Direct hydroxymethylation of furfural towards HMF over solid acid catalyst

Shun Nishimura,[a,*] **Atsuki Shibata,**[a] **Kohki Ebitani**[a]

[a]*Graduate School of Advanced Science and Technology, Japan Advanced Institute of Science and Technology (JAIST), 1-1 Asahidai, Nomi, Ishikawa 923-1292, Japan*

**Shun Nishimura: +81-(0)-761-51-1149, s_nishim@jaist.ac.jp*

Abstract: Direct hydroxymethylation of 2-furaldehyde (furfural) towards 5-hydroxymethyl-2-furaldehyde (HMF) was examined by using various solid acid catalysts. It was found that the commercial acidic resin named as Amberlyst-15, a sulfuric functionalized resin, gave the highest yield of 40% for HMF production with 57% selectivity using an aqueous formaldehyde reagent. The Amberlyst-15 was also reusable and applicable for derived hydroxymethylations of furfuryl alcohol, furfurylamine, and furoic acid towards the corresponding 5-hydroxymethyl furans. A liquid flow reaction system with a fixed Amberlyst-15 catalyst bed have notably produced approx. 36% yield for HMF with 48% selectivity during 24 h, continuously.

1. Introduction

There remains an ever-increasing interest and challenge to develop new biomass transformation technology. Among them, the upgrading of inedible biomass resources towards important chemicals and materials is a key task for sustainable development not competing with foods. The target substrate in this study, 2-furaldehyde (furfural), is well-known as a one of abundant inedible biomass-derived furaldehydes, however transformations of furfural towards versatile compounds have not been conducted in various ways[1-2]. Apparently, the structural character of furfural, a formyl group linked on a furan ring at second position, gives strenuous reaction process and limits its potential as a starting material. For instance, there has been above 100 numbers of transformation paths related on 5-hydroxymethyl-2-furaldehyde (HMF), two functional groups (formyl and hydroxyl group) in a furan ring[3-4]. In this study, we focused on catalytic upgrading of furfural to HMF through a direct hydroxymethylation over solid acid catalyst with formaldehyde as a reagent.

In previous reports, such catalytic transformation of C5 to C6 furaldehydes has been investigated by very few research groups. Important discussions have been undertaken by Moreau and co-workers, and they had achieved the maximum performance of approx. 10% yield for HMF production from furfural in formaldehyde/furfural = 240 over dealuminated mordenite catalyst[5].

2. Experimental

Direct hydroxymethyration was typically performed in a Schlenk flask attached with a condenser. 37% aqueous formaldehyde solution (Wako) was used as both a reagent and a reaction solvent. After the reaction, furfural conversion and HMF yield were determined by a HPLC equipped with a RI detector. An Aminex HPX-87H column (Bio-Rad) was applied under the 10 mM H_2SO_4 aq. flow (0.5 ml/min) at 323 K.

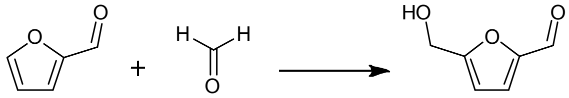
The liquid flow reaction was examined by using a MCR-1000 simple flow reactor (EYELA). As a model condition, the mixed solvent of furfural (14 mmol) in 37% aqueous formaldehyde solution (70 mL) was used as an eluent through the catalyst bed packed in a SUS tube (100 mm × φ5) at 363 K with a flow rate of 0.04 mL/min.

Acid amount of commercial acidic resin was determined by ion-exchange and successive titration as the following procedure. The acidic resin was dispersed into 0.1 M NaCl aq. solution at room temperature, and then the amount of released HCl was counted by neutralization with 0.1 M NaOH aq. agent.

3. Results and discussion

A variety of solid acid catalysts was applied for the direct hydroxymethyration of furfural to HMF (**Table 1**). Mordenite (JRC-Z-HM20(5)), zeolite Y (JRC-Z-HY5.5) and γ-Al_2O_3 (JRC-ALO-8) gave no activity for the reaction (< 3% yields) whereas ZSM-5 (JRC-Z5-90H(1)) and zeolite β (JRC-Z-HB25) served mild activities (12 % and 23%, respectively). While, on the other hand, Amberlyst-types acidic resins served higher yield than such conventional solid acid catalysts. Numerous yields were assigned over Amberlyst-15 (Ho = -2.20, acid amount: 5.04 mmol/g) with 40% and Amberlyst-35 (Ho = -2.65, acid amount: 5.62 mmol/g) with 37%. The former showed much better selectivity (57%) than the latter (44%). It is noted that Amberlyst-15 is composed by mono-sulfonic acid functionality in a polystyrene unit at the para position (*p*-toluenesulfonic acid) whereas Amberlyst-35 was composed by di-sulfonic acid functionalities in a polystyrene unit. Strong homogeneous acid of conc. H_2SO_4 served 35% HMF yield. Notably, the highly-active Amberlyst-15 was reusable for 4th runs without significant decreases in activity (38% yield at 4th run).

Table 1. Direct hydroxymethylation of furfural towards HMF over solid acid catalyst.



Catalyst	Conversion of furfural (%)	Yield of HMF (%)	Selectivity of HMF (%)
Amberlyst-15	71	40	57
Amberlyst-35	85	37	44
Zeolite β^a	61	23	38
ZSM-5^a	33	12	38
Mordenite^a	16	3	18
Zeolite Y^a	11	<1	
γ-$Al_2O_3^a$	11	<1	
Conc. $H_2SO_4^b$	77	35	46
Blank	7	<1	

Reaction conditions: furfural (1 mmol), 37% aqueous formaldehyde solution (5 mL), catalyst (200 mg), time (12 h), temp. (363 K), stirring (500 rpm). (a) Pretreated at 773 K for 5 h. (b) 1 mmol usage.

Amberlyst-15 mediated derived hydroxymethylation of 5th position on a furan ring were also challenged, and then 35% yield of 2,5-bis(hydroxymethyl)furan from furfuryl alcohol, 14% yield of 5-(hydroxymethyl)furfurylamine from furfurylamine, and 24% yield of 2,5-furandicarboxylic acid from furoic acid were respectively achieved under optimum condition.

As advanced study, a flow reactor system was also demonstrated with fixed Amberlyst-15 catalyst bed. At present condition, the continuous production of 70 mM HMF solution was successfully observed with a 200 mM furfural solution flow during 24 h reaction; *i.e.* approx. 36% yield with 48% selectivity.

4. Conclusions

Sulfonic acid functionalized resin acts as an effective catalyst for direct hydroxymethylation of C5 to C6 furaldehyde transformations; especially for furfural to HMF. The catalyst system was reusable and applicable for not only a batch but also a liquid-flow reactor system. These findings are expected to open up new avenues in inedible biomass utilization to produce highly valuable chemicals and materials[6-7].

References

1. J. Lange, E. Heide, J. Buijtenen, R. Price, ChemSusChem 5 (2012) 150.
2. S. Dutta, S. De, B. Saha, M. I. Alam, Catal. Sci. Technol. 2 (2012) 2025.
3. R. Putten, J. C. Wall, E. Jong, C. B. Rasrendra, H. J. Heeres, J. G. Vries, Chem. Rev. 113 (2013) 1499.
4. A. A. Rosatella, S. P. Simenov, R. F. M. Frade, C. A. M. Afonso, Green Chem. 13 (2011) 754.
5. J. Lecomte, A. Finiels, C. Moreau, Ind. Crop. Prod. 9 (1999) 235.
6. S. Nishimura, A. Shibata, K. Ebitani, *under revision*.
7. S. Nishimura, K. Ebitani, JP Patent Application (No. 2017-100728).

Acknowledgement

This study was supported by Grant-in-Aid for Young Scientists (A) (Grant No. 17H04966).