Experimental and modelling studies on the synthesis of 5-hydroxymethylfurfural from sugars
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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2015

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):

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Summary

Fossil resources play a key role in energy generation, the transportation sector and for the production of materials, food and pharmaceuticals and this has been the case for more or less the past 100 years. The environmental footprint of an economy based totally on fossil resources is high and the development of alternative, sustainable sources and processes for energy and materials production is of prime importance. Alternative energy sources are already used (solar, wind and water power), although significant improvements are still needed. The production of materials generally requires sources of organic carbon. The only source of sustainable organic carbon is biomass and it is for this reason that biobased chemicals need to be developed, especially for bulk applications.

When sugars are heated in the presence of Brønsted acids, 5-hydroxymethylfurfural (HMF) is formed. HMF is considered a ‘sleeping giant’, as it may be converted into a number of high-potential building blocks, especially for polymers. The synthesis of HMF presents challenges in terms of yield and work-up/purification. In order to overcome these challenges, more knowledge is required about the actual dehydration chemistry of sugars to HMF. The research discussed in the present thesis entitled ‘Experimental and modelling studies on the synthesis of 5-hydroxymethylfurfural from sugars’ was performed with two main objectives in mind: (i) to gain new insights in the reaction pathways of the dehydration of ketohexoses to HMF and (ii) to identify the most suitable hexose for HMF production from a selectivity and activity point of view.

The state of the art on the dehydration of sugars to HMF and the conversion of HMF into building blocks for chemicals, materials and fuels are reviewed in Chapter 2. It shows that the vast majority of the research performed on the synthesis of HMF so far is done on small scale in a research laboratory setting. Initially mainly fructose and glucose were used as substrates, but recent years have seen an increase in the use of polysaccharides. The state of the art clearly shows the effects of solvents on HMF yields and underpins the importance of solvent selection. For the acid-catalysed fructose dehydration in water, the maximum yield of HMF is around 50%, a value that can be increased to around 90% by using ionic liquids or polar aprotic solvents. For glucose the yields are typically below 10%. Yields from glucose
can be improved by using bifunctional catalysts, which presumably involves an initial isomerisation of glucose to fructose. The vast majority of the research so far has focused on yield optimisation by (systematic) catalyst screening studies. Mechanistic studies to intrinsically understand the chemistry and to postulate reaction mechanisms are virtually absent. In general, the highest HMF yields and selectivities have been obtained in exotic reaction systems that are difficult to translate and scale up to economically viable and industrially relevant processes.

In Chapter 3 an experimental and modelling study is reported on the reactivity of different hexoses in water using sulphuric acid as the catalyst. Three aldoses (glucose, mannose and galactose) and three ketoses (fructose, sorbose and tagatose) were tested using high-throughput experimentation and supported by DFT calculations. The aldoses are less active and less selective for HMF formation than the ketoses. Major differences in reactivity were not observed for the three aldoses. On the contrary, the ketoses show significant differences in reactivity and selectivity to HMF, explained by considering the hydroxyl group orientations on the C3 and C4 positions for the various ketoses. These findings point to a reaction mechanism involving cyclic intermediates.

Experimental studies on the use of methanol instead of water as the reaction medium for the conversions of ketoses to HMF are described in Chapter 4. The ketoses are much more reactive in methanol than in water. In addition, HMF was formed in minor amounts as it is etherified to its methyl ether, 5-methoxymethylfurfural (MMF). Fructose, sorbose, tagatose and psicose again show significant differences in reactivity and selectivity to furanics. Psicose and tagatose show the highest conversion rates, whereas fructose and psicose show the highest selectivities for HMF and MMF formation. The highest maximum MMF yield was found for psicose, at around 55%. The formation of significant amounts of an HMF isomer, 2-hydroxyacetylfuran (HAF), was observed for sorbose and tagatose. This study supports the claim (Chapter 3) that the stereochemistry of the OH groups at C3 and C4 plays a key role in the reaction network, supporting a reaction mechanism with cyclic intermediates in the rate-determining step. HAF formation was studied in more detail by performing experiments with $^{13}$C-labelled sorbose and subsequent analyses of the reaction mixtures using $^{13}$C-NMR. The results imply that HAF formation proceeds via a 1,4-anhydroketose.

Experimental studies on the reactivity of psicose in acidic water are discussed in Chapter 5 and the results are compared to fructose, sorbose and tagatose. The results are consistent with those in Chapters 3 and 4, pointing to the importance of the orientation of the hydroxyl groups on C3 and C4 regarding the reaction rate and selectivity to HMF. The
formation of HAF was only observed for tagatose and sorbose, indicating a key role of the stereochemistry of the hydroxyl group on C4 in the reaction pathway to HAF.

As shown in Chapter 4, it is beneficial to perform catalytic sugar conversions in alcohols instead of water. Since the solubility of sugars in alcohols may differ considerably from that in water, the solubility of six sugars (glucose, fructose, mannose, xylose, arabinose and sucrose) in methanol and methanol-water mixtures has been determined experimentally and the results are described in Chapter 6. The results were successfully modelled with a UNIQUAC model and may be used for further scale-up studies.