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Catalysis

Production of Hydroxyl-rich Acids from Xylose and Glucose Using Sn-BEA Zeolite

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Sn-BEA zeolite is known to catalyze the aldose-to-ketose isomerization of xylose and glucose; however, the selectivity to pentose and hexose isomers is not stoichiometric, suggesting the formation of other products. In the present study, we have observed near-complete conversion of all pentose and hexose isomers when xylose and glucose were reacted in the presence of Sn-BEA at 140 °C and 200 °C, respectively. The previously unidentified products were identified by nuclear magnetic resonance and mass spectrometry to be hydroxyalkanoic acids and their derivatives. The hydroxyl-rich acids comprise a significant fraction of the converted sugars and are potential monomers for the synthesis of hyper-crosslinked, biodegradable polymers.

Lignocellulosic biomass is an attractive and renewable feedstock for producing chemicals.^[1,2] The two major components of lignocellulosic biomass are cellulose and hemicellulose, which together comprise as much as 80 dry wt% of this feedstock.^[3] These carbohydrates can be hydrolyzed to their constituent pentose and hexose sugars, xylose and glucose. Subsequent dehydration of xylose and glucose produces furfural and 5-(hydroxymethyl)furfural (HMF), respectively, products that can be further converted to fuels, lubricants, and other commodity chemicals.^[4-6] The selective dehydration of pentoses and hexoses to furanics has been shown to be best carried out using a combination of Lewis acid and Brønsted acid catalysts.^[7,8] Brønsted acids catalyze the dehydration of sugars to furanics, whereas Lewis acids catalyze the isomerization of the most prevalent aldoses (xylose and glucose) to their ketose forms (xylulose and fructose),^[9-14] which are much more susceptible to dehydration than their respective aldoses.^[15]

One of the most promising Lewis acid catalysts for the aldose-to-ketose isomerization of xylose and glucose is Sn-BEA, a Beta zeolite containing framework Sn atoms.^[8-11,14] The hydrophobicity of this catalyst is an attractive feature that enables isomerization of pentose and hexose sugars to be carried out in aqueous solution. However, prior studies have shown that while complete consumption of xylose and glucose can be achieved at temperatures of 100 °C and above, the selectivity to the isomers of the two sugars is incomplete, suggesting the formation of additional products.^[8-10] The objective of the present study was to identify the products not accounted for in previous investigations and to suggest the reaction pathways by which they might be formed. Near-complete conversion (> 98% in both case) of all isomers of pentose and hexose sugars was observed when xylose and glucose were reacted in the presence of Sn-BEA for 1 h at 140 °C and 200 °C, respectively. The products are divided into four categories – hydroxyalkanoic acids and their derivatives, furanics and their derivatives, products of retro-aldol splitting of the sugars, and humins. For xylose, the products were 2,4,5-trihydroxypentanoic acid and its derivatives (46%), furfural (3%), lactic acid (9%), and humins (40%). For glucose, the products were 2,4,5,6-tetrahydroxyhexanoic acid and its derivative (14%); HMF, levulinic acid, and formic acid (27%); lactic acid and 2-hydroxybut-3-enoic acid (24%); and humins (33%).

A representative high-performance liquid chromatography (HPLC) chromatogram of the products of xylose reaction after 0, 10, and 120 min over Sn-BEA in water at 140 °C is shown in Figure 1. Peaks A, B, and C are attributable to xylose, lyxose, and xylulose. In addition to these expected products, two peaks, labeled D and E, were observed. Product analysis by liquid chromatography-mass spectrometry (LC-MS) showed the [M-H]⁻ m/z ratios for these peaks to be 149.0457 and 131.0348, respectively. The m/z ratio of peak D is identical to that of the pentose isomers: xylose, lyxose, and xylulose, indicating that the product represented by peak D and these pentose isomers have the same molecular weight. The m/z ratio of peak E is 18.0109 lower than that of peak D, suggesting that the product represented by peak E results from losing one molecule of water from an isomer of xylose. HPLC was used to divide the solution of reaction products into fractions each representing 15 s of retention time in the column. These fractions were then analyzed by heteronuclear single quantum coherence two-dimensional nuclear magnetic spectroscopy (HSQC 2D-NMR), and by this means peak D was identified as 2,4,5-trihydroxypentanoic acid and peak E as 2,5-dihydroxypent-3-eno-

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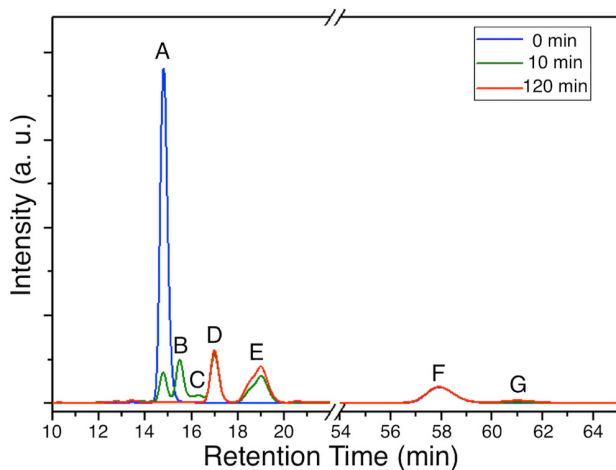
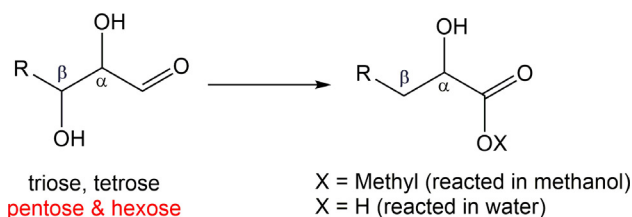


Figure 1. HPLC chromatogram of products after reacting xylose with Sn-BEA at 140 °C for 0, 10, and 120 min (A: xylose, B: lyxose, C: xylulose, D: 2,5-dihydroxypent-3-enoic acid, E: racemic 2,4,5-trihydroxypentanoic acid and lactic acid, F: 1,6-hexanediol as internal standard, G: furfural).

ic acid, as described in the SI. Gas chromatography-mass spectrometry (GC-MS) analysis also revealed a trace amount of 3-hydroxy-5-(hydroxymethyl)dihydrofuran-2(3H)-one, which was not observed by HPLC. We refer to these three products (i.e., the hydroxypentanoic acid and its two observed derivatives) collectively as HPAs. Similar products were formed upon reaction of glucose over Sn-BEA at 200 °C, as shown in Figure S5. In this case the new products were 2,4,5,6-tetrahydroxyhexanoic acid and its derivative 5-(1,2-dihydroxyethyl)-3-hydroxydihydrofuran-2(3H)-one (also known as 3-deoxy- γ -lactones, or DGL),^[16] which we refer to collectively as HHAs. The last of these products was recently discovered during the reaction of glucose over Sn-BEA in methanol.^[16]

The formation of the hydroxyalkanoic acids in water resembles the SnCl₄-catalyzed formation of methyl-4-methoxy-2-hydroxybutanoate (MMHB) from erythrulose in methanol.^[17] The formation of C₆ hydroxyalkanoates during Sn-BEA catalyzed reaction of glucose in methanol has also been reported recently.^[16] These findings, together with our observations, suggest that cationic Sn centers in the zeolite facilitate the replacement of the hydroxyl group in aldoses by a hydrogen atom on the β carbon and the subsequent conversion of the aldehyde group to a carboxylic acid or ester, depending on the solvent, as illustrated in Scheme 1.^[16,17] The hydroxyalkanoic acids can



Scheme 1. Isomerization of C₃-C₆ aldoses to acids or esters.

then undergo dehydration to form either alkenoic acids or furanone esters. Figure 2 shows the conversion of pentoses (as

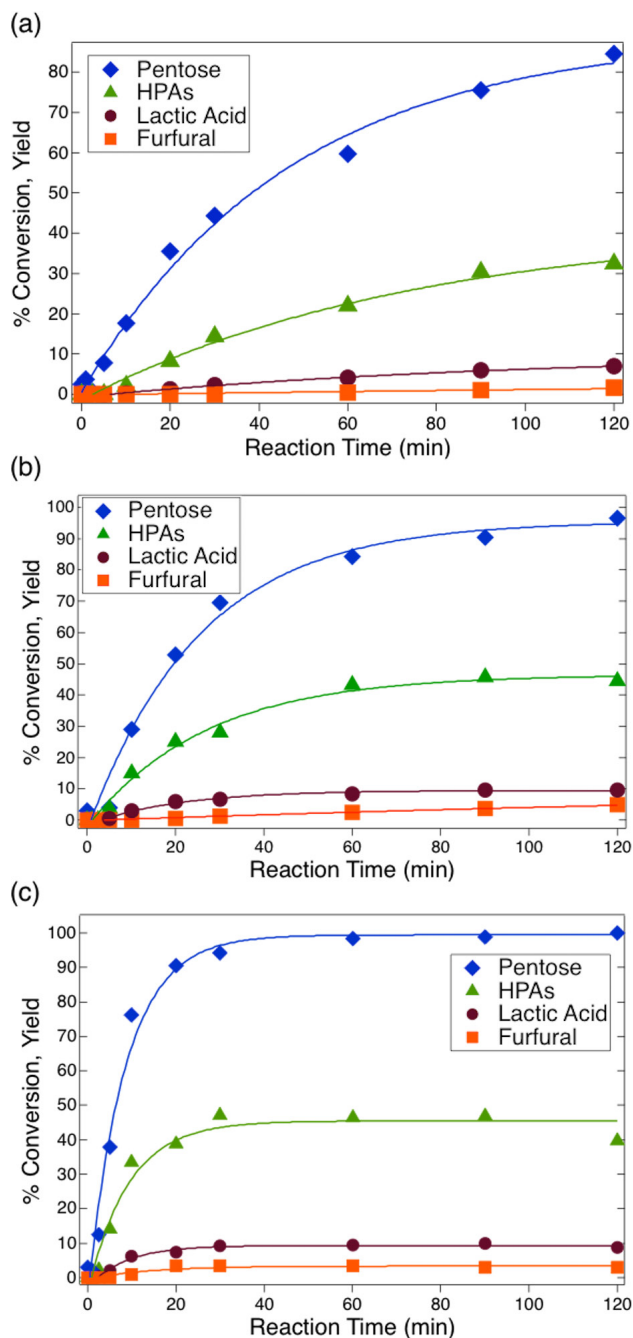


Figure 2. Conversion of pentose and yields of identified products at (a) 100 °C, (b) 120 °C, and (c) 140 °C.

defined in the SI) and the yields of all identifiable products (i.e., HPAs, lactic acid, and furfural) as a function of reaction time for the reaction of xylose over Sn-BEA at 100 °C, 120 °C, and 140 °C. We report the yields of HPAs collectively in Figure 2 for conciseness; separate plots of components of this group are shown in Figure S14. A small amount of furfural (less than 3% yield) was observed in these reactions, despite the absence of any added

Brønsted acid. It was hypothesized that the formation of furfural could be catalyzed by the acids formed in the reactions (i.e., HPAs and lactic acid).^[18] To test this idea, an aqueous solution of xylose was heated in the presence of either lactic acid or HPAs at 140 °C, using the same concentrations of those acids that were observed in the reactions using Sn-BEA. Very little furfural (less than 1%) was observed, suggesting that the formation of furfural is not catalyzed by the HPAs or the lactic acid formed in the reaction. Therefore, it is more likely that furfural formation is catalyzed by the weak Brønsted-acid $\equiv\text{Sn-OH}$ and/or silanol groups of open Sn sites in the zeolite framework, which have been shown to form upon hydrolysis of a $\equiv\text{Sn-O-Si}\equiv$ linkage.^[19,20] In support of this conclusion, we note that weak Brønsted-acid sites were observed in our samples of Sn-BEA by Fourier transform infrared spectroscopy (FTIR) of adsorbed pyridine and 2,6-ditertbutylpyridine (see SI). It should be noted that while strong Brønsted-acid sites are most often used to catalyze the formation of furfural, weak Brønsted acids have also been shown to catalyze this reaction.^[21,22] We also carried out reactions of HPAs with 3 equivalents of HCl to see whether additional Brønsted acidity would convert the HPAs to furfural. We heated xylose over Sn-BEA at 140 °C for 2 h to produce HPAs, removed the zeolite and solid waste by centrifuging the resulting solution, and added HCl to the supernatant, which we then heated to 140 °C for 3 h. This experiment showed negligible change in the concentration of HPAs, demonstrating that the HPAs are stable to the level of HCl used and do not form furfural after 3 h at 140 °C.

We found that under similar conditions, hexoses did not convert as readily as pentoses, and consequently experiments with hexoses were carried out at higher temperatures: 150 °C, 175 °C and 200 °C. The conversion of hexoses (as defined in the SI) and the yields of identifiable products (i.e., HHAs, lactic acid, HMF, and formic acid) are given in Figure 3 as functions of reaction time. We show the yields of HHAs together in Figure 3 because the peaks corresponding to the two molecules overlapped significantly in the HPLC chromatograms and we were unable to resolve them (see Figure S5). Our estimates for separated yields of HHAs are plotted in Figure S15. In addition to the products shown, small amounts of levulinic acid and 2-hydroxybut-3-enoic acid were detected. The yields of these products are not shown in Figure 3 because they are very low, reaching maximum values of 3.0% and 2.6%, respectively, at 200 °C. The imbalance between the yields of levulinic acid and formic acid observed in this study has been observed before and was attributed to the tendency of levulinic acid to undergo cyclization to form α -angelica lactone.^[23] However, no evidence was found in the present study for the formation of α -angelica lactone. An interesting observation is that for reactions carried out at 150 °C, 175 °C, and 200 °C, the selectivity to HHAs measured after 2 h is lowest at 175 °C (see Figure S16). Conversely, the selectivity to humins reaches a maximum at the same temperature. We do not understand the reason for this pattern but suspect that it may have to do with the concentration and reactivity of various components present in the reaction mixture and the way in which these factors contribute to the formation of humins. Considerably more work would need to be carried

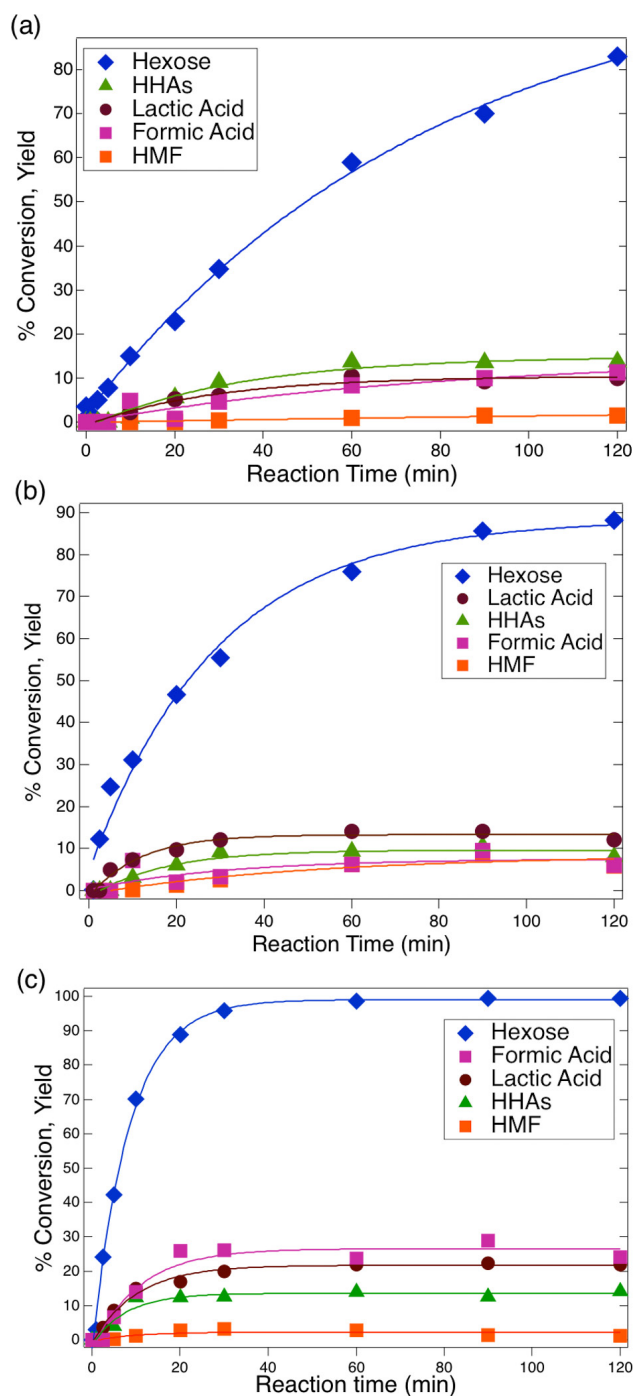


Figure 3. Conversion of hexose and yields of identified products at (a) 150 °C, (b) 175 °C, and (c) 200 °C. Yields of levulinic acid and 2-hydroxybut-3-enoic acid are not shown because their relatively low magnitude, reaching maximum values of 3.0% and 2.6% at 200 °C.

out in order to determine whether this hypothesis is correct.

In contrast with the results for the reactions of pentoses presented in Figure 2, in which HPAs were the leading products, Figure 3 does not show a clearly predominant hexose-derived product. However, it is worth noting that formic acid forms via hydrolysis of HMF, so the yield of formic acid plus

HMF should represent the total yield of furanics. As mentioned above, furanics form via a reaction pathway that is different from that by which other products are formed. We conducted an additional experiment with xylose at 200 °C, to compare the yield of furfural from pentoses to that of HMF and formic acid from hexoses under the same conditions. After 2 h, we observed that the yield of furfural (11 %) was much lower than the combined yield of HMF and formic acid (25%). For both pentoses and hexoses, the ketose form (xylulose and fructose, respectively) undergoes dehydration more readily to form furanics.^[24,25] We also observed a lower proportion of ketoses among the pentose isomers than the hexose isomers (see Figure S17) consistent with our observation of a lower yield of furfural from pentoses than HMF and its degradation products from hexoses.

The use of an extracting agent increased the yield of HPAs and furfural. The experiments presented in Figure 2c were repeated but with toluene used as an extracting agent in a 1:2 water:toluene volume ratio. The yield of HPAs after 2 h increased from 40% to 58% (the yield of 2,4,5-trihydroxypentanoic acid increased from 21% to 27%, while the yield of 2,5-dihydroxypent-3-enoic acid increased from 19% to 31%), while the yield of furfural increased from 3% to 17%, the yield of humins decreased from 49% to 11%, and the yield of lactic acid slightly increased from 8% to 13%. Previous studies have suggested that in situ extraction of furfural prevents its further reaction with intermediates derived from sugars to form humins.^[23,26–28] The production of HPAs also benefits from the furfural extraction because fewer pentose molecules are converted to humins, allowing more of the pentose to be converted to HPAs.

Scheme 2 illustrates the proposed pathways by which xylose and glucose are converted to the observed products in water when catalyzed by Sn-BEA. We hypothesize, based on the current literature,^[16–18,29–32] that Sn-BEA isomerizes the sugars between their aldose and ketose forms, and then converts them into smaller molecules via retro-aldol splitting. Pentoses are fragmented into glycolaldehyde and a triose (either glyceraldehyde or dihydroxyacetone).^[31] A very similar pathway applies to hexoses: fructose is split into two trioses (glyceraldehyde and dihydroxyacetone) while glucose and mannose form glycolaldehyde and a tetrose (2,3,4-trihydroxybutanal).^[17–18] The trioses can be interconverted by Sn-BEA and can also be dehydrated and rehydrated to produce lactic acid (see Scheme 1).^[29,31] Likewise, the tetrose fragmented from glucose and mannose can be dehydrated and rehydrated (see Scheme 1) to form 2,4-dihydroxybutanoic acid, which is further dehydrated to form 2-hydroxybut-3-enoic acid.^[17–18] The work reported here suggest that HPAs and HHAs are formed by dehydration and rehydration of C₅ or C₆ aldoses without retro-aldol splitting and subsequent dehydration to form hydroxyalkenoic acids or saturated furanone esters.

In summary, we have identified new xylose- and glucose-derived products: 2,4,5-trihydroxypentanoic acid, 2,5-dihydroxypent-3-enoic acid, and 3-hydroxy-5-(hydroxymethyl)dihydrofuran-2(3H)-one from xylose; and 2,4,5,6-tetrahydroxyhexanoic acid and 5-(1,2-dihydroxyethyl)-3-hydroxydihydrofuran-2

(3H)-one from glucose. By using toluene as an extracting agent, we were able to increase the yield of HPAs and furfural. This work suggests that by analogy to trioses and tetroses, pentoses and hexoses can also undergo a dehydration and rehydration to form carboxylic acids.

It should be noted that the HPAs and HHAs discovered in this study could be used as monomers for the synthesis of hyperbranched polymers. Typical degradable polyesters, e.g. poly(lactic acid-co-glycolic acid)s (PLAGAs), are commonly used for sutures, bone prostheses, and drug delivery systems.^[33–38] Because these polyesters are hydrophobic, their biocompatibility can be improved by copolymerizing them with functionalized molecules such as gluconic acid.^[33–34,37–41] The hydroxyalkanoic acids and hydroxypentenoic acid reported here should be similarly useful as co-monomers, since they bear very similar molecular structures to gluconic acid. Additionally, the hydroxypentenoic acid has a C=C bond, which increases its flexibility for further functionalization and cross linking. We note as well that the furanone esters observed in this study could also be used as monomers for polymer synthesis. These observations suggest that further work on the synthesis of HPAs and HHAs is warranted given their potential use as monomers for the synthesis of hydrophilic, biodegradable polymers.

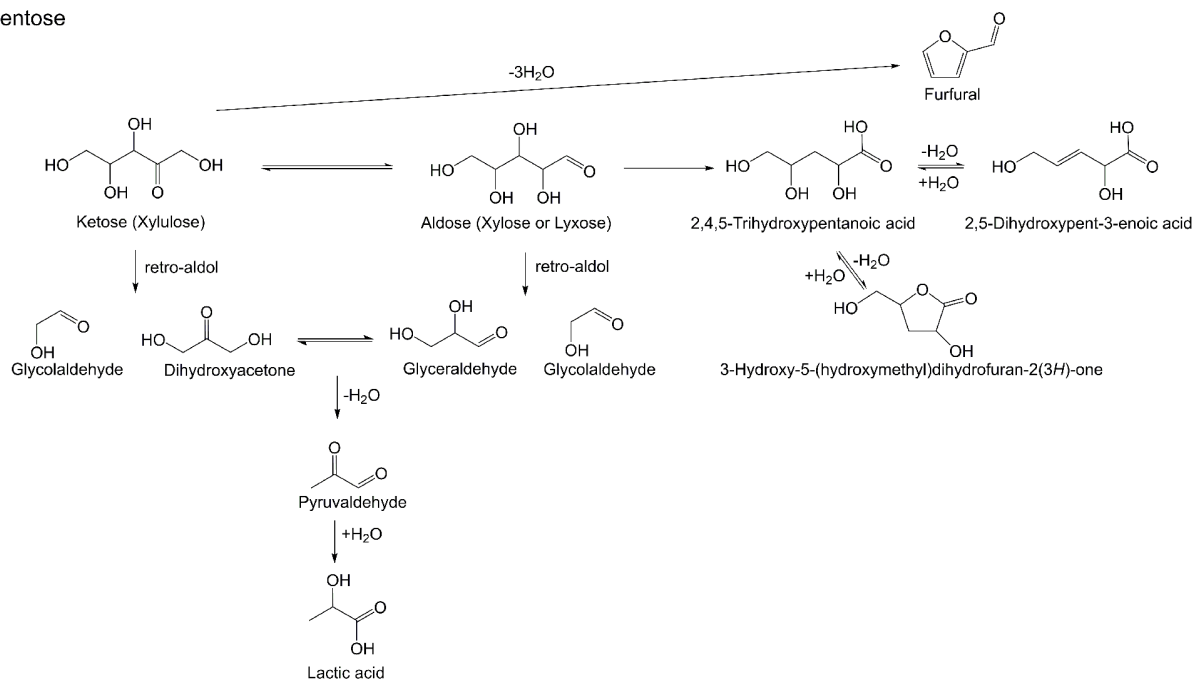
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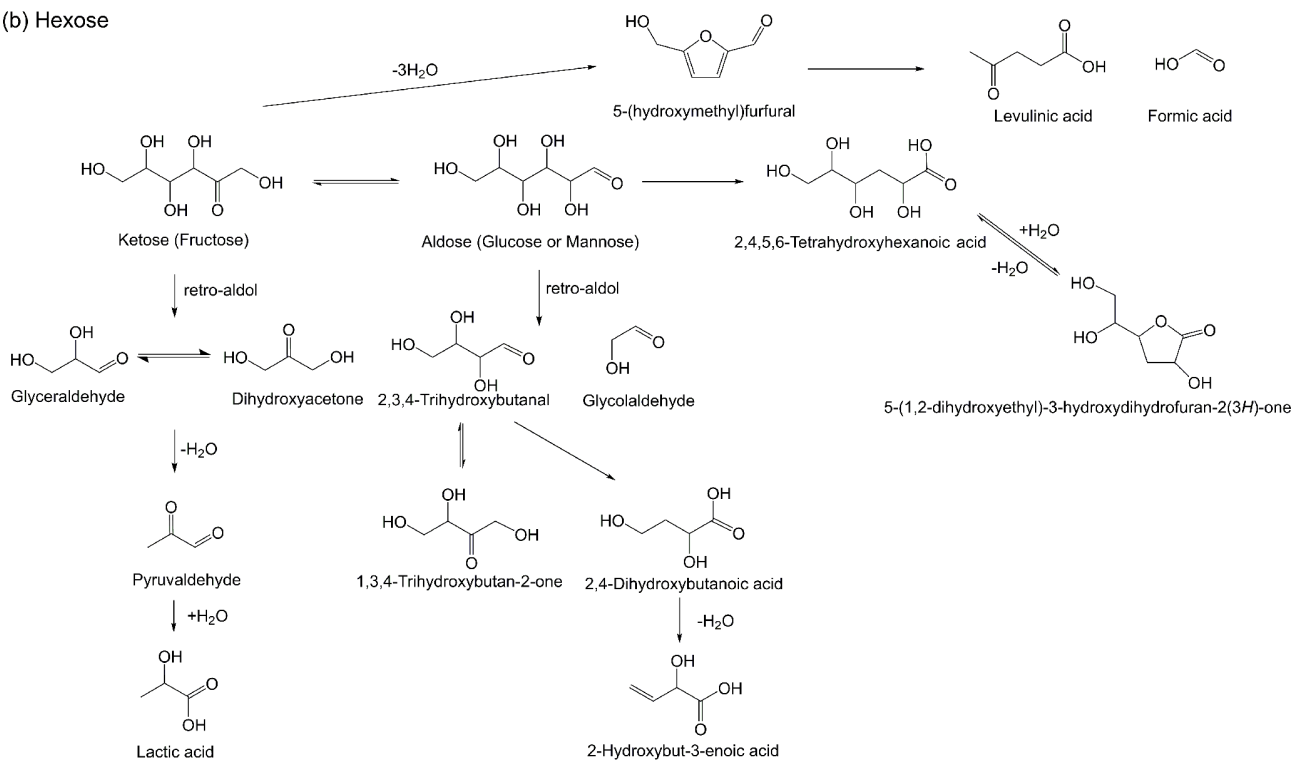
Keywords: Biomass · Carbohydrates · Heterogeneous Catalysis · Polymers · Sn-BEA

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(a) Pentose



(b) Hexose



Scheme 2. Proposed pathways for the reactions of (a) pentoses and (b) hexoses over Sn-BEA.

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