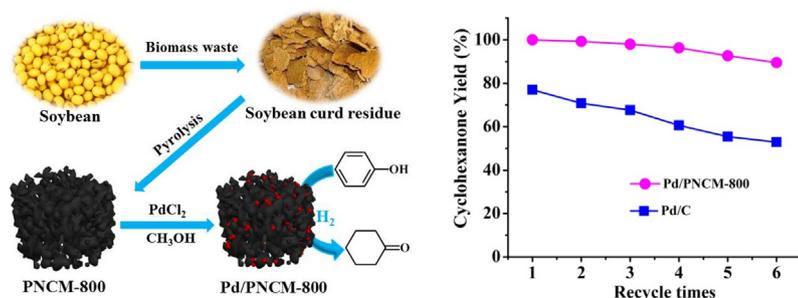


## ARTICLE INFO

## ABSTRACT

Use of renewable raw materials for fabrication catalysts with excellent catalytic performance is of considerable importance for sustainable chemistry. Here, biowaste soybean curd residue (SCR) was used to prepare porous *N*-doped carbon materials (PNCM) via the carbonization method, and subsequently modified with small Pd nanoparticles (NPs) to generate the Pd/PNCM catalyst. Pd/PNCM was used for catalytic hydrogenation of phenol to cyclohexanone, as the latter is an important chemical intermediate that is usually produced under harsh reaction conditions. The Pd/PNCM catalyst can hydrogenate phenol to cyclohexanone in aqueous solution under mild reaction conditions with excellent catalytic performance. In addition, compared to commercial Pd/C, Pd/PNCM exhibits excellent catalytic performance and stability, which is attributed to the synergetic effects of *N*-doping of porous carbon supports and stabilization of ultra-small Pd NPs. Thus, this study highlights a new pathway for preparing *N*-doped porous carbon materials using biomass waste as the precursor material, and subsequently fabricating precious metal-modified catalysts with excellent catalytic performance for sustainable and green catalysis.

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## 1. Introduction

As an important fine chemical, cyclohexanone is mainly used as a feedstock for synthesizing adipic acid, caprolactame, nylon 6, nylon 66, and polyamide resins [1]. In the chemical industry, the

main strategies for producing cyclohexanone involve oxidation of cyclohexane and the hydrogenation of phenol [2,3]. Cyclohexane oxidation requires high reaction pressure (1–2 MPa) and temperature (140–180 °C), but has low reaction conversion (<15%), consumes more energy, and generates many undesirable byproducts [4,5]. Hence, phenol hydrogenation is the desired strategy for cyclohexanone production, which can be performed under relatively mild reaction conditions. However, in many cases, cyclohexanone can be easily hydrogenated to cyclohexanol and other byproducts, which leads poor reaction selectivity [6,7]. Thus, effective catalysts for phenol hydrogenation with high phenol conversion and excellent cyclohexanone selectivity are required. Until now, many noble metal-based catalysts have been reported for the hydrogenation of phenol to cyclohexanone, including Pd/C [8,9], Pd@MgO [10], Pd/Al$_2$O$_3$ [11,12], Pd/MgO [13], Rh/C [14,15], and Ru/TiO$_2$ [16]. However, the disadvantages of these catalysts involve instability or poor selectivity for cyclohexanone, due to the weak Van der Waals interaction between the Pd active sites and the supporting materials.

In order to improve the catalysts stability and enhance the catalytic performance, supporting materials that can firmly anchor the noble metal active sites are highly needed. Based on this point, supporting materials with heteroatomic groups (N, S, and P) such as N-doped carbon, amino-functionalized mesoporous silica have been fabricated for supporting noble metal nanoparticles (NMNPs) [3,17–22]. The coordination between the heteroatoms with lone pair electrons in such supporting materials and metal atoms with unoccupied orbitals could also make the NMNPs firmly anchored in the supporting materials with high dispersion, efficiently stabilize the NPs and maintain excellent activity. For example, our group fabricated amino modified fibrous silica nanosphere and modified it with Ni@Pd NPs for hydrodechlorination of 4-chlorophenol [23]. Zhang's group has prepared thioether-containing covalent organic framework for supporting ultrafine metal NPs for catalytic applications [24]. And many other researchers also reported the fabrication of N-doped porous carbon materials with hard or soft templates for supporting NMNPs and used in various catalytic applications [25–27]. However, most of these reported supporting materials suffer from disadvantages such as complicated preparation procedure, expensive precursors, and requirement of excessive reagents or harsh conditions. Therefore, using low-cost and easily available precursor materials to fabricate supporting materials with heteroatoms for preparing NMNPs modified catalysts is still a challenge and very meaningful work.

As abundant, low price, and renewable resources, biomass materials that contain intrinsic heteroatom-doped structure with rich nitrogen- and oxygen-bearing functional groups have attracted attention for preparing porous heteroatom-doped carbon [28–30]. Developing carbon materials using biomass waste materials meets the standard for green and sustainable developing strategies. Some carbon materials derived from biomass such as chitosan, cotton, peanut shell, and corncob residue exhibit favorable electrochemical or heterogeneous catalysis properties [31–35]. In addition, the soybean curd residue (SCR) is a common biomass waste from the soybean milk and Chinese traditional daily food tofu-making process. SCR contains abundant protein and cellulose, which can be transferred to porous N-doped carbon materials (PNCM) with alkaline nitrogen groups through the carbonization process.

Considering the above viewpoints, this study used SCR as a precursor for preparation nitrogen-containing groups abundant PNCM, and modifying the PNCM with highly dispersed small Pd NPs (Pd/PNCM). Owing to the amino basic sites and the accessible Pd active sites on the Pd/PNCM catalyst, it shows high catalytic activity for hydrogenation of phenol with excellent selectivity for cyclohexanone. At the same time, Pd/PNCM also has superior catalytic stability compared to commercial Pd/C. Thus, this study will provide a useful platform for the construction of biomass waste-derived carbon-based catalysts for green and sustainable catalysis.

## 2. Experimental section

### 2.1. Materials

SCR was supplied by a local bean curd shop (Lanzhou, Chian). Palladium (II) chloride (PdCl$_2$, ≥99.9%) was purchased from Shanghai Chemical Reagent Co., Ltd.. Phenol (≥99%) and other phenolic derivatives of analytical grade were provided by Sinopharm Chemical Reagent Co. Ltd., China. 5 wt%Pd/C for comparison were commercially available and purchased from Lanzhou Aihua Chemical Company. Potassium hydroxide (KOH, AR) and anhydrous methanol (CH$_3$OH, ≥99.9%) were purchased from the Tianjin Guangfu Chemical Company. All other reagents used in this work were of analytical grade and did not require further purification.

### 2.2. Preparation of PNCM

Initially, the SCR powder was pyrolyzed under inert atmosphere at 300 °C. Next, the carbon sample was activated with KOH, thoroughly washed with distilled water, and dried overnight in a vacuum oven at 40 °C [36]. Then, the treated sample was carbonized at 700, 800, and 900 °C in a tube furnace at a heating rate of 5 °C min$^{-1}$ under nitrogen atmosphere for 2 h. The obtained PNCM samples were named as PNCM-x (x refers to the carbonization temperature). For comparison, an N-doped carbon material (SAC-800) was prepared using a similar method, but without KOH activation.

### 2.3. Synthesis of Pd/PNCM-x

The Pd/PNCM-x catalyst was prepared by methanol reduction [37]. Typically, 2 g PNCM-x and 12 mL PdCl$_2$ solution (Pd content, 12 mg mL$^{-1}$) were dissolved in 60 mL methanol in a 100 mL round-bottom flask. The mixture was stirred at 85 °C for 24 h with a reflux condenser. The 0.07-Pd/PNCM-x catalyst was obtained after filtration, washing with distilled water and ethanol, and vacuum drying. A series of y-Pd/PNCM-800 catalysts with different Pd contents (y = 0.02, 0.05), and 0.07-Pd/SAC-800 samples were successfully synthesized by the same method.

### 2.4. Catalytic hydrogenation of phenol

Typically, 0.25 mmol of phenol (23.53 mg), 0.07-Pd/PNCM-800 catalyst (Pd: 10 mol% relative to phenol), and 3 mL distilled water were placed in a 10 mL two-neck round-bottom flask. Prior to the reaction, a balloon filled with hydrogen was connected to the flask, and the air in the flask was replaced by hydrogen. Then, the mixture was stirred vigorously in an oil bath at 80 °C for approximately 3 h. The reaction products were analyzed by gas chromatography-mass spectroscopy (GC-MS, Agilent 5977E). The conversion and selectivity results were calculated using the following equations [38]:

$$\text{Conversion of Phenol} = \left( 1 - \frac{\text{mol of Phenol after reaction}}{\text{mol of Phenol initial}} \right) \times 100\%$$

(1)

$$\text{Selectivity of Cyclohexanone} = \frac{\text{mol of Cyclohexanone}}{\text{mol of the amounts of products}} \times 100\%$$

(2)