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ARTICLE TYPE

From microcrystalline cellulose to hard- and softwood-based feedstocks: their hydrogenolysis to polyols over a highly efficient ruthenium-tungsten catalyst

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The utilization of cellulose and its integration in a biorefinery concept is essential even in the near future of growing global shortage of crude oil. Here, we report the catalyzed one-pot hydrogenolysis of cellulosic materials to valuable bio-derived molecules, especially polyols (e.g. ethylene glycol). We demonstrate how a very promising bifunctional catalyst, Ru-W/AC, converted not only 100 % of microcrystalline cellulose to polyols in repeated experiments with a maximum yield of 84 % and ethylene glycol productivity of 3.7 g ($g_{catalyst}$ h)$^{-1}$) but was also active for pine-, birch-, and eucalyptus-derived materials. Moreover, we systematically investigated the problem of catalyst stability with time by detailed studies of changes of both the catalyst structure and the liquid phase, which has been often overseen when biomass is converted to fuels and chemicals. Control of active sites for the conversion of cellulosic feedstocks coupled with reaction engineering and strategies to prevent catalyst deactivation is a prerequisite to understand how high yields of platform chemicals can be achieved.

1 Introduction

The increasing demand for a new effective technology to process cellulose, which presents a perspective resource for the production of valuable fuels and chemicals, incites many research activities in the last decade. Besides the sustainability and the possible CO_2 neutrality, other advantages like inexpensiveness and abundance of cellulose feedstock can help to resolve the problem of decreasing fossil reserves in our society[1]. Although cellulose degradation offers a big variety of products[2], the great stability caused by inter- and intra- molecular hydrogen bonds yielding a robust crystalline structure makes a highly selective conversion of this biopolymer very challenging.

The depolymerization and hydrolysis of cellulose to cello-oligosaccharides and monomer building blocks (glucose molecules) is the first key reaction step. Homogenous acidic catalysis showed good results, but the negative influence of concentrated or diluted mineral acids (separation/recovery of acid, corrosion) prohibits large-scale application of these processes[3]. Therefore, the use of solid acid catalysts in an aqueous solution under hydrogen atmosphere became a promising new way for the production of desired chemicals from cellulose[4]. Various solid acid materials like zeolites, sulfated zirconia, silica (SBA-15) or carbon materials were investigated[5, 6, 7]. Additionally, the presence of different active sites on solid supports allows that in a one-pot reaction system various complex reaction pathways can occur. For example, in the presence of supported metal catalysts (Ru or Pt on support), C6 sugar alcohols like sorbitol and mannitol can be produced via the tandem reaction of hydrolysis and hydrogenation[5].

Other than that mentioned, the direct hydrogenolysis of cellulose presents an interesting route to obtain various short-chain polyols (e.g. ethylene glycol, propylene glycol, and glycerol). Polyols are an important class of platform molecules, and their sustainable production within a biorefinery is a challenge but also necessary because of the worldwide shortage of crude oil as raw material for the production of fuels and chemicals. For example, ethylene glycol is usually produced via hydrolysis of ethylene oxide which is obtained from petroleum-based ethylene[8]. Reversibly formed acid sites in hot water together with ruthenium on activated carbon were effective for the formation of hexitols (39.3% yield) at 518 K, 60 bar hydrogen pressure within 3 h[9]. Various carbon materials like carbon nanotubes (CNTs)[10] or mesoporous carbon materials (CMKs)[11,12] were developed and enabled, in combination with noble metals, the conversion of cellulose to glucose and sugar alcohols. Moreover, if a catalyst with nickel and tungsten carbide on activated carbon was applied, product distribution differed strongly and the hydrogenolysis reaction to ethylene glycol was facilitated[13]. Catalysts containing nickel or noble metals and different forms of tungsten (W[14] or WO_3[15]) were also active, and a binary catalyst system composed of tungsten acid (H_2WO_4) and Ru/C[16] or Raney Ni[17] gave ethylene glycol as main product. Besides tungsten acid, catalyst systems with heteropoly acids[17, 18, 19] (Ru/C + CsHPA, $H_4[Si(W_3O10)_4]$ or $H_3[P(W_3O_{10})_4]$) are able to convert cellulose to polyols like sorbitol or ethylene glycol. Not only activated carbon, but also SiO_2 or SiO_2-Al_2O_3 as support in combination with Ni and W were active for the polyols production[20, 21]. Beside the drawbacks of using mineral acids or expensive ionic liquids for the degradation of cellulose another critical point is that sugar alcohols can cause Ni leaching because of their chelating properties[22, 23].

Despite the increasing research activities for processing cellulose and other biomass feedstock to chemicals and fuels, the problem of catalyst stability with time-on-stream, which is self-evident due to the knowledge of catalyst action in petroleum industry but must not necessarily follow the same mechanisms, has been seldom reported[22, 23, 24, 25] or overseen.

In this work, we demonstrate the effective cellulose hydrogenolysis over a self-prepared ruthenium containing

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catalyst supported on W/AC starting with microcrystalline cellulose. Recycling tests of this bifunctional Ru/W/AC catalyst and the detailed studies of changes of both the catalyst and the liquid phase occurring during the reaction were performed in order to understand the long term stability and the degradation behaviour of the catalyst. Additionally, the prepared catalyst was used in combination with ball-milled cellulose in order to investigate the influence on cellulose reactivity and product distribution. In the end, we transfer the optimal hydrogenolysis process to different kinds of cellulosic materials.

2 Experimental

2.1 Catalyst synthesis

The support material (activated carbon, (AC), specific surface area 1200 m^2 g^{-1}, particle size 0.063–0.2 µm) SX Ultra was purchased from Cabot Norit Company/Nederland, and impregnated in the first step with an aqueous solution of ammonium metatungstate hydrate followed by drying at 383 K for 15 h, pretreatment in Ar at 823 K for 300 minutes and reduction in hydrogen in the following way: applying a heating ramp from room temperature to 808 K in 26 minutes, then to 1128 K in 64 minutes and holding this temperature for 30 minutes. After cooling down, the pre-catalyst W/AC was obtained. The latter was impregnated with an aqueous solution of ruthenium nitrosyl nitrate followed by drying at 383 K for 15 h and reduction in hydrogen flow (200 ml/min, 623 K for 3 h). This procedure gives the final catalyst Ru/W/AC which was introduced in this form into the batch reactor of the cellulose hydrogenolysis reaction. The loading of tungsten and ruthenium is 40 wt%, related to WO_3, and 2 wt%, respectively. A monometallic ruthenium catalyst was prepared in an analogous way, however, without the first step.

2.2 Hydrogenolysis of cellulose

General procedure: Typically, 0.5 g catalyst, 5 g cellulose microcrystalline (Merck) and 100 mL water were converted in a batch reactor (Parr Instrument, 300 mL). At the beginning of each experiment, the reaction solution consisting of 0.5 g catalyst, 5 g cellulose, and 100 mL water was closed in the reactor. Then, air atmosphere was flushed up with argon, the reactor was pressurized with 20 bar of hydrogen and the reaction solution was heated up to 493 K under stirring (1000 rpm). After reaching the reaction temperature, the reactor was second time pressurized to 65 bar. This was confirmed as the start of the reaction. After 3 h of reaction time, the reaction solution was cooled down to room temperature. During and after the reaction, liquid samples were taken and analyzed by HPLC, GC and GC-MS.

Catalyst recycling: In the first run, 0.5 g of Ru/W/AC was introduced for the experiment. After the reaction, the product solution was filtered, the catalyst was washed with deionized water and dried at 383 K under air atmosphere over night. After drying, the catalyst was scraped from the folded filter, re-weight and recovered for the next run (catalyst mass: Table 1).

Conversion of cellulose (X) was determined gravimetrically based on the weight loss during the reaction.

The yields (Y_i) in this work are based on the moles of carbon in the product i divided by the moles of carbon in cellulose:

$$Y_i = (z_i / z_{C_6H_{10}O_5}) \times (n_i \cdot M_{C_6H_{10}O_5} / m_{Cellulose,start}),$$

z_i is carbon number in a molecule.

Carbon efficiency coefficient (CEL) is based on the ratio of carbon of the known soluble products to carbon of all soluble products (known + unknown soluble products).

2.3 Catalyst characterisation

Powder X-ray diffraction (XRD) analysis of samples was carried out on a powder diffraction system using CuKα1-radiation at voltage of 40 kV and current of 40 mA. Scans were carried out from 2 theta = 10 to 90^o with 0.067^o steps and 40 s per step.

The amount of acid sites was determined by temperature-programmed desorption (TPD) of NH_3. After calcination at 573 K the sample was exposed to NH_3 at 308 K for 1 h. Weakly adsorbed NH_3 was removed by flowing nitrogen at 308 K. Finally, the temperature was increased with a rate of 5 K min^{-1} up to 923 K and the amount of NH_3 was measured by FT-IR spectrometry (Thermo Fischer Scientific).

Temperature-programmed reduction (TPR) measurements were performed on a TPD/R/O 1100 from Thermo Fisher Scientific using a quartz U-tube reactor. The catalyst was pretreated in Ar flow (30mL/min) at 383 K for 60 minutes and cooled to 303 K. The experiments were performed using 30mL/min of 5.1 vol.% H_2/Ar by heating the sample from 303 K to 1073 K at a heating rate of 5 K/min while monitoring the TCD signal. Additionally, the apparatus was coupled with a mass spectrometer to detect water formed during the TPR.

3 Results and discussion

The bimetallic catalyst containing ruthenium and tungsten supported on activated carbon (Ru/W/AC) was carefully prepared according to the two-step incipient wetness (IW) technique starting with ammonium metatungstate hydrate on SX Ultra as described above. After heating this pre-catalyst, denoted as W/AC, in flowing hydrogen up to 1128 K, X-ray diffraction (XRD) and temperature-programmed reduction (TPR) experiments revealed the formation of tungsten carbides, WC and W_2C (Fig. S1, S2). For the second IW step an aqueous solution of ruthenium nitrosyl nitrate was used. With this Ru precursor and after reduction at 623 K, ruthenium is highly dispersed in the virgin heterogeneous Ru/W/AC catalyst as indicated by the absence of diffraction signals for ruthenium. Moreover, in this catalyst no crystalline phases of tungsten carbides were observed indicating their dissolution and redispersion in the presence of water and hydrogen, respectively. This is supported by the TPR of Ru/W/AC which shows a high-temperature behavior similar to W/AC due to the reduction of tungsten species until the carbides were formed. Accordingly, traces of tungsten dioxide and metallic tungsten were observed.

Ru/W/AC showed remarkable performance for the hydrogenolysis of cellulose (Table 1, entry 1). Not only the cellulose conversion was very high (90 %) at 493 K, 65 bar hydrogen and within 3 h, but also the carbon efficiency coefficient (CEL= 76.7 %) which describes the ratio of carbon of the known soluble products to carbon of all soluble products (known and unknown). Interestingly, the catalyst produced the desired polyols with an overall yield of 66.6 %, and the dominant product was ethylene glycol with a yield of 34.2 %. Additionally, other valuable products such as sorbitol and erythritol were obtained with a yield of 18.5 % and 5.2 %, respectively. The monometallic catalyst Ru/AC exhibited much lower reactivity (cellulose conversion = 60 %) and gave only 19.7 % polyols (Fig. S4). With the addition of tungsten in the first step of the

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preparation protocol, acidic sites were formed which were probed by temperature-programmed desorption of ammonia (NH_3-TPD): the acid site concentrations of Ru/W/AC and Ru/AC amount to 1.157 mmol/g and 0.098 mmol/g, respectively. Remarkably, the high concentration of acid sites in the former corresponds to a level which is known from zeolites (e.g., H-BEA[26]). However, with Ru and Ni modified zeolites hexitols were the mainly formed polyols[27, 28]. The results imply that tungsten species must be involved in the formation of short-chain polyols such as ethylene glycol.

In general, the product distribution obtained during the degradation of cellulose under hydrothermal conditions and in presence of hydrogen strongly depends on reaction conditions and type of the used catalysts. The predominant reactions, which casually explain the product distribution and occurred during the cellulose hydrogenolysis over our catalyst Ru/W/AC, are shown in Scheme 1. They can be classified in cellulose hydrolysis, retro-aldol condensation of glucose (and other saccharides) and hydrogenation reactions. In the first step, cellulose is hydrolyzed to cello-oligosaccharides and glucose due to H^+ ions, which are in-situ produced in water at high temperatures (autoprotolysis of water)[9, 29]. Tungsten species, which are responsible for C-C and C-O bond scissions, also participate in the hydrolysis of cellulose to glucose and cause formation of short-chain aldehydes and ketones (e.g. glycolaldehyde, glyceraldehyde, 1-hydroxy-2-propanone, 1-hydroxy-2-butanone, 3-hydroxy-2-butanone). Importantly, retro-aldol condensation is the main reaction to form glycolaldehyde and erythrose (from glucose) or other aldehydes (e.g., glyceraldehyde from fructose). Erythrose is then rapidly hydrogenated to erythritol or converted into two glycolaldehyde molecules via retro-aldol condensation. The latter is also of synthetic value applying subcritical and supercritical water for the conversion of glucose[30] and cellobiose[31]. The aforementioned unsaturated intermediates are finally hydrogenated, by ruthenium sites, to the desired polyols like ethylene glycol, propylene glycol, 1,2-butanediol, and 2,3-butanediol (2b, 6b, 7b, 8b, Scheme 1). Besides the three-step reaction route consisting of hydrolysis, retro-aldol condensation, and hydrogenation entailing short-chain polyols, direct hydrogenation of glucose is competitive and yields sorbitol. Degradation products like methanol and ethanol are also obtained during the reaction of microcrystalline cellulose over Ru/W/AC. Gas phase analysis showed the presence of methane, ethane, CO, and CO_2 with a summarized yield of ~ 3 %, whereas methane was the dominant product.

Recycling tests of the Ru/W/AC were performed in order to test the stability of this catalyst. Due to the difficult catalyst separation from the non-converted solid cellulose rest, full conversion of cellulose during the recycling test is necessary for the re-use of the catalyst. For this reason, different from the standard reaction conditions, a reaction temperature of 498 K was chosen during the recycling test because full cellulose conversion was achieved at this temperature. Presented in Table 1 (entry 2-8), the catalyst Ru/W/AC maintained its stability during six cycles (100 % cellulose conversion, and also the overall polyol yield was always very high, in the range of 64-70 %). In the last (seventh) run, the yield of polyols decreased to 46.4 % and the product distribution differed strongly. The yield of ethylene glycol was very small, 4.9 % (note, that the yield of ethylene glycol in the first run was 36.6 %), meanwhile the yield of sorbitol increased from 15.6 % in the first run to 28.4 % in the last recycling run. As noticed in Table 1, a small loss of catalyst in each recycling run was caused because of the complicated re-use method of a heterogeneous catalyst in this gas/liquid/ solid/solid reaction system. However, no decrease in cellulose conversion and polyol yield was detected during the six consecutive runs which demonstrates that the loss of catalyst is not the main reason for the decrease of activity of Ru/W/AC in the last seventh cycle. To confirm this point, one experiment with 0.372 g fresh catalyst was carried out at the same reaction conditions as the recycling test (Table 1, entry 9). Note that the results are comparable to those obtained in the fifth recycling run, where the catalyst amount was in the same range. Therefore, leaching of active components and/or chemical and structural changes of catalyst surface must be considered. The ICP-OES analysis showed that ruthenium is very stable under our reaction conditions, and no traces were found in the liquid phase. This is in line with our previous study of glucose hydrogenation over supported ruthenium demonstrating the absence of any leaching during 1000 hours time-on-stream in a trickle-bed reactor[23]. On the other hand, tungsten in ppm range was detected in the liquid samples after each recycling run (Table 1), the overall loss of weight corresponds to 21 %. In the first run, the concentration of tungsten in the liquid phase was the highest, 121 ppm. Interestingly, when the tungsten concentration in the last cycle decreased to only 5 ppm, both the activity of the catalyst and the yield of desired short chain polyols decreased. The product solution obtained after the reaction was blue and during the filtration the solution became colorless. Typical blue compounds of tungsten are hydrogen tungsten bronzes ($H_{0.1}WO_3$, $H_{0.33}WO_3$), which can be easily oxidized by contact with air[32]. Probably, the leached tungsten species are in form of hydrogen tungsten bronze during the reaction, and during the filtration they quickly oxidize. In which form tungsten during the reaction exists, is not known yet. Although the virgin heterogeneous Ru/W/AC catalyst clearly exhibits high concentration of acidic tungsten sites which are responsible for cleavage of C-O and C-C bonds, the confirmed loss of tungsten due to leaching indicates that these species may be involved in a homogeneously catalyzed step in the degradation of cellulose. With decreasing concentration of leached tungsten species from run to run (Table 1), the retro-aldol condensation of glucose to glycolaldehyde and erythrose (with subsequent hydrogenation of both) got suppressed, and the main reaction route switches from ethylene glycol formation to the direct hydrogenation of glucose. Therefore, the yield of sorbitol achieved a high value (28 %) in the last run (Fig. 1). The ratio of ethylene glycol/sorbitol at this point corresponds to ~ 1:5.8 compared to ~ 2.4:1 in the previous runs. Remarkably, although loss of ppm of tungsten is occurred, the heterogeneous catalyst still contains metallic tungsten (Fig. S2) and is still active for cellulose hydrogenolysis after repeated runs and produces the desired polyols switching now the selectivity from one value-added product (ethylene glycol) to the other (sorbitol).

To further elucidate the performance of our heterogeneous Ru/W/AC catalyst in light of the interplay of soluble hydrogen tungsten bronze (H_xWO_3) and tungsten acid (H_2WO_4) which can act as precursor for the former under hydrothermal conditions and in presence of hydrogen[15], we compared the standard reaction with 0.5 g of Ru/W/AC catalyst containing 36.7 % of tungsten (ICP-OES analysis, corresponds to 1.8 g/L tungsten) and 0.5 g of Ru/AC + 2.5 g/L tungsten acid (corresponds to 1.84 g/L tungsten). Here, slightly higher cellulose conversions between 3-8 % were obtained in the reactions performed with Ru/AC + H_2WO_4 (Table 2). The formation of dissolved active tungsten species occurs slowly via continuously leaching from heterogeneous Ru/W/AC. Leaching kinetics follows a 0.5 order with respect to tungsten concentration (Fig. S3). The system with tungsten acid exhibits a higher concentration of homogenous active species in the liquid phase from the beginning, and because of this, the higher

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conversion of cellulose can be obtained. However, the carbon efficiency (CEL) was lower (69-80 %) in this case compared to the Ru/W/AC catalyst (76-82 %). For all of these experiments, noticeable differences could be seen in polyol distributions. Note that the yield of ethylene glycol was still 11-15 % greater (independent on reaction time), if the heterogeneous catalyst Ru/W/AC was used. On the other hand, the combination of Ru/AC + H_2WO_4 allowed higher production of sorbitol. In this case, the yield of sorbitol of 30.5 % was obtained after one hour reaction time, and a further increase was not monitored neither with increasing reaction time nor with varying concentration (Fig. S4). Under identical reaction conditions, Ru/W/AC produced only half of the sorbitol yield of the Ru/AC + H_2WO_4 system. The differences in the distribution of the main products, ethylene glycol and sorbitol, are due to the kinetics and mass transport of several steps of the complex reaction system, namely (i) tungsten leaching, (ii) retro-aldol condensation of glucose catalyzed by both the dissolved tungsten species formed via the leaching process and the remaining acid tungsten sites of the heterogeneous Ru/W/AC catalyst (in contrast to H_2WO_4 of the combined catalyst system), and (iii) glucose and glycolaldehyde hydrogenation.

The real active site of tungsten during the reaction is not known yet because the lack of in situ methods for gas-liquid-solid reactions. Because of high reaction temperature and usage of water as a solvent, possible reaction of tungsten with water in this hydrothermal environment can occur[22]. Therefore, the formation of real active sites from metallic tungsten is possible. This leads to tungsten in different valence states (WO_3, WO_2, hydrogen bronze), all of them exhibit acidic properties and principally they all can take part in the reaction beside the redispersed tungsten carbides. Therefore, regarding tailoring the active sites for hydrolysis and C-O/C-C bond scissions we conclude that the following conditions should be fulfilled: a) high tungsten loading in the pre-catalyst, b) its high-temperature reduction and c) redispersion of tungsten carbide species by the aqueous environment of the second impregnation step followed by reduction. The latter step also ensures a close position of hydrogenation and acidic sites on the catalyst surface. This is also indicated by an experiment with physical mixture of Ru/AC and W/AC in order to see the importance of synergy between ruthenium and tungsten active sites. The conversion of cellulose obtained during this reaction was 85 % and the overall polyol yield was similar to the experiment with standard Ru/W/AC catalyst. However, the product distribution differs and is similar to them obtained after the reaction with the catalyst system Ru/AC + H_2WO_4. In both these cases, more sorbitol in the range of 30-45 % was obtained, but the yield of ethylene glycol was ~ 11-15 % smaller. Therefore, we conclude that for the production of ethylene glycol with a high yield the close position of ruthenium and tungsten species is necessary. On the other hand, for the high production of sorbitol catalyst systems with separated active species of Ru and W are more essential.

It must be noted that the ICP-OES analysis of the liquid phase obtained after the reaction with Ru/AC + H_2WO_4 showed, in contrast to Ru/W/AC, the presence of small traces of nickel and iron. Therefore, the possible corrosion of the stainless steel reactor can prohibit an industrial application of the catalyst system consisting of tungsten acid and ruthenium catalyst. After standard reaction time of 3 hours, polyols were produced in the same level for both systems (overall yield of 66.1 % and 66.6 % for Ru/AC + H_2WO_4 and Ru/W/AC, respectively). Taking into account all these results, we decided to use the heterogeneous catalyst for the next step, namely the hydrogenolysis of different cellulosic materials based on pine, birch and eucalyptus.

Before we demonstrate the catalyst performance for this challenge, we kept in mind that such types of feedstock are usually pretreated. To further increase the reactivity of cellulose, various pretreatment techniques (mechanical, chemical) can be used. Ball-milling is a mechanical process, which effectively degrades the resistant cellulose crystallinity, particle size and the high degree of polymerization[33]. Usually, the time of ball-milling is between 1 hour and few days, and such pretreated cellulose was applied for the hydrolysis of cellulose[7, 18, 34, 35]. Because of the high costs of this pretreatment, it is necessary to optimize both the time for ball-milling of cellulose and for the hydrogenolysis reaction. Therefore, we ball-milled microcrystalline cellulose using ZrO_2 balls in a ZrO_2 bottle of a planetary ball mill for various times (4, 15, 30, 120, 720 minutes) and we investigated the influence of the pretreated cellulose on the hydrogenolysis reaction over the Ru/W/AC catalyst. Additionally, for 4 and 15 minutes ball-milled cellulose, experiments with shorter reaction time of 1 hour and 2 hours were carried out in order to better comparison and understanding of the influence of this cellulose pretreatment method. Higher cellulose conversions were obtained if ball-milled cellulose was used (Fig. 2). Surprisingly, very short-time ball-milling of 4 minutes is enough to increase the cellulose conversion from 65 % (no pretreatment) to 81 % after one hour reaction time, and to 94 % for 15 minutes long ball-milled cellulose. Moreover, the overall polyol yield achieved a value of 70.0 % (therefrom 39.6 % ethylene glycol yield) if the reaction took three hours for 4 minutes ball-milled cellulose. In contrast to short-time ball-milled cellulose, if the long-time ball-milled cellulose was used (30, 120, and 720 minutes), the overall polyols yield slowly decreased and for 720 minutes ball-milled cellulose achieved a value of only 15.4 % after three hours of reaction time. The mechanical pretreatment method also influenced the product distribution (Fig. 2). Interestingly, the amount of sugar hydrogenation products, i.e. sorbitol (from glucose) and erythritol (from erythrose), decreased with increasing time of cellulose ball-milling. On the other hand, the amount of short-chain polyols like propylene glycol or 1,2-butanediol increased with increasing time of ball-milling and achieved yields in the range of 4-10 %. Based on these results we can conclude that the short-time ball-milling of cellulose can improve its reactivity and the yield of desired polyols. Moreover, the reaction time of cellulose hydrogenolysis can be shorted to one hour instead of three hours: this optimization led to a modified space-time yield (productivity) of 3.2 – 3.7 g ethylene glycol $(g_{catalyst}\ h)^{-1}$.

In the final step of this pretreatment we investigated the effect of mix-milling of catalyst and cellulose, i.e. a mechanocatalytic activation of cellulose. It was reported, that mix-milling of simple carbon and cellulose (with small amounts of HCl) were effective for its hydrolysis in order to achieve a high yield of sugars, especially glucose[36]. We mix-milled 5 g of cellulose with 0.5 g of Ru/W/AC catalyst for only four minutes. After milling, we flushed out the cellulose-catalyst mixture with 100 g of water and used it for the hydrogenolysis reaction. After three hours of reaction time, full conversion of cellulose was achieved. The enhanced contact between solid cellulose and solid catalyst caused by mix-milling could increase the overall polyol yield to 84 % (Fig. 2), which is the highest polyol yield achieved during cellulose hydrogenolysis with our Ru/W/AC. Besides a high ethylene glycol yield of 37.4 %, the yields of propylene glycol, butanediol, and sorbitol were also high, 14 %, 10.8 %, and 17.3 %, respectively. Remarkeably the carbon balance in the case of mix-milling is the highest (90 %, illustrated by the CEL data of Table S1).

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Real biomass can be provided from agriculture (e.g. dedicated crops and residues), forestry (e.g. wood), industry and household (solid residues, e.g. wastepaper), and aquaculture[37]. Complex chemical composition of biomass consisting of the three main components cellulose, hemicellulose, lignin, and other small fractions (proteins, fats, etc.) images a significant challenge in its utilization. Therefore, the raw material has to be separated by physical or chemical methods. After the fractionation, the conversion of each component can improve the economical efficiency of a bio-refinery[38]. We showed above that the heterogeneous catalyst Ru/W/AC can convert microcrystalline cellulose into polyols with high yield. This catalyst system was then applied to different kinds of cellulosic materials which typically incur, for example, in wastepaper. Concretely, cellulosic material of pine (unbleached and bleached), birch, and eucalyptus were used for the hydrogenolysis reaction over Ru/W/AC at 493 K, 65 bar of hydrogen pressure within three hours of reaction time. Also the low catalyst/cellulosic material ratio of 1/10 which was used for the hydrogenolysis of microcrystalline cellulose was preserved. Again we carried out the reaction in pure water and without the use of mineral acids. All raw materials were firstly cut with scissors, pre-milled with a grinder (particle size ~ 5 mm) and finally milled in the planetary ball mill (particle size < 0.4 μm). The results obtained in the experiments are shown in Fig. 3. Surprisingly, the activity of Ru/W/AC was very high as indicated by conversions of the different cellulosic materials in the range of 89 % and 100 %. As expected, the product distribution depends strongly on the individual cellulose type. The reaction of unbleached pine cellulose gave 9.9 % of polyols and the yield of ketones was even higher, 19.3 %. On the other hand, the hydrogenolysis of bleached pine-, birch- and eucalyptus-based cellulosic feedstocks showed a high overall polyol yield, 32.1 %, 41.0 % and 60.2 %, respectively. Note that among the polyols produced by the eucalyptus-derived feedstock, ethylene glycol is the most abundant component (~ 28 %), and no formation of sorbitol was observed. This indicates that among the aforementioned competitive reaction steps the retro-aldol condensation of sugar molecules and the subsequent hydrogenation of the unsaturated intermediates to short-chain polyols proceeds much faster than the sugar hydrogenation. Moreover, we analyzed the four materials with respect to their α-cellulose content which amounts to 91, 87, 85 and 88 % for unbleached pine, bleached pine-, birch- and eucalyptus-based cellulosic feedstocks, respectively. Obviously, there is no correlation between the catalyst performance and the content of α-cellulose indicating that the latter is not a key parameter. Therefore other factors must be considered such as pretreatment (bleaching or not, sulfite vs. sulfate process) and the cellulose source (hardwood, e.g. eucalyptus vs. softwood, e.g. pine) influencing the fiber morphology, especially length and shape. In comparison to the results obtained during the hydrogenolysis of microcrystalline cellulose over Ru/W/AC, the yields of ethylene glycol and C4/C6 polyols decreased, whereas the yield of propylene glycol and 1,2-butanediol was doubled for the reaction with bleached pine-based feedstock, and tripled in the case of birch- and eucalyptus-derived feedstock. Indeed, the hydrogenolysis over our Ru/W/AC catalyst could be successfully transferred to other cellulosic materials.

Conclusions

Polyols, a class of biomass-derived platform molecules, were obtained in high yield by hydrolytic hydrogenation of different cellulosic feedstocks using a bifunctional Ru-W catalyst which exhibits a very high concentration of acid sites. Therefore the use of mineral acids can be avoided. We are aware that the next step of processing biomass to value-added chemicals by heterogeneously catalyzed hydrogenolysis should include real lignocellulosic feedstocks. Also in this case catalysts have to withstand deactivation which is expected to occur. Our aim was to show how a carefully synthesized bifunctional catalyst converts not only model cellulose but also real cellulosic materials to valuable platform chemicals and can be re-used several times without loss of activity. It is necessary to critical scrutinize the catalyst stability under the conditions of such kind of liquid phase reactions (high temperatures, aqueous environment, presence of solvents, biogenic impurities, metal-chelating properties of reactants/products).

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Notes and references

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Tables

Table 1. Cellulose conversions (X), carbon efficiency coefficients (CEL) and product yields of cellulose hydrogenolysis over Ru/W/AC[a] catalyst including recycling.

#	Exp	X [%]	CEL [%]	Yield	[%]							Leaching of tungsten [ppm]	m_{CAT} [g]
				EG	PG	BD	Ery	Sor	Other Polyols	MeOH+ EtOH	Others		
1	STD	90	76.7	34.2	4.2	3.5	5.2	18.5	1.0	(1.3+0.6)	0.4	nm	0.501
2	1.run	100	70.4	36.7	3.4	3.3	5.1	15.4	1.4	(1.4+1.0)	0.1	127	0.505
3	2.run	100	68.8	34.4	3.8	3.8	5.0	18.2	1.7	(1.0+0.8)	0.8	71	0.505
4	3.run	100	75.9	34.8	2.8	3.1	5.3	20.4	2.0	(1.2+0.8)	1.1	66	0.450
5	4.run	100	72.3	39.1	4.6	4.4	4.0	16.0	1.8	(1.7+0.9)	0.9	45	0.450
6	5.run	100	73.2	39.7	3.8	4.4	3.7	14.7	2.6	(1.7+0.9)	1.0	40	0.369
7	6.run	100	67.3	33.8	3.9	4.2	3.5	15.7	3.1	(1.0+0.9)	0.8	21	0.360
8	7.run	85	55.6	4.5	3.1	1.3	4.5	28.4	4.6	(0.3+0.2)	0.6	5	0.357
9	RED	100	76.1	42.3	5.0	4.7	5.1	12.7	2.1	(2.0+1.5)	0.04	nm	0.372

EG = ethylene glycol, PG = propylene glycol, BD = 1,2-butanediol, Ery = erythritol, Sor = sorbitol, Other Polyols = (glycerol+1,2-hexanediol), MeOH+EtOH = (methanol+ethanol), Others = (cellobiose, glucose, mannose, fructose, mannitol, xylitol, 3-hydroxytetrahydrofurane, 1-hydroxy-2-propanone, 1-hydroxy-2-butanone, 3-hydroxy-2-butanone, 2,5-hexanedione, acetic acid, levulinic acid), nm = not measured, STD = experiment at standard reaction conditions, RED = experiment with reduced amount of catalyst.

[a] Tungsten loading = 40 wt% relating to WO_3. Ruthenium loading = 2 wt%.

Table 2. Cellulose conversions (X), carbon efficiency coefficients (CEL) and product yields of cellulose hydrogenolysis over Ru/W/AC[a] and Ru/AC + H_2WO_4[b].

#	Exp	Time [h]	X [%]	CEL [%]	Yield	[%]						
					EG	PG	BD	Ery	Sor	Other Polyols	MeOH+ EtOH	Others
1	Ru/W/AC	1	65	76.4	24.4	2.0	2.0	3.9	13.8	2.8	(1.0 + 1.1)	0.6
2	Ru/W/AC	2	84	81.5	34.5	2.8	2.9	5.8	17.0	1.4	(1.4 + 1.5)	0.9
3	Ru/W/AC	3	90	76.7	34.2	4.2	3.5	5.2	18.5	1.0	(1.3 + 0.6)	0.4
4	Ru/AC+ H_2WO_4	1	73	69.6	10.4	1.3	0.7	6.5	30.5	0.5	(0.5 + 0.3)	0.3
5	Ru/AC+ H_2WO_4	2	92	73.7	19.7	3.6	2.1	7.8	30.2	1.2	(1.2 + 0.8)	0.7
6	Ru/AC+ H_2WO_4	3	95	79.5	23.1	4.2	2.2	7.2	27.0	2.4	(1.2 + 0.6)	0.1

EG = ethylene glycol, PG = propylene glycol, BD = 1,2-butanediol, Ery = erythritol, Sor = sorbitol, Other Polyols = (glycerol+1,2-hexanediol), MeOH+EtOH = (methanol+ethanol), Others = (cellobiose, glucose, mannose, fructose, mannitol, xylitol, 3-hydroxytetrahydrofurane, 1-hydroxy-2-propanone, 1-hydroxy-2-butanone, 3-hydroxy-2-butanone, 2,5-hexanedione, acetic acid, levulinic acid).

[a] Tungsten loading = 40 wt% relating to WO_3. Ruthenium loading = 2 wt%.

[b] Ru/AC: Ruthenium loading = 2 wt%. Mass of catalyst = 0.5 g. Mass of H_2WO_4 = 0.25 g.

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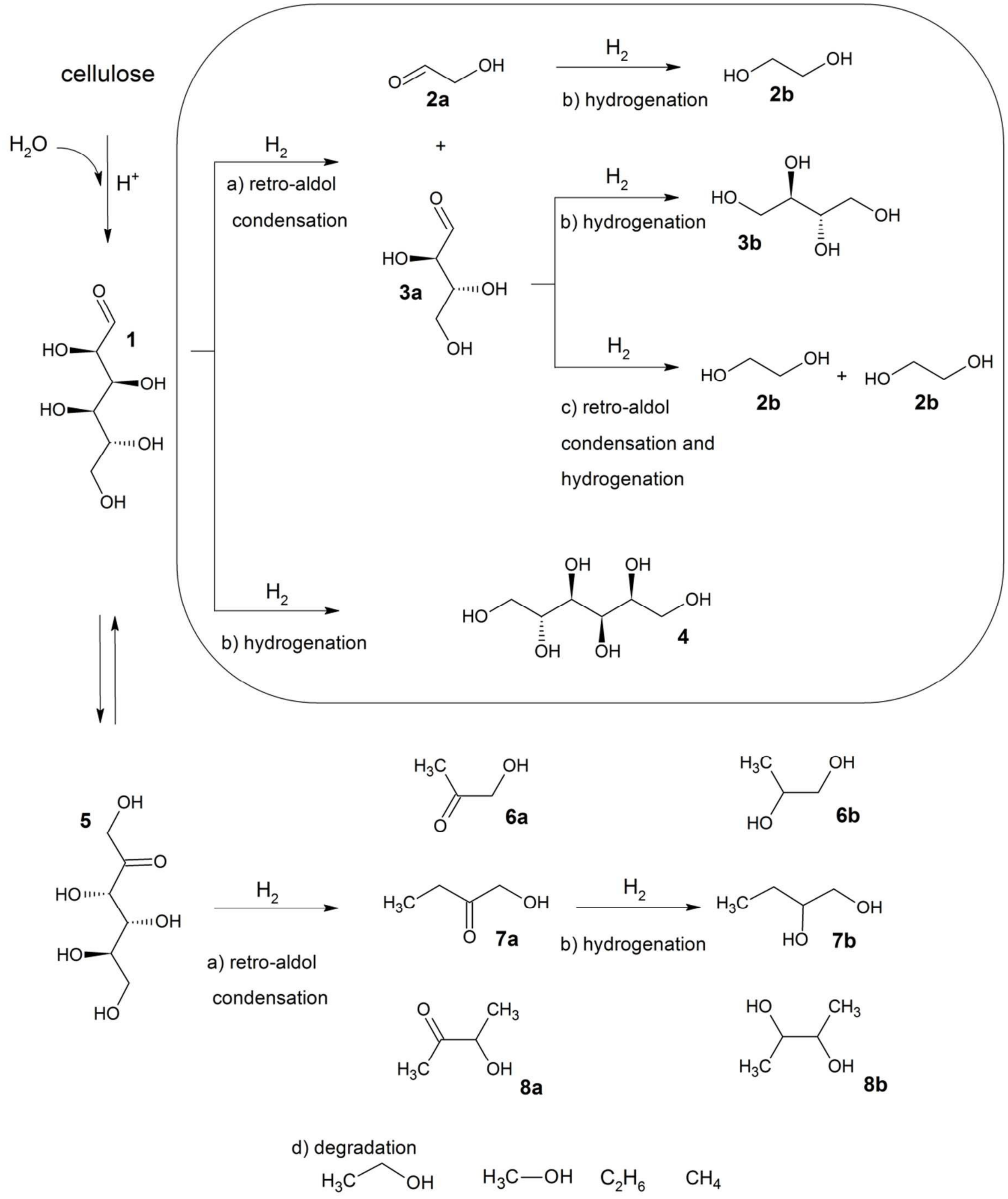
Figures

Scheme 1. Simplified reaction scheme of cellulose hydrogenolysis over Ru/W/AC catalyst: main reactions to glucose **1**, glycolaldehyde **2a**, ethylene glycol **2b**, erythrose **3a**, erythritol **3b**, sorbitol **4**, by-product formation: fructose **5**, 1-hydroxy-2-propanone **6a**, propylene glycol **6b**, 1-hydroxy-2-butanone **7a**, 1,2-butanediol **7b**, 3-hydroxy-2-butanone **8a**, 2,3-butanediol **8b**. Further degradation products which were formed during the reaction (often in trace amounts: acetic acid, levulinic acid, cellobiose, and mannose) are not included in this scheme.



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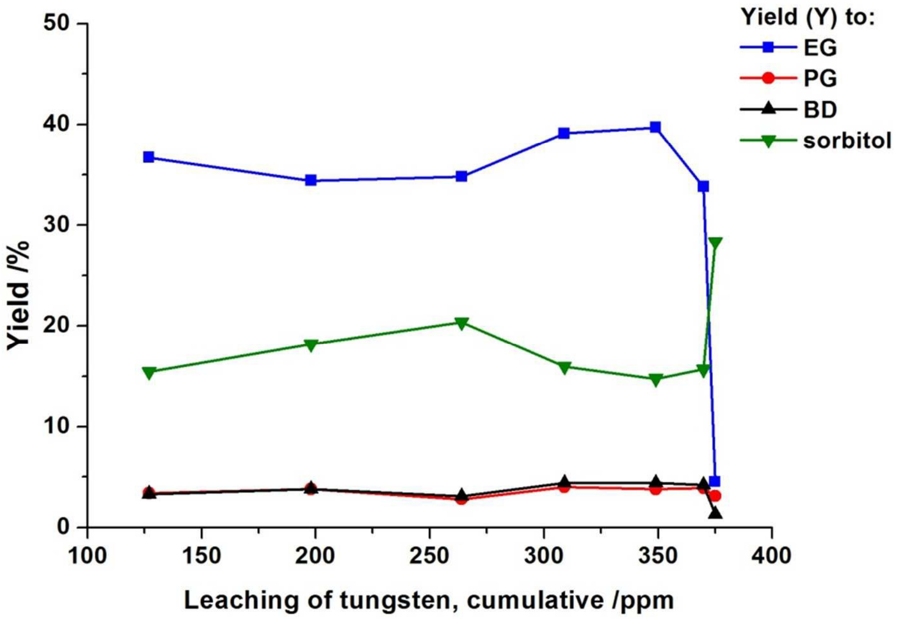

5 **Fig. 1. Yields of ethylene glycol (EG), propylene glycol (PG), 1,2-butanediol (BD), and sorbitol in dependence on tungsten leaching in the recycling test.**

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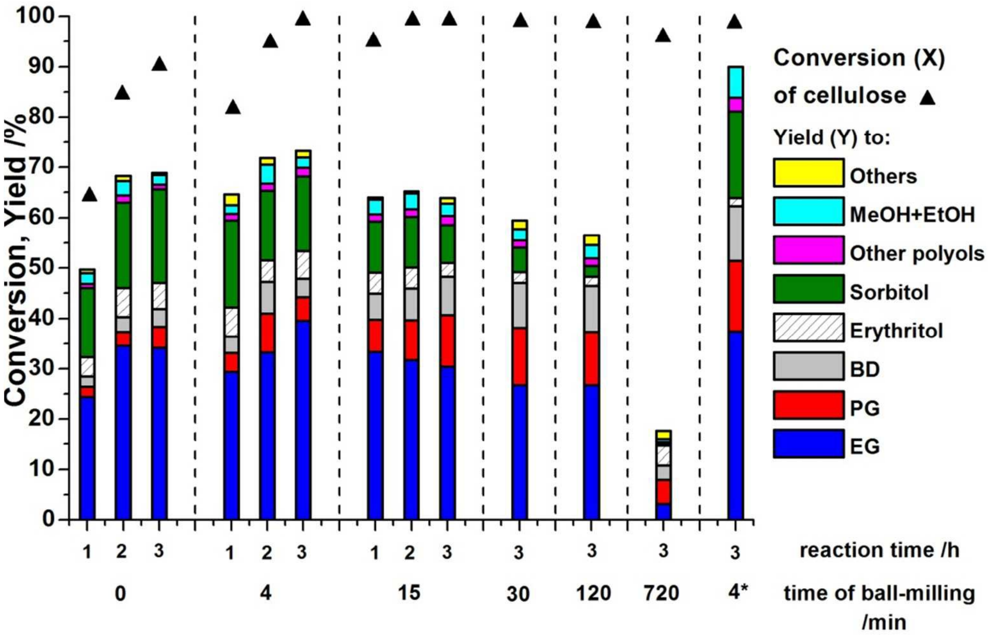

Fig. 2 Conversions and product yields for Ru/W/AC with non-pretreated cellulose (0 min) and ball-milled cellulose (4, 15, 30, 120, and 720 min). Reaction conditions: 0.5 g catalyst, 5 g cellulose, 100 mL water, reaction temperature 493 K, 65 bar of hydrogen pressure (measured at reaction temperature), 1000 rpm, * - mix-milling of catalyst and cellulose.

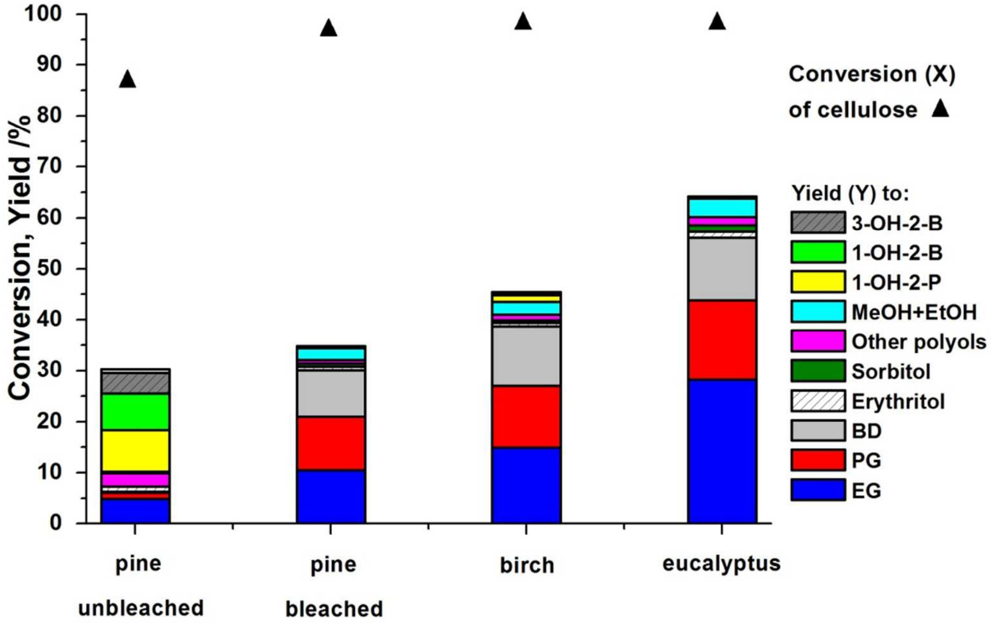

Fig. 3. Conversions and product yields for hydrogenolysis of different kinds of cellulosic material (pine unbleached, pine bleached, birch, eucalyptus) over Ru/W/AC catalyst. Reaction conditions: 0.5 g catalyst, 5 g cellulosic material, 100 mL water, reaction temperature 493 K, 65 bar of hydrogen pressure (measured at reaction temperature), 1000 rpm, 3 hours reaction time. 1-OH-2-P = 1-hydroxy-2-propanone, 1-OH-2-B = 1-hydroxy-2-butanone, 3-OH-2-B = 3-hydroxy-2-butanone.

Polyols, a class of biomass-derived platform molecules, were obtained in high yield by hydrogenolysis of different cellulosic feedstocks using a bifunctional Ru-W catalyst which exhibits a very high concentration of acid sites.

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