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Rasrendra, C. B.; Makertihartha, I. G. B. N.; Adisasmito, S.; Heeres, H. J.

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Green Chemicals from D-glucose: Systematic Studies on Catalytic Effects of Inorganic Salts on the Chemo-Selectivity and Yield in Aqueous Solutions

C. B. Rasrendra · I. G. B. N. Makertihartha ·
S. Adisasmito · H. J. Heeres

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Abstract The use of inorganic salts as catalysts for the reactions of D-glucose in aqueous solutions in a batch reactor is reported. The type of salt and effect of reaction time were examined in detail at a fixed salt (5 mM) and D-glucose concentration (0.1 M) and at a temperature of 140 °C. Al(III) and Cr(II) salts gave the highest conversion of D-glucose. Typical reaction products were organic acids like lactic acid, levulinic acid, furanics like hydroxymethylfurfural and insoluble products (humins). The chemo-selectivity is a clear function of the type of inorganic salt. For Al(III), the major water soluble product was lactic acid, for Zn(II) HMF was formed in the highest yields. A reaction scheme is proposed to explain the observed product compositions.

Keywords Inorganic salts · Lewis acids · D-glucose · HMF · Levulinic acid · Lactic acid · Biobased chemicals

1 Introduction

Research on green chemicals from renewable resources has boosted over the last decade. The C6-sugars (e.g. D-glucose, D-fructose and D-mannose) in lignocellulosic biomass like wood chips and agricultural residues (e.g. straw, corn stover) are interesting precursors for a broad range of chemicals with high application potential [1, 2]. Examples

of target molecules are organic acids like levulinic acid and lactic acid and furanics like hydroxymethylfurfural (HMF) and 2,5-dimethylfuran.

A well established synthetic methodology for levulinic acid, including HMF as an intermediate product, is the acid catalysed hydrolysis of C6-sugars in water (Scheme 1) [3, 4].

Levulinic acid may be obtained in 62 mol% yield at 140 °C in water using sulfuric acid as the catalyst when using D-glucose as the starting material [3]. The intermediate HMF may be obtained in reasonable yields by optimizing the reaction conditions. Recently, organic solvents [5] and ionic liquids [6, 7] were shown to have high potential for these conversions with respect to product selectivity and yield. A wide variety of Bronsted acid catalysts have been tested for these conversions. Examples are homogeneous catalysts like sulfuric acid, hydrochloric acid, phosphoric acid, trifluoroacetic acid [3, 8, 9] and solid acid catalysts like acidic ion exchange resins, zeolites and montmorillonites [10].

Several authors have reported the catalytic effects of metal salts on the dehydration reactions of D-glucose and D-fructose in water. An overview is given in Table 1. In some cases, the combination of Bronsted acids and salts were applied, whereas others only involve the use of inorganic salts. The reactions were carried out at a range of experimental conditions and as such do not provide a consistent picture. The main products are HMF, levulinic acid and/or lactic acid, the yield being a function of process conditions and type of salt.

The reactions performed at temperatures below 150 °C mainly yield HMF and/or levulinic acid. For instance, Van Dam et al. studied the dehydration of D-fructose using HCl as the catalyst [11]. The presence of certain salts (e.g. NaCl, AlCl₃, CrCl₃, and LaCl₃) enhanced the reaction rate

C. B. Rasrendra · H. J. Heeres (✉)
Department of Chemical Engineering,
University of Groningen, Groningen, The Netherlands
e-mail: h.j.heeres@rug.nl

C. B. Rasrendra · I. G. B. N. Makertihartha · S. Adisasmito
Department of Chemical Engineering,
Institut Teknologi Bandung, Bandung, Indonesia

Scheme 1 Acid-catalysed hydrolysis of D-glucose to levulinic acid

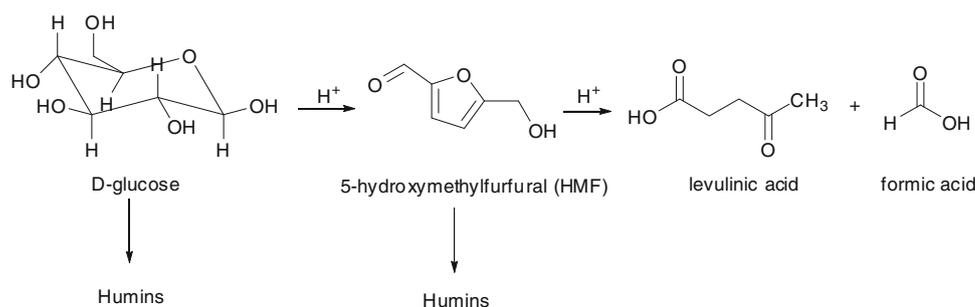


Table 1 C6-sugar conversions using salts as the catalyst

No.	Starting material	Catalyst	Conditions	Product (yield)	Ref.
1	D-fructose (0.5 M)	HCl (1 M) and AlCl ₃ (0.17 M)	88 °C, 500 min	Levulinic acid (42 mol%), HMF (15 mol%)	[11]
2	D-glucose (0.4 M)	HCl in saturated MgCl ₂	3 h under reflux	Levulinic acid (61 mol%)	[12]
3	D-fructose (0.3 M)	DyCl ₃ (2 mM)	140 °C, 120 min	HMF (25 mol%)	[14]
4	D-glucose (0.3 M)	DyCl ₃ (2 mM)	140 °C, 120 min	HMF (12 mol%)	[14]
5	D-fructose (0.055 M)	ZnSO ₄ (400 ppm)	300 °C, 250 bar	Lactic acid (48%) ^a	[19]
6	D-glucose (0.07 g)	CoSO ₄ (400 ppm)	300 °C, 12 s	Lactic acid (yield: 9.5% (g/g))	[20]

^a Selectivity value, defined in C-mol%, see Eq. 3

(8%) and increased the yield of levulinic acid (10%). Tyrlik et al. discovered that magnesium chloride has a positive effect on the formation of levulinic acid when using D-glucose as substrate and HCl as the catalyst. The highest yield of levulinic acid was 61 mol% [12, 13]. Serie et al. reported the application of lanthanum salts as active catalysts for converting D-glucose and D-fructose to HMF in water and DMSO [14, 15]. Krupenskii examined the effects of metal ions such as Al³⁺, Cr³⁺, Ti³⁺, Cu²⁺, Fe³⁺, Ag⁺, Hg²⁺ and Ce³⁺ on the decomposition of several sugars (D-xylose, L-arabinose, D-glucose, D-galactose, D-mannose) in an acidic medium ($T = 130\text{--}150$ °C) [16–18]. A positive effect of the various salts on the dehydration rates of the sugars was observed.

Besides work in aqueous systems at temperatures between 80 and 150 °C, the use of subcritical water at higher temperatures (200–360 °C, 250 bar) has also been explored and was shown to affect the product selectivity considerably. The main product appears lactic acid in this case. For instance, Bicker et al. showed that the presence of 400 ppm of ZnSO₄ gave 42 C-mol% of lactic acid (300 °C, 250 bar) [19]. Kong et al. reported the conversion of D-glucose, microcrystalline cellulose and various types of biomass to lactic acid using salts as catalyst in subcritical water [20]. The lactic acid yield for D-glucose was 9.5 wt% when using 400 ppm Co(II) as the catalyst at 300 °C and 120 s. Yan et al. studied the production of lactic acid from D-glucose in water at 300 °C under basic conditions [21]. Lactic acid was obtained at a yield of 27% when using NaOH as the base.

The studies highlighted above indicate that inorganic salts catalyse the conversion of C6-sugars to interesting biobased chemicals. However, systematic studies aiming to identify the most promising salts in aqueous solutions under comparable conditions as well as the role of the salts and insights in reaction pathways are lacking. As part of a larger program to identify novel catalysts for the production of biobased chemicals from C6-sugars, we here report our research activities on the catalytic effect of a wide range of inorganic salts on the conversion of D-glucose in aqueous solutions.

2 Experimental Section

2.1 Chemicals

The various halide and sulfate salts were obtained from Merck KGaA (Darmstadt, Germany) except for AlCl₃·6H₂O (99%) and Fe₂(SO₄)₃·xH₂O (99%) which were purchased from Sigma-Aldrich, and anhydrous CrCl₂ and LaCl₃ which were obtained from Acros Organics (Geel, Belgium). D-glucose (99%), D-fructose (99%), levulinic acid (98%), formic acid (98%) and L-lactic acid (1 M, standardized solution) were purchased from Sigma-Aldrich. Sulfuric acid (95–97%) and hydrochloric acid (37%) were obtained from Merck KGaA. DL-glyceraldehyde (95%) and dihydroxyacetone (98%) were supplied by Acros Organics (Geel, Belgium). De-ionized water was used to prepare the various solutions.

2.2 Experimental Procedures

The reactions were conducted in glass ampoules with an inside diameter of 3 mm, wall thickness of 1.5 mm and length of 150 mm. A series of glass ampoules was loaded with 0.5 mL of an aqueous solution of 0.1 M D-glucose containing a pre-determined amount of the selected inorganic salt and subsequently sealed with a torch. The sealed ampoules were placed in a constant temperature oven. At various reaction times, an ampoule was taken out of the oven and directly quenched in a water bath (20 °C) to stop the reaction. The reaction mixture was taken from the ampoule and the solid particles (humins) were separated from the reaction mixture by centrifugation using a micro centrifuge (Omnilabo International BV) for 15 min at 1200 rpm. The particle-free solution was diluted with de-ionized water and analyzed by HPLC and capillary electrophoresis (CE).

2.3 Analytical Methods

The amounts of D-glucose, D-fructose, D-mannose, hydroxymethylfurfural, dihydroxyacetone, DL-glyceraldehyde and levulinic acid in the reaction mixture were quantified using HPLC. The HPLC was equipped with a Hewlett Packard 1050 pump, a Biorad Aminex HPX-87H organic acid column and a Waters 410 refractive index detector. The mobile phase was an aqueous solution of sulfuric acid (5 mM) at flow rate of 0.55 mL/min. The column was operated at 60 °C. All samples were measured in duplicate.

A capillary electrophoresis (CE) system from Agilent Technologies was used to determine the amount of formic-, acetic-, glycolic- and lactic acid in the reaction mixture. The CE apparatus was equipped with a cassette containing a standard fuse capillary (75 µm i.d., 72 cm active length, and 80.5 total length) and a diode array detector (DAD). The CE was operated at a temperature of 20 °C and a voltage of –25 kV. Electropherograms were recorded at 350 nm with a reference at 200 nm. A buffer solution (pH = 4.6) from Agilent Technologies containing 5 mM cetyltrimethyl-ammonium bromide (CTAB) was used. The capillary was preconditioned prior to each measurement by flushing the buffer solution for 4 min at 1 bar. All samples were measured in duplicate.

An Inolab pH 730 meter equipped with a Sentix 81 probe was used to measure the pH of the reaction mixtures at room temperature.

2.4 Definitions

The conversion of starting material (X_i) was calculated using the following equation:

$$X_i = \left(1 - \frac{C_i}{C_{i,0}}\right) \times 100 \text{ mol\%} \quad (1)$$

where C_i is the concentration of reactant i after a certain reaction time and $C_{i,0}$ denoted the initial concentration of the reactant.

The yield (Y_j^C) and selectivity (S_j^C) of the reaction products were expressed as carbon-yield and calculated as follows:

$$Y_j^C = \frac{N_j^C}{N_i^C} \times \frac{\text{Concentration of product}}{\text{Initial concentration of reactant}} \times 100 \text{ C-mol\%} \quad (2)$$

$$S_j^C = \frac{Y_j^C}{X_i} \times 100 \text{ C-mol\%} \quad (3)$$

where N_i^C and N_j^C denote the number of carbon atoms of reactant and product, respectively. The carbon yield was used to compensate for the fact that not all products have a similar carbon number as the starting material D-glucose, following a procedure published by Bicker et al. [19].

3 Results and Discussion

3.1 Effect of Type of Salts on the D-glucose Conversion

The effect of a wide range of different salts on the reaction of D-glucose in water was screened at 140 °C using a 0.1 M D-glucose solution and a 5 mM solution of salt as the catalyst. Both halide and sulfate salts of alkali (Na), alkali earth (Mg), aluminum (Al) and transition metals (Mn(II), Co(II), Ni (II), Fe(II), Fe(III), La(III), Cr(II) and Zn(II)) were explored. Sulfuric and hydrochloric acid were used as the reference.

The effect of the presence of salts on the conversion of D-glucose after 6 h reaction time is shown in Fig. 1. It is clear that all salts catalyse the reaction more efficiently than the Bronsted acids HCl and H₂SO₄ under the prevailing reaction conditions. Iron, alkali and alkali earth salts gave low D-glucose conversions (<30 mol%). Significantly higher conversions were found with transition metals and aluminum salts. Essentially quantitative D-glucose conversions were observed for Al(III) and Cr(II) salts, whereas Zn(II) also showed good conversion levels.

No major differences were observed between the halide and sulfate salts of the various metals, suggesting that anion effects in this type of catalysis are of less importance than cation effects.

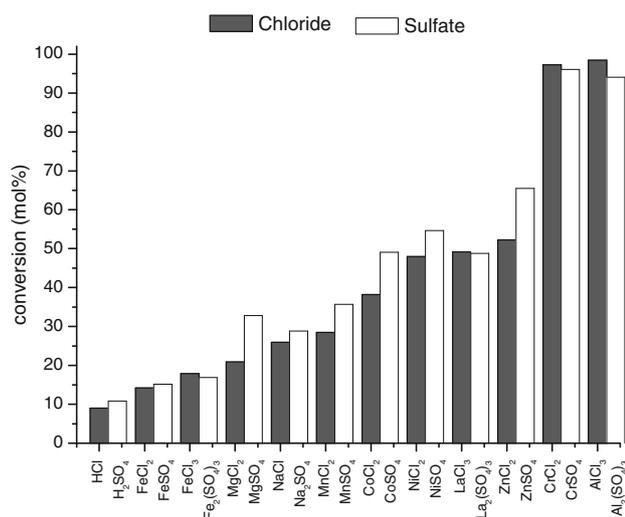


Fig. 1 Effect of various chloride and sulfate salts on the conversion of D-glucose ($C_{\text{salt}} = 5 \text{ mM}$, $C_{\text{acids}} = 5 \text{ mM}$, $T = 140 \text{ }^\circ\text{C}$, $t = 6 \text{ h}$)

3.2 Effects of salts on the chemo-selectivity of the reactions

To gain insights in the influence of the type of salts on the chemo-selectivity of the reaction, the liquid products were identified and quantified by HPLC and CE analyses. Table 2 shows the main reaction products for the various salts.

For iron, alkali and alkali earth metals as the catalyst, the formation of D-fructose and trace amounts of HMF and levulinic acid were observed. The main products for the transition metal and aluminum salts were C6-sugars (D-fructose and D-mannose), furanics (HMF) and organic acids (levulinic-, formic-, glycolic-, acetic-, and lactic acid). Besides these components, major amounts of dark brown solids were formed, known as humins. The formation of humins has been reported for acid catalysed C6-sugar conversions and under some conditions may even be the main product. The compounds are known to consist of higher molecular weight materials formed by condensation reactions. Thus we may conclude that the reaction pathways in the presence of salts appear more complicated than when using typical Bronsted acids like sulfuric acid. In the latter case, lactic acid and glycolic acid were not observed and to the best of our knowledge are also not

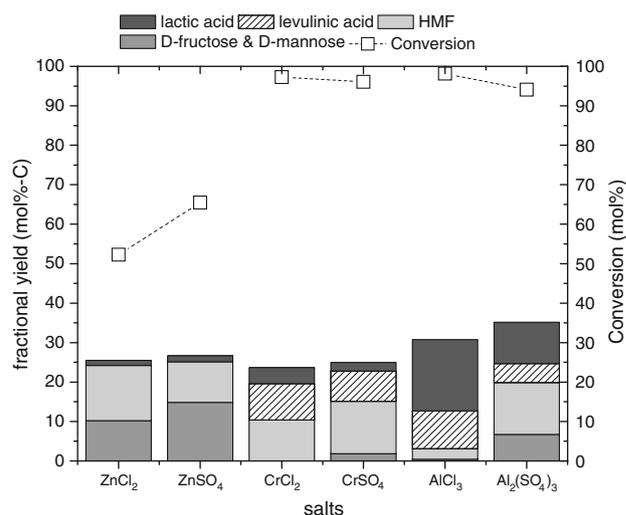


Fig. 2 Product yield after 6 h reaction time for various salts ($C_{\text{GLC}} = 0.1 \text{ M}$, $C_{\text{salt}} = 5 \text{ mM}$, $T = 140 \text{ }^\circ\text{C}$)

reported in the literature when the reactions are carried out at temperatures below $200 \text{ }^\circ\text{C}$.

For the three best performing catalysts with respect to D-glucose conversion (Zn(II), Cr(II) and Al(III), see Fig. 1), the yields of the various individual products at 6 h reaction time are given in Fig. 2. Also included are the D-glucose conversions for each run.

Clearly visible is the difference in chemo-selectivity for the three salts. The aluminum salts result in the formation of considerable amounts of lactic acid and this acid is, besides humins, actually the main product when using AlCl_3 . For Cr-salts, the amount of lactic acid is lower than for Al-salts. However, this comparison is rather difficult to make as the conversion of the intermediate C6-sugars (D-fructose and D-mannose) is not similar for both salts (vide infra). Of interest is the chemo-selectivity for Zn-salts. Lactic acid was present in only very low amounts and the major product was HMF. This implies that Zn-salts may have potential for the synthesis of HMF from C6-sugars.

3.3 Development of a Reaction Network

For AlCl_3 , the composition of the reaction mixtures was followed in time and a typical reaction profile

Table 2 Influence of type of salts on the reaction products

Type of catalyst	Products
Mineral acids	HMF, formic acid and levulinic acid
Fe(II), Fe(III), Mg and Na salts	D-fructose, HMF (trace amount), formic acid and levulinic acid
Mn(II), Co(II), Ni(II), La(III), Cr(II), Zn(II) and Al(III) salts	D-fructose, D-mannose, HMF, formic acid, levulinic acid, acetic acid, glycolic acid and lactic acid

(0.1 M D-glucose, 5 mM AlCl₃, 140 °C) is depicted in Fig. 3. At the start of the reaction, the formation of D-fructose and D-mannose was observed. However, these are clearly intermediate products as the concentrations show a clear optimum. It is well possible that the salt promotes the isomerisation of D-glucose to D-mannose and D-fructose. This isomerisation reaction is well known to be catalysed by solids (cation ion exchange resins, hydrotalcites and metal oxides such as ZrO₂ and TiO₂) and involves an 1,2-enediol as the intermediate [10, 22–24]. The D-fructose and D-mannose formed in the isomerisation reaction are not inert and also known to react to, among others, HMF and levulinic acid [1].

The main water soluble products are organic acids like lactic acid, formic acid and levulinic acid. Only minor amounts of glycolic acid and acetic acid were formed (Fig. 3b). As for the Bronsted acid catalysed reaction, levulinic acid is likely formed from HMF (Scheme 1). The reaction of HMF to levulinic acid is known to give formic acid as the co-product (Scheme 1) and the levulinic- and formic acid are expected to be formed in a 1 to 1 molar ratio. In our experiments, the amount of formic acid is slightly higher than that of levulinic acid. We do not yet have a sound explanation for this observation. It is possible that additional formic acid is formed by yet unknown pathways.

Evidence that aqueous AlCl₃ solutions catalyse the conversion of HMF to levulinic acid and formic acid comes from a separate experiment. When an aqueous solution of HMF (0.1 M) and AlCl₃ (5 mM) were heated to 180 °C for 1 h, 90% HMF conversion was observed and levulinic acid was obtained in 50 mol% yield (entry 1, Table 3).

Lactic acid, the main reaction product, is likely formed from the C6-sugars via a complex reaction pathway neither involving HMF nor levulinic acid as intermediates [19, 21]. The first step is believed to consist in the formation of dihydroxyacetone and glyceraldehyde from the C6-sugars in the mixture through a retro-aldol condensation reaction. In a subsequent step these are dehydrated to pyruvaldehyde which subsequently rearranges to lactic acid (Scheme 2).

Recently, the ability of Lewis acids to convert trioses like glyceraldehyde and dihydroxyacetone into lactic acid has been reported. For example, the application of a Sn-beta zeolite as solid Lewis acid in water gave high lactic acid yields (90%) for reactions at 125 °C and 24 h reaction time [25]. Further evidence for the involvement of glyceraldehyde or dihydroxyacetone in the conversion of C6-sugars to lactic acid under the reaction conditions and salt catalysts employed in this study was obtained by performing reactions with glyceraldehyde and dihydroxyacetone using AlCl₃ as the salt catalyst (140 °C). After 90 min reaction time, both are converted to lactic acid in high yields (90%, entries 2 and 3, Table 3), a clear indication that this reaction is well possible and likely to occur. It also implies that simple salts are efficient catalysts for lactic acid synthesis from glyceraldehyde or dihydroxyacetone.

The presence of Al(III) ions is essential for the formation of lactic acid. When reacting glyceraldehyde or dihydroxyacetone in the absence of salt catalysts or with Bronsted acids like HCl, lactic acid was not detected and the formation of the isomerisation products (dihydroxyacetone or glyceraldehyde), the dehydration product (pyruvaldehyde) and brown insoluble products were observed (entries 7 and 8, Table 3).

So far, we do not have a sound explanation for the formation of the small amounts of acetic acid and glycolic acid formed in the course of the reaction. Srokol et al. observed the formation of small amounts of glycolic acid and acetic acid when reacting C6-sugars at elevated temperatures ($T = 350$ °C) [26]. The formation of acetic acid and glycolic acid was assumed to proceed via retro-aldol condensation reactions.

On the basis of these experiments we can conclude that aqueous solutions of Al-salts catalyse (1) the isomerisation of D-glucose to D-fructose and D-mannose, (2) the conversion of these sugars to glyceraldehyde and dihydroxyacetone and subsequently to lactic acid and (3) also promote the conversion of the C6-sugars to HMF and subsequently to levulinic acid and formic acid. With Bronsted acids like

Fig. 3 Reaction profile of the conversion of D-glucose using AlCl₃ as a catalyst ($C_{\text{GLC}} = 0.1$ mol/l, $C_{\text{salt}} = 5$ mM, $T = 140$ °C)

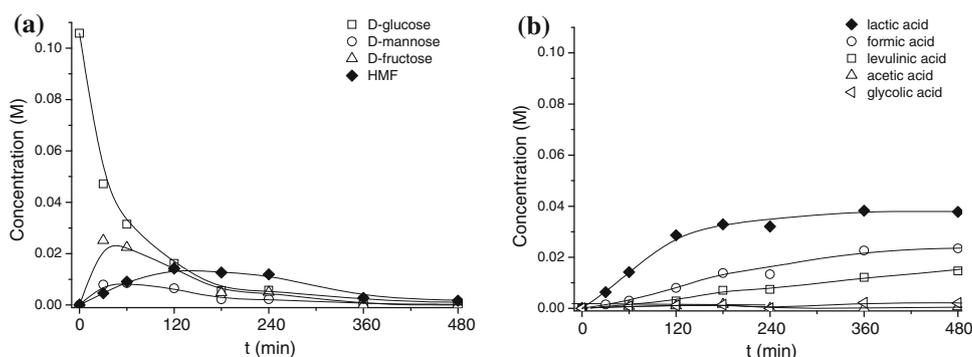


Table 3 Probing the reaction network, experimental data for reactions with intermediate products^a

No	Starting material	Catalyst	t (min)	T (°C)	Conversion (mol%)	Yield (C-mol%)	
						Levulinic acid	Lactic acid
1	HMF	AlCl ₃	60	180	90	50	–
2 ^b	DL-glyceraldehyde	AlCl ₃	90	140	100	–	89
3 ^b	Dihydroxy-acetone	AlCl ₃	90	140	100	–	91
4 ^b	DL-glyceraldehyde	AlCl ₃	40	140	100	–	78 (21) ^c
5 ^b	Dihydroxy-acetone	AlCl ₃	40	140	80	–	76
6 ^b	Dihydroxy-acetone	ZnCl ₂	40	140	43	–	6
7 ^d	Dihydroxy-acetone	HCl	40	140	68	–	–
8 ^d	Dihydroxy-acetone	No catalyst	40	140	21	–	–

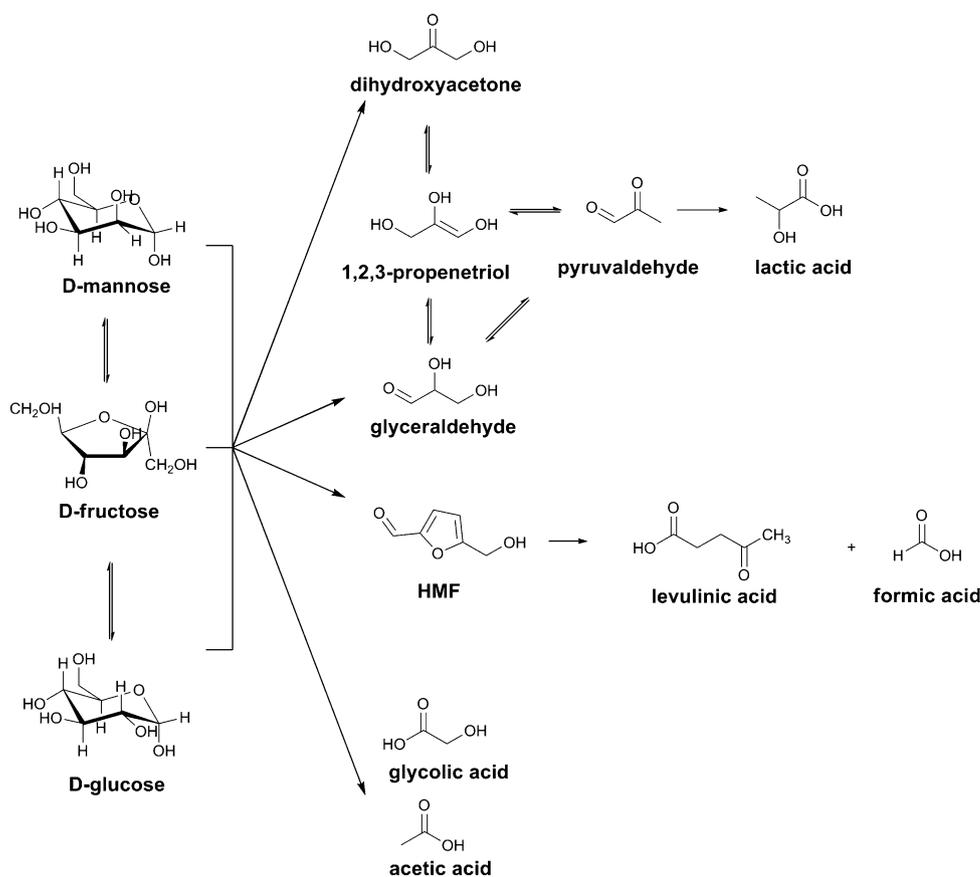
^a Catalyst concentration was always 5 mM, substrate concentration always 0.1 M

^b Clear solution after reaction was observed

^c Yield in parentheses is the C-mol% yield of dihydroxyacetone

^d Pyruvaldehyde and insoluble brown solids were observed

Scheme 2 Simplified reaction network to explain the product formation for D-glucose in the presence of inorganic salts



HCl and H₂SO₄, the pathway leading to lactic acid has not been observed at temperatures below 200 °C and the pathway to HMF/levulinic acid is dominant.

The catalytic action of the inorganic salts used in this study likely involves the Lewis acidic metal centers. The question arises whether Bronsted acidity also plays a role as most salts are amphoteric and when dissolved in water

affect the pH. For instance, the pH of the Al-solutions at room temperature (AlCl₃: 3.86, Al₂(SO₄)₃: 4.33) was far below 7, indicating that Bronsted acidity may also play a role. However, the observed high reactivity as well as the change in chemo-selectivity when using salt solutions in comparison with Bronsted acids alone clearly implies that the metal ions play a key role.

4 Conclusions

The catalytic effects of inorganic salts on the conversion of D-glucose in water have been explored in a systematic manner under similar process conditions. Zn(II), Cr(II) and Al(III) are the most active salts under the conditions employed and the activity exceeds mineral acids like HCl and sulfuric acid. The major liquid product for the Al-salts is lactic acid, an interesting biobased chemical, which is not observed when using Bronsted acids at temperatures below 200 °C. For Zn(II), the major product is HMF under the conditions employed. Further kinetic studies at a range of conditions will be required to optimize the lactic acid and HMF yields for both salts and these are currently in progress. On the basis of the experimental findings, a reaction network is proposed to explain the product compositions. Individual reactions in the network were investigated to determine their validity. An interesting observation was that the intermediate trioses like glyceraldehyde and dihydroxyacetone may be converted in high yields to lactic acid when using Al-salts, an unprecedented finding with possible application potential.

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