

"One-Pot" Synthesis of 5-(Hydroxymethyl)furfural from Carbohydrates using Tin-Beta Zeolite

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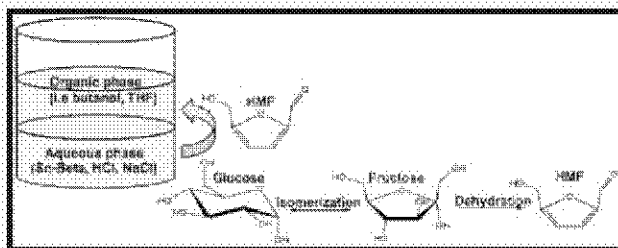
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S Supporting Information

ABSTRACT: Conversion of carbohydrates to 5-(hydroxymethyl)furfural (HMF) may provide a step forward toward achieving a renewable biomass-based chemicals and fuels platform. Recently, we reported that a tin-containing, high-silica molecular sieve with the zeolite beta topology (Sn-Beta) can efficiently catalyze the isomerization of glucose to fructose in aqueous media at low pH. Herein, we describe the combination of Sn-Beta with acid catalysts in a one vessel, biphasic reactor system to synthesize HMF from carbohydrates such as glucose, cellobiose, and starch with high efficiency. HMF selectivities over 70% were obtained using this "one-pot" biphasic water/tetrahydrofuran (THF) reactor system. The key to successfully achieving the conversions/selectivities reported is that Sn-Beta is able to convert glucose to fructose at pH near 1 and in saturated aqueous salt solutions.

KEYWORDS: Zeolite, HMF, carbohydrate conversion, glucose isomerization, heterogeneous catalysis



Biomass is being intensely investigated as feedstock for the production of the chemicals (such as biodegradable polymeric materials like polylactic acid) and transportation fuels of the future.^{1–3} Carbohydrates represent 75% of the annual renewable biomass.¹ One pathway that utilizes the conversion of carbohydrates to fuels and chemicals involves the production of 5-(hydroxymethyl)furfural (HMF). HMF is currently considered an important precursor to the production of high value polymers such as polyurethanes and polyamides, as well as for biofuels.^{4,5}

Glucose is the most abundant monosaccharide and the cheapest hexose making it a promising candidate as raw material for the production of HMF.⁶ One of the challenges of using glucose as a raw material is that the stability of the glucose ring makes processing difficult. It has been proposed that conversion of glucose to HMF can occur via isomerization of glucose to fructose in the presence of enzymes or base catalysts followed by the dehydration of fructose to HMF using acid catalysts (Scheme 1).⁶ Huang et al. have shown that combining enzymatic and acid catalysis to synthesize HMF from glucose can result in HMF selectivities of 70% at glucose conversions of 85%.⁷ Takagaki et al. have demonstrated that a combination of Amberlyst-15 (solid acid) and Mg–Al hydrotalcite (solid base) in *N,N*-dimethylformamide media can also be used to synthesize HMF from glucose.⁸ They were able to achieve HMF selectivities of 58% at glucose conversions of 73% at 180 °C. Furthermore, the use of metal chlorides in ionic liquids solvents has received attention.^{9–11} Zhao et al. have demonstrated that using CrCl₃ in 1-ethyl-3-methylimidazolium chloride [EMIM]Cl leads to HMF selectivities of 72% at glucose conversions of 94% at 80 °C.^{9,10}

Previous work on synthesizing HMF from glucose, some of which we outlined above, have several disadvantages because they employ systems that involve enzymes, numerous reactors, or environmentally unfriendly catalysts and solvents. For example "one-pot" ionic-liquid systems suffer from high separation costs, sensitivity to reaction conditions, and undesirable environmental effects. "One-pot" synthesis of HMF from glucose in aqueous media with high efficiency still remains a challenge. Here, we report an efficient "one-pot" synthesis of HMF from sugars using a tin-containing silica molecular sieve with the zeolite beta topology (Sn-Beta) in concert with acid catalysts. We find that HMF selectivities of over 70% are achieved from sugars using Sn-Beta and HCl in a biphasic (H₂O/tetrahydrofuran (THF)) system (Table 1, Entries 6, 8, 9). Our previous studies have shown that Sn-Beta zeolite facilitates the isomerization of glucose to fructose in aqueous media even at low pH.^{12,13} In this molecular sieve, the Sn atoms act as isolated Lewis acid centers and are responsible for the isomerization of glucose to fructose.^{12,13} Sn-Beta has also been shown to catalyze Meerwein–Ponndorf–Verley reduction of carbonyl compounds in methanol,^{14,15} and the production of lactate derivatives from monosaccharides in methanol.¹⁶

Sn-Beta zeolite and an acid catalyst, in this case HCl, were combined in aqueous media and tested for their activity toward conversion of glucose to HMF using single phase and a biphasic

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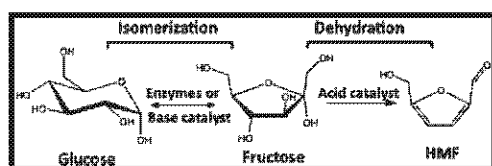
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Table 1. Results for Conversion of Glucose, Cellobiose, and Starch to HMF^a

entry	feed	system	catalyst	conv. [%]	HMF selec. [%]	time [min]	temp [°C]
1	glucose	single phase (H ₂ O)	Sn-Beta, HCl	45	6	90	160
2	glucose	biphasic (H ₂ O/1-butanol)	Sn-Beta, HCl	77	26	90	160
3	glucose	biphasic (H ₂ O/1-butanol/NaCl)	Sn-Beta	75	18	90	160
4	glucose	biphasic (H ₂ O/1-butanol/NaCl)	HCl	26	40	90	160
5	glucose	biphasic (H ₂ O/1-butanol/NaCl)	Sn-Beta, HCl	75	55	90	160
6	glucose	biphasic (H ₂ O/THF/NaCl)	Sn-Beta, HCl	79	72	70	180
7	glucose	biphasic (H ₂ O/THF/NaCl)	Ti-Beta, HCl	76	70	105	180
8	cellobiose	biphasic (H ₂ O/THF/NaCl)	Sn-Beta, HCl	36	36	40,60	180
9	starch	biphasic (H ₂ O/THF/NaCl)	Sn-Beta, HCl	75	69	40,60	180

^a Reaction Conditions: Glucose to tin molar ratio of 200, aqueous to organic phase volume ratio of 1:3, pH = 1 in HCl. Entries 1–7: Feed was 10 wt % glucose solutions. Entries 3–9: 0.35 g of salt in 1 g of water was added. Entry 8: Feed was 10 wt % cellobiose in H₂O. Entry 9: Feed was 0.1 g of starch added to 0.9 g of water. In entries 8 and 9 cellobiose and starch were first converted to glucose in the presence of H₂O and HCl at pH = 1 at 180 °C for 40 min. The reactor was then cooled down and Sn-Beta, salt and organic phase were added. The reactor was then heated at 180 °C for another 60 min.

Scheme 1. Schematic Representation of Reaction Pathway for Glucose Conversion to HMF

reactor systems (Table 1, entry 1 or 2, respectively). The single-phase system was composed of a mixture of glucose, Sn-Beta, and HCl in water, while the biphasic system contained an aqueous phase of glucose, Sn-Beta, HCl, and an organic phase, for example, 1-butanol. Detailed descriptions of the zeolite synthesis and reactor systems are provided in the Supporting Information. The data listed in Table 1, entries 1 and 2, clearly demonstrate that the use of a biphasic system results in higher glucose conversions and HMF selectivities at the same reaction time. The higher HMF selectivity obtained using the biphasic system is a consequence of the presence of a water-immiscible organic phase that allows for the extraction of HMF from the aqueous phase, thus preventing the quick degradation of HMF into undesired byproducts under aqueous acidic conditions.⁵ Furthermore, Table 1, entries 3–5 show that the combination of Sn-Beta zeolite with HCl result in higher HMF selectivity than a biphasic system with either Sn-Beta or HCl as catalyst. This is because both Sn-Beta and HCl are required to convert glucose to HMF, that is, Sn-Beta is necessary for the isomerization of glucose to fructose while HCl for the dehydration of fructose to HMF (Scheme 1).

To improve HMF selectivity, we explored the effects of adding inorganic salts to the aqueous phase of the biphasic systems containing Sn-Beta and HCl (Supporting Information, Figure S1). It has been previously shown that addition of inorganic salts to biphasic systems significantly improves the partitioning of HMF into the organic phase (i.e., the electrolytes alter the intermolecular bonding interactions between liquid components resulting in increased immiscibility between the aqueous and organic phases).^{4,17,18} Results in Supporting Information, Figure S1 clearly demonstrate that the selectivity to HMF significantly increases with the addition of the salt to the aqueous phase and suggest that the activity of Sn-Beta is not affected by the presence of the salt. It is remarkable that Sn-Beta can be so active in the presence of such high salt concentration. Sn-Beta is also stable and active in the presence of a number of different salts such as MgCl₂, KBr, and

KCl. The highest HMF selectivity was achieved using NaCl (Supporting Information, Figure S1). This result is consistent with previous reports showing that NaCl generates the highest extraction coefficient among the inorganic salts tested herein, thereby resulting in the most efficient extraction of HMF from the aqueous to the organic phase.¹⁷ The inorganic salts mainly contribute to the extraction of HMF from aqueous to the organic phase with minimal involvement in catalyzing the reactions. Reactions performed without Sn-Beta, but in the presence of salt and HCl result in glucose conversions (~30%) that are drastically lower than those obtained in the presence of Sn-Beta (~75%).

The effects of acid on the glucose conversion, HMF selectivity, and the stability of Sn-Beta were also analyzed (Supporting Information, Figure S2). Our results show that the addition of HCl (to give a pH = 1 solution) significantly improves HMF selectivity. This is not surprising since Sn-Beta mainly catalyzes the isomerization of glucose to fructose while HCl is responsible for the dehydration of fructose to HMF. Therefore, the addition of HCl should result in higher HMF yields. No reduction in glucose conversion is detected with the addition of HCl, suggesting that activity of Sn-Beta is not affected by the presence of the acid.

We have also investigated the effect of organic solvent type on the glucose conversion and HMF selectivity (Supporting Information, Figure S3). A number of solvents such as primary alcohols (1-butanol), secondary alcohols (2-butanol), and cyclic ethers (THF) were tested. The data provided in Supporting Information, Figure S3 show that the highest HMF selectivity (72%) is achieved using THF at 180 °C for 70 min. The higher HMF selectivities in THF are because THF has the highest partitioning coefficient, that is, results in highest partitioning of HMF from the aqueous to the organic phase.¹⁷ The 2-butanol system gave the lowest HMF selectivity.

Given that a THF/H₂O biphasic system containing Sn-Beta, NaCl and HCl resulted in the highest HMF selectivities, we analyzed the performance of this system over time. The data given in Figure 1 show the evolution of glucose conversions and HMF selectivities over time. We find that at low conversions (~10%) HMF selectivity exceeds 90%; at glucose conversions in the 60–90% range (60–80 min), selectivity values over 70% are achieved; and as the reaction time increases over 80 min, HMF selectivity decreases to values under 60%. The gradual decrease in HMF selectivity is likely due to the degradation/resinification

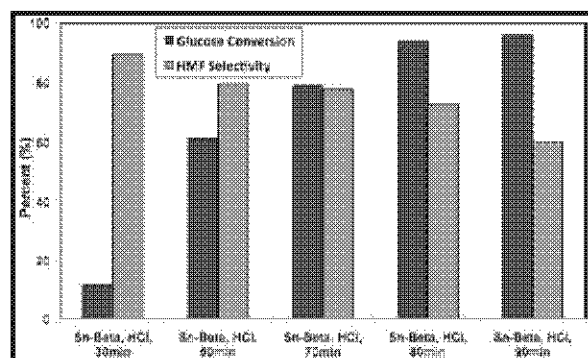


Figure 1. Conversion of glucose to HMF as a function of time using Sn-Beta and HCl in a biphasic H₂O/THF system at 180 °C. Reaction Conditions: Glucose to tin molar ratio of 200, 1:3 water to THF phase volume ratio, pH = 1 in HCl and operating temperature of 180 °C.

of HMF over time at high temperatures. We note that under these conditions no significant amount of fructose is detected suggesting that under these conditions the dehydration of fructose to HMF is fast.

Scanning electron microscopy (SEM) and powder X-ray diffraction (XRD) were used to analyze the morphology of the Sn-Beta zeolite before and after reactions in the presence of acid and salt. The results are included in the Supporting Information. X-ray diffraction data for the Sn-Beta zeolite before and after reaction in the presence of HCl and NaCl showed that no significant changes have occurred in the crystal structure of the zeolite under reaction conditions (Figure S5, Supporting Information). Similar results were obtained using SEM (Supporting Information, Figure S6). Furthermore N₂ adsorption studies show that the pore volume of Sn-Beta does not change when the material is exposed to either water at high temperatures, to water at low pH (HCl) and high temperatures, or to standard reaction conditions (see Supporting Information, Figure S4). While these characterizations provide a good start toward understanding the long-term behavior (and/or recyclability) of the Sn-Beta catalyst, much further work will be necessary to understand if this solid can be used at these conditions for extended reaction times.

The performance of Sn-Beta zeolite was compared to another Beta zeolite material containing a different Lewis acid center (Ti-Beta) in the conversion of glucose to HMF using a water/THF biphasic system. We find that Sn-Beta is more active than Ti-Beta, as it takes a longer time for the system catalyzed by Ti-Beta to reach the same glucose conversion as the system catalyzed by Sn-Beta. (Table 1, entries 6, 7). This result is consistent with our previous findings showing that Ti has a lower activity toward glucose isomerization.¹³

The robustness of Sn-Beta zeolite in synthesizing HMF from glucose opens up the possibility of using more complex carbohydrates such as starch and cellobiose as renewable raw materials. Starch is a glucose polysaccharide joined by easy to hydrolyze α -glycosidic linkages, commonly used as feedstock in first generation bioethanol facilities. On the other hand cellobiose is a glucose dimer joined by the difficult to hydrolyze β -glycosidic linkages, commonly found in cellulose, the most abundant component of biomass. Synthesis of HMF from cellobiose and starch involves their hydrolysis into their constituent glucose monomers in the presence of an acid or enzyme, followed by isomerization of glucose to fructose and subsequent dehydration of fructose to HMF. Table 1,

entries 8–9 show the results obtained using Sn-Beta and HCl for the conversion of cellobiose and starch to HMF. HMF selectivities of ~86% and 69% at cellobiose and starch conversion of ~73%, 75%, respectively, were achieved using a H₂O/THF biphasic system at 180 °C. These results are very promising since they show that Sn-Beta coupled with an acid catalyst can be used for conversion of complex carbohydrates to HMF.

■ ASSOCIATED CONTENT

S Supporting Information. Detailed description of the experimental methods, characterization techniques and additional reactor studies are provided. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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