



Title	Studies on Catalytic Conversion of Biomass-derived C6-Furanics for Polymer Applications [an abstract of dissertation and a summary of dissertation review]
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学 位 論 文 内 容 の 要 旨

博士の専攻分野の名称 博士（理学） 氏名 SHEET Nirupama

学 位 論 文 題 名

Studies on Catalytic Conversion of Biomass-derived C6-Furanics for Polymer Applications
(高分子材料への応用を志向したバイオマス由来 C6 フラン化合物の触媒変換に関する研究)

Recently, the rapid consumption of fossil resources to produce chemicals and fuels raises the substantial energy crisis along with their adverse environmental impact. The utilization of sustainable and renewable carbon sources in the chemical industry is of utmost importance for building a sustainable society. Non-edible biomass is widely recognized as one of the promising carbon sources due to its abundance and renewable nature.

Chapter 1 introduces the significance of lignocellulosic biomass and key platform molecules including biomass-derived C6 furanics for future chemical industry. A variety of biomass-derived molecules such as furfural, 5-hydroxymethylfurfural, levulinic acid, phenol, and vanillin can be obtained from lignocellulosic biomass via hydrolysis, dehydration, aldol condensation, dealkylation, etc. The conversion of biomass-derived carbohydrates (such as glucose, fructose, and xylose) into furanic aldehydes (such as furfural, 5-hydroxymethylfurfural (HMF), 5-chloromethylfurfural (CMF) and 5-bromomethylfurfural (BMF)) has gained much attention due to their diverse applications in synthesizing a wide range of new products. Among them, chemocatalytic transformation of HMF affords a variety of useful compounds in organic synthesis, pharmaceuticals, transportation fuels and chemical industries. Chapter 1 summarizes the current processes primarily focusing on oxidative and reductive transformation of HMF and its derivatives to potential monomers for bio-based polyesters and polyamides. Despite the potential of HMF, selective conversion of HMF to desired chemicals remains many challenges due to the highly reactive formyl group (-CHO) in HMF causing complex side reactions. This dissertation deals with the efficient transformation of biomass-derived C6-furanics using concentrated solutions (10-20 wt%) to possible building blocks of bio-based polymers mitigating our dependency on fossil fuel reserves.

In Chapter 2, a highly efficient catalytic process to produce dimethyl furan-2,5-dicarboxylate (MFDC) from concentrated HMF-acetal solutions (10–20 wt%) is developed based on the stepwise and protecting strategies. This process consists of three steps: 1) the oxidative esterification of HMF-dimethylacetal to the dimethylacetal form of methyl 5-formylfuran-2-carboxylate (MFFC-acetal), 2) the deprotection of MFFC-acetal to methyl 5-formylfuran-2-carboxylate (MFFC) and 3) the production of MFDC via oxidative esterification of MFFC. Two oxidative esterification steps with HMF-dimethylacetal and MFFC (10–20 wt%) were performed with CeO₂-supported Au catalyst (Au/CeO₂), which gave high product yields (90-95%). The deprotection step (MFFC-acetal to MFFC) was designed using a solid Brønsted acid catalyst, which further enhanced the sustainability of the process. Products such as MFFC-acetal, MFFC, and MFDC could be obtained from the reaction mixture in high purity after each step, extending the scope of this approach toward other valuable bio-based monomers.

Chapter 3 demonstrates the high-yielding synthesis of 2,5-bis(aminomethyl)furan (BAMF) via reductive amination of acetal-protected 2,5-diformylfuran (DFF) with 1,3-propanediol (PD-DFF). An acetal protection strategy was applied to the stepwise synthesis of BAMF

from concentrated DFF-acetal solutions (10 wt%). The reductive amination of PD-DFF (10 wt%) in a binary solvent of methanol and water (2:1, v/v) with NH₃ and Co₂P NRs catalyst afforded corresponding primary amine with retaining acetal functionality (PD-AMF) in high yield (94%). In the second step, pH of the reaction mixture was adjusted by the addition of acetic acid to promote the partial hydrolysis of the acetal moiety during the reductive amination of PD-AMF. BAMF was obtained in a high yield (95%) from a 10 wt% PD-AMF solution under the optimal reaction conditions (pNH₃ = 0.6 MPa, pH₂ = 1.2 MPa, 120 °C, 4 h). Co₂P NRs showed outstanding catalytic performance compared to state-of-art catalysts and can be reused several times while retaining its original activity. Moreover, the present process involved concentrated solutions (10 wt%) in two reductive amination steps, thus making the process industrially feasible for the large-scale production of BAMF.

In Chapter 4, Co₂P NRs was applied to the synthesis of methyl 5-aminomethylfuran-2-carboxylate (MAMFC), one of the valuable biomass-derived primary amines, which can be produced via the reductive amination of MFFC. There has been no efficient synthetic procedure to produce MAMFC in the previous papers. Herein, I studied the reductive amination of MFFC in methanolic solution using pressurized NH₃ and H₂ with Co₂P NRs catalyst. The reaction parameters were optimized to maximize the MAMFC yield. MAMFC was obtained with the highest yield of 54% at 130 °C in 2 h under the optimized reaction conditions (pNH₃ = 0.3 MPa and pH₂ = 0.5 MPa).

Chapter 5 summarizes the dissertation and discusses the future direction for my research topics to realize the possibility of value-added chemical synthesis aiming for the application of biomass-based polymers.