Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information for

The importance of pretreatment and feedstock purity in the reductive splitting of (ligno)cellulose by metal supported USY zeolite

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X-ray powder diffraction (XRD)

X-ray powder diffraction patterns of (pretreated) Avicel PH-101 cellulose and SCT 20, 50 and 101 (Figure S1) were 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 62.5°. A background signal without cellulose was also measured and subtracted from all patterns. For comparison, intensities were normalized with respect to the highest intensity in each pattern. Crystallinity indices were calculated using the XRD peak height method according to Segal *et al.*:[1]

$$CrI(\%) = \frac{(I_{002} - I_{AM})}{I_{002}} \times 100$$

In this equation, I_{002} represents the maximum intensity of the (002) plane reflection in the cellulose sample at a 2θ angle between 22° and 24° and I_{AM} the intensity of the amorphous reflection at a 2θ angle of about 18°, corresponding to the minimum intensity between the $(10\bar{1})$ and (021) plane signals (indicated in Figure S1). The crystallinity index of ball milled and ammonia-treated Avicel PH-101 cellulose could not be determined reliably with the XRD peak height method due to the absence of well-defined minimum and maximum cellulose I intensities.

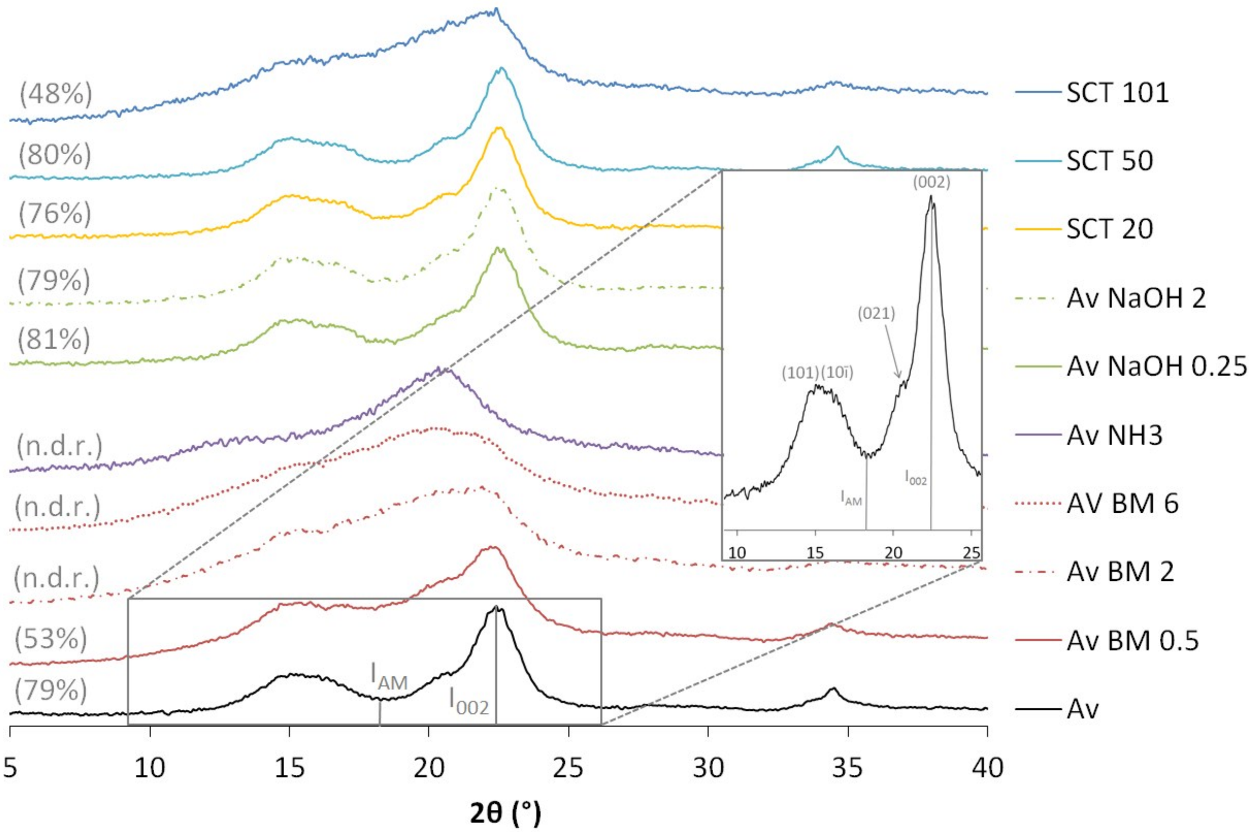

Figure S1 XRD patterns of Avicel PH-101 cellulose (Av: unpretreated; Av BM: ball milled for 0.5 h, 2 h or 6 h; Av NH_3: ammonia pretreated; Av NaOH: NaOH pretreated for 0.25 h or 2 h) and SCT 20, 50 and 101. Calculated crystallinity indices are indicated in parentheses. n.d.r.: could not be determined reliably. The insert represents the corresponding Miller indices of Avicel PH-101 cellulose.

Solid-state ^{13}C CP MAS NMR

Solid-state ^{13}C CP MAS NMR spectra of (pretreated) Avicel PH-101 cellulose and SCT 20, 50 and 101 (Figure S2) were recorded with a Bruker Avance DSX400 spectrometer (B_0 = 9.4 T). 4400 scans were accumulated with a recycle delay of 10 s, the contact time was 4 ms. Samples were packed in 4 mm zirconia rotors. The spinning frequency of the rotor was 5000 Hz. Tetramethylsilane was used as shift reference. For comparison, intensities were normalized with respect to the highest intensity in each spectrum. Crystallinity indices were calculated using the NMR C4 peak separation method according to Newman:[2]

$$CrI\ (\%) = \frac{A_{Ord}}{A_{Ord} + A_{Disord}}(\times 100)$$

In this equation, A_{Ord} (ordered) and A_{Disord} (disordered) represent the area obtained by integration of the C4 region of the solid-state ^{13}C CP MAS NMR spectrum from 86-87 to 91-93 ppm and 79-81 to 86-87 ppm chemical shift, respectively (Figure S2).

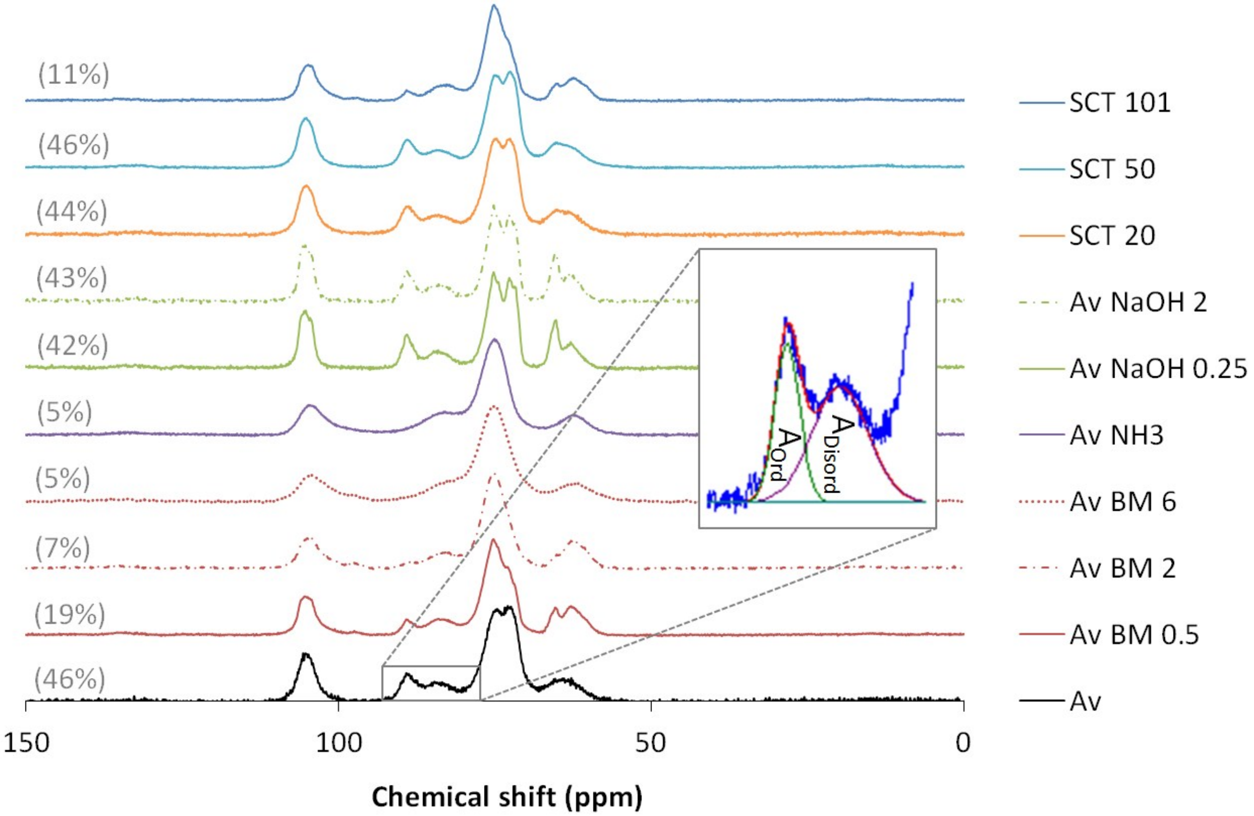

Figure S2 Solid-state ^{13}C CP MAS NMR spectra of Avicel PH-101 cellulose (Av: unpretreated; Av BM: ball milled for 0.5 h, 2 h or 6 h; Av NH_3: ammonia pretreated; Av NaOH: NaOH pretreated for 0.25 h or 2 h) and SCT 20, 50 and 101. Calculated crystallinity indices are indicated in parentheses. The NMR C4 peak separation method is graphically demonstrated in the insert (Avicel PH-101 cellulose).

Laser diffraction

Particle sizes of (pretreated) Avicel PH-101 cellulose and SCT 20, 50 and 101 (Figure S3) were determined by laser diffraction using a Microtrac S 3500. In a typical measurement 0.2 g of cellulose powder was loaded in a turbotrac autofeeder. The machine was first flushed with air to remove all particles from earlier measurements, after which a series of blank measurements was performed. When blank measurements were found adequate, cellulose powders were systematically sucked for 10 s towards the cell where particles were measured with a TRI-LASER multi-detection system. The data was handled and analyzed with Microtrac flex 11.0.0.3 software. Multiple measurements were performed.

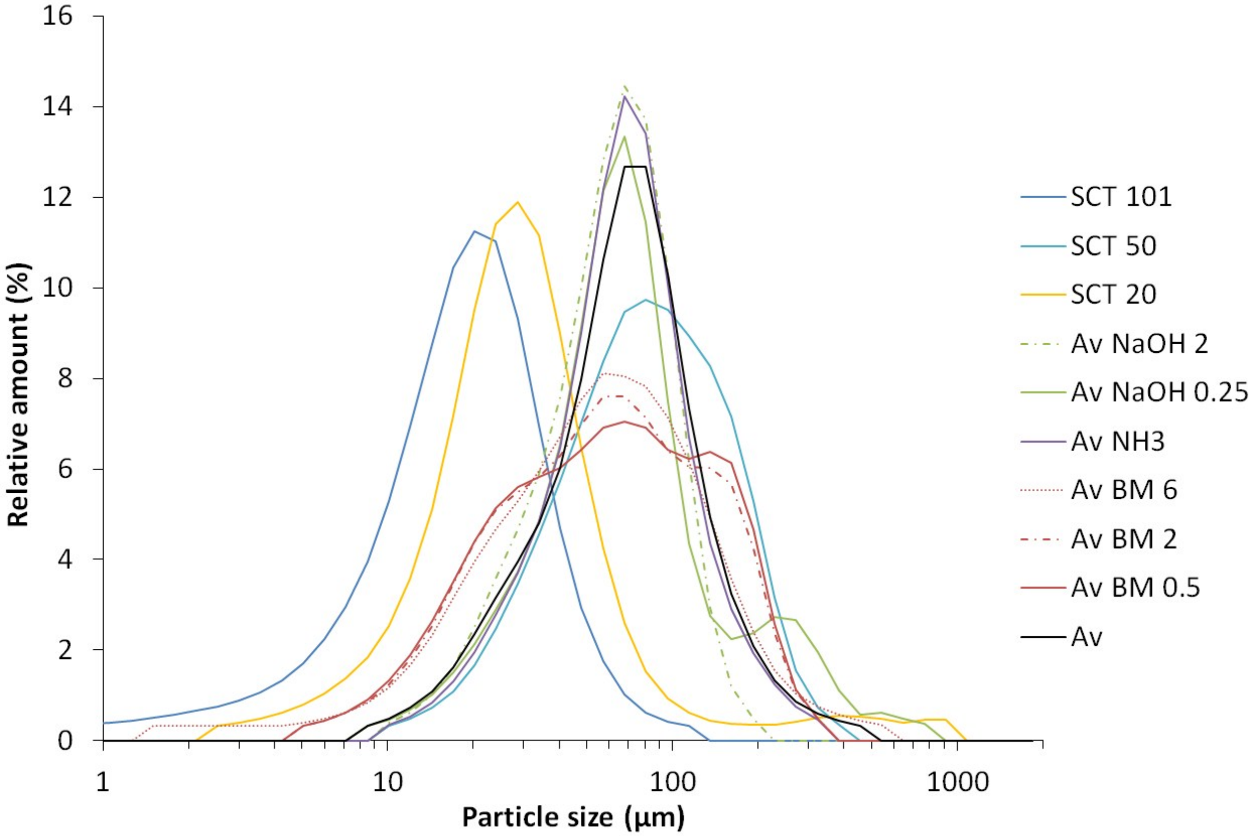

Figure S3 Particle size distributions of Avicel PH-101 cellulose (Av: unpretreated; Av BM: ball milled for 0.5 h, 2 h or 6 h; Av NH_3: ammonia pretreated; Av NaOH: NaOH pretreated for 0.25 h or 2 h) and SCT 20, 50 and 101.

Fourier-transformed infrared (FTIR)

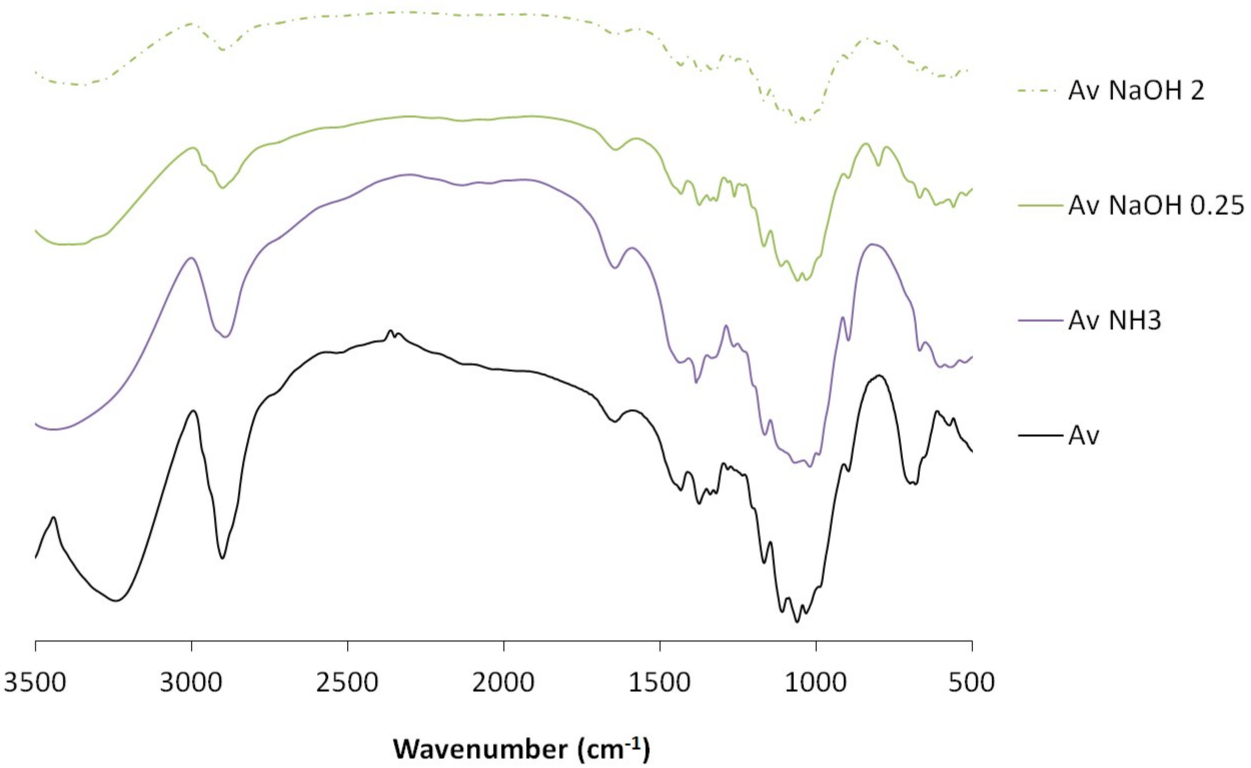

Figure S4 FTIR spectra of (chemically pretreated) Avicel PH-101 cellulose (Av: unpretreated; Av NH_3: ammonia pretreated; Av NaOH: NaOH pretreated for 0.25 h or 2 h).

Pretreatment effectiveness data

Table S1. Pretreatment effectiveness data.

Sample	Conditions	Pulp yield (dw%)	Glucan recovery (%)	Xylan/mannan hydrolysis[a] (%)	Delignification (%)
Wheat straw	90 min, 483 K 50 wt% EtOH	48	93	81	56
	60 min, 463 K 30 mM H_2SO_4 60 wt% EtOH	41	94	94	61
Spruce	60 min, 463 K 5 mM H_2SO_4 60 wt% EtOH	47	76	96	66
Birch wood	30 min 473 K 5 mM H_2SO_4 50 wt% EtOH	41	93	94	88

[a] Xylan hydrolysis in case of wheat straw and birch. Mannan hydrolysis in case of spruce.

References

1. L. Segal, J. J. Creely, A. E. Martin and C. M. Conrad, *Text. Res. J.*, 1959, **29**, 786-794.
2. R. H. Newman, *Holzforschung*, 2004, **58**, 91-96.