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| Description | Supervisor:海老谷幸喜，マテリアルサイエンス研究科，修士 |

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# One-pot Synthesis of Furfurals from Sugars over Solid Acid and Base Catalyst

Mika Ohara (Ebitani Laboratry)

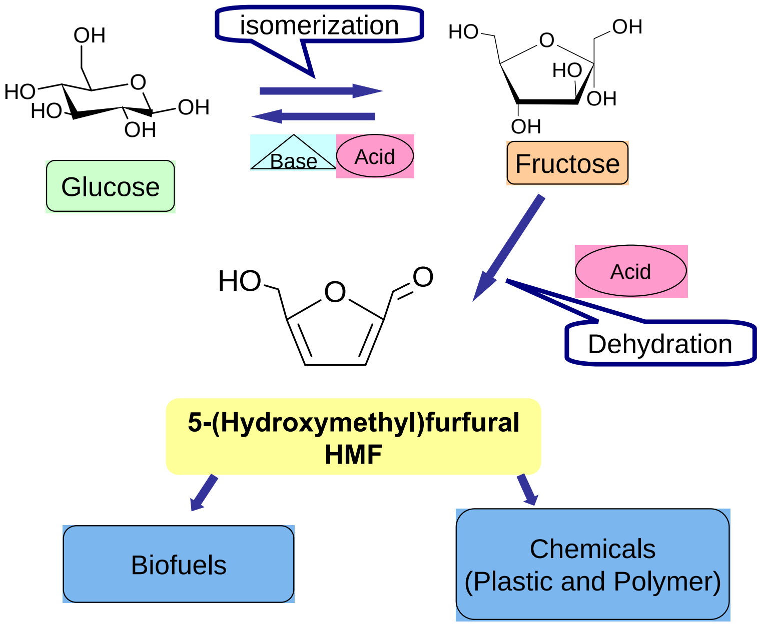
## Introduction

Currently, the world faces serious environmental and economic issues related to our overwhelming dependence on fossil fuels for energy and chemical production and the resulting global warming that arises from their conversions to carbon dioxide. Biomass offers a promising alternative to fossil fuels as a renewable resource as it can be produced in a carbon neutral way.[1] To avoid competition for land resources dedicated to food and animal-feed production, it is strongly desirable to utilize an inedible biomass. Wood-based biomass offers an abundant resource comprising cellulose (35~50 %), hemicellulose (25~30 %) and lignin (25~30 %). Cellulose and hemicellulose can be depolymerized into monosaccharides including glucose, fructose and xylose. Among them, glucose is the most abundant monosaccharide, and therefore transformation of glucose has attracted much attention for the production of alternative chemicals as an efficient biorefinery.

5-Hydroxymethylfurfural (HMF) as a furan derivative can be formed by elimination of three water molecules from hexoses (glucose or fructose), and is a desirable intermediate for plastics, polymers and fuels. For instance, HMF can be oxidized to form 2,5-diformylfuran and 2,5-furandicarboxylic acid. These derivatives are expected to be highly useful intermediates for a variety of polymers and plastics. Levulinic acid, which is obtained by rehydration of HMF, is also an important intermediate for polymers.

Efficient production of HMF has been reported using an organic-water biphasic system, in which hydrochloric acid in the water phase dehydrates fructose or glucose to form HMF, which is subsequently extracted into the organic phase, resulting in high HMF selectivity.[2] The use of ionic liquids containing metal ions such as chromium has also been a notable method for HMF production, providing high selectivity with high conversion.[3] HMF can be much more easily synthesized from fructose than glucose by dehydration because of the difference in their chemical structures. Fructose, as a ketohexose, readily dehydrates to form HMF under mild acid conditions. In contrast, glucose, as an aldohexose, gives poor HMF selectivity in direct dehydration due to considerable side reactions, including cross-condensation resulting in the formation of humins and oligomers.

In this thesis, I have adopted an alternative approach for HMF synthesis from glucose through a two-step reaction in one-pot.[4,5] It is known that glucose can be transformed into fructose by base-catalyzed aldose-ketose isomerization. The obtained fructose could be easily converted into HMF in the presence of acid (Scheme 1). This simple methodology can be performed using a solid acid catalyst along with a solid base catalyst in one-pot. The combination of solid acid and base catalysts offers the opportunity to utilize acid or base activity separately even in one reactor, whereas for a liquid acid-base pair, neutralization and subsequent deactivation would naturally occur. Here, a strong acidic ion-exchange resin, Amberlyst-15 and Nafion NR50 were used as the solid acid catalyst, and a layered clay compound, hydrotalcite, was used as the solid base catalyst.



**Scheme 1.** One-pot synthesis of HMF from glucose using solid acid and base catalysts.

## Experimental

The reactions were performed using D-glucose, (0.1 g), hydrotalcite (0.2), Amberlyst-15 (0.1 g), *N*,*N*-dimethylformamide (DMF) (3 ml) at 373 K for 3 h under $N_2$ atmosphere. The conversion and yield were estimated by using a high-performance liquid chromatography (HPLC) (Waters) with Aminex HPX-87H column from Bio-Rad Laboratories, Inc. Samples were diluted by water before the HPLC measurement. The products were analyzed by using refractive index (RI) detector. The analysis condition was as follows: eluent; 10 mM $H_2SO_4$, flow rate; 0.5 mL/ min, column temperature; 323 K.

## Result and Discussion

The results of transformation of glucose over solid acid and/or base are listed in Table 1. Although hydrotalcite (HT) as base catalyst could convert glucose into fructose (yield; 17%), HMF was not formed (entry 1). In the presence of solid acids such as Amberlyst-15, glucose was not transformed into HMF and fructose, but anhydroglucose like levoglucosan was formed through dehydration (entry 2).[6] It should be noted that HMF was considerably produced using solid base and acid by one-pot reaction (entry 3-5), whereas coexistence of homogeneous base and acid did not produce HMF (entry 6). High HMF selectivity (57%) at high glucose conversion (72%) was obtained in the presence of 0.2 g of hydrotalcite and 0.1 g of Amberlyst-15 (entry 4).

Table 1 One-pot synthesis of HMF from glucose over hydrotalcite and Amberlyst-15[a]

| Entry | Base | Acid | Conversion of glucose/% | HMF | |
|---|---|---|---|---|---|
| | | | | Yield/% | Selectivity/% |
| **1** | **Hydrotalcite** | **—** | **62** | **0** | **0** |
| **2** | **—** | **Amberlyst-15** | **68** | **0** | **0** |
| **3** | **Hydrotalcite** | **Amberlyst-15** | **64** | **24** | **35** |
| **4[b]** | **Hydrotalcite** | **Amberlyst-15** | **73** | **43** | **58** |
| **5** | **Hydrotalcite** | **Nafion NR50** | **60** | **16** | **58** |
| **8[c]** | **Piperidine** | ***p*-TsOH** | **0** | **0** | **0** |

[a] Reaction conditions; Glucose ( 0.1g), Catalyst (base 0.1 g, acid 0.1 g), DMF (3 ml), 373 K, 3 h. [b] Hydrotalcite 0.2 g, 353 K, 9 h.
[d] Piperidine (0.2 mmol), *p*-Toluenesulfonic acid (0.07 mmol)

This system can be also applied to the direct formation of HMF from disaccharides. Disaccharides such as sucrose (a disaccharide of glucose and fructose) and cellobiose (a disaccharide of glucose) are decomposed by acid catalysis into the monosaccharides. Amberlyst-15 is known as a powerful acid catalyst for the hydrolysis of disaccharides. The results of one-pot synthesis of HMF from disaccharides and monosaccharides using HT and Amberlyst-15 are shown in Table 2. Sucrose and cellobiose were also directly converted into HMF with high selectivity, indicating that sequential reactions, including the hydrolysis of disaccharides by acid, isomerization of glucose by base, and dehydration of fructose by acid, are successfully achieved. It is considered that a small amount of adsorbed water on the catalyst triggers the initial hydrolysis of disaccharides. Once HMF was formed by dehydration to remove three water molecules, hydrolysis of disaccharides should proceed smoothly. High selectivity of HMF from disaccharides is presumably attributed to the continuous formation of glucose, which prevents side reactions such as anhydroglucose formation, and results in satisfactory cascade reactions.

Table.2 Direct synthesis of HMF from sugars using solid base and acid catalysts

| Entry | Substrate | temp/time | DMF/mL | Yield of HMF /%[a] |
|---|---|---|---|---|
| 1[a] | Sucrose | 373 K/6 h | 6 | 71 |
| 2[b] | Cellobiose | 393 K/1 h | 8 | 59 |
| 3[c] | Glucose | 373 K/3 h | 3 | 35 |

Reaction conditions ;[a.] sucrose (0.05 g), hydrotalcite (0.2 g), Amberlyst -15 (0.1 g), [b] cellobiose (0.02 g), hydrotalcite (0.3 g), Amberlyst -15 (0.1 g). [c] glucose(0.1 g), hydrotalcite (0.2 g), Amberlyst-15 (0.1 g).

The one-pot system using solid acid and base catalysts afford efficient production of furfural from xylose, a major component of hemicellulose. Furfural is the useful intermediate for solvent, polymer and resins. The results of one-pot synthesis of furfural from xylose using HT and Amberlyst-15 are shown in Table 3. In the presence of Amberlyst-15, small amount of furfural was obtained from xylose at 373 K (entry 3). Increasing temperature at 393 K could increase furfural yield (entry 4). In contrast, combination of hydrotalcite and Amberlyst-15 can be formed furfural at high yield at much lower temperature (353-373 K) (entry1-2).

Table 3 One-pot synthesis of furfural from xylose over hydrotalcite and Amberlyst-15[a]

| Entry | Reaction temp / K | Acid Catalyst | Base Catalyst | Conversion /% | Selectivity /% |
|---|---|---|---|---|---|
| 1 | 373 | Amberlyst-15 | hydrotalcite | 72 | 51 |
| 2 | 353 | Amberlyst-15 | hydrotalcite | 26 | 52 |
| 3 | 373 | Amberlyst-15 | — | 51 | 1 |
| 4 | 393 | Amberlyst-15 | — | 62 | 43 |
| 5[b] | 373 | — | hydrotalcite | 47 | 0 |

[a] Reaction conditions; Xylose (0.1 g), Amberlyst-15 (0.1 g), HT (0.2 g), DMF (3 ml), 3 h. [b] HT (0.1 g)

## Conclusion

Furfurals, one of the most important intermediates derived from biomass, was directly produced from hexose (fructose and glucose), pentose (xylose) and disaccharides (sucrose and cellobiose) by a simple one-pot synthesis using a heterogeneous solid acid and base under mild reaction conditions.

## References

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