



Title	Transformation of Sugar-Derived Compounds over Supported Metal Catalysts [an abstract of dissertation and a summary of dissertation review]
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## 学位論文内容の要旨

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### 学位論文題名

## Transformation of Sugar-Derived Compounds over Supported Metal Catalysts

(担持金属触媒による糖化合物の変換)

Use of non-edible lignocellulosic biomass as a feedstock for chemical production is attractive in terms of carbon neutrality. The use of biomass requires development of synthetic routes to a variety of chemicals that are currently produced from fossil fuels. Chemicals with two, three, five and six carbon atoms can be easily synthesized from biomass and some of these are currently produced industrially. On the contrary, four carbon chemicals are still prepared from fossil sources because of lack of biomass derived platform chemical with four carbon atoms. Hence, this thesis discusses pathways for four carbon chemicals from biomass derived furfural. As sugar isomerization is a key step in furfural production, Chapter 2 is dedicated to catalyst development for glucose isomerization to fructose. Chapter 3 discusses furfural oxidation to succinic acid using reusable Lewis acidic catalysts and Chapter 4 discusses catalyst development for hydrogenation of succinic acid to  $\gamma$ -butyrolactone.

Chapter 1 starts with a general introduction to lignocellulosic biomass and the chemicals that can be derived from it. This is followed by analysis of current bio-based chemical synthesis scenario and the need for C4 chemical synthesis. Then an introduction of possible pathway for C4 chemical synthesis from glucose and xylose is presented, which followed discussion on individual steps in this pathway. The subsequent sections introduce glucose isomerization reaction, furfural oxidation reaction to succinic acid and succinic acid hydrogenation to  $\gamma$ -butyrolactone. For each individual process step the reaction mechanism is discussed along with aspects of catalyst design, current state of art and the aspects that must be addressed for this reaction to be successful.

In Chapter 2, a catalytic process for glucose to fructose isomerization is explored. Glucose is the most abundant biomass derived platform chemical and its conversion to fructose is the first step in several catalytic pathways, including the formation of furfural. For glucose isomerization, a Lewis acid catalyst was developed by anchoring highly dispersed Sn species on the surface of SBA-15. The dispersed Sn species with tetrahedral open sites were created on the surface of SBA-15 via simple impregnation by taking advantage of the abundance of hydroxyl groups and high surface area. Characterizations revealed that one active site could form with five silanol groups on catalyst surface. Isotopic labeling study proved that glucose was isomerized via the 1,2-hydride shift mechanism, which validated the role of Lewis acid sites in our reaction. Turn over frequency over this Sn/SBA-15 catalyst was two times in comparison to conventional Sn-Beta catalyst.

Chapter 3 discusses oxidative C-C cleavage of carbonyl group in furfural to produce succinic acid.

Succinic acid can be a gateway to biobased four carbon chemicals. For this reaction we have used a purely Lewis acidic Sn-Beta catalyst prepared by post-impregnation method. This catalyst was selective and reusable for furfural oxidation to succinic acid. NMR analysis of reaction mixture revealed that 2(3H)-furanone was the key intermediate. Sn-Beta accelerated the formation of 2(3H)-furanone via Baeyer-Villiger oxidation. Increase in Lewis acid density of the catalyst had a positive effect on initial rate of reaction. Sn-Beta polarized the carbonyl group of furfural making the carbon atom more electrophilic, which was then attacked by hydrogen peroxide to do Bayer-Villiger oxidation reaction. In contrast, when TS-1 was used as Lewis acid catalyst for comparison, maleic acid was produced, which was due to the formation of M-OOH species leading to epoxidation of furfural ring. Similarly, Brønsted acidic HBeta-38 zeolite produced a mixture of products as it reacted with hydrogen peroxide. The peculiar nature of Sn-Beta to activate furfural and not to react with hydrogen peroxide makes it a suitable catalyst for this reaction.

In Chapter 4, the use of succinic acid as precursor to synthesis of  $\gamma$ -butyrolactone (GBL) is discussed. GBL is a four-carbon lactone that serves a green aprotic solvent and chemical precursor. All the catalysts reported in literature for this reaction, use 1,4-dioxane as solvent and expensive metals like Pd or Au as catalysts. In contrast, we found that Ru can also activate succinic acid in aqueous phase when supported on a suitable metal oxide. Ru/V<sub>2</sub>O<sub>3</sub> catalyst showed improved activity compared to other supports such as V<sub>2</sub>O<sub>5</sub>, SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>. In situ DRIFTS study with pivalic acid as model carboxylic acid suggested that succinic acid undergoes dissociative adsorption at the interface of Ru metal and V<sub>2</sub>O<sub>3</sub> support. The catalytic activity was stable for at least five cycles. Some amount of VO<sub>2</sub> phase was observed after the reaction which remained constant through multiple cycles. We propose a mechanism involving dissociative adsorption of succinic acid on Ru/V<sub>2</sub>O<sub>3</sub> followed by hydrogenation in which the ability of V<sub>2</sub>O<sub>3</sub> support to localize abstracted proton of succinic acid played a crucial role.

Chapter 5 summarizes the thesis and discusses the future direction for research in this field to realize the possibility of value-added chemical synthesis from biomass derived sugars.