Cellulose Conversion

DOI: 10.1002/anie.200802879

# Depolymerization of Cellulose Using Solid Catalysts in Ionic Liquids**

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Many recent studies have addressed the conversion of sugars into fuels[1,2] or chemicals[3,4] in order to tap renewable feedstocks instead of fossil fuels. The crucial step in the production of biofuels or chemicals from biomass is the hydrolysis of cellulose to fermentable sugars.[5–7] However, the major fraction of the sugar molecules in biomass is contained in cellulose or lignocellulose, in which the sugar molecules are efficiently protected against chemical processing. Because of the protection of the β-glycosidic linkages by the tight packing of cellulose chains in microfibrils,[8] hydrolysis of cellulose requires severe conditions, such as the use of dilute sulfuric acid at high temperatures. However, cellulose[9] and wood[10] dissolve in alkylmethylimidazolium ionic liquids, which leaves the cellulose chains accessible to chemical transformations.[11] Consequently, depolymerization/hydrolysis of cellulose over solid catalysts, which sounds inapplicable to conventional cellulose slurries in water, should become feasible. Herein we show that solid acids are powerful catalysts for the hydrolysis of cellulose dissolved in an ionic liquid.[12] Cellulose undergoes selective depolymerization to yield cellulose oligomers (cellooligomers) without any substantial formation of side products. Even wood, a lignocellulosic material, can be hydrolyzed by using our methodology. The cellooligomers are readily precipitated by addition of water. The ease of cellulose processing using solid catalysts could lead to novel process options and allow the large-scale use of cellulose depolymerization as the first step in biorefineries.

Macroreticulated styrene–divinylbenzene resins functionalized with sulfonic groups (-$SO_3H$) are powerful catalysts for the selective depolymerization of cellulose dissolved in ionic liquids. These sulfonated resins are commercially available (under the brand name Amberlyst), inexpensive, and stable catalysts, which are employed in many large industrial plants for several alkylation processes.[13] Initially, we monitored the hydrolysis of cellulose by following the release of reducing sugars from purified cellulosic substrates (microcrystalline cellulose and α-cellulose), and from wood (spruce), by using the 3,5-dinitrosalicylic acid (DNS) assay for quantification (Figure 1).

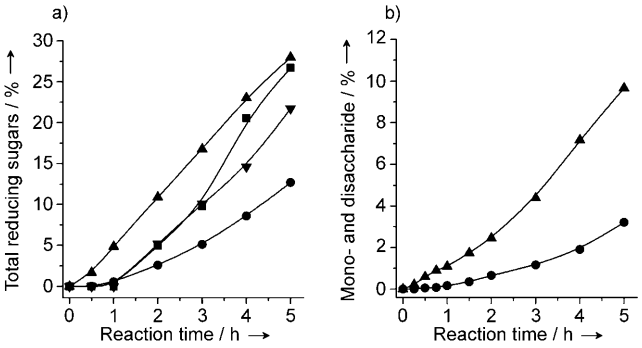


***Figure 1.*** a) Total release of reducing sugars from ▲ α-cellulose (using *p*-TSA), ■ microcrystalline cellulose, ▼ wood (spruce), ● α-cellulose (using Amberlyst 15DRY), determined by DNS assay. b) Production of mono- and disaccharides, monitored by HPLC, for the hydrolysis of α-cellulose catalyzed by ▲ *p*-TSA and by ● Amberlyst 15DRY. Reaction conditions: cellulose (5 g, corresponding to approximately 31 mmol of anhydroglucose, $C_6H_{10}O_5$) dissolved in 100 g BMIMCl, Amberlyst 15DRY (1.00 g, 4.6 mmol $H^+$) or *p*-TSA (4.6 mmol), water (111 mmol), 373 K.

Purified cellulosic substrates dissolved in 1-butyl-3-methylimidazolium chloride (BMIMCl) release reducing sugars in the presence of Amberlyst 15DRY. Even microcrystalline cellulose, which cannot be processed by conventional methods, is easily hydrolyzed using Amberlyst 15DRY in the process described here. Remarkably, cellulose in untreated wood chips is also hydrolyzed, giving a similar reaction profile for the release of reducing sugars (Figure 1).

All reactions using Amberlyst 15DRY for the production of reducing sugars show an induction period of approximately 1 h. However, with the molecular catalyst *p*-toluenesulfonic acid (*p*-TSA), which resembles the acid sites of Amberlyst 15DRY but is soluble in BMIMCl, no induction period is observed. In a more detailed analysis of the reaction, the release of mono- and disaccharides from the hydrolysis of α-cellulose catalyzed by Amberlyst 15DRY or by *p*-TSA was monitored by HPLC (Figure 1). The reaction catalyzed by Amberlyst 15DRY again showed negligible production of mono- and disaccharides during the initial 1.5 h of the reaction, whereas the production of small sugars had no induction period for the reaction catalyzed by *p*-TSA. Mono- and disaccharides constitute approximately 25 and 35% of the total reducing sugars formed after 5 h in the reactions catalyzed by Amberlyst 15DRY and *p*-TSA, respectively. The majority of reducing sugars consisted of water-soluble oligosaccharides, which also respond positively in the DNS assay.

Cellulose is readily precipitated and recovered by addition of water to the cellulose/BMIMCl solution. At the start of the reaction, the cellulose isolated from the ionic liquid appears as bulky fibers (Figure 2). These fibers become successively smaller with increasing reaction time, resulting in

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[**] We acknowledge financial support from the Max-Planck-Society and from the Cluster of Excellence RWTH-Aachen "Tailor-Made Fuels from Biomass".

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200802879.

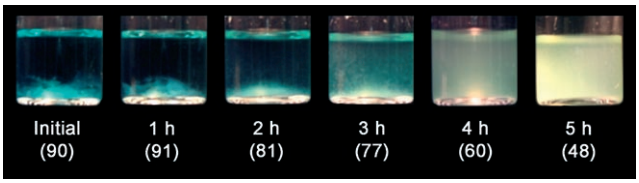


***Figure 2.*** Hydrolysis of microcrystalline cellulose. Appearance of cellulose recovered from BMIMCl by addition of water after the reaction times indicated. The values between parentheses represent the percentage of isolated cellulose.

a colloidal dispersion for the material recovered after 5 h of reaction. The visual appearance of the isolated cellulose suspensions indicated that substantial changes occurred in the cellulose. To explore these changes, the isolated celluloses were derivatized with phenylisocyanate. This reaction gives THF-soluble cellulose derivatives, which allow the determination of the apparent distribution of the degree of polymerization (DP) by gel-permeation chromatography (Figure 3).[14]

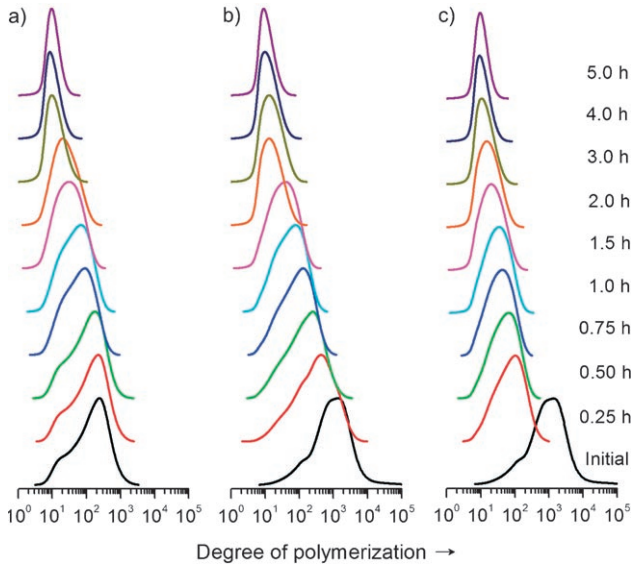


***Figure 3.*** Distribution of apparent degree of polymerization of the celluloses isolated from BMIMCl solution during the reaction: a) microcrystalline cellulose (Amberlyst 15DRY); b) α-cellulose (Amberlyst 15 DRY); and c) α-cellulose (*p*-TSA).

In contrast to synthetic polymers, naturally occurring cellulose exists in a high polydispersity. Both microcrystalline cellulose and α-cellulose show broad DP distributions (Figure 3). Microcrystalline cellulose cannot be hydrolyzed by conventional dilute-acid processes. Indeed, this cellulose is commercially isolated as an insoluble residue from the hydrolysis of the amorphous regions of α-cellulose.[8] As a result, the DP of microcrystalline cellulose lies in a lower range than that found for α-cellulose (Figure 3).

The changes in the degree of polymerization show that either α-cellulose or even microcrystalline cellulose are effectively depolymerized in the presence of Amberlyst 15DRY in ionic liquids. In the absence of acid catalysts, only minor changes in the distribution of the apparent degree of polymerization are observed (see the Supporting Information). Remarkably, the reaction using solid catalysts proceeds with a high preference to cleave the longer cellulose chains. The depolymerization of cellulose proceeds progressively, resulting in the formation of soluble oligosaccharides if the reaction is carried out over a long enough time. Interestingly, after a reaction time of 5 h, the isolated cellooligomers consisted of approximately ten anhydroglucose units (AGU). As shown in Figure 2, the amount of isolated cellulose decreased during the reaction from 90% at the initial time to 48% after 5 h. These results are not expected on the basis of the experience gained for conventional diluted acid hydrolysis of cellulose in aqueous slurries. Under such conditions, the DP quickly drops from 1500 to 300 AGU after 0.5 h, but then indefinitely remains constant at 300 AGU,[15] as a result of the inability of conventional acid hydrolysis to break down the microcrystalline cellulose domains.

The differences between Amberlyst 15DRY and *p*-TSA are also reflected in the DP of the isolated celluloses (Figure 3). In the reaction catalyzed using Amberlyst 15DRY, cellulose initially depolymerizes in a very controlled fashion with a size-specific preference for the cleavage of large chains. This preference is so high that only negligible amounts of reducing sugar are released at the beginning of the reaction, which results in the induction time observed in Figure 1. In contrast, the reaction catalyzed by *p*-TSA proceeds much faster and with no size selectivity.

The complex pathway of the hydrolysis of cellulose is generically described as:[7] cellulose→cellooligomers→sugars→dehydration products (see the Supporting Information). The preferential breakdown of larger cellulose chains by Amberlyst 15DRY in BMIMCl is highly attractive, and the best use of this process is probably the production of cellooligomers and not of fermentable sugars such as glucose. Firstly, the conversion of cellulose into cellooligomers proceeds very selectively using Amberlyst 15DRY (Figure 1). Since a negligible amount of sugar is formed during the induction period, only traces of dehydration products, such as furfural and 5-hydroxymethylfurfural, which would act as poisons in later enzymatic stages, are obtained (0.053 and 0.17%, respectively, after 5 h; for more detailed information on the products see the Supporting Information). Furthermore, cellooligomers with a degree of polymerization around 30, as found for the material isolated after 1.5 h of hydrolysis of microcrystalline cellulose, are readily precipitated in high yields (90%) by the addition of water (Figure 2), which is a crucial advantage of this process. In contrast, the high solubility of sugars in ionic liquids[16] makes the workup for sugar extraction and ionic-liquid recovery extremely difficult, which is a severe disadvantage for the practical use of the system using the homogeneous conditions reported by Zhao and co-workers.[17,18] Therefore, the most interesting transformation of cellulose in ionic liquids using heterogeneous catalysis is its depolymerization to cellooligomers instead of its total hydrolysis to fermentable sugars.

  

The screening of other organic and inorganic solid acids for depolymerization of α-cellulose in BMIMCl (Figure 4) was conducted only up to 1 h, to maintain the high selectivity for isolable cellooligomers. The nature and concentration of

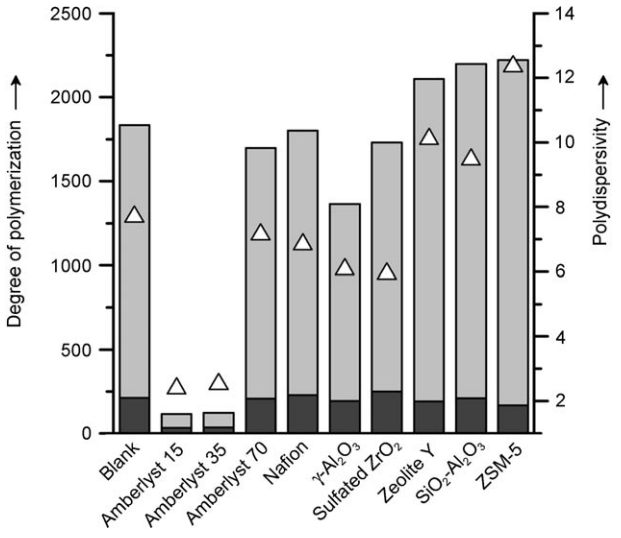


***Figure 4.*** Performance of other catalysts in the depolymerization of α-cellulose. The light-gray and dark-gray bars represent $DP_n$ and $DP_w$, respectively. Triangles indicate polydispersivity.

the accessible acid sites on these solids are rather different, so it does not appear to be useful to compare turnover frequencies. Figure 4 gives the number and weight-averaged degree of polymerization ($DP_n$ and $DP_w$) as well as the polydispersity calculated from these values, and includes a comparison with the values obtained for a reference experiment without the addition of any solid acid.

Among the acid resins, only Amberlyst 35 (dried) showed a similar potential to depolymerize α-cellulose as that of Amberlyst 15DRY. Amberlyst 15DRY and Amberlyst 35 resins are macroreticulated materials with average pore sizes of 36 and 28 nm, respectively. However, the low activity of Amberlyst 70 (dried) is strongly related to its small surface area ($< 1\ m^2 g^{-1}$) compared to Amberlyst 15DRY ($36\ m^2 g^{-1}$) and Amberlyst 35 ($40\ m^2 g^{-1}$).[19] Likewise, Nafion has a limited performance because of the low surface area of the polymer beads ($0.02\ m^2 g^{-1}$).[20]

Inorganic oxides were also investigated. γ-$Al_2O_3$ shows some depolymerization activity, but at a substantially lower level than the Amberlyst catalysts; whereas sulfated $ZrO_2$ depolymerizes cellulose to a much lower extent than γ-$Al_2O_3$. The lower performance of these materials is related to their smaller pore sizes (12.5 and 8.2 nm, respectively, for γ-$Al_2O_3$ and sulfated $ZrO_2$). Although the performance of these materials is not as good as that of Amberlyst 15DRY, these results clearly prove that inorganic materials can catalyze reactions in ionic liquid media. Indeed, these results contradict the initial notion that inorganic materials would be poisoned by the strong interaction between ionic liquids and material surfaces.[11,21] Silica–alumina, zeolite Y, and ZSM-5 do not show activity for depolymerization of cellulose. In fact, these materials do not have a large external surface area that would be accessible to cellulose chains; in fact, the pores of these solids are too narrow (0.7 and 1.2 nm, respectively, for the zeolites Y and ZSM-5, and 4.5 nm for silica–alumina) to be reached by the polymer. The apparent increase in the degree of polymerization for these samples, as analyzed by GPC, arises from the formation of molecular aggregates linked by interfacial interaction between the cellulose and the aluminosilicate surfaces. These are not broken in the isolation process of the cellulose and thus a higher apparent DP is determined.

The screening results strongly suggest that the ideal solid catalyst for depolymerization of cellulose in ionic liquids should be a macroporous acidic material with a large external surface area, because solutions of cellulose in ionic liquids are very viscous, which makes the transport of cellulose chains to the catalytic sites a highly demanding process. Macroreticulated resins functionalized with sulfonic groups (-$SO_3H$) fulfill practically all of these requirements. However, the stability of solid catalysts in ionic liquids is an important issue, which, amongst other considerations, such as melting point and viscosity, also governs the choice of the ionic liquid. For example, Amberlyst 15DRY was highly stabile in BMIMCl, but the simple change to BMIM($CH_3COO$), which could be a more suitable solvent because of its lower viscosity, led to rapid destruction of the catalyst.

The range of catalyst performances in the depolymerization of cellulose (Figure 4) is clear evidence that the hydrolysis of β(1→4) glycosidic linkages is catalyzed by the solid acid surfaces. In the systems studied, the solid acid materials are not acting as an $H^+$ reservoir which releases protons into the reaction medium. The results obtained here form a strong contrast with those obtained almost half a century ago, in which acid resins were used for the hydrolysis of cellulose in aqueous slurries.[22] In this earlier report, the acid resins were merely an acidifier of the aqueous slurries, having a similar effect as an aqueous solution of $H_2SO_4$.[22]

In summary, solid acids, especially acidic resins with relatively large pores, are highly suitable catalysts for the depolymerization of cellulose, even microcrystalline cellulose or wood, in ionic liquids. The reaction proceeds in the most selective process reported to date, that is, in the first stage cellooligomers are formed, which are subsequently further broken down into sugars. If the process is terminated at the right time, cellulose fragments ideally suited for further processing by, for example, enzymatic hydrolysis, can easily be isolated. Cellooligomers instead of sugars could be an ideal entry point into advanced value chains for biorefineries, starting from cellulose as a sustainable feedstock available in most parts of the world in very large amounts.

## Experimental Section

A solution of cellulose in BMIMCl was depolymerized at 373 K using Amberlyst 15DRY and other catalysts. The amount of reducing sugars was determined by DNS assay. Mono- and disaccharide yields were determined by HPLC. The depolymerization of cellulose was followed by gel-permeation chromatography of the tricarbanilate derivative of the cellulose samples. Further experimental details and

  

the textural properties of the catalytic materials are provided in the Supporting Information.

Received: June 17, 2008
Published online: September 22, 2008

**Keywords:** cellulose · depolymerization · heterogeneous catalysis · hydrolysis · ionic liquids

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