

Title	コハク酸の選択的水素化を指向したCuPdバイメタル触媒に関する研究
Author(s)	LE, Dinh Son
Citation	
Issue Date	2021-03
Type	Thesis or Dissertation
Text version	ETD
URL	<a href="http://hdl.handle.net/10119/17486">http://hdl.handle.net/10119/17486</a>
Rights	
Description	Supervisor:西村 俊, 先端科学技術研究科, 博士

## Studies on CuPd Bimetallic Catalysts for Selective Hydrogenation of Succinic Acid

Doctoral Degree  
Nishimura's Laboratory  
Le Dinh Son (1820036)

Succinic acid (SA) was identified as one of the most potentially bio-derived platform chemicals which can be converted to a number of value-added products via hydrogenation, esterification, and amination reactions. Among these main three conversion routes of SA, the hydrogenation is by far the most investigated transformation due to the importance of its products including  $\gamma$ -butyrolactone (GBL), tetrahydrofuran (THF), and 1,4-butanediol (BDO). However, the selective hydrogenation of SA is generally a challenging reaction due to the low electrophilicity of the carbonyl group and the complexity in its reaction pathways, which have provided a strong spur for chemists to design effective catalysts for this transformation. Despite that, the heavy dependence on precious metals such as Pd, Pt, Re, Ir, Ru, and Rh in previously reported catalysts is economically disadvantageous, which possibly limits them from industrial applications. Therefore, the studies embodied in this thesis aim to develop efficient earth-abundant metal-based bimetallic catalysts for selective hydrogenation of SA to BDO, THF, and GBL.

In the initial attempt to search for a suitable catalyst system, hydroxyapatite (HAP) supported  $\text{Cu}_x\text{Pd}_y$  ( $x + y = 10$  wt%) was found to be potential bimetallic catalysts for the production of BDO from SA. The effect of metal ratio was examined, and the  $\text{Cu}_8\text{Pd}_2/\text{HAP}$  was found to be the best catalyst, affording a high selectivity of BDO (>80%) at a quantitative conversion of SA. A strong Cu–Pd interaction resulted from alloying formation led to an enhanced catalytic activity to the intermediate GBL, compared to that over the  $\text{Cu}_{10}/\text{HAP}$  monometallic catalyst. While on the other hand, the Cu-rich CuPd nanoparticles (NPs) suppressed the over-reactivity of Pd, preventing the side reaction to butyric acid (BA), which is typically encountered in the  $\text{Pd}_{10}/\text{HAP}$  monometallic catalyst. Subsequently, the Cu species that existed closely to CuPd alloying NPs promoted further hydrogenation of GBL, achieving BDO with high yield.

Since the metal–support interaction can have pronounced effects on the catalyst structures and thus their catalytic performances, the influences of various supports i.e.,  $\text{SiO}_2$ ,  $\text{TiO}_2$ , and  $\gamma\text{-Al}_2\text{O}_3$ , on the constructions of Cu-rich CuPd alloy nanoparticles (NPs) were investigated. In-depth characterizations revealed that randomly homogeneous CuPd NPs were prevalently constructed on  $\text{TiO}_2$  and  $\text{SiO}_2$ , whereas the heterogeneous CuPd alloy NPs with a great extent of Cu segregation were dominantly formed on  $\gamma\text{-Al}_2\text{O}_3$ . As a result, the catalytic activity and product selectivity are distinctly different among these catalysts. Particularly, a selectivity of GBL (90%) can be attained over the  $\text{CuPd}/\text{TiO}_2$  catalyst at 73% conversion of SA, which was attributed to the presence of large CuPd NPs preventing further hydrogenation of GBL and lowering the catalytic activity. On the other hand, the higher activity and selectivity toward BDO of  $\text{CuPd}/\text{SiO}_2$  were ascribed to its small CuPd NPs and the presence of isolated Cu species which promoted the formation of BDO at a high yield of 86%. Notably, the strong Lewis acid sites in the  $\text{CuPd}/\gamma\text{-Al}_2\text{O}_3$  was revealed as the decisive factor in the formation of highly selective THF with 97% at a quantitative conversion of SA.

To broaden knowledge in the  $\gamma\text{-Al}_2\text{O}_3$  supported CuPd catalysts, the influence metal ratio on the catalytic performance has been extended. Excellent catalytic performance toward THF was achieved over the Cu-rich  $\text{Cu}_6\text{Pd}_4/\gamma\text{-Al}_2\text{O}_3$  and  $\text{Cu}_8\text{Pd}_2/\gamma\text{-Al}_2\text{O}_3$  catalysts, achieving the product yield and selectivity of 85–90%. In addition, the present catalyst can maintain its high activity and selectivity for several recycling runs under high temperature and pressure conditions. Extensive characterization methods revealed that major factors that were responsible for the superior performance and stability of this catalyst for THF production include CuPd alloy NPs with isolated Cu species and strong Lewis acid sites of the  $\gamma\text{-Al}_2\text{O}_3$  support. The strong interaction in CuPd alloy NPs resulted in the enhanced reactivity compared to that of the monometallic Cu, while the Cu-rich component helped to restrain the strong reactivity of Pd species which favors the formation of BA. Alternatively, the Cu-rich CuPd NPs were proposed to promote the formation of the intermediate BDO which was easily converted to THF via cyclodehydration under the influence of strong Lewis acid sites in the support  $\gamma\text{-Al}_2\text{O}_3$ .

Finally, the influence of the capping agent on the catalytic performance of CuPd NPs was studied for SA hydrogenation. A highly efficient PVP-capped CuPd NPs constructed on HAP was discovered for selective hydrogenation of SA to GBL. The inhibition effect of the capping agent PVP was revealed to play a key role in the formation of GBL with excellent selectivity. The catalyst was able to proceed at extremely low hydrogen pressure from 1 MPa while maintaining high selectivity of GBL (>90%). Besides, the catalyst showed remarkable reusability, offering the catalyst with enormous potential for applying to the hydrogenation of not only SA but also other oxygen-rich biomass resources from laboratory to industrial scale.

In conclusion, the present thesis provides feasible and versatile methods to design effective CuPd bimetallic catalysts for selective hydrogenation of SA. Depending on the purpose, the product selectivity toward a specific product including BDO, THF, and GBL can be controlled by adjusting the Cu:Pd ratio, changing the catalyst support, and stabilizing with capping agent. The important findings derived from the present thesis might be useful to apply and design other earth-abundant bimetallic catalysts for hydrogenation reactions of other carboxylic acids.

**Keywords:** Succinic acid, CuPd alloy, Gamma-butyrolactone, 1,4-butanediol, Tetrahydrofuran