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論文名	「Sub-Critical Water Conversion of D-fructose as Model for Carbohydrates and Biomass: Formation of Bio-based Building Block Chemicals」 (糖質及びバイオマスのモデル物質として用いたD-フルクトースの亜臨界水転化ーバイオ由来の基礎物質の生成ー)
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#### 論文要旨

Fossil fuels are indispensable resources in the world. However, it is obvious that fossil fuels are a finite resources and their availability is limited. On the other hand, it is estimated that about 170 billion tons of biomass are biosynthesized a year. Today, the uses of biomass as cheap and sustainable alternative resources, for the supply of primary energy and as raw materials in synthesis of organic chemistry represent an important facet of present and future technologies. The transition to a sustainable raw material base will be one of the most important challenges facing society in the 21st century. As part of this endeavor, substantial increases in the use of biomass-derived feedstock in the chemical industry are expected over the next years. On the other hand, in recent years supercritical water and particularly sub-critical water have received more attention as a novel and clean medium for chemical processes of environmental and industrial importance. The use of sub- and supercritical water for many kinds of chemical reactions has been gaining interests due to its potential as green solvent. More recently, growing attention has been devoted to the hydrolysis and decomposition of biomass in sub-critical water for the synthesis of industrial chemicals and related materials. Our aim is using this clean technique to conversion of biomass and carbohydrates to valuable chemicals in order to find direct replacements for fossil derived chemicals.

The present work is aimed at developing sub-critical water technique to produce biobased chemical compounds using fructose and/or other monosaccharides as models of renewable biomass and carbohydrates. In the experimental study both batch and flow-type sub-critical water reaction systems were used. The effect of the temperature, pressure, and other operating parameter were investigated in detail. It is well known that, in the dehydration of saccharides, acids are necessary in normal pressure as catalyst. In the present work, different homogeneous and heterogeneous acids were used in the sub-critical water conditions. The major and important results of the present work are summarized as follows:

In chapter one, the general introduction and importance of the present work as well as review of previous works were presented.

In chapter two, the optimization of conversion of fructose to 5-hydroxymethylfurfural (hereafter HMF) was an essential aim of this investigation. A batch-type sub-critical water reaction system was used to perform the decomposition of fructose over a temperature range of 473-593 K. Generally two series of experiments; reaction in absence and presence of acid catalysts were carried out. Although, under the normal temperature and pressure conditions, the presence of acid catalysts is necessary for the production of HMF, the results of sub-critical water experiments showed that the dehydration of fructose to HMF can be conducted even in the absence of acids. However lower amount of HMF was obtained in the absence of acids at 533 K. Later, the catalytic effects of various organic and inorganic acids with pH values in the range of 1.5-5 were evaluated. In this study, *hydrochloric, sulphuric, phosphoric, oxalic, citric, maleic, and p-toluenesulfonic acids* that have previously been used to decompose the saccharides under normal temperature and pressure conditions, were selected as the common homogeneous acids, for evaluation of their applicability to the dehydration of fructose in sub-critical water. Other pertaining parameters such as concentration of initial fructose, sub-critical water temperature and reaction time, which influenced the production yield of HMF and of by-products, were investigated too.

It was found that not only the pH but also the nature of the acids had great influence on the decomposition pathway. At lower pH, a rehydration of HMF to levulinic and formic acids occurred, whereas at higher pH, polymerization reactions occurred. *Phosphoric acid* (at pH 2) was determined to give the best balance between activity, yield, and by product amounts in the homogenous acid catalysts used in this study. The optimum condition for the best yield of HMF (65%) was achieved at a temperature of 513 K for a residence time of 120 s.

The decomposition reaction of some other monosaccharides and disaccharides, which

were sorbose, mannose, galactose, glucose, sucrose, and cellobiose, were also investigated. It was found that the ketohexoses gave higher yield of HMF than aldohexoses. However, all saccharides showed the possibility of the conversion to HMF in sub-critical water. The UV-Vis absorbance showed the formation of soluble polymers from oligomerization and polymerization of saccharides and HMF. These soluble polymers can not be quantitated; however it could be detected by absorbance at 350-450 nm. One of the main by-products of decomposition of saccharides was the formation of these soluble polymers. In sub-critical water with *phosphoric acid* catalyst, since the higher yield of HMF was obtained, the formation of these polymers was found to be much smaller than other cases.

Another reason for causing the decrease of HMF yield is decomposition of HMF into other compounds. The decomposition of fructose is consecutive-type reaction, by which formed

HMF can rehydrate to levulinic and formic acids. It is worth noting that good catalytic activity of *hydrochloric acid* was observed at lower pH among all homogeneous acids used in this study to rehydration of HMF into levulinic and formic acids.

In chapter three, possibility of applying solid acid catalysts in batch-type sub-critical water dehydration of fructose and or glucose, which were used as models of carbohydrate, were investigated. Eighteen laboratory-made zirconium phosphate solid acids were prepared. Wide range of catalysts from amorphous to high crystalline forms was obtained by refluxing in concentrate *phosphoric acid* and/or by calcination in two temperatures (i.e. 573 and 873 K). Physicochemical properties of the prepared solid acids were studied. The experimental results showed that the surface area decreased almost linearly by refluxing time and/or by heat treatment. By increasing the crystallinity, the surface area decreased. Therefore, with respect to the data of surface areas, it can be realized that both refluxing and calcination may increase the crystallinity of solids toward higher crystal forms. On the other hand, results showed that calcining have a more noticeable effect on the amorphous forms than on higher crystalline forms.

Based on IUPAC classification on adsorption isotherms, it was found that the prepared samples have nonporous or macroporous structures. Other experimental results showed that the amorphous and crystalline forms zirconium phosphates had different pore-size and its distribution. Crystalline form had narrow range of pore distribution compared to the amorphous one. Specific pore volume decreased with increasing crystallinity; however it was found that in all solid samples their volumes of macroporous were small.

As application of zirconium phosphates, dehydration of fructose and glucose to HMF in

batch type sub-critical water was performed in the presence of different kinds of these solid acids at 513 K. In the presence of amorphous form of zirconium phosphate, about 80% of fructose was decomposed in sub-critical water at after 120 s, and the selectivity of the dehydration reaction of fructose to HMF rose to 61%. No rehydration products were identified. Soluble polymers and 2-furfuraldehyde were the only major and minor side-products found, respectively. As result, it was realized that zirconium phosphate solid acids were stable in sub-critical water and they can easily be recovered without changing the catalytic properties. At the experimental conditions, no corrosion of stainless steel reactors was observed when using solid acids as catalyst.

In chapter four, home made flow-type sub-critical water system was used for decomposition of fructose and formation of HMF, levulinic and formic acids simultaneously. Previous results showed that in presence of *hydrochloric acid*, produced HMF can be rehydrating to equimolar amounts of levulinic and formic acids. The experimental conditions were 483 to 543 K, 4 to 15 MPa, and residence time of 0.5 to 300 s. The pH of initial feed solution was adjusted at 1.8. The pressure of sub-critical water did not affect the decomposition reactions; this differed from other operating variables.

The main products were found to be HMF, 2-furfuraldehyde, levulinic acid, formic acid, and soluble polymers. The HMF, levulinic and formic acids were also individually subjected for decomposition at the same condition. From the decomposition of HMF, the products were obtained as levulinic acid, formic acid, and soluble polymers; from decomposition of levulinic and/or formic acids, we did not identified any decomposition products, however it was realized that soluble polymers can not be produced from levulinic and or formic acids. 2-furfuraldehyde was found to be produced only from fructose and not from HMF.

A simplified reaction pathway was proposed. Based on the experimental data obtained from decomposition products, a kinetic model, in which all identified pathways were taken into consideration, was developed. This model distinguished between two different soluble polymers based on the source of production. Theoretical lines matched well with the experimental decomposition and formation curves of fructose, 2-furfuraldehyde, HMF, levulinic and formic acids. The best-fit parameters were determined by nonlinear regression analysis. The proposed kinetic model can accurately predict the rate constant of fructose as well as other decomposition products, especially of two kinds of soluble polymers, which can not be quantified experimentally.

These results showed that the rate constants increase with the reaction temperature obeying the Arrhenius equation. The activation energies of the reactions with rate constants regarding to the kind of substrate along with the average activation energies (without concerning the kind of substrate) were calculated for the reactions.

In chapter five, general conclusions of the present work were given.

From the results obtained in this thesis, it is concluded that conversion of not only monosaccharides, but also any kind of biomass-derived feedstock (and particularly various waste biomasses) to valuable bio-based chemical compounds using sub-critical water as simple, clean, and environmentally friendly method is a feasible process. Also the author believed that the potentially ease of scale-up of this operationally simple method are attractive for large-scale production of valuable chemical compounds in order to replace fossil derive chemicals.

### 審査結果の要旨

本論文は、木質系バイオマスから化学物質を作るための基礎研究として、その単位化学構造であるフルクトースや他の単糖類を出発物質とし、各種ポリマーの原料に使われている 5-hydroxymethylfurfural (以下HMFと略)を合成することを試みたもので、以下の成果を得ている。

(1) 現在、HMFは単糖類を原料として有機溶媒中で合成されているが、この方法では大量生産が困難であり、また環境問題から脱有機溶媒反応が強く求められている。本研究では、臨界点以下の高温高压水である亜臨界水反応の適用を試み、収率及び大量生産の可能性も含め極めて有効であることを示した。

(2) バッチ型亜臨界水反応器を用いて反応温度 473~593K の範囲でフルクトースの分解実験を行った。常温常圧においてはフルクトースの分解は酸触媒無しでは起こらない。しかし、亜臨界水中では、酸触媒無しでもHMFが収率 21%で生成することを明らかになった。さらに水に溶解する種々の酸触媒について検討した結果、リン酸触媒 (pH 2) を用いた場合、触媒効果が最も大きく、513K、反応時間 120 秒で収率 65%を得た。

(3) 上記の反応は極めて複雑であるが、生成物の詳細な分析結果を基に、反応パスウェイを提案した。

(4) 固体酸触媒の適応の可能性について検討を加えた。18種類のリン酸ジリコニウムを合

成した。これらは、アモルファス型から結晶質まで広範囲に内部構造を変化させたものである。アモルファス型の方が表面積は大きく細孔分布も広範囲に及んでいた。これらを亜臨界水反応に用いたところ、触媒粒子の表面積や細孔分布に無関係にほぼ同程度の触媒効果を示し、513K、反応時間 120 秒でHMFの収率が61%という大きな値を示した。

(5) 連続亜臨界水処理装置を用いてフルクトースを分解しHMFを生成する亜臨界水反応を塩酸触媒下で、温度、圧力、pH及び反応時間を様々に変化させて実験した。反応は非常に複雑であるがそれらを簡略化した反応パスウェイとそのパスウェイに基づく反応動力学モデルを提案し、汎用性のある解析解を求めた。この理論解析結果は各種反応生成物の経時変化の実測値と良好な一致を示した。

本委員会は本論文の審査及び最終試験の結果から、博士（工学）の学位を授与することを適当と認める。