Glucose isomerization in Dioxane/Water with Sn-β catalyst: improved catalyst stability and use for HMF production

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Glucose isomerization in Dioxane/Water with Sn-β catalyst: improved catalyst stability and use for HMF production

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Qiang Guo,[a+]* Limin Ren,[a+] Saeed M. Alhassan[d] Michael Tsapatsis[a,b,c]*

Abstract: The stability of zeolite Sn-Beta (Sn-β) was greatly improved for glucose isomerization to fructose and fructose yield of 41.5 % has been obtained when dioxane/water was used as solvent. The effect of dioxane/water solvent mixtures for fructose dehydration on Amberlyst-131 was also studied and it was found that small amounts of water in dioxane increase the yield of HMF (up to 74 %) by limiting the formation of oligomers like Difructose Anhydride (III). 56 % yield of HMF from glucose, maltose, trehalose or cellobiose and 60 % from sucrose were produced when hydrolysis of disaccharides, glucose isomerization and fructose dehydration were coupled in a mixture of dioxane/water (5 wt%).

Hydroxymethylfurfural (HMF) is a versatile biomass-derived platform chemical[1-7] that can be produced via glucose to fructose isomerization[8-11] followed by fructose dehydration.[12-14] Lewis acids are selective glucose isomerization catalysts,[9-10,15-19] while Brønsted acids can be used for fructose dehydration to HMF.[12,20-21]

For glucose isomerization, Sn-β zeolite has been studied extensively as a Lewis acid catalyst[9-10,22-24] but it has been documented that in water[19] and in alcohol solvents[25-26] it can deactivate under reaction conditions within minutes. Hammond and co-workers prevented Sn-β deactivation in methanol by adding small amounts of water to mitigate Si-OR and Sn-OR formation preserving a desirable level of Si-OH and Sn-OH active sites in their relatively hydrophilic catalyst, prepared by stannation of dealuminated zeolite-β.[25] Gounder and co-workers attributed deactivation in pure water solvent to the progressive hydrophilization of their initially highly hydrophobic Sn-β (synthesized in fluoride media).[27] They suggest that hydrolysis of siloxane bridges and the Si-OH groups lead to increased rates initially, when present in small amounts, but at higher amounts, the intrapore water, eventually, entropically destabilize the hydride-shift transition state of glucose to fructose isomerization, reducing the observed reaction rates. The above studies as well as other reports that zeolite catalysts can be modified by solvents like alcohol and water,[28-29] highlight the importance of solvent not only for affecting phase equilibria (sugar and product solubility and micropore adsorption) and the relative stabilization/destabilization of reactants, intermediates, transition states and products,[30-32] but also as a catalyst modifier by reacting with the Sn-β framework.

The Brønsted acid catalyzed fructose dehydration has been studied in various solvents and solvent mixtures, also highlighting the importance of the solvent for this reaction. In addition to the use of biphasic systems enabling HMF extractive removal for increased yield and its coupling with glucose isomerization,[33-35] single phase solvent mixtures have also been investigated.[21,36-37]. Aellig and Hermans reported that addition of dimethyl sulfoxide (DMSO), which is known to increase the rate of fructose conversion to HMF and suppress the formation of condensation by-products,[12] would increase the selectivity of HMF when fructose dehydration was performed in dioxane.[38] Dumesic, Neurock and co-workers have shown that dioxane-water and other one-phase organic-water mixtures are effective in improving activity and suppressing by-product formation; increased HMF yields using homogeneous and heterogeneous catalysts, observed in DMSO, dioxane, tetrahydrofuran (THF), gamma-valerolactone (GVL) and other solvent mixtures with water were attributed to the differences in solvation stabilization of the reactant and transition states.[39-42].

Here, we report that at a certain water content (ca. 2.5-5%) of a dioxane/water mixture, hydrophobic Sn-β (made in a

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[a] *Department of Chemical Engineering and Materials Science University of Minnesota, 421 Washington Ave SE, Minneapolis, MN, 55455, USA.*
[b] *Department of Chemical and Biomolecular Engineering & Institute for NanoBioTechnology Johns Hopkins University 3400 N. Charles Street, Baltimore, MD 21218, USA*
[c] *Applied Physics Laboratory Johns Hopkins University 11100 Johns Hopkins Road, Laurel, MB 20723, USA*
[d] *Department of Chemical Engineering, Khalifa University of Science and Technology, P. O. Box 127788, Abu Dhabi, UAE*
† These authors contributed equally.
Email: E-mail:qguo@umn.edu; tsapatsis@jhu.edu

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x fluoride containing mixture) is a remarkably stable glucose to fructose isomerization catalyst achieving fructose yield (ca. 41.5%) close to that of the immobilized enzymes.[8,43] Although, it is known that even small amounts of water can decrease the selectivity of fructose conversion to HMF by accelerating the degradation of 5-HMF to levulinic acid and formic acid,[38,44-46] motivated by the findings of Dumesic and co-workers on improved fructose dehydration rates and yield in dioxane/water,[41] we also explore the one-pot synthesis of HMF from glucose and other saccharides using Sn-β combined with Amberlyst 131.

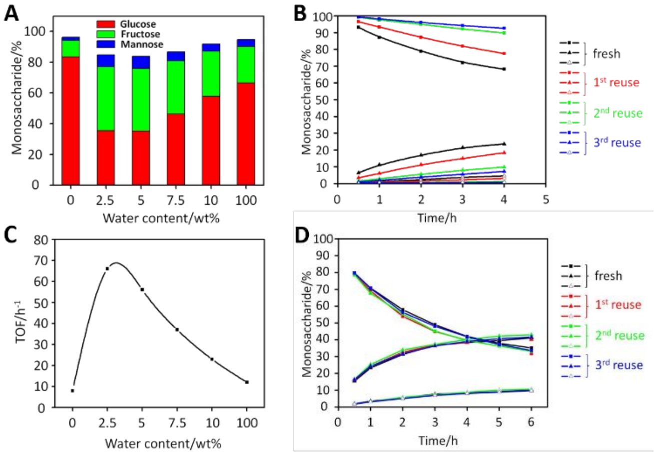

Figure 1 A) Glucose, fructose and mannose percentages (based on initial amount of glucose) for glucose isomerization using Sn-β in dioxane with different amounts of water after 4 hrs at 90 °C; B) Glucose (solid square), fructose (solid triangle) and mannose (hollow triangle) percentages (based on initial amount of glucose) for glucose isomerization on fresh and reused Sn-β in water; C) TOF calculated within the first 15 mins of reaction; D) Glucose (solid square), fructose (solid triangle) and mannose (hollow triangle) percentages (based on initial amount of glucose) for glucose isomerization on fresh and reused Sn-β in dioxane/water (5 wt% water). Reaction conditions: 50 mg glucose, 4.95 g solvent, 20 mg Sn-β, 90 °C.

When glucose isomerization was performed in pure water using Sn-β as the catalyst, the product distribution is similar to the earlier reported behavior (Figure 1A).[9,19] The catalyst was then used four times for the glucose isomerization in water and it was found that its activity gradually decreased (Figure 1B), in agreement with the earlier findings that Sn-β deactivates during the glucose isomerization in water.[19] Dioxane is a low boiling-point H_2O-miscible solvent from which it has been suggested that HMF can be separated in a cost-effective way.[38] When the glucose isomerization was performed in pure dioxane, 83.6 % glucose, 10.6 % fructose and 2.1 % mannose were obtained after 4 hrs (Figure 1A). When water was added as the co-solvent, the fructose yield was greatly enhanced. Yields comparable with those obtained from xylose isomerase (41.5 % fructose and 9 % mannose) were obtained after 4 hrs in the presence of 2.5 wt% water. This could be due to increased density of open Sn sites in the presence of water.[47-49] Figure 1C shows the turnover frequency (TOF) of glucose isomerization to fructose on Sn-β with different contents of water in dioxane. TOF increased from 8 to 55 and from 8 to 66 h^{-1} when 5 and 2.5 wt% water was used, respectively, and gradually decreased with increasing amount of water (Table S1).

The TOF of 8 h^{-1} at 90 °C corresponds to ca. 0.4×10^{-4} mol fructose (mol Sn*s*(mol glucose m^{-3}))$^{-1}$, which is in agreement with the ca. 0.6×10^{-4} mol fructose (mol Sn*s*(mol glucose m^{-3}))$^{-1}$ reported at 100 °C.[27] 66 h^{-1} corresponds to ca. 4×10^{-4} mol fructose (mol Sn*s*(mol glucose m^{-3}))$^{-1}$ which is approximately equal to the highest 1st order isomerization rate constant obtained after 10 min exposure to liquid water.[27] However, unlike in pure water,[27] no loss of activity is observed in dioxane/water. Sn-β was used four times for the glucose isomerization in dioxane/water (5 wt%) and its activity remains unchanged (Figure 1D).

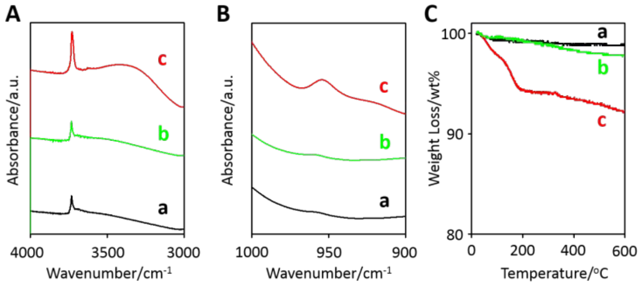

Figure 2. A,B) FTIR spectra; and C) TGA profiles of: fresh Sn-β (a); Sn-β used three times in dioxane/water (5 wt% water) solvent (b); and Sn-β used three times in pure water (c).

The catalysts were analyzed by FTIR and TGA after the third run. Figure 2A shows the hydroxyl IR region of the fresh and used Sn-β catalysts. The intensity of the peak at 3735 cm^{-1}, which arises from the isolated silanol groups,[50] increased significantly after the catalyst was used three times in pure water but it remained unchanged in dioxane/water (5 wt%) mixture. Moreover, an intense and broad band centered at 3400 cm^{-1} assigned to H-bonded silanols and a peak at 960 cm^{-1}, which was ascribed to Si-O vibration of the silanol groups[29,50] that appeared after Sn-β was used in pure water are not visible in dioxane/water (5 wt%) (Figures 2A and B). Figure 2C shows the TGA profiles of the fresh and used Sn-β catalysts in different reaction media and further supports that Sn-β can be hydroxylated when glucose isomerization is performed in pure water, while it remains unaltered when the reaction is performed in dioxane/water (5 wt%) mixture. The weight losses for the fresh Sn-β and the Sn-β used in dioxane/water (5 wt%) mixture before 200 °C are lower than 1 %, indicating their hydrophobicity. But the weight loss of the spent Sn-β in water in this region is about 6 %. This finding is in agreement with the IR data and confirms that that Sn-β after being used in water becomes more hydrophilic. It is also in agreement with the findings of Gounder and co-workers[27] that Sn-β hydrophilization is correlated with loss of catalytic activity in water. In contrast, with a small amount of water (2.5-5 wt%) in dioxane the improved activity remains unchanged and correlates with preservation of its hydrophobicity. XRD, SEM and elemental analysis do not reveal significant changes for Sn-β before and after use (Figures S1 and S2).

Having established superior glucose isomerization activity and stability of Sn-β in dioxane-water, we attempted to combine glucose isomerization with fructose dehydration in one pot using a Brønsted acid catalyst like Amberlyst-131. Dumesic and co-workers have shown that homogeneous and heterogeneous Brønsted acid catalysts in water/organic solvent mixtures, including 10 % water in dioxane exhibit superior activity and yield to HMF.[39-41] We therefore, anticipated to combine the beneficial role of water in dioxane for both isomerization and dehydration.

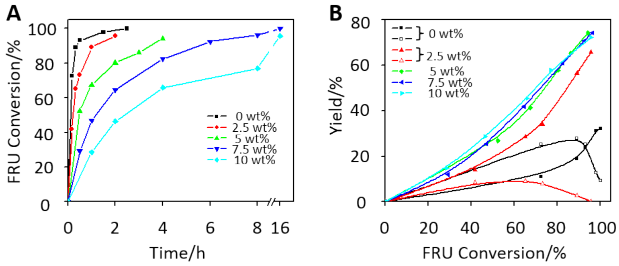

Figure 3. Fructose dehydration in dioxane with different water contents using Amberlyst-131: A) FRU conversion versus reaction time; and B) HMF and Difructose anhydride (III) yield versus FRU conversion (Solid symbol: HMF yield; Hollow symbol: Difructose anhydride (III)). Reaction conditions: 50 mg fructose, 4.95 g solvent, 40 mg Amberlyst-131, 90 °C

In pure dioxane, high fructose conversion can be achieved but HMF selectivity is low (Figure 3). This is in agreement with the earlier report by Aellig and Hermans.[38] Unidentified byproducts and Difructose Anhydride (III) were observed by HPLC. The Difructose Anhydride (III) yield was even higher than that of HMF when the fructose conversion was lower than 90 % (Figure 3B). This indicates that fructose oligomerization is a key side-reaction when fructose dehydration was done in pure dioxane. The addition of water, which is miscible with dioxane and a product of the oligomerization side-reactions, could deter the formation of oligomers. The conversion of fructose on Amberlyst-131 gradually decreased as water content increased (Figure 3A) while the yield of Difructose Anhydride (III) decreased and was kept at a low level (Figure 3B). For example, the conversion of fructose drops from 98 % (1.5 h) to 46 % (2 h) when the solvent consists of 10 wt% of water in dioxane, while the yield of Difructose Anhydride (III) was lower than 10 % when 2.5 % water was added and it is negligible (< 3 %) when more water was used. As a result, the yield of HMF increased from 30 % to 65 % when 2.5 wt% water was added and to 74 % when 5 to 10 wt% water was used (Figure 3B). We conclude that water in dioxane limits the oligomerization of fructose and promotes the formation of HMF on Amberlyst-131.

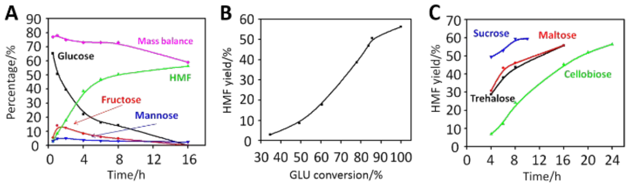

Figure 4. Saccharide conversion to HMF using Sn-β and Amberlyst-131 in dioxane/water solvent (5 wt% water): A) Monosaccharide and HMF percentages (based on initial amount of glucose) versus reaction time; B) HMF yield versus glucose conversion: and C) HMF yield versus reaction time from sucrose, maltose, trehalose and cellobiose in one-pot. Reaction conditions: 50 mg glucose/47.5 mg disaccharide, 4.7 g dioxane, 0.25 g water, 20 mg Sn-β, 40 mg Amberlyst-131, 90 °C.

Considering the above findings for glucose isomerization and fructose dehydration, we synthesized HMF in one-pot from glucose in the mixture of dioxane/water. 5 wt% water in dioxane was used as the reaction solvent to achieve optimal isomerization and dehydration performance for Sn-β and Amberlyst-131, respectively. Figure 4A shows the product distribution versus reaction time. Glucose was gradually converted and maximum fructose yield was obtained in 1 h. Mannose yield was at a low level over the entire course of the reaction. 60 % HMF selectivity was obtained at 85 % conversion of glucose (Figure 4B) after 8 hrs and finally, the HMF yield reached 56 % after 16 hrs. The recyclability of the catalysts was tested and despite its drastically improved stability for glucose isomerization in dioxane/water, the Sn-β catalyst still deactivates when used for one-pot production of HMF from glucose. This deactivation is probably due to the deposition of dehydration products as suggested by the color change of Sn-β and the full recovery of catalytic activity by calcination (Figure S3).

Disaccharides were also used as the starting materials for HMF production (Table S3). Water can be used to hydrolyze the disaccharides using the Brønsted acid Amberlyst-131. Sucrose will be cleaved to glucose and fructose, while trehalose, maltose and cellobiose will all be converted to glucose before isomerization and dehydration. Figure 4C shows the HMF yield versus reaction time from different disaccharides catalyzed by Sn-β and Amberlyst-131 in one-pot. The maximum yields of HMF from maltose, trehalose and cellobiose are all around 56 %, which are similar as that obtained from glucose. The HMF formation rate from cellobiose is much lower compared with other disaccharides. This comes from the fact that the hydrolysis rate of cellobiose is lower at the same conditions.[51] Sucrose consists of one glucose and one fructose and the maximum HMF yield from it is 60 %. We conclude that the hydrolysis process of these disaccharides produced glucose selectively and the byproducts were almost all formed during the process of glucose isomerization and fructose dehydration.

In summary, the effect of dioxane/water solvent mixtures for glucose isomerization and fructose dehydration on Sn-β and Amberlyst-131, respectively, were studied. In dioxane/water mixtures (2.5-5 wt%), Sn-β attains higher isomerization catalytic activity compared to those in either pure solvents or mixtures thereof, and this activity is retained upon multiple uses in contrast to the well-established deactivation observed in water. A higher yield of fructose (41.5 % vs 23.6 % in pure water) can be obtained in the mixture of dioxane and water. Addition of water in dioxane can also increase the yield of HMF (up to 74 %) from fructose dehydration over Amberlyst-131 by limiting the formation of oligomers like Difructose Anhydride (III). By coupling hydrolysis of disaccharides, glucose isomerization and fructose dehydration in a mixture of dioxane/water (5 wt%), 56 % yield of HMF was achieved using glucose, maltose, trehalose or cellobiose and 60 % if starting from sucrose.

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Conflicts of interest

There are no conflicts to declare.

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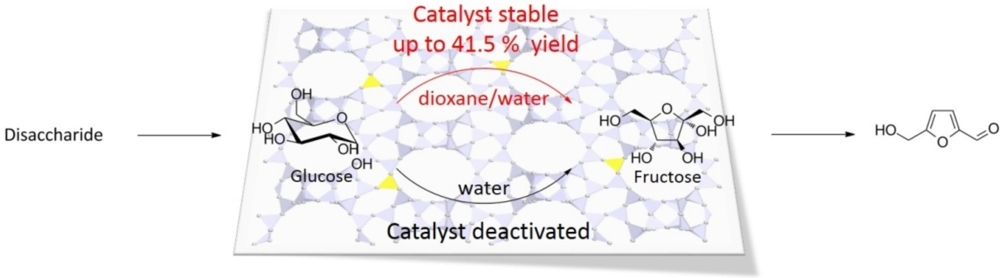

The stability of zeolite Sn-*β* was greatly improved for glucose isomerization to fructose when dioxane/water was used as solvent, and fructose yield (ca. 41.5%) close to that of the immobilized enzymes has been achieved.

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