



# Reaction media dominated product selectivity in the isomerization of glucose by chromium trichloride: From aqueous to non-aqueous systems



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## ABSTRACT

While chromium trichloride hydrate ( $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ ) effectively catalyzed the isomerization of glucose into fructose in aqueous solution, a general product selectivity behavior was observed independent of reaction variables such as reaction time, temperature, catalyst loading, halide ion, and initial glucose concentration. By studying the mixed solution of dimethylsulfoxide (DMSO) and water at varied DMSO/ $\text{H}_2\text{O}$  ratios, it was found that deviation from the general water-phase fructose yield curve, with concomitant 5-hydroxymethylfurfural (HMF) formation, occurred when the fructose concentration in available water became sufficiently high in DMSO rich solvent mix. Therefore, tuning the solvent system was the most effective approach to change the product distribution from  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  catalyzed glucose conversion. The apparent activation energy of glucose conversion in the studied system was estimated to be  $58.6 \text{ kJ mol}^{-1}$ . Special attention was also given to gain some mechanistic insights by control experiments with simple model compounds and additives,  $^{13}\text{C}$  NMR and UV–vis spectroscopic analyses.

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## 1. Introduction

With the growing consumption of fossil fuels and the consequential emission of green house gases, the world faces increasing pressure to develop technologies that enable the efficient utilization of alternative sources of energies and renewable feedstocks. Biomass has recently been proposed as a potential feedstock toward sustainable development in both alternative energy and chemicals [1].

In the past decade, saccharides have attracted tremendous attention toward the development of a new biorefinery industry, since they can be utilized to synthesize a variety of valuable chemicals [1]. Dehydration of fructose into 5-hydroxymethylfurfural (HMF) was a mostly studied pathway for this purpose. The fructose dehydration proceeds relatively easily, which can be catalyzed by mineral acid [2–7], organic acid [8,9], metal salt [10–13], solid acid [14–18] in varieties of reaction media, such as

dimethylsulfoxide (DMSO) [8,11,13,19,20], dimethylacetamide (DMA)-LiCl [21], water/organic solvent biphasic system [2,9,17,18], ionic liquid [3,4,12,14–16], and even water [5,22]. Establishing a protocol to produce HMF based chemicals from sugars offers the potential to reduce society's reliance on traditional fossil resources to some extent. Unfortunately, fructose has a low abundance in nature [1], with high cost [23], and is not a suitable feedstock for industrial development. By contrast, glucose is the most abundant monosaccharide and available from many non-edible cellulosic materials. However, the effective conversion of glucose into HMF based products always remained a great challenge until Zhang and co-workers discovered that chromium chloride ( $\text{CrCl}_2$  or  $\text{CrCl}_3$ ) significantly facilitated HMF production from glucose in ionic liquids [24]. The key role of  $\text{CrCl}_x$  was to isomerize glucose into fructose in situ [24]. Thereafter, a spate of researches focused on the conversion of glucose based feedstocks into HMF by employing  $\text{CrCl}_x$  in ionic liquids as well as DMSO or DMA-LiCl system [21,25–32]. Other metal salts, such as tin chloride ( $\text{SnCl}_2$  or  $\text{SnCl}_4$ ) and germanium chloride ( $\text{GeCl}_4$ ), were also found to be effective for the dehydration of glucose in ionic liquids via fructose intermediate [33–35]. In general, the bottleneck of converting glucose into HMF lies on effectively isomerizing glucose into fructose in a reaction medium.

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Up to now, Cr-catalyzed systems are still the most active for HMF production from glucose based feedstocks, and almost all of these systems employ ionic liquids or other non-aqueous solvents [21,24–32]. However, the chemistry of Cr catalysts in isomerizing glucose to fructose is shadowed by that of fructose dehydration to HMF which is rapidly formed as the most abundant product in the non-aqueous solvent systems. Some solvents used above are expensive and some may display toxicity, so alternative cheaper and greener solvents are more desirable. One may be concerned of the potential toxicity of Cr catalyst. In fact, hexavalent chromium is highly toxic while trivalent chromium, found in most foods and nutrient supplements, is an essential nutrient with very low toxicity [36]. Thus, trivalent chromium catalysts should be avoided in an oxidation reaction. Because glucose is a reducing sugar, the oxidation of Cr(II, III) to Cr(VI) is unlikely to occur. Water is the most environmentally benign and naturally abundant solvent. Exploring the ability to utilize water for glucose conversion will be highly attractive for reducing cost of solvent and potential pollution. Recently, a series of studies on the isomerization of glucose into fructose have already been carried out in aqueous solution with solid bases or zeolites as catalysts [37–40]. However, most of the above systems have not been extended for the further use of the in situ formed fructose yet. Nikolla and co-workers have showed reasonable potential for one-pot synthesis of HMF from glucose over Sn-Beta zeolite in water/tetrahydrofuran biphasic system at 160–180 °C [41]. However, the Sn-Beta also has drawbacks, for examples, the aging time for the preparation of this catalyst is very long (>1 month) and it can be poisoned by a certain solvent/additive, such as DMSO [42]. Choudhary et al. recently studied the consecutive conversion of glucose into levulinic acid and xylose into furfural, respectively, in aqueous solution with CrCl<sub>3</sub>·6H<sub>2</sub>O and hydrochloric acid (HCl) as catalysts, and demonstrated that Cr complexes isomerized glucose and xylose into fructose and xylulose, respectively [43,44]. The results offer an opportunity to realize efficient conversion of sugars in aqueous media.

In this work, we investigated the effect of reaction variables on the CrCl<sub>3</sub>·6H<sub>2</sub>O catalyzed isomerization of glucose into fructose in aqueous media in great detail. It is remarkable that these results for the first time revealed a general behavior of glucose isomerization in the studied system independent of the process parameters. It is also noted that other published works involving aqueous systems used for glucose conversion fit into this general behavior. In this work, special attention was also given to gain some mechanistic insights using simple model compounds and additives. Ultraviolet–visible spectroscopic analyses provided information on the interaction between chromium species and glucose during the reaction process.

## 2. Experimental

### 2.1. Materials

D-glucose (99%), D-fructose (99%), 1,6-anhydro-β-D-glucose (AGP, 99%), D-cellobiose (98%) and chromium bromide hexahydrate (CrBr<sub>3</sub>·6H<sub>2</sub>O, 98%) were purchased from Alfa Aesar. Chromium chloride hexahydrate (CrCl<sub>3</sub>·6H<sub>2</sub>O, 96%) and DL-glyceraldehyde (≥90%) were purchased from Sigma–Aldrich. 5-Hydroxymethylfurfural (HMF, 98%), levulinic acid (LA, 99%) and 1,3-dihydroxyacetone dimer (97%) were purchased from Aladdin. Glycerol (99%), dimethyl sulfoxide (DMSO, 99%) and 1,2-propylene glycol (99%) were purchased from Sinopharm (China). Hydrochloric acid (HCl, 36–38 wt%) was provided by a local supplier. All the chemicals were used as received. Deionized water (DI H<sub>2</sub>O) was produced by a Milli-Q Integral 5 system, having a resistivity of 18.2 MΩ cm.

### 2.2. Typical reaction procedure

Glucose (50 mg), CrCl<sub>3</sub>·6H<sub>2</sub>O (3.7 mg, 5 mol% with respect to glucose) and 1 mL of DI H<sub>2</sub>O were added into each reaction vial (5 mL) with a magnetic stir bar. Then, the reaction vials were sealed, inserted into a heating and stirring module (TS-18821, Thermo Scientific, USA), and stirred at 500 rpm for a specified time at the reaction temperature. After the reaction was quenched in ice water bath, 1 mL of DI H<sub>2</sub>O and the internal standard were added into the reaction mixture. Then, a small amount of sample was taken out and further diluted by ~15 times and analyzed by high performance liquid chromatography (HPLC).

### 2.3. Analysis method

HPLC analysis was performed on an Agilent 1260 series with a refractive index detector and a PL Hi-Plex H column (300 mm × 7.7 mm, 8 μm). Diluted H<sub>2</sub>SO<sub>4</sub> solution (0.005 M) at a flow rate of 0.6 mL/min was used as the mobile phase. The column and detector temperatures were 65 and 50 °C, respectively. Authentic chemical compounds were used to identify the retention times. Glycerol was added as an internal standard for the quantitative calculations. For the control experiments with glycerol, DL-glyceraldehyde or 1,3-dihydroxyacetone as simple model compounds or additives, 1,2-propylene glycol was used as the internal standard instead of glycerol. Glucose conversion and product yield are defined as in Eqs. (1) and (2). The pH values were measured by a Mettler-Toledo G20 Titrator with a DG115-SC electrode or Core Module 3 (CM3) System (Freeslate). <sup>13</sup>C NMR spectra were recorded on a Bruker DRX-400 spectrometer. Ultraviolet–visible (UV–vis) spectra were collected on a Shimadzu UV-2600 spectrophotometer.

Glucose conversion (mol%)

$$= \left( 1 - \frac{\text{Mole of remaining glucose detected by HPLC}}{\text{Mole of initially added glucose}} \right) \times 100\% \quad (1)$$

Yield (mol%)

$$= \left( \frac{\text{Mole of product detected by HPLC}}{\text{Mole of ideal amount of product from added feedstock}} \right) \times 100\% \quad (2)$$

## 3. Results and discussion

### 3.1. Isomerization of glucose into fructose in aqueous solution

Chromium dichloride (CrCl<sub>2</sub>) has been mostly reported to be the effective catalyst for HMF production in non-aqueous solvent system [24,25,27,28,31]. However, to avoid CrCl<sub>2</sub> oxidation by air, especially in H<sub>2</sub>O which may cause the oxidation [45,46], chromium trichloride (CrCl<sub>3</sub>) is used in this work. CrCl<sub>3</sub> is also an effective catalyst [24], of which the hydrated form, CrCl<sub>3</sub>·6H<sub>2</sub>O, has better solubility in the solvents [30]. Since water is used as a reaction medium in this work and anhydrous CrCl<sub>3</sub> has poor solubility in H<sub>2</sub>O [30], CrCl<sub>3</sub>·6H<sub>2</sub>O was selected as the catalyst for isomerization of glucose into fructose.

Fig. S1 shows the results of glucose isomerization at 90, 110, and 130 °C for 0.5–4 h in 1 mL of H<sub>2</sub>O each, to which 50 mg of glucose and 3.7 mg of CrCl<sub>3</sub>·6H<sub>2</sub>O (5 mol%, with respect to glucose) were added. The reaction proceeded very slowly at 90 °C, at which glucose conversion and fructose yield reached 13.6% and 10.8%, respectively, after 4 h. Elevating the reaction temperature boosted the isomerization of glucose. At 110 °C, the yield of fructose increased to 21.8% after 4 h, while it reached the maximum

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