Hydrogenation of 4-propylphenol over carbon supported metal catalyst in aqueous ethanol solution

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Abstract: The ring hydrogenation of 4-propylphenol to 4-propylcyclohexanone, *cis*- and *trans*-4-propylcyclohexanols proceeded over a carbon supported palladium catalyst in aqueous ethanol solution at 573 K without using any external hydrogen gas. Hydrogen gas was formed over the carbon supported palladium catalyst in ethanol; however, the ring hydrogenation did not proceed. Both water and ethanol were indispensable for the ring hydrogenation in aqueous ethanol solution at 573 K.

Keywords: Ring hydrogenation, Liquid phase hydrogenation, Palladium catalyst

1. Introduction

The development of value-added chemicals production from lignocellulose, especially, by reacting two or more biomass-derived compounds with each other, is indispensable for sustainable society. The ring hydrogenation of alklyphenols to the corresponding alkylcyclohexanone and alkylcyclohexanols, which are useful intermediates for fragrance and perfume, is an important chemical process. Because hydrogen gas is highly explosive and inflammable, hydrogenation processes without using hydrogen gas is desirable. In this paper, we report the catalytic hydrogenation of 4-propylphenol with aqueous ethanol solution. This approach will open a new way to convert lignin-derived alkylphenols into valuable chemicals using cellulose-derived ethanol as a hydrogen donor.

2. Experimental

Catalytic hydrogenation was studied with a butch reaction system with a 316 stainless steel tube reactor [1]. Gaseous products were analyzed by a gas chromatograph with a thermal conductivity detector. Liquid products were analyzed by a gas chromatograph with a flame ionization detector and by a gas chromatograph with a mass spectrometer.

3. Results and discussion

Various gaseous products (H_2, CO, CO_2, CH_4, and C_2H_6) were formed over the supported metal catalysts in aqueous ethanol solution at 573 K, indicating that ethanol was gasified over supported metal catalysts in water. Among the several catalysts screened, a carbon supported platinum catalyst (Pt/C) was found to be the most active for the hydrogen production in aqueous ethanol solution system; however, the hydrogenation of 4-propylphenol did not proceed over Pt/C. On the other hand, a carbon supported palladium catalyst (Pd/C) was found to be solely active for the hydrogenation of 4-propylphenol to give 4-propylcyclohexanone, *cis*- and *trans*-4-propylcyclohexanols. Figure 1 shows the effect of ethanol-water molar fraction on the hydrogenation of 4-propylphenol over the Pd/C catalyst in aqueous ethanol solution at 573 K. Gaseous products were not produced and the ring hydrogenation did not proceed over Pd/C in pure water. By the addition of ethanol, gaseous products were formed and their amounts increased with increasing ethanol molar fraction. The maximum amount of hydrogen gas was obtained at 0.60 molar fraction of ethanol; however, the yield of ring hydrogenation products reached a maximum at 0.13. Ethylpropylphenol was formed in aqueous ethanol solution and its yield increased with an increase in ethanol molar fraction. In spite of the formation of hydrogen in ethanol solvent (1.0 molar fraction of ethanol), the ring hydrogenation did not proceed over Pd/C; however, the alkylation proceeded under supercritical conditions in ethanol over Pd/C.

We checked the effect of external gaseous hydrogen on the hydrogenation of 4-propylphenol over the Pd/C catalyst in water for 1 h 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 4-propylphenol did not proceed over Pd/C in water solvent under external gaseous hydrogen pressure of 1.0 MPa. The hydrogen atoms generated from ethanol would be more active than the adsorbed hydrogen atoms from gas phase under high-pressure conditions.

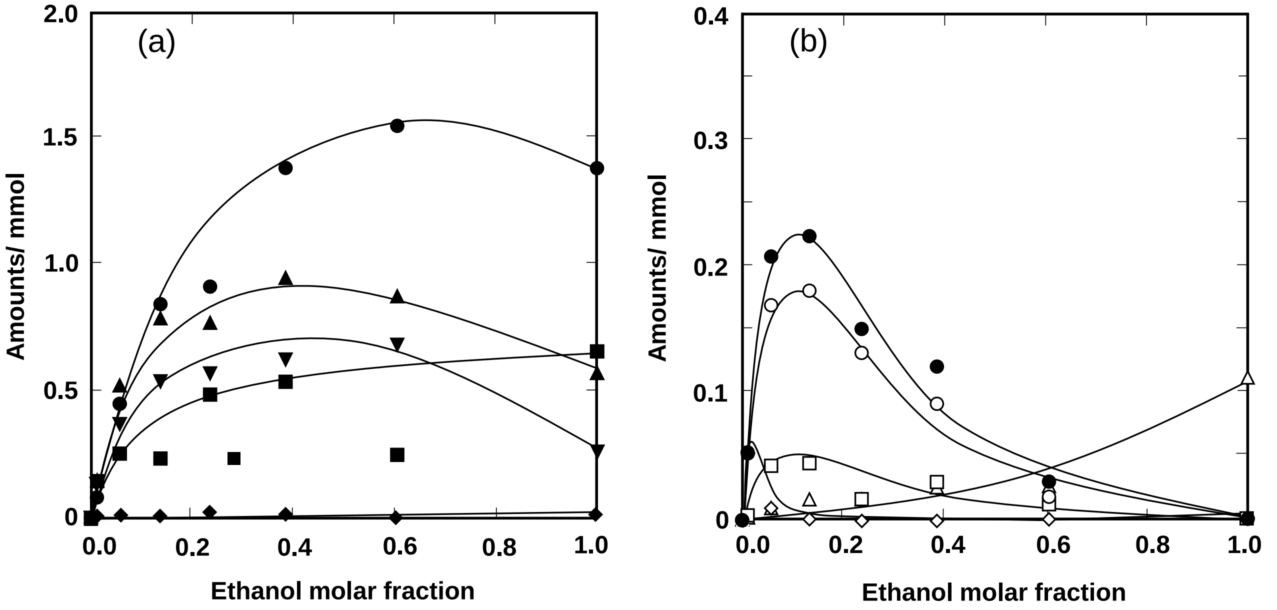

Figure 1. 4-propylphenol hydrogenation over Pd/C. (a) gas products determined by GC-TCD (●) H_2, (▲) CH_4, (■) CO, (▼) CO_2, (◆) C_2H_6. (b) liquid products determined by GC-FID (○) 4-propylcyclohexanone, (□) 4-propylcyclohexanol (cis + trans), (◇) propylbenzene, (△) ethylpropylphenol, (●) 4-propylcyclohexanone + 4-propylcyclohexanols. Reaction conditions: reaction time, 1.0 h; reaction temperature, 573 K; 4-propylphenol, 0.74 mmol; Catalyst, 0.15 g.

4. Conclusions

The hydrogenation of aromatic ring of 4-propylphenol to 4-propylcyclohexanone and 4-propylcyclohexanols proceeded over a carbon supported palladium catalyst in aqueous ethanol solution without using external hydrogen gas. Both water and ethanol are indispensable for the ring hydrogenation of 4-propylphenol in aqueous ethanol solution at 573 K. The ring hydrogenation activities in aqueous ethanol solution over a carbon supported palladium catalyst were higher than those with the system using externally supplied hydrogen gas.

References

1. Y. Nagasawa, H. Nanao, O.Sato, A. Yamaguchi, and M. Shirai, Chem. Lett. 45 (2016) 643.