Catalysis
Science & Technology

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Cite this: *Catal. Sci. Technol.*, 2013, **3**, 1565

Simultaneous hydrolysis and hydrogenation of cellobiose to sorbitol in molten salt hydrate media

Jianrong Li, Helena S. M. P. Soares, Jacob A. Moulijn and Michiel Makkee*

Received 22nd November 2012,
Accepted 11th March 2013

DOI: 10.1039/c3cy20808g

www.rsc.org/catalysis

The hydrolysis and hydrogenation of cellobiose (4-*O*-β-D-glucopyranosyl-D-glucose) in $ZnCl_2{\cdot}4H_2O$ solvent was studied to optimize the conditions for conversion of lignocellulose (the most abundant renewable resource) into sorbitol (D-glucitol). Water at neutral pH does not allow hydrolysis of cellobiose under the conditions of the experiments (up to 125 °C, 4 h), but relatively fast hydrogenation of cellobiose into 3-β-D-glucopyranosyl-D-glucitol over a Ru/C catalyst in the presence of H_2 takes place. In $ZnCl_2{\cdot}4H_2O$ hydrolysis does take place in the range of temperatures studied (75–125 °C) and simultaneously hydrogenation (H_2, Ru/C), though at a lower rate than that in neutral water. Thus, a one-pot conversion of cellobiose into sorbitol is possible. The hydrolysis is the rate limiting reaction, but the selectivity to sorbitol is determined by the rate of hydrogenation. Under optimal conditions the yield of sorbitol is ≥95%. The kinetic pathways are discussed.

Introduction

The sustainable production of fuels and chemicals from biomass has attracted broad interest from the catalysis and chemical engineering community.[1,2] At present much attention is given to the so-called 2nd generation of biomass resources, *viz.*, lignocellulosics, mainly because of their abundant presence without direct competition with the food chain. Cellulose as the most abundant fraction of lignocellulosics especially deserves attention (i) because of its crystalline structure and since the glucosidic linkages are in the β configuration, it is much more stable in most processes, for instance under fermentation conditions; and (ii) because of its simple, regular structure and well-defined composition, it is well suited for the production of platform molecules for the chemical industry.[3–9]

Conversion of cellulose into different platform chemicals is a hot topic.[10,11] These platform chemicals include glucose, hexitols (sorbitol), HMF,[12] gluconic acid, alkyl glycosides, ethylene glycol,[13] and levulinic acid.[14] Conversion of cellulose into sorbitol through glucose is possible by a combination of hydrolysis and hydrogenation.

Hydrolysis of glycosidic bonds in cellulose to glucose can be achieved with hot water;[3,4] with concentrated or diluted mineral acids such as H_2SO_4,[15–17] HCl; solid acid catalysts such as, Nafion, Amberlyst, H-mordenite (H-zeolite), carbon based solid acids,[18,19] and sulfonated silica–carbon nanocomposites which were found to be more active and selective than the pure carbon based solid acid catalysts;[20] phosphate salts;[21] enzymes;[22] ionic liquids such as 1-butyl-3-methylimidazolium chloride;[23,24] basic solvents such as NaOH in water;[25] inorganic molten salt hydrates such as $ZnCl_2{\cdot}4H_2O$ and $LiCl{\cdot}4H_2O$.[6,26]

Inorganic molten salt hydrates as solvents for cellulose have been studied earlier by Fischer *et al.*[27,28] Zhang and coworkers used ionic liquids in the hydrolysis of cellulose to glucose and further dehydration of D-glucose *via* D-fructose into 5-hydroxymethylfurfural (HMF).[29,30]

Hydrogenation catalysts commonly used in the literature are supported metal catalysts,[31] such as ruthenium on carbon,[32–38] ruthenium on carbon nanotubes,[39,40] Ru-loaded zeolites,[41] nickel on carbon nanofibers,[42] tungsten carbide on carbon nanotubes;[43] ruthenium nano-particles and promoted nickel catalysts were also reported as catalysts for conversion of cellulose into polyols.[44,45] In this study Ru/C catalysts have been selected, because in contrast to RANEY®-type Ni catalysts in the hydrogenation of glucose no leaching was observed.[37]

In previous work, we have selected molten salt hydrate $ZnCl_2{\cdot}4H_2O$ as the solvent and 5 wt% ruthenium on carbon as a hydrogenation catalyst for the study of cellulose conversion. We reported the conversion of cellulose into sorbitol (D-glucitol) and subsequent dehydration into isosorbide in molten salt hydrate $ZnCl_2{\cdot}4H_2O$, as illustrated in Fig. 1.[6]

The yield of glucose from cellulose was over 90%. Compared to reported processes converting biomass, this number is high. Nevertheless the development of a practical process calls for an

Catalysis Engineering, ChemE, Delft University of Technology, Julianalaan 136, 2628 BL, Delft, The Netherlands. E-mail: m.makkee@tudelft.nl; Fax: +31 15 278 5006; Tel: +31 15 278 1391

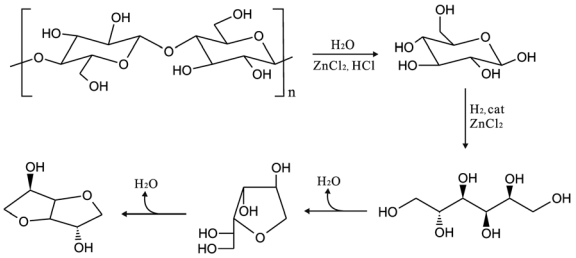

Fig. 1 Conversion of cellulose into isosorbide. The reaction pathway consists of hydrolysis of cellulose to glucose, hydrogenation of glucose to sorbitol, dehydration of sorbitol to sorbitan (only 1,4-anhydrosorbitol is shown in the scheme), and sequential dehydration of sorbitan to isosorbide.[6]

intensive programme because (i) the intermediate product glucose is prone to degradation, calling for a precise engineering of the process; and (ii) the separation of this type of products from the solvent, $ZnCl_2{\cdot}4H_2O$, has not been reported in the literature.

In this paper, we focus on the production of sorbitol and the conditions for obtaining high sorbitol yield. Primary study of this work is a part of a PCT international application.[46]

In the hydrolysis step the glucose produced is a thermally rather unstable molecule. At higher temperature isomerization to fructose occurs and large amounts of degradation products are formed.[4] An advantage of the reaction scheme, as illustrated in Fig. 1, is that glucose is converted into the much more stable sorbitol. It is self-evident that the engineering of coupling of the two reactions, glucose formation and conversion, is crucial.

An exploratory study aimed at optimizing the conversion of the solid cellulose into glucose is expected to be very time-consuming. When a simple model compound could be used the research would be greatly facilitated. An obvious choice is cellobiose, (4-*O*-β-D-glucopyranosyl-D-glucose), which is the repeat unit of cellulose ($(1,4\text{-}O\text{-}\beta\text{-glucopyranosyl})_{n-1}$-D-glucose).

Several articles on a one-pot conversion of cellobiose or cellulose into sorbitol have been reported. Deng *et al.* used 68% concentrated HNO_3 pretreated carbon nano-tube supported ruthenium as catalyst, and successfully converted cellobiose into sorbitol, a sorbitol yield of 87% was achieved at 185 °C after 3 hours reaction.[3] Luo *et al.* showed that in water at elevated temperature in the presence of Ru/C catalysts up to 20% hexitols were produced from cellulose.[4] Yan *et al.* reported the use of ruthenium nano-clusters as a hydrogenation catalyst under acidic conditions (pH = 2, HCl is generated during the formation of Ru nanoparticles) and 100% sorbitol yield was obtained at 120 °C after 12 hours reaction with a catalyst to cellobiose ratio of 1 : 500 (on weight basis).[5] Fukuoka and Dhepe studied one-pot conversion of cellulose into sugar alcohols by supported metal catalysts and reported 30% sugar alcohols yield after 24 hours at 50 bar hydrogen and 190 °C with a catalyst to cellulose ratio of 1 : 2.[47]

For a practical process the yield of sorbitol has to be high (typically >90%) and the catalyst to substrate ratio should be economically acceptable, the rates of the conversion steps involved (dissolution cellulose, hydrolysis, hydrogenation steps) should be satisfactory. The results of the model compound study should be representative for cellulose conversion. In this paper, we report an exploratory optimization study on the one-pot conversion of cellobiose into sorbitol in $ZnCl_2{\cdot}4H_2O$ solvent. The reaction pathway and the kinetics network will be discussed.

Experimental

Materials

Zinc chloride (≥98.0%), D-(+)-glucose (>99.5%), ruthenium 5 wt% on carbon and D-(−) fructose (≥99%) were obtained from Sigma-Aldrich. D-Sorbitol (D-glucitol) (≥99.5%) and D-(+)-cellobiose (≥99.0%) were obtained from Fluka.

Reactions

The reactions were carried out in a mini-multi-batch reactors set-up (ProSense); the reactors (autoclaves) have a volume of 16 ml, are made of Hastelloy C, equipped with a magnetic stirrer (stirring rate up to 2000 rpm) and a K-type thermocouple to measure the temperature of the liquid (T_{liquid}). A separate heater is available allowing a temperature of up to 300 °C, and the maximum operation pressure is 100 bar.

Hydrolysis. Transparent molten salt hydrate $ZnCl_2{\cdot}4H_2O$ was prepared prior to use. 0.5 g of cellobiose was dissolved in 6 g of $ZnCl_2{\cdot}4H_2O$ at room temperature and, subsequently, this mixture was added to the reactor. The reactor was flushed three times with nitrogen. The pressure in the reactor was increased to 30 bar with nitrogen, the reactor was placed in the heater, which already was at the desired set point, and the stirrer was started (1500 rpm). The time when the reactor was placed in the heater was defined as $t = 0$. After about 15 min, the temperature of liquid inside the reactor was constant. At the end of the experiment heating and stirring were stopped and the autoclave was removed from the heater and quenched in cold water. When the temperature of the reactor reached room temperature, the pressure was released and, subsequently, a sample was taken and prepared (diluted and filtrated) for HPLC analysis.

Hydrogenation. The procedure was identical to the hydrolysis procedure, except for the addition of a specified amount of catalyst (Ru/C) to the reactor. The reactor was flushed three times with nitrogen and subsequently three times with hydrogen and at ambient temperature the hydrogen was set at a total initial hydrogen pressure of 40 bar.

Analysis and characterization methods

High performance liquid chromatography (HPLC) analysis. After the reaction, the sample was diluted with the eluent used for HPLC, then the solid catalyst and, if present, tars were separated by filtration, and the liquid phase was analyzed using a HPLC (Hewlett Packard) set-up, equipped with a Refractive Index (RI) detector. Two types of columns were used, *i.e.* Phenomenex Rezex RCM-Monosaccharide HPLC Column (8% Ca^{2+}, 300 × 7.80 mm) and Supelco apHera™ NH2 HPLC Column (5 μm particle size, 250 × 4.6 mm). The eluents used were water and acetonitrile–water (75 : 25), respectively.

Scanning electron microscopy (SEM). A (Philips XL20) SEM operated at 15.0 kV was used to image original cellobiose powder. Sample was coated with gold using a vacuum sputter-coater to

improve the conductivity of the sample and thus the quality of the SEM images.

X-ray diffraction (XRD). XRD patterns were recorded in a Bragg–Brentano geometry in a Bruker D5005 diffractometer equipped with a Huber incident-beam monochromator and a Braun PSD detector. Data collection was carried out at room temperature using monochromatic Cu Kα1 radiation (λ = 0.154056 nm) in the 2θ region between 10° and 30°. Si-reference powder (NBS640b), thin layer specimen, was measured to determine the instrumental width, under identical measurement conditions to the sample. Data evaluation was done with the Bruker program EVA.

Thermogravimetric analysis (TGA). A METTLER TOLEDO TGA/SDTA851^e was used for investigating the contents of free moisture in cellobiose crystalline powder and the degradation temperature of cellobiose. Two protocols were applied, *i.e.*, (1) 25 °C, He 100 ml min^{-1} drying for 15 min, then 25–150 °C, 3 °C min^{-1}; (2) 25 °C, He 100 ml min^{-1} drying for 15 min, then 25–400 °C, 3 °C min^{-1}, respectively.

Results

Cellobiose characterization

SEM and XRD results showed that cellobiose has a high crystallinity; using Scherrer's equation, we calculated that the crystals had a lateral dimension of 140 nm. TGA data showed that the cellobiose crystals contained very little free moisture, about 0.6% weight. In the region of 235–360 °C, cellobiose lost main part of its weight, corresponding with the thermal decomposition/degradation of cellobiose.

Hydrolysis

In demi-water cellobiose did not react under the conditions applied (up to 125 °C, 4 h). In $ZnCl_2$ hydrate hydrolysis of cellobiose occurred. The results of a typical example at 95 °C at varying reaction times are given in Fig. 2. Besides glucose, mannose and fructose are observed, showing the mild isomerization/epimerization activity of the system. Furthermore, 5-hydroxymethylfurfural (HMF) is observed, probably formed by dehydration of fructose. Some "unknown" products are observed.

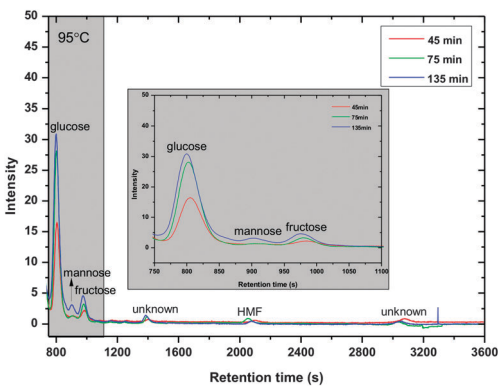

Fig. 2 Hydrolysis of cellobiose at 95 °C at varying reaction times (0.5 g cellobiose, 6 g $ZnCl_2{\cdot}4H_2O$).

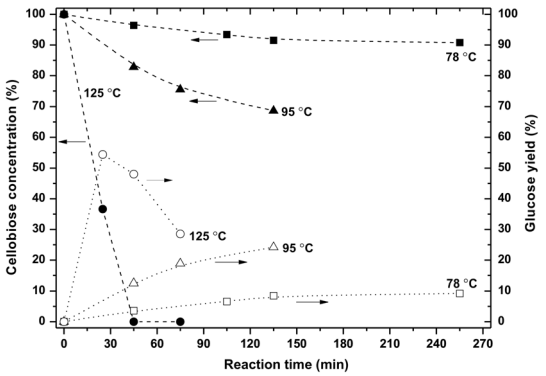

Fig. 3 Product distribution of the hydrolysis of cellobiose at varying times and temperatures (0.5 g cellobiose, 6 g $ZnCl_2{\cdot}4H_2O$). The dashed lines are guidance for the eyes.

The structures of the unknowns have not yet been identified. The amount of byproducts (HMF and unknowns) increases with the reaction time.

The conversion at various temperatures is shown in Fig. 3. At around 80 °C the conversion was limited, but the selectivity to glucose was high. No byproducts were formed, only glucose was observed. At 95 °C the rate was 2–3 times higher, but byproducts were observed (Fig. 2), resulting in loss of selectivity.

Full conversion was only achieved at 125 °C but at the expense of a low selectivity to glucose. At this temperature the glucose yield went through a maximum, illustrating the serial kinetic pathway with glucose as the main primary product. The maximum yield of glucose was only 55%.

The loss of selectivity as a function of temperature and conversion can be best seen in Fig. 4. Clearly, at high temperature the conversion is high but the selectivity is disappointing. The relatively high glucose selectivity point at 125 °C corresponds to, compared to the low temperature data, a short reaction time; at prolonged reaction time the glucose selectivity drops enormously, as is shown in Fig. 4.

Simultaneous hydrolysis and hydrogenation

Water as solvent. The hydrogenation of cellobiose in water was used as reference. Cellobiose dissolved very well in water,

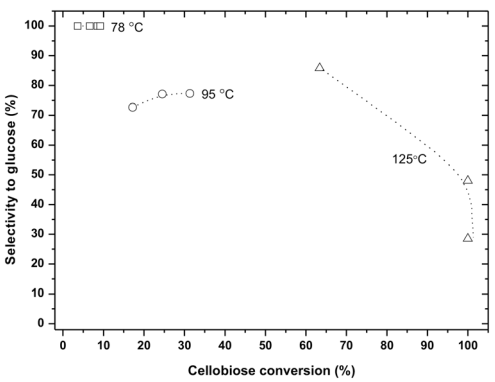

Fig. 4 Plot of selectivity to glucose *versus* conversion for the hydrolysis of cellobiose (0.5 g cellobiose, 6 g $ZnCl_2{\cdot}4H_2O$). The dashed lines are guidance for the eyes. The data correspond to those in Fig. 3.

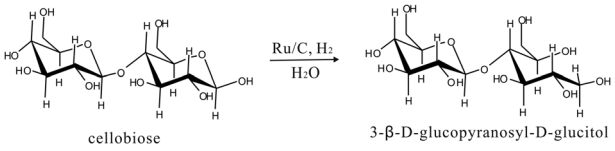

Fig. 5 Cellobiose conversion into 3-β-D-glucopyranosyl-D-glucitol.

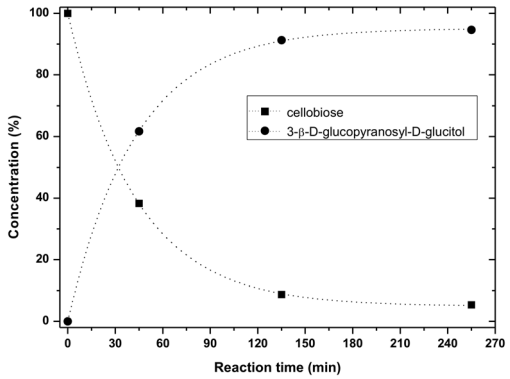

Fig. 6 Cellobiose hydrogenation in water at 95 °C (0.5 g cellobiose, 6 g water, 0.025 g Ru/C, P_{H2} 40 bar). The dashed lines are guidance for the eyes.

but hydrolysis did not take place, as expected. Hydrogenation did take place, forming 3-β-D-glucopyranosyl-D-glucitol: (Fig. 5)

Typical results are shown in Fig. 6. A clean reaction was observed with only one product, being 3-β-D-glucopyranosyl-D-glucitol. After 135 min at 95 °C, 90% conversion was reached with 100% selectivity to 3-β-D-glucopyranosyl-D-glucitol.

$ZnCl_2 \cdot 4H_2O$ as solvent. In $ZnCl_2$ hydrate the product spectrum strongly differs from that in pure water as solvent. At 95 °C the major product was 3-β-D-glucopyranosyl-D-glucitol, but also glucose and sorbitol are observed. With increasing time the sorbitol concentration continuously increased, whereas the 3-β-D-glucopyranosyl-D-glucitol concentration went through a maximum. At 500 minutes the 3-β-D-glucopyranosyl-D-glucitol and the sorbitol yields were 60 and 20%, respectively, as shown in Fig. 7.

Apparently, 15% of the cellobiose or the intermediate product glucose were converted into byproducts. Clearly, compared to

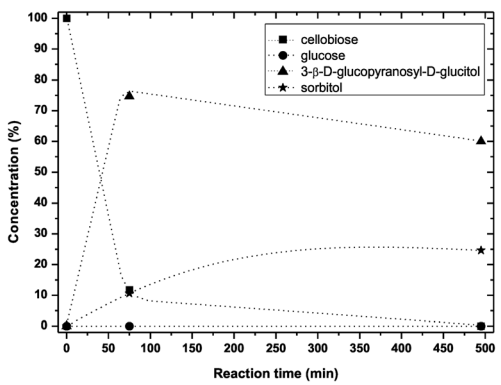

Fig. 7 Cellobiose conversion at 95 °C (0.5 g cellobiose, 6 g $ZnCl_2 \cdot 4H_2O$, 0.125 g Ru/C, P_{H2} 40 bar). The dashed lines are guidance for the eyes.

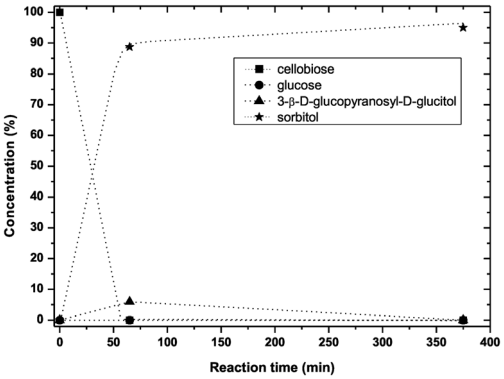

Fig. 8 Product distribution for simultaneous hydrolysis and hydrogenation at a high catalyst loading at 125 °C (0.5 g cellobiose, 6 g $ZnCl_2 \cdot 4H_2O$, 0.125 g Ru/C, P_{H2} 40 bar). The dashed lines are guidance for the eyes.

hydrogenation rate the rate of hydrolysis is low, in agreement with the earlier observation that in hydrolysis full conversion is only achieved at 125 °C. Fig. 8 shows the results of simultaneous hydrolysis and hydrogenation at this temperature. Already after 65 minutes 90% yield of sorbitol was realized. At longer reaction time full conversion was observed. Again 3-β-D-glucopyranosyl-D-glucitol as one of the intermediates was formed and the profile shows a maximum. At this temperature the concentration of 3-β-D-glucopyranosyl-D-glucitol did not exceed 10%. The reaction is proceeding in a remarkably clean way. A yield of 95% of sorbitol was obtained with only 5% of byproducts (mannitol and un-assigned products).

The interplay between hydrolysis and hydrogenation can be illustrated by tuning the rate of hydrogenation. Hydrogenation can be switched on by adding a catalyst.

The effect of different amounts of catalyst on the reaction results at 95 °C is shown in Fig. 9. The higher the loading of Ru/C, the larger is the rate of conversion of cellobiose. At 95 °C with 25 wt% catalyst, the conversion reached 88% after 75 min; with 50 wt% catalyst, full conversion of cellobiose was observed after 75 min. Although high conversions can be obtained, the selectivity to sorbitol was not high. Only 13% of sorbitol and 85% of 3-β-D-glucopyranosyl-D-glucitol were obtained when the

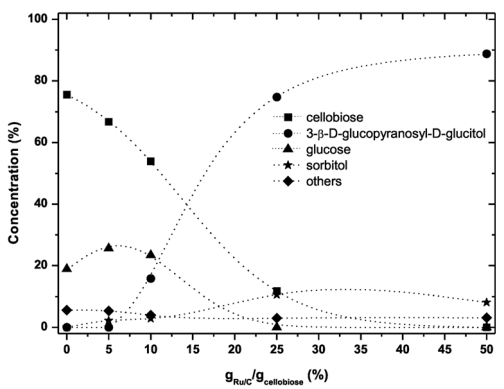

Fig. 9 Effect of catalyst loading on the product distribution at 95 °C (0.5 g cellobiose, 6 g $ZnCl_2 \cdot 4H_2O$, varying amounts of Ru/C, P_{H2} 40 bar, 75 min). The dashed lines are guidance for the eyes.

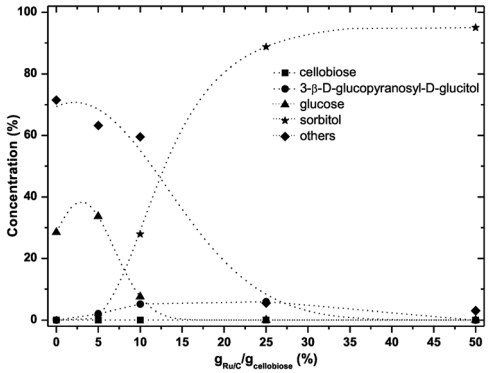

Fig. 10 Effect of catalyst loading on the product distribution at 125 °C (0.5 g cellobiose, 6 g $ZnCl_2{\cdot}4H_2O$, varying amounts of Ru/C, P_{H2} 40 bar, 75 min). The dashed lines are guidance for the eyes.

catalyst amount was 25 wt% with respect to the cellobiose weight with a reaction time of 75 min.

At 125 °C, when the amount of catalyst was varied the product distribution dramatically changes as is illustrated in Fig. 10. At low catalyst loading significant amounts of glucose and excessive amounts (>60%) of degradation products (''others'') were observed, whereas at highest catalyst loading essentially a clean production of sorbitol (95% of yield) was observed.

Discussion

The simultaneous hydrolysis and hydrogenation of cellobiose has a spectacular impact on the selectivity of the reacting system. In Fig. 11 we summarize at 125 °C the beneficial influence of coupling hydrolysis with hydrogenation. In the absence of favorable hydrogenation conditions (H_2, Ru/C) extensive side reactions are observed (epimerization to mannose and isomerization to fructose, followed by degradation of fructose to HMF and char, unknowns). When the reaction is carried out under favorable hydrogenation conditions the reaction product is very clean. Obviously, $ZnCl_2{\cdot}4H_2O$ is a good solvent for dissolving cellulose, but it causes degradation reactions of glucose.

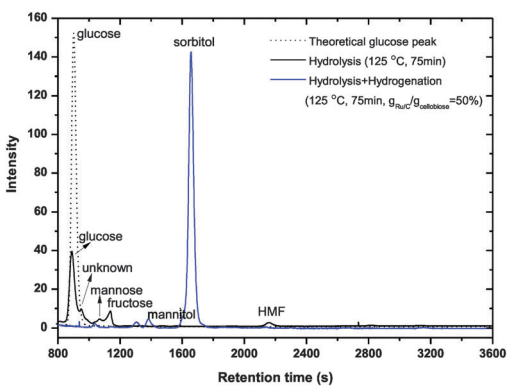

Fig. 11 HPLC patterns showing the influence of hydrogenation on the occurrence of glucose degradation reactions at 125 °C (hydrolysis and hydrogenation conditions, see Experimental).

Fortunately, hydrogenation in this solvent is possible, producing the more stable sorbitol and, as a consequence, a clean reaction is feasible if we push sufficiently the hydrogenation reaction rate. It should be noted that with the simultaneous hydrolysis and hydrogenation, the carbon-balance is closed and the char formation is avoided.

The data for water as solvent show that hydrolysis of cellobiose is not occurring in a neutral environment. This observation is not surprising and agrees with the conclusion that cellobiose will be dissolved, but cannot be hydrolysed in water under the conditions of this study. Hydrogenation does occur and 3-β-D-glucopyranosyl-D-glucitol is formed,[3] where the C–O bond in the pyranose ring structure of cellobiose is adsorbed at the catalyst surface, followed by bond breaking and reaction with two activated H atoms.[51] An alternative mechanism would be the hydrogenation of the aldehyde bond in the open chain form.

The rate of hydrogenation is high and this route might be an attractive route to the β-isomer of the well-known sugar-free sweetener, isomalt.[48,49]

In $ZnCl_2{\cdot}4H_2O$ under hydrogenation conditions 3-β-D-glucopyranosyl-D-glucitol is also observed, but in addition sorbitol is produced. At lower temperature (95 °C) 3-β-D-glucopyranosyl-D-glucitol is the main product, whereas at higher temperature (125 °C) sorbitol is more predominant, suggesting that under our reaction conditions hydrolysis is the limiting reaction.

The reaction pathways from cellobiose to sorbitol have been studied previously. Yan and coworkers[5] proposed that under acidic conditions, cellobiose is firstly hydrolyzed to glucose, subsequently glucose is hydrogenated to sorbitol with a hydrogenation catalyst. Deng and coworkers[3] proposed for their system (nitric acid, Ru/C, H_2) a different pathway, first hydrogenation takes place of cellobiose to 3-β-D-glucopyranosyl-D-glucitol, followed by consecutive hydrolysis resulting in sorbitol formation.

We conclude that in the $ZnCl_2$ hydrate solvent hydrolysis of cellobiose to glucose and hydrogenolysis of cellobiose to 3-β-D-glucopyranosyl-D-glucitol proceed simultaneously. By tuning the conditions, the acidity, the temperature, the reaction time and the hydrogenation catalyst activity the selectivity can be chosen. We found that the hydrolysis requires higher temperature than the hydrogenation reaction.

We propose the pathway as presented in Fig. 12.

According to this scheme, the first step could be either the hydrogenation reaction to form 3-β-D-glucopyranosyl-D-glucitol, followed by the hydrolysis to sorbitol and glucose, or the hydrolysis to two glucose molecules, followed by hydrogenation to sorbitol.

The question arises which of the two pathways to sorbitol is the most important. In order to get information on the relative reactivity we studied the reactivity of the methyl ether, 1-β-*O*-methylcellobiose (for structure, see Fig. 13):

Hydrogenation reactivity of glucose and methyl glucose have been compared.[49] The reactivity of methyl glucose appeared to be relatively low. It is well-known that the methyl group hinders the ring opening of the pyranose structure.[50,51] From our observation

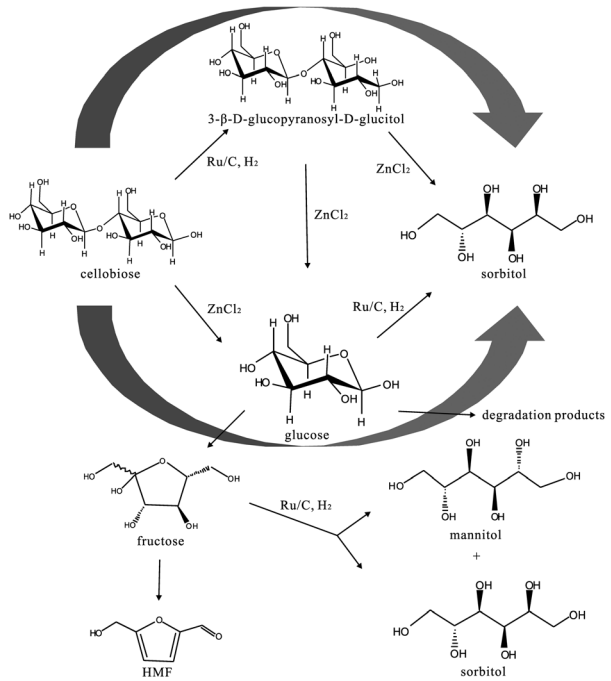

Fig. 12 Scheme of the main hydrolysis and the hydrogenation conversion pathway of cellobiose in $ZnCl_2{\cdot}4H_2O$.

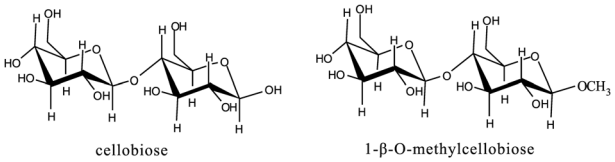

Fig. 13 Structures of cellobiose and 1-β-*O*-methylcellobiose.

that the hydrogenation of methylcellobiose hardly occurred with respect to the hydrogenation of cellobiose, we conclude that the hydrogenation takes place *via* a ring opening hydrogenolysis mechanism.[51] This nicely agrees with the conclusion that the hydrogenation step involves ring structure opening, though a mechanism involving a sequential keto-group hydrogenation is not ruled out. Thus the pathway involves either hydrolysis, followed by hydrogenation or hydrogenation followed by hydrolysis. From the observation that at mild temperature the rate of hydrogenation of cellobiose far exceeds the rate of hydrolysis we tentatively conclude that in our solvent the hydrolysis is the limiting reaction. Referring to the kinetic scheme in Fig. 12, we conclude that both pathways to sorbitol, *via* 3-β-D-glucopyranosyl-D-glucitol followed by hydrolysis or *via* direct hydrolysis of cellobiose to glucose followed by hydrogenation, are operative, but the first one is kinetically most important.

It should be noted that the selectivity of the process is critically dependent on the conditions. If the hydrogenation activity is not high enough, glucose will undergo isomerization and extensive degradation reactions. Several products will be formed such as HMF (dehydration product of fructose),[29,30] mannitol (hydrogenation product of fructose) and to some extent mannose and fructose. Similarly, if the reaction conditions are changed, the reaction depth might be changed accordingly, and sorbitol might undergo extensive sequential reactions, as for instance reported in the work of Huber *et al.*[52,53] The strategy and importance of tuning parameters for hydrolysis of cellulose has also been reported recently by Van de Vyver *et al.*[54] To control the reaction depth of this work, tuning of the $ZnCl_2$ hydrate medium concentration, the hydrogenation catalyst amount, reaction temperature and reaction time can be done. In addition, adding extra mineral acid such as HCl has been reported, which accelerates the rate determining step, *i.e.* the hydrolysis step.[6,41] However, addition of HCl leads to an increase of the rate of degradation reactions and it might interfere with the hydrogenation catalysis. For a better understanding and evaluation of the $ZnCl_2$ hydrate medium effects, it was decided to use no additional HCl.

In this study sorbitol was the desired product. The kinetic scheme shows that by tuning the conditions the severity of hydrolysis and of hydrogenation can be tuned independently of each other. Thus, the technology presented is flexible and in principle allows the production of different platform molecules, such as glucose, 3-β-D-glucopyranosyl-D-glucitol, sorbitol, and HMF.

For the hydrogenation step the heterogeneous catalyst Ru/C has been selected. The catalyst stability is critical for the process economics. Recently it was reported by Op de Beeck *et al.*,[55] that the stability of the Ru/C hydrogenation catalyst is an issue, because of deposition of polymeric byproducts. Investigations regarding the catalyst stability should have high priority.

Cellobiose has been studied as a model for cellulose. The results suggest that when cellulose is reacted under combined hydrolysis and hydrogenation conditions the oligomers formed are quickly transformed by hydrogenations into the 3-β-D-(poly)-glucopyranosyl-D-glucitol analogues and, as a consequence, the selectivity to sorbitol will be comparable with that presented here for cellobiose. In an exploratory study this was shown to be the case.[46]

Conclusions

Simultaneous hydrolysis and hydrogenation of cellobiose reduces following reactions as degradation and isomerization, allowing high conversion of cellobiose with extremely high selectivity to sorbitol (95% sorbitol yield). Optimizing the reaction conditions (amount of catalyst, hydrogen partial pressure, the reaction temperature, composition of the molten salt hydrate) allows producing sorbitol at high yield. Reaction pathways have been assigned.

The technology presented here allows a flexible production of platform molecules from cellulose. The potential sweetener 3-β-D-glucopyranosyl-D-glucitol can be easily produced from cellulose by hydrogenation of cellobiose.

Acknowledgements

The authors would like to thank BIO^{e}CON for the financial support; Prof. Dr. Ir. Herman van Bekkum is acknowledged for his stimulating discussions.

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