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Author(s)	TAT, BOONYAKARN
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博士の専攻分野の名称 博士（理学） 氏名 Tat Boonyakarn

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Protection Strategies for Catalytic Conversion of Biomass-derived Furanics to Monomers for Polyamides

（保護基活用戦略に基づくバイオマス由来フラン化合物からポリアミド原料への触媒変換）

Lignocellulosic biomass is widely regarded as an abundant, easily accessible, and renewable carbon resource that can replace fossil fuels. Catalytic valorization of its main constituents (cellulose, hemicellulose, and lignin) into platform molecules has been extensively studied to realize sustainable production of fuels and commodity chemicals. Hydrolysis of cellulose into glucose and its subsequent dehydration yields HMF.

This thesis starts with chapter 1 focusing on general introduction to lignocellulosic biomass using heterogeneous catalysts. A number of cascaded reactions such as hydrolysis, dehydration, aldol condensation, hydrogenation, and reductive amination are required to convert lignocellulose biomass into valuable chemicals. The biggest challenge of biomass utilization curtails its selective conversion into a handful of chemicals, so-called platform molecules, which can be used in the same way as petroleum-sourced intermediates. Holocellulose moiety is depolymerized by the acid-catalyzed hydrolysis to yield simple hexose and pentose sugars, which can then be dehydrated to 5-(hydroxymethyl)furfural (HMF) and furfural. HMF and furfural are both very versatile molecules, comprising an aromatic 5-membered furan ring and an aldehyde, as well as a hydroxymethyl moiety in the case of HMF. Chapter 1 mainly describes research background of HMF conversion to monomers for polyesters and polyamides. Representative studies on oxidative transformation and reductive amination of HMF-derived furanics are summarized comprehensively. HMF is very versatile molecules, comprising an aromatic 5-membered furan ring and an aldehyde, as well as a hydroxymethyl moiety in the case of HMF. HMF can be transformed into transport fuels, but especially HMF lends itself exceptionally well to the production of fine chemicals and monomers due to its hydroxymethyl and aldehyde functionalities.

In Chapter 2, an acetal protection strategy for HMF was used to obtain 2,5-diformylfuran (DFF) using concentrated HMF solutions and a γ - Al_2O_3 -supported Ru catalyst (Ru/ γ - Al_2O_3). The HMF-acetal with 1,3-propanediol can be oxidized to DFF-acetal with a yield of 84.0% at an HMF conversion of 94.2% from a 50 wt% solution. In contrast, aerobic oxidation of nonprotected HMF using a 10 wt% solution afforded DFF only in a moderate yield (52.3%). Kinetic studies indicate that the six-membered ring acetal group not only prevents side reactions but also accelerates aerobic oxidation of the $-\text{CH}_2\text{OH}$ moiety to $-\text{CHO}$ under retention of the acetal functionality. Organic deposits formed during the reaction explained the significant decrease in the activity of the Ru/ γ - Al_2O_3 catalyst, which could be recovered neither by washing in water or organic solvents, nor by a calcination-reduction treatment. Sonication of the used Ru/ γ - Al_2O_3 catalyst in an aqueous NaOH solution successfully removed the deposits and allowed reuse of the catalyst for at least four times without activity loss.

Chapter 3 deals with an efficient strategy for preparing 5-(aminomethyl)furan-2-carboxylic acid (AMFCA) from renewable biobased 5-formylfuran-2-carboxylic acid (FFCA) as a monomer for polyamides through reductive amination using catalytic single-crystal cobalt phosphide nanorods (Co_2P NRs). Strongly alkaline ammonia solutions, commonly used for reductive amination, caused severe degradation of FFCA, but no degradation occurred when using ammonium acetate (NH_4OAc) as a nitrogen source. Moreover, among binary water-organic solvent mixtures (Toluene, DMF, alcohol, etc.), AMFCA yield was the highest in

water-methanol mixing solvent, due to in-situ acetal formation which provides protection of the labile aldehyde of FFCA and so suppresses degradation and other side reactions. Under optimized conditions, i.e., 0.5 mmol of substrate, 5 mmol of NH_4OAc , substrate to catalyst ratio of 10 mol/mol, under 0.5 MPa H_2 at 393 K for 3 hours in methanol/water 2:1 v/v, near-stoichiometric amounts of AMFCA (90% yield) were formed at full conversion.

The benefits of using FFCA-acetal (dimethylacetal of FFCA) in AMFCA synthesis was explored in Chapter 4. Strongly alkaline methanolic ammonia solutions, commonly used for reductive amination, caused severe degradation of FFCA, but no degradation occurred when using FFCA-acetal. AMFCA was directly produced in 97% selectivity from FFCA-acetal in methanolic ammonia solution without production of the free FFCA as an intermediate. The acetal protected the aldehyde from any side reactions, but the alkaline environment and absence of water retarded the reaction rate significantly. Reductive amination of FFCA-acetal using NH_4OAc as an amphoteric nitrogen source in methanol : water mixtures was faster than when using ammonia in anhydrous conditions. In this case, FFCA was detected as the more acidic and aqueous conditions caused some hydrolysis of the dimethyl acetal. The rate for AMFCA formation was improved using an optimized ratio of methanol : water 2:1 v/v (80 mmol g-cat⁻¹ h⁻¹) compared to pure methanol (30 mmol g-cat⁻¹ h⁻¹). Under optimized conditions, i.e., 0.5 mmol of FFCA-acetal, 5 mmol of NH_4OAc , substrate to catalyst (Co_2P NRs) ratio of 10 mol/mol, under 0.5 MPa H_2 at 393 K for 3 hours in methanol/water 2:1 v/v, a 91% yield of AMFCA (91% yield) was achieved at full conversion.

Chapter 5 covers reductive amination of DFF-acetal, which is obtained from oxidation from HMF-acetal in chapter 2. Reductive amination of DFF for the synthesis of 2,5-bis(aminomethyl)furan (AMF) was studied using cobalt phosphide nanorods (Co_2P NR) catalyst. Because of severe degradation of DFF, using acetalized DFF with 1,3-propanediol (DFF-acetal) was required. In the first step, the reductive amination of the DFF-acetal selectively converted the formyl group to amine with retaining the acetal moiety, yielding an intermediate in the maximum yield of 90% at full conversion of DFF-acetal. AMF can be produced from the intermediate in 65% yield when the intermediate was heated at 393 K for 3 hours in methanol-water 2:1 v/v-mixture with NH_3 and Co_2P NR catalyst.

Chapter 6 summarizes the thesis and discusses the future direction for research in this field to realize the possibility of value-added chemical synthesis aiming for the application of biomass-based polymers.