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Electronic Supplementary Information for

Catalytic production of levulinic acid from cellulose and other biomass-derived carbohydrates with sulfonated hyperbranched poly(arylene oxindole)s

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1 Materials and method

Avicel® PH-101, cellobiose, sucrose, maltose, xylose, α-cellulose, Sigmacell Type 20, Sigmacell Type 50, Nafion® NR50, Nafion® SAC-13, furfural and formaldehyde were purchased from Sigma-Aldrich. Levulinic acid, glucose, fructose, 1,6-anhydro-β-D-glucopyranose, 5-hydroxymethylfurfural and Amberlyst® 15 were supplied by Acros Organics. Cellohexaose was supplied by Seikagaku Biobusiness, formic acid and xylan by Merck Chemicals, and Orafti® inulin by BENEO-Orafti. All chemicals were used without further purification as received.

For typical runs, desired amounts of substrates, catalyst and water were loaded into a batch reactor under air. The temperature of the reactor was elevated to the target temperature under continuous stirring. After each reaction, the product mixture was sampled, centrifuged, syringe filtered and analyzed by HPLC (Agilent 1200 Series) on a Varian Metacarb 67H column (300 x 6.5 mm), using an aqueous solution of sulfuric acid (5 mM) at a flow rate of 0.8 ml min^{-1} and a column temperature of 308 K. Figure S1 shows a typical chromatogram of the liquid recovered from a reaction of cellulose with the sulfonated hyperbranched polymers.

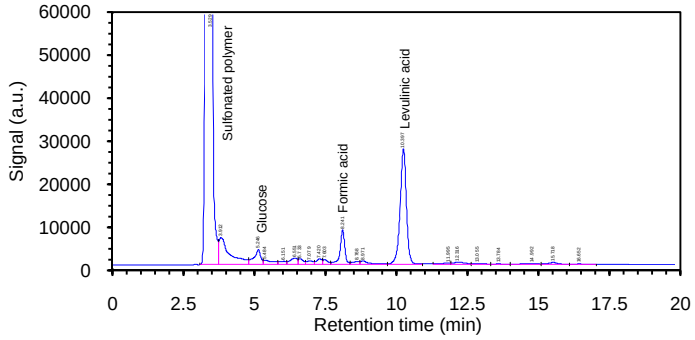

Fig. S1 Typical chromatogram of the reaction mixture obtained from the catalytic conversion of cellulose over sulfonated hyperbranched poly(arylene oxindole)s.

For some selected samples, identification of compounds was carried out by GC-MS using an Agilent 5973 Network Mass Selective Detector coupled to an Agilent 6890N GC with HP5MS capillary column (30 m x 0.25 mm). The representative mass spectrum of LA is shown in Figure S2.

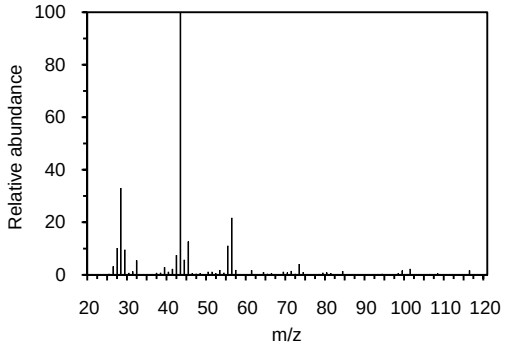

Fig. S2 Mass spectrum of LA detected by an ion trap mass spectrometer.

2 Cellulose pretreatment and characterization

Avicel® PH-101 was characterized (i) as received from Sigma-Aldrich and (ii) after 24 h ball-milling pretreatment. Ball-milling with 25 g of cellulose was carried out using ZrO2 balls (mass 7.5 g; diameter 1.8 cm). SEM images in Figure S3 were taken with a high resolution Scanning Electron Microscope (Philips XL-30 FEG).

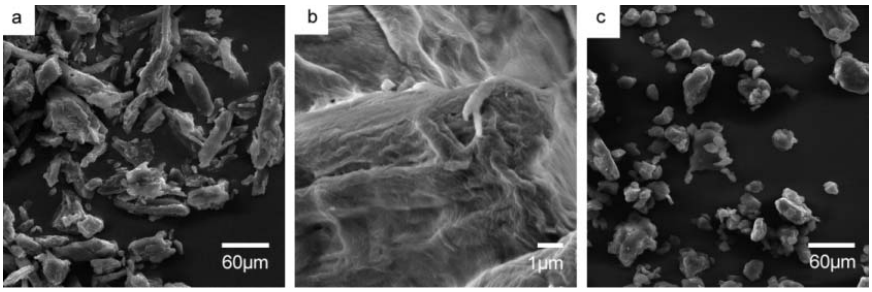

Fig. S3 SEM characterization of Avicel® PH-101 before (a-b) and after ball-milling (c).

X-ray diffraction (XRD) patterns of the Ni/CNF catalyst were recorded at room temperature with a STOE STADI P Combi diffractometer. The diffracted intensity of CuKα radiation (wavelength of 0.154 nm) was measured in a 2θ range between 0° and 75°. Figure S4 displays XRD patterns taken of cellulose samples unmilled and ball-milled for 24 h. In the untreated cellulose, the major peak at $2\theta = 22.5°$ can be assigned to the crystalline plane 002. A comparison of the patterns clearly reveals a decrease in crystallinity of cellulose after ball-milling pretreatment.

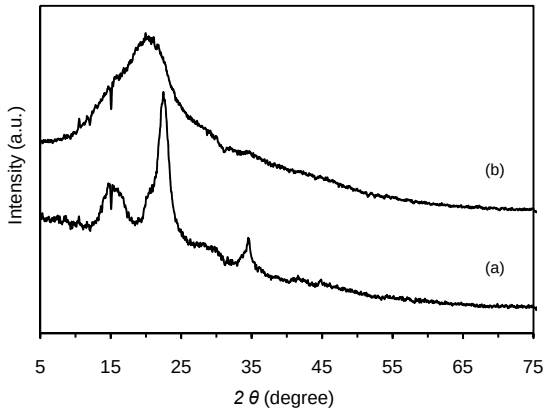

Fig. S4 Powder X-ray diffraction patterns of Avicel® PH-101 before (a) and after ball-milling (b).

IR spectra were recorded under vacuum from KBr pellets on a Bruker IFS 66v/S instrument. The spectra in Figure S5 also show the changes in the cellulose structure after ball-milling. The less pronounced band at 1430 cm^{-1} is another strong indication of a less ordered cellulose sample, since it is assigned to the CH_2 scissoring motion in the cellulose I crystal. The ball-milling allows the regular arrangement of the CH_2OH group on C_6 to relax into a more random one, resulting in a broader band at 1430 cm^{-1}.

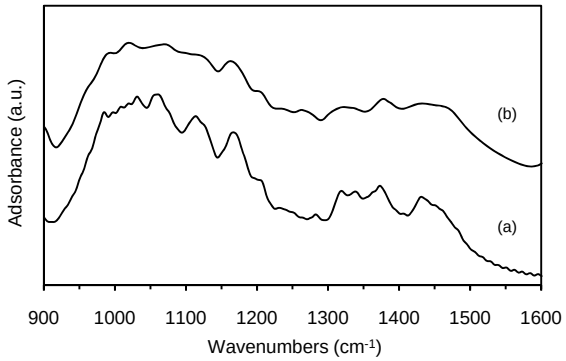

Fig. S5 IR spectra of Avicel® PH-101 cellulose before (a) and after ball-milling (b).

The ^{13}C CP MAS NMR spectra in Figure S6 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 cellulose samples were packed in 4 mm rotors, and the spinning frequency of the rotor was 5000 Hz. Tetramethylsilane was used as shift reference. The crystallinity indices (*CrI*) presented in this manuscript are calculated after deconvolution of C4 regions (80 to 94 ppm) of the ^{13}C CP MAS NMR spectra into crystalline and amorphous peaks.

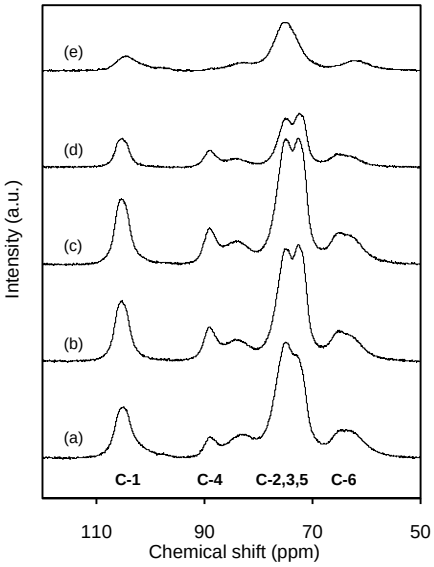

Fig. S6 ^{13}C CP MAS NMR spectra of α-cellulose (a), Sigmacell Type 50 (b), Sigmacell Type 20 (c), Avicel® PH-101 (d), ball-milled cellulose (e).

3 ^{1}H NMR characterization of the hyperbranched polymer

^{1}H NMR spectra of the hyperbranched poly(arylene oxindoles)s before and after sulfonation were recorded on a Bruker AMX 400 (400 and 100 MHz).

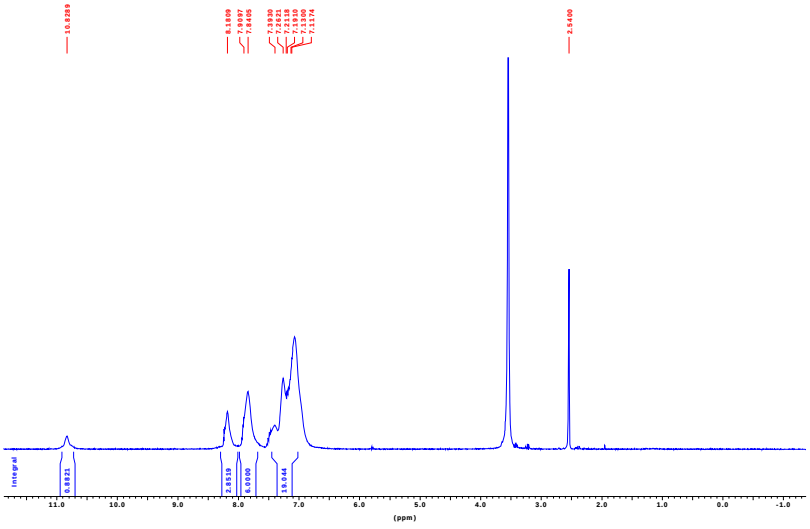

Fig. S7 ^{1}H NMR spectrum of the hyperbranched poly(arylene oxindole)s before sulfonation.

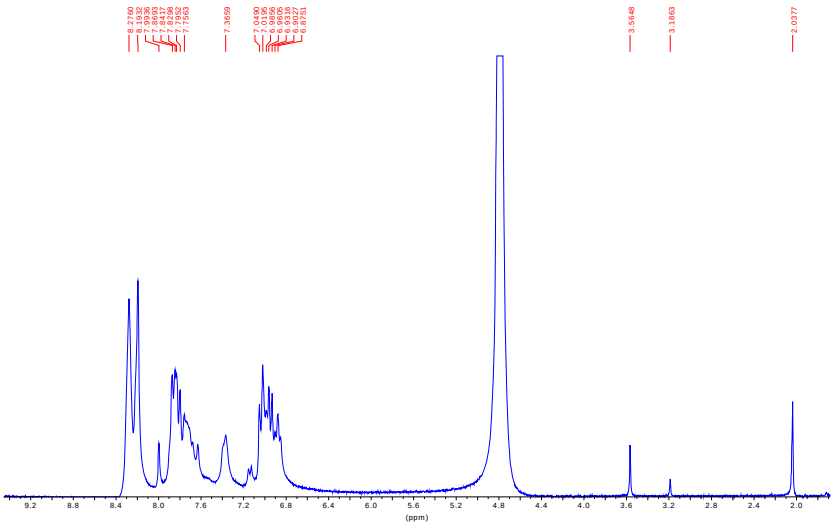

Fig. S8 ^{1}H NMR spectrum of the hyperbranched poly(arylene oxindole)s after sulfonation.