

Title	不均一系触媒を用いた非可食性バイオマス資源からの 化成品原料合成プロセスの開発に関する研究
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Studies on Development of Heterogeneous Catalytic System for Transformations of Inedible Biomass into Valuable Chemicals

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Introduction

During the last century, the standard of living of our society has been reached to a high level on the cost of utilization of natural fossil resources. Considering the diminishment of these resources, it is imperative to make the transition from non-renewable fossil fuel to renewable biomass resources to meet the future demands. A fundamental challenge in the conversion of biomass into tailor-made fuels is to develop cost effective processes for transformation of the high oxygen content of saccharides. The current biomass conversion methods are dominated by high-temperature pyrolysis and acid-catalyzed dehydration, which leads to difficulty in recovering catalyst from the reaction mixture and pose environmental and health risks. The aforementioned difficulties associated with the previous reports can be alleviated by developing suitable heterogeneous catalytic system for desired chemical transformations.

Results and Discussion

For achieving the goal of shifting the load away from non-renewable sources to biomass resources for sustainable development, the following studies were conducted in this thesis. As sugars comprise the main class of biomass compounds, the selective conversions of sugars to produce furan compounds were carried out over solid acid and base catalysts in one-pot manner in **chapter 2**. The effective synthesis of furans from various saccharides are likely progressed by the aldose-ketose isomerization of sugars over Hydrotalcite (solid base) followed by successive dehydration to furans over Amberlyst-15 (solid acid). Furan compounds are versatile intermediates of biomass based and petroleum based industries. Among them 5-hydroxymethylfurfural (HMF) has received a considerable attention owing to its potential in bio-refinery. Subsequently in **chapter 3**, HMF was selectively transformed into 1,6-hexanediol (HDO) *via* Brønsted acid-catalyzed hydrogenolytic ring opening of HMF by transfer hydrogenation methodology using formic acid (FA). The hydrogenolysis of HMF to HDO supposedly proceeds through 2 key reactions; (1) deoxygenation of furan ring (C-O bond cleavage) (2) hydrogenation of C=O and C=C bond. I found that Pd/ZrP exhibited a significant activity due to the specific Brønsted acidity on ZrP support, which accelerates the cleavage of C-O bond in the furan ring. Further hydrogenation was achieved over Pd metal sites together with the presence of FA as a source of hydrogen instead of high pressured-hydrogen. The produced HDO from renewable resources has immense advantages in polymer industry owing to its terminal hydroxyl groups. The same molecule can be further transformed into other valuable chemicals. One chemical of such immense value is 6-hydroxycaproic acid (HCA) that has potential applications in polycaprolactone production. Accordingly, the selective oxidation of HDO using *N,N*-dimethyldodecylamine *N*-oxide (DDAO) stabilized AuPd bimetallic nanoparticles supported on hydrotalcite as heterogeneous catalyst is demonstrated in basic aqueous media with hydrogen peroxide as oxidizing agent in **chapter 4**. The spectroscopic investigations suggested AuPd interactions to provide negatively charged-Au species, which might be responsible for the excellent catalysis in the selective oxidation of one primary OH group of C6 aliphatic diol, HDO. To substantiate the versatility of Pd/ZrP (catalyst from chapter 2) in catalytic transfer hydrogenation (CTH) reactions, selective hydrogenation of various substituted nitroarenes was investigated over Pd/ZrP in presence of FA as a hydrogen source in **chapter 5**.

Conclusion

In conclusion, new pathways have been developed to produce important industrial commodities directly from inedible biomass-resources employing novel heterogeneous catalytic systems. HDO and HCA like important industrial entities whose synthesis were only dependent on fuel resources can now be produced from biomass in just few steps. Furthermore, a new CTH methodology is developed using bio-based FA as hydrogen source over reusable Pd/ZrP catalyst. The chemoselective, eco-friendly, cost-effective methodology which can work under base-free conditions will lead to a new direction of CTH reactions.

Keywords: Biomass, Heterogeneous Catalysis, Sustainable Chemistry, Analytical Techniques, Organic Transformations.