

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
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Description	Supervisor:西村 俊, 先端科学技術研究科, 博士

氏名	LE, Dinh Son		
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論文審査委員	主査	西村 俊	北陸先端科学技術大学院大学 准教授
		金子 達雄	同 教授
		谷池 俊明	同 教授
		松見 紀佳	同 教授
		大山 順也	熊本大学 准教授

論文の内容の要旨

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 γ -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 Cu_xPd_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., SiO_2 , 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 TiO₂ and SiO₂, whereas the heterogeneous CuPd alloy NPs with a great extent of Cu segregation were dominantly formed on γ -Al₂O₃. 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 CuPd/TiO₂ 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 CuPd/SiO₂ 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 CuPd/ γ -Al₂O₃ 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 γ -Al₂O₃ 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 Cu₆Pd₄/ γ -Al₂O₃ and Cu₈Pd₂/ γ -Al₂O₃ 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 γ -Al₂O₃ 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 γ -Al₂O₃.

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

論文審査の結果の要旨

バイオマス資源は従来の天然炭素資源と比較して、再資源化プロセスの速度が速く地域偏在性が少ない資源特性から、次世代社会の中核を担う資源・エネルギー源としての利用が期待されている。一方で、従来資源とは異なり含水・含酸素率が高いことから、特に脱水・還元を経る触媒変換技術の開発が求められている。本研究では、バイオマス由来資源コハク酸の水素化反応をターゲットに、異種金属・担体から成る複合構造触媒を構築し、より高機能性（高活性・高選択性・高安定性）を発現する触媒開発を進めた。

第一章では、バイオマス由来資源変換における工業ターゲット、合金触媒に関する研究動向、およびコハク酸水素化における従来技術をレビューすることで、本研究の位置づけを行い、目的と意義を示した。

第二章では、安定なハイドロキシアパタイト（HAP）を母材とした種々の貴金属＋典型元素の組み合わせから成る合金触媒の検討から見出した CuPd/HAP 複合触媒が、コハク酸の水素化反応において 1,4-butandiol を直接合成可能な触媒となることを示した。特に Cu 含有量が多い CuPd 触媒が高収率であり、安価で汎用な Cu を中心とする複合触媒開発の可能性を示した。

第三章では、Cu 含有量が多い CuPd 触媒に対して性質が異なる母材を作用させた複合触媒を調製し、コハク酸の水素化反応の生成物選択性制御を可能とした。特に、酸性質を有する Al_2O_3 との複合化により得た CuPd/ Al_2O_3 触媒が tetrahydrofuran の直接合成に高収率・高選択合成を発現することを示した。

第四章では、CuPd/ Al_2O_3 触媒による tetrahydrofuran 直接合成プロセスにおける Cu/Pd 比の影響を考察し、Cu 含有量が大きいに形成される遊離した Cu 種の存在が、中間経路の反応である g-butyrolactone から 1,4-butandiol を生じる水素化プロセスに機能する触媒因子であるとの知見を示した。

第五章では、第二～第四章の検討では改善が困難であった触媒の安定性向上をターゲットに、高分子配位剤であるポリビニルピロリドン（PVP）とのハイブリッド化を検討し、金属リーチングが極めて少ない CuPd-PVP/HAP 複合触媒の開発に成功した。

第六章では、すべての章を総括し、CuPd 触媒を用いたコハク酸の水素化反応における複合触媒構造の要素と反応性を関連付け、体系的な説明を行った。また、今後の技術課題についても明確に示した。

以上、本論文は、バイオマス由来資源であるコハク酸の水素化変換を切り口に 1,4-butandiol や tetrahydrofuran 合成を高収率・高選択率で可能とする CuPd 触媒を開発し、触媒の安定性向上の方策として高分子とのハイブリッド化の指針を示しており、学術上・応用上の両方の観点から貢献する

ところが大きい研究である。よって博士（マテリアルサイエンス）の学位論文として十分価値あるものと認めた。