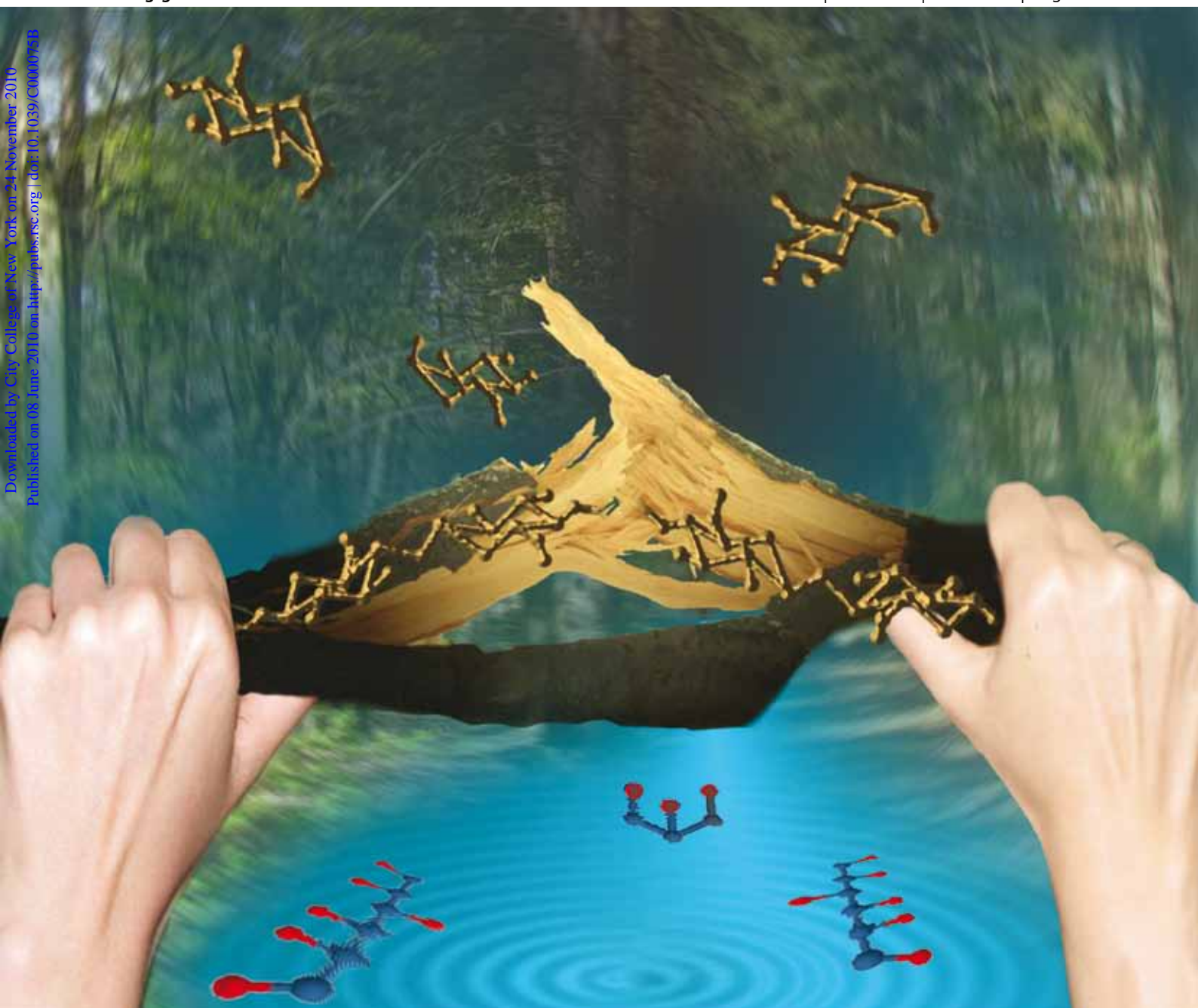


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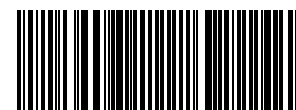
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Hydrogenolysis of cellulose combining mineral acids and hydrogenation catalysts†

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A catalytic system capable of reaching high performance in the hydrogenolysis of cellulose at low reaction temperature and short reaction times has been developed. Therefore, supported noble metal catalysts based on Pt, Pd and Ru have been combined with dilute mineral acids. A broad variable set in terms of type of noble metal, type of acid, acid concentration and reaction time could be evaluated based on chemical interpretation and supported by a Design of Experiment (DoE) approach. The variables significantly influenced conversion of cellulose, product range and selectivity towards sugar alcohol formation. Thus, at 160 °C, above 60% yield in sugars and sugar alcohols with 84% selectivity at a cellulose conversion of 72% could be reached. Besides, glycerol, propylene glycol, ethylene glycol and methanol were formed as additional valuable by-products leading to an overall carbon utilization above 89%. Furthermore, the concept was successfully transferred to real feedstocks in the form of spruce reaching close to 60% conversion in only one hour reaction time.

Introduction

Conventional methods to convert cellulose to glucose include acid hydrolysis and enzymatic saccharification, and are used on small scale only, due to several problems. While enzymatic saccharification suffers from rather low reaction rates and consequently low space-time yields, acid hydrolysis – as in the traditional wood saccharification processes, *e.g.* the Bergius-Rheinau or the Scholler-Tornesch process – raises the problem of by-product formation and acid recovery.¹ Therein, further acid catalyzed degradation of glucose to furfural compounds reduces the overall sugar yield and most degradation products are potential inhibitors for further enzymatic transformations. Although a lot of research effort has been made concerning cellulose degradation with the application of enzymes or mineral acids and bases, integral progress has not been reached yet. Nevertheless, depletion of fossil fuel reservoirs together with an indispensable shift of the feedstock base towards a biorefinery approach necessitates utilizing lignocelluloses on a large scale for chemical and fuel production, and makes efficient and environmental benign technology an imperative.

Recently, different chemo- and thermo-catalytic approaches were investigated to tackle the conversion of cellulose. Therein,

catalytic pyrolysis and decomposition at high temperatures demonstrated to yield valuable chemicals including aromatic species or syngas *via* reforming of biomass.^{2–4} These attempts are certainly technically promising but rather energy intense, and especially syngas formation does not make use of the defined chemical structure of biomass. Further mechanistic investigations will be necessary to understand processes associated with thermal decomposition of biomass to allow high selectivity to certain target molecules.⁵

Concerning controlled chemical transformations, ionic liquids with their ability to dissolve cellulose on a molecular level attracted increasingly attention and studies on hydrolysis of cellulose in these solvents have been carried out either using acidic ionic liquids, mineral acids to yield glucose, or metal chlorides aiming for synthesis of 5-hydroxymethylfurfural.^{6–8} The results were quite promising but separation of the products from the ionic liquids is tedious and hampers an application on the industrial scale. Using solid acid catalysts in the ionic liquid 1-butyl-3-methylimidazolium chloride, cellulose could be depolymerized selectively to cello-oligomers which appear interesting as their further enzymatic hydrolysis to glucose could be much faster.⁹ Therein, the solid acid catalyst substitutes not only mineral acids but allows a tailored depolymerization to avoid formation of sugars and further degradation products. Recycling of the expensive ionic liquids, however, remains a challenge so far.

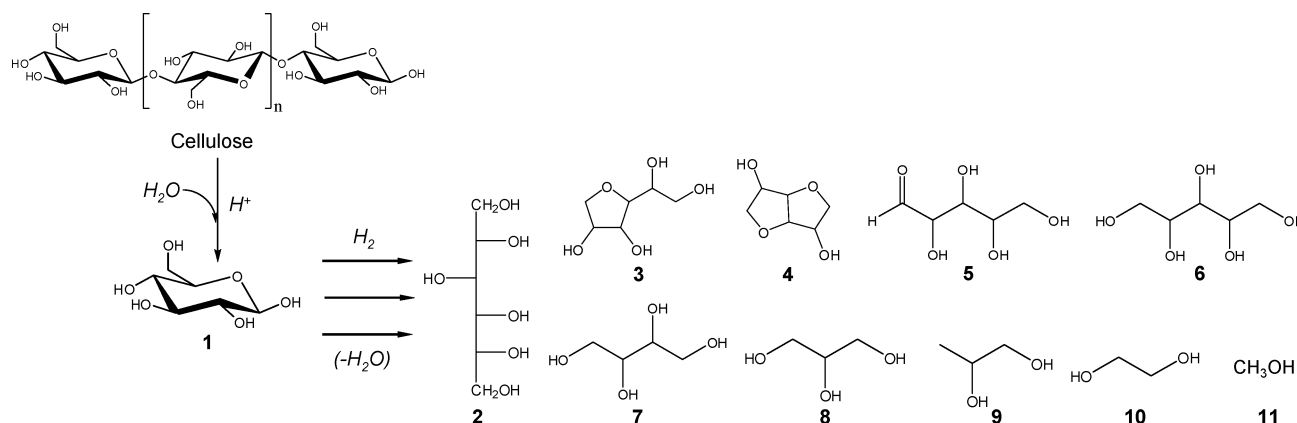
Regarding hydrolysis of cellulose in aqueous phase using solid acid catalysts, little progress has been made, although several studies demonstrated hydrolysis of cellulose using functionalized polymers, carbons or silica materials.^{10–13} In fact, the heterogeneously catalyzed hydrolysis of cellulose in aqueous media appears to be hampered by the fact that both the substrate and the catalyst are present in solid state. Consequently, very

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Scheme 1 Reaction scheme of the hydrogenolysis of cellulose with the major products: glucose **1**, sorbitol **2**, sorbitan **3**, isosorbide **4**, xylose **5**, xylitol **6**, erythritol **7**, glycerol **8**, 1,2-(or 1,3-)propanediol **9**, ethanediol **10** and methanol **11**. Further possible products which were identified in trace amounts and not included in the analysis are 1,3-butanediol, 5-hydroxymethylfurfural, levulinic acid and formic acid.

little contact between the substrate and the active sites results, reflected by a maximum conversion even of physically pre-treated cellulose (ball milling) of only 50%, with 90% selectivity to glucose.¹¹

Interestingly, current investigations showed that the combination of cellulose hydrolysis and hydrogenation can significantly improve the conversion of cellulose and prevent consecutive reactions towards undesired furfural components.¹⁴ Instead, more valuable sugar alcohols, glycerol, propylene or ethylene glycol, and methanol may be formed. The reaction scheme of cellulose hydrogenolysis is illustrated in Scheme 1. Dependent on reaction conditions and catalyst system, either a two-step reaction combining simple acid hydrolysis to yield glucose and further hydrogenation/hydrogenolysis to polyols can appear, or direct hydrogenolysis catalyzed by supported metal catalysts becomes possible. While in the first case, cleavage of the glycosidic linkages is achieved *via* addition of water catalyzed by acid catalysts, the latter was suggested to be catalyzed by supported metals *via* dissociation of hydrogen which may spill-over on the surface of the support, migrate to Lewis acid sites and release an electron to form protonic acid sites.¹⁴ These sites could consequently act as active sites for acid-catalyzed hydrolysis of cellulose as suggested by Fukuoka *et al.*¹⁵

In line with this, the first studies were carried out over supported noble metal catalysts in water at relative high temperatures of 190 or 245 °C and 120 bar hydrogen pressure. At 245 °C within 30 min a 40% yield of sugar alcohols could be reached. This result was at the expense of full conversion of cellulose, which means in fact that rather low carbon utilization towards the desired products was achieved. In contrast, another study worked at 190 °C with supported ruthenium nanoparticles and reported 30% yield of sugar alcohols in 24 h reaction time.¹⁶ Although no further information regarding cellulose conversion was given, our previous experiences point towards reasonable carbon utilization under such reaction conditions. Recently, Zhang *et al.* presented an interesting approach using nickel promoted tungsten carbide catalysts.¹⁷ Such noble metal-free catalysts could be low-cost alternatives to Pt and Ru systems and under similar reaction conditions (245 °C, 60 bar H_2 at 25 °C) reached full cellulose conversion within 30 min. Therein, the

main product proved to be ethylene glycol with a maximum of 61% mass-based yield. Further studies showed that also simple bimetal catalysts can exhibit comparable selectivity, although superior yields of up to 72% were obtained over tungsten carbide supported on three dimensional mesoporous carbons.¹⁸

These results are quite promising, but have not been transferred to real substrates yet. Additionally, overall high yields in combination with high carbon utilization in reasonable reaction time and a flexible product spectrum will be essential to render this process type feasible. Moderate reaction conditions are preferred to reduce material and installation costs for such processes. Indeed, at these high temperatures, inter- and intramolecular hydrogen bonding within the substrate is reduced which significantly facilitates consequent hydrolysis of cellulose. Unfortunately, at the same time the corrosion potential of water increases substantially and therewith, causes higher costs of potential construction materials. Consequently, attempts are necessary to reduce the reaction temperature and gain basic knowledge on factors influencing cellulose conversion and product distribution.

Our investigation focuses on the development of a catalytic system capable to reach reasonable performance in the combined hydrolysis – hydrogenation/hydrogenolysis of cellulose and real feedstocks at significantly lower temperature and short reaction times.^{19,20} Earlier on, Sharkov indicated that the conversion of cellulose under such reaction conditions could be efficient and Robinson *et al.* revisited this approach also reporting promising results.²¹ Based on these reports, a comprehensive investigation on the combined hydrolysis and hydrogenation of cellulose has been carried out.

Therefore, supported noble metal catalysts based on platinum, palladium and ruthenium on carbon have been combined with dilute sulfuric and phosphoric acid at a reaction temperature of 160 °C. Based on a broad variable set in terms of type of noble metal, type of acid, acid concentration and reaction time, the influence of the different variables could be evaluated to identify correlations between these variables and cellulose conversion, carbon utilization, and product distribution. The impact of these variables is discussed based on chemical interpretation of the data, while the study has additionally

been supported by a Design of Experiment approach (DoE) and a full description of further studies on the development of a quantitative composition-activity relationship (QCAR) model to allow quantitative prediction of conversion and yield under certain reaction conditions will be in the focus of further investigations. In the present study, however, the most promising reaction conditions were applied to spruce as real feedstock and efficient conversion of this substrate to a range of defined products could be demonstrated.

Experimental

All catalyst materials (5 wt% Ru/C, Pd/C and Pt/C) were provided from Johnson Matthey and used as delivered. α -Cellulose (fibres) from wood (spruce), sulfuric and phosphoric acid were purchased from Aldrich and used without any pre-treatment or purification. In general, α -cellulose is the insoluble fibrous residue obtained by extraction of wood, straw pulps and holocelluloses with strong alkali under carefully controlled conditions and contains about 10% of hemicellulose. The degree of polymerization of α -cellulose was determined by gel-permeation chromatography of the tricarbonyl derivative of the cellulose samples and showed a broad distribution with the maximum around $1.5 \cdot 10^3$.^{9,22,23}

Catalytic experiments

In a typical experiment, 500 mg α -cellulose, 100 mg catalyst, and 10 ml acid solution were combined in a 36 ml stainless steel autoclave equipped with Teflon inserts. The reactor was flushed several times with hydrogen and finally pressurized to 50 bar hydrogen pressure. Within 15 min, the autoclave was heated to 160 °C and kept there 1 or 5 h. After reaction, the reactor was cooled down, remaining pressure was released, and the reaction mixture was centrifuged to separate remaining solid components and the product solution.

Characterization

Quantification of the products in the reaction solution was achieved *via* HPLC measurements in 2 mM TFA on a Shimadzu LC-10A based on calibration curves of the pure compounds. The setup was equipped with a column switch, combining a 100 and a 300 mm organic acid resin column (8 mm i.D.), wherein, sugars and sugar alcohols were analyzed using a RI detectors, while analysis of by-products, *e.g.* furfurals, was carried out using a UV-detector.

The conversion of cellulose $X_{\text{Cellulose}}$ was determined based on the weight of cellulose utilized in the reaction $m_{\text{Cellulose},0}$ and the solid recovered after reaction taking into consideration the fraction of the solid catalyst in the remainings with $m_{\text{Cellulose}} = m_{\text{recovered solid}} - m_{\text{Catalyst}}$.

$$X_{\text{Cellulose}} = \frac{m_{\text{Cellulose},0} - m_{\text{Cellulose}}}{m_{\text{Cellulose},0}} \quad (1)$$

Concerning calculation of yields, previous studies on cellulose hydrogenolysis described mass-based yields deviding the weight of polyols in the product mixture by the weight of cellulose used in the reaction.⁶ Such a description has the advantage

to summarize the results of HPLC analysis very straight forward. Though, differences in the oxygen content of the various products is not accounted for. Therefore, the amount of oxygen-rich products will be overestimated, while products of dehydration reactions will be underestimated. Consequently, a more general representation of the observed product spectrum would be desirable. Therefore, the yields Y_{Products} presented in this manuscript are based on the standard definition, where the stoichiometric coefficient of the substrate $\nu_{\text{Substrate}}$ is equal to one for a $(\text{C}_6\text{H}_{10}\text{O}_5)_n$ cellulose unit as starting material:

$$Y_{\text{Product}} = \frac{n_{\text{Product}} - n_{\text{Product},0}}{n_{\text{Substrate},0}} \frac{\nu_{\text{Substrate}}}{\nu_{\text{Product}}} \quad (2)$$

with $n_{\text{Substrate}}$ equal to the molar amount of $(\text{C}_6\text{H}_{10}\text{O}_5)$ in the starting substrate, $n_{\text{Product},0}$ equal zero and n_{product} equal the molar amount of the certain product as determined by HPLC.

Therein, 100% yield has to correspond to the case that 100% of the carbon atoms of cellulose can be found in the analyzed products. Due to the fact that the reaction mechanism is not fully clear yet, calculation of reaction yields has to be carried out using theoretical stoichiometric coefficients ν_{Product} corresponding to the carbon content of the particular products compared to $(\text{C}_6\text{H}_{10}\text{O}_5)_n$. Consequently, the theoretical stoichiometric coefficient ν_{Product} would be one for all C₆ compounds, while a C₅ product would be accounted for with 6/5 and a C₄ with 6/4 and so on, resulting in a closed carbon balance for every single compound.

Results and discussion

The investigated variables significantly influence cellulose conversion, product distribution and selectivity towards the various products formed in hydrogenolysis of α -cellulose. Fig. 1 illustrates the relation between conversion of α -cellulose and these variables for a reaction temperature of 160 °C. Interestingly, independently of the type of metal catalyst used, overall higher conversion of cellulose can be reached in the reaction performed with H_2SO_4 than in those carried out with H_3PO_4 . This effect

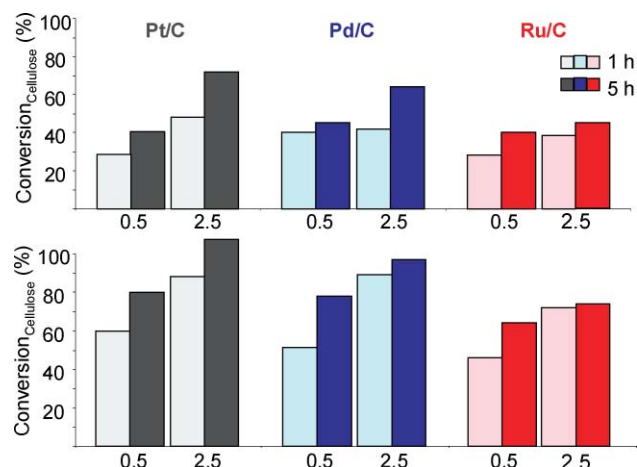


Fig. 1 Cellulose conversion in 0.5 or 2.5 wt.% H_3PO_4 (top) or H_2SO_4 (bottom) for 1 or 5 h over 5% Pt, Pd or Ru catalysts on carbon. (160 °C, $p(\text{H}_2) = 50$ bar (25 °C)).

may be attributed to the higher acid strength of sulfuric acid ($pK_a -3.9$) compared with phosphoric acid ($pK_a 2.16$) for the first dissociation. Indeed, previous studies indicate the reaction rate of cellulose hydrolysis to be strongly dependent on acid concentration.^{24,25} Besides, the nature of the substrate in terms of crystallinity, degree of polymerization, or pretreatment together with the reaction conditions certainly influence the reaction.^{23,25} In agreement, our results emphasize that the conversion of cellulose increases for higher H_3O^+ concentrations and longer reaction times. Less pronounced changes for phosphoric acid may be attributed to the overall lower variation in H_3O^+ concentration.^{24,26}

Regarding the influence of the supported metal catalysts, Pt/C in combination with sulfuric acid shows the highest conversion of cellulose reaching 100%. Likewise, Pd/C allows achieving quite high conversion of cellulose of up to 96%. In contrast, hydrogenolysis of cellulose over a Ru/C catalyst leads to a maximum conversion of cellulose of only 74%. These significant differences in overall conversion of cellulose over different catalysts are, at first glance, difficult to rationalize. In principle, the reaction causing conversion of cellulose should be basically cellulose hydrolysis, which is predominantly determined by acid concentration, reaction temperature and reaction time. Control experiments have been carried out under identical reaction conditions, but in the absence of any metal catalysts. Interestingly, a maximum conversion of cellulose of 69% could be reached with 2.5 wt% H_2SO_4 after 5 h. The results are summarized in the ESI† including detailed information about the resulting product spectrum. Therein, mainly glucose and xylose, resulting from a fraction of around 10% of hemicellulose in α -cellulose, and degradation products including hydroxymethylfurfural, furfural and levulinic acid are formed. In the absence of metal catalyst, however, in no case full conversion of cellulose could be observed. Consequently, the presence of metal catalysts under hydrogenolysis conditions influences the depolymerization of cellulose and severe differences in conversion of cellulose at identical reaction conditions but over varying metal catalysts seem either to point towards an influence of the metal catalyst on the hydrolysis step of cellulose or towards other means of cellulose degradation, e.g. via C–C and C–O bond cleavage.

Concerning the first point, Fukuoka *et al.* suggested the mentioned spillover effect, wherein hydrogen could be dissociated on the metal surface, transferred onto the support material forming acid sites which are supposed to catalyze the hydrolysis of cellulose.¹⁵ Beside hydrogen spillover, another explanation could be based on the reforming, namely, the C–C and C–O bond cleavage activity of the different catalysts. In line with the observed conversion of cellulose, the reforming activity of the investigated catalysts decreases in the order Pt/C > Pd/C > Ru/C.¹ This effect is additionally reflected in the product distribution over the different catalysts shifting from gaseous and short chain products to C_5 – C_6 products for Ru/C. Interestingly, both explanations would require contact between active sites of the solid catalyst and the bulky biopolymer cellulose that would most probably involve steric hindrance and transport limitations. Nevertheless, to tackle these points, further investigations will be necessary to elucidate the nature of the interaction between cellulose and supported metal catalyst resulting in an accelerated and therewith somewhat

facilitated hydrolysis of cellulose under hydrogenolysis reaction conditions.

Carbon utilization factor

Beside high conversion of cellulose, the decisive point for an efficient process transforming cellulose in a one step reaction to a mixture of value-added chemicals is based on the yield of desired products. Certainly, the term “desired” may be defined differently depending on the aim of the study. Herein, however, we consider all products dissolved in the water phase as desirable; while gaseous compounds as methane or carbon dioxide are undesired. Consequently, based on the conversion of cellulose and the yield of products in the liquid phase ($Yield_{Liquid}$), an overall selectivity to liquid phase products expressed as carbon efficiency (E_c) may be calculated:

$$E_c = \frac{Yield_{Liquid}}{X_{Cellulose}} \quad (3)$$

Table 1 summarizes conversion, product distribution and carbon efficiency under various reaction conditions. Obviously, a higher carbon efficiency results if more carbon atoms of the converted cellulose end-up in the desired liquid-phase products. Therein, over Pt/C and Pd/C rather low carbon efficiencies below 60% are reached with a maximum of 65% for Pd/C after 1 h reaction time in 2.5 wt% phosphoric acid (entry 7) and only 10% combining Pt/C with 2.5 wt% sulfuric acid at 5 h reaction time (entry 16).

Concerning the influence of acid concentration on carbon efficiency, no clear trend can be observed, although the results point out a slight decrease of carbon efficiency for higher acid concentrations. Beside acid concentration and metal catalyst, the reaction time significantly influences carbon efficiencies. For longer reaction times, the hydrogenolysis reaction proceeds further and a higher fraction of smaller and, therewith, potentially gaseous molecules is formed, consequently, resulting in a lower carbon efficiency. This effect is in particular considerable in the case of Pt/C and Pd/C at high concentrations of sulfuric acid (entries 16 and 20).

These points, namely decreasing carbon efficiency for increasing acid concentrations and longer reaction times, also apply to reactions over Ru/C catalysts, but the decline in carbon efficiency in this system is only little. Thus, although reactions over Ru/C result in rather low conversion of cellulose compared to Pt/C and Pd/C, superior yields of liquid phase products and carbon efficiency up to 83 and 89% for 1 h reaction in 0.5 or 2.5 wt% sulfuric acid can be reached. Additionally, over Ru/C these values even remain high after 5 h reaction time, still reaching 70 and 84% carbon efficiency, respectively.

As mentioned, an explanation of the differences in the conversion of cellulose and the yield to liquid phase products depending on the metal catalyst may be related to the tendency to catalyze C–C and C–O bond cleavage. Consequently, over Pt- and Pd-catalysts longer reaction times yield a higher fraction of C_1 to C_3 molecules and the overall carbon efficiency for liquid phase products drops. In contrast, Ru/C exhibits a high activity in hydrogenation reactions resulting in sugar alcohol formation but further C–C cleavage reactions are only catalyzed to a smaller extent. Therefore, carbon efficiency does not

Table 1 Cellulose conversion, carbon yield, carbon efficiency and product selectivities in the hydrogenolysis of cellulose over supported Pt, Pd and Ru catalysts on carbon with phosphoric or sulfuric acid. ($m(\text{cellulose}) = 0.5 \text{ g}$, $m(\text{catalyst}) = 0.1 \text{ g}$, $V(\text{acid}) = 10 \text{ ml}$, $T = 160 \text{ }^\circ\text{C}$, $p(\text{H}_2) = 50 \text{ bar}$ ($25 \text{ }^\circ\text{C}$))

Entry	Catalyst	Conc. [wt%]	Time/h	Conv. ^a [%]	Yield _{Liq.} ^b [%]	E_C [%]	Yield [%] ^b										
							C ₆				C ₅		C ₄	C ₃	C ₂		C ₁
							1	2	3	4	5	6	7	8	9	10	11
Phosphoric acid																	
1	Pt/C	0.5	1	41.6	23.8	57	7.4	0.0	0.0	0.0	10.9	0.4	0.0	0.9	0.0	0.0	4.1
2	Pt/C	0.5	5	40.8	25.2	62	13.9	0.0	0.0	1.1	6.2	1.8	0.0	0.8	0.3	1.1	0.0
3	Pt/C	2.5	1	48.0	27.8	58	12.7	0.0	0.0	0.6	10.3	1.3	0.0	0.9	0.6	1.4	0.0
4	Pt/C	2.5	5	72.0	19.5	27	12.9	0.0	0.0	0.4	1.5	1.7	0.0	1.0	0.6	1.4	0.0
5	Pd/C	0.5	1	40.0	25.0	63	8.9	1.1	0.0	0.1	9.1	4.2	0.0	1.2	0.2	0.0	0.0
6	Pd/C	0.5	5	58.6	24.3	42	14.2	0.8	0.0	0.3	5.8	2.1	0.0	1.1	0.0	0.0	0.0
7	Pd/C	2.5	1	42.0	27.1	65	12.0	1.3	0.0	0.2	8.0	4.4	0.0	0.9	0.3	0.0	0.0
8	Pd/C	2.5	5	64.0	24.6	38	12.9	3.0	0.0	0.6	0.8	4.6	1.7	1.0	0.0	0.0	0.0
9	Ru/C	0.5	1	28.0	23.9	85	0.0	8.9	4.8	1.2	0.0	6.8	0.6	1.6	0.0	0.0	0.0
10	Ru/C	0.5	5	40.0	27.2	68	0.0	12.5	6.2	0.3	0.0	4.3	1.8	2.0	0.0	0.0	0.0
11	Ru/C	2.5	1	38.6	31.5	82	0.0	14.8	4.8	0.3	0.0	10.2	0.4	1.0	0.0	0.0	0.0
12	Ru/C	2.5	5	59.0	35.4	60	0.0	17.7	7.1	0.2	0.0	7.3	1.0	2.2	0.0	0.0	0.0
Sulfuric acid																	
13	Pt/C	0.5	1	60.0	23.6	39	13.1	0.0	0.0	0.3	6.1	1.3	0.0	0.7	1.0	1.3	0.0
14	Pt/C	0.5	5	84.6	33.2	39	28.3	0.0	0.0	1.5	2.4	0.0	0.0	1.0	0.0	0.0	0.0
15	Pt/C	2.5	1	88.0	30.8	35	24.6	0.0	0.2	1.1	1.9	0.4	0.0	1.2	0.0	1.5	0.0
16	Pt/C	2.5	5	100	10.0	10	1.0	0.4	0.5	4.8	0.1	0.3	1.7	1.2	0.0	0.0	0.0
17	Pd/C	0.5	1	51.4	26.9	52	15.8	0.0	0.0	0.3	6.2	4.2	0.0	0.0	0.4	0.0	0.0
18	Pd/C	0.5	5	78.0	21.1	27	7.3	4.1	0.0	1.0	0.0	4.4	0.0	1.3	0.0	0.3	2.7
19	Pd/C	2.5	1	89.2	46.7	52	29.8	1.2	0.8	1.7	1.6	1.4	0.0	0.8	0.5	0.2	8.7
20	Pd/C	2.5	5	96.8	12.2	13	0.3	0.8	0.8	1.7	0.0	0.8	0.0	1.1	0.0	0.3	6.5
21	Ru/C	0.5	1	39.6	33.0	83	0.0	16.5	6.0	0.5	0.0	8.5	0.0	1.5	0.0	0.0	0.0
22	Ru/C	0.5	5	64.0	44.8	70	0.0	25.6	8.6	0.0	0.0	7.7	0.0	2.9	0.0	0.0	0.0
23	Ru/C	2.5	1	72.0	63.8	89	0.0	33.2	13.6	1.8	0.0	11.3	0.0	2.2	0.0	0.0	1.7
24	Ru/C	2.5	5	74.0	62.2	84	0.0	11.7	25.6	5.7	0.0	10.5	0.0	5.7	0.0	0.0	3.1

^a Conversion was calculated by the weight difference of cellulose before and after reaction. ^b Based on theoretical stoichiometric coefficients corresponding to the carbon content of the reaction products.

change significantly for longer reaction times, but the product distribution shifts towards the dehydration products **3** and **4** formed in subsequent C–O cleavage and dehydration reactions.

Product distribution

Besides carbon efficiency, the ability of the different catalyst materials for C–C and C–O bond cleavage is additionally reflected in the product distribution. For reactions over Ru/C and independently of the type of acid, C₅–C₆ sugar alcohols including sorbitol **2**, sorbitan **3**, isosorbide **4** and xylitol **6** are the main products with selectivities up to 83% (entry 23). Therein, formation of xylitol can be attributed again to hemicellulose incorporated in α -cellulose. Besides, small amounts of glycerol **8** and methanol **11** are formed in the case of high sulfuric acid concentrations (entry 23 and 24), while for phosphoric acid erythritol **7** is formed (entries 9–12). The absence of any sugar in the form of glucose **1** or xylose **5** emphasizes the fast hydrogenation of these molecules over the ruthenium-based catalyst. Therefore, after hydrolysis of cellulose to form glucose, hydrogenolysis over Ru/C appears to be primarily determined by fast hydrogenation of sugars together with subsequent dehydration reactions to form **3** and **4**.

In the case of Pt/C and Pd/C and independently of the reaction conditions, only low yields of C₅–C₆ sugar alcohols can

be observed. Instead, the product spectrum constitutes mainly from glucose **1** and xylose **5**. Besides, xylitol **6** is formed in yields up to 4.6% for the Pd/C catalyst (entry 8). Certainly, higher acid concentrations and longer reaction times shift the product distribution towards shorter and potentially gaseous products. Interestingly however, for most reactions glucose remains among the main products. Therefore, Pt/C and Pd/C do not seem to be active enough to sufficiently hydrogenate sugars under these reaction conditions to yield sugar alcohols. With regard to C–C cleavage, however, it is questionable if hydrogenation to sorbitol is required as an intermediate step before hydrogenolysis proceeds further or if glucose is rather directly cleaved to form smaller molecules.

Hydrogenolysis of lignocellulosic feedstocks

Certainly, efficient utilization of cellulose poses an important challenge to be tackled. Concerning future biorefinery approaches, however, efficient conversion of real feedstocks will be mandatory to achieve economic processes. Therein, a crucial point to be mentioned, relates to the impact of the substrate utilized in the reaction. All previous investigations have been carried out with α -cellulose, but achieved conversions and yields may vary significantly dependent on nature, origin and pretreatment of the substrate, and its properties in terms of degree

Table 2 Hydrogenolysis of lignocellulosic feedstocks in the form of spruce chips ($m(\text{spruce}) = 0.5 \text{ g}$, $m(\text{catalyst}) = 0.1 \text{ g}$, $V(\text{acid}) = 10 \text{ ml}$, $T = 160 \text{ }^\circ\text{C}$, $p(\text{H}_2) = 50 \text{ bar}$ ($25 \text{ }^\circ\text{C}$))

Entry	Cat.	Time/h	Conv. ^a [%]	Cellulose Conv. ^b [%]	Yield _{Liq.} ^{b,c} [%]	E_c [%]	Yield [%] ^{b,c}										
							C ₆				C ₅		C ₄	C ₃	C ₂	C ₁	
							1	2	3	4	5	6	7	8	9	10	11
25	Pt/C ^d	1	44.2	68.0	38.0	56	11.3	1.0	2.4	0.2	18.3	0.7	1.1	0.5	0.0	1.8	0.8
26	Ru/C ^e	1	59.2	91.1	61.9	68	0.7	36.0	7.3	0.6	0.0	6.5	4.5	0.7	0.0	2.3	3.2
27	Ru/C ^d	5	50.8	78.2	72.0	92	4.3	24.3	8.8	0.6	0.0	7.1	7.6	3.7	1.3	6.0	8.4

^a Conversion was calculated by the weight difference of spruce before and after reaction. ^b Cellulose conversion was based on a content of 40% cellulose and 25% hemicellulose, calculated as 65% cellulose. ^c Yield was calculated based on theoretical stoichiometric coefficients corresponding to the carbon content of the reaction products. ^d Carried out with 2.5 wt.% phosphoric acid. ^e Carried out with 2.5 wt.% sulfuric acid.

of polymerization or crystallinity.²² Nevertheless, the general impact of the different reaction variables on the substrate may at least allow a first assessment of suitable reaction conditions for an efficient conversion of various types of feedstocks.

Consequently, the most promising reaction conditions for Pt/C and Ru/C were applied in the hydrogenolysis of wood chips in the form of spruce. The results are summarized in Table 2. Indeed, the reaction could be transferred successfully to spruce as biomass feedstock. Therein, conversions between 44 and 59% could be achieved. Cellulose content in spruce was estimated with around 40% together with 25% of hemicellulose resulting in yields between 38 and 72% based on these contents of cellulose and hemicellulose.¹⁰ Related to the product distribution, for Ru/C mainly C₆ sugar alcohols are formed with additional amounts of C₅ and C₄ compounds which are most probably due to transformation of hemicellulose under reaction conditions. Interestingly, combination of Ru/C with phosphoric acid (entry 27) results not only in C₄ to C₆ polyol but also the whole range of C₁ to C₃ compounds is covered with above 8% yield of methanol. Nevertheless, the observed yields correspond well to the results for pure α -cellulose and the presented approach to combine mineral acids and supported noble metal catalysts for the hydrogenolysis of cellulose can indeed be transferred to real feedstocks without the need for any pretreatment of the utilized biomass.

Based on these results the application of hydrogenolysis as alternative entry point for a biorefinery concepts appears feasible. Certainly, utilization of mineral acids is unfavorable and further studies will concentrate on suitable solid acid systems. Additionally, the need for hydrogen in the reaction may be of concern and efficient routes to reform parts of the biomass to yield hydrogen will be required before efficient water splitting technologies are in place. Nevertheless, hydrogenolysis offers the possibility to convert the cellulosic fraction of biomass in a one step reaction into a wide range of potential bulk chemicals for further chemical transformations, *e.g.* in surfactant applications *via* telomerization with bioethanol derived 1,3-butadiene, further hydrogenolysis reactions aiming for a certain product distribution or dehydration reactions as recently demonstrated by Lehr *et al.*^{27–30}

Conclusions

In summary, combination of Pt, Pd or Ru catalysts supported on carbon with dilute phosphoric or sulfuric acid allows an

efficient conversion of cellulose and even spruce in a one step hydrogenolysis reactions to form C₄ to C₆ sugar alcohols. The variables including type of noble metal, type of acid, acid concentration and reaction time significantly influence cellulose conversion, carbon efficiency and product distribution. The effects may be summed up as follows:

(I) Overall, higher conversion of cellulose can be reached for sulfuric compared to phosphoric acid. This can be explained based on the lower pK_a value of sulfuric acid when compared to phosphoric acid.

(II) Interestingly, significantly higher conversions of cellulose can be achieved combining hydrolysis and hydrogenation/hydrogenolysis reactions, emphasizing the supporting effect of the metal catalyst in the hydrolysis of cellulose.

(III) Pt/C and Pd/C allow almost complete conversion of cellulose but due to slow hydrogenation, glucose and xylose are the main products. Additionally, a high fraction of volatile products from consequent hydrogenolysis reactions occurs resulting in an overall low carbon efficiency.

(IV) Ru/C yields predominantly C₄ to C₆ sugar alcohols resulting from simple hydrolysis of cellulose followed by hydrogenation of the released sugars. As little further C–C cleavage occurs, high carbon efficiencies of up to 89% may be reached.

(V) Furthermore, the concept can be transferred to real biomass in the form of spruce. Therein, 60% conversion in only one hour reaction time could be achieved with close to 55% yield of C₄ to C₆ sugar alcohols.

Thus, overall, hydrogenolysis of cellulose combining mineral acids and supported noble metal catalysts presents an interesting approach for a direct conversion of cellulose into valuable platform chemicals with the ability to control cellulose conversion and product distribution.

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