Supporting Information

Mechanocatalytic depolymerization of cellulose combined with hydrogenolysis as a highly efficient pathway to sugar alcohols

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1. Experimental Details

1.1. Chemicals

Microcrystalline cellulose (MC, Avicel PH-101, Fluka), α-cellulose (C8002, Sigma-Aldrich), H_2SO_4 (96 %, J.T. Baker), Ruthenium 5% on carbon (Ru/C, Sigma-Aldrich, 206180) were used as received.

1.2. Impregnation of the cellulosic substrates

The cellulosic substrate (10.00 g, 62 mmol anhydroglucose units) was dispersed in MTBE (150 mL) and stirred for 10 min prior to the dropwise addition of H_2SO_4 (0.52 mL, 10 mmol). The suspension was stirred for 30 min. In sequence, the solvent was removed under reduced pressure at 40 °C. H_2SO_4-impregnated microcrystalline cellulose (IMC) was obtained as a colorless powder.

1.3. Ball milling

The cellulosic substrates were milled in a stainless steel vial (12 mL; six stainless steel milling balls at 3.95 g each), using a ball mill (Fritsch, Pulverisette P7) at room temperature. Under working conditions, the temperature inside the mill was not higher than 42 °C after 0.5 h. To avoid overheating in reactions carried out longer than 0.5 h, milling was turned off every 0.5 h for 10 min. Reaction times refer exclusively to overall milling time. Acid-impregnated cellulose powder (1.2 g) was processed, directly after the impregnation step “1.2”, at 800 rpm for the indicated times. Ball milled IMC was obtained as a powder and used directly in the hydrolytic hydrogenolysis experiments.

1.4. Hydrolytic hydrogenolysis

Ru/C (100 mg), substrate (500 mg) and water (10.0 ml) were added into a glass inlet (30 mL). The experiment was performed in a stainless steel autoclave (45 mL). Typically, the autoclave was pressurized with H_2 (50 bar, *r.t.*) and heated to 160 °C for 1 h. Afterwards, the reaction was stopped by cooling the reactor in an ice-bath.

1.5. Sugar alcohol analysis by HPLC

The analysis of the aqueous product mixtures were performed on a HPLC Shimadzu LC-10 equipped with a column switch, combining two organic acid resin columns [CS Chromatographie, (1st column) 8 mm ID × 100 mm in length and (2nd column) 8 mm ID × 300 mm in length]. The mobile phase was an aqueous solution of trifluoroacetic acid (2 mM) and the flow rate was 1 mL min^{-1}. The sugars and sugar alcohols were analyzed by a RI detector.

The carbon yields (Y) were calculated as given by:

$$Y_{product} = \frac{\upsilon_{product} \cdot n_{product}}{\upsilon_{substrate} \cdot n_{substrate}}$$

where: $\upsilon_{product}$ is the number of carbons present in the compound, for glucans $\upsilon_{substrate}$ is 6, $n_{product}$ is the quantity of a product (in mmol, determined by HPLC), $n_{substrate}$ was calculated as follows:

$$n_{substrate} = \frac{m_{substrate} \cdot f_{acid}}{M_{C_6H_{10}O_5}}$$

where: $m_{substrate}$ is the weight of microcrystalline cellulose (98 % of glucan content), corrected by the acid content, using the factor $f_{acid} = 0.916$ and assuming that the substrate consists only of anhydroglucose units (AGU, $C_6H_{10}O_5$).

As α-cellulose comprises 76 % of glucans (X_{glucans}) and 16 % of xylans (X_{xylans}), the carbon yield was calculated by:

$$Y_{product} = \frac{n_{product} \cdot \upsilon_{product}}{6 \cdot n_{glucans} + 5 \cdot n_{xylans}}$$

where:

$$n_{glucans} = \frac{X_{glucans} \cdot f_{acid} \cdot m_{substrate}}{M_{C_6H_{10}O_5}} \qquad n_{xylans} = \frac{X_{xylans} \cdot f_{acid} \cdot m_{substrate}}{M_{C_5H_8O_4}}$$

1.5. Determination of the apparent degree of polymerization

The cellulosic substrate (30 mg) was suspended in DMSO (5 mL, Fluka). Into the suspension 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 by R. Evans, R. H. Wearne and A. F. A. Wallis (*J. Appl. Polym. Sci.* 1989, **37**, 3291-3303). 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, Tosoh TSKgel SuperHZM-M, 4.6 mm ID × 15.0 cm) and stabilized THF as eluent (0.2 mL min^{-1}, inhibitor-free, Aldrich). For detection, a UV/Vis detector at 236 nm was used. The system was calibrated with polystyrene standards ($5 \cdot 10^2$ to $7 \cdot 10^6$ Da, Aldrich). The apparent weight-average degree of polymerization, DP, was calculated by dividing the weight average molecular weight values by molar mass of the anhydroglucose tricarbanilate (519 g mol^{-1}).

1.6. GPC analysis of water-soluble products

After ball milling IMC, water-soluble products were analyzed, without derivatization, by GPC using water as mobile phase. Analyses were performed at 80 °C on a Perkin-Elmer HPLC 200 outfitted with a set of four columns (4 × TSKgel G-Oligo-PW: 7.8 mm I.D. × 30 cm, Tosoh) in series, and milli-Q water as the eluent (0.8 mL min^{-1}). For detection, a refractive index detector was used.

TEM images of the Ru/C catalyst

Transmission Electron microscopy (TEM) images of samples were collected with a HF 2000 microscope (Hitachi) equipped with a cold-field emission gun. The acceleration voltage was 200 kV.

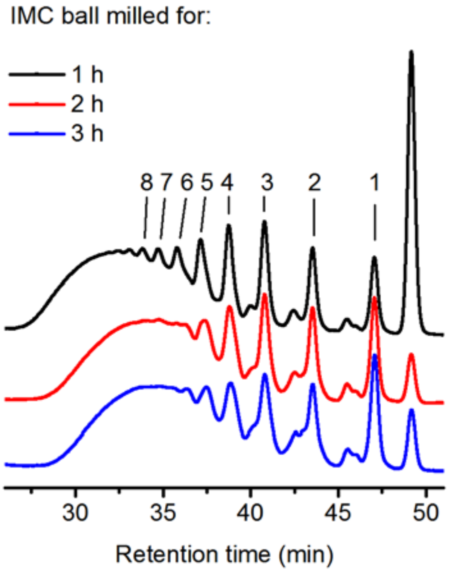

Figure S1. Gel-permeation-chromatogram of water-soluble products obtained by milling IMC for 1, 2 and 3 h. Numbers indicate the DP of the eluting species.

Table S1. Yields of other products obtained from the hydrolytic hydrogenation of unprocessed and ball milled substrates, as indicated in Table 1.

Entry	Carbon Yields [%]					
	Erythritol	Glycerol	Isosorbide	Ethylene glycol	Glucose	Sum
1	0.00	0.82	0.00	0.00	0.00	0.8
2	0.00	0.74	0.07	0.02	0.00	0.8
3	0.29	0.36	0.00	0.00	0.02	0.7
4	0.48	0.00	0.00	0.00	0.00	0.5
5	0.43	0.36	0.00	0.00	0.00	0.8
6	1.72	2.33	0.00	0.00	2.42	6.5
7	1.74	1.03	0.00	0.00	1.57	4.3
8	1.79	0.97	0.24	0.00	0.63	3.6
9	0.80	0.79	0.00	0.00	0.00	1.6
10	0.43	0.00	0.00	0.00	0.00	0.4
11	1.18	0.37	0.00	0.00	0.00	1.6