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Author(s)	Takagaki, Atsushi; Ohara, Mika; Nishimura, Shun; Ebitani, Kohki
Citation	Chemical Communications, 2009(41): 6276-6278
Issue Date	2009-09-07
Type	Journal Article
Text version	author
URL	http://hdl.handle.net/10119/19042
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Description	

A one-pot reaction for biorefinery: combination of solid acid and base catalysts for direct production of 5-hydroxymethylfurfural from saccharides

Atsushi Takagaki, Mika Ohara, Shun Nishimura and Kohki Ebitani*

5 Received (in XXX, XXX) Xth XXXXXXXXXX 200X, Accepted Xth XXXXXXXXXX 200X

First published on the web Xth XXXXXXXXXX 200X

DOI: 10.1039/b000000x

5-Hydroxymethylfurfural (HMF), one of the most important intermediates derived from biomass, was directly produced from monosaccharides (fructose and glucose) and disaccharides (sucrose and cellobiose) by a simple one-pot reaction including hydrolysis, isomerization and dehydration using solid acid and base catalysts under mild conditions.

The efficient utilization of biomass has recently received considerable attention as a potential alternative to petroleum for the production of fuels and chemicals.^{1,2} One of the most desired processes is the transformation of lignocellulosic biomass because of its inedibility, abundance and worldwide distribution.³ Glucose, an abundant monosaccharide obtained from the depolymerization of cellulose, is further converted to 5-hydroxymethylfurfural (HMF) via isomerization into fructose and subsequent dehydration, as shown in Figure 1. HMF is considered to be a significant intermediate for the synthesis of a wide variety of chemicals and alternative fuels.⁴ Selective formation of HMF is therefore highly desirable to establish successful biorefinery.

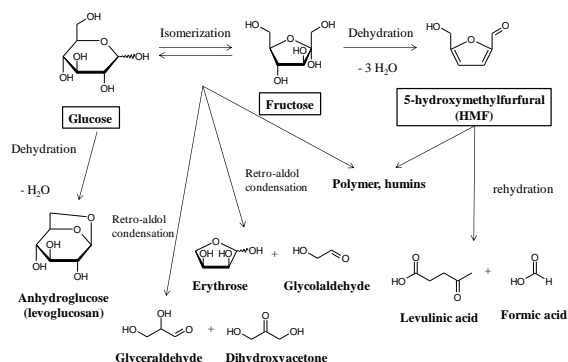


Fig. 1. A typical reaction scheme for glucose transformation

HMF is selectively formed from fructose by dehydration in the presence of liquid⁵ or solid acids.⁶ Direct production of HMF from glucose is, however, unsuccessful because isomerization of glucose into fructose seems to be more difficult by acid catalysis,² resulting in poor selectivity and considerable amounts of by-products such as levulinic acid and oligomers. Although notable methods for HMF production from glucose and/or fructose have been demonstrated using a two-phase modifier⁷ and an ionic liquid containing chromium chloride,⁸ development of a more environmentally-benign system is strongly preferred in order

to realize green and sustainable chemistry.⁹

One-pot reactions using heterogeneous catalysts afford remarkably unique and environmentally-friendly benefits, including avoidance of isolation and purification of intermediate compounds, which saves time, energy and solvent.¹⁰ The concept of site isolation can be realized by the coexistence of acid and base without neutralization, which has been demonstrated using acid-base pairs of polymers, sol-gel matrices, porous silicas and layered clays.

Here, we report selective HMF formation from glucose over solid acid and base catalysts via a one-pot reaction under mild conditions. Simple use of conventional solid acids and bases has afforded the efficient production of HMF. Our strategy involves separating HMF synthesis from glucose into two reactions, (1) isomerization of glucose into fructose catalyzed by solid base and (2) dehydration of fructose into HMF by solid acid. Such an approach has never been adopted for liquid acid-base pair due to their neutralization.

To select efficient heterogeneous catalysts for the one-pot reaction, two individual reactions were first tested, the isomerization of glucose and dehydration of fructose. Isomerization of glucose to fructose is known as the Lobry-de Bruyn-van Ekenstein transformation and is generally catalyzed by base.¹¹ Among solid bases tested, Mg-Al hydrotalcite (HT), consisting of layered clays with HCO₃⁻ groups on the surface,¹² was found to display the highest activity for isomerization (See ESI† Table S1†).¹³ For acid-catalyzed dehydration of fructose into HMF, ion-exchange resins, such as Amberlyst-15⁶ and Nafion NR50, as well as sulfated zirconia exhibited high activity, whereas niobic acid and H-type zeolites were inactive under the conditions listed in Table 1. The transformation of glucose over solid acids, also shown in Table 1, indicates that ion-exchange resins did not produce HMF directly from glucose but caused intramolecular dehydration into anhydroglucoses (1,6-anhydro-β-D-glucopyranose and 1,6-anhydro-β-D-glucofuranose).¹⁴ This is one of the major drawbacks in using only an acid catalyst for the direct formation of HMF from glucose. From these results, HT and Amberlyst-15 were chosen as the solid base and acid, respectively. It was confirmed that these catalysts could be recycled for each reaction at least three times without loss of the activity. Although the appearance of humins on the surface of hydrotalcite was observed after isomerization of glucose, the activity for isomerization remained unchanged by washing

with solvent and drying in vacuo for further experiment.

Table 1. Transformations of fructose and glucose over solid acid catalysts^a

Substrate	Catalyst	Conversion /%	Yield /%	
			HMF	AHG ^b
Fructose	Amberlyst-15	>99	73	0
	Nafion NR50	>99	45	0
	SO ₃ /ZrO ₂	57	21	0
	Nb ₂ O ₅ ·nH ₂ O	8	0	0
	H-ZSM5 ^c	trace	0	0
Glucose	H-Beta ^d	trace	0	0
	Amberlyst-15	69	0	32
	Nafion NR50	34	0	26
	SO ₃ /ZrO ₂	7	0	0
	Nb ₂ O ₅ ·nH ₂ O	12	0	0
H-ZSM5 ^c	trace	0	0	
H-Beta ^d	trace	0	0	

^a Reaction conditions: Substrate (0.1 g), catalyst (0.1 g), *N,N*-dimethylformamide (3 mL), 373 K, 3 h ^b Anhydroglucose ^c SiO₂/Al₂O₃ = 90, JRC-Z-5-90H ^d SiO₂/Al₂O₃ = 25, JRC-Z- HB25

Table 2. One-pot synthesis of 5-hydroxymethylfurfural (HMF) from glucose using acids and bases^a

Entry	Base	Acid	Conversion /%	HMF selectivity /%
1	HT	Amberlyst-15	64, 73, ^b 60 ^c	38, 58, ^b 76 ^c
2	HT	Nafion NR50	60	27
3	HT	–	62	0
4	–	Amberlyst-15	69	0
5	–	HCl (pH 1)	>99	0
6 ^d	Piperidine	<i>p</i> -TsOH·H ₂ O	0	0

^a Reaction conditions: Glucose (0.1 g), HT (0.1 g), Amberlyst-15 (0.1 g), *N,N*-dimethylformamide (3 mL), 373 K, 3 h ^b Using 0.2 g of HT, 353 K, 9 h ^c Using 0.2 g of HT, 4.5 h. Amberlyst-15 was added after 2.5 h ^d Piperidine (0.2 mmol), *p*-Toluenesulfonic acid (0.07 mmol)

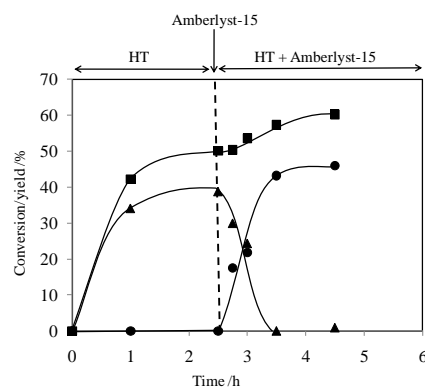


Fig. 2. Plot of glucose conversion (■), fructose yield (▲), and 5-hydroxymethylfurfural (HMF) yield (●) for the transformation of glucose as a function of reaction time. Amberlyst-15 was added after 2.5 h. Reaction conditions: glucose (0.1 g), hydrotalcite (0.2 g), Amberlyst-15 (0.1 g), DMF (3mL), 373 K.

Direct formation of HMF from glucose using solid acid and base in the one-pot reaction is shown in Table 2 (see ESI†). Remarkably, HMF synthesis from glucose was successfully achieved in the presence of both HT and Amberlyst-15 catalysts (entry 1).¹⁵ 64% of glucose conversion and 38% of HMF selectivity were obtained at 373 K for 3 h. Anhydroglucoses (AHG; 1,6-anhydro-β-D-glucopyranose and 1,6-anhydro-β-D-glucofuranose) and small amount of fructose were detected as by-products (AHG selectivity: 28 %, fructose selectivity 3%). Other compounds including retro-aldol condensation products such as erythrose and glycolaldehyde, and levulinic acid as rehydration of HMF were not detected. The mass balance was estimated to be 69 % from the sum of amount of detected products. Glucose conversion and HMF yield continually increased with increasing reaction time. HMF selectivity was almost the same after 3 h reaction. After 9 h, glucose was fully converted (>98%), resulting in HMF selectivity of 34% (see ESI†, Figure S1†). At 353 K for 9 h, HMF selectivity was 58% at high glucose conversion (73%). It should be noted that this one-pot reaction operates at lower temperature (353 K). Increasing the temperature results in the formation of anhydroglucose and oligomers by acid catalysis. The pair of HT and Nafion NR50 also produces HMF from glucose (Glucose conversion: 60%; HMF selectivity: 27%) (entry 2). As mentioned above, glucose was converted, not into HMF, but fructose, over only solid base (HT) (entry 3) and anhydroglucoses over only solid acid (Amberlyst-15) (entry 4). On the other hand, HMF was not formed using a liquid acid-base pair (entry 6). A control experiment confirmed the occurrence of sequential reactions, as the addition of solid acid (Amberlyst-15) into a solution containing a considerable amount of fructose (39%), which had formed from glucose in the presence of solid base (HT), resulted in the disappearance of fructose and simultaneous formation of HMF within 1 h (Figure 2). 76 % of HMF selectivity was obtained after 4.5 h (Table 2, entry 1) and anhydroglucoses and other products were not detected (mass balance: 76 %).

The acid-base catalysts were simply recovered by decantation, washing with the solvent (DMF, 6 mL) and

drying in vacuo overnight, and recycled for further reaction. It was confirmed that a pair of HT and Amberlyst-15 could be reused for this HMF synthesis at least three times without loss of activities (see ESI† Figure S2†). HMF was also produced in other polar aprotic solvents including *N,N*-dimethylacetamide and dimethyl sulfoxide in the presence of both HT and Amberlyst-15 (see ESI† Figure S3†). It should be noted that HMF was formed in acetonitrile which is a lower boiling solvent, much easier to separate HMF from solvent. Moreau et al. have examined isomerization of glucose over NaOH and solid base catalysts.¹³ Although high glucose conversion was observed at high concentration of NaOH (pH 12.8), selectivity to fructose was below 50%. In the pH range from 9.6 to 12.8, moderate basicity (pH 11.4) gave the highest selectivity of fructose though glucose conversion was about half to that in the case of pH 12.8. The carbonate form of HT also exhibited similar activity of NaOH solution with pH 11.4. The high selectivity of HMF using Amberlyst-15 could explain compared to Nafion NR50. Strong acidity of Nafion NR50 ($H_0 < -12$) affords to undesired by-products like humins. The pair of moderate basicity of HT and acidity ($H_0 = -2.2$) of Amberlyst-15 is considered to display high selectivity.

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 component monosaccharides. Amberlyst-15 is a powerful acid catalyst for the hydrolysis of disaccharides.³

Table 3. One-pot synthesis of 5-hydroxymethylfurfural (HMF) from mono- and disaccharides using HT and Amberlyst-15^a

Entry	Substrate		Conversion /%	HMF selectivity /%
1 ^b	Monosaccharide	Fructose	> 99	76
2 ^c		Glucose	73	58
3 ^d	Disaccharide	Sucrose	58	93
4 ^d		Cellobiose	52	67

^a Reaction conditions: Substrate (0.1 g), HT (0.1 g), Amberlyst-15 (0.1 g), *N,N*-dimethylformamide (3 mL) ^b 373 K, 3 h ^c Using 0.2 g of HT, 353 K, 9 h ^d 393 K, 3 h

The results of one-pot synthesis of HMF from disaccharides and monosaccharides using HT and Amberlyst-15 are shown in Table 3. HMF was produced from both fructose and glucose with high conversion and selectivity. 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. We used Amberlyst-15 and hydrotalcite without pretreatment for one-pot synthesis of HMF from disaccharides. It is considered that 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.

In conclusion, 5-hydroxymethylfurfural, one of the most important intermediates derived from biomass, was directly produced from monosaccharides (fructose and glucose) and disaccharides (sucrose and cellobiose) by a simple one-pot synthesis using a conventional solid acid and base under mild reaction conditions.

This work was supported by a Grant-in-Aid for Young Scientists (Start-up) (No. 20860038) of the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

Notes and references

School of Materials Science, Japan Advanced Institute of Science and Technology (JAIST), 1-1 Asahidai, Nomi, Ishikawa 923-1292, Japan.

Fax: +81-761-51-1625; Tel: +81-761-51-1611; E-mail:

⁴⁵ ebitani@jaist.ac.jp

† Electronic Supplementary Information (ESI) available: Experimental procedure, isomerization of glucose, recycle test, solvent effect. See DOI: 10.1039/b000000x/

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- Acid and base amounts of catalysts used are 4.8 mmol/g for Amberlyst-15 and 0.7 mmol/g for HT, respectively. 0.2 mmol of HMF was produced from 0.55 mmol of glucose in the presence of Amberlyst-15 (25 mg, acid amount; 0.12 mmol) and hydrotalcite (0.2g, base amount; 0.14 mmol) in DMF (3 mL) at 373 K for 3 h. TONs were estimated to be 1.7 and 1.4 for Amberlyst-15 and hydrotalcite, respectively.