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Palladium and carbon synergistically catalyzed room-temperature hydrodeoxygenation (HDO) of vanillyl alcohol – A typical lignin model molecule

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ABSTRACT

Vanillyl alcohol, which is made up of an aromatic ring, an alcoholic hydroxyl group, a phenolic hydroxyl group and a methoxy group, was selected as the model molecule of lignin. Various carbon materials supported Pd catalysts were chosen to catalyze the HDO of vanillyl alcohol. The catalysts were characterized via TEM, TPD, XRD, XPS and CO-chemisorption. It was found that different carbon materials could obviously influence the particle sizes, dispersion and distribution of Pd or PdO particles. Palladium and carbon can synergistically catalyze the room-temperature HDO of vanillyl alcohol even at room temperature, and the carboxyl group was found to be the effective active acid site during the reaction. Possible reaction mechanism was also proposed. The existence of the effective active acid sites on the carbon supports could obviously lower the reaction temperature without decreasing the selectivity, as a result, making the production of renewable fuels by HDO much more economically feasible, which is of much importance.

1. Introduction

Biomass can be divided into three categories [1]: carbohydrates, lignin and fats/oils. Among the three categories, lignin is the most underutilized high energy resource that is available in massive quantities and chemically similar to petroleum [2]. To satisfy the energy needs of future generation, developing efficient routes to convert lignin into transportation fuels is necessary [3]. However, the high oxygen content of lignin derivatives, which always leads to chemical instability, corrosion, immiscibility with fossil fuels [4], terribly delays the application of the liquid. To lower the oxygen content of lignin derivatives, catalytic hydrodeoxygenation (HDO), which eliminates oxygen as water without the loss of carbon atoms and produces saturated hydrocarbons over aromatics, is the preferred route [5].

Recently, Mu et al. [6] summarized the components in lignin pyrolysis oils detected by GC-MS, and Rahimi et al. [7] proposed a model lignin structure and strategies for depolymerization. It can be concluded that a large part of lignin derivatives are basically made up of aromatic rings and substituent groups such as phenolic hydroxyl groups, methoxy groups, alcoholic hydroxyl groups and aldehyde groups. The alcoholic hydroxyl group is one of the most abundant groups in lignin derivatives. Even the aldehyde group, another most abundant group in lignin derivatives, always gets converted to the alcoholic hydroxyl group in HDO processes. Therefore, it seems that the HDO of lignin cannot proceed without taking off the alcoholic hydroxyl group. As is also the same case for carbohydrates and fats/oils. This process really plays an important role in biomass HDO processes, and is of particular concerns.

HDO reactions are always performed under high H_2 partial pressures (as high as 10–20 MPa) and high temperatures (523–873 K) [2,8,9]. The harsh reaction conditions greatly increase the energy consumption and the requirement of the machine. Only the amount of energy released from the renewable fuels obtained from the lignin conversion is larger than the amount of energy required in their production processes, it makes sense. And the larger the difference is, the more meaningful it is for the human. So, much milder HDO processes are invariably expected to get an economically feasible lignin conversion. Whereas, this demands a thorough understanding of the HDO catalysts.

It is well known that, a hydrogenation component for hydrogenation and an acid component for dehydration are necessary for a catalyst for HDO reactions [5,10]. The hydrogenation components, such as transition metals or noble metals, have been described in

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detail in various literatures [2,5,6,11,12]. However, except the generally accepted opinions that the acid components can be introduced by the supports [13], and the acidity of a support has a significant influence on catalyst selectivity [14], as far as we know, it is not easy to find any reports about how the acid component cooperates with the hydrogenation component to influence HDO reactions or how to balance them in a catalytic system.

Palladium is active in hydrogenation reactions, and therefore popular to be used as the hydrogenation component in HDO catalysts. Among various supports, carbon materials are attractive since they have been reported to have many distinctive advantages: (i) resistant to acidic environments, (ii) resistant to coke formation, (iii) positive to higher deoxygenation performances of catalysts, (iv) able to be tailored to meet specific needs, (v) the facile recovery of supported metals [11,15–17]. The activated carbon supported palladium has already been one of the most popular used catalysts in HDO reactions.

In the present work, vanillyl alcohol, with an aromatic ring, a phenolic hydroxyl group, an alcoholic hydroxyl group and a methoxy group connected to the aromatic ring, which we think can most basically represent the structure of lignin derivatives, was chosen as the lignin model molecule. Various carbon materials supported palladium were used as the catalysts to take off the alcoholic hydroxyl group. We elucidate how different carbon materials influence the active palladium and how palladium and carbon synergistically catalyze the room-temperature HDO of vanillyl alcohol. Possible mechanism for the HDO of vanillyl alcohol is also proposed.

2. Experimental

2.1. Materials

Carbon nanotubes (surface area, 215 m^2/g) were obtained from Shandong Dazhan Nano Materials Co., Ltd. (Zouping County, Binzhou City, Shandong Province, China). Ultra dispersed nanodiamond powders (high-purity grade) were bought from Beijing Grish Hitech, PR China, and were synthesized by the detonation explosive method followed by acid washing for purification. Palladium(II) chloride, vanillyl alcohol and 2-methoxy-4-methylphenol were bought from Alfa Aesar. Actived carbon, tetrahydrofuran (THF), concentrated nitric acid and concentrated hydrochloric acid were supplied by Sinopharm Chemical Reagent Co., Ltd. 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) was from Aladdin. 4-hydroxy-3-methoxybenzaldehyde was from TCI.

2.2. Sample preparation

The p-CNT was obtained after treating the pristine CNTs with concentrated HCl at room temperature for 24 h, followed by washing with distilled water to neutral. The o-CNT was obtained after the pristine CNTs were refluxed at 393 K in concentrated HNO_3 for 2 h, followed by washing with distilled water to neutral.

The catalysts with a nominal Pd loading amount of 5 wt% were prepared by incipient wet impregnation on different carbon materials with H_2PdCl_4 solution as precursor. The H_2PdCl_4 solution was prepared by dissolving calculated amount of $PdCl_2$ into a certain amount of concentrated HCl solution. After drying at 353 K overnight, the samples were reduced by H_2 at 523 K for 2 h, and the obtained samples were referred as Pd/AC, Pd/UDD, Pd/o-CNT and Pd/p-CNT, respectively. After treated in an aqueous ammonia solution overnight, and followed by drying in an oven at 333 K, the Pd/o-CNT was turned to the NH_3–Pd/o-CNT.

2.3. Sample characterization

The XRD patterns of the samples were obtained using a D/MAX-2500 PC X-ray diffractometer with monochromatized Cu *Kα* radiation (λ = 1.54 Å). Transmission electron microscopy (TEM) images were obtained by a FEI Tecnai T12 operated at 120 kV. The X-ray photoelectron spectroscopy (XPS) spectra were carried out on an ESCALAB 250 XPS system with a monochromatized Al *Kα* X-ray source (1486.6 eV). The temperature-programed desorption (TPD) was performed on Catlab with a QIC-20 mass Spectrometer from Hiden Analytical, and the samples were heated in He with 10 K/min from 353 K to 1173 K, then kept at this temperature for 20 min. The CO-chemisorption was also performed on the Catlab at 310 K. The reduction processes were performed at 523 K for 1 h in a 10% H_2/He atmosphere.

2.4. Catalyst tests

The hydrodeoxygenation (HDO) of vanillyl alcohol was performed in a Limbo 350 high-pressure reactor from Büchi Glas UsterIt (autoclave A), which is available with a 90 mL stainless vessel and a cyclone 075 magnetic drive. The jacket-temperature was programed by a jacket temperature controller to increase the inner-temperature. For a typical run, vanillyl alcohol, catalyst and THF were mixed in the stainless vessel, and then sealed and purged with hydrogen for 5 times. The hydrodeoxygenation reaction was performed at the target temperature with target hydrogen pressure under stirring at 500 r/min. After the autoclave was cooled to the room temperature, H_2 was released, then, the solution was filtered and analyzed by GC.

The comparison experiments and the HDO of 4-hydroxy-3-methoxybenzaldehyde were carried out in autoclave B with a 95 mL PTFE vessel, and a PTFE-coated magnetic bar was used to give a vigorous stirring.

All the experiments in this work were started with 200 mg reactant, 20 mg catalyst and 20 mL THF.

2.5. Product analysis

Vanillyl alcohol, 2-methoxy-4-methylphenol and 4-hydroxy-3-methoxybenzaldehyde were analyzed by GC (Agilent 7890A) equipped with a FID detector and an HP-5 capillary column. For GC analysis, the initial column temperature of 323 K was held for 2 min, and then, the temperature was ramped at 5 K/min until 363 K was reached and held for 2 min, after that, the temperature was ramped at 30 K/min until 543 K was reached and held at that temperature for 10 min. The vanillyl alcohol conversion, 2-methoxy-4-methylphenol selectivity and yield were calculated using the following equations:

$$\text{The vanillyl alcohol conversion (\%)} = (1-(\text{moles of reactant in products}) / (\text{starting moles of reactant})) \times 100 \quad (1)$$

$$\text{The 2-methoxy-4-methylphenol selectivity (\%)} = (\text{moles of target product}) / (\text{moles of converted reactant}) \times 100 \quad (2)$$

$$\text{The 2-methoxy-4-methylphenol yield (\%)} = (\text{the reactant conversion} \times \text{the target product selectivity}) / 100 \quad (3)$$

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