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Catalytic effect of aluminium chloride on the example of the conversion of sugar model compounds

Martin Schwiderski^{a,*}, Andrea Kruse^{b,1}

^a Karlsruhe Institute of Technology, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany ^b University of Hohenheim, Garbenstrasse 9, 70599 Stuttgart, Germany

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1. Introduction

ABSTRACT

In this work, the catalytic effect of the Brønsted acid hydrochloric acid, the Brønsted base sodium hydroxide and the Lewis acid AlCl₃ on the conversion of biomass derived carbohydrates is investigated. On the example of the glycolaldehyde conversion, it is shown that the Lewis acid catalyses the ketol-endioltautomerism, the dehydration, the retro-aldol-reaction and the benzilic-acid-rearrangement. The main products are C₄- and C₆-carbohydrates as well as their secondary products 2-hydroxybut-3-enoic acid 1 and several furans. Under the same reaction conditions hydrochloric acid catalyzes mainly the dehydration and sodium hydroxide the tautomerism and subsequent aldolization.

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In the hydrothermal conversion of lignocellulosic biomass, the catalyst is of special importance for the production of chemicals. Herein', Brønsted acids and bases are often used for catalysis. Using a Brønsted acid as the catalyst, biomass can be direct converted into platform chemicals: in the 1920's, the Quaker Oats process had been patented [1]. Herein, biomass is treated in aqueous media containing sulphuric acid under elevated temperatures for several hours. The acid catalyzes mainly two reactions. First, the hydrolysis of the hemicellulose to xylose and second the triple dehydration of xylose to furfural. The yield of furfural in the Quaker Oats process is limited to about 50% (mol/mol). In recent years, production processes underwent several improvements. In the BIOFINE process, the yield is increased up to 75% (mol/mol) [2]. Furthermore, levulinic acid is formed from the biomass containing cellulose. Furfural and levulinic acid 2 are both important platform chemicals. They are designated under the top ten carbohydrates derived molecules by Bozell and Petersen [3]. However, no industrial application for the production of 5-hydroxymethylfurfural HMF 3 from

Andrea_Kruse@uni-hohenheim.de (A. Kruse).

¹ Tel.: +49 711 459 24700; fax: +49 711 459 24702.

http://dx.doi.org/10.1016/i.molcata.2015.03.018 1381-1169/© 2015 Elsevier B.V. All rights reserved. glucose or biomass has been established yet. Since, the conversion of glucose to HMF 3 requires severe reaction conditions glucose undergoes several undesired side reactions, especially the formation of humins. Also, the formed HMF 3 tends to hydrolyze to levulinic acid **2** [4].

The conversion of cellulosic biomass using an alkaline catalyst is well investigated in the literature. Often used catalysts are sodium hydroxide and calcium hydroxide. Starting from cellulose, the main reaction products are organic acids including oxalic, acetic, formic, lactic and succinic acid. Herein, high catalyst dosages of about 1 g catalyst per g biomass and elevated temperatures above 160 °C are required for the conversion. A good overview of the direct conversion of cellulose using alkaline catalysts is given by Knill and Kennedy [5]. At comparable catalyst loadings but lower temperatures cellulose is not converted, but most of the lignin is removed. This makes the cellulose more accessible for the enzymatic hydrolysis to glucose [6–8]. Following, the glucose solution can be fermented to platform chemicals [3].

The use of metal salts for the catalytic conversion of biomass to furans as well as levulinic acid is also investigated in the literature. Herein, it is shown that multivalent metal ions, especially chromium(III), copper(II), iron(III) and aluminium(III) salts catalyze the conversion of hemicellulose and cellulose [9,10]. On the example of the Sn-beta-catalyst, it is shown that metal ions also catalyze the isomerization of aldoses to ketoses [11]. The dehydration of the formed ketoses to furans is much faster than the dehydration of

^{*} Corresponding author. Tel.: +49 721 608 26511; fax: +49 721 608 22244. E-mail addresses: martin.schwiderski@kit.edu (M. Schwiderski),



Scheme 1. Formation of C₄- and C₆-carbohydrates starting from glycolaldehyde 4.

the corresponding aldoses. However, tin containing catalysts are not effective on the dehydration, thus a Brønsted acid needs to be added. A mixture of the tin-beta-catalyst and HCl leads to quite good yields of furfural or HMF **3** starting from xylose or glucose, respectively [12]. Using aluminium chloride in pulping processes of lignocellulosic biomass furfural is obtained without addition of any Brønsted acids. At a temperature of 120 °C and pure water as the solvent furfural yields below 5% are achieved [13]. Using a solvent mixture like THF/water or ethanol/water and higher temperatures, the furfural yield increases up to about 50% [14,15]. One of the major byproducts of the conversion of C₅- and C₆-carbohydrates using metal ion catalysts is lactic acid [14,16].

The metal salt aluminium chloride plays a special role. After dissolving in water, the formed hexahydrate hydrolyzes furthermore. Many hydrolysis products are suggested in the literature. A good overview is given by Bottero et al. [17]. The hydrolysis products are strongly dependent on the pH of the solution [18,19]. However, all of these hydrolysis reactions lead to similar products. On the one hand, hydrochloric acid is released, on the other hand, a complex consisting of one or more aluminium ions (in one special case 13 aluminium ions are coordinated to 4 oxygen ions) coordinated to aqua- and hydroxyligands is formed. Due to these structural similarities, the hydrolysis of aluminium chloride will be discussed according to the simplified Eq. (1) in the following part of this paper.

$$AlCl_3 + 6H_2O \iff [Al(H_2O)_6]Cl_3 \iff Al(OH)_3 + 3H_3O^{\oplus} + 3Cl^{\ominus}$$
(1)

In this work, the catalytic effect of AlCl₃ is investigated on the example of the conversion of the sugar model compounds fructose, methylglyoxal and glycolaldehyde. Since, AlCl₃ decomposes in aqueous solution to hydrochloric acid and the hydroxyl compound, the catalytic effect is compared to those of HCl and NaOH. Of special interest is the ability to catalyze the ketol-endiol-tautomerism, the dehydration, the retro-aldol-reaction and the benzilic-acid-rearrangement. These reactions are the most common ones in the conversion of carbohydrates.

2. Reactions of carbohydrates - literature overview

2.1. Enolisation and aldolisation of glycoladehyde

The formose reaction starting with formaldehyde is a well investigated reaction in the literature. Herein, Ca(OH)₂ is often used as the catalyst and the reaction is carried out at room temperature [20-22]. A cascade of aldol-reactions leads to a mixture of straight- and branched- chain C₃-C₇-carbohydrates. In the recent literature, it is shown that also metal ions like the bivalent zinc or the tetravalent tin are able to catalyze aldol reactions starting from glycolaldehyde 7 to form higher carbohydrates [23,24]. Due to their Lewis acid- character, multivalent metal ions coordinate multiple OH- bonds and stabilize the transition state of enols. In this work, the trivalent aluminium ions are used as the catalyst. In Scheme 1, the possible aldol-reactions starting from glycolaldehyde are shown. The key step is the enolisation of glycoladehyde 4 to the endiol 5 and the subsequent aldolization to form aldotetroses 6. The aldotetroses 6 can isomerize to the corresponding enols 7 and to tetruloses 8. Thus, there is a variety of aldol- reactions possible.



Scheme 2. Reaction mechanism of the formation of HMF 3 starting from an aldohexose 9.

As can be seen in Scheme 1, possible reaction products are straightchain aldohexoses 9, ketohexoses 10 and 3-keto-hexoses 11. Also branched- chain C_6 -carbohydrates 12–14 can be formed, however, they are not reported in the literature yet. The formation of octoses is also possible but it is not part of the investigation in this work.

2.2. Dehydration of C_6 - carbohydrates – formation of furans

There are several mechanisms of the formation of HMF **3** from aldohexoses **9** or one of their tautomers postulated [25]. However, the isomerisation of the aldose **9** to the ketose **10** and then triple dehydration seems to be the dominant reaction path (Scheme 2) [26]. One widely accepted mechanism is the dehydration starting from a ketohexose **10**. The first step is the isomerisation to a furanose **16**. The next step is Brønsted acid catalyzed. Protonation and dehydration of the hemiacetal hydroxyl group at C₂ lead to a tertiary carbenium ion. Subsequent deprotonation and double dehydration lead to HMF **3**. As already mentioned HMF **3** is an intermediate and it tends to hydrolyze to levulinic acid **2**.

Considering these facts, the open chained carbohydrates **11–14** first isomerize to their corresponding furanoses **17–20**. Herein, there are two possibilities to form a five membered ring for the carbohydrate **13** leading to the furanoses **18** and **19**. All the furanoses dehydrate in an analogue mechanism as the furanose **16**. The initial step is the dehydration of the highest substituted alcohol to form a tertiary carbenium ion followed by deprotonation and two consecutive dehydrations in the ring to form 1-(furan-2-yl)-2-hydroxyethanone **21**, 1-(furan-3-yl)-2-hydroxyethanone **22**, 2-(hydroxymethyl)-3-furaldehyde **23**, 3-(hydroxymethyl)-2-furaldehyde **24** (Scheme 3).

2.3. Benzilic acid rearrangement

The mechanism of the benzilic acid rearrangement starting from glyceraldehyde is postulated in the literature. Herein, zinc sulphate is used as the catalyst and the main reaction product is lactic acid [16]. Applying this mechanism on the conversion of tetroses and aluminium chloride as the catalyst, the acid **1** is formed (Scheme 4). The first step is the ketol-enol-tautomerism of aldotetroses **6** followed by two dehydration steps of the enols **7** to form vinylglyoxal **25**. Aluminium chloride decomposes in aqueous solutions into aluminium hydroxide Al(OH)₃ and hydrochloric acid HCl. In the next step, these OH— groups function as nucleophiles and attack the aldehyde carbon. Subsequent hydrid shift and hydrolysis lead to the acid **1**.

3. Materials and methods

Glycolaldehyde-dimer (98%), aqueous methylglyoxal solution (\sim 40%), p-fructose (p.a.), water free aluminium chloride (p.a.), HMF (p.a.) were purchased from "Sigma–Aldrich". Aqueous hydrochloric acid (0.1 M), aqueous sodium hydroxide (0.25 M), both with a purity of p.a. were purchased from "Merck".

3.1. General procedure

In separate volumetric flasks 2.4g (20 mmol) glycolaldehydedimer, 6.15 ml (40 mmol) methylglyoxal-solution, 7.2 g (40 mmol) D-fructose and 0.27 g (2 mmol) aluminium chloride were dissolved in 100 ml water. The resulting concentrations of the sugar compounds were 0.4 M and of aluminium chloride 0.02 M. Before use, the solutions were stirred over night. As the reactor steel autoclaves with 10 ml volume were used. Then 3 ml of the sugar compound solution and 3 ml of the AlCl₃- solution or 1.8 ml 0.1 M (0.18 mmol) HCl and 1.2 ml water or 0.24 ml 0.25 M (0.06 mmol) NaOH and 2.76 ml water were added. The initial concentrations for all experiments were 0.2 M glycolaldehyde-monomer or methylglyoxal or D-fructose and 0.01 M AlCl₃ or 0.01 M NaOH or 0.03 M HCl. Then, the reactor was placed in a GC-oven and heated up for different heating rates. When the oven reached the desired temperature, the time was set to be zero. Therefore, only the time at this temperature was called "reaction time" here. During the reaction, the autoclave was mechanically turned with 20 rpm. After the desired reaction time, the oven was cooled down and the autoclave was left in the oven. After cooling down the product, solution was poured into a 10 ml volumetric flask and the reactor was washed twice with 2 ml water.

3.2. Isolation of the products

As the reactor a non stirred steel autoclave with 500 ml volume was used. The reaction solution was prepared by adding 100 ml 0.4 M aqueous glycolaldehyde to 100 ml 0.02 M aqueous AlCl₃- solution. The mixture was stirred with a spatula for 1 min. Then the reactor was sealed and placed in a GC- oven. The oven was heated to 170 °C and the reaction time was 60 min. After cooling down the product, solution was three times extracted with 200 ml dichloromethane. The organic layer was dried over magnesium sulphate, concentrated and purified over a column using mesoporous silica as the stationary phase and ethylacetate/cyclohexane (1:1 = v/v) as the solvent. Following furans could be isolated: **1-(furan-3-yl)-2-hydroxyethanone22** ($R_F = 0.48$): ¹H



Scheme 3. Formation of furans from open chained hexoses via furanose intermediates.

NMR (250 MHz, CDCl₃): δ = 8.11 (m, 1-H₁), 7.52 (m, 2-H₁), 6.81 (m, 3-H₁), 4.65 (s, 4-H₂) ppm. ¹³C NMR (250 MHz, CDCl₃): δ = 147 (1-C), 145 (2-C), 108 (3-C), 66 (4-C), 194 (q-C), 124 (q-C) ppm. 2-(Hydroxymethyl)-3-furaldehyde23 ($R_F = 0.42$): ¹H NMR $(250 \text{ MHz}, \text{ CDCl}_3)$: $\delta = 10.00 \text{ (s, } 1\text{-H}_1), 7.41 \text{ (d, } 2\text{-H}_1), 6.80 \text{ (d. } 3\text{-}$ H₁), 4.88 (s, 4-H₂) ppm. ${}^{3}J_{2,3}$ = 2.0 Hz. ${}^{13}C$ NMR (250 MHz, CDCl₃): δ = 187 (1-C), 142 (2-C), 110 (3-C), 57 (4-C), 162 (q-C), 123 (q-C) ppm. **3-(Hydroxymethyl)-2-furaldehyde24** (R_F = 0.32): ¹H NMR (250 MHz, CDCl₃): δ = 9.83 (s, 1-H₁), 7.64 (d, 2-H₁), 6.62 (d, 3-H₁), 4.82 (s, 4-H₂) ppm. ${}^{3}J_{2,3}$ = 1.6 Hz. ${}^{13}C$ NMR (250 MHz, CDCl₃): δ = 181 (1-C), 148 (2-C), 113 (3-C), 57 (4-C), 150 (q-C), 138 (q-C) ppm. **5-(Hydroxymethyl)-2-furaldehyde HMF 3** (*R_F* = 0.26): ¹H NMR (250 MHz, CDCl₃): δ = 9.61 (s, 1-H₁), 7.24 (d, 2-H₁), 6.54 (d, 3-H₁), 4.74 (s, 4-H₂) ppm. ${}^{3}J_{2,3}$ = 3.5 Hz. The remaining extracted aqueous phase was adjusted with 0.25 M NaOH- solution to a pH of 10 and three times extracted with 200 ml diethylether. The diethylether layers were discarded. Then the aqueous phase was adjusted with 1 M HCl- solution to a pH of 2 and again three times extracted with 200 ml diethylether. The combined organic phases were dried over magnesium sulphate and the solvent was removed under reduced pressure. The resulting yellow solid was identified as **2-hydroxybut-3-enoic acid 1**. ¹H NMR (250 MHz, C₃D₆O): δ = 4.69 (ddd, 1-H₁), 5.21 (ddd, 2-H₁), 5.48 (ddd, 3-H₁), 6.04 (ddd, 4-H₁) ppm. ${}^{2}J_{2,3}$ < 2.0 Hz, ${}^{3}J_{1,4}$ = 4.8 Hz, ${}^{3}J_{2,4}$ = 10.4 Hz, ${}^{3}J_{3,4}$ = 17.2 Hz,

 ${}^{4}J_{1,2} < 2$ Hz, ${}^{4}J_{1,3} < 2$ Hz. 13 C NMR (250 MHz, C₃D₆O): δ = 71 (1-C), 118 (2,3-C), 133 (4-C), 176 (q-C) ppm. The ¹H NMR-spectra of the identified compounds are shown in supplement Fig. S1–S5. The ¹³C-signals were assigned with their corresponding 2D-NMR-spectra (HMQC, HMBC).

3.3. Analytical methods

Glycolaldehyde **4**, methylglyoxal, levulinic acid **2** and 2hydroxybut-3-enoic acid **1** were measured using HPLC on a Merck Hitachi device. The column is Aminex® HPX-87H. The eluent is aqueous 0.004 M sulphuric acid, the flow rate is 0.5 ml min⁻¹ and the temperature 60 °C. Glycolaldehyde **7** and methylglyoxal were quantified using an RI- detector, the acid **1** using an UV-vis-detector at a wavelength of 210 nm and levulinic acid **2** at a wavelength of 280 nm. Furans were also measured using HPLC on a Merck/Hitachidevice. It is a "Hypersil ODS" column. The mobile phase is a 9:1 (v:v)- mixture of acetonitrile and water with a flow rate of 0.5 ml min⁻¹, the temperature is 30 °C. The samples are detected with an UV-vis- detector at a wavelength of 290 nm. Before measuring on HPLC basic samples were adjusted to a pH of 2 and acidic samples were measured directly.

Calibration of the furans (except HMF **3**) and the acid **1** was done as following described: a small portion of the puri-



Scheme 4. AlCl₃ catalyzed reaction mechanism of the formation of 2-hydroxybut-3-enoic acid 1.



Fig. 1. (A) Conversion of glycolaldehyde **7** and (B) product yields: ■ C₄-carbohydrates, △ C₆-carbohydrates, ● 2-hydroxybut-3-enoic acid **1**, X Furans. Reaction conditions: $c_{0,glycolaldehyde} = 0.2$ M, $c_{0,AlCl3} = 0.01$ M, $V_{H20} = 6$ ml, T = 170 °C, t = 20 min.

fied compounds was dissolved in 0.2 ml D₂O and 0.2 ml of 3-(trimethylsilyl)-2,2',3,3'-tetradeuteropropionic acid TMSP-d₄ in D₂O (c_{TMSP} = 6.34 g l⁻¹) was added. A ¹H NMR-spectrum was measured. Then three dilutions with water were made and measured on the HPLC- devices. HMF **3** was calibrated using commercial available substance.

Carbohydrates were quantified as their alditol acetates. The derivatisation procedure is described elsewhere [27]. Basic samples were derivatised directly and acidic samples were adjusted to a pH of 10. Xylose was added as an internal standard. Quantitative measurements of the carbohydrates were carried out on an Agilent GC 6890 on a Resteck 13323 column. The carrier gas is helium with a flow rate of 1.4 ml min⁻¹. The injection temperature is 35 °C and the GC-oven is heated to 280 °C within 10 min. The split is 30.8:1 and the FID temperature 310 °C. GC-MS- analysis is carried out on a Trace Ultra GC coupled with a DSQ II quadrupole MS detector from the Thermo Scientific. The samples are measured at 250 °C (injector temperature) on a 25-m ULTRA 2 silica column ((5% phenyl)-methylpolysiloxane) from Agilent Technologies. A constant gas flow rate of 1 ml min⁻¹ with the following temperature program are applied: initial temperature 40 °C, increased at $6 \circ C \min^{-1}$ to 200 $\circ C$, further increased with $8 \circ C \min^{-1}$ to a final 300 °C, kept for 5 min. The MS detector is operated in positive ionization mode at 70 eV with an ion source temperature of 200 °C. A GC-chromatogram and the mass spectra of the carbohydrates are shown in supplement Fig. S6-S14.

4. Results and discussion

4.1. AlCl₃ catalyzed conversion of glycolaldehyde at various temperatures

In this section, the conversion of glycolaldehyde **4** using AlCl₃ as the catalyst is discussed. Therefore, the simplified reaction scheme including the main reactions aldolisation, dehydration and the benzilic acid rearrangement is shown in Scheme 5. In Fig. 1A, the conversion of glycolaldehyde **4** and in Fig. 1B, the product yields at various temperatures are shown. At 130 °C, the conversion of glycolaldehyde **7** is 41% and at 170 °C and higher temperatures it is completely converted. At 130 °C besides glycolaldehyde **4** only C₄and C₆-carbohydrates are found in the product mixture. The C₄carbohydrates achieve a maximum yield of 40% at a temperature of 150 °C. The C₆-carbohydrates are in the whole temperature range from 130 °C to 180 °C with maximum 3% less concentrated. Herein, no branched- chain carbohydrates can be detected. At 180 °C, no C₆-sugars are found at all. The secondary products of the carbohydrates are present at 140 °C for the first time. With increasing temperature their yield is also increasing. At temperatures above 170 °C, the acid **1** is the main product. The yield of the furans is with below 6% low. Their distribution is shown in Fig. 2.

With the results shown on Fig. 2, the reaction schemes 1, 3 and 4 will be discussed. The yield of HMF 3 compared to the other furans is at every temperature low and furan 21 is not found at all. Except the aldohexose 9, all carbohydrates are able to form a furanose ring which is suitable for the dehydration to furans. Thus an isomerisation of the aldose 9 to the ketose 10 is required to form HMF 3. The low yield of HMF 3 and that exclusively straight- chain carbohydrates are found lead to the assumption that the isomerisaton of C_6 -carbohydrates is the rate limiting step in the formation of furans. The isomerisation of 10 to 11 is more unlikely and thus no furan 21 is formed. Another possibility to produce carbohydrate 11 and thus furan **21** is the aldolisation of the C₄-enol **7** and glycolaldehyde **4**. However, in a competitive reaction the enol 7 dehydrates to form vinylglyoxal 25. Probably, the dehydration is much faster and the sugar 11 and thus furan 21 are not present. The carbohydrate 13 is able to dehydrate without further isomerisation to any tautomers. That's why in the whole temperature range the secondary products 22 and 23 are the most present furans in the product mixture.

4.2. Conversion of glycolaldehyde using different catalysts

Aluminium chloride $AlCl_3$ decomposes in aqueous solutions to aluminium hydroxide $Al(OH)_3$ and hydrochloric acid HCl. The cat-







Scheme 5. Simplified reaction scheme of the AlCl₃ catalyzed conversion of glycolaldehyde 4.

Table 1	
Conversion of glycolaldehyde 7 and product yields using different catalysts. Reaction conditions: $c_{0,glycolaldehyde} = 0.2$ M, $V_{H2O} = 6$ ml, $T = 170$ °C, $t = 20$ min.	

Entry	Catalyst	Conversion glycolaldehyde 4 [mol-%]	Yield C ₄ -carbohydrates [mol-%]	Yield acid 1 [mol-%]	Yield C ₆ -carbohydrates [mol-%]	Yield furans [mol-%]
1	none	34%	8%	0	Traces	0
2	0.03 M HCl	51%	12%	0	Traces	0
3	0.01 M NaOH	100%	20%	0	27%	Traces
4	0.01 M AlCl ₃	100%	20%	23%	2%	5%

alytic effect of aluminium ions compared to the effect of a Brønsted acid HCl and a Brønsted base sodium hydroxide NaOH is examined. Therefore the conversion of glycolaldehyde **4** using these three catalysts is investigated (Table 1).

The non catalyzed (entry 1) and the HCl catalyzed (entry 2) reaction show a similar product distribution. The conversion of gly-colaldehyde **4** and the yield of C₄- carbohydrates in entry 2 are just slightly higher than in entry 1. In both cases C₆- carbohydrates are formed just in traces and no acid **1** and no furans are formed. In the ¹H NMR-spectrum of the extracted product solution of entry 2 (Supplement Fig. S15) just glycolaldehyde **4** in its monomeric form can be determined.

Using NaOH (entry 3) as the catalyst glycolaldehyde **4** is fully converted. The main products are C_4 - and C_6 -carbohydrates. The distribution of the C_6 -carbohydrates is about 75% straight- chain and 25% branched- chain (Supplement Fig. S6 and Fig. S7). In entry 3 no acid **1** is present and just HMF **3** is formed in traces.

Also, in the AlCl₃ catalyzed reaction (entry 4) glycolaldehyde **4** is fully converted. The main products using AlCl₃ as the catalyst are tetroses and the acid **1**. The C₆-carbohydrates are the minor products, the main part of them is further converted to furans.

Evaluating these results, it can be concluded that both $AlCl_3$ and NaOH are efficient catalysts for the enolisation and subsequent aldolization. In the case of using HCl, there is just a minor catalytic effect of the enolisation of glycoladehyde **4**. Furthermore, AlCl₃ catalyzes the dehydration of the formed carbohydrates, whereas in the NaOH catalyzed reaction just traces of the dehydration products are formed.

4.3. Conversion of fructose

On the example of the fructose conversion, the ability of HCl, NaOH and AlCl₃ to catalyze the dehydration, the retro-aldol-reaction and the benzilic acid rearrangement is investigated. The results are given in Table 2.

In the case of using HCl, fructose is completely converted after 60 min reaction time. The yield of the dehydration products (HMF **3** and the secondary product levulinic acid **2**) is 74%. No retro-aldol-products like dihydroxyacetone, glyceraldehyde, methylglyoxal or lactic acid are formed.

In the AlCl₃, catalyzed reaction fructose is also completely converted and the yield of the dehydration products is 42%. In this reaction a quite high amount of 27% of lactic acid is produced. Lactic acid derives from the retro-aldol-products dihydroxyacetone or its isomer glycerinaldehyde. Double dehydration leads to methyl-glyoxal and a benzilic acid rearrangement to the final product lactic acid. This mechanism is equal to the one shown in Scheme 4.

Та	bl	e	2

Conversion of fructose and product yields using different catalysts. Reaction conditions: $c_{0,fructose} = 0.2 \text{ M}, V_{H2O} = 6 \text{ ml}, T = 170 \degree \text{C}, t = 60 \text{ min}.$

Entry	Catalyst	Conversion fructose [mol-%]	Yield HMF 3 [mol-%]	Yield levulinic acid 2 [mol-%]	Yield lactic acid [mol-%]
1	0.03 M HCl	100%	11%	63%	0
2	0.01 M NaOH	54%	11%	0	0
3	0.01 M AlCl ₃	99%	13%	29%	27%

Table 3

Conversion of methylglyoxal and product yields using different catalysts. Reaction conditions: $c_{0,methylglyoxal} = 0.2 \text{ M}$, $V_{H20} = 6 \text{ ml}$, $T = 170 \circ \text{C}$, t = 20 min.

	Entry	Catalyst	Conversion methylglyoxal [mol-%]	Yield lactic acid [mol-%]
Ì	1	0.03 M HCl	29%	0
	2	0.01 M NaOH	100%	0
	3	0.01 M AlCl ₃	100%	87%

If glucose is used as the starting material much more HMF **3** is produced, if $AlCl_3$ is used as the catalyst [14]. Although HCl is a very efficient catalyst for dehydration reactions, it fails to enolize and isomerize glucose to fructose. Aluminium chloride decomposes in aqueous solutions to triaquatrihydroxyaluminium and hydrochloric acid. The aluminium ions catalyze the isomerisation to fructose and the hydrochloric acid the dehydration to HMF **3**.

NaOH has the weakest effect on both the conversion and HMF **3** yield. Just 54% of the initial fructose is converted and the yield of the dehydration products is 11%. Conspicuous is that the secondary product levulinc acid 2 is not formed. Also, no retro-aldol-products are detected. In the literature, it is shown that Brønsted bases are effective catalysts for the retro-aldol-reaction and the benzilicacid-rearrangement to form lactic acid from C₆-carbohydrates. Treating an aqueous glucose solution containing Ca(OH)₂ at the boiling point, on the one hand lactic acid is formed with a yield of 26%. On the other hand, cyclic enols and phenols are found in the product solution [28]. That means an alkaline catalyst is efficient for the retro-aldol-reaction. Next to the benzilic acid rearrangement to form lactic acid other reactions such as recombination, aldolcondensation and cyclisation to form cyclic compounds take place [29]. In this work, it is shown that at higher temperatures also the dehydration of C₆-carbohydrates to form HMF 3 plays an important role. But the effect of the dehydration of NaOH is low compared to HCl and AlCl₃.

4.4. Conversion of methylglyoxal

To form the acid **1** or lactic acid, an enolization step of the C_4 - or C_3 -carbohydrates is necessary (Scheme 4). To form lactic acid from C_6 -carbohydrates, the retro-aldol-reaction to form C_3 -carbohydrates is additionally needed. In the previous results, it is shown that there is either just a weak or no catalytic effect of HCl on the enolisation and retro-aldol-reaction. To prove the ability of HCl, to catalyze the benzilic acid rearrangement additional experiments of the conversion of methylglyoxal are done. The results are shown in Table 3. The AlCl₃ catalyzed conversion is completely and leads to a high yield of 87% of lactic acid. Also, in the NaOH catalyzed reaction methylglyoxal is completely converted. However, no lactic acid is formed. As mentioned above at higher temperatures other reactions than the benzilic acid rearrangement are favoured. The effect of HCl on the reaction is weak. Just 29% of methylglyoxal is converted and no lactic acid is formed.

5. Conclusion

In this work, the catalytic effect of NaOH, HCl and AlCl₃ on the example of the conversion of glycolaldehyde **4**, fructose and methylglyoxal is investigated. It is shown that the Brønsted acid catalyzes the dehydration but it has a weak effect on the ketol-endiol-tautomerism, retro-aldol-reaction and the benzilic-acid-rearrangement. The catalytic effect of the Brønsted base is opposite. It is a weak dehydration catalyst but it mostly catalyzes

the tautomerism. Aluminium chloride combines the catalytic properties of a Brønsted acid and a Brønsted base. All the previously mentioned reactions are catalyzed by the Lewis acid.

In view of biorefineries, especially in the production of the platform chemical 5-Hydroxymethylfurfural **3**, Brønsted bases are not suitable because of their low dehydration ability on carbohydrates. If inulin containing biomass, such as Jerusalem artichoke or chicory roots, is used as the starting material Brønsted acids are very effective catalysts for the formation of HMF **3**. However, Brønsted acids fail in the direct conversion of cellulosic biomass to HMF **3** because of their missing ability to catalyze the tautomerism of glucose to fructose. Since the Lewis acid AlCl₃ catalyzes both, the tautomerism and the dehydration, it is an effective catalyst for the direct conversion of cellulose to platform chemicals. But AlCl₃ also catalyzes the retro-aldol-reaction and the benzilic-acid-rearrangement. Both are undesired side reactions. Thus there are extensive kinetic studies required to optimize the yield of HMF **3**.

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Appendix A. Supplementary data

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