



Full Length Article

Selective hydrogenation of phenol to cyclohexanone over Pd@CN (N-doped porous carbon): Role of catalyst reduction method

Shuo Hu, Guangxin Yang, Hong Jiang, Yefei Liu, Rizhi Chen*

State Key Laboratory of Materials-Oriented Chemical Engineering, Jiangsu National Synergetic Innovation Center for Advanced Materials, Nanjing Tech University, Nanjing 210009, China

ARTICLE INFO

Article history:

Received 28 August 2017

Received in revised form

17 November 2017

Accepted 21 November 2017

Keywords:

Phenol

Selective hydrogenation

Cyclohexanone

Reduction method

Pd@CN

ABSTRACT

Selective phenol hydrogenation is a green and sustainable technology to produce cyclohexanone. The work focused on investigating the role of catalyst reduction method in the liquid-phase phenol hydrogenation to cyclohexanone over Pd@CN (N-doped porous carbon). A series of reduction methods including flowing hydrogen reduction, in-situ reaction reduction and liquid-phase reduction were designed and performed. The results highlighted that the reduction method significantly affected the catalytic performance of Pd@CN in the liquid-phase hydrogenation of phenol to cyclohexanone, and the liquid-phase reduction with the addition of appropriate amount of phenol was highly efficient to improve the catalytic activity of Pd@CN. The influence mechanism was explored by a series of characterizations. The results of TEM, XPS and CO chemisorption confirmed that the reduction method mainly affected the size, surface composition and dispersion of Pd in the CN material. The addition of phenol during the liquid-phase reduction could inhibit the aggregation of Pd NPs and promote the reduction of Pd (2+), and then improved the catalytic activity of Pd@CN. The work would aid the development of high-performance Pd@CN catalysts for selective phenol hydrogenation.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Cyclohexanone is an important intermediate for producing nylon 6 and nylon 66 [1]. Generally, cyclohexanone can be produced by cyclohexane oxidation or phenol hydrogenation [2–6]. There are many advantages of the selective phenol hydrogenation as compared to the cyclohexane oxidation, as it avoids harsh reaction conditions, undesirable byproducts and difficult separation [3,7]. Considering that the degree of hydrogenation mainly depends on the properties of the support and the type of catalyst, and the development of highly active and highly selective catalysts for this reaction attracts considerable interest [8].

Up to date, a lot of catalysts including Pd [3–8], Pt [9,10], Ni [11,12] and Rh [13–15] have been developed for the selective hydrogenation of phenol. Among them, Pd-based catalysts are the relatively better choices in most cases owing to their high selectivity and relatively low price [8]. Multiple supports such as metal oxides [16,17], activated carbon [18], zeolites [19], carbon nanofibers [20], carbon nanotubes (CNTs) [21], mesoporous silica nanoparticles (MSN) [22], hydrophilic carbon [23] and N-doped

porous carbon (CN) [24–27] have been used for the immobilization of Pd due to their high surface area and uniform distribution of Pd nanoparticles (NPs) on them [8]. The synthesis of Pd@CN catalysts has been extensively investigated due to their superior catalytic performance [5,24–28]. On one hand, the incorporation of nitrogen atoms in the CN support can enhance the electronic density of Pd nanoparticles and provide more structural defects, thereby improving the catalytic activity [28]. On the other hand, the nitrogen functionalities may act as strong Lewis base sites, and their interaction with cyclohexanone can restrain the further hydrogenation of cyclohexanone to cyclohexanol, leading to higher cyclohexanone selectivity [5]. For example, Wang et al. has reported that Pd NPs supported on a mesoporous CN could achieve superior conversion and selectivity under mild reaction conditions [5,24]. Very recently, our group reported a Pd@CN catalyst made of Pd NPs loaded on a CN material derived from ZIF-67, which exhibited better catalytic activity, selectivity and excellent catalytic stability during recycling experiments [26,27].

In general, the catalytic activity and selectivity are sensitive to the type of active metal and acid and/or base co-catalyst [28,29]. More important factors controlling the activity and selectivity are particle size and metal dispersion which in turn are governed by the type of metal precursors and catalyst reduction conditions [30–32]. Mahata et al. systematically investigated the influence

* Corresponding author.

E-mail address: rizhichen@njtech.edu.cn (R. Chen).

of Pd precursor on the structural properties and catalytic performance of Pd/Al₂O₃, and they found that when Pd(OOCCH₃)₂ was used as the precursor the as-prepared Pd/Al₂O₃ catalyst exhibited good metal dispersion and phenol hydrogenation activity [33]. The catalysts for hydrogenation reactions are usually reduced by flowing hydrogen in a tube furnace or by reducing chemicals, such as hydrazine, formaldehyde and NaBH₄ [33,34]. Divakar et al. synthesized Pd/bentonite catalysts by three different reduction methods including H₂, NaBH₄ and ethanol, and applied for citral hydrogenation [35]. It was found that the Pd/bentonite reduced by ethanol and NaBH₄ had the highest activity and selectivity, respectively, which was attributed to the uniform distribution of Pd NPs for the former and presence of boron species for the latter. To the best of our knowledge, there are few reports on the effect of reduction method on the Pd@CN catalyst performance in the liquid-phase hydrogenation of phenol.

The aim of this work is to investigate the role of catalyst reduction method in the liquid-phase phenol hydrogenation to cyclohexanone over Pd@CN by designing a series of experiments. To explore the influence mechanism of reduction method, many characterization techniques including XRD, TEM, XPS, ICP and CO chemisorption were applied for investigating the dispersion, particle size, loading and chemical nature of Pd@CN catalysts.

2. Experimental

2.1. Chemicals

All chemicals were used as received without further purification: dicyandiamide (C₂H₄N₄) and acetone (CH₃COCH₃) (Shanghai Lingfeng Chemical Reagent Co., Ltd., China), citric acid monohydrate (C₆H₈O₇·H₂O) and phenol (C₆H₅OH) (Sinopharm Chemical Reagent Co., Ltd., China), methanol (CH₃OH) (Shandong Yuwang Industrial Co. Ltd., China), activated carbon (AC) (Jiangsu Zhuxi Activated Carbon Co., Ltd., China), Palladium acetate (Pd(OAc)₂) (Sin-platinum Metals Co., Ltd., China), and cyclohexane (C₆H₁₂) (Shanghai Shenbo Chemical Reagent Co., Ltd., China).

2.2. Catalyst preparation

The synthesis of Pd@CN catalyst included three steps: CN preparation, Pd(OAc)₂@CN preparation, Pd(OAc)₂@CN reduction.

2.2.1. Preparation of CN

The CN was synthesized according to the previous report by our group [36]. In a typical procedure, 20 g of dicyandiamide and 33.3 g of citric acid monohydrate were mixed in 500 mL of methanol with stirring for 4 h. Then, 60 g of AC was added into the above solution and the mixture was stirred for 12 h. After removing the methanol by rotary evaporation, the obtained solid was dried under vacuum at 60 °C overnight, followed by calcining under nitrogen atmosphere at 550 °C for 4 h to yield the CN material.

2.2.2. Preparation of Pd(OAc)₂@CN

The Pd(OAc)₂@CN was prepared by a wet impregnation route as follows: 40 g of CN material was added into 1 L of acetone solution containing 1.72 g of Pd(OAc)₂, and the suspension was agitated at room temperature for 12 h and then heated at 70 °C in a vacuum evaporator to remove excess acetone.

2.2.3. Reduction of Pd(OAc)₂@CN

Three reduction methods were attempted for reducing Pd(OAc)₂ to Pd NPs in CN.

The first was flowing hydrogen reduction. Specifically, the Pd(OAc)₂@CN material was calcined in a tube furnace under hydro-

gen atmosphere from room temperature to 300 °C at 2 °C/min for 4 h, and the yielded catalyst was denoted as Pd@CN-G.

The second was in-situ reaction reduction, which was performed in a 2 L autoclave (Parr Instrument Co., Ltd., U.S.A.). When 600 mL (467 g) of cyclohexane, 200 g of phenol and 6.4 g of Pd(OAc)₂@CN were added into the reactor, the autoclave was sealed, and the air in the autoclave was removed by purging with hydrogen for five times under 0.5 MPa. Then, the reactor was heated under a low stirring rate (200 rpm). As the temperature reached the set temperature (110 °C), the hydrogen was added into the reactor to 0.5 MPa and the stirring rate was then increased to 500 rpm. After that, the reduction of Pd(OAc)₂@CN started, and the phenol hydrogenation happened at the same time. After 2.5 h, the reaction was stopped, and the solid catalyst was filtered and denoted as Pd@CN-R.

The third was liquid-phase reduction, which was also carried out in the above autoclave. The procedure was similar to the second method except the absence of phenol and the reduction time of 1 h. The obtained catalyst was marked as Pd@CN-L. To further investigate the influence of reduction method on the catalytic activity of Pd@CN catalyst in the liquid-phase hydrogenation of phenol to cyclohexanone, the experiments with different amount of phenol added during the reduction process were designed. The yielded catalyst was denoted as Pd@CN-L-X, where X expressed the added phenol amount (wt.%).

2.3. Catalyst characterization

X-ray diffraction (XRD) was conducted on a Rigaku Smartlab TM 9 KW powder diffractometer at 40 kV and 40 mA. The patterns were recorded from 10° to 80° with a scanning rate of 0.2°/s. Transmission electron microscopy (TEM) images of Pd@CN catalysts were obtained using a JEOL-2100F microscope operated at 200 kV. X-ray photoelectron spectrometry (XPS, Thermo ESCALAB 250) was applied for investigating the surface composition of the catalyst. After the Pd@CN catalyst sample was treated by digestion solution, the amount of Pd was measured by inductively coupled plasma emission spectroscopy (ICP-AES, Optima 7000 DV). CO chemisorption analyses were performed on a Micromeritics ASAP 2010 device by a volumetric method. Samples (about 100 mg) were first dried in a He flow (30 mL/min) at 100 °C for 30 min. Then, total and reversible CO adsorption isotherms were measured at 35 °C, and the Pd dispersion on the catalyst was calculated according to the molar ratio of the chemically adsorbed CO on the catalyst and the Pd in the catalyst (assuming a chemisorption stoichiometry of CO/Pd = 1).

2.4. Catalytic tests

Liquid-phase selective hydrogenation of phenol to cyclohexanone over Pd@CN with cyclohexane as the solvent was also carried out in a 2 L autoclave. The experimental procedure was the same as the second reduction method as presented above. The reaction products were analyzed by a gas chromatograph (GC-2014), and the phenol conversion and cyclohexanone selectivity were calculated based on the initial phenol concentration and the final phenol and cyclohexanone concentrations [37]. GC-MS (Agilent 7890B-5977A) was used to analyze the composition of products.

3. Results and discussion

3.1. Effect of reduction method

In order to investigate the role of catalyst reduction method in the liquid-phase hydrogenation of phenol to cyclohexanone over Pd@CN, three reduction methods were designed and performed.

Download English Version:

<https://daneshyari.com/en/article/7836080>

Download Persian Version:

<https://daneshyari.com/article/7836080>

[Daneshyari.com](https://daneshyari.com)