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Production of monocyclic phenols by the liquid-phase hydrogenolysis of benzofuran and dibenzyl ether using in situ hydrogen production from methanol

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Graphical Abstract



Highlights

- Hydrogenolysis of benzofuran in methanol without gaseous hydrogen was conducted
- Furan moiety of benzofuran was selectively reacted with hydrogen produced in situ
- $Pt/\gamma-Al_2O_3$ exhibited a higher catalytic performance than Pt/ZrO_2 and Pt/TiO_2
- Hydrogen produced in situ was more effective in the reaction than hydrogen gas
- Dibenzyl ether was hydrogenolyzed under the same reaction conditions as benzofuran

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Abstract

We herein report our study into the hydrogenolysis of benzofuran, a model compound for the poorly decomposable compounds derived from lignin, over Pt supported catalysts in methanol in the absence of gaseous hydrogen. In this in situ hydrogenolysis reaction system, it was elucidated that both hydrogen production from methanol and selective hydrogenolysis of the furan moiety proceeded simultaneously to yield monophenolic compounds and gaseous hydrogen. This in situ hydrogenolysis reaction was investigated at temperatures between 180 and 220 °C and with reaction times ranging from 1 to 48 h. We found that the hydrogenolysis reaction was accelerated

with increased hydrogen concentrations in the solvent. The molar ratio of consumed hydrogen to net hydrogen production increased gradually upon increasing the reaction temperature and time. In addition, the in situ hydrogenolysis of benzofuran under a hydrogen gas atmosphere revealed that the hydrogen produced in situ was more effective in the reaction than gaseous hydrogen, likely due to the dissolution and diffusion resistances of the solvent. Furthermore, dibenzyl ether was hydrogenolyzed to give monocyclic aromatic compounds under the same reaction conditions, suggesting that this in situ hydrogenolysis process could be effective in converting the by-products obtained during lignin depolymerization into valuable aromatic compounds.

Keywords: Hydrogenolysis; Benzofuran; Dibenzyl ether; Methanol; Pt/γ -Al₂O₃; Reaction mechanism

1. Introduction

The effective utilization of biomass as a chemical feedstock has attracted increasing attention in recent years. Lignin, which is one of the main components of lignocellulosic biomass, is a biopolymer consisting of various aromatic ethers, irregularly connected by a variety of linkages [1], and hence it is considered an excellent raw material for producing valuable products, such as phenolic compounds. To convert lignin into valuable chemical compounds, both depolymerization and deoxygenation reactions are required. For example, during the depolymerization of lignin through hydrolysis and pyrolysis, monophenolic compounds (e.g., phenylpropanoids) and various by-products containing poorly decomposable moieties such as furan rings, ether bonds, and aliphatic chains, are obtained [2, 3]. These components can then be further converted into aromatic products by hydrogenolysis and hydrogenation reactions.

As illustrated in **Figure 1(a)**, hydrogenolysis reactions are usually performed in solution in the presence of a catalyst under a hydrogen atmosphere. To date, the hydrogenolysis of depolymerized lignin [4, 5] and model compounds for lignin monomers, such as guaiacol [6–8], cresols [9], and phenols [8] have been reported using metal catalysts based on Pt [4, 6–9], Pd [5, 8], and Ru [8]. Such transformations resulted in the formation of demethoxylated compounds, benzene, and cyclohexane derivatives. However, in this system, a high hydrogen pressure (>1 MPa) is generally required to maintain a suitably high hydrogen concentration in the solvent due to the low solubility of hydrogen in typical reaction solvents. As such, the transportation of high-pressure hydrogen from the hydrogen source to the biomass processing plant is necessary for the hydrogenolysis of biomass, which is both dangerous and costly.

To overcome this hydrogen transportation issue, the development of a novel hydrogenolysis reaction system, namely in situ hydrogenolysis, has recently been investigated [10–12]. In this system (see **Figure 1(b)**), the reactant is dissolved in a hydrogen donor solvent, such as an alcohol, in the presence of a catalyst, and the hydrogen produced through decomposition of the hydrogen donor solvent by the

catalyst is used for the hydrogenation step. The use of a hydrogen donor solvent thereby reduces the risks and costs associated with the transportation of high-pressure hydrogen. For example, Nagasawa et al. [10] carried out the hydrogenation of 4propylphenol using a mixture of ethanol and water over a Pd/C catalyst to produce 4propylcyclohexanone and 4-propylcyclohexanol. In addition, Otromke et al. [11] found that removal of the methoxy group from guaiacol proceeded using a supported Pt catalyst in an aqueous methanol solution, while Song et al. [12] used lignin fragments as the reactants for a similar reaction system. They conducted the in situ hydrogenolysis of birch lignin in methanol using a Ni/C catalyst, and found that cleavage of the ether bond and the hydroxyl groups proceeded using hydrogen produced in situ from the reaction solvent. However, the hydrogenolysis of poorly decomposable compounds such as furan moieties and aromatic ethers, which are derived from the depolymerization of complex of lignin with cellulose and hemicellulose, has yet to be performed under such conditions. Moreover, few quantitative studies into the hydrogen produced and consumed in the in situ hydrogenolysis reaction system have reported, despite the minimization of hydrogen consumption being a key advantage of this system compared with gaseous hydrogenbased hydrogenolysis techniques.

Thus, we herein report our investigation into the in situ hydrogenolysis of poorly decomposable compounds using methanol both as a solvent and a hydrogen source in the presence of a metal oxide-supported noble metal catalyst, mainly Pt/γ -Al₂O₃. Benzofuran was selected as a model reactant bearing the furan moiety, as it is derived from the depolymerization of complex of lignin with cellulose and hemicellulose biomass. Quantification of both the gaseous and liquid products will be carried out to allow estimation of the hydrogen efficiency (i.e., the molar ratio of consumed hydrogen to net produced hydrogen) as an index for the reaction. Initially, an effective hydrogenolysis reaction system will be established by comparing different catalyst supports and active metals, and the reaction system will be examined in the absence of the reactant and the noble metal. Subsequently, the effects of reaction temperature

and time on the product yields and the hydrogen efficiency will be investigated. In addition, the potential advantages of this in situ hydrogenolysis process will be examined by comparing its efficiency with a comparable hydrogenolysis reaction under a gaseous hydrogen atmosphere. Finally, we will conduct the in situ hydrogenolysis of dibenzyl ether, a model compound for aliphatic ethers, under the reaction conditions optimized for the in situ hydrogenolysis of benzofuran.

2. Experimental

2.1. Chemicals

All chemicals obtained commercially were used without further purification. The 8 wt% aqueous H₂PtCl₆ solution was purchased from Sigma-Aldrich Japan, γ-Al₂O₃ (99.5 % purity) was purchased from Strem Chemicals Ltd., benzofuran (99 % purity) was obtained from Tokyo Chemical Industry Co., Ltd., Japan, and PdCl₂ (99 % purity), rutile TiO₂ (99 % purity), ZrO₂ (99 % purity), methanol (99.5 % purity), dibenzyl ether (97 % purity), and *m*-xylene (98 % purity) were obtained from Wako Pure Chemical Industries, Ltd., Japan.

2.2. Catalyst preparation

Pt/ γ -Al₂O₃, Pt/ZrO₂, and Pt/TiO₂ catalysts containing 1 wt% Pt were prepared by an incipient wetness impregnation method. More specifically, the diluted H₂PtCl₆ solution (1.9 wt% for Pt/ γ -Al₂O₃; 2.3 wt% for Pt/ZrO₂; and 2.0 wt% for Pt/TiO₂) was added dropwise to the support and mixed for 15 min at room temperature. The wetted support was then dried at 80 °C and 200 kPa using a rotary evaporator, followed by calcination at 500 °C for 2 h. As the same procedure, 2 wt% Pt/ γ -Al₂O₃ and 0.54 wt% Pd/ γ -Al₂O₃ were prepared. 0.54 wt% Pd/ γ -Al₂O₃ had the same mole of metal as 1 wt% Pt/ γ -Al₂O₃. The obtained catalyst was then reduced under a nitrogen stream containing 10 % hydrogen at 350 °C over 1 h prior to analysis and use. The pore volumes and Brunauer-Emmett-Teller (BET) surface areas of the catalysts were determined by N₂ adsorption isotherms at –196 °C using a BESORP-mini High Precision Volumetric Gas Adsorption Apparatus (MicrotracBEL Corp.), while the Pt particle sizes

and active metal surface areas were estimated by pulsed CO chemisorption at 50 °C using a BEL-METAL instrument (MicrotracBEL Corp.). The properties of the prepared catalysts can be found in **Table 1**, where it is apparent that the Pt particles were loaded in high dispersion on the supports and the catalysts loaded on γ -Al₂O₃ exhibits the much larger surface area than those on TiO₂ and ZrO₂. 2 wt%/ γ -Al₂O₃ had twice larger particle size for Pt than 1 wt%/ γ -Al₂O₃, indicating that the Pt particles in 2 wt% Pt/ γ -Al₂O₃ was sintered during the catalyst preparation.

2.3. In situ hydrogenolysis

A 1/2 in stainless-steel batch reactor (8.7 mL volume) was used for the reaction. Typically, the reactant (6.3 mmol), methanol (53 mmol), and the catalyst (0.5 g) were added to the reactor, and any air remaining in the reactor was purged with argon at 25 °C and ambient pressure. The reactor was then placed in an oil bath and heated at the desired reaction temperature (i.e., 180–220 °C). After the desired reaction time (i.e., 1–48 h), the reactor was cooled rapidly in a cold oil bath (20 °C) to terminate the reaction. The gaseous reaction products were collected in a gas bag by purging with N₂, while the liquid products and used catalysts were collected and separated by centrifugation. The gaseous products were analyzed using a gas chromatograph (GC-2014; Shimadzu Co., Ltd.) equipped with a thermal conductivity detector and a Shincarbon ST column (Shinwa Chemical Industries Ltd., Japan). Argon gas was used as an internal standard. The liquid products were quantified using a gas chromatograph (GC-2014, Shimadzu Co. Ltd) equipped with a flame ionization detector and a gas chromatograph coupled to a mass spectrometer (GC-17A with GCMS-QP5050; Shimadzu Co., Ltd.) equipped with a DB-WAX capillary column (Agilent Technologies Japan, Ltd,). *m*-Xylene was employed as an internal standard for the liquid products. The conversions of benzofuran (X_{BZ}) and dibenzyl ether (X_{DBE}) and the yields of the liquid products were calculated based on the quantity of aromatic ring in the reactants put into the reactor. The hydrogen efficiency ($\eta_{\rm H}$) was estimated from the molar ratio of hydrogen consumed during hydrogenolysis and the net hydrogen production. The

quantity of hydrogen consumed during the hydrogenolysis reaction was calculated by assuming that all the liquid products were formed through hydrogenolysis.

3. Results and discussion

3.1. Determination of the reaction mechanism for in situ hydrogenolysis

We initially examined the effect of the catalyst support on the in situ hydrogenolysis reaction, and so the hydrogenolysis of benzofuran was carried out in methanol using 1 wt% Pt/γ-Al₂O₃, Pt/TiO₂, Pt/ZrO₂, 2 wt% Pt/γ-Al₂O₃, or 0.54 wt% Pd/γ-Al₂O₃ at 220 °C over 24 h. The yields of the liquid products and the quantities of gases produced by each catalyst are presented in Figure 2 and Table 2. For all catalysts, the quantities of H₂, CO, CO₂, and CH₄ gas produced were measured, in addition to those of three monophenolic liquid compounds, namely 2,3-dihydrobenzofuran, o-ethylphenol, and phenol. The observation of these products in all systems confirmed that both hydrogen production and hydrogenolysis took place for all catalysts examined. Other liquid products, such as cyclohexane derivatives, were not observed, indicating that the furan moiety was selectively reacted. For the hydrogenolysis of aromatic compounds under high-pressure hydrogen atmosphere, there are some researches reporting that the hydrogenation of aromatic rings into cyclohexane derivatives proceeds [8–10, 13]. We expect that the hydrogenation of aromatic ring did not proceed in our study because of the molar ratio of hydrogen produced to the reactant and the hydrogenolysis reactivity of benzofuran. The hydrogenation of aromatic ring requires the excess molar amount of hydrogen against the aromatic ring, while in our reaction system the quantity of hydrogen was smaller than the quantity of benzofuran, which was unfavorable for the hydrogenation of aromatic ring. In addition, for the hydrogenation of benzofuran at 300–400 °C, the hydrogenation of the furan moiety is followed by the hydrogenation of the aromatic ring or the hydrogenolysis with the cleavage of C–O bond [14, 15]. Because our reaction condition was milder than that reported, the hydrogenation of benzofuran was terminated at the initial step.

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As listed in Table 2, the composition of carbon containing gases was different among the catalysts, indicating that both the active metal and the catalyst support affected the selectivity of gas formation reaction. CO_2 was major carbon-containing gas product, accounting for more than 70 %, for all the catalysts except for Pt/TiO₂. CH₄ and CO_2 could be formed via methanation reaction ($CO + 3H_2 \rightarrow CH_4 + 2H_2O$) and water gas shift reaction ($CO + H_2O \leftrightarrow CO_2 + H_2$). Though C_2H_6 could be formed with the conversion of *o*-ethylphenol into phenol, we could not detect the formation of C_2H_6 gas by the GC. In order to collect the whole gas product, the gas in the reactor was sufficiently purged with N₂. Assumed that the same molar of C_2H_6 was formed with the production of phenol, C_2H_6 accounts for less than 0.01 % including N₂ used for purging for all experiments, which was smaller than the detection limit. Therefore it would be reasonable that the comparable quantity of C_2H_6 with phenol was formed during the reaction while C_2H_6 was not detected.

When comparing 1 wt% Pt/y-Al₂O₃ and 0.54 wt% Pd/y-Al₂O₃ catalysts which had the same metal content on molar basis, $Pt/\gamma-Al_2O_3$ showed higher catalytic activity for both the benzofuran conversion and the hydrogen production than Pd/γ -Al₂O₃, while the higher hydrogen efficiency of 38.2 % was obtained by 0.54 wt% Pd/γ -Al₂O₃. Pt was therefore more effective for this in situ hydrogenolysis reaction system. Among the 1 wt% Pt loaded catalysts, the highest catalytic activities for hydrogen production and in the hydrogenolysis reaction were observed for 1 wt% $Pt/y-Al_2O_3$, where 2.62 mmol of gaseous hydrogen was produced along with a benzofuran conversion of 7.32 %. We expect that this result was due to the smaller Pt particle sizes in 1 wt% Pt/ γ -Al₂O₃ compared to those in the Pt/ZrO₂ and Pt/TiO₂ catalysts. In addition, the hydrogen efficiencies for 1 wt% Pt/ γ -Al₂O₃ and Pt/TiO₂ were calculated to be ~18 %, while that of Pt/ZrO_2 was only 4.2 %. Comparing Pt/γ -Al₂O₃ catalysts with different metal loading, 2 wt% Pt/ γ -Al₂O₃ exhibited the lower conversion of benzofuran at 4.53 % and the smaller hydrogen production at 2.33 mmol than 1 wt% Pt/y-Al₂O₃, while the metal loading was doubled. The lower catalytic activity for 2 wt% Pt/y-Al₂O₃ was mainly due to its large Pt particle size (2.9 nm), which was larger than 1 wt% Pt/ γ -Al₂O₃ (1.4 nm) as

listed in Table 1. This result therefore indicates that the Pt particle size strongly affects both the hydrogen production and the hydrogenolysis reactions. Based on the above results, 1 wt% Pt/γ -Al₂O₃ was employed for all subsequent experiments.

We then moved on to examine the reaction mechanism by comparing three different systems at 220 °C over 24 h: (a) The in-situ hydrogenolysis of benzofuran over Pt/y-Al₂O₃ in methanol; (b) the decomposition of methanol over $Pt/y-Al_2O_3$ in the absence of benzofuran; and (c) the reaction of benzofuran over the y-Al₂O₃ support in methanol in the absence of Pt. Figure 3 shows the yields of liquid products and the quantities of hydrogen produced for these three reaction systems. As expected, gaseous hydrogen, 2,3-dihydrobenzofuran, o-ethylphenol, and phenol were obtained for the in situ hydrogenolysis reaction system (a). For the methanol decomposition reaction system (b), the same gaseous products detected for the in situ hydrogenolysis reaction system were also observed. In this case, 3.40 mmol of hydrogen was produced, which is slightly larger than that of the in situ hydrogenolysis reaction system. More specifically, when the amount of hydrogen consumed during hydrogenolysis was considered, the net amount of hydrogen produced in the in situ hydrogenolysis reaction system was ~3.22 mmol. It therefore appears that benzofuran did not inhibit the decomposition of methanol to produce hydrogen. Furthermore, as shown in Fig. 3, no reaction was observed in reaction system (c), indicating that the Pt catalyst is required to produce hydrogen from methanol, which is subsequently consumed in the hydrogenolysis reaction. These results therefore indicate that the in situ hydrogenolysis reaction proceeded through the decomposition of methanol over the Pt catalyst to produce hydrogen, followed by adsorption of the furan moiety of benzofuran onto the γ -Al₂O₃ support and subsequent hydrogenation with the produced hydrogen to yield 2,3dihydrobenzofuran, o-ethylphenol, and phenol.

3.2. Optimization of the reaction conditions for the in situ hydrogenolysis of benzofuran

To determine the optimal reaction conditions for the in situ hydrogenolysis reaction of benzofuran and examine the reaction mechanism in further detail, the reaction was

carried out in methanol over a Pt/γ -Al₂O₃ catalyst at various temperatures and over a range of reaction times.

Figure 4 shows the yields of liquid products and the quantities of hydrogen produced under these conditions over 24 h at 180, 200, and 220 °C. As shown, upon increasing the reaction temperature, the conversions of both benzofuran and methanol increased. The hydrogen efficiency was apparently high at 14.3 % at 180 °C. This would be because both the conversion of benzofuran and the quantity of hydrogen produced were small. While extremely low conversions were observed at 180 °C, the quantity of gaseous hydrogen produced increased remarkably to 2.18 mmol at 200 °C. However, at this temperature, yields of the liquid products remained low, resulting in a poor hydrogen efficiency of 4.8 %. In contrast, at 220 °C, the conversion of benzofuran and the quantity of hydrogen produced respectively increased to 7.32 % and 2.62 mmol and the hydrogen efficiency was improved to 18.6 %. This result suggests that methanol decomposition occurs at lower temperatures than the hydrogenolysis reaction, and so higher temperatures favored both the conversion of benzofuran and the hydrogen efficiency.

We then examined the effect of reaction time on the in situ hydrogenolysis of benzofuran over Pt/γ -Al₂O₃ in methanol at 220 °C, where **Figure 5** and **Table 3** show the different quantities of liquid products and hydrogen produced following reaction times ranging from 1 to 48 h. As indicated, between 1 and 24 h, the quantities of both the liquid products and gaseous hydrogen produced increased gradually, and the hydrogen efficiency remained relatively constant at ~20 %. As the hydrogen efficiency indicates the ratio of the average hydrogenolysis reaction rate to that of hydrogen production, a constant hydrogen efficiency value indicates that the hydrogen production and hydrogenolysis reactions proceeded at a constant ratio of reaction rates. However, upon increasing the reaction time from 24 to 48 h, the quantities of liquid products produced increased despite the quantity of gaseous hydrogen produced remaining relatively constant. As such, the hydrogen efficiency increased from 18.6 to 53.0 % over this time period. Interestingly, after allowing the reaction to

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proceed for 48 h, only 2,3-dihydrobenzofuran, *o*-ethylphenol, and phenol were detected as liquid products. In addition, the relatively constant hydrogen production observed suggests that the quantity of hydrogen consumed during hydrogenolysis over 48 h was comparable to the quantity produced during this period. More specifically, the concentration of hydrogen in the solvent, which correlates positively with the quantity of gaseous hydrogen produced, increased gradually for the first 24 h, and then remained relatively constant over the second 24 h period. Thus, since the hydrogenolysis reaction rate increased gradually during the initial 24 h, it was apparent that this reaction could be accelerated by increasing the hydrogen concentration in the solvent.

To investigate the reaction mechanism taking place, the variation in the molar ratios of the liquid products was examined between 1 and 48 h. More specifically, upon increasing the reaction time from 5 to 48 h, the molar ratio of *o*-ethylphenol to 2,3dihydrobenzofuran increased gradually from 0.27 to 0.41. As the molar ratio of a second to a first intermediate tends to increase for a consecutive reaction, but remain constant for a parallel reaction, the hydrogenolysis of benzofuran can be described as a consecutive reaction. Assuming that the reaction rate equations for the hydrogenation of benzofuran to yield 2,3-dihydrobenzofuran and the hydrogenolysis of 2,3-dihydrobenzofuran to give o-ethylphenol are expressed as first-order against the liquid reactants, which is generally employed to formulate the reaction rate for liquid phase reaction, and have the same reaction order against the hydrogen concentration [15, 16], the ratio of the rate constants was estimated, assuming phenol production to be negligible. Indeed, the molar ratio of phenol to *o*-ethylphenol was small for all reaction times examined, thereby suggesting that the conversion of o-ethylphenol to phenol was minimal. Thus, the rate constant for the hydrogenolysis of 2,3dihydrobenzofuran was calculated to be 2.2 times larger than that for the hydrogenation of benzofuran, indicating that the hydrogenation of benzofuran was slower than the hydrogenolysis of 2,3-dihydrobenzofuran.

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From these results, we proposed the reaction scheme illustrated in **Scheme 1**. As indicated, benzofuran was initially hydrogenated by the hydrogen derived from methanol to yield 2,3-dihydrobenzofuran. Subsequent hydrogenation of 2,3-dihydrobenzofuran accompanied by cleavage of the C-O bond produced *o*-ethylphenol. In addition, small quantities of *o*-ethylphenol were also converted into phenol through cracking of the ethyl group. These reactions can therefore be accelerated by increasing the hydrogen concentration of the solvent. As discussed in Section 3. 1., the concentration of C₂H₆ in the collected gas including the purging gas was significantly small. We therefore considered C₂H₆ could be produced during the conversion of *o*-ethylphenol into phenol and this reaction scheme should be reasonable.

3.3. Comparison of the in situ hydrogenolysis reaction with hydrogenolysis carried out using gaseous hydrogen

To investigate the differences between a hydrogenolysis reaction carried out using hydrogen produced in situ and an equivalent reaction carried out using gaseous hydrogen, the hydrogenolysis of benzofuran was performed over $Pt/\gamma-Al_2O_3$ in methanol at 220 °C for 1 and 5 h under a hydrogen atmosphere. Gaseous hydrogen was introduced into the reactor at room temperature and the initial pressure was set at 0.1 MPa. As the hydrogen partial pressure of the in situ system was estimated as 1.4 MPa after 24 h, the effect of the hydrogen atmosphere became negligible after 24 h under a hydrogen atmosphere at ambient pressure. The yields of the liquid products obtained after hydrogenolysis for 1 and 5 h under the hydrogen atmosphere are shown in Figure 6. Due to the high concentration of hydrogen in the gas collected after the reaction, the gaseous products could not be quantified. However, as expected, hydrogenolysis under a hydrogen atmosphere enhanced the yields of the liquid products, although the yields were increased by only 1.7 times, despite the quantity of hydrogen in the reactor being estimated to be 4.7 times greater for this reaction after 1 h. This result could be explained by the dissolution and diffusion resistances of the solvent towards the transportation of gaseous hydrogen to the catalyst surface. Indeed, the dissolution and diffusion in methanol are essential to

allow the gaseous hydrogen to reach the catalyst surface and take part in the reaction. In contrast, for the in situ system, the hydrogen produced on the catalyst surface takes place in the reaction directly. As such, any advantageous contributions from the gaseous hydrogen were limited, thereby indicating that the hydrogen produced from methanol in situ was more effectively consumed in the hydrogenolysis reaction.

3.4. The in situ hydrogenolysis of aliphatic ether bonds

Finally, to investigate the applicability of our in situ hydrogenolysis reaction system to the conversion of other poorly decomposable compounds, the in situ hydrogenolysis of dibenzyl ether, a model compound containing an aliphatic ether bond, was performed under the optimal reaction conditions determined for the in situ hydrogenolysis of benzofuran. As shown in **Figure 7**, four different monoaromatic compounds were observed as liquid products, namely benzyl methyl ether, benzyl alcohol, toluene, and benzene. No other liquid products were detected. Interestingly, both the conversion and the hydrogen efficiency were larger for dibenzyl ether than for benzofuran, indicating that the aliphatic ether bond was hydrogenolyzed more easily than the furan moiety. In addition, the net quantity of hydrogen produced for the in situ hydrogenolysis of dibenzyl ether was estimated to be 1.86 mmol, which is significantly smaller than the quantities produced in the decomposition of methanol and the in situ hydrogenolysis of benzofuran, as indicated in Fig. 2. This may be due to the bulkier dibenzyl ether being adsorbed onto the catalyst and inhibiting methanol decomposition. In this case, cleavage of the C-O bond and the aliphatic C-C bond appeared to be the dominant reactions. Furthermore, for these reactions, the molar ratios of benzyl ethyl ether to benzene, and of toluene to benzyl ether must be equal to 1. However, the observed molar ratios observed were not equal to 1, thereby suggesting that the side reaction involving dibenzyl ether and methanol proceeded to produce benzyl alcohol and benzyl methyl ether. It therefore appears that this in situ hydrogenolysis reaction system was capable of converting both furan and aliphatic ether moieties simultaneously. Thus, to clearly demonstrate the practical applicability

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of this system, it is necessary to further examine the in situ hydrogenolysis of aromatic ethers and alkyl chains.

4. Conclusion

We herein described our studies into the in situ hydrogenolysis of benzofuran (a model compound for the poorly decomposable compounds derived from complex of lignin with cellulose and hemicellulose) over a noble metal supported catalyst in methanol, which was used as both the reaction solvent and the hydrogen source. Pt showed higher catalytic activity for in situ hydrogenolysis reaction than Pd. Compared to ZrO_2 and TiO_2 supports, Pt supported on γ -Al₂O₃ exhibited the highest catalytic activity in both hydrogen production and hydrogenolysis. 1 wt% Pt/γ -Al₂O₃ having Pt particle size of 1.4 nm showed the higher conversion of benzofuran and the higher hydrogen production than 2 wt% Pt/ γ -Al₂O₃ having Pt particle size of 2.9 nm, indicating that Pt particle size in the catalyst strongly affects the catalytic activity. In this in situ hydrogenolysis reaction system, it was elucidated that the decomposition of methanol to produce hydrogen over the Pt catalyst proceeded simultaneously with the hydrogenolysis of benzofuran. Upon optimization of the reaction conditions, the furan moiety of benzofuran reacted selectively with the hydrogen produced from methanol decomposition to produce 2,3-dihydrobenzofuran, o-ethylphenol, and trace quantities of phenol at 220 °C over 48 h. In addition, these hydrogenolysis reactions proceeded according to a consecutive reaction mechanism. We also found that the reaction could be accelerated by increasing the concentration of hydrogen in the reaction solvent (i.e., methanol), and hence the hydrogen produced in situ was more effective in the hydrogenolysis reaction than a gaseous hydrogen atmosphere. We expect that this was due to likely due to the dissolution and diffusion resistances of the solvent towards hydrogen gas. Furthermore, aliphatic ethers were also converted into monophenolic compounds by the in situ hydrogenolysis reaction under the conditions optimized for furan, thereby suggesting that this process could be effective for the simultaneous conversion of various poorly decomposable compounds obtained during lignin depolymerization into useful chemical products.

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References

[1] E. Dorrestijn, L. J. J. Laarhoven, I. W. C. E. Arends and P. Mulder, J. Anal. Appl. Pyrolysis, 54 (2000) 153–192.

[2] C. Xu, R. A. D. Arancon, J. Labidi and R. Luque, Chem. Soc. Rev., 43 (2014) 7485– 5000.

[3] F. P. Bouxin, A. McVeigh, F. Tran, N. J. Westwood, M. C. Jarvis and S. D. Jackson, Green Chem., 17 (2015) 1235–1242.

[4] A. L. Jongerius, P.C.A. Bruijnincx and B.M., Weckhuysen, Green Chem., 15 (2013)3049–3056.

[5] K. M. Torr, D. J. Pas, E. Cazeils and I. D. Suckling, Bioresour. Technol., 102 (2011)7608–7611.

[6] A. Gutierrez, R. K. Kaila, M. L. Honkela, R. Slioor and A. O. I. Krause, Catal. Today, 147 (2009) 239–246.

[7] T. Nimmanwudipong, R. C. Runnebaum, K. Brodwater, J. Heelan, D. E. Block and B.C. Gates, Energy Fuels, 28 (2014) 1090–1096.

[8] B. Güvenatam, O. Kurşun, E. H. J. Heeres, E. A. Pidko and E. J. M. Hensen, Catal.Today, 233 (2014) 83–91.

[9] H. Wan, R. V. Chaudhari and B. Subramaniam, Top. Catal., 55 (2012) 129–139.

[10] Y. Nagasawa, H. Nanao, O. Sato, A. Yamaguchi and M. Shirai, Chem. Lett., 45 (2016) 643–645.

[11] M. Otromke, L. Theiss, A, Wunsch, A. Susdorf and T. Aicher, Green. Chem., 17(2015) 3621–3631.

[12] Q. Song, F. Wang, J. Cai, Y. Wang, J. Zhang, W. Yu and J. Xu, Energy Environ. Sci., 6(2013) 994–1007.

[13] H. Ohta, H. Kobayashi, K. Hara and A. Fukuoka, Chem. Commun., 47 (2011) 12209–12211.

[14] C. Liu, Z. Shao, Z. Xiao, C. T. Williams and C. Liang, Energy Fuels, 26 (2012) 4205–4211.

[15] M. C. Edelman, M. K. Maholland, R. M. Baldwin and S. W. Cowley, J. Catal., 111(1988) 243–253.

[16] C. L. Lee and D. F. Ollis, J. Catal., 87 (1984) 325–331.

Figure Captions



Figure 1. Schematic representation of the reaction systems for (a) hydrogenolysis with gaseous hydrogen, and (b) in situ hydrogenolysis.



Figure 2. Yields of the liquid products and quantities of hydrogen produced in the in situ hydrogenolysis of benzofuran over the catalysts prepared (benzofuran 6.3 mmol; CH₃OH 53 mmol; catalyst 0.5 g; Ar atmosphere; 220 °C; 24 h).



Figure 3. Yields of the liquid products and quantities of hydrogen produced in (a) the in situ hydrogenolysis of benzofuran (benzofuran 6.3 mmol; CH_3OH 53 mmol; Pt/γ - Al_2O_3 0.5 g), (b) the decomposition of methanol (CH_3OH 53 mmol; Pt/γ - Al_2O_3 0.5 g), and (c) the reaction in the absence of Pt (6benzofuran 6.3 mmol; CH_3OH 53 mmol; γ - Al_2O_3 0.5 g) at 220 °C over 24 h in an Ar atmosphere.



Figure 4. Effect of reaction temperature on the liquid product yields and the quantities of hydrogen produced in the in situ hydrogenolysis of benzofuran (benzofuran 6.3 mmol; CH₃OH 53 mmol; Pt/ γ -Al₂O₃ 0.5 g; Ar atmosphere; 180–220 °C; 24 h).



Figure 5. Effect of reaction time on the quantities of liquid products and hydrogen produced in the in situ hydrogenolysis of benzofuran (benzofuran 6.3 mmol; CH₃OH 53 mmol; Pt/ γ -Al₂O₃ 0.5 g; Ar atmosphere; 220 °C; 1–48 h).



Figure 6. Effect of the gas atmosphere on the liquid product yields in the in situ hydrogenolysis of benzofuran (benzofuran 6.3 mmol; CH_3OH 53 mmol; Pt/γ - Al_2O_3 0.5 g; Ar or H_2 atmosphere; 220 °C; 1 or 5 h).



Figure 7. Yields of the liquid products and quantities of hydrogen produced in the in situ hydrogenolysis of dibenzyl ether (dibenzyl ether 6.3 mmol; CH₃OH 53 mmol; Pt/ γ -Al₂O₃ 0.5 g; Ar atmosphere; 220 °C; 24 h).



Scheme 1. Possible reaction mechanism for the in situ hydrogenolysis of benzofuran over Pt/γ -Al₂O₃ in methanol at 220 °C.









Figr-4









	1 wt%	1 wt%	1 wt%	2 wt%	0.54 wt%
	Pt/TiO ₂	Pt/ZrO ₂	Pt/y-Al ₂ O ₃	Pt/y-Al ₂ O ₃	Pd/y-Al ₂ O ₃
BET surface area $[m^2/g]$	5.5	10.6	118.3	128.0	129.5
Total pore volume [cm ³ /g]	0.012	0.070	0.47	0.42	0.42
Pt metal surface area $[m^2/g]$	0.94	0.94	2.01	1.90	0.81
Pt particle size [nm]	3.0	3.0	1.4	2.9	3.3

Table 1. The properties of the catalysts prepared

	1 wt%	1 wt%	1 wt%	2 wt%	0.54 wt%
	Pt/TiO ₂	Pt/ZrO ₂	Pt/y-Al ₂ O ₃	Pt/y-Al ₂ O ₃	Pd/y-Al ₂ O ₃
CO ₂ [mol%]	33.9	71.4	85.3	75.4	81.0
CO [mol%]	34.2	23.2	5.5	11.2	10.8
CH ₄ [mol%]	31.9	5.2	9.2	13.5	8.3

Table 2. The composition of carbon-containing gases produced during the in situhydrogenolysis of benzofuran at 220 $^{\circ}$ C for 24 h over the prepared catalysts.

Table 3. The change of the conversion of benzofuran and the hydrogen efficiency in reaction time for the in situ hydrogenolysis of benzofuran over $1 \text{ wt\% Pt/}\gamma\text{-Al}_2\text{O}_3$ at 220 °C.

	1 h	5 h	10 h	24 h	48 h
Conversion of benzofuran, X _{BZ} [mol%]	0.12	0.77	1.75	7.32	31.1
Hydrogen efficiency, $\eta_{\rm H}$ [mol%]	23.4	13.5	22.5	18.6	52.8