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.

Key words: Room-temperature hydrodeoxygenation; Palladium; Carbon; Lignin; Biomass conversion

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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 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 m²/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, P.R. 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. Activated 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 HNO₃ 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 H₂PdCl₄ solution as precursor. The H₂PdCl₄ solution was prepared by dissolving calculated amount of PdCl₂ into a certain amount of concentrated HCl solution. After drying at 353 K overnight, the samples were reduced by H₂ 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 333K, the Pd/o-CNT was turned to the NH₃-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 K α 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 K α X-ray source (1486.6 eV). The temperature-programmed 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% H₂/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 programmed 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, H₂ 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:

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

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

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

3. Results and discussion

3.1. How different carbon materials influence the active palladium

For various carbon materials, activated carbon (AC) is a typical disordered carbon. Ultra dispersed nanodiamond (UDD), HNO₃ oxidized carbon nanotube (o-CNT) and HCl washed carbon nanotube (p-CNT) were selected as representatives of ordered carbon. Among them, UDD is a sp^3 -hybridized carbon material, o-CNT and p-CNT are sp^2 -hybridized carbon materials. o-CNT represents the oxidized sp^2 -hybridized carbon material and p-CNT represents the pristine sp^2 -hybridized carbon material. After impregnation with H₂PdCl₄ solution and reduction in H₂ atmosphere, 5 wt% Pd/AC, 5 wt% Pd/UDD, 5 wt% Pd/o-CNT and 5 wt% Pd/p-CNT were obtained. For Pd's nature that can be easily oxidized in air, there should be the coexistence of Pd and PdO, and it is proven by the following XRD and XPS analyses. The incipient wet impregnation method is one of the most effective ways to get rid of the impurities involved in the preparation processes, which may influence the catalytic reactions. Without adding the organic molecules in, it can be also regarded as one of the most natural ways to reveal how the supports influence the active metals during their formation processes.

Different carbon materials can obviously influence the Pd in the as-prepared Pd/AC, Pd/UDD, Pd/o-CNT and Pd/p-CNT catalysts. Figure 1 gives the TEM images of the four catalysts. It could be observed that, the Pd or PdO particles have quite nonuniform particle size (the sizes of most particles vary from 1 nm to 12 nm) on AC, while it is hard to distinguish between Pd species (Pd and PdO) and UDD particles in Figure 1(b). This means a uniformly similar particle size of the particles of Pd species to the particles of UDD, which is about 5–8 nm [18]. The particles of Pd species can be seen uniformly distributed on CNTs, with an average particle size of 1.66 nm for Pd/o-CNT and 2.43 nm for Pd/p-CNT (Figure 1e, f).

Figure 1. TEM images of Pd/AC (a), Pd/UDD (b), Pd/o-CNT (c) and Pd/p-CNT (d); particle size distribution of Pd/o-CNT (e) and Pd/p-CNT (f).

XRD patterns of the four catalysts along with the fresh UDD's are shown in Figure 2. For Pd, the 2θ values of reflections appear at 40.04° , 46.60° , 68.04° and 82.04° , corresponding to (111), (200), (220) and (311) planes, respectively. For PdO, the obvious 2θ value of reflection only appears at 33.80° in the XRD pattern of Pd/AC, which corresponds to (101) plane. Although the catalysts were reduced by H_2 at 523 K for 2 h, the diffraction peak of PdO always exists due to the easy oxidation of Pd during the unavoidable air contact in the transfer steps. The deconvolution of Pd 3d XPS spectra also verifies the existence of PdO in Figure 3. Obvious diffraction peaks of Pd and PdO can be seen in the XRD pattern of Pd/AC, which proves the existence of large crystalline grains of Pd and PdO. The main peaks of Pd at 40.04° become sharper and sharper from Pd/o-CNT, Pd/p-CNT to Pd/UDD, which means the average Pd crystalline size gets larger and larger. The average crystalline sizes of Pd and UDD in Pd/UDD, calculated according to the Scherrer's equation, are 7.0 nm and 7.5 nm, respectively. And the average crystalline size of Pd species in Pd/AC is 8.3 nm. The informations obtained from the XRD patterns are in accordance with the TEM images shown.

Figure 2. XRD patterns of Pd/AC, Pd/UDD, UDD, Pd/o-CNT and Pd/p-CNT.

The surface elemental composition derived from XPS analysis is shown in Figure 3 and Table 1. For the ordered carbon supported palladium, increasing the surface O content from Pd/p-CNT (4.29%), Pd/o-CNT (8.58%) to Pd/UDD (10.73%), the surface Pd content decreases. The phenomenon shows the influence to the distribution of Pd by O functional groups for ordered carbon materials. O functional groups could also show a positive role to disperse Pd species particles. Increasing surface O content from p-CNT to o-CNT, the average particle size of Pd species gets larger on Pd/p-CNT than on Pd/o-CNT (Figure 1), which is consistent with our previous work [19]. UDD is composed of a nanodiamond core and an outer shell of unstructured amorphous carbon [18]. Recent work [20] in our group studied the detailed role of defects in a similar core-shell structure to the supported Pd nanoparticles, and proved a strong metal-support interaction.

Figure 3. Pd 3d and O 1s XPS spectra of the four catalysts (The intensities are not in the same scale).

Table 1. XPS analyses of the various carbon materials supported palladium catalysts.				
Elements and relevant chemical states	Pd/AC	Pd/UDD	Pd/o-CNT	Pd/p-CNT
Pd	0.42%	0.24%	0.32%	0.45%
Pd ⁰ (335.3–335.9 eV) ^a	0.12%	0.12%	0.12%	0.24%
Pd ²⁺ (337.0–337.5 eV) ^b	0.30%	0.12%	0.20%	0.21%
O	9.03%	10.73%	8.58%	4.09%
highly conjugated carbonyl oxygen (530.7 eV)	3.37%	-	-	-
C=O (531.5–531.8 eV)	2.51%	0.93%	0.75%	0.88%
O=C—O (532.5–532.8 eV)	1.93%	4.59%	3.91%	1.88%
C—OH (533.5–533.9 eV)	1.23%	5.21%	3.92%	1.33%

^a The peak position of Pd⁰ 3d_{5/2}.

^b The peak position of Pd²⁺ 3d_{5/2}.

3.2. How palladium and carbon synergistically catalyze the room-temperature HDO of vanillyl alcohol

The conversion of 5-hydroxymethylfurfural (HMF) to 2, 5-dimethylfuran (DMF) is a typical HDO reaction. From a recent review on the HDO of HMF by Hu et al. [21], some conclusions can be obtained. With the noble metal or the transition metal as the hydrogenation component in a catalytic system, when there is no acid component or quite weak acid component on the support, high temperatures (as high as 403–493 K) are always needed. However, when there is stronger acid component like H₂SO₄ or just H₂CO₃, the reaction temperature could decrease to 343–353 K. From these studies, it seems that the acid component is a key point to lower the reaction temperature. As we mentioned before, the acid component in a HDO catalyst is responsible for the dehydration. Then, it is assumed that the dehydration step might be significantly influenced by the acid component when the reaction occurs at relatively low temperatures. The only acid source in the present catalytic system should be the oxygenated groups on the carbon supports. The acidic O functional groups on the surface of carbon materials are mainly carboxyl, anhydride, lactone, phenol, and carbonyl groups. Phenol and carbonyl groups are such weak acidic groups that only can be neutralized by strong bases like NaOH and C₂H₅ONa [22]. For the only hydrogenation component in the present reaction system is the Pd species and the main acid component in the present reaction system is the O=C—O species (carboxyl, anhydride, lactone group), the Pd and the

O=C—O species are most probably active sites for the reaction. Based on these understandings on the HDO of vanillyl alcohol, a series of experiments were carried out (Table 2).

Table 2. Experiments of the HDO of vanillyl alcohol to 2-methoxy-4-methylphenol by the various carbon materials supported palladium catalysts.

Entry	Catalyst	H ₂ partial pressure (MPa)	Temperature (K)	Reaction time ^a (h)	Conversion (%)	Selectivity (%)	Yield ^b (%)
1	-	1	470	8	25	59	15
2	Pd/UDD	1	470	8	100	>98	100
3	Pd/AC	1	470	8	100	>98	100
4	Pd/AC	1	420	8	100	>98	100
5	Pd/AC	1	382	8	96	>98	96
6	Pd/AC	1	358	8	91	>98	91
7	Pd/AC	1	335	8	78	>98	78
8	Pd/AC	1	358	4	80	>98	80
9	Pd/AC	1	358	2	52	>98	52
10	Pd/AC	1	335	4	73	>98	73
11	Pd/AC	0.5	335	4	25	94	24
12	-	1	room temperature	19	7	0	0
13	Pd/AC	1	room temperature	19	51	94	48
14	Pd/o-CNT	1	room temperature	19	100	>98	100
15	Pd/p-CNT	1	room temperature	19	100	>98	100
16	Pd/o-CNT	1	room temperature	8	100	>98	100
17	Pd/p-CNT	1	room temperature	8	100	>98	100
18	Pd/o-CNT	1	room temperature	3	100	>98	100
19	Pd/p-CNT	1	room temperature	3	63	>98	63
20	Pd/AC	1	room temperature	1	15	58	9
21	Pd/UDD	1	room temperature	1	8	46	4
22	Pd/p-CNT	1	room temperature	1	57	>98	57
23	Pd/o-CNT	1	room temperature	1	74	>98	74
24 ^c	Pd/o-CNT	1	room temperature	1	100	>98	100
25 ^c	NH ₃ -Pd/o-CNT	1	room temperature	1	14	0	0
26 ^{c,d}	Pd/o-CNT	1	room temperature	1	100	0	0

^a Time required to get to the required temperature and for cooling is not included. It is the duration that the autoclave is hold at the desired temperature.

^b Yield (%) = (Conversion×selectivity) /100, during the calculation processes, >98% is regarded as 100%.

^c The comparison experiments were performed in autoclave B.

^d 400 mg TEMPO was added.

Aqueous ammonia is a base of moderate strength. The adsorbed ammonia can react with carboxyl groups to form ammonium carboxylate species, but fails to react with phenol groups [23]. In order to give a proof to the indispensable influence of the acid component in HDO reactions, aqueous ammonia was used to neutralize the acidic functional groups on the Pd/o-CNT catalyst. Then, the as-received NH_3 treated Pd/o-CNT catalyst was used for the reaction. Another advantage for choosing aqueous ammonia is its easy removal by evaporation. The comparison experiments were carried out at room temperature and 1 MPa H_2 pressure. 100% conversion of vanillyl alcohol and $> 98\%$ selectivity to 2-methoxy-4-methylphenol were obtained by the Pd/o-CNT catalyst (entry 24), however, when the NH_3 treated Pd/o-CNT catalyst was used, no 2-methoxy-4-methylphenol was detected by the GC (entry 25). This may suggest an irreplaceable role of the acid component, and rules out the possible influence by phenol groups, let alone carbonyl groups that of even weaker acidity. As mentioned in the introduction section that the acid component in a HDO catalyst is responsible for the dehydration process, so the low conversion of vanillyl alcohol by NH_3 -Pd/o-CNT also suggests the dehydration process most probably starts in the first step of the present HDO reaction.

The HDO reaction can be obviously influenced by the free spaces of autoclaves. Two experiments were carried out in two autoclaves with quite different free spaces for H_2 under the same reaction conditions. The experiment in the autoclave with more free space (autoclave B, entry 24) showed much better catalytic performance compared to that in the autoclave with less free space (entry 23). In the following work, the autoclave with a small free space was used to limit the catalytic performance and get insight to the catalytic behaviors of the catalysts.

The blank reaction performed at 470 K (entry 1) showed a conversion of 25% and a selectivity of 59%, however, the blank reaction at room-temperature (entry 12) didn't give any HDO product. It proves the positive effect of the high temperature to take off the alcoholic hydroxyl group. When increasing the temperature from 335 to 420 K (entry 7, 6, 5, 4), the conversion increased obviously from 78% to 100% on Pd/AC, while the selectivity stabilised at $> 98\%$. Even at a much higher temperature (470 K, entry 3), the selectivity still stabilised at $> 98\%$ without the hydrogenation of the aromatic ring. For the reason that lignin's high aromatic content is responsible for its high energy content, the stability of the benzene ring of the product on the catalysts is quite meaningful for the conversion of lignin to petroleum-like aromatic fuels. The H_2 partial pressure can also greatly influence the reaction. Lowering the H_2 partial pressure from 1 MPa to 0.5 MPa, the conversion of vanillyl alcohol decreased obviously (entry 10, 11).

Surprisingly, it was found that the Pd/AC catalyst could show 51% conversion of vanillyl alcohol with 94% selectivity to 2-methoxy-4-methylphenol after 19 h even at room temperature (entry 13). Getting rid of the influence of the high temperature, this phenomenon should mean the existence of effective acid sites on the carbon supports. Then, also at room temperature, it was found the Pd/p-CNT catalyst could give 100% conversion of vanillyl alcohol and $> 98\%$ selectivity to 2-methoxy-4-methylphenol after 8 h, however, the Pd/o-CNT catalyst only need 3 h to give a full

conversion (entry 17, 18). The Pd/UDD showed almost no catalytic activity at room temperature (entry 21). The catalytic performances of the four catalysts at room temperature for 1 h decreased in the order: Pd/o-CNT > Pd/p-CNT > Pd/AC > Pd/UDD (entries 20–23), and the blank reaction did not show any yield of the product at room temperature even after 19 h (entry 12).

The surface chemical properties of the four catalysts were probed by X-ray photoelectron spectroscopy (XPS) analysis to try to reveal the relationship between the catalytic performances and the active components (the hydrogenation component and the acid component). The spectra of Pd 3d and O 1s were presented in Figure 3. The peak within the range of 340.8–343 eV is ascribed to Pd 3d_{3/2}, while the peak within the range of 335.2–337.6 eV is assigned to Pd 3d_{5/2} [24–26]. In this work, the Pd⁰ 3d_{5/2} and Pd²⁺ 3d_{5/2} for the four catalysts were observed within the range of 335.3–335.9 eV and 337.0–337.5 eV, respectively. The O 1s spectra were deconvoluted into four peaks at 530.7 eV, 531.5–531.8 eV, 532.5–532.8 eV, 533.5–533.9 eV, corresponding to highly conjugated forms of carbonyl oxygen such as quinone groups, C=O (ketonic carbonyl groups), O=C–O (a sum of carboxyl, anhydride, lactone, and ester groups), C–OH (phenol groups), respectively [27,28]. Detailed information on various chemical states of Pd and O were obtained after the deconvolution of the spectra (Table 1). The HDO of vanillyl alcohol is also a hydrogenolysis reaction, which was found to be first order with respect to catalyst [29]. That means the real active sites of the HDO catalyst can be identified by the liner relationship between the amount of them and the catalytic performance, and the line should pass through the origin (no active sites, no yields). The reaction conducted in the absence of catalysts (entry 12, blank reaction) showed no yield of the product, which just happened as expected. In the following work, the (0, 0) point by the blank reaction is tried to satisfy the liner relationship between the amount of them and the catalytic performance. The active components of HDO catalysts are the acid component and the hydrogenation component. The only possible acid components in the present catalytic system are the acidic O groups, and the only possible hydrogenation component is the Pd species. Since the phenol group and the carbonyl group were ruled out as the active acid sites in the comparison experiments (entries 24 and 25), O=C–O species are the only possible acid component left. It can be seen from Figure 4(a) that, the yields of the product could show similar variation trend with the increase of the contents of the O=C–O species under the same reaction conditions for only Pd/p-CNT (entry 22), Pd/o-CNT (entry 23) and the blank (entry 12, the reaction conducted in the absence of catalysts). Then, there should be a linear relationship between the yield of the product and the content of the hydrogenation component under the same reaction conditions for at least Pd/AC (entry 20), Pd/UDD (entry 21) and the blank (entry 12). By comparing the relationships between the yields of the product and the possible hydrogenation components (Figure 4b and c), a nice linear relationship was obtained between the Pd content and the yield of the product (Figure 4b) for Pd/AC, Pd/UDD and the blank.

Figure 4. Relationships between the possible hydrogenation components (Pd, Pd⁰), the O=C–O content and the yield of the product (entries 12, 20–23).

Only the Pd content instead of the Pd⁰ content could show similar variation trend with the yield of the product for Pd/AC, Pd/UDD and the blank (Figure 4b and c). And only for Pd/AC, Pd/UDD and the blank, there shows a nice linear relationship between the Pd content and the yield of the product with the increase of the Pd content (Figure 4b). Getting rid of the acid components (Figure 4a), the hydrogenation step is most probably the rate determining step, therefore, the reaction rates showed to be influenced by the surface Pd content rather than other possible acid components for Pd/AC, Pd/UDD and the blank. Due to the “cage effect” [30] of liquid phase reactions and the limited solubility of H₂ in liquid phase, the same supported Pd catalyst may give different active Pd content in gas phase and liquid phase reactions. Then, CO-chemisorption is no longer suitable to be used to determine the active Pd content for this reaction. The fact is proven by determining the active surface areas of Pd/AC and Pd/UDD both before and after reduction by CO-chemisorption (Table S1). No obvious relationship could be found, when we tried to relate them with the yield of the product for Pd/AC, Pd/UDD and the blank (Figure S1). Quantifying the active Pd content in liquid-phase reactions seems still a challenge. In the present work, the similar average crystalline sizes of Pd species in Pd/UDD and Pd/AC may give similar active surface areas on the reaction conditions. Then, it results to the approximate linear relationship between the surface Pd content and the yield of the product. When there are similar sizes of Pd species, the surface

Pd content obtained from the XPS data seems reliable for relating it with the catalytic performance. Moreover, once the reaction started, most of the surface PdO should also be quickly reduced by H₂.

The O=C–O species is the only possible acid component left. Only for Pd/p-CNT, Pd/o-CNT and the blank, there shows a nice linear relationship between the O=C–O species content and the yield of the product with the increase of the content of the O=C–O species (Figure 4a). Getting rid of the hydrogenation component (Figure 4b), It was assumed that the dehydration step is the rate determining step, and the O=C–O species (the main acid component in the reaction system) work as the active acid component to influence the reaction rate for Pd/p-CNT, Pd/o-CNT and the blank. As a result, the acid component for the system is most probably the sum of carboxyl, anhydride and lactone groups.

It is well known that the decomposition of O=C–O species always gives CO₂. By the deconvolution of the evolution profiles of CO₂ intensity to temperature, four peaks can be obtained that are identified as strongly acidic carboxylic groups, weakly acidic carboxylic groups, carboxylic anhydrides and lactones, respectively [31]. To confirm the relationship between the content of the O=C–O species and the yield of the product for Pd/o-CNT, Pd/p-CNT and the blank, temperature-programmed desorption (TPD) was applied to give out the relative amounts of the different O=C–O species (Figure 5a, Table 3). One carboxylic anhydride group is easy to be hydrolyzed to two carboxyl groups, so the acid sites from the anhydride group could be described as 2*anhydride (two times the amount of the anhydride group). One anhydride group releases one CO₂ molecule and one CO molecule during the TPD process, thus the number of anhydride groups could be obtained from the deconvolution of the evolution profiles of CO₂ (Table 3). Then, the amount of the O=C–O species could be described as the amount of “Carboxyl + 2*Anhydride + Lactone”. A nice linear relationship between the yield of the product (entries 12, 22, 23) and the amount of (Carboxyl + 2*Anhydride + Lactone) for Pd/o-CNT, Pd/p-CNT and the blank can be found and shown in Figure 5(b). However, no such linear relationship could be found for the carboxyl group, the anhydride group or the lactone group, respectively (Figure S2). The results are in accordance with the former conclusion that the reactions are most probably influenced by the content of the O=C–O species for Pd/o-CNT, Pd/p-CNT and the blank.

Figure 5. Evolution profiles of CO₂ during the TPD tests of Pd/o-CNT and Pd/p-CNT, and the relationship between the yield of the product (entries 12, 22, 23) and the amount of (Carboxyl + 2*Anhydride + Lactone).

Samples	Carboxyl ^a	Anhydride ^a	Lactone ^a	Carboxyl + 2*Anhydride + Lactone ^a	Yield ^b
Pd/o-CNT	30.37 a.u.	30.98 a.u.	22.32 a.u.	114.65 a.u.	0.74
Pd/p-CNT	13.02 a.u.	38.90 a.u.	5.11 a.u.	95.93 a.u.	0.57
Pd/o-CNT to Pd/p-CNT ratio	2.33	0.80	4.37	1.20	1.30

^a The relative amounts of the functional groups obtained from the deconvolution of the evolution profiles of CO₂.

^b Reaction conditions: room temperature, 1 MPa, 1 h (entries 22, 23).

The comparison experiments suggest the active acid site for the reaction should be at least one of the carboxyl, anhydride and lactone group. As a first order reaction with respect to catalyst, both the XPS and TPD results show that the contents of the O=C–O species varies in the similar trend with the increase of the yields of the product for Pd/p-CNT, Pd/o-CNT and the blank. One carboxylic anhydride group contains two O=C–O structures, and can be easily hydrolyzed to two carboxyl groups by water in the reaction system. The lactone group could also be hydrolyzed to produce the carboxyl group. Under reaction conditions, carboxyl and phenolic hydroxyl groups are the protogenic surface groups [23]. Then, these clues tend to give out such information that the O=C–O species are the active acid sites for the reaction and work in the form of carboxyl groups under the reaction conditions.

Detailed summaries on the recent HDO results of lignin derived model compounds from noble metal catalysts and non-noble transition metals were made by Daniel A. Ruddy et al. [5] and Majid Saidi et al. [2]. However, high H₂ partial pressures and high reaction temperatures seem to be unavoidable. As far as we know, the present work by the Pd/o-CNT seems to be the very rare room-temperature HDO of lignin derivatives. It seems that the well synergism between the acid component and the hydrogenation component cannot be ignored. Recently, Similar experiments were also performed by Trenton H. Parsell et al. [32]. They chose 4-hydroxy-3-methoxybenzaldehyde and vanillyl alcohol as the same type monomeric lignin surrogates to carry out the HDO reactions. Commercial 5 wt% Pd/C and Zn modified commercial 5 wt% Pd/C were chosen as their catalysts. However, the best HDO result of vanillyl alcohol (>99% conversion and 80% yield of 2-methoxy-4-methylphenol) were obtained at 2 MPa and 150 °C after 8 h, which was much more severe compared to the present work.

4-Hydroxy-3-methoxybenzaldehyde, a typical and common component of pyrolysis oil derived from the lignin fraction, as the same type lignin model molecule with vanillyl alcohol, was also tried in the present work. Pd/o-CNT, which give the best performing in the present HDO of vanillyl alcohol, was employed in the HDO of 4-hydroxy-3-methoxybenzaldehyde. It was found that 4-hydroxy-3-methoxybenzaldehyde could also be completely converted to the HDO product at room temperature and 1 MPa in just 3 h. Compared with the recent results of the HDO of

4-hydroxy-3-methoxybenzaldehyde in literatures (Table S2), the catalytic performance of the Pd/o-CNT shows obvious advantage.

It is noticed that none of the catalysts used in the above mentioned works in literatures was treated by acid or some other ways that can introduce acid components in. The only acid components just came from the pristine support materials. Comparing with the present work, this may mean there are not enough acid sites in these catalytic systems. The lack of the active acid components is most probably the reason for the difference between the results by the Pd/o-CNT in the present work and the results in the aboved mentioned literatures. The phenomenon gives evidence to the ability of acid components to influence the HDO reaction and the importance of the synergism between the hydrogenation component and the acid component by another way.

3.3. Proposed mechanism of the HDO of vanillyl alcohol

The dehydration here, to be more exact, should be the taking off of alcoholic hydroxyl groups or the cleaving of the alkyl–OH bond. The S_N2 or S_N1 type reaction mechanism was proposed for the hydrogenolysis of benzylic alcohols [33], which also include vanillyl alcohol. However, both S_N2 and S_N1 type reactions are nucleophilic substitution processes, which should have nucleophilic hydrogen species in the catalytic system to continue the hydrogenolysis reactions. During the process of dissociating hydrogen molecules into atomic hydrogen by Pd, the adsorption of H on Pd is due to H-vacancy pairs (H atoms adsorb on the empty face-centred cubic sites) [34]. And though there may be palladium hydride formed, it is also just the absorbed hydrogen atoms that occupy interstitial octahedral sites of the face-centered cubic lattice [35]. It just likes an alloy of palladium with metallic hydrogen. In other words, it is hard to find any nucleophilic hydrogen species in the present reaction system. For the lack of the nucleophilic hydrogen species, neither S_N2 nor S_N1 type reaction mechanism is reasonable for the present work.

In 2014, a free-radical theory based mechanism was proposed to the hydrogenolysis of the C–O bond of benzyl phenyl ether in undecane by DFT calculation [30]. In 2015, the free-radical pathway was proved by electron paramagnetic resonance (EPR) and the free radical quenching agent TEMPO in the hydrogenolysis of benzyl phenyl ether into phenol and toluene by using Pd/C as the catalyst [36]. Since the existence of atomic hydrogen in the present system, the free-radical theory seems to be much more reliable. In order to prove this conjecture, TEMPO is used as the free radical quenching agent to quench the free radicals in this work. The experiment by Pd/o-CNT could show 100% conversion of vanillyl alcohol and >98% selectivity to 2-methoxy-4-methylphenol in entry 24. However, after adding TEMPO, the selectivity decreased to 0 while the conversion still remained at 100%. This phenomenon gives evidence to a free-radical process. The stable conversion also means the free-radical process most probably happened in the steps after the cleaving of the alkyl–OH bond.

The blank reaction at room-temperature (entry 12) didn't show any HDO product, which might be ascribed to the strong bond energy of alkyl–oxygen bond (385 kJ/mol) [5,37]. Therefore the cleaving of

the alkyl–oxygen bonds should be catalyzed by the acid component. When these acid components were poisoned, the dehydration process, which was assumed to start in the first step of the present HDO reaction, was severely suppressed (entry 25).

A possible mechanism of the HDO of vanillyl alcohol was then proposed and shown in Figure 6. The H_2 molecules are decomposed into atomic hydrogen on metallic Pd (including the Pd reduced from PdO under reaction conditions with water produced). These atomic hydrogen could also reduce the PdO into Pd. The carboxylic anhydride group and the lactone group are hydrolyzed to produce the carboxyl group by water in the reaction system. The vanillyl alcohol molecule is prone to interact with the carboxyl group and then decomposes and releases water molecules. Under the induction by the atomic hydrogen, the corresponding radicals are formed. Then, the atomic hydrogen can quickly react with the radicals to recover the carboxyl groups, and produce the 2-methoxy-4-methylphenol.

Figure 6. Proposed mechanism of the HDO of vanillyl alcohol over various carbon materials supported palladium (Water in the reaction system could come from the dehydration and the reduction of PdO).

4. Conclusions

In summary, the present work gives some illustrations on how different carbon materials influence the active palladium and how palladium and carbon synergistically catalyze the room-temperature HDO of vanillyl alcohol. The carboxyl group was found to be the effective active acid site during the reaction.

Different carbon materials have different influences on the active Pd species. The ordered carbon (UDD, o-CNT, p-CNT) results in uniform particles of Pd species, however, the disordered carbon (AC) results in nonuniform particles. The sphere-like sp^3 carbon (UDD) is much easier to lead to a larger particles size of Pd species than the tube-like CNT. The O functional groups play a positive role to disperse the Pd species. For ordered carbon, O functional groups can also influence the distribution of Pd to some extent.

The room-temperature HDO of vanillyl alcohol can be synergistically catalyzed by palladium and carbon. Pd species and O=C–O species are the two active sites for this reaction. During the reaction, the Pd⁰ serves as the hydrogenation component and the carboxyl group on carbon materials is the effective active acid component. The carboxyl group is effective to take off the alcoholic hydroxyl group even at room temperature, which means the easy removal of alcoholic hydroxyl groups in lignin derivatives could happen under quite mild conditions. A possible reaction mechanism is proposed to understand the room-temperature HDO of vanillyl alcohol.

5. Prospect

Nowadays, with the rapid development of society but limited fossil fuels, the demand for renewable fuels becomes more and more urgent. Developing an economic way for biomass conversion is highly desired. One of the most important parts should be trying to lower the energy consumption by HDO processes. The present work proves the carboxyl group as an effective acid site for the room-temperature HDO of vanillyl alcohol—a typical lignin model molecule, and proposes a reaction pathway for the reaction. It gives hope to avoid high reaction temperatures in the HDO of lignin derivatives by taking good advantage of the effective acid component. The carboxyl group can make the reaction conditions of the HDO reactions much milder. For its moderate acid strength, it could also work effectively without the occurrence of the side reactions caused by other acid components (like generally used H₂SO₄). The present understanding of the catalysts gives the possibility to balance the hydrogenation speed and the dehydration speed of the alcoholic hydroxyl groups by tuning the hydrogenation sites and the active acid sites on the catalysts. Making good use of the hydrogenation component and the acid component should be a good solution to give an excellent HDO reaction performance. Then, much milder and more effective HDO processes can be expected. A well-developed biomass conversion system with quite limited energy consumption and much larger energy contained biofuel products will be no longer a dream.

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Graphical abstract

Description portion: The discovery and understanding of the very rare room-temperature HDO of lignin derivatives, and how carbon materials influence the active palladium is described.