Transfer Hydrogenation of 4-Propylphenol Using Ethanol and Water over Charcoal-supported Palladium Catalyst

Yoshiyuki Nagasawa,¹ Hidetaka Nanao,¹ Osamu Sato,² Aritomo Yamaguchi,^{2,3} and Masayuki Shirai^{*1,2}

¹Department of Chemistry and Bioengineering, Faculty of Engineering, Iwate University, 4-3-5 Ueda, Morioka, Iwate 020-8551

²Research Institute for Chemical Process Technology, National Institute of Advanced Industrial Science and Technology (AIST),

4-2-1 Nigatake, Miyagino, Sendai, Miyagi 983-8551 ³JST, PRESTO, 4-2-1 Nigatake, Miyagino, Sendai, Miyagi 983-8551

(E-mail: mshirai@iwate-u.ac.jp)

The aromatic hydrogenation of 4-propylphenol to 4propylcyclohexanone, *cis*- and *trans*-4-propylcyclohexanols proceeded over a charcoal-supported palladium catalyst (Pd/C) in water–ethanol cosolvent at 573 K without using any external hydrogen gas. The ring hydrogenation activities in water– ethanol cosolvent over Pd/C were higher than those with a conventional method using externally supplied hydrogen gas. Both water and ethanol were indispensable for the ring hydrogenation in the water–ethanol cosolvent at 573 K.

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Many important chemicals are produced from petroleum, which is a finite resource. For the sustainable production of chemicals, it is inevitable to utilize renewable resources like biomass (mainly lignocellulose). Valuable chemicals can be obtained by partial decomposition, dehydration and/or hydrogenation of lignocellulose, which is a polymer containing functional group with several oxygen atoms. The research on catalytic conversion of lignocellulose to chemicals is being pursued extensively over last two decades.¹⁻¹⁰ Here, we report the development of synthetic strategies to obtain high-valueadded chemicals from lignocellulose by reacting two or more biomass-derived compounds with each other. As an example, hydrogenation of lignin-derived alkylphenols with cellulosederived bioethanol to produce alkylcyclohexanone and alkylcyclohexanols will be demonstrated in this communication. Liquid-phase hydrogenation of alkylphenols to the corresponding alkylcyclohexanone and alkylcyclohexanols, which are useful intermediates for fragrance and perfume, is well reported over supported rhodium catalysts under high pressure of external hydrogen gas.¹¹⁻¹⁴ However hydrogen gas is highly explosive and inflammable; thus, use of external hydrogen gas poses a serious problem of its safe handling and it becomes a major cost center in the whole process economics. This can be overcome using ethanol as a hydrogen donor.^{15,16} So far, there is no report on the ring hydrogenation of aromatic compounds with ethanol and supported metal catalysts, which will be reported in this paper for the first time. This approach will open a new route to convert lignin-derived phenols into valuable chemicals using cellulose-derived ethanol as a hydrogen donor.

Commercially available charcoal-supported 5 wt % palladium (Pd/C), rhodium (Rh/C), platinum (Pt/C), and ruthenium (Ru/C) catalysts, and 4-propylphenol (97%) procured from Wako Pure Chemical Ind. Ltd., Japan, were used in this study without any further pretreatment.¹⁷ Catalytic hydrogenation was conducted in a 316 stainless steel tube reactor having an internal volume of 6.0 cm^{3} .¹⁸ Desired amounts of catalyst, 4-propylphenol, and a mixture of water and ethanol as solvent, were loaded into the reactor. Composition of water-ethanol mixture was varied as 3.0 mL of water (0 ethanol molar fraction), 2.9 mL of water + 0.1 mL of ethanol (0.011), 2.5 + 0.5 (0.057), 2.0 + 0.51.0 (0.13), 1.5 + 1.5 (0.23), 1.0 + 2.0 (0.38), and 0.5 + 2.5(0.60), and 3.0 mL of ethanol (1.0). The reactor was thoroughly purged by argon gas ten times for the removal of any residual air. Then the reactor was submerged in a sand bath (ACRAFT, model AT-1B) and was maintained at 573 K. After a given reaction time, the reactor was taken out from the sand bath and submerged in a water bath for rapid cooling to room temperature. Gaseous products were collected by a syringe through sampling loops attached to a gas chromatograph with a thermal conductivity detector (GC-TCD) (SHIMADZU, model GC-8A). After sampling the gaseous products, the slurry was filtered to remove the catalyst and the clear liquid fraction was recovered with tetrahydrofuran (THF). The products dissolved in THF were analyzed by a gas chromatograph with a flame ionization detector (GC-FID) (SHIMADZU, model GC-14B) and by a gas chromatograph with a mass spectrometer (GC-MS) (Agilent Technologies, model HP-7890) with a DB-WAX capillary column.

Hydrogenation over Pd/C with gaseous hydrogen was carried out as follows. After the removal of residual air in the reactor having 0.10 g of 4-propylphenol, 0.15 g of Pd/C, and 3.0 mL of water, 1.0 and 3.0 MPa of hydrogen gas was introduced into the reactor. Then the reactor was heated in the sand bath at 573 K. After 1 h, the reactor was cooled in a water bath and the gaseous and liquid products were analyzed by GC-TCD and GC-FID, respectively.

No gaseous product was formed and the hydrogenation of 4-propylphenol did not proceed in the absence of any supported metal catalysts in a water-ethanol cosolvent system (2.0 mL of water and 1.0 mL of ethanol (ethanol molar fraction 0.13)) at 573 K. However, various gaseous products were formed over the supported metal catalysts in the water-ethanol cosolvent, indicating that ethanol would be gasified over the supported metal catalysts in water. Among the several catalysts screened in this study, Pt/C was the most active for the hydrogen production in the water-ethanol cosolvent system; however, the hydrogenation of 4-propylphenol did not proceed over Pt/C. On the other hand, a Pd/C catalyst was active for the hydrogenation of 4-propylphenol to give 4-propylcyclohexanone, and cis- and trans-4-propylcyclohexanols under the present reaction conditions. A control experiment without 4-propylphenol showed the formation of hydrogen along with carbon monoxide, carbon dioxide, and hydrocarbons (methane and ethane), indicating that ethanol could be gasified over Pd/C also and hydrogen formed would be responsible for the hydrogenation of 4-propylphenol, which will be discussed later. Compared with the Pt/C and Pd/C catalysts, a large amount of methane was formed among the gaseous products over Ru/C and Rh/C catalysts in the water–ethanol cosolvent system; however, the aromatic hydrogenation did not proceed. Pd/C was the sole active catalyst for the hydrogenation of the aromatic ring of 4-propylphenol in water–ethanol cosolvent without using gaseous hydrogen. The gasification of ethanol proceeded at the lower reaction temperatures; however, the hydrogenation did not proceed over Pd/C in water–ethanol cosolvent at 523 K. Hence, we focused on the hydrogenation behavior of the Pd/C catalyst in water–ethanol cosolvent at 573 K.

Figure 1 shows the effect of ethanol-water molar fraction on the hydrogenation of 4-propylphenol over the Pd/C catalyst at 573 K. Gaseous products were not produced and hydrogenation of 4-propylphenol did not occur over Pd/C in pure water i.e. when ethanol molar fraction was zero; gaseous products were formed by the addition of ethanol. The amount of each gas increased with an increase in ethanol molar fraction, and a greater amount of hydrogen gas could be obtained than the other gases at all the molar fractions of ethanol in water. The maximum amount of hydrogen gas was obtained at 0.60 molar fraction of ethanol (Figure 1a). The yield of ring hydrogenation products increased with an increase in ethanol molar fraction and reached maximum at 0.13 (Figure 1b). Formation of propylbenzene was observed at 0.011 of ethanol molar fraction by the hydro-deoxygenation of 4-propylphenol. Ethylpropylphenol was formed in water-ethanol cosolvent and its yield increased with an increase in ethanol molar fraction, as a result of alkylation of aromatic compounds with ethanol. In spite of the formation of hydrogen along with other gases in ethanol solvent (1.0 molar fraction of ethanol), hydrogenation of 4-propylphenol did not proceed over Pd/C; however, the formation of ethylpropylphenol (determined by GC-MS but unable to ascertain the position of ethyl group) was observed, indicating that alkylation proceeded under supercritical conditions in ethanol over Pd/C. Figure 1 shows that hydrogen was formed from ethanol over Pd/C in water at 573 K and the amount of hydrogen increased with an increase in ethanol molar fraction; however, the



Figure 1. Hydrogenation products of 4-propylphenol over a charcoal-supported palladium catalyst (Pd/C) in water–ethanol cosolvent: (a) Products determined by GC-TCD, (\bigcirc) hydrogen; (\triangle) methane; (\bigtriangledown) carbon dioxide; (\square) carbon monoxide; (\diamondsuit) ethane. (b) Liquid products determined by GC-FID, (\bigcirc) 4-propylcyclohexanone; (\blacklozenge) 4-propylcyclohexanols (*cis* + *trans*); (\blacksquare) propylbenzene; (\blacktriangle) ethylpropylphenol; (\bigcirc) 4-propylcyclohexanone + 4-propylcyclohexanols. Reaction conditions: reaction time, 1.0h; reaction temperature, 573 K; 4-propylphenol, 0.74 mmol; Pd/C, 0.15 g.

hydrogenation product yields were maximized at an intermittent ethanol molar fraction of 0.13. One probable explanation for this observation is that the transferred hydrogen from ethanol was active for the hydrogenation of 4-propylphenol molecules dissolved in the given composition of water-ethanol system. Phase of water-ethanol mixture at 573 K was estimated with a process simulation software (VMG, VMG-Sim) and it showed that two phases (liquid and gas) exist in water-ethanol mixture from 0 to 0.13 of ethanol molar fraction while, a single phase of steam dissolved in supercritical ethanol was formed from 0.23 to 1.0 ethanol fraction at 573 K. We could not determine the solubility of 4-propylphenol in the system; however, the amount of 4-propylphenol molecules dissolved in the liquid phases would be larger and the adsorbed 4-propylphenol molecules react with activated hydrogen atoms on palladium sites. The hydrogenation product yields would increase in the liquid phase up to 0.13 ethanol molar fraction with an increase in the number of activated hydrogen atoms on the palladium sites. On the other hand, the yield decreased beyond 0.23 ethanol molar fraction in a single phase in spite of the fact that larger amount of hydrogen molecules was present. The amount of 4-propylphenol molecules dissolved in the supercritical phase would be lower than those in the liquid phase; hence, lower ring hydrogenation yields were obtained for more than under 0.23 ethanol molar fraction. Further study is necessary on this aspect; however, the water molecules would be involved in the hydrogenation steps (formation of transfer hydrogen atoms and/or adsorption of 4propylphenol molecules) on palladium sites because the product yield decreased with an increase in ethanol molar fraction and it became zero in ethanol solvent.

Table 1 shows the effect of external gaseous hydrogen on the hydrogenation of 4-propylphenol over the Pd/C catalyst in water for 1 h at 573 K under 1.0 and 3.0 MPa pressure. Under 1.0 MPa of hydrogen pressure at 573 K, 4-propylcyclohexanone and 4-propylcyclohexanols were not formed; however, propylbenzene was formed indicating that the hydrogenation of 4propylphenol did not proceed over Pd/C in water solvent under external gaseous hydrogen pressure of 1.0 MPa. Nevertheless, as hydrogen pressure was increased to 3.0 MPa, aromatic hydrogenation proceeded and both 4-propylcyclohexanone and 4propylcyclohexanols were formed in water, although yields of 4-propylcyclohexanone and 4-propylcyclohexanols were onesixth and one-third, respectively, of those in water-ethanol cosolvent system (0.13 ethanol molar fraction), indicating that ethanol addition is more effective for the hydrogenation of the aromatic ring of 4-propylphenol in water than the external hydrogen gas under high-pressure conditions. The hydrogen atoms generated from ethanol and activated on palladium sites, would be more active than the adsorbed hydrogen atoms from gas phase under high-pressure conditions.

Table 2 shows the results of hydrogenation of 4-propylphenol over the Pd/C catalyst in water-methanol and water-2-propanol cosolvents. The gaseous yields in water-methanol cosolvent were higher than those in water-ethanol cosolvent; however, the gaseous product distribution and hydrogenation of 4-propylphenol behavior were similar in water-methanol and water-ethanol cosolvent systems.

Gaseous products were formed by the addition of methanol. The amount of each gas increased with an increase in methanol molar fraction, and showed maximum yields of hydrogen,

Table 1.	Hydrogenation	products of	4-propylphenol	over Pd/C in	water + hydrogen	gas ^a and in	water-ethanol c	cosolvent
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Salvente	Amounts/mmol							
Solvents	Hydrogen	4-Propylphenol	4-Propylcyclohexanone	4-Propylcyclohexanols	Propylbenzene	Ethylpropylphenol		
Water $+ 1.0$ MPa H ₂	0.83	0.61	0.0	0.0	0.012	0.0		
Water $+ 3.0 \text{ MPa H}_2$	3.3	0.56	0.032	0.014	0.041	0.0		
Water-Ethanol ^b	0.85	0.34	0.18	0.045	0.0	0.015		

^aReaction conditions: reaction time, 1 h; reaction temperature, 573 K; 4-propylphenol, 0.74 mmol; Pd/C, 0.150 g; water 3.0 mL. ^bWater and ethanol cosolvent (water (2.0 mL) + ethanol (1.0 mL), ethanol molar fractions 0.13).

	Alcohol molar fraction	Gaseous products/mmol					Liquid products/mmol			
Alcohol		Hydrogen	Carbon monoxide	Methane	Carbon dioxide	Ethane	4-Propylcyclohexanone	4-Propylcyclohexanols	Alkylpropylphenol	
Methanol	0.10	0.79	0.13	0.018	0.47	0	0.19	0.068	0	
	0.48	2.35	0.67	0.10	0.75	0	0.038	0	0	
	1.0	3.6	2.1	0.28	0.67	0	0	0	0.044 ^b	
2-Propanol	0.11	0.16	0.20	0.045	0.11	0	0.13	0.077	0	
	0.34	0.56	0.17	0.019	0.083	0	0.25	0.27	0	
	1.0	1.2	0.55	0.086	0.080	0	0.073	0.32	0	

Table 2. Hydrogenation products of 4-propylphenol over Pd/C in water-alcohol cosolvent

^aReaction conditions: reaction time, 1 h; reaction temperature, 573 K; 4-propylphenol, 0.74 mmol; Pd/C, 0.15 g. ^bMethylpropylphenol.

carbon monoxide, and methane. The hydrogenation of the aromatic ring of 4-propylphenol to 4-propylcyclohexanone and 4-propylcyclohexanols proceeded in methanol-water cosolvent. The yield of ring hydrogenation products was maximized at 0.10 methanol molar fraction. Propylbenzene was not formed in the water-methanol system. A small amount of methylpropylphenol was formed in water-methanol cosolvent and its yield increased with increasing methanol molar ratio; however, the yields were lower than ethylpropylphenol yields in water-ethanol cosolvent system.

The ring hydrogenation yields in water-2-propanol cosolvent were higher than those in water-ethanol cosolvent. The hydrogenation yields increased with an increase in 2-propanol molar fraction and aromatic ring hydrogenation of 4-propylphenol also proceeded in 2-propanol (1.0 of 2-propanol molar fraction). Catalytic transfer hydrogenation of p-cresol to 4methylcyclohexanol and 4-methylcyclohexanone proceeds over Pt/C and Pd/C in 2-propanol solvent by the dehydrogenation of 2-propanol to acetone.¹⁹ We also confirmed that acetone was detected among the products in the water-2-propanol cosolvent system. It is noteworthy that the yield of ring hydrogenation (4-propylcyclohexanone, cis- and trans-4-propylcyclohexanols) was obtained at 0.34 molar fraction of 2-propanol, which was higher than that in pure 2-propanol, indicating that water molecules enhanced the yield for transfer hydrogenation with secondary alcohol in high-temperature conditions.

The hydrogenation of aromatic ring of 4-propylphenol to 4-propylcyclohexanone and 4-propylcyclohexanols proceeded over a charcoal-supported palladium catalyst (Pd/C) in water– ethanol mixed solvent without using external hydrogen gas. The hydrogenation product yields in the water–ethanol cosolvent system with an optimum ethanol fraction of 0.13 were higher than that obtained under 3.0 MPa of external hydrogen pressure in water alone over Pd/C at 573 K. Hydrogen derived from ethanol was active for the hydrogenation of aromatic ring of 4-propylphenol over Pd/C in water. Both water and ethanol are indispensable for the ring hydrogenation of 4-propylphenol in water–ethanol cosolvent at 573 K.

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