Conversion of cellulose to glucose and levulinic acid via solid-supported acid catalysis

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ABSTRACT

Cellulose is hydrolyzed to glucose, which is further converted to levulinic acid in the presence of surface-supported Brønsted and Lewis acid catalysts. Nafion catalysts, in particular, have the potential to be recycled or applied to a continuous flow reactor for the synthesis of these biofuel precursors.

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Cellulose, the principle structural component of plants, is the most abundant organic compound on earth. It is a biopolymer that consists of glucose units joined by $\beta(1\rightarrow4)$ linkages. This bond, by itself, is not partially strong, as it can be readily hydrolyzed by simple acids such as HCl or by cellulolytic enzymes. However, the cellulose polymer, as a whole, is very robust. The individual glucose monomers are so densely packed together by an extensive network of hydrogen bonds that enzyme catalysts and most aqueous solvents cannot penetrate the structure. Consequently, cellulose is virtually insoluble in water and is generally regarded as a difficult material to work with. The development of methods for hydrolyzing raw biomass from renewable, non-food bearing plants, either to glucose or directly to biofuels, is highly desirable. These difficult transformations are not readily feasible using the current best technology, which employs cellulolytic enzymes, as they require water solvents and mild conditions under which cellulose is not readily soluble. Herein, we report an improved chemical method to convert raw cellulose to biofuel precursors.

The chemical conversion of cellulose to fuel feedstocks has received significant attention recently.[1] A method for converting C6-sugars such as glucose and sorbitol to fuels suitable for use in automobiles and aircraft has recently been reported. However, the process employs a Pt–Re catalyst on a graphite support, and is energy intensive, requiring temperatures >500 K and pressures of 27 bar.[2–4] While sugars are cheap and readily available commodities, their refinement from biomass adds to the overall energy consumption of the process. Reducing conditions have also been applied to the conversion of cellulose to sugar alcohols. Either platinum or ruthenium catalysts at high temperatures and under high-pressure of H_2 can convert cellulose to a mixture of polyols, whose main component (80%) was sorbitol.[5]

The current best method for converting biomass to a fuel was reported in 2008. The process employs refluxing HCl (a Brønsted acid) in the presence of LiCl, resulting in an 80% conversion. The primary product of the reaction is 5-(chloromethyl)furfural, which is not a biofuel, but this intermediate can be readily converted to 5-(ethoxy)furfural, which can be used as a diesel additive.[6]

Ionic liquids have been used to dissolve cellulose[7] and even raw wood chips.[8] These solvents have the added benefit that they are generally considered to be 'green' due to their low vapor pressure. These solvents have been used with Brønsted acid catalysts to convert fructose to hydroxymethylfuran.[9] Recently, Schüth and co-workers degraded cellulose in [BMIM][Cl], an imidazolium-based ionic liquid, with an Amberlyst catalyst. A combined yield of less than 4% was observed for the production of both mono- and disaccharides.[8] Subsequently, Binder and Raines described a reaction medium containing dimethylacetamide, LiCl, $CrCl_2$, and an ionic liquid that is capable of processing both sawdust and corn stover to furfurals in good yields.[10]

Minimal attention has been given to the use of solid-supported acid catalysis for the depolymerization of cellulose in water. Recent reports describe the hydrolysis of cellulose by acid-modified amorphous carbon,[11] layered transition metal oxides,[12] or Amberlyst resin.[8] These surface acidic species were quite efficient for the conversion of cellulose into smaller, water-soluble $\beta(1\rightarrow4)$ glucans, but conversion to glucose or other small biofuel precursors was limited.

In this Letter we report the chemical conversion of cellulose to glucose and levulinic acid by hydrolysis of silica-supported acid catalysts under relatively mild conditions. The reaction is catalyzed by both Nafion and $FeCl_3$ supported on amorphous silica.[13] Nafion SAC 13 (Nafion polymer on amorphous silica), in particular, has the potential to be recycled or applied to a continuous flow reactor, providing that residual, unreacted cellulose can be removed from the system.

Our initial experiments were conducted with cellobiose as a substrate (Scheme 1). Cellobiose is a water-soluble single repeat unit of cellulose and is frequently used as a cellulose model compound. A Teflon-capped glass reaction flask was charged with

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catalyst	conversion (2 : 3)
Nafion SAC 13	100% (1 : 0)
FeCl₃/ silica	100% (1 : 2)
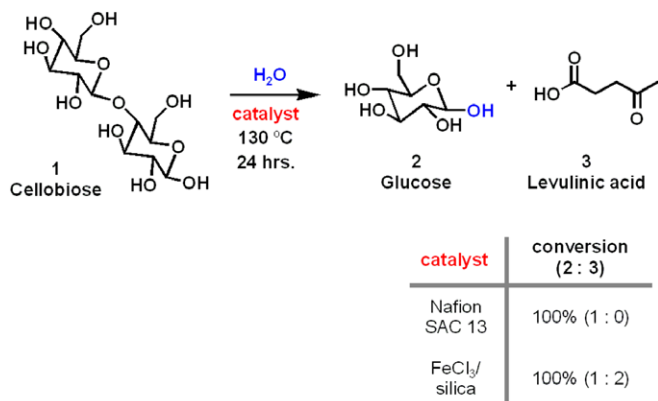
Scheme 1. Hydrolysis of cellobiose using solid-supported Brønsted and Lewis acid catalysts.

Table 1
Conversion of cellulose by solid-supported acid catalysts at different temperatures

Catalyst	Temp.	% Yield cycle 1[a]	% Yield cycle 2[a]	% Yield cycle 3[a]
Nafion SAC 13	130 °C	2 (0)	1 (0)	1 (0)
Nafion SAC 13	160 °C	6 (0)	8 (0)	2 (0)
Nafion SAC 13	190 °C	9 (2)	4 (4)	2 (5)
FeCl₃/Silica	130 °C	3 (0)	1 (0)	1 (0)
FeCl₃/Silica	160 °C	7 (0)	1 (0)	1 (0)
FeCl₃/Silica	190 °C	9 (1)	2 (1)	1 (0)

[a] Isolated yield of glucose (and levulinic acid). The ratio between the two compounds was determined by ^1H NMR.
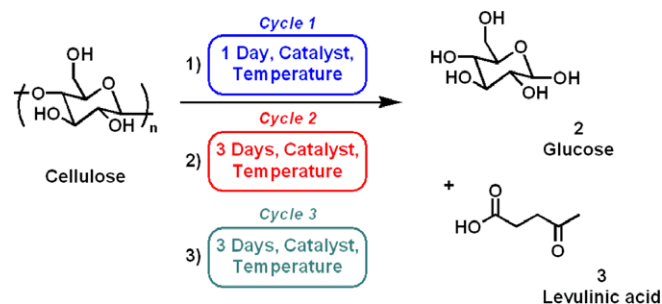
cellobiose (1.0 g, 3 mmol), Nafion SAC 13 (0.47 g), and 15 mL of water. The flask was heated to 130 °C for 24 h followed by filtration to remove the catalyst and concentrated in vacuo to remove the water, providing a quantitative conversion of cellobiose to glucose. The catalyst can then be reused under identical reaction conditions to quantitatively convert cellobiose to glucose confirming the recyclability of the catalyst. Identical experiments were conducted with FeCl₃/silica with similar quantitative conversions and recyclability. However, reaction with the Lewis acid provided a 1:2 mixture of glucose and levulinic acid. Control experiments with silica, FeCl₃, and an aqueous dispersion of Nafion confirmed that the acidic species (FeCl₃ and Nafion) were the reactive species while the silica is a relatively inert surface under the reaction conditions. Furthermore, control experiments in which aqueous glucose solutions were heated in the presence of FeCl₃ produced a quantitative conversion to levulinic acid; indicating that the reaction proceeds by a cellobiose → glucose → levulinic acid sequence.[14] The formic acid by-product of the final step of this process was presumably removed during the rotary evaporation.

We then expanded our investigation to probe the solid-supported acid-catalyzed hydrolysis of cellulose. A stainless steel Parr reactor was charged with Nafion SAC 13 (0.94 g), cellulose (2.0 g, 6 mmol), and water (30 mL). The reactor was heated in an oil bath for one day followed by two sequential three day periods. After each cycle, the reaction mixture was filtered to separate the solids, which contained both the catalyst and unreacted cellulose, which had been partially hydrated during the course of the reaction. The solid was washed with warm water (5 mL) to extract any water-soluble components. The water was removed by rotary evaporation followed by high vacuum, leaving a residue of the hydrolysis products, which were analyzed by ^1H and ^{13}C NMR spectroscopy and compared to commercial standards. The water-insoluble residue, which contained both the catalyst and cellulose, was combined with additional cellulose (1.0 g) and water (30 mL) and returned to the reaction conditions for the next cycle. This process was repeated to determine the recyclability of the catalyst. Similar procedures were utilized for the FeCl₃/silica-catalyzed hydrolysis of cellulose. In all cases, the only water-soluble products observed were glucose and levulinic acid (Table 1).

Hydrolysis of cellulose by Nafion SAC 13 is highly dependent upon the reaction temperature. At lower temperatures (130 °C) there is little conversion of cellulose to glucose (2%) after one day. As the temperature is increased, the conversion rates improve. The increased conversion is likely related to increased solubility of cellulose at higher temperatures. The conversion at 190 °C is very good (11%) after the first cycle (1 day), In addition, the catalyst shows good recyclability. Reuse of the catalyst provides efficient

conversions for both the second (8%) and third (7%) reaction cycles. Though Nafion SAC 13 is generally regarded to be a robust catalyst at moderate temperatures, the side-chain rearrangement of Nafion-type polymers has been observed above its glass transition temperature (100–110 °C).[15] Additionally, the decrease in yield as a result of catalyst cycling may be attributed to the presence of residual insoluble cellulose on the catalyst surface. Even though these yields are low when compared to most organic reactions, the data in Table 1 are notable when compared to the majority of work in the field of cellulose degradation chemistry. In particular, our yields are superior to those that were observed with solid-supported catalysts in ionic liquids, and with more complex catalysts, such as acid-modified graphite.[8,11]

At higher temperatures glucose is not the only product observed in the reaction mixture. Significant concentrations of levulinic acid are also observed. Interestingly, the ratio of glucose to levulinic acid is dependent upon the storage time. As the storage times are gradually increased from one to four days the concentration of levulinic acid gradually increases while the concentration of glucose decreases. This observation is consistent with two mechanistic hypotheses. First, the glucose generation is limited to a fraction of the total available cellulose. This percentage is dependent upon temperature and is likely related to a soluble or accessible component of the cellulose structure. Second, the levulinic acid is only generated via the reaction of glucose and the rate of glucose conversion to levulinic acid is slower than the rate of hydrolysis of cellulose. This was confirmed by a simple control reaction, in which glucose was heated to 190 °C in the presence of Nafion SAC 13 for one day, resulting in a 1:1 mixture of unreacted glucose and levulinic acid. This suggests that the reaction conditions can be optimized for the production of either glucose or levulinic acid.

Hydrolysis of cellulose by FeCl₃/silica provides similar results (Table 1, 1 day). However, the recyclability of the catalyst is less adequate for the FeCl₃/silica catalyst. This is likely due to Fe³⁺ leaching from the silica surface under hydrolytic conditions and limits the utility of these catalysts.

In summary, we have demonstrated that solid-supported acid catalysts (Nafion SAC 13 and FeCl₃/silica) are active for the hydrolysis of cellulose to glucose and levulinic acid at 190 °C. The recyclability of the Nafion SAC 13 is good; suggesting that this is a promising catalyst for the conversion of cellulose into liquid biofuel precursors. Assuming that the solid catalyst can be mechanically separated from

residual cellulose material, solid-supported acidic catalysts, such as those described herein, could be employed *en masse* for the conversion of cellulose to biofuel precursors.

Acknowledgments

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