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主 論 文 の 要 旨

論文題目 **Studies on the heterogeneous catalytic process for production of liquid fuels and fine chemicals from hemicellulose derived furfural and furfuryl alcohol**

(へミセルロース由来のフルフラールおよびフルフリルアルコールからの液体燃料およびファインケミカル製造のための不均一系触媒プロセスに関する研究)

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論 文 内 容 の 要 旨

Interest in the generation of biofuels and green chemicals from biomass, particularly lignocellulosic biomass, which is a high-potential renewable feedstock, has grown significantly in recent years. This work focused on the utilization of hemicellulose derived furfuryl alcohol (FAL) to produce a sustainable aviation fuel (SAF) or gasoline additive such as butyl levulinate (BL) through butanolysis reaction and furfural hydrogenation to obtain an industrial green solvent tetrahydrofurfuryl alcohol (THFA). Thus, making a good use of lignocellulosic biomass to contribute to the fuels and fine chemicals sectors to cope with the depleting fossil fuels. This work also aimed at developing process catalysts that can accommodate these reactions in achieving high yields of BL and THFA. It is highly advantageous and desirable to

synthesize suitable catalysts that are efficient and versatile in chemical reactions.

The first part of the thesis discusses the butanolysis of FAL over a solid acid catalyst to produce BL. Considering butanolysis of furfuryl alcohol is a strong function of acidity, tungstated zirconia ($\text{WO}_3\text{-ZrO}_2$), a robust solid acid catalyst, and a sulfonated carbon catalyst were employed to achieve high yields BL while targeting a lower initial molar ratio of butanol to FAL. The catalytic activity of $\text{WO}_3\text{-ZrO}_2$ with respect to BL yield was optimized in calcination temperature (800 °C) and WO_3 loading (15 Wt.%). However, a maximum of 28 mol% of BL yield was achieved at a reaction temperature as high as 240 °C. At such high temperature, FAL polymerization was promoted rapidly resulting in low yield of BL. Using noble (Pd & Pt) and non-noble (Fe, Co, Ni, and Cu) promoters to increase the acidic strength also resulted in the same activity as neat $\text{WO}_3\text{-ZrO}_2$. As the acidity of the catalysts is a key factor for butanolysis of FAL, a carbon catalyst was synthesized by partial carbonation of biomass derived sucrose to obtain acidic carboxyl, phenolic, and hydrophilic groups in the carbon structure. This carbon structure was further enhanced with strong Bronsted $-\text{SO}_3\text{H}$ groups by sulfonation. Thus, prepared sulfonated carbon catalyst possessed an acidic strength of 2.357 mmol/g, resulting in 80 mol% of BL yield at as low as 8.5 initial mole ratio of butanol: FAL.

The second part of the thesis focused on developing a bi-metallic catalysts to employ for furfural hydrogenation to THFA. In this regard, Ni-Cu-Al hydrotalcite catalysts were prepared by dispersing equal moles of Ni and Cu on varying amount of Al by the co-precipitation method to synthesize Ni-Cu alloy particles. The nickel species were active for both the furan ring ($\text{C}=\text{C}$) and carbonyl group ($\text{C}=\text{O}$) of furfural molecule, while Cu species were highly active for only the carbonyl group of furfural molecule.

Systematic characterization of the prepared catalysts by XRD, TPR, STEM-EDS, and XPS analysis revealed the formation of highly active Ni-Cu alloys and near-equal Ni/Cu surface contents were achieved for the equimolar catalyst, which showcased a maximum of 98 mol% yield of THFA at 140 °C, 30 bar, 4h. The reaction pressure and temperature showed a substantial effect on the product yield. The solvent selection also influenced the product selectivity, particularly with 2-butanol, which promoted the reaction with its hydrogen donor capacity and supported the ring hydrogenation of FAL to THFA. Moreover, the reduced Ni₁Cu₁-Al₁ catalyst displayed good recyclability for three runs and an equal activity to that of a fresh catalyst after the regeneration.

The next section of the thesis focused on exploring the electrocatalytic hydrogenation (ECH) of furfural, which has a broad range of conversion to FAL, THFA, and 2-methyl furan (2-MF). In this work, furfural hydrogenation is carried out using Ni-Cu-Al mixed oxide catalysts in thermal catalytic conversion (TCH) and ECH to report the catalytic activity of these mixed oxides. The Ni-Cu-Al mixed oxide catalysts are prepared as working electrodes by depositing the catalyst ink on a Cu foam substrate. 98 mol% selectivity of THFA with complete conversion was observed in the TCH route using Ni₁-Cu₁-Al₁ R catalyst at 140 °C under 30 bar H₂ pressure after 4 hours of the reaction. However, the electrocatalyst (Ni₁-Cu₁-Al₁ R on Cu foam) through the ECH route displayed 89 mol% conversion of furfural with 58 % selectivity of 2-MF and 23.8 % selectivity of FAL. The pH (0.5) of the electrolyte used in the ECH process controlled the selectivity between 2-MF and FAL. Moreover, the formation of THFA was not observed in the ECH route.

The final section of the thesis aimed at developing a simulation model of furfural hydrogenation to evaluate the techno-economic analysis. In this work, an Aspen Plus

model was developed using the PENG-ROB estimation method to hydrogenate furfural to THFA and furfuryl alcohol (FAL) to estimate the economics and the energy scenario of the process. The best results obtained by Ni1Cu1-Al1 R catalyst (100 mol% conversion and 98 mol% THFA yield, 1.5 mol% of FAL yield at 140 °C and 30 bar H₂ pressure) are used in the RSTOIC reactor to estimate its economic potential. As the reaction was exothermic, the liberated heat source was integrated to make use of the process heat.