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Which Controls the Depolymerization of Cellulose in Ionic Liquids: The Solid Acid Catalyst or Cellulose?

Roberto Rinaldi,* Niklas Meine, Julia vom Stein, Regina Palkovits, and Ferdi Schüth*[a]

Cellulose is a renewable and widely available feedstock. It is a biopolymer that is typically found in wood, straw, grass, municipal solid waste, and crop residues. Its use as raw material for biofuel production opens up the possibility of sustainable biorefinery schemes that do not compete with food supply. Tapping into this feedstock for the production of biofuels and chemicals requires—as the first-step—its depolymerization or its hydrolysis into intermediates that are more susceptible to chemical and/or biological transformations. We have shown earlier that solid acids selectively catalyze the depolymerization of cellulose solubilized in 1-butyl-3-methylimidazolium chloride (BMIMCl) at 100 °C. Here, we address the factors responsible for the control of this reaction. Both cellulose and solid acid catalysts have distinct and important roles in the process. Describing the depolymerization of cellulose by the equivalent number of scissions occurring in the cellulosic chains allows a direct correlation between the product yields and the extent of the polymer breakdown. The effect of the acid strength on the depolymerization of cellulose is discussed in detail. Practical aspects of the reaction, concerning the homogeneous nature of the catalysis in spite of the use of a solid acid catalyst, are thoroughly addressed. The effect of impurities present in the imidazolium-based ionic liquids on the reaction performance, the suitability of different ionic liquids as solvents, and the recyclability of Amberlyst 15DRY and BMIMCl are also presented.

Introduction

Currently, the production of biofuels from carbohydrates is a field of intense research activity.[1] In particular processes for biofuels that start from glucose have been attracting immense attention.[1] However, there is concern that sugars obtained directly from saccharose (typically produced from sugarcane or sugar beet) or semi-directly from the hydrolysis of starch (present in corn and other crops) can compete with food supply.[2a] Accordingly, cellulose emerges as a feedstock that is more suitable than starch or saccharose. Firstly, this biopolymer is the most abundant organic compound on the planet.[2] In addition, the utilization of cellulose, present in lignocellulosic materials such as wood, straw, grass, municipal solid waste, and crop residues, does not compete with food supply.[3a] Nevertheless, the recalcitrance of this biopolymer poses serious challenges to the chemical and biological processing of cellulose.[3–5]

Many attempts to hydrolyze lignocellulosic materials into glucose and other fermentable sugars have been reported during the last century.[5] These processes are commonly referred to as saccharification of wood. Several mineral acids, such as H_2SO_4,[6c,h,i] HCl,[6d,f] or even HF,[6j] have been employed as liquid acid catalysts for the hydrolysis of cellulose. Some of these processes were scaled up to pilot-plant level.[6c–e,h,i] Although valuable results were obtained during the pilot tests, the full-scale production of glucose via saccharification of lignocellulosic materials was never commercially implemented because of problems concerning corrosion, energy demand, catalyst recovery, and decomposition of sugars.[5,6a,b]

In the majority of saccharification processes, the lignocellulosic raw material is typically not solubilized in the reaction medium.[5] Under such conditions the supramolecular/crystalline structure of cellulose imposes important restrictions on the kinetics of the heterogeneous hydrolysis of cellulose.[7] In practice, a specific pretreatment of the lignocellulosic material (e.g., by partial chemical degradation, mechanical comminution, activation by swelling, or by several other processes) is usually applied to partially disrupt the supramolecular structure of the cellulosic fibers, enhancing the reactivity of cellulose towards hydrolysis.[8] The solubilization of cellulose in ionic liquids, however, completely disassembles the supramolecular structure of the cellulosic fibers.[9] This strongly improves the reactivity of cellulose.[10]

We have shown earlier that solid acids catalyze the depolymerization of cellulose dissolved in 1-butyl-3-methylimidazolium chloride (BMIMCl) under mild conditions.[11] This reaction is performed efficiently using macroreticulated acid resins (known by the brand name Amberlyst 15DRY[12]). The total depolymerization of cellulose can easily be achieved. In practice, however, it is much more interesting to stop the process at the stage in which cellooligomers are the main products.[11]

At first glance, the use of this acidic resin shows several significant advantages over molecular acids. Firstly, the breakdown of cellulose by Amberlyst 15DRY in BMIMCl is more con-

[a] Dr. R. Rinaldi, N. Meine, J. vom Stein, Dr. R. Palkovits, Prof. F. Schüth
Department of Heterogeneous Catalysis
Max-Planck-Institut für Kohlenforschung
Kaiser-Wilhelm-Platz 1, 45470 Mülheim an der Ruhr (Germany)
Fax: (+49) 208 306 2995
E-mail: rinaldi@mpi-muelheim.mpg.de
schueth@mpi-muelheim.mpg.de
Homepage: http://www.mpi-muelheim.mpg.de/kofo/

trollable.[4] Stopping the reaction at the cellooligomer stage (Figure 1) allows the separation of the cellooligomers from the ionic liquid by addition of water.[4] This enables recycling of the ionic liquid. In contrast, the hydrolysis of cellulose is very fast when using soluble acids [e.g., mineral acids or *p*-toluenesulfonic acid (*p*-TSA)] leading to the formation of a multitude of dehydration and polymeric byproducts, making work-up of the product mixture extremely difficult.[13] Up to now, the efficient extraction of glucose and its dehydration products from the reaction medium has not been achieved.[4,14]

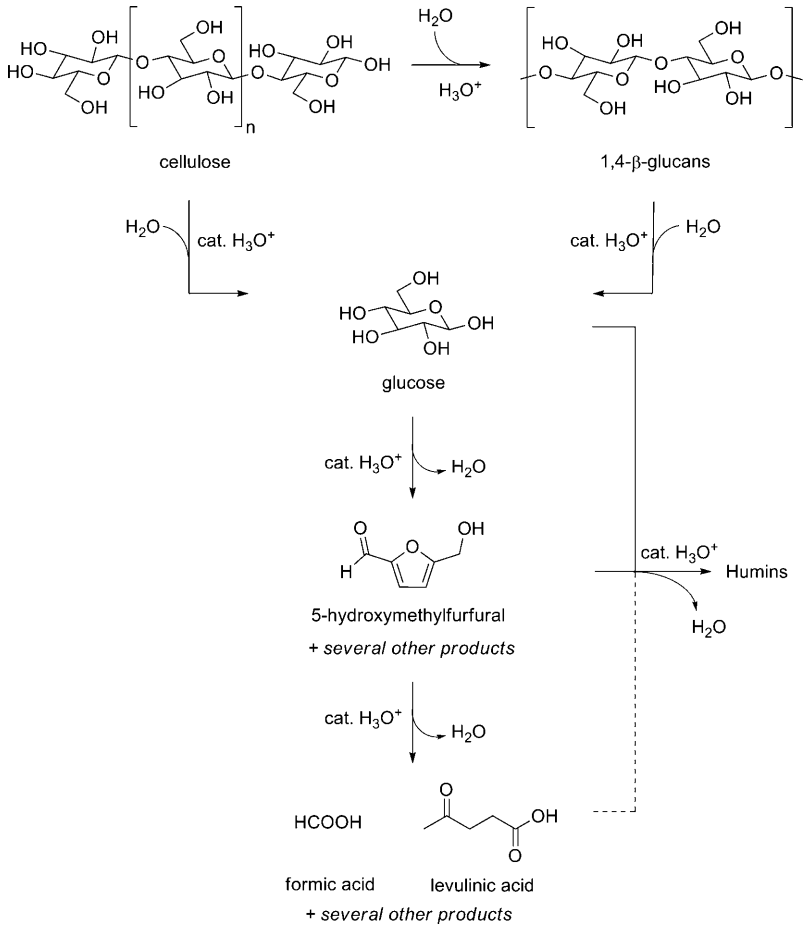

Figure 1. Selected products formed by acid-catalyzed reactions starting from cellulose. Hemicelluloses are typical impurities of cellulose. Therefore, xylose and other monosaccharides as well as their degradation products (furfural, furoic acid, and others) are also present in the reaction mixture.

Herein, we comprehensively address the factors responsible for controlling the depolymerization of cellulose when using Amberlyst 15DRY in BMIMCl. The effects of catalyst amount and of temperature on the distribution of the products are investigated. The description of the reaction by the equivalent number of scissions occurring in the cellulosic chains allows a direct correlation between the yield of products and the progress of the depolymerization reaction. As a result, the roles of the properties of cellulose and of the solid acid catalyst in controlling of the reaction could be elucidated. Regarding the properties of the catalyst, acid strength is an important factor in the activation of cellulose towards hydrolysis. Practical aspects of the reaction, concerning the homogeneous nature of the catalysis in spite of using a solid catalyst, are discussed in detail. We correct our previous conclusion on the heterogeneous nature of the catalyst.[11] The effect of impurities in the imidazolium-based ionic liquids on the reaction performance, the suitability of different ionic liquids as reaction medium, and the recyclability of catalyst and ionic liquid are also presented here.

Results and Discussion

Effect of the amount of acid catalyst

The addition of H_3O^+ species into a solution of cellulose in BMIMCl initiates a complex reaction chain, as described in Figure 1. In the first step, cellulose undergoes depolymerization via hydrolysis of 1,4-β-glycosidic bonds. Either smaller 1,4-β-glucans (cellooligomers) or glucose can be formed at this stage. In the presence of acidic species, glucose is likely to be dehydrated, producing a number of compounds[15] such as 5-hydroxymethylfurfural (5-HMF), levulinic acid, formic acid, and several others (Figure 1).[16,17] These products are prone to recombination with sugars or oligosaccharides via aldol condensation, resulting in polymers with undefined structures and stoichiometry called humins.[15,18]

The formation of the mentioned products in Figure 1 is catalyzed by acid. It is thus expected that by changing the amount and/or the nature of the acid catalyst, the reaction rates for the different steps should change differently, altering the distribution of products obtained from cellulose.[13d] The effect of the amount of catalyst on the depolymerization of cellulose was investigated by performing the reactions with Amberlyst 15DRY amounts ranging from 0.46 to 6.90 mmol of H_3O^+ for the reaction batch. These amounts correspond to concentrations of H_3O^+ ranging from 4.25 to 63.7 $\mu mol\,g^{-1}$ of reaction mixture, respectively.

Figure 2 shows the effect of the amount of Amberlyst 15DRY on the reaction performance. As expected, the higher the loading of Amberlyst 15DRY in the reaction, the faster the hydrolysis rate. Starting from an amount of Amberlyst 15DRY equivalent to 0.46 mmol of H_3O^+, a glucose yield of 0.58%

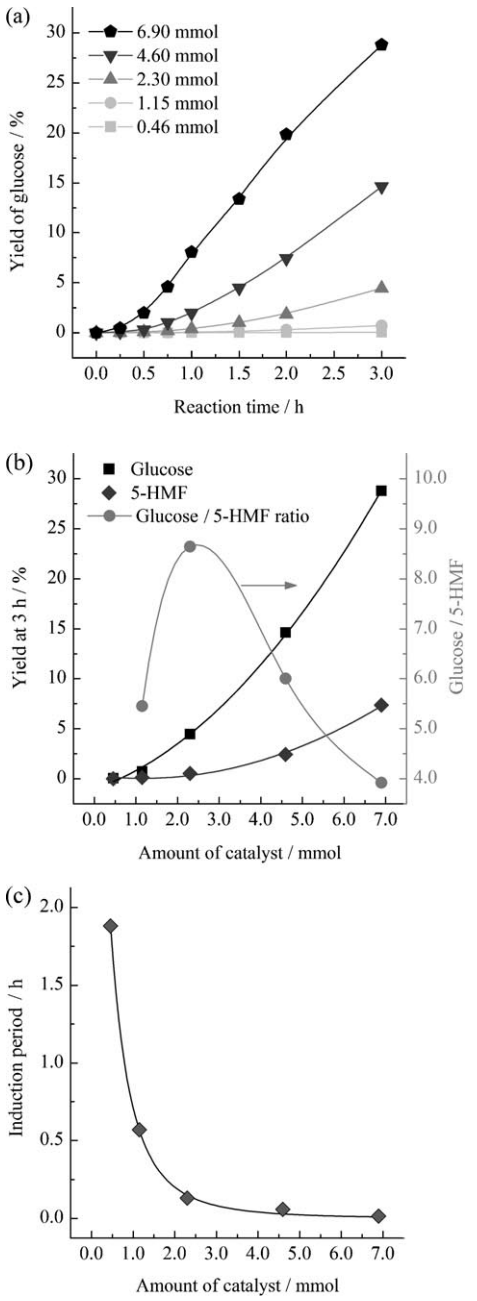

Figure 2. Depolymerization of cellulose over Amberlyst 15 DRY. a) Effect of the amount of catalyst on the yield of glucose. b) Yield of glucose and 5-HMF for reactions performed at 100 °C for 3 h using different amounts of catalyst. c) Dependence of the induction period on the amount of catalyst. Reaction conditions: cellulose [5 g, corresponding to ca. 31 mmol of anhydroglycose units (AGU); $C_6H_{10}O_5$: DP_o 650 AGU] dissolved in 100 g BMIMCl, Amberlyst 15DRY (4.6 mmol H_3O^+ g^{-1}), water (111 mmol), 100 °C.

was reached after 3 h. Under these conditions the formation of 5-HMF was not detected. Both, yields of glucose and of 5-HMF, did not increase linearly with the amount of acid used in the reaction (Figure 2b). Increasing the amount of Amberlyst 15DRY by 15 times (equivalent to 6.9 mmol of H_3O^+) resulted in a yield of glucose 50 times higher (28.8%, 3 h) than that observed when using an amount of acid resin equivalent to 0.46 mmol of H_3O^+. However, the formation of 5-HMF was also strongly enhanced when using 6.9 mmol of H_3O^+, reaching 7.35% at 3 h.

Figure 2b shows that the glucose/5-HMF ratio reached a peak at around 2.3 mmol of H_3O^+. At this value, the yield of glucose was 8.6 times higher than that of 5-HMF (100 °C, 3 h). In sequence, for the reactions performed with larger amounts of acid catalyst, there was a marked decrease of the glucose/5-HMF ratio. This suggests that the formation of 5-HMF is strongly favored when using larger amounts of acid catalyst (Figure 2b). However, as will be discussed in the next sections, an assessment of the product distribution with respect to the extent of depolymerization is necessary to correctly evaluate the influence of the amount of Amberlyst 15DRY on the reaction selectivity.

Extrapolating the trends for the yields of glucose and 5-HMF shown in Figure 2b, a maximum yield of glucose would be expected when using an amount of Amberlyst 15DRY equivalent to 11.9 mmol of H_3O^+. Under these conditions, the predicted yields of glucose and 5-HMF are 74.8 and 25.2%, respectively. In practice, however, the reaction produced only 25.0% of glucose and 11.8% of 5-HMF at 100 °C for 3 h. These low yields were due to the substantial formation of humins as byproducts.

The reaction performed with Amberlyst 15DRY displays an induction period for the production of glucose. This is not observed using equivalent amounts of *p*-toluenesulfonic acid (*p*-TSA).[11] The induction period depends heavily on the amount of acid resin used for the reaction (Figure 2c). Here, the induction period is defined as the reaction time required for a yield of glucose of 0.02%. The increase in the catalyst amount from 0.46 to 6.9 mmol of H_3O^+ makes the induction period much shorter. The induction period decreased from 1.9 h to less than 5 min under the latter reaction conditions (Figure 2c). In other words, performing the reaction with a large amount of Amberlyst 15DRY resembled carrying out the reaction with a soluble strong acid, for which no induction period for the production of glucose was noticed.[11]

Assessing the depolymerization of cellulose

The yield of glucose cannot describe fully the extent of the breakdown of cellulose in the course of the process (Figure 2). For this purpose, an assessment of the degree of polymerization (*DP*) of the cellulose solubilized in the reaction mixture is needed to describe the number of scissions that have occurred in the cellulosic chains at a given reaction time [Equation (1)].[19] Figure 3 shows the number of scissions over time for reactions performed with different amounts of Amberlyst 15DRY.

In contrast to the release of glucose, which showed an induction period (Figure 2a), the depolymerization of cellulose started immediately when Amberlyst 15DRY was added to the cellulose/BMIMCl solution (Figure 3). Furthermore, the linear correlation between the scission rates and the catalyst amounts (Figure 4) showed that depolymerization of cellulose solubilized in BMIMCl is a first-order reaction with respect to the amount of acid catalyst. The frequency of scissions at

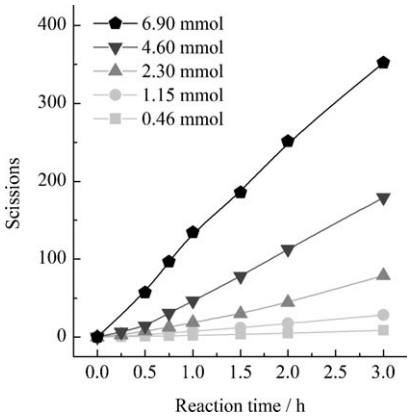

Figure 3. Equivalent number of scissions occurring in the cellulose chains during the course of the depolymerization using Amberlyst 15DRY. Reaction conditions: 5 g cellulose (corresponding to ca. 31 mmol of AGU; $C_6H_{10}O_5$: DP_o 650 AGU) dissolved in 100 g BMIMCl, Amberlyst 15DRY (4.6 mmol H_3O^+ g^{-1}), water (111 mmol), 100 °C.

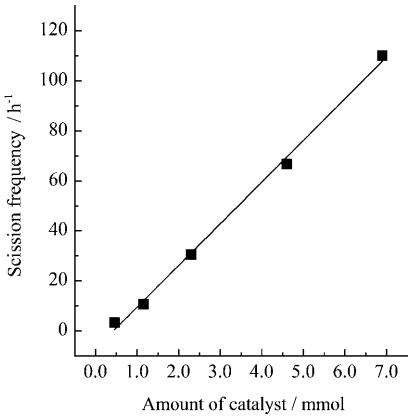

Figure 4. Correlation between the amount of catalyst and the scission frequency for reactions performed at 100 °C using Amberlyst 15DRY as H_3O^+ source.

100 °C was about 17 scissions h^{-1} (mmol H_3O^+)$^{-1}$ (Amberlyst 15DRY).

The extent of depolymerization and the distribution of products

Revisiting the set of data shown in Figures 2 and 3, it is apparent that the high concentration of acid not only enhanced the rate of depolymerization of cellulose but also appeared to favor the decomposition of glucose into 5-HMF. To understand how the extent of depolymerization regulates both yields of glucose and of 5-HMF, the correlation between these yields and the number of scissions occurring in the cellulosic chains was plotted, as shown in Figure 5.

The single most striking observation that emerges from the data comparison shown in Figure 5 is that the formation of glucose displays a rather consistent trend directly associated

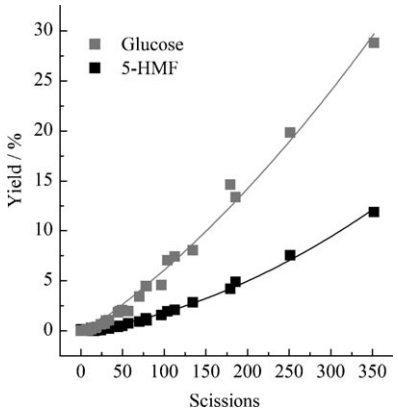

Figure 5. Depolymerization of cellulose over Amberlyst 15 DRY. Yield of selected products versus the number of scissions occurring in the cellulosic chains. These correlations were performed using the whole set of data gathered from the reactions displayed in Figure 2.

with the extent of the depolymerization of cellulose. A similar consistent pattern emerges in the correlation between yield of 5-HMF and the number of scissions occurred in the cellulosic chains. It is interesting to note that the selectivity for the products depends heavily on the extent of depolymerization. Therefore, for a fair comparison between yields or selectivities of different reactions, these values must be taken at the same extent of reaction.

To determine whether the concentration of acid catalyst altered the product distribution, the glucose/5-HMF ratio, obtained from reactions performed with 4.6 and 6.9 mmol of H_3O^+ (Amberlyst 15DRY), were analyzed with respect to the extent of depolymerization, as shown in Figure 6. Contrary to expectations, this study did not find a large difference between the glucose/5-HMF ratios, at a given depolymerization extent, for the reactions performed with 4.6 and 6.9 mmol of H_3O^+ (Amberlyst 15DRY). Increasing the amount of catalyst from 4.6 to 6.9 mmol of H_3O^+, that is, by 50%, favors the formation of 5-HMF by only about 10%. In fact, the consistent trends between yields and reaction extent, as shown in Figure 5, are only possible because of the small influence of

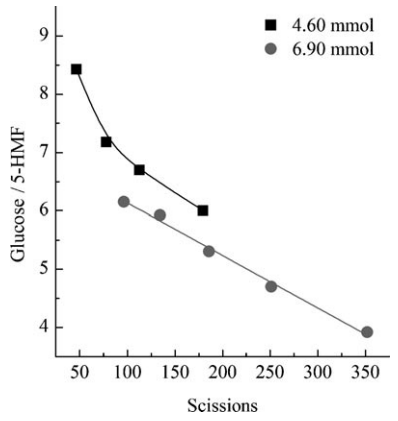

Figure 6. Effect of acid catalyst amount on the glucose/5-HMF ratio.

the amount of acid catalyst on the product yields at a given reaction extent.

Effect of temperature

Temperature seriously affects the depolymerization rate of cellulose. The reaction carried out at 120 °C was ca. 100 times faster than a reaction performed at 80 °C (Figure 7). This enhancement in the reaction rate is comparable to an increase of the catalyst amount from 1.15 to 6.9 H_3O^+ mmol in the batch (see Figure 3). The apparent activation energy for the depolymerization of cellulose was determined from the data shown in Figure 7. The value obtained in BMIMCl, 108 ± 5 kJ mol^{-1}, is slightly lower than that reported for the dilute-acid hydrolysis of cellulose in water-based systems (118–131 kJ mol^{-1}).[5,20] However, the present value of apparent activation energy for the depolymerization of cellulose in BMIMCl is identical to that reported elsewhere (111 ± 12 kJ mol^{-1}) for the hydrolysis of cellobiose in 1-ethyl-3-methyl-imidazolium chloride (EMIMCl).[13d] Thus, cellulose dissolved in ionic liquids appears to behave similarly to cellobiose. This indicates that the solubilization of cellulose does disassemble the supramolecular structure of this polymer, fully removing its physical protections against hydrolytic processes.[10]

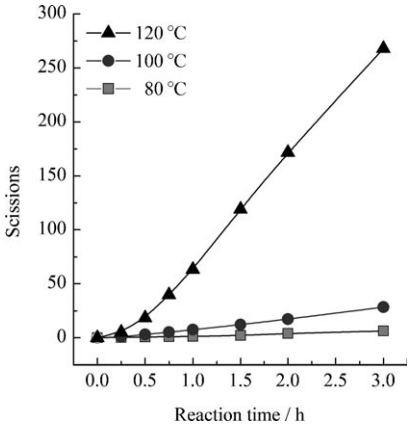

Figure 7. Effect of temperature on the depolymerization rate of cellulose. Reaction conditions: cellulose (5 g, corresponding to ca. 31 mmol of AGU; $C_6H_{10}O_5$: DP_o 650 AGU) dissolved in 100 g BMIMCl, Amberlyst 15DRY (1.15 mmol of H_3O^+), water (111 mmol).

Although cellulose dissolution in BMIMCl leads to a lowering of the apparent activation energy for hydrolysis, this value is still almost identical to that found by us for the acid-catalyzed degradation of glucose in BMIMCl (114 ± 6 kJ mol^{-1}). This indicates that the further decomposition of glucose should easily take place parallel to the hydrolysis of cellulose in a batch reaction. Because of the almost identical activation energies, the effect of temperature on the glucose to 5-HMF ratio, at a given reaction extent, is not very pronounced, as shown in Figure 8.

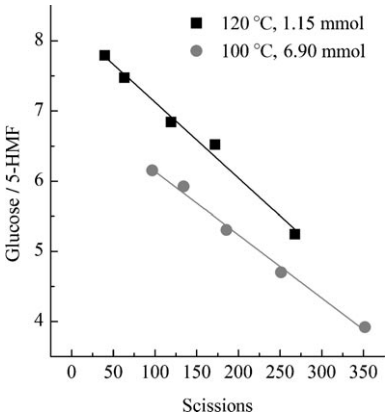

Figure 8. Effect of temperature on the glucose/5-HMF ratio.

The nature of Amberlyst 15DRY-catalyzed hydrolysis

Performing the depolymerization of cellulose in a controlled manner is one of the main motivations for the use of Amberlyst 15DRY instead of *p*-TSA.[11] At first glance, *p*-TSA seems to be a more active catalyst than Amberlyst 15DRY. Indeed, the formation of glucose (Figure 9a) and the cellulose breakdown (Figure 9b) take place at a faster rate using *p*-TSA than with sulfonated acidic resin. Furthermore, the reactions performed with Amberlyst 15DRY always display an induction period for the production of glucose, which depends heavily on the amount of solid acid present in the reaction medium (Figure 2c). In the case of the *p*-TSA-catalyzed reaction, the induction period for production of glucose is not evident (Figure 9a). Although Amberlyst 15DRY and *p*-TSA appear to be different, as discussed so far, the correlation between yield of glucose and extent of the depolymerization process (Figure 9c) shows that the real performance of both catalysts is otherwise the same considering the amount of glucose released in the progress of the reactions, as can be seen in Figure 9c.

Because Amberlyst 15DRY and *p*-TSA display similar performances concerning the production of glucose over the reaction extent, the question arises: Where does the reaction take place—on the catalyst surface or in the bulk solution?

Adding Amberlyst 15DRY into BMIMCl starts an ion-exchange process, as shown in Figure 10. Our former conclusion on the heterogeneity of the reaction with Amberlyst 15DRY as catalyst[11] was disguised due to presence of impurities found in the technical-grade BMIMCl *(*vide infra) and thus has to be corrected. In those experiments,[11] the amount of acid was determined directly by pH measurements of aqueous solutions of the reaction aliquots. The basic impurities (mainly *N*-methylimidazole) present in the technical-grade BMIMCl establish buffer equilibria, resulting in much higher pH values than would be expected without the buffer effect. Thus, reliable results on the acid amount present in the ionic liquid medium can be obtained by acid–base titration only.

Titrating the ionic liquid phase, separated from a suspension of Amberlyst 15DRY in BMIMCl, revealed that H_3O^+ was progressively released in this liquid within the first hour of contact between both phases (Figure 11). In sequence, the concentra-

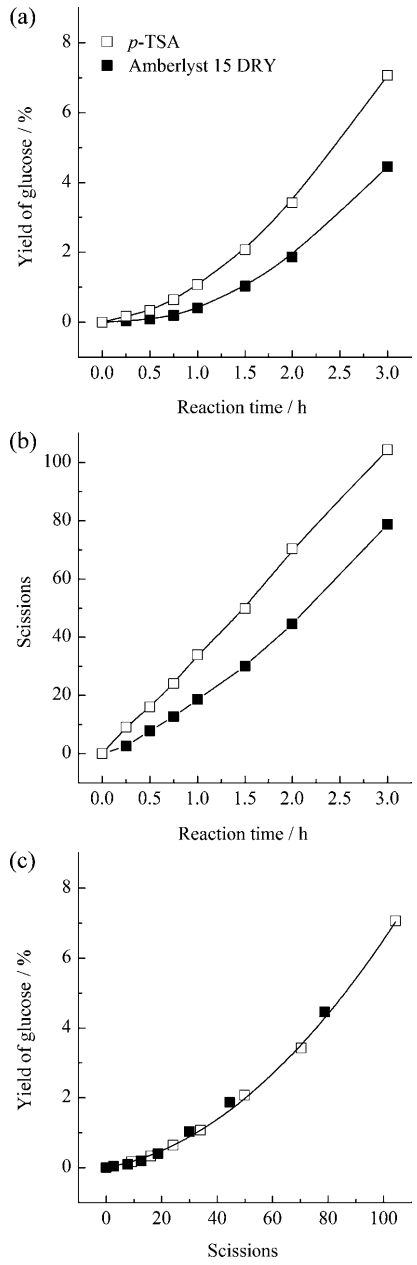

Figure 9. Depolymerization profiles of cellulose with Amberlyst 15DRY or *p*-TSA as catalyst. a) Yield of glucose. b) Equivalent number of scissions. c) Correlation between yield of glucose and equivalent number of scissions. Reaction conditions: cellulose (5 g, corresponding to ca. 31 mmol of AGU; $C_6H_{10}O_5$: DP_o 650 AGU) dissolved in 100 g BMIMCl, Amberlyst 15DRY or *p*-TSA (2.3 mmol of H_3O^+), water (111 mmol), 100 °C.

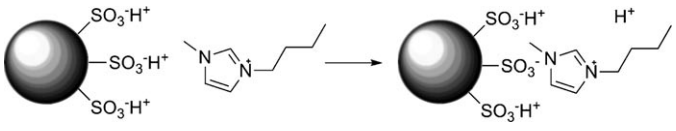

Figure 10. Ion-exchange process involving $BMIM^+$ and H^+ species.

tion of acid remains constant indefinitely. At this stage, ca. 75–80% of the initial acidic content of Amberlyst 15DRY is present in the ionic liquid phase. The slow release of H_3O^+ species is in

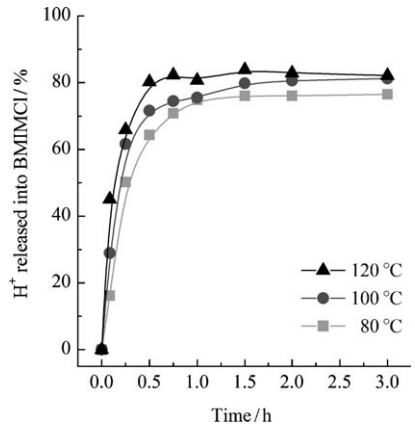

Figure 11. H^+ release profile of Amberlyst 15DRY in contact with BMIMCl at different temperatures.

agreement with the low initial rate of depolymerization found for the reaction performed with Amberlyst 15DRY (Figure 9b). Furthermore, because only ca. 80% of the acidic content of Amberlyst 15 DRY is present after the equilibration time (1 h), this acidic resin appears to be accordingly less active than *p*-TSA. Taking into account the real amount of acid present in both reaction media, the catalysts display otherwise similar activity, as expressed by the frequency of scissions found for the reactions performed with *p*-TSA and Amberlyst 15DRY (16 and 17 scissions h^{-1} (mmol H_3O^+)$^{-1}$, respectively).

Regarding the fact that the depolymerization of cellulose with Amberlyst 15DRY occurs in the solution phase, an explanation for the slower initial rate for the formation of glucose is still required. Depolymerization of cellulose solubilized in ionic liquid takes place preferentially at the larger cellulose molecules, as we have reported recently.[11] Accordingly, the induction period for the release of glucose is observed. The results obtained so far showed that the production of cellooligomers is preferred over the formation of glucose in the earlier stages of the reaction. This preference can be understood considering that cellooligomers can be produced by cleaving the polymeric chain at any position, while formation of glucose requires specific cleavage at the ends of cellulose. In this manner, the formation of glucose is not favored statistically in the beginning of the depolymerization process, because the reaction mixture contains large polymeric chains at this reaction stage. Therefore, the induction period for production of reducing sugars and the high selectivity for cellooligomers are features linked to cellulose rather than to the acid catalyst used.

Amberlyst 15DRY should be regenerated before reuse, due to the release of its H_3O^+ content into the cellulose/BMIMCl solution. The spent Amberlyst 15DRY possessed no catalytic activity for depolymerization of cellulose. However, washing this material with a H_2SO_4 solution regenerated its original catalytic performance, as shown in Figure 12. The regenerated resin (dried) was able to produce similar number of scissions in the cellulosic chains per time as the original Amberlyst 15DRY. Likewise, the yields of glucose obtained with the regenerated resin (dried) and with Amberlyst 15DRY were very similar, 0.29 and 0.26% at 2 h, respectively.

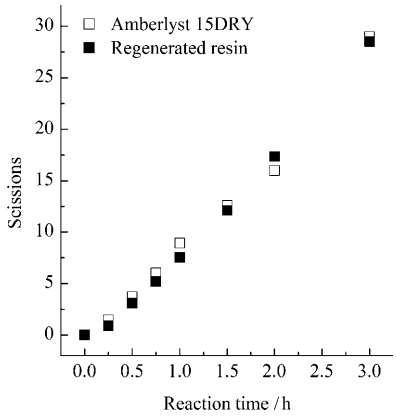

Figure 12. Equivalent number of scissions produced by Amberlyst 15DRY and by the regenerated resin after its first use. Reaction conditions: cellulose (5 g, corresponding to ca. 31 mmol of AGU; $C_6H_{10}O_5$: DP_o 650 AGU) dissolved in 100 g BMIMCl, Amberlyst 15DRY (1.15 mmol of H_3O^+), water (111 mmol), 100 °C.

Mimicking the solid acidic resin Amberlyst 15DRY

The evidences for the homogeneous nature of the catalysis, in spite of using a solid acid, indicate that the slow release of H_3O^+ species governs the initial rate of the depolymerization of cellulose using Amberlyst 15DRY. In order to simulate the H_3O^+ release process, a reaction was performed by dosing an HCl solution with a syringe pump over 1 h (2.3 mmol). Figure 13 shows the profiles for the reactions performed using Amberlyst 15DRY, dosing HCl over 1 h, and with *p*-TSA. The depolymerization of cellulose and the formation of glucose occurred very rapidly when adding a soluble acid at once (*p*-TSA, 2.3 mmol) into the reaction medium, as can be seen in Figure 13. In contrast with this result, the initial profile for the reaction fed with an HCl solution over 1 h was identical to that obtained using Amberlyst 15DRY, as H_3O^+-source (Figure 13a and b). This confirms the hypothesis that the slow release of H_3O^+ is the special feature of the Amberlyst resin for the control of the depolymerization of cellulose in BMIMCl. At 0.75 h, however, the reaction fed with HCl started to become faster than the reaction using Amberlyst 15DRY. This is due to the fact that Amberlyst 15DRY can release only ca. 75–80% of its nominal acidic content (Figure 11). Thus, the amount of acid present in the reaction mixture that was fed continuously with HCl over 1 h, is higher than that provided by Amberlyst 15DRY. Consequently, from 0.75 h on, a higher yield of glucose and a larger number of scissions were observed for the HCl-catalyzed reaction compared with those values found for Amberlyst 15 DRY (Figure 13a and b).

The profiles for the production of glucose against the number of scissions are identical for the reactions performed with *p*-TSA, Amberlyst 15DRY and HCl (Figure 13c). In fact, in the mentioned reactions, the catalytic species is H_3O^+ present in the ionic liquid phase. Accordingly, the formation of glucose depends solely on the number of scissions occurring in the cellulosic chains in the depolymerization process.

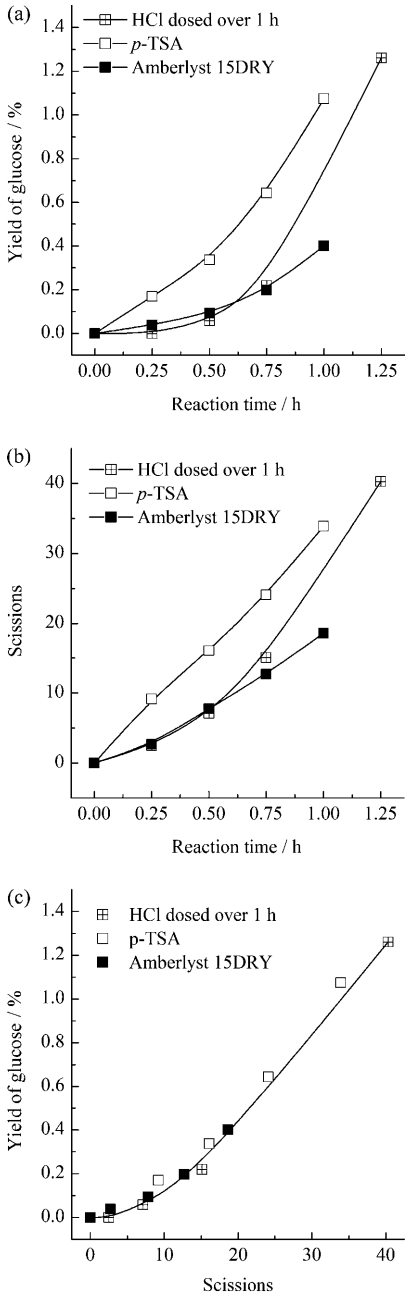

Figure 13. Profiles for the reactions performed using Amberlyst 15DRY, dosing HCl over 1 h and with *p*-TSA. a) Yield of glucose. b) Equivalent number of scissions. c) Correlation between yield of glucose and equivalent number of scissions. Reaction conditions: cellulose (5 g, corresponding to ca. 31 mmol of AGU; $C_6H_{10}O_5$: DP_o 650 AGU) dissolved in 100 g BMIMCl, Amberlyst 15DRY or *p*-TSA (2.3 mmol of H_3O^+), water (111 mmol), 100 °C. In the reaction performed with HCl, a 4.6 mol L^{-1} HCl solution was dosed by a syringe pump over 1 h (0.50 mL, 2.3 mmol of H_3O^+). The initial amount of water added in this reaction was 83 mmol.

Revisiting the mechanism of hydrolysis of cellulose

In the last sections, we have shown that the overall rate of depolymerization of cellulose depends both on the amount of H_3O^+ present in the reaction medium and on the temperature. The most striking result to emerge from that is the low turnover frequency (TOF) of acid-catalyzed depolymerization in

BMIMCl. We found a TOF value of 17 scissions h^{-1} (mmol H_3O^+)$^{-1}$ at 100 °C using Amberlyst 15DRY as H^+ source. Unfortunately, for several reasons it is not possible to directly compare this value with other systems already studied. Firstly, in the heterogeneous reactions, the hydrolytic process occurs on the surface of cellulose. Therefore, the reaction rate is governed by a series of other phenomena (such as adsorption, swelling of the polymeric structure, diffusion of the reactants, and so on) rather than by the chemical reactivity of cellulose.[3c,5] Secondly, in the homogeneous systems, such as in those cases in which cellulose is solubilized in mineral acids,[6d,21] the amount of H_3O^+ is much too high to establish a proper comparison with the homogeneous systems based on cellulose solubilized in imidazolium-ionic liquids, in which catalytic amounts of H_3O^+ are used. For example, cellulose and hemicellulose easily hydrolyze to a mixture of water-soluble oligosaccharides and monosaccharides at room temperature, if fuming HCl is used as a reactive solvent.[5,6d] In contrast, cellulose dissolved in BMIMCl depolymerizes sluggishly when using catalytic amounts of H_3O^+ already at 80 °C (Figure 7).

Another interesting feature of the depolymerization of cellulose is the effect of the acid strength on the reaction rate. The extent of depolymerization of cellulose over time, using molecular acids, with pK_a values ranging from −3 to 14, is directly associated with the acid strength, as shown in Figure 14. Al-

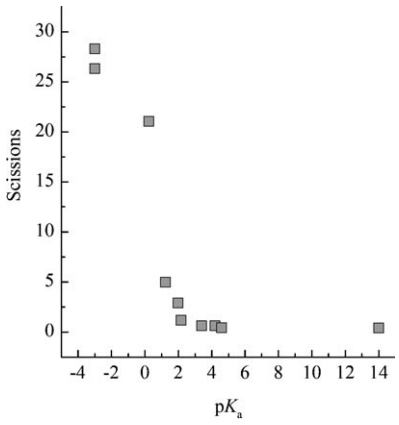

Figure 14. Influence of the acid strength on the number of equivalent scission occurring in cellulose. Acids tested (pK_a values in parentheses): sulfuric acid (−3.0), *p*-TSA (−3.0), CF_3COOH (0.23), oxalic acid (1.23), $BMIMHSO_4$ (1.99), H_3PO_4 (2.16), malic acid (3.40), benzoic acid (4.19), levulinic acid (4.59), and water (14). Reaction conditions: cellulose (0.25 g, corresponding to ca. 1.6 mmol of AGU; $C_6H_{10}O_5$: DP_o 100 AGU) dissolved in 5 g BMIMCl, molecular acid (0.23 mmol), water (5.5 mmol), 100 °C for 2 h. The pK_a values were taken from the CRC Handbook of Chemistry and Physics (79th Ed.).

though acidity in ionic liquids is a concept still in its infancy, it is already known that the ranking of acid strength of several organic and inorganic acids—in ionic liquids—resembles generally that observed in water.[22] Our results show that cellulose is cleaved extensively in the presence of molecular acids with pK_a < 1. However, weaker acids display much lower catalytic activity. A comparable trend for the hydrolysis of cellobiose in EMIMCl was recently reported.[13d]

Both the low scission frequency observed in the reaction performed using Amberlyst 15DRY and the reaction rate dependence on the acid strength are thought-provoking facts. Analyzing the mechanism of hydrolysis of cellulose, which was derived mostly from the experience gained with the hydrolysis of soluble glycosides,[23] the activation of cellulose is proposed to proceed through protonation of the glycosidic oxygen (Figure 15).[23b,c,e] Sequentially, a cyclic carbocation is formed by the slow unimolecular scission of the glycosidic linkage.[23c] The nucleophilic attack of water on the cyclic carbocation re-establishes the hydroxyl group at the C(1) position of the anhydroglucose unit.[23]

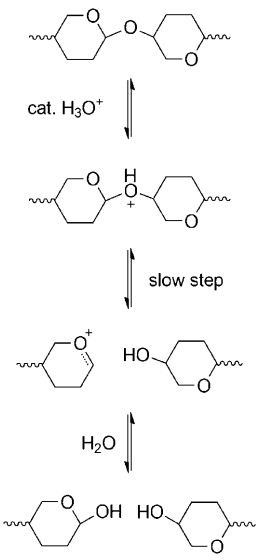

Figure 15. Proposed mechanism for hydrolysis of cellulose.[23e] Hydrogen, hydroxyl, and hydroxymethyl groups are omitted for clarity.

Although the formation of the cyclic carbocation is regarded to be the decisive step of the mechanism (Figure 15),[23] the protonation of the glycosidic oxygen was already reported to be cumbersome in some electron-deficient acetals.[24] In the case of cellulose, the *O*-sites can be roughly classified, according to their basicity, into two groups: the acetal *O*-sites and the hydroxyl *O*-sites. The acetal *O*-sites are considerably less basic than the hydroxyl ones. For the sake of comparison, monoprotonated formaldehyde acetals, R–O–CH_2–O–R, where R is methyl-, ethyl-, and isopropyl, show pK_a values −4.57, −4.13, −3.70, respectively.[25] It is then expected that the pK_a value of the protonated glycosidic *O*-site should lie within this range. On the other hand, the protonated hydroxyl *O*-sites of cellulose should have a pK_a value lying between those values found for protonated methanol (pK_a −2.4) and for protonated isopropanol (pK_a −3.2). Therefore, the hydroxyl *O*-sites are expected to be 10 to 100 times more basic than the glycosidic *O*-site. In other words, the protonation of the glycosidic oxygen—as proposed in the mechanism shown in Figure 15—is favored at high H^+ concentration, because the protonation is more preferable at the hydroxyl groups than at the glycosidic *O*-site. In addition, strong acids are required to activate cellulose towards hydrolysis due to the weak basicity of the glycosidic *O*-site. However, in presence of water, the acidity of strong acids is leveled out to the acidity of H_3O^+ species (pK_a −1.7). Regarding the acidity of H_3O^+ species (pK_a −1.7), the prevalence of the protonated glycosidic *O*-sites (pK_a ~ −4) is around 1:200, while this prevalence is ca. 1:20 for the protonated hydroxyl *O*-sites (pK_a ~ −3). Indeed, the low prevalence of the protonated glycosidic *O*-sites explains the observed low scission frequency of the cellulosic chains.

A serious consequence of the requirement of a strong acid for the catalytic hydrolysis of cellulose is the restriction on the number of ionic liquid suitable as solvent for this reaction. Al-

kylimidazolium ionic liquids containing weakly basic anions - such as acetate or organophosphates - are great solvents for cellulose.[26] However, we observed that these solvents are not appropriate for acid-catalyzed hydrolytic processes. Actually, acetate or phosphonic anions are protonated easily by strong acids, resulting in acetic acid (pK_a 4.78) or phosphonic acids (methylphosphonic acid, pK_{a1} 2.38).[27] Consequently, cellulose cannot be sufficiently protonated to result in its hydrolysis at reasonable rates in these ionic liquids.

Impurities of the ionic liquid

Residues of *N*-methylimidazole are commonly found as the main impurity of 1-alkyl-3-methylimidazolium ionic liquids.[28] To study systematically the effect of this basic impurity on the depolymerization of cellulose, *N*-methylimidazole (3.3 mmol) was added in a reaction performed using Amberlyst 15DRY (6.7 mmol of H_3O^+). In a reference reaction carried out with Amberlyst 15DRY (6.9 mmol of H_3O^+), no *N*-methylimidazole was added. Comparing the results of both reactions (Figure 16), a decrease in the depolymerization rate from 162

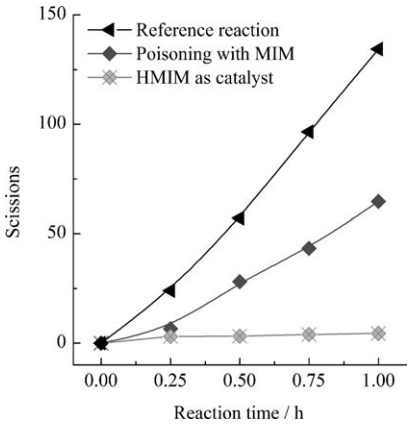

Figure 16. Effect of methylimidazole (added as impurity) and methylimidazolium chloride (used as catalyst) in the depolymerization of cellulose. Reaction conditions: (reference) cellulose (5 g, corresponding to ca. 31 mmol of AGU, $C_6H_{10}O_5$) dissolved in 100 g BMIMCl, Amberlyst 15DRY (6.9 mmol of H_3O^+), water (111 mmol), 100 °C; (poisoning with methylimidazole) cellulose (5 g, corresponding to ca. 31 mmol of AGU, $C_6H_{10}O_5$) dissolved in 100 g BMIMCl, Amberlyst 15DRY (6.7 mmol of H_3O^+), methylimidazole (3.3 mmol), water (111 mmol), 100 °C; (HMIM as catalyst) cellulose (5 g, corresponding to ca. 31 mmol of AGU, $C_6H_{10}O_5$) dissolved in 100 g BMIMCl, HMIMCl (4.6 mmol of H_3O^+), water (111 mmol), 100 °C.

to 75 scissions h^{-1} (calculated from the slope at steady state) was observed in the reaction poisoned with *N*-methylimidazole (Figure 16). This result is consistent with the fact that only 3.4 mmol of H_3O^+ effectively participates in the activation of cellulose in the reaction poisoned with *N*-methylimidazole. Therefore, in the acid-catalyzed depolymerization of cellulose, the presence of residual *N*-methylimidazole is an issue because H^+ species are readily neutralized by this organic base. The resulting *N*-methylimidazolium (HMIMCl, pK_a 7.2)[29] cannot activate cellulose towards hydrolysis as can also be seen in Figure 16.

Recycling of ionic liquid

The main concern for ionic-liquid based processes is the reutilization of the solvent because of its high cost. In the depolymerization of cellulose, the cellooligomers can be removed from the reaction medium by addition of water. Nevertheless, small sugars, dehydration products, and H_3O^+/H_2O remain solubilized. Therefore, these compounds should be removed prior to reutilization of the ionic liquid. The acid content was successfully neutralized by passing the aqueous solution of BMIMCl through a neutral alumina column. The neutralization is believed to occur by the exchange of the labile surface hydroxyl groups by Cl^-, forming Al–Cl surface groups. The liberation of OH^- neutralizes the acidic content of the ionic liquid. Starting from an initial acid content of ca. 45 μmol H_3O^+ g^{-1}, the acid content of the recycled ionic liquid was 3.5 mmol H_3O^+ g^{-1}. The content of water in BMIMCl was reduced via vacuum distillation. It is important to point out that the recycled ionic liquid does not need to be anhydrous to be reused in the process. In fact, some water is actually required as a reactant for the hydrolysis of the glycosidic bond. Cellulose can be solubilized in BMIMCl even in the presence of 2 wt% water. The recycling of the ionic liquid was possible without damage to the catalytic performance. Figure 17 shows the performance of the recycled

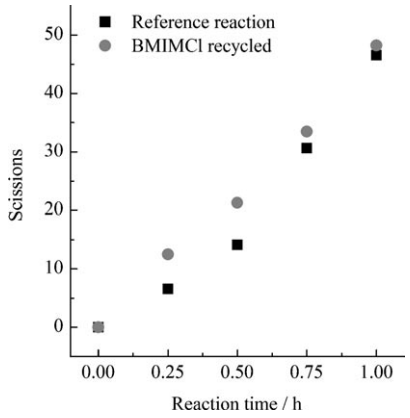

Figure 17. Recycling of BMIMCl. Reaction conditions: cellulose (5 g, corresponding to ca. 31 mmol of AGU, $C_6H_{10}O_5$) dissolved in 100 g BMIMCl, Amberlyst 15DRY (4.6 mmol H_3O^+), water (111 mmol), 100 °C.

ionic liquid compared with the fresh ionic liquid. Due to the small scale of the process, however, a recovery ratio could not be precisely determined. In our experiments, the recovery ratio could be estimated to approximately 91%, but this value could be vastly improved for a larger scale implementation.

The treatment steps described above, however, are not efficient for removing the sugars and other small molecules. The separation of sugars from the ionic liquid is still the most challenging issue in the recycling of BMIMCl. Removal of glucose, cellobiose, and other small sugars from the ionic liquid solution was attempted by adsorption on alumina or charcoal, but these were not very effective. Therefore, small sugars and dehydration products would be accumulated over successive cycles of re-utilization of the ionic liquids. This can only be

avoided by stopping the reaction at the cellooligomer stage. However, whether the build-up of impurities would then be a problem after hundreds of regeneration steps remains to be seen.

Conclusions

The factors responsible for the control of depolymerization of cellulose in ionic liquid using Amberlyst 15DRY as H_3O^+ source were determined in detail. Based on these findings the following conclusions can be drawn for the Amberlyst 15DRY-catalyzed depolymerization of cellulose:

(1) Although the amount of catalyst positively affects the depolymerization rate, this reaction parameter, surprisingly, has only a small effect on the distribution of products at a given reaction extent.

(2) Depolymerization of cellulose is a first-order reaction with respect of the catalyst concentration.

(3) The reaction temperature seriously affects the rates of the reactions. The activation energy for the depolymerization of cellulose is 108 kJ mol^{-1}. The selectivity at identical conversion of glycosidic bonds is not strongly affected by changes in reaction temperature, because of the similar activation energies for hydrolysis of the glycosidic bonds and for further dehydration of glucose formed.

(4) The depolymerization of cellulose catalyzed by Amberlyst 15DRY happens in solution. The acidic resin releases H^+ into the solution, controlling the initial rate of depolymerization. The preferential cleavage of large polymeric molecules occurs because of statistical reasons. A soluble catalyst is not able to change this preference. In other words, the initial size of the cellulose chains is crucial in the control of initial product distribution. Large chains are preferably cleaved into smaller ones instead of producing glucose, which explains the induction period observed for the release of glucose or total reducing sugars.

(5) A high degree of control of the depolymerization reaction can be achieved also in the case of molecular acids, if they are added slowly over time to the reaction batch, thus mimicking the slow ion exchange process occurring over the solid acids.

(6) Activation of cellulose towards hydrolysis requires a strong acid. This prohibits the utilization of acetate- or phosphonate-based ionic liquids - or any other kind of ionic liquid composed of a weakly basic anion. These anions capture essentially the available H_3O^+ species, which prevents the activation of the glycosidic bonds. Additionally, the presence of *N*-methylimidazole, often found at different concentration levels as impurity in BMIMCl, decreases proportionally the catalytic performance of this system.

(7) Both the ionic liquid and Amberlyst 15DRY can be recycled, the ionic liquid by neutralization with alumina and vacuum distillation; the acidic resin by washing with sulfuric acid.

In principle, the homogeneous nature of the reaction with Amberlyst 15DRY, as solid acid, can be extended to any other solid Brønsted acid catalyst. For any such catalyst, the ion-exchange process, resulting in H^+-release, will proceed to some extent, although differences may be observed, depending on the pore size of the catalyst and its acid strength and acid site concentration.

Experimental Section

Materials

α-Cellulose (fibers, Aldrich) and 1-butyl-3-methylimidazolium chloride (≥99.9%, Iolitec) were used without prior treatment. Amberlyst 15DRY (Aldrich) and *p*-toluenesulfonic acid monohydrate (≥98.5%, Fluka) were used as received.

Depolymerization of cellulose

Typically, the solution of cellulose in 1-butyl-3-methylimidazolium chloride (BMIMCl) was prepared by dissolving 5 g of α-cellulose [31 mmol, calculated as anhydroglucose unit (AGU) $C_6H_{10}O_5$] in 100 g of BMIMCl at 100 °C. The mixture was stirred by a mechanical overhead stirrer. To the cellulose/BMIMCl solution, 2.00 mL of distilled water (111 mmol) were added under mechanical stirring. The mixture was stirred for 15 min. Subsequently, the desired amount of Amberlyst 15DRY (4.6 mmol H_3O^+ g^{-1}) was added to the mixture containing cellulose. The depolymerization of cellulose was carried out at 100 °C for 3 h. The aliquots were taken at the reaction times indicated. Cellulose from the aliquots was precipitated by addition of water. The cellulose was separated from the aqueous solution by centrifugation. The aqueous solutions were collected and stored for later HPLC analysis.

HPLC analysis of sugars and dehydration products

The chromatographic separations were carried out using a Nucleogel OA HY (300×7.8 mm, 10 μm) column and an aqueous solution of sulfuric acid (5 mmol L^{-1}) as mobile phase. The samples were analyzed in isocratic mode at a flow rate of 0.5 mL min^{-1} at 80 °C, using a Perkin–Elmer HPLC 200. Glucose and cellobiose were analyzed using a refractive index detector. 5-Hydroxymethylfurfural (5-HMF) was analyzed using a diode-array UV/Vis detector at 254 nm. The mentioned components were identified by comparison of retention times with those of the corresponding reference compounds. The amounts of products were quantified using external calibration curves.

Determination of the apparent degree of polymerization

An aliquot of the reaction mixture (0.5 g) was suspended in DMSO (5 mL, Fluka). BMIMCl does not interfere in the carbanilation of cellulose.[30] Into the suspension of cellulose in DMSO was added 1.0 mL of phenylisocyanate (>99%, Aldrich). The reaction was carried out for 4–5 h at 80 °C, resulting in cellulose tricarbanilates (CTC), which are soluble in DMSO. The cellulose derivative was then worked up as described in Ref. [31]. The isolated CTC was dissolved in THF (2 mg mL^{-1}) and analyzed by gel permeation chromatography. The analyses were performed at 50 °C using a Perkin–Elmer HPLC 200 using mix-bed GPC columns (2 columns, TSKgel SuperHZM-M, 4.6 mm ID×15.0 cm) and stabilized THF as eluent (0.2 mL min^{-1}, LiChrosolv, Merck). For detection, a UV/Vis detector at 236 nm was used. The system was calibrated with polystyrene standards (5×10^2 to 7×10^6 Da, Aldrich). The apparent number-average and weight-average degree of polymerization, DP_n and

DP_w respectively, were calculated by dividing the respective average molecular weight values by molar mass of the anhydroglucose tricarbanilate (519 g mol^{-1}). The equivalent number of scissions was calculated by using Equation (1):

$$s = \frac{DP_0}{DP} - 1 \quad (1)$$

where DP_o and DP are the weight-averaged degree of polymerization at $t = 0$ and at a given time, respectively.

Titrations

The acid concentrations given in the text were determined via titration with a 0.01 mol L^{-1} NaOH solution using a Metrohm Titrino Plus 848 automated titrator.

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Keywords: catalysis · cellulose · hydrolysis · ionic liquids · polymerization

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