

1. Experimental

a. Materials

Hydrates of $\text{H}_3\text{PW}_{12}\text{O}_{40}$, $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ and $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ were purchased from Fluka and were used as received. Microcrystalline cellulose, Avicel PH-101, was obtained from Sigma-Aldrich. The carbon supported Ru (5%) hydrogenation catalyst was purchased from Sigma-Aldrich. The USY zeolites were supplied by Zeolyst. These samples were saturated with water over an NH_4Cl saturated solution before use. H_2SO_4 (96%), HNO_3 (65%), HCl (37%) and all other chemicals were commercially supplied. Water content of all the substrates and catalysts was determined by thermogravimetric analysis (TGA) under an inert N_2 atmosphere with a TGA Q500 from TA Instruments before use and the weight of each component and yield calculations were adjusted accordingly.

b. Cellulose ball milling procedure

Ball-milling of cellulose was carried out in batches of 25g cellulose using seven ZrO_2 balls (mass of 7.5 g and diameter of 1.8 cm) in a 500 mL ZrO_2 bottle, for 24 one hour sessions. This assured that the cellulose temperature never exceeded 323K and therefore no thermal decomposition of the cellulose occurred during ball milling.

c. Catalytic reactions

In a typical reaction (hydrolysis or combined hydrolysis + hydrogenation) cellulose (or cellobiose), the acid catalyst, and water were loaded in a 100ml reactor (Parr Instruments Co.). In the reductive conversion of cellulose carbon supported Ru (5%) was added as the hydrogenation catalyst. The reactor was then flushed with N_2 to remove O_2 . The mixture was stirred at 750 rpm and heated to the desired reaction temperature. For the reductive cellulose conversion, the reactor was pressurized with 50 bar H_2 upon prior to heating to the reaction temperature. This moment was chosen as the reaction starting time. Samples were taken during the reaction, which were quickly cooled in an ice bath and centrifuged. The product mixture was then derivatised to trimethylsilylethers and analysed on a Hewlett Packard 5890 GC equipped with an HP 7673 autosampler, a 50m CP-Sil-5CB column and a FID. Product yields are expressed in C mol% and are calculated as follows: $\text{yield}(\%) = [\text{moles C in product} / \text{total moles C loaded in reactor}] \times 100\%$. Selected samples were also analysed (for oligosaccharide formation) after filtration over a $0.45\mu\text{m}$ PTFE filter by an Agilent 1200 Series HPLC equipped with a Varian Metacarb 67C column (300 x 6.5 mm) and a RI detector. Water was used as mobile phase. The conversion of cellulose was determined by total organic carbon (TOC) analysis of the product mixture.

2. Characterisation of ball milled cellulose

Both the microcrystalline and ball milled cellulose were characterised using XRD, FTIR, CP MAS NMR and SEM. Crystallinity of all samples was checked by powder X-ray diffraction patterns, recorded at room temperature on a STOE STADI P Combi diffractometer. The diffracted intensity of Cu-K α radiation ($\lambda=0.154$ nm) was measured in a 2θ range between 0° and 60° . FTIR was measured under vacuum on a Bruker IFS 66v/S instrument (KBr method). The ^{13}C CP MAS NMR spectra were recorded on a Bruker Avance DSX400 spectrometer (9.4 T). 4400 scans were accumulated with a recycle delay of 10 s. The contact time was 4 ms. The samples were packed in 4 mm rotors, and the spinning frequency of the rotor was 5000 Hz. Tetramethylsilane was used as shift reference. SEM characterisation was done using a high resolution SEM (Philips XL-30 FEG), equipped with an EDS detector system (from EDAX).

The powder X-ray diffractograms in figure S1 clearly demonstrate the reduced crystallinity of the cellulose after the ball milling pretreatment. In the microcrystalline cellulose, the major peak at $2\theta = 22.5^\circ$ is assigned to the [002] crystal plane. In figure S2 FTIR data in the region $900\text{-}1600\text{ cm}^{-1}$ are given. The decreasing intensity of the band at 1430 cm^{-1} has been recognized to be indicative for a less crystalline cellulose sample¹. Figure S3 shows ^{13}C CP MAS NMR data of both cellulose samples. The decreasing peak ratios of C4(86-92 ppm)/ C4(79-86 ppm) and C6(63-67 ppm)/C6(56-63 ppm) are in good agreement with literature data². Furthermore, line widths are larger in the amorphous sample, which can be attributed to a larger distribution of molecular orientations. This, in combination with the above XRD and FTIR data, strongly suggests that a more disordered form of cellulose is produced by the ball milling pretreatment. Finally, figure S4 shows SEM micrographs that clearly indicate that the cellulose particles are significantly reduced in size. In conclusion, the ball milling pretreatment has produced a less crystalline cellulose sample with reduced particle dimensions. This allows easier access of the acid catalyst to the glycosidic bonds and therefore faster and more complete conversion of the cellulose.

Figure S1. Powder XRD patterns of (a) microcrystalline and (b) ball milled cellulose.

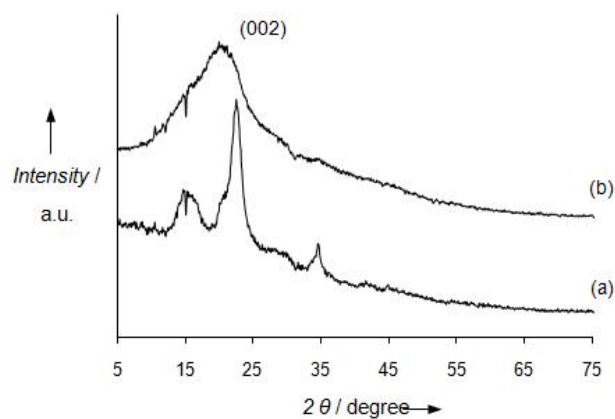


Figure S2. FTIR spectrum of (a) microcrystalline and (b) ball milled cellulose.

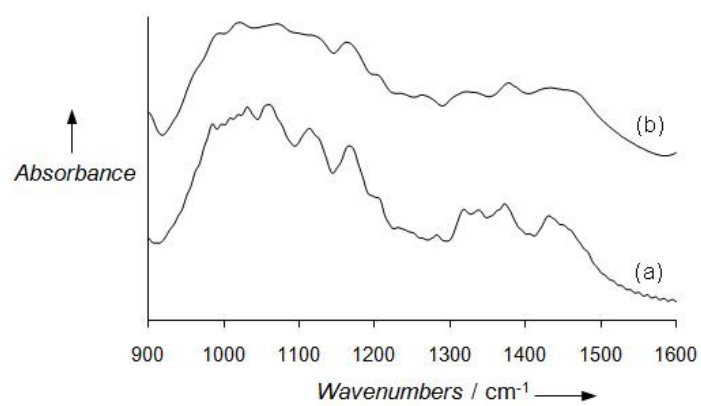


Figure S3. ¹³C CP MAS solid state NMR spectra of (a) microcrystalline and (b) ball milled cellulose.

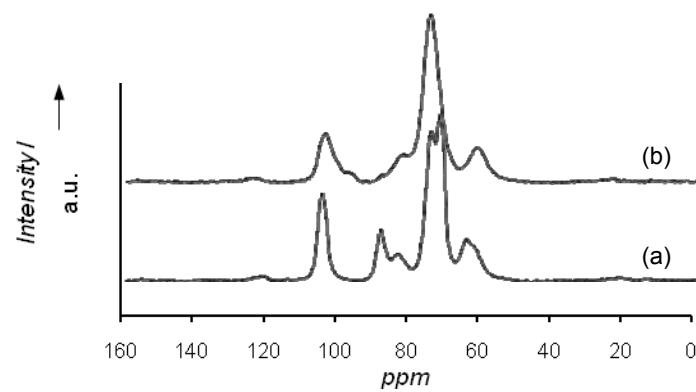
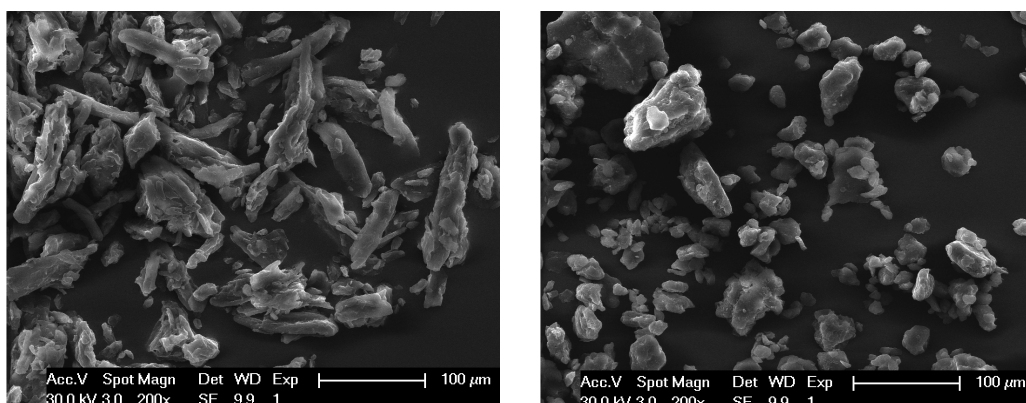


Figure S4. SEM micrographs of (a) microcrystalline and (b) ball milled cellulose.



3. Cellobiose hydrolysis: screening of acid catalysts

At the start of the study, several heteropoly acids, mineral acids and USY zeolites were tested in cellobiose hydrolysis. Cellobiose is a water soluble glucose dimer, in which the glucose monomers are linked by a β -1,4-glycosidic bond, as in cellulose. It is therefore an interesting model substrate to test the intrinsic hydrolysis potential of acids for this bond without interference of chemico-physical influences such as the crystallinity and insolubility of a cellulose crystal, surface adsorption issues etc. For the zeolite acid catalysts, USY was chosen because this topology was reported to be very active in maltose and starch hydrolysis⁹. The results, given in table S1, do not constitute maximum obtainable yields.

Table S1. Cellobiose hydrolysis over various acid catalysts[a].

Catalyst	Hexose yield (%)	Conversion (%)	Hexose Selectivity (%)
$\text{H}_3\text{PW}_{12}\text{O}_{40}$	44.5	44.8	>99
$\text{H}_4\text{SiW}_{12}\text{O}_{40}$	42.1 (82.9) ^[b]	42.4 (84) ^[b]	>99 (99) ^[b]
$\text{H}_3\text{PMo}_{12}\text{O}_{40}$	39.4	40.8	97
H_2SO_4	27.2	27.2	>99
HCl	46.6 (71.8) ^[b]	46.8 (73.4) ^[b]	>99 (98) ^[b]
HNO_3	46.1 (82.1) ^[b]	46.6 (86.5) ^[b]	99 (95) ^[b]
H^+ -CBV300	0.9	1.7	53
H^+ -CBV500	0.8	2.2	36
H^+ -CBV712	1.2	4	30

H⁺-CBV720	1.8	4.2	43
H⁺-CBV760	3.8	4.6	83

[a] Reaction conditions: cellobiose 1g, water 50g, $[H^+] = 1.22 \cdot 10^{-2}$ M for homogeneous acids assuming full dissociation; solid acid catalysts 0.5g, 398K, 1.5h, N₂ atmosphere.

[b] data in parentheses refer to a reaction time of 7h.

The table shows a large difference in both activity and selectivity between the homogeneous and heterogeneous catalysts. All of the homogeneous catalysts, except H₂SO₄, exhibit a high selectivity and activity for the reaction under these conditions, whereas the USY zeolite catalysts are almost inactive and far less selective. Our observation agrees well with recent paper of Shimizu *et al*³, who showed that H⁺-BEA zeolite has a low hydrolysis activity and hydrolyses unselectively. Of the homogeneous catalysts, the heteropoly acids consistently exhibit much higher activities than H₂SO₄, the industrial standard for acid hydrolysis of cellobiose and cellulose. Since all of the homogeneous acids used are considered to be fully dissociated in water, this result shows that the proton concentration in solution is not the only factor determining the speed of hydrolysis. The same behavior was very recently observed by Shimizu *et al*³ in their screening of Brønsted acids in cellobiose hydrolysis.

4. References

1. R. T. O'Connor, E. F. DuPré, D. Mitcham, *Text. Res. J.*, 1958, **28**, 382 – 392.
2. H. Zhao, J. H. Kwak, Y. Wang, J. A. Franz, J. M. White, J. E. Holladay, *Energy Fuels*, 2006, **20**, 807 – 811.
3. K. Shimizu, H. Furukawa, N. Kobayashi, Y. Itaya and A. Satsuma, *Green Chem.*, 2009, **11**, 1627-1632.