

Hydrogenolysis of benzofuran over Pt/Al₂O₃ in methanol used as solvent and hydrogen source

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Lignin is regarded as a raw material for valuable aromatic compounds. To obtain these chemicals at a high yield, not only the depolymerization of lignin but also the hydrogenolysis of hardly decomposable compounds produced as by-products during the depolymerization are essential. High-pressure hydrogen atmosphere is required for hydrogenolysis and hence it is difficult to apply this reaction to biomass conversion. Then, a new hydrogenolysis reaction system, "in-situ hydrogenolysis", was proposed [1]. In this reaction system, the reactant is treated in a hydrogen carrier solvent with a catalyst, and it is hydrogenated by the hydrogen produced in-situ by the decomposition of the hydrogen carrier. In this study, we carried the in-situ hydrogenolysis of benzofuran, which is a model compound for the hardly decomposable compounds from lignin, to yield phenols using methanol as hydrogen carrier solvent and Pt/Al₂O₃ as catalyst. The effects of reaction conditions on product yield were examined.

1 wt% Pt/Al₂O₃ catalyst was prepared by an incipient wetness impregnation of γ -Al₂O₃ (Stem Chemicals) with an aqueous solution of H₂PtCl₆ (Aldrich). A 8.7 mL stainless batch reactor was used for the reaction. 0.67 mL of benzofuran (6.3 mmol), 2.5 mL of methanol (53 mmol), and 0.5 g of Pt/Al₂O₃ catalyst were put into the reactor, and the reactor was purged with Ar at ambient temperature and pressure. The reactor was then put into an oil bath preheated at 220 °C. After heated for the predetermined time, the reactor was cooled in a cold oil bath. The gaseous and liquid products were entirely collected and analyzed by gas chromatography (GC-2014, Shimadzu).

The in-situ hydrogenolysis of benzofuran in methanol was performed at 220 °C for 24 h. It

was found that the 7.3 mol-% of benzofuran was converted into 2,3-dihydrobenzofuran, *o*-ethylphenol, and phenol and no other compounds were obtained. This result indicates that the furan moiety of benzofuran was hydrogenated and the desired phenolic compounds were selectively formed. Because no reaction occurred in the absence of catalyst, hydrogenolysis of benzofuran proceeded using hydrogen produced from methanol.

Next, in-situ hydrogenolysis was performed at 220 °C for different reaction times. As shown in **Figure 1**, with the increase of the reaction time, the benzofuran conversion was increased whereas hydrogen efficiency, η_H , which is a ratio of hydrogen used in hydrogenolysis against net production, was almost constant. This result suggests methanol decomposition and the hydrogenolysis reaction occurred in parallel. The reaction scheme is illustrated in **Scheme 1**. Furthermore, the in-situ hydrogenolysis reaction was performed using various catalyst supports or other model compounds containing ether group.

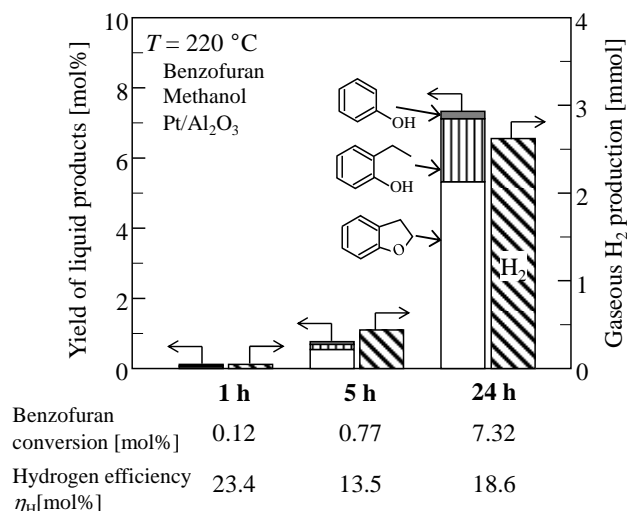
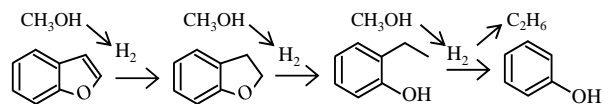


Figure 1 Change in the product yield and the hydrogen efficiency with reaction time of in-situ hydrogenolysis of benzofuran in methanol at 220 °C



Scheme 1 Reaction scheme of in-situ hydrogenolysis of benzofuran in methanol

REFERENCES

- [1] A.L. Jongerius, P.C.A. Bruijninx and B.M. Weckhuysen, *Green Chem.*, 15 (2013) 3049.