

Article

High Efficient Hydrogenation of Lignin-Derived Monophenols to Cyclohexanols over Pd/ γ -Al₂O₃ under Mild Conditions

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Abstract: The catalytic hydrogenation of lignin-derived monophenols with high efficiency and selectivity is important for the sustainable production of chemicals and fuels. Here, Pd/ γ -Al₂O₃ was prepared via impregnation and used as catalyst for the hydrogenation of phenols to cyclohexanols under mild conditions in aqueous solution. 3 wt. % Pd/ γ -Al₂O₃ exhibited good catalytic activity for the selective hydrogenation of 4-ethylphenol into 4-ethylcyclohexanol, and a conversion of 100% with selectivity of 98.9% was achieved at 60 °C for 12 h. Other lignin-derived monophenolic model compounds such as 4-methyl phenol and 4-propyl phenol could be hydrogenated into cyclohexanols selectively under optimal conditions. Moreover, the Pd/ γ -Al₂O₃ catalyst displayed good activity for the hydrogenation of the mixture of monophenols directly derived from raw biomass system to cyclohexanols as the main products, and was favorable for the depolymerization of lignin oligomers under milder conditions. Pd/ γ -Al₂O₃ catalyst showed good water resistance and stability after recycling four times. This result might provide a promising approach to selectively producing cyclohexanol directly from raw biomass material under mild conditions in aqueous solutions.

Keywords: 4-ethylphenol; lignin; hydrogenation; 4-ethylcyclohexanol; Pd/ γ -Al₂O₃ catalyst

1. Introduction

As the only renewable resource which can be converted into carbon-based fuels and chemicals, biomass is recognized as the optimal feedstock to replace the exhausted fossil fuels [1]. Lignin, constituting 15–30 wt. % and carrying about 40% of its energy of biomass, represents an ideal renewable source of aromatics for the production of value-added chemicals [2,3].

Currently, many efforts have been made to depolymerize lignin to monophenols because of its high degree of polymerization and complex structure. Hydrogenolysis, catalytic cracking, and solvothermal treatment were the main methods adopted [4,5], and a satisfied yield of monophenols was obtained [6,7]. A high yield of monophenols was achieved by Zhao *et al.* via the catalytic hydrogenation process [8]. Very recently, Van den Bosch *et al.* reported the selective delignification of lignocelluloses in methanol through simultaneous solvolysis and catalytic hydrogenolysis, resulting in a lignin oil consisting of above 50% monophenols [9]. In our previous work [10], selective conversion of lignin in corncob residue resulted in 24.3 wt. % of monophenols. Among the obtained monophenol products, 4-ethylphenol was the common and predominant product. Therefore, the further conversion of 4-ethylphenol to produce value-added chemical intermediates and fuels is becoming necessary and crucial.

Cyclohexanol derivatives are important value-added chemical intermediates, which are widely applied to the fields of pesticide, pharmacy and cosmetics. Cyclohexanol derivatives can be produced from the hydrogenation of phenols. Much effort had been directed towards the hydrogenation of phenols over the decades in the gas or liquid phase. In the case of gas phase hydrogenation, high temperatures (120–300 °C) are usually required [11–16]. However, the formation of coke due to high temperatures in the reaction process causes the deactivation of catalysts, which involves the limitation of circulation and further utilization. Additionally, high temperatures require more energy consumption and thus an increase in cost. Recently, much attention has been focused on the liquid phase hydrogenation of phenols [8,17–25]. For example, Huang *et al.* [26] prepared a high-performance PdRu bimetallic catalyst on mesoporous silica nanoparticles for the hydrogenation of phenol in CH₂Cl₂ solvent. Rode *et al.* [27] reported that a charcoal-supported rhodium catalyst was highly active for the ring hydrogenation of phenol and cresols under scCO₂, and high conversions of phenol were achieved under such conditions as 328 K, 10 MPa H₂ and 12 MPa CO₂. Although high catalytic efficiency was achieved, some environmentally unfriendly organic solvents and tough reaction conditions were indispensable. Compared to organic solvent, water is much greener in the view of environmental protection [28–31], although most of the catalysts could deactivate in aqueous solutions. Moreover, most of the reports involving the cyclohexanol production usually employed commercial phenols as starting material. There are limited studies about the production of cyclohexanol directly from lignin in raw biomass.

Here, Pd/ γ -Al₂O₃ was prepared via impregnation and used as a catalyst for the selective hydrogenation of 4-ethylphenol into cyclohexanols in an aqueous phase under mild conditions. In addition, the catalytic system was further applied to other phenolic model compounds and liquid mixture with monophenols directly from the lignin in raw biomass material.

2. Results and Discussion

2.1. Catalyst Characterization

The surface area, pore structure parameters and the actual Pd loading of all the samples are summarized in Table 1. The average pore diameter of all the samples ranged from 82.0 Å to 92.5 Å, confirming that all the samples possessed a mesoporous structure. The BET surface area and pore volume of samples decreased distinctly by the loading of palladium on the bare support. Both the BET surface area and pore volume gradually decreased with increasing Pd loading from 1 to 5 wt. %, whereas the average pore diameter gradually increased. It seemed that more porous space inside the support was occupied, and the smaller pores were blocked, with an increasing amount of palladium introduced. Meanwhile, the blocking of smaller pores gave rise to the enlarging of average pore diameters. The ICP-AES results suggest that most of the actual Pd loadings are slightly less than or close to the controlled Pd loadings.

Table 1. BET and ICP-AES analyses of the catalysts.

Sample	Surface Area (m ² /g)	Pore Volumes (cm ³ /g)	Average pore diameter (Å)	Pd ^a (wt. %)
γ -Al ₂ O ₃	230	0.471	82.0	-
1Pd/ γ -Al ₂ O ₃ ^b	223	0.468	83.1	0.71
2Pd/ γ -Al ₂ O ₃	218	0.463	84.7	1.79
3Pd/ γ -Al ₂ O ₃	197	0.423	86.0	3.05
5Pd/ γ -Al ₂ O ₃	174	0.403	92.5	4.54

^a Total Pd loadings determined by ICP; ^b 1 wt. % Pd/ γ -Al₂O₃ was abbreviated to 1Pd/ γ -Al₂O₃ and other samples were also abbreviated analogously.

Figure 1A shows the XRD patterns of samples with different treatments. Characteristic diffraction peaks of γ - Al_2O_3 were observed at 2θ of 37.2° , 42.4° , 45.5° and 67.3° . The XRD pattern of γ - Al_2O_3 impregnated with PdCl_2 aqueous solution (UC-Pd/ γ - Al_2O_3) showed no difference from γ - Al_2O_3 . After calcinations at 500°C for 4 h, two diffraction peaks corresponding to PdO at 2θ of 33.8° and 54.9° were detected, indicating that PdCl_2 was transformed into PdO by calcination in air. The diffraction peaks of Pd/ γ - Al_2O_3 at 2θ of 39.9° and 46.4° in the XRD patterns can be assigned to the (111), (200) planes of face-centered cubic (fcc) crystallographic structure of metallic palladium, respectively [32]. This indicated that PdO was reduced to Pd^0 via the reduction treatment. The characteristic diffraction peaks of metallic Pd can be observed in the XRD patterns of Pd/ γ - Al_2O_3 catalysts with varied Pd loadings (see Figure 1B). The average particle sizes of Pd particles were calculated from the Scherrer equation. With increasing Pd loading to 5 wt. %, the average particle sizes of Pd particles increased from 9 to 16 nm, resulting in a lower surface area and a lower degree of dispersion. This result was consistent with that of the BET analyses.

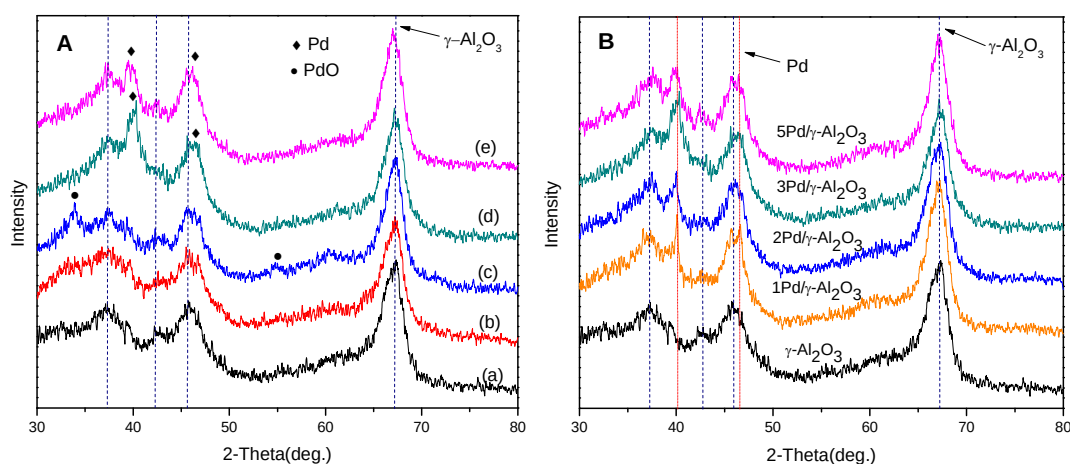


Figure 1. XRD patterns of the samples. (A): (a) γ - Al_2O_3 : γ - Al_2O_3 support; (b) UC-3 wt. % Pd/ γ - Al_2O_3 : γ - Al_2O_3 support was only impregnated with aqueous liquid of PdCl_2 ; (c) UR-3 wt. % Pd/ γ - Al_2O_3 : UC-Pd/ γ - Al_2O_3 catalyst was calcined at 500°C for 4 h; (d) 3 wt. % Pd/ γ - Al_2O_3 : UR-Pd/ γ - Al_2O_3 catalyst was reduced with H_2 at 450°C for 2 h; (e) used 3 wt. % Pd/ γ - Al_2O_3 : Pd/ γ - Al_2O_3 catalyst recycled after reaction; (B): patterns of catalysts with different Pd loading on γ - Al_2O_3 .

The XPS spectra of calcined (UR-Pd/ γ - Al_2O_3) and reduced (Pd/ γ - Al_2O_3) samples are shown in Figure 2. The Pd $3d_{5/2}$ and $3d_{3/2}$ binding energies were given in Table S1 along with a quantitative estimation of the surface elements. The XPS spectra of the calcined sample exhibited two prominent peaks at 336.8 and 342.2 eV, assigning to $\text{Pd}^{2+} 3d_{5/2}$ and $\text{Pd}^{2+} 3d_{3/2}$, respectively [30,33]. This implied that PdO was the primary oxidation state of palladium on UR-Pd/ γ - Al_2O_3 . In addition, two small peaks observed at 335.1 ($\text{Pd}^0 3d_{5/2}$) and 340.3 eV ($\text{Pd}^0 3d_{3/2}$) indicated the presence of metallic Pd, possibly attributing to the partial decomposition of PdCl_2 during calcination. The XPS spectra of the reduced sample indicated that significant changes occurred in the relative amounts of Pd^0 and Pd^{2+} . For the reduced sample, the percentage of Pd^{2+} decreased markedly, and Pd^0 was the predominant species (*ca.* 60%). However, a small amount of Pd^{2+} was also detected after hydrogen reduction.

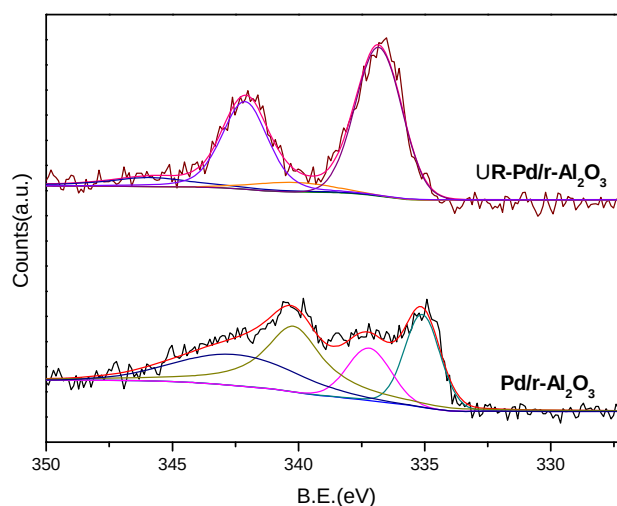


Figure 2. XPS spectra of samples.

2.2. The Selective Hydrogenation of 4-Ethylphenol

2.2.1. Effect of Reaction Temperature and Time on the Hydrogenation of 4-Ethylphenol

Aqueous-phase hydrogenation of 4-ethylphenol was conducted at different reaction temperatures (40–120 °C) (see Figure 3). 4-Ethylphenol was found to be converted to 4-ethylcyclohexanone and 4-ethylcyclohexanol with the catalysis of 5 wt. % Pd/ γ -Al₂O₃ at a very low temperature, and the conversion of 4-ethylphenol reached up to 94.6% at 40 °C. Higher temperatures than 60 °C led to the complete conversion of 4-ethylphenol. This result might provide an energy saving and lower cost approach for the hydrogenation of lignin model compounds.

4-Ethylcyclohexanone and 4-ethylcyclohexanol were the main products detected in the hydrogenation processes at various reaction temperatures. However, the selectivity to the product was greatly dependent on the reaction temperature. The selectivities to 4-ethylcyclohexanone and 4-ethylcyclohexanol were 51% and 29% at 40 °C, respectively. With increasing temperature, the selectivity to 4-ethylcyclohexanone was markedly decreased to only 2% at 120 °C. The selectivity to 4-ethylcyclohexanol remained around 66% at a temperature of 60 °C or higher. The total selectivity to 4-ethylcyclohexanone and 4-ethylcyclohexanol was first increased, reached up to 100% at 60 °C, and was then gradually decreased with increasing reaction temperature. The carbon balance of 4-ethylphenol hydrogenation showed a similar tendency, reaching a maximum of 100% at 60 °C (see Table 2). Only 68% products were identified at 120 °C. To further analyze the reaction products, the liquid products were further conducted by LC-MS analysis (see Figure S1). Besides 4-ethylcyclohexanone and 4-ethylcyclohexanol, some products with a molecular weight from 200 to 400 (about 2 to 3 benzene rings) were also detected, and their amount was gradually increased with increasing temperature from 80 to 120 °C. This indicated that dimers or polymers could be formed at higher temperatures even in the hydrogenation system, which led to the decrease of total selectivity. Full conversion and a total selectivity of 100% was achievable over 5 wt. % Pd/ γ -Al₂O₃ catalyst at 60 °C for 6 h.

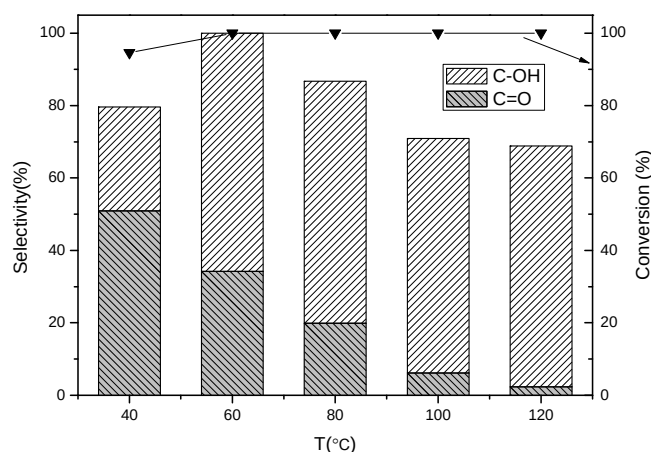


Figure 3. Effect of reaction temperature on the conversion of 4-ethylphenol and the selectivity to the products. Reaction conditions: 25 mL H₂O, 0.82 mmol 4-ethylphenol, 0.20 g Pd/ γ -Al₂O₃, 2 MPa H₂, 6 h.

Table 2. Carbon balance of 4-ethylphenol hydrogenation on 5 wt. % Pd/ γ -Al₂O₃ at different reaction temperature and on Pd/ γ -Al₂O₃ with different Pd loading at 60 °C.

T/°C ^a	40	60	80	100	120
Carbon balance/%	79.6	100	86.8	70.9	68.9
Pd loading/wt. % ^b	0	1	2	3	5
Carbon balance/%	-	100	100	100	100

^a Reaction conditions: 25 mL H₂O, 0.82 mmol 4-ethylphenol, 0.20 g 5 wt. % Pd/ γ -Al₂O₃, 2 MPa H₂, 6 h;

^b Reaction conditions: 25 mL H₂O, 0.82 mmol 4-ethylphenol, 0.20 g Pd/ γ -Al₂O₃, 2 MPa H₂, 12 h, 60 °C.

The effect of reaction time on the aqueous-phase hydrogenation of 4-ethylphenol over 5 wt. % Pd/ γ -Al₂O₃ is illustrated in Figure S2. In a short reaction time of 2 h, only about 53.7% of 4-ethylphenol was converted to 4-ethylcyclohexanone and 4-ethylcyclohexanol with selectivities of 84.9% and 15.1%, respectively. When the reaction time was 6 h, the conversion of 4-ethylphenol significantly increased to 100%. By further prolonging the reaction time from 6 to 14 h, the selectivity to 4-ethylcyclohexanol was gradually increased, while the selectivity to 4-ethylcyclohexanone decreased significantly. This indicates that prolonging reaction time could facilitate the conversion of 4-ethylphenol and promote the selectivity to 4-ethylcyclohexanol. When the reaction time was 12 h, 4-ethylphenol was converted completely to 4-ethylcyclohexanol with a selectivity of 98.3%.

2.2.2. Effect of Pd Loading on the Hydrogenation of 4-Ethylphenol

To investigate the effect of Pd loading on γ -Al₂O₃, a series of reactions were conducted in the presence of Pd/ γ -Al₂O₃ with different Pd loadings (see Figure 4). When a bare γ -Al₂O₃ catalyst (0 wt. % Pd/ γ -Al₂O₃) was used, 4-ethylphenol was almost unconverted. The conversion of 4-ethylphenol was significantly enhanced with Pd loading increasing from 0 to 3 wt. %. A conversion of 100% was obtained over 3 wt. % Pd/ γ -Al₂O₃ for 12 h at 60 °C. This implied that Pd/ γ -Al₂O₃ was an effective catalyst for 4-ethylphenol hydrogenation. In addition, different Pd loadings on γ -Al₂O₃ significantly influence the selectivity to hydrogenation products of 4-ethylphenol. With increasing Pd loading, the selectivity to 4-ethylcyclohexanone gradually decreased, while the selectivity to 4-ethylcyclohexanol greatly increased. A selectivity of 99% to 4-ethylcyclohexanol was achieved when 3 wt. % Pd/ γ -Al₂O₃ was used. When 5 wt. % Pd/ γ -Al₂O₃ was employed, the conversion of 4-ethylphenol remained at 100%. All the carbon balances remained at 100% when Pd loading increased from 1 to 5 wt. % (see Table 2). Based on the result of the XRD, it was found that higher Pd loading led to a larger particle of catalyst, which further resulted in better catalytic activity for the production of 4-ethylcyclohexanol.

This result is similar to that in the literature. [34] Thus, the selective hydrogenation of 4-ethylphenol was achievable over a 3 wt. % Pd/ γ -Al₂O₃ catalyst with a conversion of 100% and a selectivity of 99%. Compared to a commercial Pd catalyst such as Pd/C in the literature [29], 3 wt. % Pd/ γ -Al₂O₃ showed better catalytic activity for phenol hydrogenation to cyclohexanol under mild conditions in an aqueous solution.

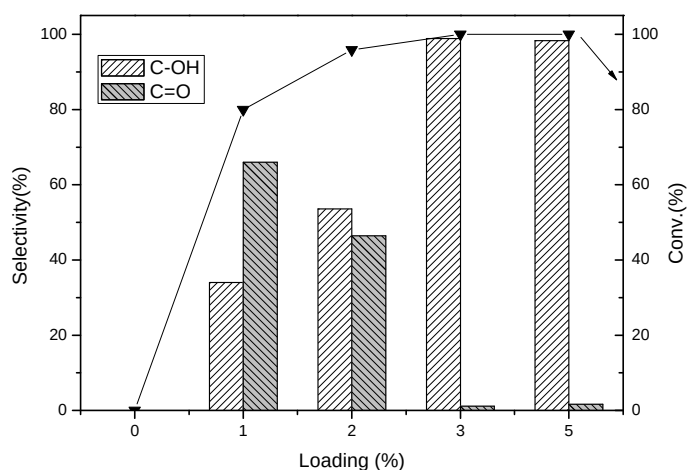
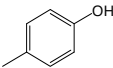
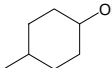
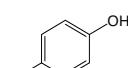
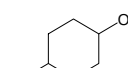
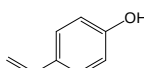
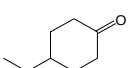
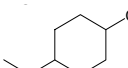
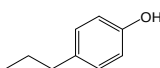
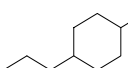
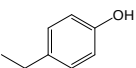
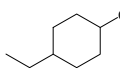
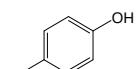
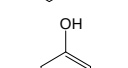
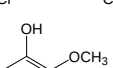
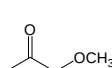
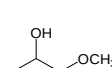


Figure 4. Effect of Pd loading on the hydrogenation of 4-ethylphenol. Reaction conditions: 25 mL H₂O, 0.82 mmol 4-ethylphenol, 0.20g Pd/ γ -Al₂O₃, 2 MPa H₂, 12 h, 60 °C.

2.3. Hydrogenation of Other Substituted Phenols

The aqueous phase hydrogenation of phenols with different substituent groups was performed over a 3 wt. % Pd/ γ -Al₂O₃ catalyst. Under the optimized conditions (60 °C, 2 MPa H₂, 12 h), a range of bio-derived phenols with electron-donating groups such as -CH₃, CH₃CH₂, -(CH₂)₂CH₃ and -CH(CH₃)₂ were selectively hydrogenated into cyclohexanols with both high conversion of substituted phenols and high selectivity to products (see Table 3). Unexpectedly, the chosen chlorophenols exhibited full conversion under this reaction condition. The products of chlorophenol hydrogenation were cyclohexanone and cyclohexanol with different selectivities depending on both the different substituted position of -Cl and the number of -Cl. This result indicated that dechlorination occurred in the reaction process. According to the reports [35,36], it was found that the -Cl was very difficult to remove from a benzene ring of chlorophenol. Therefore, this work might provide a possible pathway to remove the -Cl of chlorophenol in the treatment of chlorophenols as pollutants [35]. However, guaiacol showed a much lower conversion, which might have been caused by one of the following. On the one hand, the methoxy group displayed electrophilic property when it was connected with a benzene ring in an elimination or addition reaction, and thus could have decreased the electron density of the benzene ring and made the ring more stable. On the other hand, a probable mechanism for the hydrogenation of phenols on Pd-based catalysts indicated that phenols were adsorbed and activated on the support [37], while H₂ was activated on the Pd and induced the hydrogenation of adsorbed phenols. If the adsorption of phenols occurred through the hydroxyl, the methoxy group in ortho-position may have increased steric hindrance of the reaction such that guaiacol had more trouble being hydrogenated than the other phenols did [19,37].

Table 3. The catalytic efficiency of the catalysts on the hydrogenation of different lignin-derived monophenols ^a.

Entry	Reactant	Conversion (%)	Products			
			Selectivity (%)		Selectivity (%)	
1		100	-	-		100
2		100	-	-		100
3		100	-	-		100
4		100	-	-		100
5		100		9.8		90.2
6		100	-	-		100
7		92.9	-	-		100
8		100		21.7		78.3
9		100		80.3		19.7
10		100		65.7		34.4
11		56.9		58.4		41.6

^a Reaction conditions: reactant (0.82 mmol), H₂O (25 mL), 3 wt. % Pd/γ-Al₂O₃ (0.200 g, 0.056 mmol Pd), 60 °C, 2 MPa H₂, 12 h, reaction mixture stirred at 500 rpm.

2.4. The Probable Reaction Pathway of 4-Ethylphenol Hydrogenation

To study the probable reaction pathway of 4-ethylphenol hydrogenation, a series of kinetic experiments were conducted over 3 wt. % Pd/γ-Al₂O₃ (see Figure 5). The conversion of 4-ethylphenol gradually increased with prolonging reaction time, and 4-ethylphenol was almost converted when the reaction was performed for 10 h. After 12 h, the conversion of 4-ethylphenol reached up to 100%. At the initial stage of the reaction, the predominant products were 4-ethylcyclohexanone, and the detected 4-ethylcyclohexanol was very limited. With prolonging the reaction time, the amount of 4-ethylcyclohexanone was gradually reduced before 6 h, and afterward sharply decreased. On the contrary, the amount of 4-ethylcyclohexanol gradually increased before 6 h, and afterward sharply improved. Nearly all of the 4-ethylphenol was converted to 4-ethylcyclohexanol after 12 h. This result suggested that 4-ethylphenol was firstly hydrogenated to 4-ethylcyclohexanone as an intermediate, and then 4-ethylcyclohexanone was further hydrogenated to produce 4-ethylcyclohexanol. Some prior research indicates that the hydrogenation of phenols proceeded mainly in a sequential manner [13,32].

The benzene ring of phenols was partially hydrogenated to an enol in the first step, which was unstable and isomerizes rapidly to form cyclohexanone; and cyclohexanone can be converted into cyclohexanol in a further hydrogenation process [32]. Thus, it was inferred that 4-ethylphenol was hydrogenated to an enol and rapidly isomerized to form 4-ethylcyclohexanone in the first step, and 4-ethylcyclohexanone was further hydrogenated into 4-ethylcyclohexanol in a subsequent process.

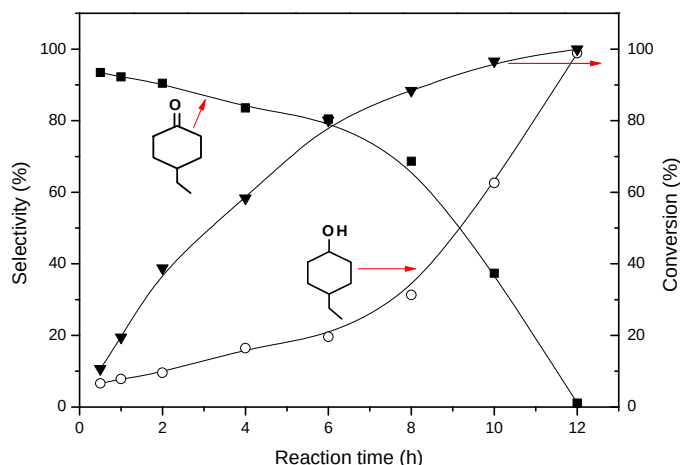
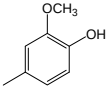
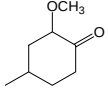
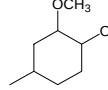
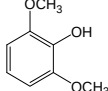
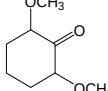
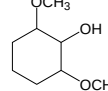
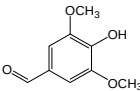
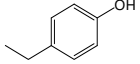
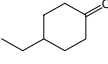
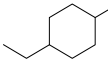


Figure 5. Effect of reaction time on the conversion of 4-ethylphenol and selectivity to products. Reaction conditions: reactant (0.82 mmol), H₂O (25 mL), 3 wt. % Pd/ γ -Al₂O₃ (0.200 g/0.056 mmol Pd), 60 °C, 2 MPa H₂.

2.5. The Hydrogenation of Phenols Directly from Raw Biomass on Pd/ γ -Al₂O₃

Given the good activity of the Pd/ γ -Al₂O₃ catalyst for the hydrogenation of phenols, the catalyst was also applied to the hydrogenation of monophenols directly derived from the raw biomass system. In our previous work [38], a liquid mixture with lignin-derived phenols was obtained from the selective degradation of lignin in pubescens via a two-step process in an ethanol solvent, and 4-ethylphenol was the primary monophenols identified. So we chose the liquid mixture as our reaction substrate for the hydrogenation of monophenols in the raw biomass system. 4-ethylcyclohexanone and 4-ethylcyclohexanol as the hydrogenation products of 4-ethylphenol were detected, and the amount of 4-ethylcyclohexanol was three times that of 4-ethylcyclohexanone. This indicated that 4-ethylphenol in a liquid mixture derived from raw biomass was able to be hydrogenated under this catalytic system. In addition, some other monophenols such as guaiacol, 4-methyl guaiacol, 2,6-dimethoxyphenol and syringaldehyde was also able to be partly hydrogenated (see Table 4). Therefore, we deem that the catalyst exhibits a good activity for the hydrogenation of phenols directly derived from a raw biomass system. Moreover, it was unexpected that the yield of 4-ethylphenol after hydrogenation treatment would greatly increase, though its hydrogenation products were definitely detected. According to our previous investigations [38], it was found that many lignin oligomers existed in the liquid mixture, since the yield of identified monophenols was less than 10%. Therefore, we speculate that the Pd/ γ -Al₂O₃ catalyst is favorable for the depolymerization of lignin oligomers for producing monophenols, especially 4-ethylphenol under very mild conditions. It is known that fairly high temperatures are usually required for the depolymerization of lignin to monophenols. Thus, this catalytic system might provide a promising approach to yield monophenols directly from lignin under milder conditions in an aqueous solution instead of the conventional severe reaction conditions in an organic solvent.

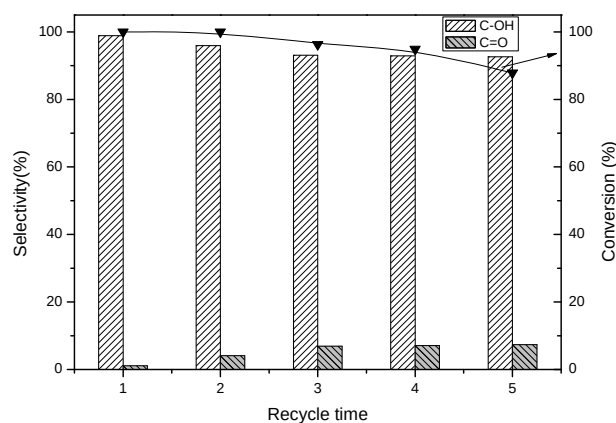
Table 4. The yield of monophenols before and after the catalytic hydrogenation of lignin-derived liquid mixture.

Entry	Monophenols	Yield (mg)		Hydrogenation Products (mg)			
		Before ^a	After ^b				
1		3.4	1.5		1.2		0.7
2		3.8	2.7		- ^c		- ^c
3		4.4	3.7		- ^c		- ^c
4		25.9	3.4	- ^c	- ^c	- ^c	- ^c
5		27.9	49.2		2.5		12.1

^a The yield of the monophenols from lignin-derived liquid mixture in our previous work [38]; ^b the yield of monophenols by the hydrogenation of the lignin-derived liquid mixture obtained in our previous work [38]; reactant (0.45 mmol), H₂O (25 mL), 3 wt. % Pd/ γ -Al₂O₃ (0.200 g, 0.056 mmol Pd), 60 °C, 2 MPa H₂, 12 h; reaction mixture stirred at 500 rpm; ^c the hydrogenation products were detected in GC-MS, but not quantified by GC due to the lack of standard substances.

2.6. Recyclability of the Catalyst

After reaction, the catalyst was separated by filtration from the liquid products, and then dried at 100 °C. After that, the catalyst was calcined in a muffle furnace at 500 °C for 4 h. Prior to the next reaction, the catalyst was pre-reduced with H₂ at 450 °C for 2 h. As shown in Figure 6, the catalyst continued to have high activity after three runs. Both the conversion of 4-ethylphenol and the selectivity to 4-ethylcyclohexanol had no significant decrease compared to the fresh catalyst. However, there was some loss in activity after the fourth and fifth cycles. In order to investigate the reason of the activity loss, the catalyst after the fifth cycle was analyzed by ICP and XRD (see Figure S3). The results indicated that the Pd loading of the catalyst decreased from 3.05 to 2.47 wt. % after five cycles, while the average particle size remained unchanged. This implied that the activity loss of the catalyst was mainly ascribed to the loss of Pd in the recycle process.

**Figure 6.** Recycle of the catalyst. Reaction conditions: reactant (0.82 mmol), H₂O (25 mL), 3 wt. % Pd/ γ -Al₂O₃ (0.200 g/0.056 mmol Pd), 60 °C, 2 MPa H₂.

3. Experimental Section

3.1. Materials

The pubescens sample (80 meshes, Huzhou, China) was washed three times with distilled water and dried at 110 °C in an oven before use. The materials for catalyst preparation (γ -Al₂O₃, Shanxi Taiyuan Daily Chemicals Factory, Taiyuan, China; PdCl₂, Sino-Platinum Metals Co., Kunming, China) were purchased commercially. Other chemicals such as 4-ethylphenol, *p*-cresol, *p*-*n*-propylphenol, *p*-isopropylphenol, *p*-vinylphenol were purchased from J&K SCIENTIFIC LTD (>99%, Beijing, China). Guaiacol was obtained from the Sheshan Chemical Factory (99%, Shanghai, China). Phenol, catechol, hydroquinol, *o*-chlorophenol, *p*-chlorophenol, 2,4-dichlorophenol and ethanol as a solvent were purchased from Chengdu Changlian Chemical Regent Co., LTD (>99%, Chengdu, China). All the materials were used directly from commercial resources without further purification.

3.2. Methods

3.2.1. Catalyst Preparation

Pd/ γ -Al₂O₃ catalysts were prepared using PdCl₂ as a metal precursor, employing the wetness impregnation method. Before use, γ -Al₂O₃ was calcined at 350 °C for 4 h. Typically, a desired amount of an aqueous solution of PdCl₂ was dropped on γ -Al₂O₃ support and ultrasonically dispersed for 1 h, and the slurry was then left for 24 h at room temperature. After removing the excess H₂O in a water bath at 80 °C, the resulting solid was dried overnight at 100 °C, and was then calcined in muffle furnace at 500 °C for 4 h. Before reaction, the obtained catalyst was pre-reduced by H₂ at 450 °C for 2 h.

3.2.2. Catalyst Characterization

N₂ adsorption-desorption isotherms were measured by static N₂ physisorption with a Micromeritics Tristar 3020 analyzer (Micromeritics, Atlanta, GA, USA). Before measurement, the samples were degassed at 100 °C for 2 h and then evacuated at 300 °C for 4 h to remove the physically adsorbed impurities under vacuum. The surface area of these samples was calculated using the Brunauer-Emmett-Teller (BET) method. The total pore volume resulted from the adsorbed N₂ volume at a relative pressure of approximately 0.99. The average pore diameters and the pore size distribution were determined by the Barrett-Joyner-Halenda (BJH) method.

X-Ray Diffraction (XRD) measurements of the samples were performed with a DANDONG FANGYUAN DX-1000 diffraction instrument (Dandong Fangyuan Instrument Co., Ltd., Jinan, China) using Cu-K α radiation ($\lambda = 0.15406$ Å) with a scanning angle (2θ) from 10° to 80°. The tube voltage was 40 kV and the current was 25 mA.

X-Ray photoelectron spectroscopy (XPS) was carried out using an AXIS Ultra DLD (KRATOS) spectrometer (Shimadzu, Kyoto, Japan) Al-K α radiation. The energy scale was internally calibrated by setting the C_{1s} peak at 284.8 eV. The samples were powdered and flaked into sheet, and kept in a vacuum drier before measurement.

Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was used to analyze the actual Pd loading of the samples using Thermo Elemental IRIS Advantage ER/S spectrometer (Thermo Elemental, MA, USA). The pump rate was 110 rpm (2.035 mL min⁻¹), and the nebulizer pressure (PSI) was 27 with a low auxiliary gas rate. 0.05 g sample was dissolved in aqua regia and diluted with water to 100 mL before ICP-AES measurement.

3.2.3. Hydrogenation Reactions of Phenols

The hydrogenation of phenols was carried out in a 60 mL stainless steel autoclave reactor equipped with a magnetic stirrer. In a typical run, 0.82 mmol 4-ethylphenol and 0.20 g Pd/ γ -Al₂O₃ were placed in the reactor with 25 mL high purity water. Air in the reactor was blown out with nitrogen three times, and the inner nitrogen was then replaced with hydrogen. The initial pressure of hydrogen was

added to 2.0 MPa. The reactor was heated from room temperature to the designated temperature with continuous stirring at 500 rpm, and then kept in the designated temperature for a different time. The reactor was cooled down to room temperature naturally after reaction. The mixture in the autoclave was collected by simply pouring it out, and the reactor was washed with high-purity water three times. After filtration, the filtrate was extracted with ethyl acetate three times. The organic phase was analyzed by Fuli 9750 Gas Chromatography (GC) (Fuli, Taizhou, China) equipped with Flame Ionization Detector (FID) and a HP-innowax column (30 m × 0.25 mm × 0.25 μm) using benzyl alcohol as an internal standard. The temperature of both the detector and injector were 280 °C. The oven was heated from 50 °C to 250 °C at a rate of 5 °C/min, and then held at 250 °C for 10 min. Each sample was tested three times to confirm the reproducibility of reported results. The error of the each result was less than 3%. The molar yield and selectivity of the hydrogenation product were calculated with the following equations:

$$\text{Yield (mol\%)} = \frac{\text{Mole of product}}{\text{Mole of reaction material}}$$

$$\text{Selectivity (\%)} = \frac{\text{Mole of product}}{\text{Mole of converted material}}$$

4. Conclusions

In conclusion, 3 wt. % Pd/γ-Al₂O₃ showed remarkable catalytic activity for the selective hydrogenation of 4-ethylphenol to cyclohexanols under mild conditions in an aqueous phase. The conversion of 4-ethylphenol reached up to 100%, and all of the 4-ethylphenol was converted to 4-ethylcyclohexanol and 4-ethylcyclohexanone with a carbon balance of 100%. High selectivity to 4-ethylcyclohexanol (98.9%) was achieved at 60 °C for 12 h. Additionally, the –Cl of chlorophenols were removable during the hydrotreatment process, which might provide a possible pathway to reduce the pollution of chlorophenols. Meanwhile, the Pd catalyst is also applicable to the hydrogenation of other monophenols in raw biomass systems, and exhibits good activity and selectivity. Kinetic experiments indicated that 4-ethylphenol hydrogenation passed through the formation of 4-ethylcyclohexanone as an intermediate, and then further hydrogenated into 4-ethylcyclohexanol. The 3 wt. % Pd/γ-Al₂O₃ catalyst showed good water resistance and stability after recycling four times. Due to the milder reaction temperature and green water as solvent, this result might provide a low-cost, green, and promising approach to selectively producing cyclohexanol directly from raw biomass material.

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