

Conversion of Xylose to Furfural Using Lewis and Brønsted Acid Catalysts in Aqueous Media

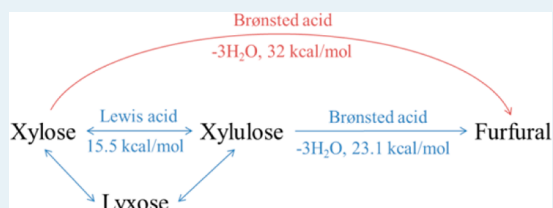
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ABSTRACT: The role of molecular structure on pentose dehydration to furfural has been examined using HCl as a Brønsted acid catalyst in a single phase aqueous media. It is shown that xylulose dehydration results in a much higher furfural yield than xylose dehydration under similar reaction conditions. Furthermore, a cascade of reactions for the efficient conversion of xylose to furfural in a single pot reactor is presented whereby a Lewis acid, CrCl_3 , is used to isomerize xylose to xylulose, and a Brønsted acid, HCl, is employed to dehydrate xylulose to furfural.

Using the combination of Lewis and Brønsted acids, a furfural yield of $\sim 39\%$ is achieved compared to $\sim 29\%$ using HCl alone, at a moderate reaction temperature ($\sim 418\text{ K}$) in a single aqueous phase, with an associated decrease in the residence time by a factor of 5. With this combined catalyst functionalities, a much higher yield (76%) to furfural can be obtained in a biphasic system at low temperatures and short times. Aside from increasing performance, our results indicate that the combined Lewis and Brønsted acids change the pathway for the conversion of xylose to furfural compared to carrying out the reaction in Brønsted acids alone.

KEYWORDS: xylose, xylulose, furfural, Lewis acid, Brønsted acid



INTRODUCTION

Recently there has been interest in converting biomass into biofuels and biochemicals as a result of the declining availability of petroleum reserves and growing environmental concerns over greenhouse gas emissions.^{1–5} A challenge lies in developing economically efficient and environmentally benign technologies to transform lignocellulosic biomass into fuels and chemicals.

Lignocellulose is composed mainly of cellulose, hemicellulose, and lignin. The hemicellulose fraction of the lignocellulosic biomass, which constitutes $\sim 25\text{--}35\%$ on a dry basis, is rich in pentoses.² Xylose is the most prevalent pentose produced via acid hydrolysis. One approach to utilize xylose entails its thermochemical conversion into furfural, which is a common industrial chemical derived from lignocellulosic biomass with an annual production of more than 400,000 tons.^{6,7} Furfural is envisaged as a potential platform chemical for the biofuel, biochemical and biopolymer industries. In addition, 2-methyl furan, 2,5-dimethylfuran, 2-methyltetrahydrofuran, 5-methylfurfural (MF), and 5-(ethoxymethyl)furfural (EMF) have been reported as promising biofuel components.^{6,8,9} Furfural, MF, and EMF have energy densities of 28.2, 29.9, and 30.3 MJ/L, respectively, in comparison to 23.5 MJ/L for ethanol.⁹ Avantium tested successfully EMF as a blend in commercial diesel engines.¹⁰ Other furfural derivatives, such as tetrahydrofuran (THF) and 2-methyltetrahydrofuran are used as industrial solvents,^{11,12} whereas 2,5-furandicarboxylic acid (FDCA) has been identified by the U.S. Department of Energy as one of 12 top value-added chemicals from biomass.¹³

Typically C6 furans are derived from 5-(hydroxymethyl)-furfural; however, these can also be produced from furfural.¹⁴

Industrial furfural production is based on biomass hydrolysis and subsequent dehydration of the obtained pentoses using a homogeneous Brønsted acid catalyst in aqueous media.¹⁵ The first industrial furfural production process was established by Quaker Oats in 1921.¹⁶ In this process, oat hulls are converted into furfural using concentrated sulfuric acid and high pressure steam to supply heat and strip out furfural. Presently, most of the furfural is produced in China using small-scale fixed bed reactors.¹⁵ The current furfural process is not only environmentally harsh but also quite inefficient, achieving only $\sim 50\%$ of the theoretical furfural yield. This suggests a need for more efficient processes given the importance of furfural in green chemistry.

Over the past decade, substantial research has been conducted on developing a heterogeneous Brønsted acid catalyst for furfural production from xylose.³ Many different Brønsted acid catalysts, such as various zeolites,^{17–20} Amberlyst,^{21,22} Nafion,²³ and MCM-41 based materials,^{22,24} have been tested.^{25–28} A key shortcoming in the Brønsted acid catalyzed xylose dehydration process is a high activation barrier of $\sim 30\text{--}32\text{ kcal/mol}$, necessitating high operating temperatures ($>423\text{ K}$) and long residence times in aqueous media.^{29,30} A furfural yield of only $\sim 30\%$ is reached in a single-aqueous phase, mainly because of side reactions leading to soluble

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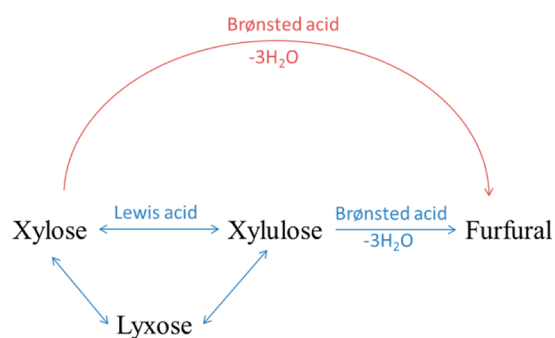
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polymers and humins. The furfural yield is typically increased using continuous extraction with an organic solvent in a liquid–liquid biphasic system^{3,29,31} or using a carrier gas to strip out the furfural.^{16,32} Recent studies reported improvement in furfural yield using various halides at high reaction temperatures (>443 K).³³ It was postulated that the halide ion assists the enolization reaction via proton transfer and dehydration reactions by stabilizing the transition states leading to intermediates.³⁴

Recently we demonstrated xylose conversion to furfural at much lower reaction temperatures in aqueous media using a cascade of reactions, wherein xylose is first isomerized to xylulose followed by xylulose dehydration to furfural.³⁵ This was achieved in a one-pot reactor using the Sn-beta zeolite, a Lewis acid, as an isomerization catalyst and HCl or Amberlyst-15, a Brønsted acid, as a dehydration catalyst. Xylulose was the main product and lyxose another product in the Sn-beta catalyzed xylose isomerization, as shown at the bottom of Scheme 1. The results were encouraging as a high xylose

Scheme 1. Schematic Representation of the Overall Paths to Produce Furfural from Xylose in the Presence of a Single Brønsted Acid Catalyst and of Both Lewis and Brønsted Acid Catalysts



conversion was obtained at a low reaction temperature (<383 K), but the furfural yield was low, ~15%. A similar approach in organic reaction media gave furfural yield of the order of 40–50% at low to moderate temperatures;^{21,36} however, such high furfural yield has not yet been achieved at similar temperatures in a single aqueous phase, the most suited solvent for green chemistry. Recently, a high yield of furfural (~75%) from xylose was reported in a biphasic system containing $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ and NaCl using microwave heating at ~413 K.³⁷

In this work, we further explore the cascade of reactions for xylose conversion in aqueous media using a different Lewis acid catalyst, CrCl_3 , and show that this approach could play a key role in improving the process efficiency of xylose conversion to furfural. The dehydration of various pentoses to furfural has also been compared to determine whether the molecular structure of the sugar affects its conversion to furfural. Furthermore, xylulose and xylose dehydration to furfural using a Brønsted acid catalyst are compared to understand the increasing furfural yield using the cascade of reactions and to obtain further mechanistic insights. Finally, it is demonstrated that the furfural yield from xylose can be significantly improved in a single aqueous phase by combining a Lewis acid, CrCl_3 , with a Brønsted acid, HCl, in appropriate proportions.

EXPERIMENTAL SECTION

The reactions were carried out in 10 mL thick-walled glass vials (Sigma-Aldrich) heated in a temperature-controlled oil bath on a digital stirring hot plate (Fisher Scientific). All the chemicals used in this study were purchased from Sigma-Aldrich and were used as received. In a typical experiment, 1 mL of an aqueous solution of reactant (1 wt %) was added to the reactor and sealed. A magnetic stirrer was used for mixing during reaction. The kinetics experiments were carried out using multiple such vial reactors, which were taken from the oil bath at specified times and quenched in water at room temperature.

The liquid samples were analyzed with high performance liquid chromatography (HPLC) using a Waters Alliance System (e2695) equipped with a refractive index (RI) detector and a photodiode array (PDA) detector. A challenging task was to quantify xylulose and lyxose as they elute at almost the same time, which may be the reason that earlier studies have not reported lyxose as a xylose isomerization product. This issue was overcome by using two Biorad HPX87C (300×7.8) columns in series at a column temperature of 363 K and using HPLC grade water as mobile phase at a flow rate of 0.60 mL/min. Xylose, xylulose, and lyxose eluted at 22, 26, 26.9 min, respectively, as shown in Figure 1. Furfural was separated from

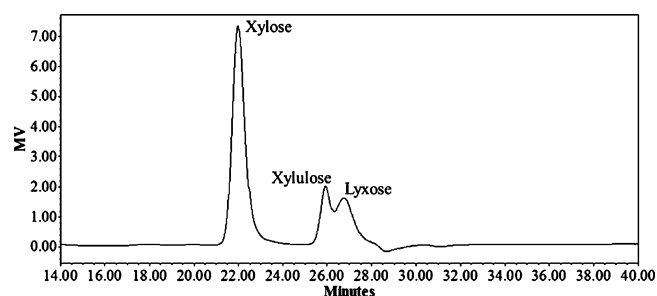


Figure 1. Separation of pentoses using two Biorad-HPX87C columns in series in the HPLC. The sugars were detected using a refractive index (RI) detector.

the reaction mixture using a Biorad HPX87H (300×7.8) column, with water (0.005 molar sulphuric acid) as the mobile phase at a flow rate of 0.65 mL/min and a column temperature of 338 K. The typical relative standard error is <1% for multiple injections from the same sample and ~5–8% for replicas. The yields of the products are calculated on a molar basis.

RESULTS AND DISCUSSION

We start describing the results using a Brønsted acid (HCl) only and turn to the Lewis acid results later. Figure 2 compares the conversion of different aldopentoses, xylose, lyxose, and arabinose, to furfural using HCl (0.1 M) as a catalyst in an aqueous medium at ~418 K. These aldopentoses differ from each other in the arrangement of the –OH groups, as shown in Scheme 2. In pentose dehydration, the furfural yield passes through a maximum with time, which implies the participation of the furfural in side reactions. The conversion of lyxose resembles closely that of xylose, as shown in Figure 2a, and leads to a similar furfural yield, as shown in Figure 2b. On the other hand, arabinose conversion is lower and results in a significantly lower furfural yield compared to the other sugars. In these reactions, a small amount of formic acid was detected (yield <0.5%).

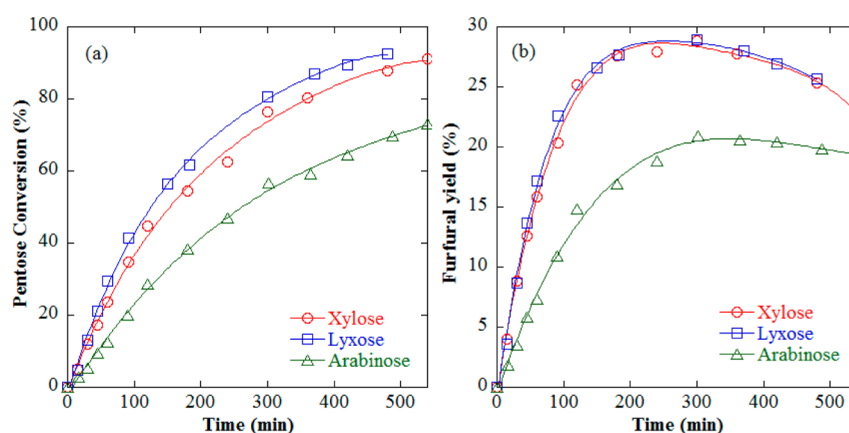
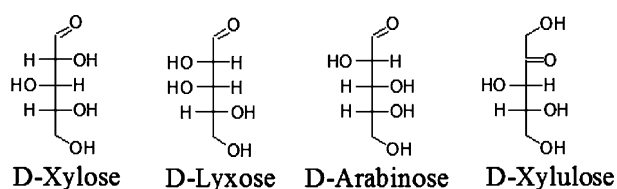


Figure 2. Comparison of the dehydration of various aldopentoses to furfural in aqueous media using a Brønsted acid catalyst at ~ 418 K. Reaction conditions: initial reactant ~ 1 wt % and HCl (0.1 M).

Scheme 2. Molecular Structure of the Various Pentoses



The reaction kinetics of xylulose, a ketopentose, dehydration to furfural catalyzed by HCl (0.1 M) in aqueous media at various temperatures is shown in Figure 3. As expected, the xylulose dehydration rate increases with increasing temperature; more importantly, the furfural yield also improves with increasing temperature. Additionally, xylulose dehydration to furfural produces a higher furfural yield than xylose dehydration at similar conditions. For example, at 418 K a furfural yield of $\sim 66\%$ (Figure 3b) was obtained in 45 min from xylulose dehydration compared to $\sim 29\%$ (Figure 2b) in 300 min from xylose at the same conditions. By fitting a first-order reaction rate expression to the initial xylulose dehydration kinetics, the apparent activation barrier of xylulose was estimated to be 23.1 kcal/mol (Figure 4), considerably lower than that of xylose dehydration reported in the literature (~ 30 – 32 kcal/mol).^{3,29} Since the reaction mechanism of pentose dehydration to

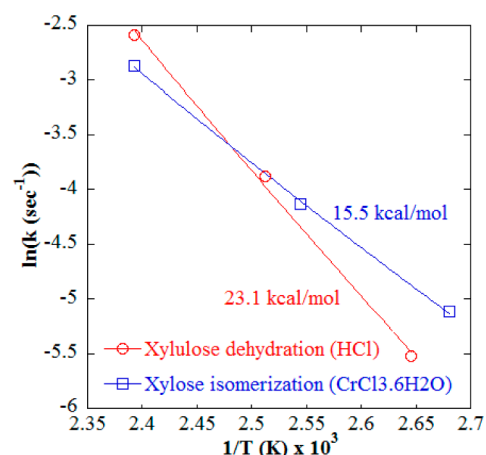


Figure 4. Arrhenius plot based on initial reaction rates of (1) xylulose (~ 1 wt %) dehydration using HCl (0.1 M), (2) xylose (~ 1 wt %) isomerization using $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ (~ 6 mM). The estimated apparent activation energies are indicated.

furfural is not well understood, it remains a challenge to explain the observed differences in the dehydration rates of the various pentoses. However, these results clearly suggest that the dehydration of xylulose is faster than that of xylose, that is, xylose isomerization is rate controlling in its conversion to

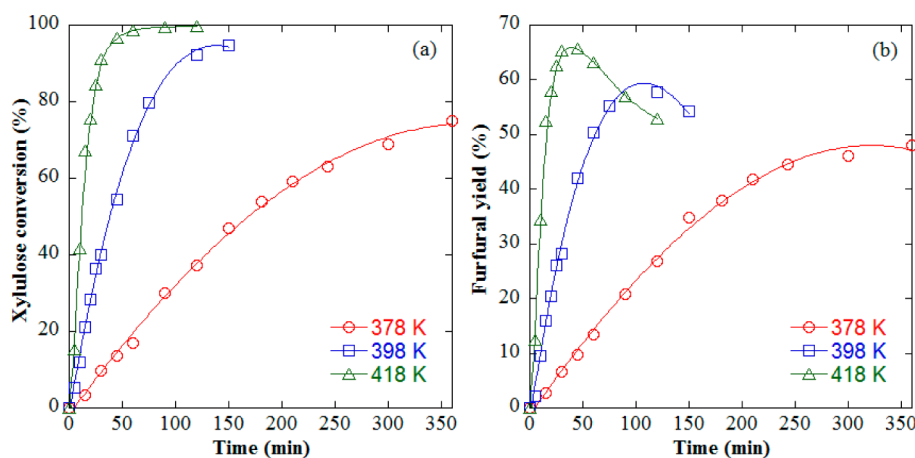


Figure 3. Xylulose dehydration to furfural in aqueous media at various temperatures using a Brønsted acid catalyst. Reaction conditions: initial reactant ~ 1 wt % and 0.1 M HCl.

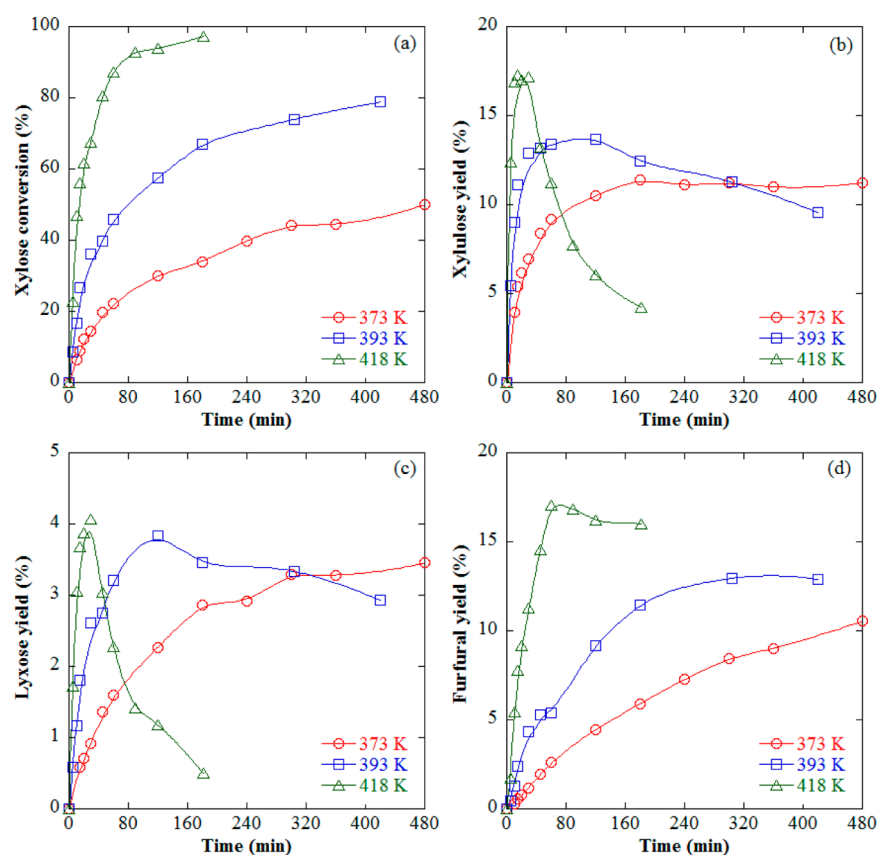


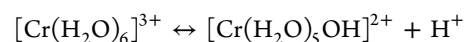
Figure 5. Xylose isomerization and dehydration to furfural in aqueous medium using $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$. Reaction conditions: initial xylose ~ 1 wt %, CrCl_3 (6 mM) and $T \sim 418$ K.

furfural through xylulose, or xylose dehydration follows a different mechanism that does not involve xylulose as an intermediate. We address this issue below.

Recently chromium chloride, a Lewis acid, was reported to be an effective catalyst to isomerize glucose to fructose in various reaction media including water.^{38–40} Drawing an analogy to the glucose isomerization, chromium chloride was tested here for xylose isomerization to xylulose in aqueous media. Figure 5 shows the results of the xylose isomerization reactions using $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ (~ 6 mM) as a catalyst at varying temperatures. [For simplicity, we will refer to $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ as CrCl_3 here onward.] The conversion of xylose increases with increasing temperature (Figure 5a). Xylulose was the main isomerization product (Figure 5b), and lyxose (Figure 5c) was identified as a secondary isomerization product, similar to the Sn-beta catalyzed xylose isomerization reactions we reported recently (bottom of Scheme 1).³⁵ The maximum xylulose yield increases as the reaction temperature is raised. The apparent activation energy of xylose isomerization, estimated from the initial reaction rate, is 15.5 kcal/mol (Figure 4).

It is clear that CrCl_3 is an effective Lewis acid catalyst in isomerizing xylose into its two isomers. At the same time, furfural is observed that is typically the product of Brønsted acid catalyzed dehydration. A notable point is that when CrCl_3 is dissolved in water, the pH of the solution drops. Initially, the pH was ~ 3 at room temperature (after overnight stirring), and upon heating the vial, the pH dropped to ~ 2.1 (measured from the quenched samples at room temperature). In aqueous media, CrCl_3 forms hexa-aqua complexes characterized by ions,

such as $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$, and the Brønsted acidity primarily results from the hydrolysis of the aqueous complex as follows⁴¹



At higher temperatures, the reaction equilibrium is shifted to the right resulting into further drop in solution pH. Further, the aforementioned difference in the measured pH of the solution before and after heating may arise because of kinetic barriers in establishing equilibrium but most probably results from $[\text{Cr}(\text{H}_2\text{O})_5\text{OH}]^{2+}$ further reacting to make chromium oligomers.⁴¹ This is a practically irreversible process and thus, even when the solution is cooled down, the pH of the solution does not return to the higher preheated value. This Brønsted acidity could catalyze the dehydration of xylulose (detected in these experiments) to furfural. A maximum furfural yield of $\sim 17\%$ was obtained at 418 K (Figure 5d), which was lower than $\sim 29\%$ obtained using only HCl (0.1 M) as a catalyst. A possible reason for the lower yield of furfural was the nonselective dehydration of the sugars at higher pH.^{31,42}

Next CrCl_3 was used in combination with HCl (0.1 M) in an attempt to combine Lewis and Brønsted acid catalysts for the production of furfural from the isomerization of xylose to xylulose, and subsequent the dehydration of xylulose to furfural. The kinetics of xylose conversion is shown in Figure 6. The CrCl_3 concentration was varied in the range 2 to 13.5 mM, while keeping the other reaction conditions fixed. It was noticed that the rate of xylose consumption was slightly slower compared to the only CrCl_3 experiment (without the addition of Brønsted acid) indicating that the addition of HCl adversely affects CrCl_3 reactivity. To understand the reason for this

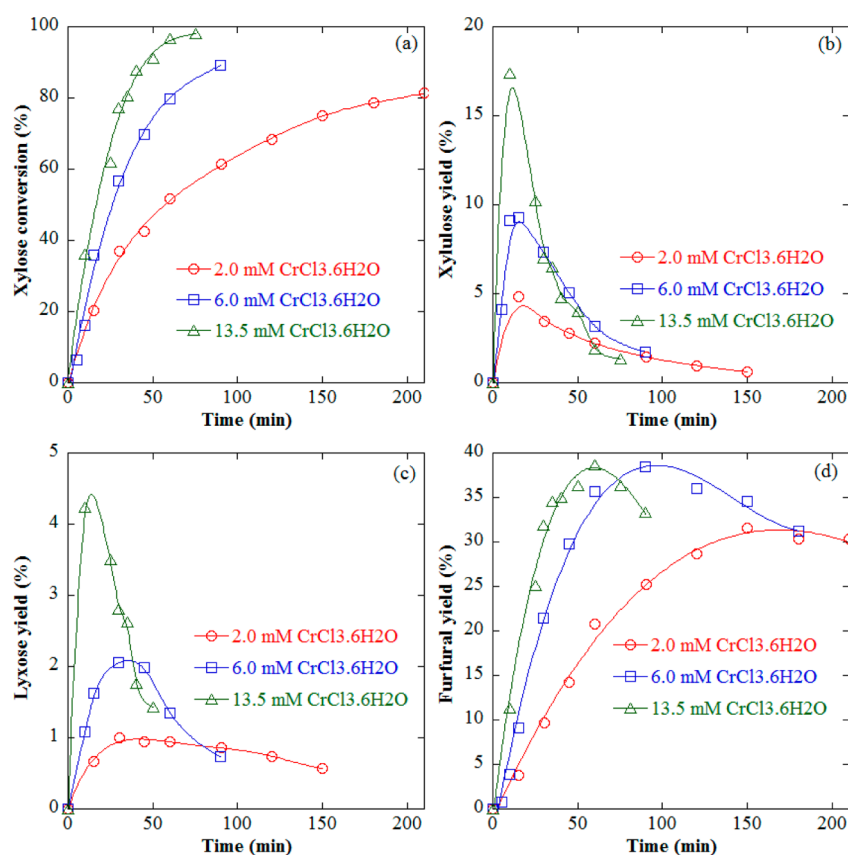


Figure 6. Xylose dehydration to furfural in aqueous media at varying $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ concentration. Reaction conditions: initial xylose ~ 1 wt %, HCl (0.1 M) and $T \sim 418$ K.

behavior, we performed UV–vis absorption spectroscopy on the CrCl_3 solution with and without HCl at room temperature, and significant differences in the spectra were observed. Specifically, the peaks around 410 and 575 nm shift to the right (not shown) in the presence of HCl. This indicates that HCl probably influences the CrCl_3 speciation in the aqueous solution. This could be explained with the aforementioned hydrolysis reaction of the $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$. In the presence of HCl, the reaction equilibrium is displaced to the left,⁴¹ and thus adversely affects the formation of $[\text{Cr}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$. Further, $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ and $[\text{Cr}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$ react to form dimers, trimers, and oligomers of Cr(III), which would also be affected by a change in solution pH.⁴¹ Hence addition of HCl alters the CrCl_3 speciation in the aqueous medium, which probably causes the decrease in the xylose conversion rate when HCl is used together with CrCl_3 . Further, these results implicitly indicate that all Cr(III) aqueous complexes are not equally active for xylose isomerization. An in-depth study of CrCl_3 speciation in aqueous media at the reaction temperature will be needed to draw any further conclusion.

Even though the rate of xylose conversion (Figure 6a) in the presence of HCl with CrCl_3 was slower compared to the only CrCl_3 case, it was much faster compared to having only the Brønsted acid (HCl) (Figure 2a), and increased monotonically with increasing CrCl_3 concentration. In addition, a few measurable unknown peaks, which were observed during HPLC analysis in CrCl_3 , almost disappeared when HCl was used together with CrCl_3 . This suggests that the addition of HCl affects the side reactions in the reaction cascade.

The xylulose and lyxose concentrations increase with time and pass through a maximum indicating a competition between isomerization of xylose to these isomers and their dehydration to furfural (bottom of Scheme 1). The maximum concentration of xylulose and lyxose increases with increasing CrCl_3 concentration. However, these concentrations are lower than those when CrCl_3 alone is used because they dehydrate faster at the lower pH used when we combine CrCl_3 and HCl. Similarly, the furfural yield passes through a maximum with time.

Table 1 compares the maximum yield of furfural at various CrCl_3 concentrations. The numbers shown in brackets are the

Table 1. Effect of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ Concentration on Maximum Furfural Yield in the Xylose Dehydration Reactions^a

reaction #	catalyst	maximum % yield of furfural
1	HCl (0.1 M)	28.8 (300)
2	HCl (0.1 M) + $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ (2 mM)	31.6 (150)
3	HCl (0.1 M) + $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ (6 mM)	38.4 (90)
4	HCl (0.1 M) + $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ (13.5 mM)	38.7 (60)

^aReaction conditions: initial xylose ~ 1 wt %, and $T \sim 418$ K. The numbers in brackets with the yields are the corresponding reaction time in minutes.

reaction times (in minutes). The furfural yield increases with an increase in CrCl_3 concentration, but there is no significant gain when the CrCl_3 concentration is increased beyond 6 mM, a concentration that corresponds to a Cr-to-xylose molar ratio of $\sim 9:100$. However, the reaction rate increases linearly (not

shown) with an increase in the CrCl_3 concentration indicating that the xylose isomerization is rate controlling when combined Lewis and Brønsted acids are employed.

Overall, a maximum furfural yield of $\sim 39\%$ is obtained, compared to $\sim 29\%$ when only HCl (0.1 M) is used. In addition, an associated decrease in the contact time by a factor of 5 is achieved, while operating at the maximum furfural yield at each concentration. To the best of our knowledge, this is the highest furfural yield achieved in a single aqueous phase at these moderate temperatures. Furthermore, by incorporating an organic phase (toluene) to continuously extract the furfural in a biphasic system, a furfural yield of $\sim 76\%$ was achieved in 120 min at 413 K (Table 2) using CrCl_3 along with HCl compared to $\sim 27\%$ when only HCl was used, and $\sim 35\%$ for the only CrCl_3 was used.

Table 2. Xylose Conversion to Furfural and Furfural Yield in the Biphasic System after 120 min^a

reaction #	catalyst	xylose % conversion	furfural % yield
1	CrCl_3 (~ 6 mM), HCl (0.1 M)	95.8	76.3
2	HCl (0.1 M)	31.1	26.7
3	CrCl_3 (~ 6 mM)	95.5	34.5

^aReaction conditions: initial xylose ~ 1 wt % (2 mL of aqueous solution), toluene (2 mL) as the extracting solvent, and $T \sim 413$ K. Catalyst concentrations are based on the aqueous phase.

It should be noticed that in the case of Brønsted acid-catalyzed xylose dehydration, xylulose was not detected, whereas it is a clear intermediate when both Lewis and Brønsted acids are used. This indicates that the reaction pathways could be different in the case of Brønsted acid catalyzed xylose dehydration compared to having both acids. A DFT study comparing three different schemes for the Brønsted acid catalyzed xylose dehydration to furfural has shown that the lowest energy reaction pathway does not go through xylulose.⁴³ This is consistent with the absence of xylulose in our experiments. On the other hand, xylulose was detected and proposed as an intermediate in xylose dehydration to furfural in water at high temperature (623–673 K) and high pressure (40–100 MPa);⁴⁴ however, it could be argued that at high temperatures, xylulose is formed as a side product. In brief, the reaction pathway of the Brønsted acid catalyzed xylose

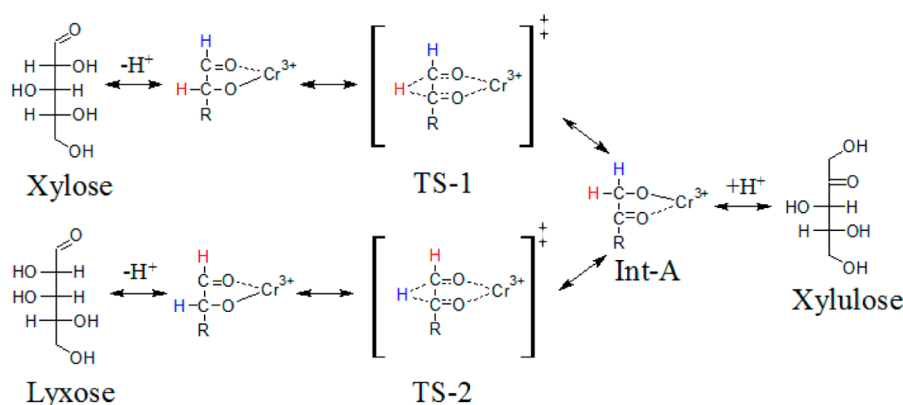
dehydration (top of Scheme 1) might differ from that in the presence of Lewis plus Brønsted acid catalyzed xylose conversion to furfural (bottom of Scheme 1). In the cascade for the Lewis and Brønsted acid reactions, both pathways (Scheme 1) can contribute to the conversion of xylose to furfural, and the extent depends on the conditions. For example, it takes ~ 60 min for 97% conversion at CrCl_3 concentration of 13.5 mM, whereas for the same reaction time only $\sim 23\%$ conversion is observed when using only HCl. This suggests that while using the combined Lewis and Brønsted acids, xylose isomerization and subsequent dehydration (bottom of Scheme 1) dominates over the direct conversion of xylose to furfural by the Brønsted acid (top of Scheme 1), and this is expected to be the case at lower temperatures and higher values of pH.

A plausible reaction pathway for the xylose isomerization to xylulose catalyzed by the chromium ion in aqueous media is presented in Scheme 3. The xylose isomerization to xylulose requires hydrogen transfers from O2 to O1 and from C2 to C1. The H transfer from C2 to C1 is a hydride transfer, and it is activated by a proton abstraction from O2 to a solvation water molecule. This initial proton donation from O2 allows the formation of a Cr(III) chelate with the O2 and O1 oxygens of the saccharide molecule; the hydride transfer ensues and proton back-donation to the O1 oxygen completes the isomerization. The proposed mechanism is shown in Scheme 3 and is predicated on earlier studies on metal catalyzed aldose to ketose isomerization reactions.^{45,46} In addition, Scheme 3 shows a pathway bifurcation at intermediate A, involving hydride transfer from C1 to C2, which accounts for the formation of lyxose in addition to xylulose. This is similar to the mechanism that has been proposed for Sn-beta catalyzed xylose isomerization.³⁵

CONCLUSIONS

In summary, we have found that the rate of pentose dehydration to furfural depends on its molecular structure; xylulose dehydrates more rapidly than xylose in aqueous media catalyzed by a Brønsted acid with an increase in the furfural yield by a factor of greater than 2. CrCl_3 , a Lewis acid, was found to be an efficient aqueous media catalyst for xylose isomerization to xylulose and lyxose as the main isomerization products, similar to using the Sn-beta catalyst. A 35% increase in furfural yield in single aqueous phase over Brønsted acid (HCl) and a 5-fold decrease in the contact time, while

Scheme 3. Plausible Reaction Mechanism for Xylose Isomerization into Xylulose and Lyxose Using CrCl_3 as a Catalyst in Aqueous Media



operating at the maximum furfural yield, were achieved using CrCl_3 in combination with HCl. Furthermore, a 76% yield of furfural was obtained in the biphasic system using toluene as an extracting phase and the same combination of Lewis and Brønsted acid catalysts at 413 K in 120 min. On the basis of these results, it can be inferred that the combination of Lewis and Brønsted acids to produce furfural from xylose via xylulose can substantially improve the process efficiency in aqueous media. Mechanistically, it appears that the dehydration of xylose in the presence of a Brønsted acid site follows a direct path (top of Scheme 1), whereas the combination of Lewis and Brønsted acids follows primarily a cascade (bottom of Scheme 1), whereby xylose first isomerizes to xylulose and lyxose using the Lewis acid that subsequently dehydrate to furfural using the Brønsted acid. It is expected that the contribution of each pathway depends on the ratio of concentrations of Lewis and Brønsted acid catalysts and the temperature.

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Notes

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