The impact of salts formed by the neutralisation of (ligno)cellulose hydrolysates on the hydrogenation of sugars

Jakob Hilgert,[a] Sérgio Lima,[b] Atte Aho,[c] Kari Eränen,[c] Dmitry Yu. Murzin,*,[c] and Roberto Rinaldi*,[b]

Abstract: The dilute acid hydrolysis of lignocellulose often requires a neutralisation step to utilise the hydrolysate's sugars. In this context, it is expected that acids or their corresponding salts produced by neutralisation can affect the catalyst performance. Nonetheless, very little is known regarding the impact of salts on the catalyst performance in the hydrogenation of sugars. In this work, the influence of a series of ammonium and alkali metal salts [i.e. NH_4NO_3, $NaNO_3$, $(NH_4)_2SO_4$, Na_2SO_4 and K_2SO_4] on the hydrogenation of glucose and xylose is addressed. This study also encompasses 'real-world' hydrolysates obtained by the mechanocatalytic depolymerisation of microcrystalline cellulose, α-cellulose and beechwood. The influence of acids and their salts were examined for the hydrogenation of sugars to sugar alcohols (alditols) in the presence of a commercial Ru/C catalyst (Ru/C, 0.7 wt% Ru) at 110 °C using batch and continuous flow reactors. The results showed that the presence of salts leads to a considerable decrease in the alditols yields. Notably, salt anions exert an effect stronger than that of cations in the catalyst deactivation. For glucose solutions, nitrates had a more significant effect on the decrease in the alditols yield than sulfates, while chlorides had the lowest impact. In this study, we also present the effect of degradation products (e.g. HMF and furfural) upon hydrogenation of lignocellulose hydrolysates. The activated carbon pre-treatments of the hydrolysates showed a positive effect on the catalyst activity, adsorbing hydrolysis by-products. Overall, this study has significant implications for the practical aspects of hydrogenation of lignocellulose hydrolysates, aspects that are often neglected in the current literature.

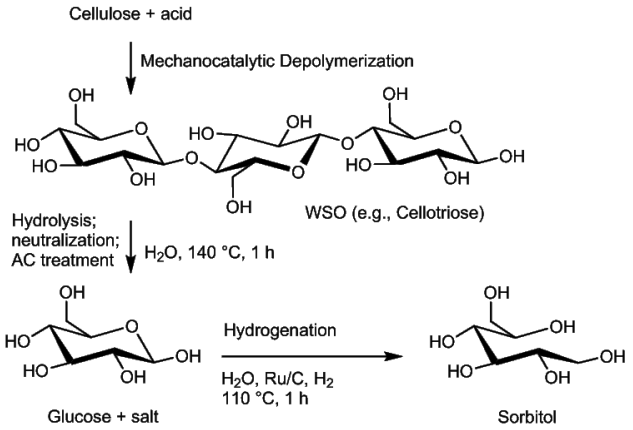
1. Introduction

Sugar alcohols or alditols show several applications in the food, pharmaceutical, and cosmetic industries (e.g. sugar substituents and tooth-friendly sweeteners, moisture stabilisers, softeners, carrier or a general conditioning agent).[1] Alditols can be produced by hydrogenation of monosaccharides obtained from the hydrolysis of lignocellulose biomass.[2] From hexoses (e.g. glucose from cellulose), a mixture of sorbitol and mannitol can be produced. From pentoses (e.g. xylose from hemicelluloses or arabinose), xylitol is obtained. Hydrogenation of glucose to sorbitol is a well-studied reaction. Currently, sorbitol is produced with excellent selectivity at full conversion on a scale of 1 Mt per annum, mostly in batch reactors by catalytic hydrogenation of high-purity glucose over Raney Ni.[1] Sorbitol also constitutes a highly promising platform chemical for the production of renewable fuels,[3] H_2,[4] and isosorbide and sorbitan.[5] In the last two decades, research related to cellulose-based oligomers hydrogenation to sugar alcohols was aimed at understanding the active phase of Raney Ni,[6] replacing Raney Ni with Ru catalysts,[7], and optimising catalyst properties and tailoring active sites and support.[8] Recently, several review articles have appeared covering hydrogenation of sugars in a great deal of detail.[5, 9] The direct use of lignocellulosic biomass as feedstock to produce alditols faces several challenges, some of which are related with its recalcitrance and insolubility in water. The recalcitrance nature and insolubility of cellulose can efficiently be overcome by the solid-state mechanocatalytic depolymerisation of acidified dry lignocellulose, which generates an acidified solid mixture of oligosaccharides soluble in water[10] As the inorganic acid catalyst is not consumed throughout the process chain, the further catalytic upgrading of the water-soluble oligosaccharides (WSO) may be performed beginning with the acidified sugar solutions (e.g. in the production of furfurals,[11] levulinic acid,[12] or sugar alcohols).[13] For the production of sugar alcohols, hydrolytic hydrogenation can be carried out at temperatures as low as 150 °C[13a] when water-soluble products obtained by mechanocatalytic depolymerisation are employed as the starting material, instead of insoluble cellulose (190-240 °C).[14]

Although the direct use of lignocellulose hydrolysates without prior separation or purification for chemocatalytic production of value-added chemicals has been demonstrated, the effect of impurities, or residual salts from the acid neutralisation, has not been addressed in detail. By-products, such as 5-hydroxymethylfurfural or furfural, formed in low levels in the cellulose hydrolysis step, and inorganic salts also present in low concentrations (due to neutralisation step) might influence the further catalytic downstream upgrading. From another angle, $ZnCl_2 \cdot 4H_2O$, a salt hydrate which is liquid at room temperature,[15] has been employed as an inexpensive alternative to ionic liquids[16] acting as a cost-effective reaction medium for efficient hydrolysis of cellulose.[17] The high salt concentration could first be hypothesised to affect the hydrogenation course due to strong ion/dipole interactions established between ions and sugar dissolved in molten salt hydrates,[18] which could change the adsorption of sugars on the hydrogenation catalyst. In practice, however, Moulijn et al.[15] reported an elegant approach rendering high yield of sorbitol from the hydrolytic hydrogenation of cellobiose in the presence of Ru/C employing $ZnCl_2 \cdot 4H_2O$ as the reaction medium. Despite a good performance of Ru/C catalyst in $ZnCl_2 \cdot 4H_2O$, recycling experiments have not been reported.[15]

Considering the dilute acid hydrolysis of cellulose, the impact of salts, derived from the neutralisation of sugar stream, on the prolonged performance of hydrogenation catalysts is still a subject of too much speculation. Usually, the experiments are performed with high loading of highly active Ru/C catalysts (e.g. 100 mg[13a] or higher loadings[15]), which hinder the prompt verification of small decays in catalyst productivity, because Ru/C is generally a very stable catalyst. In this study, catalytic hydrogenation of neat sugar solutions and sugars derived from hydrolysis of cellulosic and beechwood substrates over a commercial Ru/C catalyst, in batch and continuous trickle-bed reactors, was investigated. The current study assesses the effects of NaCl, NH_4NO_3, $NaNO_3$, $(NH_4)_2SO_4$, Na_2SO_4, K_2SO_4 on the performance of Ru/C. We chose these salts because only strong mineral acids (HCl, HNO_3 or H_2SO_4) are active for mechanocatalytic depolymerisation of cellulosic feedstock to WSO (Scheme 1, stage 1). In addition, NaOH and KOH are common, inexpensive bases that are considered for the

neutralisation of sugar feeds obtained from hydrolysis of the resulting oligomers (Scheme 1, stage 2). We also provide insight into the effect of degradation products (i.e. furfurals) upon the catalytic hydrogenation of sugars. In this context, the use of activated carbon to prevent catalyst deactivation on the hydrogenation reaction of sugar solutions was also investigated (Scheme 1, stage 2). Overall, this study provides an assessment of the effect of inorganic salts and trace organic impurities on the performance of Ru/C in the hydrogenation of C_5/C_6-sugars (Scheme 1, stage 3).



Scheme 1. The three-stage process to produce sugar alcohols (alditols). In a first stage, water-soluble oligomers (WSO) are obtained by mechanocatalytic depolymerisation of the lignocellulosic feedstocks impregnated with a strong mineral acid (e.g. H_2SO_4 or HCl). In the second, the saccharification of WSO is performed by heating a 10wt% WSO solution (pH 1) at 140 ºC for 1 h. In the third stage, the hydrogenation of C_5/C_6 sugars is performed in the presence of Ru/C.

2. Results and Discussion

2.1 Hydrogenation of sugar solutions in batch reactor

In our previous study,[13a] we have demonstrated Ru/C catalyst to yield a cumulative productivity of about 600-g of hexitols per g-Ru, after six consecutive uses of Ru/C on WSO obtained from α-cellulose at 160 °C for 1 h each. In that study, we have employed a considerably high catalyst loading (100 mg) for the batch reactions. In light of the findings that will be presented in this report, the authors understand that, under the conditions of our previous report, a full assessment of a slow decline of the catalyst performance would not be possible. Herein, as the emphasis is placed on the quantitative assessment of the impact of salts derived from neutralisation of the WSO hydrolysates on the catalyst performance, it was decided to screen conditions under which Ru/C catalyst would provide high, but not the full conversion of glucose into C_6-alditols.

In this quest, to optimise the glucose conversion for the recycling experiments in the presence of Ru/C (0.7 wt%) in a batch reactor operating at 110 °C for one hour, two experiment sets were designed in which we varied (a) the catalyst loading (Figure 1a, H_2 pressure kept at 50 bar) or (b) H_2 pressure (Figure 1b, catalyst loading maintained at 10 mg).

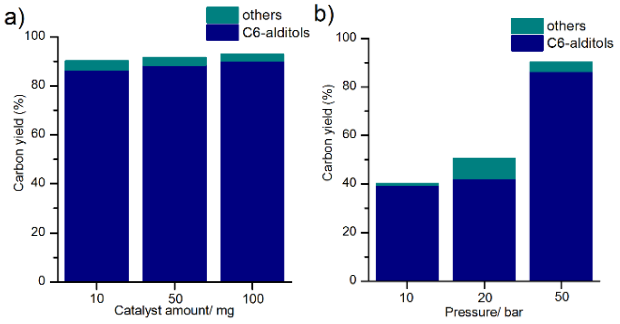


Figure 1. Results of the screening of initial experimental conditions. (a) Total carbon yield (indicated as the sum of C_6-alditols and other products) as a function of catalyst loading; (b) total carbon yield as a function of pressure. Reaction conditions: glucose solution (10 mL, 0.1 mol L^{-1}), 0.7 wt% Ru/C catalyst, 110 °C for 1 h.

Figure 1a clearly shows that Ru/C is highly active. Even at a catalyst loading as low as 10 mg, an 88% conversion of glucose into C_6-alditols at 87% C-yield was achieved. For the highest catalyst loading (100 mg of Ru/C), a 90% C_6-alditol yield was obtained at a 98% conversion. In this manner, to identify a decrease in the catalyst performance, we chose to work with a catalyst load of 10 mg. Under this condition, the effect of the H_2 pressure on the glucose conversion was assessed. Figure 1b displays the total carbon yields as a function of H_2 pressure with 10 mg Ru/C. With a reduction in H_2 pressure (from 50 to 10 bar), the total C-yield markedly decreased (from 87 to 40%, respectively). Based on these preliminary results, we set the conditions of the recycling experiments (at 10 mg Ru/C, 50 bar H_2, 110 °C for one hour), to assess the effect of salts on the catalyst deactivation.

Reproducibility of the four parallel reactors setup was also evaluated. Four parallel reactions were conducted on a glucose solution (10 mL, 0.1 mol L^{-1}) in the presence of Ru/C (10 mg) under 50 bar H_2 for one hour. In this set of experiments, glucose conversions between 85 and 91%, and C_6-alditols yields between 78 and 85% were obtained. These results confirm the very good reproducibility between the batch experiments (±3%). Apart from sorbitan (accounting for 1% C-yield), no other products than C_6-alditols and glucose were detected by HPLC. In the current experiments, the carbon balance was typically 93-95%.

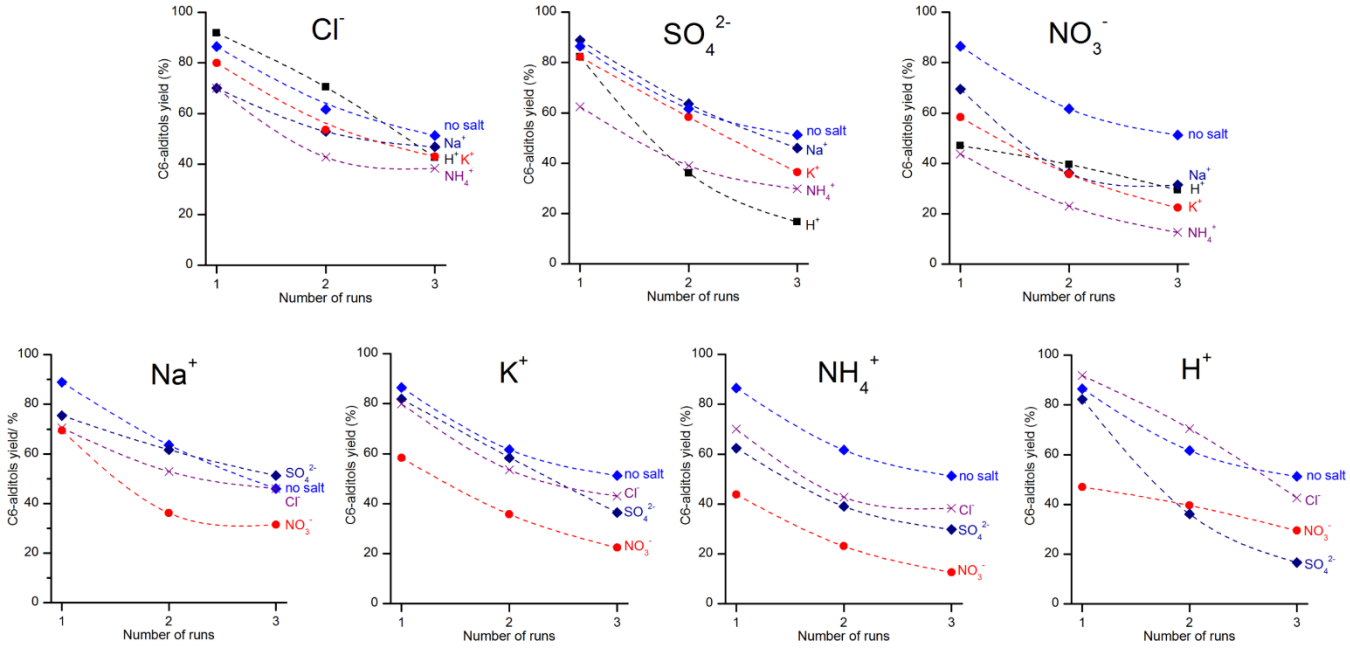


Figure 2. Recycling experiments for the evaluation of the anions (top) and cations (bottom) effects on the deactivation of Ru/C in the hydrogenation of glucose. Reaction conditions: 0.1 mol L^{-1} glucose solutions (10 mL) prepared from 18 mmol L^{-1} ammonium/alkali salt/acid solutions or ultrapure water (no salt), Ru/C catalyst (0.7 wt% Ru, 10 mg), 50 bar H_2, 110 ºC for 1 h.

2.1.1 Effects of cations and anions upon the hydrogenation of glucose solutions

Considering that only strong acids (HCl, H_2SO_4, HNO_3) are suitable as catalysts for the mechanocatalytic depolymerisation of lignocellulosic raw materials[19] and that NaOH, NH_4OH, and KOH constitute plausible choices for the work-up of sugars streams for the heterogeneously-catalysed downstream processing, the effect of NaCl, NH_4Cl, KCl, Na_2SO_4, $(NH_4)_2SO_4$, K_2SO_4, $NaNO_3$, NH_4NO_3 or KNO_3 upon the catalytic performance of Ru/C in recycling experiments was assessed. Additionally, reactions were performed in the absence of salts, but in the presence of mineral acids (18 mmol L^{-1} HCl, H_2SO_4 or HNO_3). As a reference experiment, hydrogenation of a glucose solution in ultrapure water was also carried out. In this section, the focus is on the cation and

anion effects on the catalyst stability. Accordingly, we decided to employ as the substrate, analytical grade glucose. However, we anticipate that sugars' degradation products can also deactivate Ru/C, as will be presented in Section 2.2.5.

Figure 2 summarises the results obtained from recycling experiments performed in 18 mmol L^{-1} salt solutions, 18 mmol L^{-1} mineral acid solutions, or ultrapure water as the reaction medium. Deactivation of Ru/C in the presence of an alkali cation follows the general trend: $NH_4^+ > K^+ > Na^+$. The deactivation effect of the cations seems to depend inversely on the ionic radii (NH_4^+: 175 pm, K^+: 152 pm, Na^+: 116 pm). In turn, Figure 2 reveals also the general trend $NO_3^- > SO_4^{2-} > Cl^-$ for the catalyst deactivation. Finally, conducting the experiments in dilute mineral acid solutions showed the general trend $H_2SO_4 > HNO_3 > HCl$ for the catalyst deactivation. From these trends, one fact is indeed rather surprising. Nitrate, which, at first sight, could be regarded as an innocent ion, has the most potent deactivation effect, compared against the strongly coordinating anions, SO_4^{2-} and Cl^-, which are well-known to poison metal surfaces.

Figure 3 compares the product distributions after the first run for the experiments performed in 18 mmol L^{-1} HNO_3 or nitrate salt

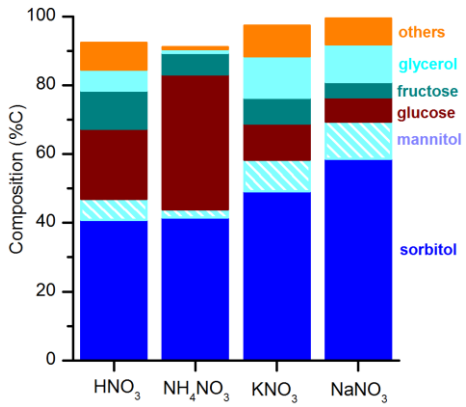


Figure 3. Products distribution after hydrogenation of glucose with fresh catalyst in the presence of nitrates. Reaction conditions: salts (18 mmol L^{-1}), glucose solution (10 mL, 0.1 mol L^{-1}), Ru/C (0.7 wt%, 10 mg) at 110 ºC for 1 h.

solutions. By stark contrast to the experiments carried in the solutions containing no NO_3^-, three major distinguishing features were found. The first corresponds to the presence of high levels of fructose observed. Fructose can easily be formed from glucose via isomerisation, especially under alkaline conditions.[20] The second feature is the high selectivity to mannitol. This observation is a consequence of the high levels of fructose found in the reaction mixtures. In fact, the hydrogenation of fructose produces a *ca.* 50:50 sorbitol-mannitol mixture,[20] while the hydrogenation of glucose forms sorbitol selectively (sorbitol:mannitol ratio of 94:6), as observed for the reaction performed in the other reaction media.[13a] The third feature is the formation of shortened sugar alcohols (i.e. xylitol, erythritol, glycerol, ethylene glycol and propylene glycol), which occurs to a much lesser extent in the reaction carried out in water (Figure 1). These compounds were formed via hydrogenolysis of C_6-alditols even at temperatures as low as 110 ºC. For example, a 12% C-yield of glycerol was observed in the experiment performed in the presence of KNO_3. Overall, these findings demonstrate that NO_3^- exerts an negative effect on Ru/C activity and selectivity.

Stimulated by the finding of fructose formation when nitrate salts or nitric acid is present in the reaction medium, we decided to determine the pH value of the reaction media before and after the reactions (1st and 3rd runs). Table 1 lists the pH values of reaction media and reveal an interesting feature. The experiments conducted in NO_3^--based reaction medium showed a massive increase in pH values. Remarkably, even the experiment performed in an 18 mmol L^{-1} HNO_3 presented an increase in pH from 2.1 to 9.4-9.6. The solutions containing nitrate salts were slightly acidic before reaction. They became alkaline, explaining the formation of fructose via isomerisation of glucose.[21] For other salt solutions with no nitrate, the reduction in pH was considerably lower (ΔpH > 1). However, when employing ultrapure water as the reaction medium,

which had a pH of 6.2 before the reaction, a decrease (to 5.4-4.7) was observed after the reaction.

Table 1. Measured pH values before the reaction, after 1st run and after the 3rd run and Ru particles size after the 3rd run.

Entry	Salt/acid	pH_0[a]	pH_1[b]	pH_3[c]	Particle size [nm][d]
1	NaCl	4.0	5.6	5.9	2.0±0.8
2	Na_2SO_4	4.1	5.0	5.2	1.8±0.5
3	$NaNO_3$	3.7	9.0	9.0	2.0±0.9
4	None	6.2	5.4	4.7	2.2±0.6
5	HCl	2.1	2.1	2.3	2.0±0.7
6	H_2SO_4	1.9	2.2	2.3	2.2±0.6
7	HNO_3	2.1	9.6	9.4	1.9±0.6
8	KNO_3	3.6	8.4	7.4	n.d.
9	NH_4NO_3	3.8	9.1	9.2	n.d.

[a] Initial pH of the solution. [b] pH of the solution after 1 run. [c] pH of the solution after the 3rd run. [d] Size of the Ru particles after 3 runs; Fig. S1 shows TEM images and particle size distributions.

The increase in pH in the nitrate-containing reaction media is hypothetically explained by the reduction of NO_3^- to NH_3, where hydroxide anions are formed, as proposed:

(1) $Ru(0) + NO_3^- + H_2O \rightarrow Ru^{3+} + NO + 4\ OH^-$

(2) $Ru^{3+} + {}^3/_2\ H_2 + 3\ OH^- \rightarrow Ru(0) + 3\ H_2O$

∑: $NO_3^- + {}^3/_2\ H_2 \rightarrow NO + OH^- + 3\ H_2O$

(3) $NO_3^- + 4\ H_2 + 2\ H^+ \rightarrow NH_4^+ + 3\ H_2O$

Nitrate anion can act as an oxidising agent converting Ru(0) into Ru(III) (equation 1).[22] The presence of H_2 during the reaction creates a reducing atmosphere, counteracting the oxidation and consuming partly the hydroxide ions formed upon reduction of ruthenium(III). However, the net equation shows that hydroxide ions are formed during the reduction of NO_3^- to NO. In a parallel pathway, Ru catalysts can selectively reduce nitrates to ammonium in aqueous media via sequential hydrogenation of NO at 25 ºC and 1 bar of H_2 (equation 3).[23] As this reaction also consumes H^+ species, the pH of the medium will logically increase. Tentatively, the formation of Ru-NO stable complexes may be a reason for the decay in catalytic activity for sugar hydrogenation when the reactions were carried out in nitrate-containing media. However, further investigation utilising operando spectroscopy is still needed to elucidate the deleterious effect of nitrate species on Ru/C catalysts.

2.2 Hydrogenation of sugar solutions in the flow reactor

2.2.1 Effect of residual salts on the hydrogenation of glucose in flow-through reactor

To assess the effects of ammonium and alkali metal salts on the catalytic performance of Ru/C in the hydrogenation of sugar solutions a series of experiments were performed using a glucose solution of 0.1 mol L^{-1}. Practically, the neutralised hydrolysate would resemble a 0.1 mol L^{-1} glucose solution with a salt concentration of 18 mmol L^{-1}.

Figure 4 presents the sorbitol yields as a function of time-on-stream (TOS) for the hydrogenation of 0.1 mol L^{-1} glucose solutions containing the investigated salts (at a concentration level of 18 mmol L^{-1}). With no added salt, the C_6-alditol productivity slightly decreased from 6.9 $mol_{C6\text{-}Alditol}$ g_{Ru}^{-1} h^{-1} at 0.5 h to 6.3 $mol_{C6\text{-}Alditol}$ g_{Ru}^{-1} h^{-1} at 8 h of TOS. All the salts investigated in this study had an adverse effect on the catalytic performance of Ru/C, as verified by the marked decrease in C_6-alditol productivity. As expected from the batch reactor results, the deactivation of Ru/C in the presence of nitrates was significantly stronger than that in the presence of sulfates, while chlorides had the lowest impact on the Ru/C performance. In the presence of NH_4NO_3 or $NaNO_3$, C_6-alditol productivity dropped considerably especially in the first 1.5 h when compared with the data in the absence of any salt, resulting in C_6-alditol productivities of 2.3-2.4 $mol_{C6\text{-}Alditol}$ g_{Ru}^{-1} h^{-1} at 1.5 h, slowly decreasing after that (to 1.7-2.3 $mol_{C6\text{-}Alditol}$ g_{Ru}^{-1} h^{-1} at 8h). Sulfate salts, $(NH_4)_2SO_4$, Na_2SO_4, K_2SO_4 led to C_6-alditol productivities of 3.4-3.8 $mol_{C6\text{-}Alditol}$ $g_{Ru}^{-1}h^{-1}$ at 1.5 h. As observed for the nitrates, the cation seems to be of less importance. In the presence of NaCl, the C_6-alditol productivity was the least affected (4.8 $mol_{C6\text{-}Alditol}$ g_{Ru}^{-1} h^{-1}).

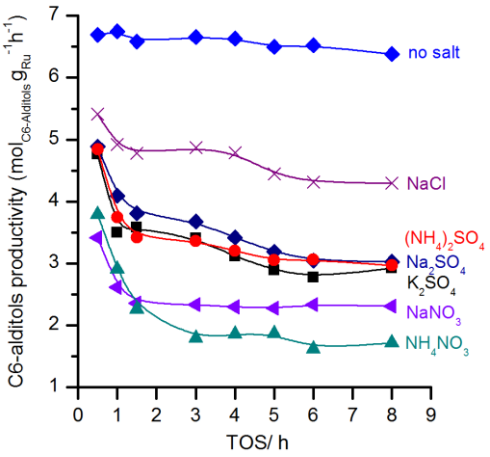


Figure 4. C_6-alditols productivity as a function of time-on-stream (TOS) in a flow-through reactor. Reaction conditions: Ru/C (0.1 g), glucose solutions (0.1 mol L^{-1} glucose and 18 mmol L^{-1} salt, 1 mL min^{-1}), H_2 pressure of 20 bar and 110 °C.

2.2.2 Hydrogenation of hydrolysates derived from α-cellulose

In several cases, a neutralisation step may constitute an important process option before hydrogenation. Considering that Cl^- presents the weakest deactivation effect on the Ru/C catalyst, HCl was employed as the acid catalyst in the mechanocatalytic depolymerisation of α-cellulose. To verify the effect of salts formed by the HCl neutralisation, a 10% solution of WSO was saccharified in water (pH 1) at 140 °C for 1 h, and subsequently neutralised with NH_4OH or NaOH. After a solution treatment with activated carbon to remove HMF and furfural (vide infra), the hydrolysate was diluted, rendering a 0.1 mol L^{-1} glucose solution with an 18 mmol L^{-1} salt concentrations. The solutions were fed to the reactor with a liquid flow of 2 mL min^{-1} and hydrogenated over 500 mg Ru/C (0.7 wt% Ru) at a temperature of 130 °C (to improve the C_6-alditol productivity).

Figure 5 compares the yields as a function of TOS for the solution neutralised with NH_3 and NaOH. Regarding the activity

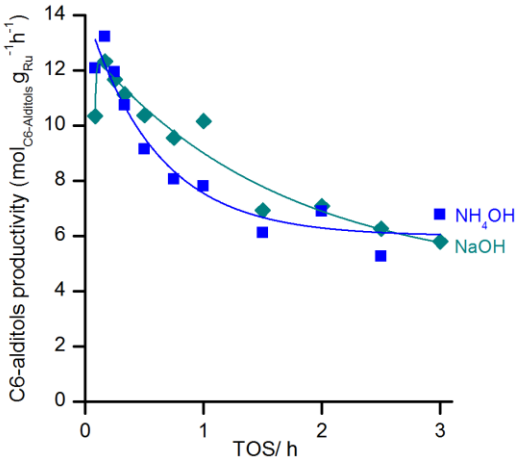


Figure 5. Productivity of C_6-alditols as a function of TOS in the continuous hydrogenation of hydrolysates obtained from α-cellulose (HCl was used as the acid catalyst), neutralised with NH_4OH or NaOH, and purified with activated carbon before hydrogenation. Reaction conditions: 500 mg Ru/C, glucose solution (0.1 mol L^{-1}, 2 mL min^{-1}), H_2 pressure of 20 bar and 130 °C. The pH value of the neutralised glucose stream was 7.0±0.5.

and deactivation of the catalyst, the results are similar. Using NH_3 for the neutralisation, the catalyst productivity decreased from 13 $mol_{C6\text{-}Alditol}$ g_{Ru}^{-1} h^{-1} after 0.17h to 7 $mol_{C6\text{-}Alditol}$ g_{Ru}^{-1} h^{-1} after 3 h, while employing NaOH, the productivity declined from ca. 12 mol $g_{Ru}^{-1}h^{-1}$ after 0.17 h to 6 $mol_{C6\text{-}Alditol}$ g_{Ru}^{-1} h^{-1} after 3 h. However, in the conversion of the NaOH-neutralised hydrolysate, a high level of side-products, mainly fructose, particularly in the later part of the experiment, was found. Fructose concentrations, equivalent to a yield of 10%, were found after 3 h. Overall, these findings are in line with the results presented in Figures 4 and 5 demonstrating that the decay in catalyst productivity has a stronger dependence on the anion (chloride) compared to that of the cation (Na^+ or NH_4^+).

2.2.3 Effect of furfurals and other species on the continuous hydrogenation of beechwood hydrolysates

The difficulties created by the strong adsorption of furfural and 5-hydroxymethylfurfural on Ru surface has been recognised in the recent literature of hydrodeoxygenation of pyrolysis oils.[24] Considering that furfurals will invariably be formed in the acid-catalysed saccharification of lignocellulose,[19, 25] we chose to test activated carbon in the purification of the hydrolysates. From aqueous solutions, to remove 95% of both HMF and furfural at an initial concentration of 10 mmol L^{-1}, it suffices to stir the solution in the presence of activated carbon (57 mg) for 10 min. As a result, the decolourisation of the hydrolysate is achieved. Notably, colouration is caused not only by the presence of furfurals but also from lignin degradation products in addition to oligomeric (soluble) humins. Importantly, despite the efficacy of activated carbon in removing furfurals and other polar compounds, this pre-treatment also reduces glucose and xylose concentrations by about 10%.

To investigate the effect of the base and decolourisation with activated carbon, three experiments were designed. In the first, the beechwood hydrolysate was neutralised with NH_3 and treated with activated carbon before feeding it into the reactor (experiment represented by '1·AC'). In the second experiment, the hydrolysate was treated twice with activated carbon ('2·AC'). In the third experiment, the hydrolysate was neutralised with NaOH and not treated with active carbon ('no AC'). Figures 6 presents the C_6-alditol productivities.

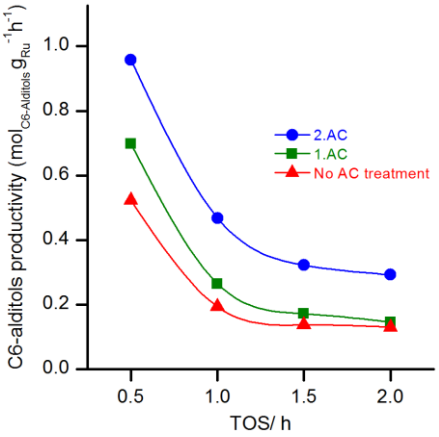


Figure 6. C_6-alditols productivity as a function of time-on-stream (TOS) in the catalytic hydrogenation of beechwood hydrolysate, treated with AC before reaction (1·AC), treated twice with AC (2·AC), and treated with no AC. Reaction conditions: 500 mg Ru/C, glucose solutions (0.1 mol L^{-1}, 2 mL min^{-1}), hydrogen pressure 20 bar, 130 °C.

The most substantial decrease in activity was observed when the stream was not treated with activated carbon. The productivity of C_6-alditols decreased from 0.5 $mol_{C6\text{-}Alditol}$ g_{Ru}^{-1} h^{-1} at 0.5 h to 0.1 $mol_{C6\text{-}Alditol}$ g_{Ru}^{-1} h^{-1} after 2 h. The best results were achieved when the solution was pre-treated twice with activated carbon. In this case, the productivity reduced from 1.0 $mol_{C6\text{-}Alditol}$ g_{Ru}^{-1} h^{-1} at 0.5 h to 0.3 $mol_{C6\text{-}Alditol}$ g_{Ru}^{-1} h^{-1} after 2 h. Compared with the hydrogenation of sugars and α-cellulose hydrolysate (Figure 4 and 5), deactivation in the hydrogenation of beechwood hydrolysate appears to be more severe even after the treatment with AC. This observation indicates that other impurities in the 'real-world' sugar stream may strongly affect the time-on-stream catalyst performance. This problem is often neglected in the catalysis literature dealing predominantly with model substrates.

To shed light on the effect of stream pre-treatment on the catalyst performance, the textural analysis of fresh and spent catalysts was performed. Figure 7 compares the N_2 sorption isotherms of the catalysts before and after the hydrogenation of the three

different streams. The decay in catalyst performance can be correlated with a decrease in BET surface area. The catalyst after the reaction with the twice treated solution had a BET surface area (1290 m^2 g^{-1}) comparable to the catalyst before the reaction (1340 m^2 g^{-1}), and the catalyst showed the best on-stream performance in the sugar hydrogenation. Spent catalysts from the experiments with a once treated solution and the untreated solution had a diminished BET surface area (i.e. 730 m^2 g^{-1} and 420 m^2 g^{-1}, respectively), and showed accordingly worsen hydrogenation performances. The findings confirm that a decrease of the surface area is one of the primary reasons for deactivation. In addition to the preferential adsorption of furfurals and lignin-derived phenolics could also play a role in the marked decrease in the C_6-alditol productivity.

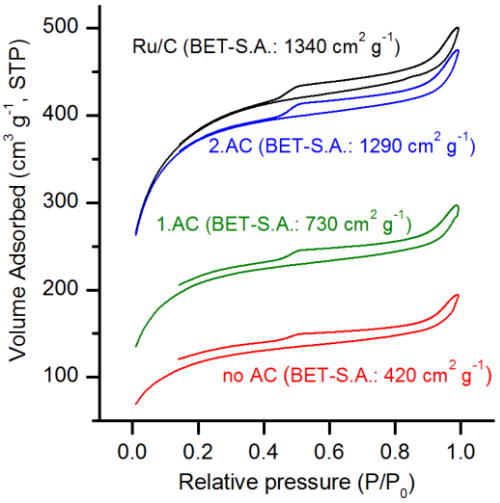


Figure 7. N_2 isotherms of fresh and spent Ru/C catalyst exposed to different hydrolysate streams.

3. Conclusions

The presence of the salts in the hydrolysates led to considerable decay in catalytic performance in the hydrogenation of sugar solutions to sugar alcohols. The presence of sulfate anions gave in more severe losses in catalyst performance than chlorides.

Surprisingly, however, nitrate anions had the most severe deactivation effect. Poor catalyst performance in nitrate-containing reaction media seems to be hypothetically associated with strong adsorption of NO formed upon reduction of nitrate by Ru/C under an H_2 atmosphere. Regarding the effect of cations on the catalyst deactivation, less pronounced differences were observed among the ammonium and alkali metals investigated in this study. From the salts studied, there exists a direct correlation between the deactivation potency and the ionic radii of the cations. After hydrolysis, low concentration levels of HMF, furfural and soluble lignin fragments and humins suffice to decrease the performance of Ru/C dramatically. It was found that the pre-treatment of hydrolysates is conducive to a sustained catalyst performance, as a less pronounced decrease of surface area was observed.

In a broader context, the current findings urge the catalytic community to consider the "quality" of the hydrolysates for the catalytic upgrading.[9b] This subject is often neglected in the current literature and reveals that, besides strong efforts devoted to efficient cellulose hydrolysis process, much more attention should also be given to the cost-efficient work-up/purification of the hydrolysates. This research aspect has been considered in considerable length in the case of biotechnological applications of hydrolysates. However, it is still a field in its infancy for heterogeneously catalysed transformations of sugars derived from cellulose hydrolysis.

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4. Experimental Section

Mechanocatalytic depolymerisation of lignocellulosic substrates

The substrate (10.0 g; microcrystalline cellulose Avicel PH101 (Fluka), α-cellulose (Aldrich), or beechwood powder) was dispersed in methyl *tert*-butyl ether (MTBE, Aldrich, 99.8%, 150 ml) and the acid (0.52 mL, 10 mmol, H_2SO_4, 95-97%, J. T. Baker or HCl 37-38%, J. T. Baker) was added dropwise to the stirred suspension. After 30 min stirring, the solvent was removed under reduced pressure. The obtained acid-impregnated solid substrate (1.00 g) and 5 milling balls (stainless steel, 5 mm diameter) were filled into a planetary ball mill (Fritsch Pulverisette 7) at 800 rpm for 2 h, with 10 min break after 30 min milling intervals resulting in water-soluble oligosaccharides (WSO), or water-soluble products from beechwood, as reported elsewhere.[19, 25]

Hydrolysis of water-soluble oligomers and activated carbon treatment

The solid substrate WSO (0.5 g) was dissolved in water (10.0 mL) and heated in a glass-reactor to 130 °C for 3 h. Then, the yellow-coloured hydrolysate was filtrated.[26] In order to remove furanic compounds from the hydrolysates, activated carbon (Adsortech, E1252F) or AC extrudates (Chemviron, CPGLF, particle size 1 mm) was added into the solution as described in the main text.

Hydrogenation of sugar solutions in a batch reactor

The hydrogenation of glucose (0.1 mol L^{-1}, 10 mL) was carried out using 50 mL 316L stainless steel autoclaves fitted with a borosilicate glass inset. In these experiments, we employed a commercial Ru/C catalyst (0.7 wt% Ru, particle size 125 µm – 250 µm, Engelhard). Typically, the reaction mixture was heated to 110ºC under H_2 (50 bar at room temperature) at a stirring rate of 300-400 rpm. After 20 min the reactions temperature was reached, and the temperature was held for 1 h. The reactions were stopped by quenching the autoclaves in an ice bath and sequentially releasing the H_2 pressure. To recover the spent catalyst, the reaction mixture was carefully transferred from the glass inset into a glass apparatus for vacuum filtration fitted with a tared membrane filter (1.0 µm, regenerated cellulose, RC 60, Whatman). The clear reaction medium was set apart for HPLC analysis. All the reactor parts contacting the solution were rinsed with deionised water, and filtered through the same filter membrane used for the filtration of the reaction medium. The catalyst was washed with deionised water. The dried membrane was placed in a Petri dish. The catalyst was dried at 60 ºC in an oven. For the next catalytic test, to avoid catalyst losses, the residual catalyst on the membrane was washed to the glass inset with the 0.1 mol L^{-1} glucose solution. This procedure allowed for at least 95% recovery of the spent catalyst, as determined by weight difference.

Hydrogenation of aqueous glucose solutions in a trickle-bed reactor

A reactor setup of six-parallel tube reactors (constructed in stainless steel 316L) was used for the continuous hydrogenation.[13b, 27] The inner diameter of the reactor tubes was 10 mm, and the catalyst was placed into the reactor by using glass wool and metal nets as supports for the catalyst bed. The liquid was pumped into the reactor using an

HPLC-pump (Agilent 1100 Quaternary pump), for the introduction of gases, mass flow controllers (Brooks 5850S) were used. The reactors were surrounded by separate aluminium blocks heated by cartridge heaters. The temperature was controlled separately using temperature controllers (CAL controls 9500P) and the temperature was recorded inside the catalyst bed by using internal thermocouples. In a typical experiment, the reactor was filled with quartz sand (particle size 125 µm – 250 µm, ~16 g) and commercial Ru/C (0.7 wt% ruthenium, particle size 125 µm – 250 µm, 0.100 or 0.500 g, Engelhard), flushed first with argon, then H_2, and heated to the reaction temperature under H_2 pressure. The feed solution was degassed with helium. The degassed solution (0.1 M) was pumped into the reactor with a flow of 1 mL min^{-1} at an H_2 pressure of 20 bar and temperature of 110 °C. Samples were taken at the outlet of the reactor after predetermined times. After the reaction, the hydrogen pressure was released, the reactor was cooled, and the reaction mixture removed.

HPLC analysis

High-performance liquid chromatography (HPLC) analysis was performed using a Shimadzu LC-20 equipped with a column switch, combining a 100 and a 300-mm organic resin column of 8 mm ID. The eluent was an aqueous solution of TFA (2 mM) and the flow rate was 1 mL min^{-1}. The sugars and polyols were analysed using an RI detector, while 5-hydroxymethylfurfural and furfural were measured using a UV detector.

Nitrogen physisorption

Nitrogen physisorption measurements were carried out on a Micrometrics ASAP 2010 instrument. Prior to analysis, the sample was degassed under vacuum overnight at 100°C. The measurements were performed at 77 K using a static-volumetric method.

The empty volume was determined with nitrogen. The BET surface area was calculated from the adsorption data in the relative pressure interval from 0.04 to 0.2.

TEM analysis

Transmission electron microscopy (TEM) images of samples were collected with a HF 2000 microscope (Hitachi) equipped with a cold-field emission gun. The acceleration voltage was 200 kV. For the particle size distribution, the size of 200 particles were determined.

Keywords: sorbitol • glucose • cellulose • batch • continuous • salts • deactivation • mechanocatalytic depolymerisation • hydrogenation • Ru/C

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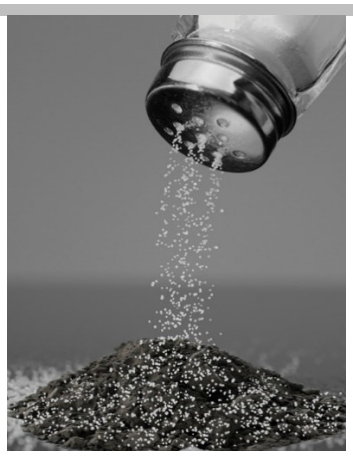
Sweet and salty: Produced by the neutralisation of (ligno)cellulose hydrolysates, the influence of salts on the hydrogenation performance of heterogeneous catalyst is an often neglected topic in the literature. Herein, we assess the effects of salts on the hydrogenation of glucose over Ru/C conducted in batch and trickle-bed reactors.



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On the impact of salts formed by the neutralisation of (ligno)cellulose hydrolysates on the hydrogenation of sugars