



Nanofiber-like mesoporous alumina supported palladium nanoparticles as a highly active catalyst for base-free oxidation of benzyl alcohol

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ARTICLE INFO

Keywords:

Palladium nanoparticles
Nano-fibrous mesoporous alumina
Benzyl alcohol oxidation
Benzaldehyde

ABSTRACT

A nanofiber-like mesoporous alumina supported palladium catalyst, Pd/ γ -Al₂O₃-fibr, was successfully prepared by a hydrothermal method and used in the aerobic oxidation of benzyl alcohol to benzaldehyde with molecular oxygen under base-free conditions. The material was characterized by N₂ physisorption, FT-IR, X-ray powder diffraction (XRD), transmission electron microscopy (TEM), and X-ray photo-electron spectroscopy (XPS). XRD and TEM results revealed that the palladium nanoparticles were uniformly dispersed in the framework of nanofiber-like mesoporous γ -alumina. The higher activity of Pd/ γ -Al₂O₃-fibr compared to Pd/ γ -Al₂O₃ and Pd/SBA-15 in the aerobic oxidation of benzyl alcohol reaction suggested that the unique fibrous architecture of our material and synergic effect between Pd species and γ -Al₂O₃ are beneficial to enhance the reactivity of palladium NPs. Furthermore, the unique architecture of Pd/ γ -Al₂O₃-fibr catalyst also offers it good mass-transfer property and accessibility, which make it an effective catalyst for aerobic oxidation of steric bulk alcohol substrate. The Pd NPs supported on nano-fibrous mesoporous alumina in this paper is demonstrated to be a recoverable noble metal-based nanocatalyst with easy accessibility and may be great potential as a promising candidate for numerous catalytic applications.

1. Introduction

Benzaldehyde is of important value due to its application as intermediate and raw material in perfumery, pharmaceuticals, dyestuff and agrochemical industry. The tradition production of benzaldehyde via the toluene chlorination and subsequent hydrolysis process requires complicated preparation procedures and generates large amount of toxic acidic wastes, leading to serious environmental contaminations and costly separation process [1–3]. As an alternative green route to produce chlorine-free benzaldehyde, the aerobic oxidation of benzyl alcohol with molecular oxygen or air has attracted significant attention in recent years, being water the only by-product of the reaction. In this regards, the active catalysts concerning transition metal and noble metal such as Cu [4,5], Cr [6], Mn [7,8], Ru [9], Pt [10], Au [11,12], Pd [13–15], bimetallic Au-Pd [16,17] have been reported, among them, the Pd-based catalysts displays interesting and promising catalytic performance in both activity and selectivity, especially under the mild conditions.

Due to the environmental friendly and safety property, aerobic

oxidation of benzyl alcohol in water is more appreciable because it helps to reduce the amount of waste after reaction and avoid explosion and hazards associated with the application of other toxic and oxidizable organic solvent. Palladium nanoparticles supported on various supporting materials are attractive catalyst for aerobic oxidation of alcohols [18–21]. However, owing to the high surface energy of catalytically active Pd NPs, Pd NPs supported on numerous conventional supports usually suffered from the problems such as gradual growth of Pd NPs into inactive large particles and poor accessibility of active sites that entrapped in the pores and channels of supports. Thus, for the purpose of improving the accessibility of active sites to reactant and reduce the propensity of Pd NPs to coalesce, many heterogenized Pd NPs catalysts with well-designed nanocomposite structures were developed for catalytic applications, including hollow core-shell structured Pd NPs-based nanocatalysts [22–25], Pd NPs@ metal–organic frameworks [26–28], and Pd NPs/CNT nanohybrids [29,30]. These nanocatalysts show promising properties to suppress aggregation, leading to enhanced catalytic activity. However, the fabrication of these nanocomposites also suffers from problems such as difficult synthesis

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procedures, the poor mechanical and chemical stability, poor control over the shell thickness and difficulty of obtaining a core particle of sufficiently small size, which greatly hinders their further application in catalysis field. Therefore, it is highly desirable to develop a simple and effective strategy to synthesize Pd NPs-based nanocomposite with high catalytic stability, uniform dispersion of small Pd NPs and improved accessibility.

Porous alumina is one of promising support materials due to its essential properties of high surface area, tunable porosity and good chemical, mechanical, and especially thermal stability. It has been reported that porous alumina with different three-dimensional stacked configurations can not only function as effective barrier to prevent NPs from aggregation but also improve the chemical and thermal stability of supported NPs. For example, Au NPs immobilized on a novel alumina with architecture of thin sheets exhibit excellent sintering-resistant property, despite calcination at 700 °C, the size of supported Au NPs at predominate 2 ± 0.8 nm is unchanged [31]. Pd NPs supported on a spherical porous alumina, Al₂O₃(PB) exhibits high Pd distribution and thin Pd dispersion depth [32]. However, in these cases, the immobilization of metal NPs on porous alumina is achieved through an impregnation-reduction method, the supported precursors in oxidation state need to be reduced to metal NPs by a time-consuming or complex reduction procedure.

Herein, we reported a controlled hydrothermal synthesis of in situ immobilization of Pd NPs in mesoporous alumina with stacked nanofiber like configuration. The hydrothermal treatment of mixture of colloidal Pd NPs, microporous graphitic microspheres, Al(NO₃)₃·9H₂O and urea can generate boehmite (γ -AlO(OH)) nanofibers attached to graphitic microspheres, Pd NPs were thus homogeneously dispersed in the framework of boehmite nanofibers. This prepared mesoporous γ -Al₂O₃ of 3D nanofiber-stacked morphology can effectively stabilize the loaded Pd NPs, retaining the high dispersion of small Pd NPs despite calcination at 550 °C. The 3D hierarchical architecture containing large mesopores can also promote the mass diffusion of reactant/product. The resultant Pd/ γ -Al₂O₃ nanocomposites can offer a highly recyclable, effective, environment-friendly and robust catalytic system for aerobic oxidation of benzyl alcohol to benzaldehyde in water.

2. Experimental section

2.1. Materials

Anhydrous D-glucose was purchased from the national pharmaceutical industry of china, polyvinylpyrrolidone K15 (PVP, Mw ~10,000) was purchased from Aldrich, Al(NO₃)₃·9H₂O, concentrated hydrochloric acid, PdCl₂, ethanol (> 99.5%) and benzyl alcohol were analytical grade and used as received without further purification. commercial γ -Al₂O₃ powder was obtained from Nanjing Chemical Reagent Company ($S_{\text{BET}} = 185$ m²/g).

2.2. Preparation of graphitic microspheres (GM)

The carbon microspheres (GM) were prepared through the hydrothermal treatment of aqueous glucose solution. In a typical synthesis, 4 g of anhydrous D-glucose was dissolved in 30 mL deionized water to form transparent solution, then the solution was sealed into a 40 mL Teflon-lined stainless steel autoclave and maintained at 180 °C for 12 h. The dark brown products were collected by centrifugation, washed repeatedly with deionized water and ethanol, and air-dried at 80 °C overnight. The graphitic microspheres were obtained by pyrolyzing the carbon microspheres at 800 °C for 2 h under N₂ flow.

2.3. Preparation of Pd/Al₂O₃-fibr catalyst

Pd/ γ -Al₂O₃-fibr catalyst with Pd loading of 1.0 wt% was prepared by a controlled hydrothermal synthesis method. In a typical synthesis,

0.12 mmol PdCl₂ and 0.02 mL concentrated hydrochloric acid were added to 30 mL of water and 70 mL of ethanol under vigorous stirring to form a clear solution. 0.5 g of PVP was then added to the solution, and the solution was heated to boiling and refluxed for 3 h to generate a homogeneous dispersion of PVP-Pd NPs. Subsequently, 0.3 g of graphitic microspheres was ultrasonically dispersed in the aqueous solution containing 0.935 g of Al(NO₃)₃·9H₂O and 1.2 g of urea (80 mL), and then another 40 mL of ethanol was added. Next, the resulting suspension was added with 10 mL of the above PVP-Pd NPs dispersion, sonicated for 1 h at room temperature and transferred into a 150 mL Teflon-lined stainless steel autoclave. The autoclave was sealed and maintained at 120 °C for 20 h, the black products were then collected, washed five times with water and ethanol. After being dried at 80 °C for 6 h, the dried products were calcined at 550 °C under static air for 3 h to produce Pd/ γ -Al₂O₃-fibr catalyst. For comparison, Pd/ γ -Al₂O₃ with similar Pd content was prepared by incipient wetness impregnation using commercial γ -Al₂O₃ support.

2.4. Characterization

X-ray diffraction patterns of the synthesized samples were measured by Bruker AXS D8 Advance diffractometer using Cu K α radiation with a scanning speed of 10° min⁻¹. Transmission electron microscopy (TEM) images of the samples were collected on a JEM 3010 instrument operated at 200 kV. More than 100 particles for each sample were randomly counted to determine the particle size distributions. N₂ adsorption and desorption isotherms were obtained on a micromeritics ASAP 2010 instrument at 77 K, samples were degassed at 473 K for 4 h under high vacuum prior to measurements. Specific surface areas and pore distribution were calculated by Brunauer-Emmett-Teller (BET) and Barret-Joyner-Hallender (BJH) methods, respectively. Elemental analysis of samples was performed with an inductively coupled plasma-optical emission spectrophotometer Shimadzu ICPs-7500. IR spectra were recorded on KBr pellets by a Nicolet Niclet 6700 spectrophotometer. The binding energy of Pd was determined by X-ray photoelectron spectroscopy (XPS) using monochromatic Al K α radiation (ESCALAB 250).

2.5. Catalytic test

Typical aerobic oxidation was carried out in a two-necked round flask provided with a reflux condenser and an electrically controlled magnetic stirrer, was loaded with 30 mg of solid catalyst and 1 mL (9.6 mmol) of benzyl alcohol in 40 mL of water. The flask was heated to 353 K in an oil bath with stirring rate of 800 rpm. Oxygen gas was bubbled into the liquid reaction mixture at a speed of 20 mL/min starting the reaction. After 2 h of reaction, the catalyst was separated by centrifugation, and the reaction solution was extracted with diethyl ether twice, 5 mL for each time. The combined organic layer was dried with MgSO₄, analyzed using a Shimadzu 2014 gas chromatograph (GC) equipped with a HP-5 capillary column (30 m \times 0.32 mm \times 0.25 μ m) to determine the yield of target product.

3. Results and discussion

3.1. Catalyst preparation and characterization

After hydrothermal treatment of the suspension containing aluminum precursor, PVP-Pd NPs and graphitic microspheres, centrifugation of the reaction mixture can produce a colorless supernatant and a black solid reflecting that the Pd NPs were completely immobilized in the resulting boehmite gel. The TEM images of graphitic microspheres, boehmite gel with Pd NPs and Pd/ γ -Al₂O₃-fibr were shown in Fig. 1. As shown in Fig. 1(b) and (c), in the presence of graphite microspheres, boehmite particles grown on the surface of graphite microspheres to produce boehmite nanofiber, the boehmite nanofibers enwrapped

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