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Graphical abstract



The introduction of HCl decreases  $k_1$  and increases  $k_2$  and  $k_3$ .

Highlights

The route via fructose is the dominant pathway for the conversion of glucose to HMF in  $AlCl_3-H_2O/THF$ .

The Lewis acidic sites are responsible for isomerization as well as dehydration.

The introduction of a suitable amount of HCl improved the selectivity for HMF.

An optimal HMF yield of 62% can be obtained with 0.1 M HCl added to AlCl<sub>3</sub>-H<sub>2</sub>O/THF.

The introduction of HCl improved the direct dehydration route of glucose to HMF.

The effect of hydrochloric acid on the conversion of glucose to 5-hydroxymethylfurfural in  $AlCl_3-H_2O/THF$  biphasic medium

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**Abstract:** The effect of hydrochloric acid (HCl) on the conversion of glucose to 5-hydroxymethylfurfural (HMF) in AlCl<sub>3</sub>-H<sub>2</sub>O/THF biphasic system was investigated. The route via isomerization to fructose followed by tandem dehydration to HMF is the dominant pathway. Lewis acid sites of  $Al^{3+}$  aqua/hydroxo complexes play the leading role for the dehydration step. The introduction of a suitable amount to HCl increases the amount of Brønsted acid sites and improves the selectivity for HMF. The maximum HMF yield from glucose is enhanced from 51% to 62% in the presence of 0.1 M HCl. The introduction of HCl lowers the reaction rate of glucose-to-fructose isomerization but enhances the reaction rate of fructose dehydration. Higher loading of HCl (1.0 M) leads to increased direct dehydration of glucose to humins and results in lower selectivity to HMF.

Keywords: Glucose; 5-Hydroxymethylfurfural; AlCl<sub>3</sub>; Fructose; HCl.

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### **1. Introduction**

Glucose, which is the monomer unit of cellulose in biomass, will be one of the most important raw materials of the future as society moves towards biomass utilization for renewable fuels and chemicals [1,2]. Among the products derived from glucose, 5-hydroxymethylfurfural (HMF) is of high value. HMF can be transformed into liquid fuel and other important chemicals [3,4]. It serves as a precursor for levulinic acid (LA), 2,5-furandicarboxylic acid, 2,5-diformylfuran, and dihydroxymethylfuran, to name a few. Liquid alkanes [5] and dimethylfuran [6], which could directly serve as a high heating value fuel, can also be produced from HMF. Hence, efficient and environmentally responsible production of HMF from abundant and cheap glucose has received considerable attention recently [7-15].

The conversion of glucose to HMF may proceed by two routes as illustrated in Fig. 1 [3,16,17], via fructose or direct dehydration of glucose. Brønsted acids such as HCl, H<sub>2</sub>SO<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub> are typically used for the conversion of glucose to HMF via the direct route because Brønsted acids do not affect glucose isomerization [7]. However, mineral acids give only low HMF yield and produce additional byproducts [7]. The route via fructose involves two main steps: (1) isomerization of glucose to fructose; (2) dehydration of fructose to HMF. Using a bifunctional catalyst that can affect glucose-to-fructose isomerization and subsequent dehydration should give higher HMF yield/selectivity [10-14]. Some Lewis acids such as CrCl<sub>2</sub> [10], SnCl<sub>4</sub> [11], and AlCl<sub>3</sub> [12] can be used for glucose conversion giving reasonable HMF yield. Among these catalysts, AlCl<sub>3</sub> is the cheapest with the lowest toxicity. Unlike CrCl<sub>2</sub> and SnCl<sub>4</sub>,

which require the use of expensive ionic liquid as solvent, AlCl<sub>3</sub> displays high activity in cheap H<sub>2</sub>O/THF biphasic medium, which can inhibit the further reaction of HMF and lead to a high HMF yield [12]. Dumesic, Shanks, and coworkers have reported recently on the combination of Lewis and Brønsted acids for the conversion of glucose in biphasic water and alkyl phenols [15]. The effect of Brønsted acid and its mechanistic implication on the conversion of glucose to HMF in the AlCl<sub>3</sub>-H<sub>2</sub>O/THF biphasic system is the subject matter of this study. In order to avoid the effect of anions with the introduction of Brønsted acid, HCl was used to adjust the concentration of Brønsted acid in the AlCl<sub>3</sub>-H<sub>2</sub>O/THF biphasic system.

### 2. Experimental

#### **2.1 Materials**

Glucose, fructose, AlCl<sub>3</sub>·6H<sub>2</sub>O, HCl (37 wt%), THF, HMF, all of analytical grade, were purchased from Sigma Aldrich, and used as received.

#### 2.2. General procedure for the reaction

All reactions were performed under microwave heating in a Discover TM System (CEM Corporation) using a 10 mL batch reaction vessel. Reaction solutions were mixed using a magnetic stir bar. The reactor temperature was measured by a fiber optic sensor. In a typical dehydration experiment, 10 mL reaction tube was charged with glucose or fructose (0.25 mmol), catalyst (HCl or/and AlCl<sub>3</sub>·6H<sub>2</sub>O (0.1 mmol)), nanopure water (1 mL) and THF (3 mL); the reaction was heated to 160 °C for the desired time. In a typical isomerization of glucose-to-fructose experiment, 10 mL reaction tube was charged with glucose (0.25 mmol), catalyst (HCl and AlCl<sub>3</sub>·6H<sub>2</sub>O)

(0.1 mmol)) and nanopure water (1 mL); the reaction was heated to 120  $^{\circ}$ C for 30 min. The reaction was stopped by nitrogen flow cooling. Samples were filtered with a 0.2  $\mu$ m syringe filter prior to analysis.

#### 2.3 Analytic methods

Quantitative analysis of the aqueous phase was performed by HPLC using a Waters 1525 pump, an aminex column HPX-87 column (Agilent) and Waters 2412 Refractive Index detector. 0.005 M H<sub>2</sub>SO<sub>4</sub> solution was used as the mobile phase at a flow rate of 0.6 mL/min, and the column temperature was maintained at 338 K. The concentration of HMF in the organic phase was determined by HPLC using a Waters 1525 pump, a XDB-C18 column, (Agilent) and Waters 2487 UV detector. 0.5 wt% formic acid solution was used as the mobile phase at a flow rate of 0.4 mL/min, and the column temperature was maintained at 303 K. All concentrations of carbohydrates in the aqueous phase and HMF in the aqueous phase and organic (THF) phase were determined by comparison to standards calibration curves.

Conversion of carbohydrates and selectivity of products are defined as follows: Glucose conversion = moles of glucose reacted/moles of starting glucose Fructose conversion = moles of fructose reacted/moles of starting fructose Fructose selectivity = moles of fructose produced/ moles of glucose reacted Glucose selectivity = moles of glucose produced/ moles of fructose reacted HMF selectivity = moles of HMF produced/(moles of starting carbohydrate- moles of carbohydrate unreacted)

HMF yield = moles of HMF produced/moles of starting carbohydrate

The pH value was measured on an Accumet AB15/15+ pH meter ( 0.01 pH units) calibrated with standard buffer solutions. The temperature of the solution was controlled by a thermostated water bath ( $\pm$  0.1 °C).

#### **3. Results and Discussion**

Although AlCl<sub>3</sub> can be used as a Lewis acid in water [18-19], it is moisture-sensitive and hydrolyzes to form Brønsted acid (H<sub>3</sub>O<sup>+</sup>). At 25 °C, the pH of 0.1 M AlCl<sub>3</sub> aqueous solution is 3.03. At higher temperature, the hydrolysis of AlCl<sub>3</sub> in H<sub>2</sub>O is even more significant. For example, at 80 °C the pH of 0.1 M AlCl<sub>3</sub> aqueous solution is 2.63. However, it is difficult to reliably measure the pH at the reaction conditions (120-160 °C), and therefore, one cannot use HCl to emulate exactly the same  $[H_3O^+]$  of 0.1 M AlCl<sub>3</sub> aqueous solution at these high temperatures. Alternatively, one can use InCl<sub>3</sub>, which bears similar character to AlCl<sub>3</sub>, but higher Brønsted acidity and lower Lewis acidity [19], to decipher which kind of acid in AlCl<sub>3</sub> system play the major role for the conversion of glucose to HMF. We tested InCl<sub>3</sub> for the conversion of glucose. While the AlCl<sub>3</sub>-H<sub>2</sub>O/THF biphasic system affords 98% conversion of glucose with 48% yield of HMF after 10 min of reaction at 160 °C, the InCl<sub>3</sub>-H<sub>2</sub>O/THF system under the same conditions affords 86% conversion of glucose with HMF yield of only 7%. However, the indium system gives fructose as the major product (59% yield). In summary, InCl<sub>3</sub> shows high activity for glucose-to-fructose isomerization, but much lower activity than AlCl<sub>3</sub> for the dehydration of fructose to HMF. Since the Brønsted acidity of InCl<sub>3</sub> in water is higher than that of AlCl<sub>3</sub>, a plausible interpretation of these results is that Lewis acid sites in

AlCl<sub>3</sub> system are crucial in the dehydration step.

As discussed above the AlCl<sub>3</sub>-H<sub>2</sub>O/THF system provides both Lewis and Brønsted acid sites. Brønsted acids, however, do not catalyze the isomerization of glucose-to-fructose [20]. On the contrary, the dehydration of fructose can be catalyzed by both Lewis and Brønsted acids [21]. Thus, the fructose dehydration reaction was used as a probe reaction to provide insight into the acidic strength of AlCl<sub>3</sub> under our reaction conditions.

The effect of pH on the dehydration of fructose is shown in Fig. 2. At pH = 2 the conversion of fructose and HMF yield are quite low. As the pH is decreased, fructose conversion and HMF yield increase, reaching a plateau at pH 1.0. Increasing the Brønsted acidity to  $[H_3O^+] = 1.0$  M results in a decline in HMF yield due to rehydration to make levulinic acid (LA) [22]. In comparison with AlCl<sub>3</sub> as a catalyst, fructose conversion of 67% and HMF yield of 38% are observed (filled triangles in Figure 2). Accordingly, the acidic strength of AlCl<sub>3</sub> aqueous solution is equal to HCl solutions pH values in the range of 1.35-1.61 (Figure 2). Next we investigated HCl at different pH values for the conversion of glucose to HMF. The results are displayed in Fig. 3. Fructose was not observed over the investigated pH range. Kuster and Temmink [22] had investigated the influence of pH on the conversion of glucose; they observed no glucose-to-fructose isomerization at pH < 4.5. Thus, with HCl in the pH range of 0-2, the conversion of glucose to HMF most likely proceeds through direct dehydration of glucose. However, HMF yield of only ca. 2% is observed in the pH range of 1.61-1.35 (which is comparable to the acidic strength of AlCl<sub>3</sub>, *vide supra*).

In comparison the use of AlCl<sub>3</sub> gives HMF yield of 43%. So far the results indicate that direct dehydration of glucose to HMF has little contribution to HMF formation from the AlCl<sub>3</sub>-catalyzed reaction.

In comparison to HCl, AlCl<sub>3</sub> shows higher activity for the conversion of glucose to HMF, but lower activity for the conversion of fructose to HMF. With AlCl<sub>3</sub> as catalyst, HMF selectivity (based on converted fructose) is only 57%, compared to 82% for HCl. Some fructose is isomerized to glucose in the presence of AlCl<sub>3</sub>; a glucose yield of 7% is observed. Correcting for glucose formation, HMF selectivity affords only 64%, which is lower than the 82% observed for HCl. Huber at al. [23] studied the effect of Lewis and Brønsted acid sites on the dehydration of xylose. They found that a lower ratio of Brønsted acid sites versus Lewis acid sites results in lowered furfural selectivity because Lewis acid sites are principally responsible for the further conversion of furfurals to intractable humins. Thus Lewis acids show lower HMF selectivity from fructose than Brønsted acids [24]. While the AlCl<sub>3</sub>-H<sub>2</sub>O/THF biphasic system is superior in HMF selectivity from glucose in comparison to HCl, it is inferior in the selective dehydration of fructose.

In an attempt to increase HMF selectivity, we introduced HCl as an additive to  $AlCl_3-H_2O/THF$  biphasic system. The effect of HCl on  $AlCl_3$  catalyzed fructose conversion is summarized in Fig. 4. The introduction of HCl increases the total Brønsted acid sites, and as a result fructose conversion increases. In the absence of HCl, fructose conversion of 67% and HMF selectivity of 63% are observed. As HCl is added the selectivity to HMF are increased reaching a maximum at ca. 80% with [HCl]

= 0.316 M (pH = 0.5). Further increase in HCl beyond this optimal value results in further degradation of HMF to LA and humins [21]. Furthermore, it is worth noting that the introduction of HCl inhibited the isomerization of fructose to glucose.

The effect of adding HCl on the AlCl<sub>3</sub> catalyzed glucose conversion is summarized in Fig. 5. The introduction of HCl does not show a discernible increase in glucose conversion. On the contrary, a decrease of glucose conversion was observed at pH values lower than 1. Considering that the dehydration reaction rate increases as the pH decreases, the decrease in glucose conversion must be caused by the decrease in the rate of isomerization. The effect of pH on the isomerization of glucose-to-fructose was investigated at 120 °C, a temperature under which the dehydration of fructose to HMF is significantly retarded. As evident in Fig. 6, fructose yield decreases as the pH is decreased. At pH = 0, nearly no fructose was detected. The introduction of HCl not only increased the amount of Brønsted acid sites, but also

affected the equilibrium of  $Al^{3+}$  aqua/hydroxo complexes ( $Al^{3+}+H_2O \rightleftharpoons Al^{3+}$  hydroxo

complexes +  $H^+$ ). These results imply that  $Al^{3+}$  hydroxo complexes are responsible for the glucose-fructose ismerization reaction. When pH=0, glucose conversion with HCl alone was 52%, and 60% with AlCl<sub>3</sub>. The introduction of HCl affected the contribution from two routes, direct glucose conversion and via fructose. As a result, a maximum HMF selectivity is observed over the pH range of 0.5-1.

Given that the AlCl<sub>3</sub>-HCl-H<sub>2</sub>O/THF (pH=1) biphasic system resulted in the highest HMF selectivity, a time profile of the reaction was obtained (Fig. 7), and

compared to the profile for the AlCl<sub>3</sub> catalyzed reaction without HCl (Fig. 8). In the absence of HCl, fructose builds up to 35% yield after 1 min. In the presence of HCl (pH=1), the maximum fructose yield was only 14% and tmax = 2.5 min. The isomerization of glucose-to-fructose is somewhat slower with added HCl. However, the total conversion of glucose was comparable under both conditions. The introduction of HCl increases the selectivity of HMF from 51% to 62%. The route via fructose remains the dominant route for glucose conversion to HMF in the AlCl<sub>3</sub>-HCl-H<sub>2</sub>O/THF (pH=1) biphasic system.

#### 4. Conclusions

For the AlCl<sub>3</sub> catalyzed glucose conversion to HMF in H<sub>2</sub>O/THF biphasic medium, the route via fructose as an intermediate is the dominant pathway. The Lewis acidic sites are responsible for isomerization as well as dehydration. The introduction of HCl as an additive/co-catalyst to AlCl<sub>3</sub> can improve the selectivity to HMF as long as the pH is not low enough so that direct dehydration of glucose becomes dominant. An optimal HMF yield of 62% can be obtained from glucose with 0.1 M HCl added to AlCl<sub>3</sub>-H<sub>2</sub>O/THF medium. Our results are consistent with the report from Dumesic and co-workers on the effect of HCl in conjunction with Lewis acids in alkyl phenol aqueous biphasic medium [15].

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#### **Caption of Figures**

Fig. 1. Reaction routes from glucose to HMF

Fig. 2. The effect of pH (Brønsted acidity) on the conversion of fructose to HMF.

Reaction condition: fructose = 0.25 mmol in H<sub>2</sub>O/THF (1:3 mL) at 160 °C under microwave

heating for 2.5 min. pH is adjusted by HCl and are the values measured at 25 °C.

<sup>a</sup> Results with 0.1 mmol AlCl<sub>3</sub>·6H<sub>2</sub>O as catalyst.

Fig. 3. The effect of pH on the conversion of glucose to HMF with HCl.

Reaction condition: glucose = 0.25 mmol in H<sub>2</sub>O/THF (1:3 mL) at 160 °C under microwave

heating for 5 min. pH is adjusted by HCl.

Fig. 4 The effect of HCl on AlCl<sub>3</sub>·6H<sub>2</sub>O catalyzed fructose conversion.

Reaction condition: fructose = 0.25 mmol, AlCl<sub>3</sub>·6H<sub>2</sub>O = 0.10 mmol in H<sub>2</sub>O/THF (1:3 mL) at 160 °C under microwave heating for 2.5 min. pH is adjusted by HCl.

**Fig. 5.** The effect of HCl on AlCl<sub>3</sub>·6H<sub>2</sub>O catalyzed glucose conversion.

Reaction condition: glucose = 0.25 mmol, AlCl<sub>3</sub>·6H<sub>2</sub>O = 0.10 mmol in H<sub>2</sub>O/THF (1:3 mL) at 160

°C under microwave heating for 2.5 min. pH is adjusted by HCl.

Fig. 6. The effect of HCl on AlCl<sub>3</sub>·6H<sub>2</sub>O catalyzed glucose-fructose isomerization.

Reaction condition: glucose = 0.25 mmol, AlCl<sub>3</sub>·6H<sub>2</sub>O = 0.10 mmol in H<sub>2</sub>O (1 mL) at 120 °C under microwave heating for 30 min. pH is adjusted by HCl.

**Fig. 7.** Conversion of glucose as a function of time using  $AlCl_3 \cdot 6H_2O$ -HCl (pH = 1) in  $H_2O$ /THF biphasic medium.

Reaction condition: glucose = 0.25 mmol, AlCl<sub>3</sub>·6H<sub>2</sub>O = 0.1 mmol, HCl= 0.1 mmol in H<sub>2</sub>O/THF

(1:3 mL) at 160 °C under microwave heating.

**Fig. 8.** Conversion of glucose as a function of time using AlCl<sub>3</sub>·6H<sub>2</sub>O in H<sub>2</sub>O/THF biphasic medium.

Reaction condition: glucose = 0.25 mmol, AlCl<sub>3</sub>·6H<sub>2</sub>O = 0.1 mmol in H<sub>2</sub>O/THF (1:3 mL) at 160

°C under microwave heating.

















