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

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ABSTRACT

In this work, the catalytic effect of the Brønsted acid hydrochloric acid, the Brønsted base sodium hydroxide and the Lewis acid AlCl$_3$ 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-endiol-tautomerism, the dehydration, the retro-aldol-reaction and the benzilic-acid-rearrangement. The main products are C$_4$- and C$_6$-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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1. Introduction

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 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

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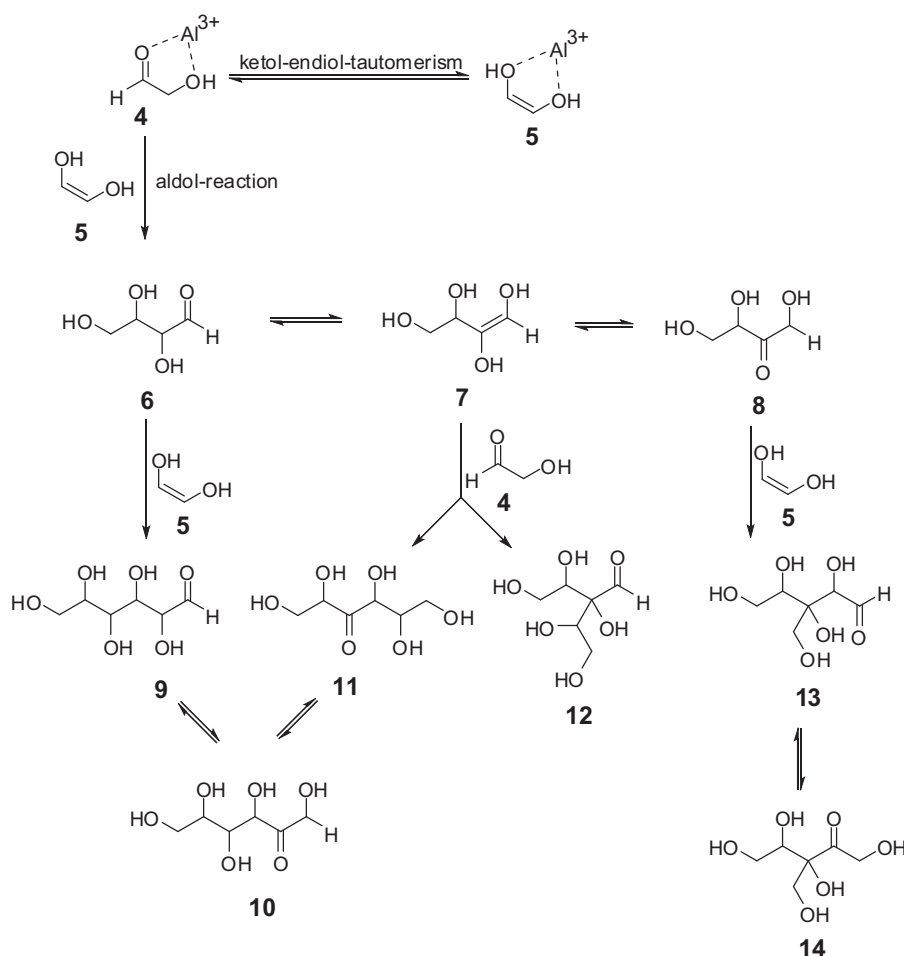
Scheme 1. Formation of C_4- and C_6-carbohydrates starting from glycolaldehyde **4**.

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 C_5- and C_6-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.

$$AlCl_3 + 6H_2O \leftrightarrows [Al(H_2O)_6]Cl_3 \leftrightarrows Al(OH)_3 + 3H_3O^{\oplus} + 3Cl^{\ominus} \quad (1)$$
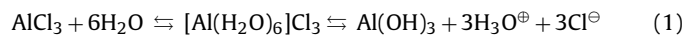
In this work, the catalytic effect of $AlCl_3$ is investigated on the example of the conversion of the sugar model compounds

fructose, methylglyoxal and glycolaldehyde. Since, $AlCl_3$ 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 C_3–C_7-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.