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# Cellulose Conversion into Polyols Catalyzed by Reversibly Formed Acids and Supported Ruthenium Clusters in Hot Water[**]

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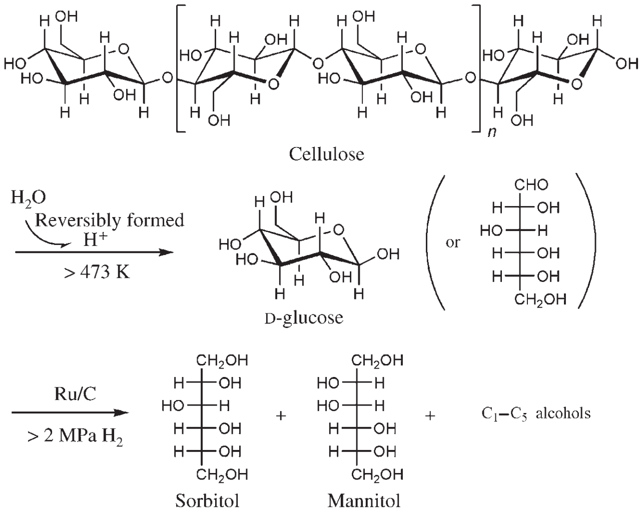
Cellulose is the most abundant source of biomass, and holds impressive potential as an alternative to fossil fuels for sustainable production of fuels and chemicals.[1–5] To this end, cellulose conversion into polyols, among the various primary conversion routes explored to date,[1,3] is evolving as a very viable option in terms of energy efficiency and atom economy. The biomass-derived polyols such as sorbitol and glycerol are being considered as new bioplatform molecules,[6–9] which can be efficiently converted into $H_2$, synthesis gas, alkanes, liquid fuels, and oxygenates, for example, by the aqueous-phase processing developed recently by Dumesic and co-workers.[8,9]

Cellulose, a linear polymer of D-glucose with β-1,4-glycosidic bonds, can be readily hydrolyzed by mineral acids into glucose, which is then hydrogenated to form sorbitol and other polyols.[1,10] However, this process is not green and suffers from the common problems associated with the use of liquid acids, for example, corrosion and acid recovery or disposal. In attempts to solve these problems, Fukuoka and Dhepe[4] recently showed that liquid acids can be replaced by solid acids for cellulose conversion into sorbitol and mannitol, but at relatively low yields, most likely owing to the robust structure of crystalline cellulose and its limited accessibility to surface acid sites. In parallel with this work, we reported a one-step approach to cellulose conversion into polyols by hydrogenation on soluble Ru clusters in ionic liquids,[5] but it encounters difficulties associated with separation of the Ru clusters and polyol products from the ionic liquids. These problems render the two processes unfeasible for industrial practice. For these reasons, it is apparent that hydrolysis of cellulose by liquid acids is currently the best method, provided that the existing acid problems can be circumvented.

It is known that liquid water at elevated temperatures (above 473 K) can generate $H^+$ ions capable of performing acid-catalyzed reactions.[3,11] Such in situ formation of the acid is reversible, and the protons automatically disappear at ambient temperatures, thus leading to complete elimination of the problems of acid recovery and waste disposal.[11] Herein, we report an efficient conversion of cellulose into polyols by combination of hydrolysis using $H^+$ ions, reversibly formed in situ in hot water, with instantaneous hydrogenation on carbon-supported Ru clusters (Ru/C; Scheme 1).



**Scheme 1.** Catalytic cellulose conversion into polyols.

Ru/C catalysts were chosen in this work as a result of their reported superior activity for glucose hydrogenation to sorbitol.[12] As shown in Table 1, cellulose reaction occurred rapidly on Ru/C in hot water; 38.5 % conversion and 22.2 % yield of hexitols (sorbitol and mannitol at a molar ratio of about 3.6:1) were obtained in 5 min at 518 K and 6 MPa $H_2$, which sharply increased to 85.5 % and 39.3 %, respectively, upon prolonging the reaction time to 30 min (Table 1, entry 1). Cellulose was also converted under these conditions into dehydration products of sorbitan and into degradation products of xylitol, erythritol, glycerol, propylene glycol, ethylene glycol, and methanol, as well as trace amounts of undesired $CH_4$; the reaction selectivity slightly increased as the reaction time was increased from 5 to 30 min. These degradation products appear to originate predominantly from the decomposition of glucose, as based on our results from glucose and sorbitol reactions under the same conditions, consistent with the general finding that glucose is much less stable toward further reactions than the corresponding polyols.[10] This result suggests that high selectivity for hexitols

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***Table 1:*** Cellulose conversion and selectivity at 518 K.[a]

| Entry | | Conversion [%] | Hexitol yield [%] | Selectivity [%] | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Sorbitol | Mannitol | Sorbitan | Xylitol | Erythritol | Glycerol | Propylene glycol | Ethylene glycol | $CH_3OH$ | $CH_4$ |
| 1[a] | $H_2O$ + 4 wt% Ru/C | 38.5<br>(85.5)[b] | 22.2<br>(39.3) | 45.2<br>(34.6) | 12.6<br>(11.4) | 11.1<br>(13.4) | 4.2<br>(6.0) | 5.9<br>(7.1) | 5.3<br>(7.5) | 5.9<br>(7.9) | 5.3<br>(6.6) | 3.5<br>(4.0) | 1.1<br>(1.5) |
| 2[a] | $H_2O$ or $H_2O$ + C | 38.6<br>(87.5)[b] | – | – | – | – | – | – | – | – | – | – | – |
| 3 | $C_2H_5OH$ or dioxane + 4 wt% Ru/C | 0 (0) | – | – | – | – | – | – | – | – | – | – | – |
| 4 | 25 mL $C_2H_5OH$ + 25 mL $H_2O$ + 4 wt% Ru/C | 10.2 | 6.4 | 43.9 | 18.9 | 19.1 | 3.1 | 3.2 | 2.1 | 2.3 | 3.2 | 3.2 | 1.0 |
| 5 | $H_2O$ + 8 wt% Ru/C | 37.9 | 21.1 | 43.7 | 12.0 | 11.3 | 4.1 | 5.9 | 6.6 | 6.0 | 5.9 | 3.3 | 1.2 |
| 6 | $H_2O$ + 2 wt% Ru/C | 38.2 | 23.2 | 47.4 | 13.4 | 11.4 | 4.1 | 5.5 | 4.7 | 4.1 | 5.0 | 3.1 | 1.3 |
| 7 | $H_2O$ + 1 wt% Ru/C | 38.1 | 13.7 | 24.2 | 11.8 | – | 2.9 | – | – | – | – | – | – |

[a] 5 min reaction time, 6 MPa $H_2$, 50 mL $H_2O$, 1 g cellulose, 0.04 mmol Ru. [b] Data in parentheses refer to a reaction time of 30 min.

necessitates immediate hydrogenation of glucose once it is formed from cellulose hydrolysis.

Such hydrolysis did not lead to any changes in the cellulose crystal structure as evidenced from the identical XRD patterns in Figure S1 of the Supporting Information, which show that the native cellulose I structure[13] remained intact after the reactions even at 85.5 % cellulose conversion (at 518 K for 30 min). This result indicates that cellulose hydrolysis occurs at its crystal surface, with no swelling or dissolution, which otherwise would lead to formation of the cellulose II crystal form, as generally observed under near-supercritical or supercritical conditions, which require much higher temperatures and pressures (593–673 K and 25 MPa).[3]

Recycling the Ru/C catalyst over five runs did not lead to any significant decline in cellulose conversion and selectivity (see the Supporting Information, Figure S2). Analysis of the aqueous reaction solutions by ICP after each cycle showed no detectable leaching of Ru. Characterization of the catalyst by TEM (Figure 1) showed no essential change in the mean diameters of the Ru clusters and their size distributions after the five reaction cycles. These results demonstrate that the catalyst is stable and reusable under the conditions in this work.

To confirm the in situ formation of acid and its role in the aqueous system, several experiments were performed with no Ru/C catalyst or no water. Similar cellulose conversions (about 38.6 % and 87.5 % after 5 min and 30 min, respectively) were obtained in water in the absence of Ru/C (Table 1, entry 2), but such conditions led to brown solutions (versus colorless solutions in the presence of Ru/C), and coke-like precipitates apparently formed from the acid-catalyzed condensation reactions of the primary product glucose and its derivatives (Table 1). Substitution of either protic solvents (for example, ethanol) or aprotic solvents (for example, dioxane) for water did not give any cellulose conversion on Ru/C under similar conditions (Table 1, entry 3). However, addition of water to ethanol (1:1 volume ratio) led to a 10.2 % cellulose conversion with 62.8 % selectivity for hexitols in 5 min under similar conditions (Table 1, entry 4). This lower conversion compared to that with the pure water system reflects the lower dielectric constant of the mixed solvent system and in turn its lower acidity.[11] Taken together, these

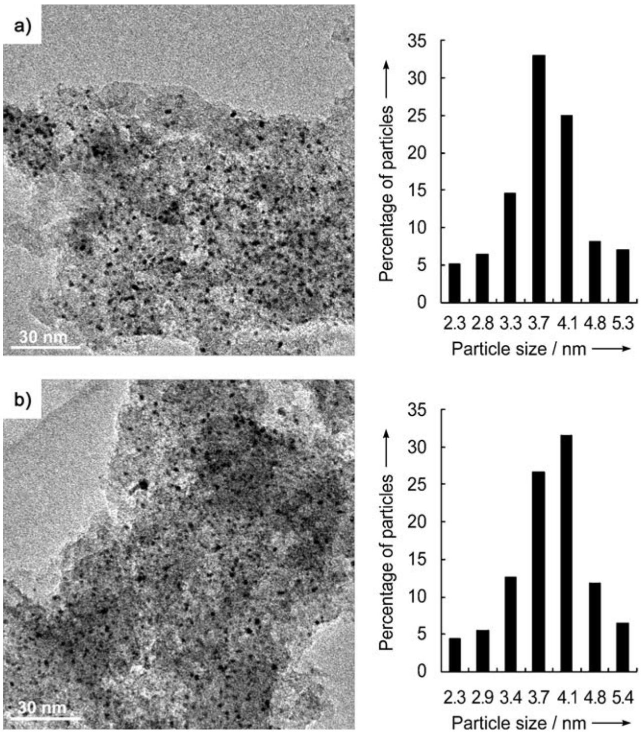

***Figure 1.*** TEM images and histograms of Ru particle size distribution of the Ru/C catalyst (4 wt% Ru) before (a) and after (b) five cycles of cellulose reaction at 518 K.

results demonstrate that water is required for in situ formation of the acid that effects the cellulose hydrolysis step responsible for determining the cellulose conversion, and Ru/C is required for instantaneous hydrogenation of the hydrolyzed product glucose to form polyols (Scheme 1) instead of the above-mentioned condensation products or cokes.

It was indeed found that the product distributions depend on the activities of the hydrogenation catalysts. When the Ru loading was changed from 8% to 2%, the combined hexitol selectivity increased slightly from 55.7% to 60.8% with a concurrent decrease in the combined selectivity for the degradation alcohol products from 31.8% to 26.5% (Table 1, entries 1, 5, and 6). Further decreasing the Ru loading to 1% led to a much lower hexitol selectivity of 36.0% with a large fraction of unsaturated products (Table 1, entry 7) that, although not yet identified, were found to contain C=O and C=C bonds as tested by Fehling's and $KMnO_4$ solutions. These results agree well with the performances in glucose hydrogenation carried out by loading glucose as the reactant under the same conditions. TEM characterization shows that these catalysts have narrow unimodal size distributions of Ru particles with diameters of 1.5, 3.2, 3.7, and 4.2 nm from 1% to 8% loading (see the Supporting Information, Figures S3–S5), thus indicating that Ru particle size for the glucose hydrogenation is important, as generally found with nanoparticle catalysts.[14]

We have also explored the effects of reaction temperature on cellulose conversion and selectivity. As shown in Figure 2, cellulose conversion on 4 wt% Ru/C in water increased sharply from 5.6% to 83.1% upon increasing the temperature from 478 K to 533 K. This result is consistent with the stronger acidity at higher reaction temperatures,[15] which are required for cellulose hydrolysis, as also reflected by the disappearance of the partially hydrolyzed products cellobiose and cellotriose (not included in Figure 2) above 503 K. Hexitol selectivity increased slowly from 55.1% to 61.1% as the temperature increased in the range 478–513 K, and then decreased to 44.5% at 533 K. Selectivity for the degradation alcohol products monotonically increased from 14.6% to 44.2%, while selectivity for sorbitan decreased from 19.8% to 10.2% upon increasing the temperature from 478 K to 533 K. It is noteworthy that selectivity for $CH_4$ was as low as about 1% even at the highest temperature (533 K) after 20 min, and these reaction conditions give rise to a 100% conversion of cellulose.

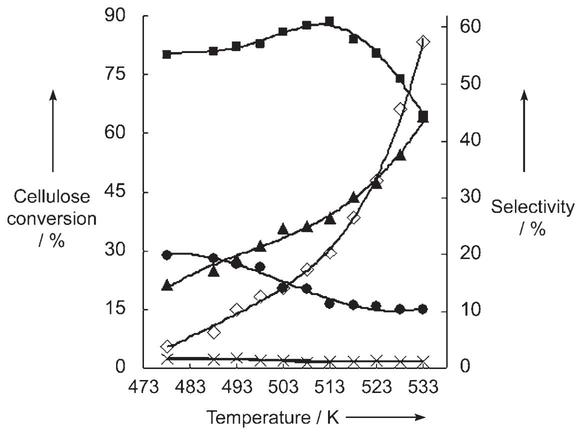

*Figure 2.* Cellulose conversion and selectivity on Ru/C (4 wt% Ru) as a function of reaction temperature in the range 478–533 K after 5 min (6 MPa $H_2$, 50 mL $H_2O$, 1 g cellulose, 0.04 mmol Ru). Left-hand axis: conversion (◇); right-hand axis: selectivity for hexitols (■), for $C_1$–$C_5$ alcohols (▲), for sorbitan (●), and for $CH_4$ (×).

These results show that our approach can lead to almost complete conversion of cellulose into hexitols and other useful alcohol products, including sorbitan and methanol. Such aqueous alcohol solutions can be directly converted into $H_2$ and synthesis gas, among other products, by an aqueous-phase reforming (APR) process,[1,8,9b] in which it is reported that selectivity for $H_2$ production is higher from lighter alcohols like ethylene glycol and methanol than from heavier ones like sorbitol.[8] Therefore, it appears that our approach is suitable for combination with the APR process for production of $H_2$ and synthesis gas directly from cellulose. Nonetheless, such mixed-alcohol solutions are not desirable as feedstocks for the synthesis of pure chemicals. For this purpose, our current studies are focused on increasing the product selectivity (to 100% hexitol) by designing more selective and efficient hydrogenation catalysts and by choosing optimal reactor configurations and reaction conditions.

In conclusion, we have presented a green approach to efficient conversion of cellulose into hexitols together with other lighter polyols through two steps: cellulose hydrolysis to glucose by acids that are reversibly formed in situ from hot water and subsequent glucose hydrogenation by supported Ru clusters. Further advances in understanding these green aqueous catalytic systems will lead to rational control of the polyol distributions, and thus to efficient conversion of cellulose into renewable fuels and chemicals.

## *Experimental Section*

Ru/C catalysts were prepared by impregnating activated carbon with acetone solutions of $RuCl_3$, subsequent drying at 393 K, and then reduction at 673 K in a 20% $H_2$ flow. Cellulose (Alfa Aesar, microcrystalline; relative crystallinity of about 84%, as estimated from its XRD pattern shown in Figure S1 a in the Supporting Information, according to the method reported in reference [3a]) reactions were carried out in a teflon-lined stainless steel autoclave (150 mL) typically at 518 K and 6 MPa $H_2$ for 5 min with vigorous stirring. Liquid-phase products were analyzed by HPLC and ESI-MS, and gas-phase products were analyzed by GC. Cellulose conversions were determined by the change in the weight of cellulose loaded before and after the reactions, and selectivities are reported on a carbon basis; carbon mass balance is better than 98 ± 3% in this work.

XRD patterns for the cellulose were measured on a Rigaku D/Max-2000 diffractometer using $Cu_{K\alpha}$ radiation ($\lambda = 1.5406$ Å), operated at 30 kV and 100 mA, in the range of 10–40°. TEM images for the Ru/C catalysts were taken on a Philips Tecnai F30 FEG-TEM operated at 300 kV. The samples were prepared by uniformly dispersing Ru/C catalysts in ethanol and then placing them onto carbon-coated copper grids. The average size of the Ru particles and their size distributions were calculated by averaging of at least 200 particles randomly distributed in TEM images.

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