Electronic Supplementary Information

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Mechanical depolymerisation of acidulated cellulose: Understanding the solubility of high molecular weight oligomers

Abhijit Shrotri,[a] Lynette Kay Lambert,[b] Akshat Tanksale[c] and Jorge Beltramini*[a]

[a] *ARC Centre of Excellence for Functional Nanomaterials, University of Queensland, Brisbane, QLD 4072 Australia. Fax: +61 7 3346 3973; Tel: +61 7 3346 3803; E-mail: j.beltramini@uq.edu.au*
[b] *Centre for Advanced Imaging, University of Queensland, Brisbane, QLD 4072, Australia. Fax: +61 7 3346 0346; Tel: +61 7 3345 9737; E-mail: lynette.lambert@cai.uq.edu.au*
[c] *Department of Chemical Engineering, Monash University, Clayton, VIC 3800, Australia. Fax: +61 3 9905 5686; Tel: +61 3 9902 4388; E-mail: akshat.tanksale@monash.edu*

Catalyst Preparation

γ Alumina acquired from Alcoa World Chemicals was used as the support for all catalysts prepared. Alumina was dried overnight at 100 °C to remove physisorbed water prior to catalyst preparation. Nickel and Platinum were impregnated using appropriate quantities of their chemical precursors, $Ni(NiO_3)_2.6H_2O$ (Fluka), 8 wt% H_2PtCl_6 in water (Sigma) respectively. The precursors were added to the support and heated to 50 °C in the presence of a small amount of water and stirred constantly for 5–6 hours. The resultant solution was dried overnight in a 90 °C oven and calcined at 500 °C for 4 h. The catalysts were reduced under hydrogen flow in a fixed bed reactor at 400 °C for 4 h prior to the catalytic run.

Catalyst Characterisation

Alumina support was characterised with N_2 physisorption using a Micromeritics Tristar instrument at liquid nitrogen temperature, for pore size distribution, pore volume and surface area. Carbon monoxide (CO) TPD was carried out to determine the dispersion of metals on bimetallic alumina catalyst. In a typical method about 200 mg of catalyst was loaded on the reaction cell and was reduced at 400 °C for 4 hours using a hydrogen and nitrogen gas mixture (50 mL min-1). The catalyst was purged with helium at 400 C to remove adsorbed H2. The sample was cooled to room temperature under He flow. A 10% CO–He mixture was passed for 15 min to complete adsorption of CO on metal sites. Residual CO was purged with helium until the CO base line reading was constant. Temperature programmed desorption was carried out in the temperature range of 30 °C to 500 °C at a heating rate of 10 °C min-1 under a He flow of 40 mL min-1. The desorbed gas was detected using a thermal conductivity detector. Metal dispersion was calculated assuming that surface concentration of metals was equal to bulk concentration.

Result and Discussion

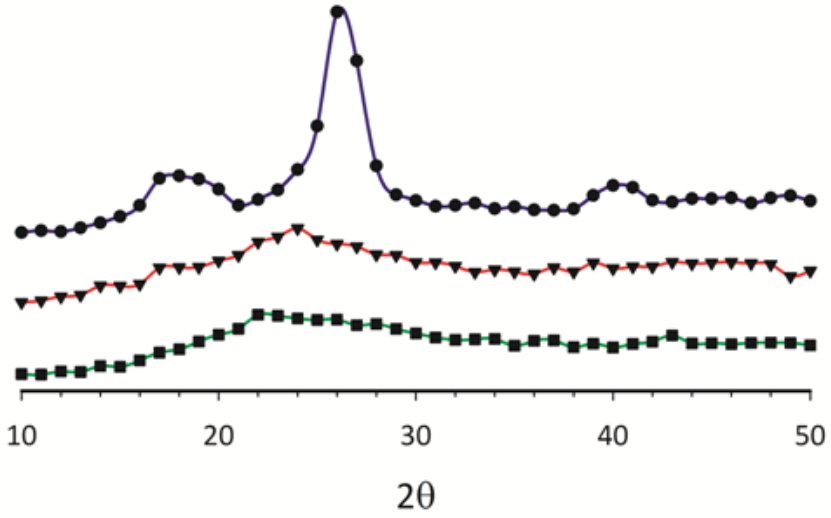

Fig. S1 XRD of cellulose after treatment (●) C-0/0 (▼) C-0/10 (■) C-0.25/10

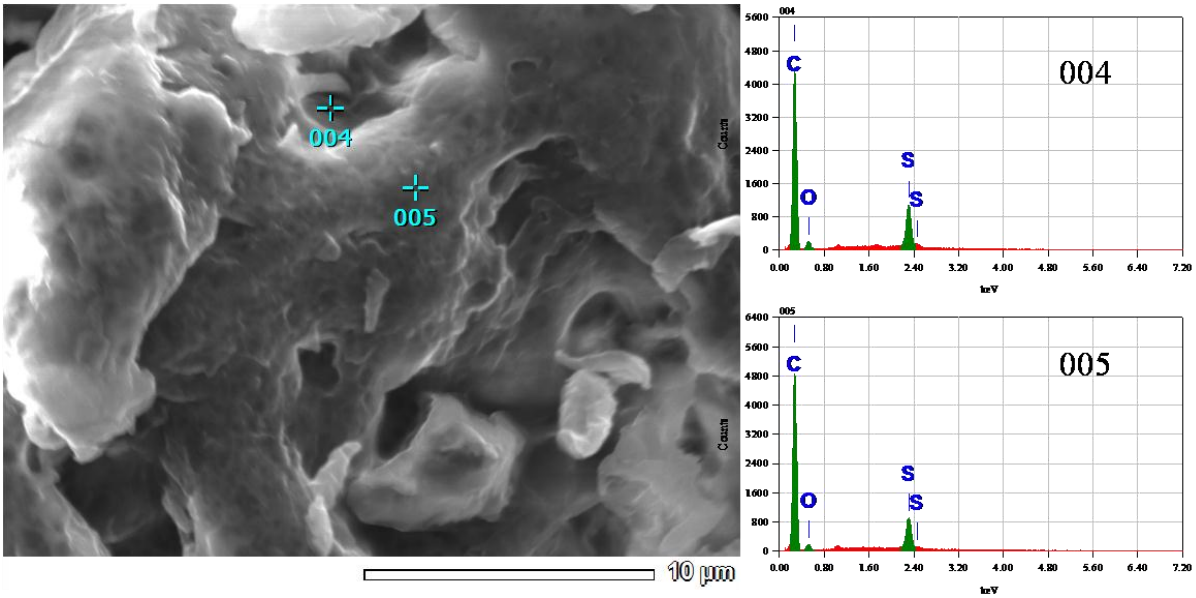

Fig. S2 SEM-EDS of cellulose impregnated with 0.25mmol/g of H2SO4

Table S1. Comparison of chemical shifts between α (1→6) linked sugar unit in iso-maltose with the α (1→6) sugar unit in soluble cellulose oligomer sample

Atom Number	α (1→6) sugar in iso-maltose		α (1→6) sugar in our sample	
	proton shift δ_H (ppm)	carbon shift δ_C (ppm)	proton shift δ_H (ppm)	carbon shift δ_C (ppm)
1	4.95	100.5	4.98	101.3
2	3.55	74.0	3.55	74.1
3	3.72	75.6	3.79	75.6
4	3.42	72.1	3.41	72.3
5	3.72	74.4	x	x
6	3.84	63.0	x	63.2
6’	3.76	-	x	

x – assignment not unequivocal due to overlap of signals

Assignment of chemical shifts for the α (1→6) linked sugar units

In the HSQC spectrum (Fig. S3) at least three cross-peaks between the H1 signals in the region of 4.98 ppm and the directly attached carbon signals (C1) in the region 100.4-101.3 ppm were observed. These were interpreted as multiple components of α (1→6) sugar units attached to different oligomeric chain lengths. Chemical shifts for the most abundant component are shown in Table S1. H1 (4.98 ppm) and C1 (101.3 ppm) for this component were assigned from the HSQC spectrum. Gradient-selected 1D TOCSY spectra were obtained using a selective pulse at H1 (4.98 ppm) and mixing times of 30, 50 and 80 ms. The assignment for the major components at 4.98 ppm were obtained for H2 (3.55 ppm), H3 (3.79 ppm) and H4 (3.41 ppm) by overlaying the 1D TOCSY experiments with the COSY experiment. It was not possible to assign H5, H6 and H6’ because of overlap with other components. However by observing the proton cross-peaks to C1 at 101.3 ppm in the HSQC-TOCSY spectrum, it was noted that additional proton signals were present at 3.72 and 3.86 ppm. These are similar to H5 and H6 at 3.72 and 3.84 ppm respectively for iso-maltose. The H6’ proton in iso-maltose is at 3.76 ppm which if present at a similar shift in the cellulose oligomer sample would be overlapped with the H3 cross-peak at 3.79 ppm. C2 (74.1 ppm) was assigned by observing the 2-bond coupling correlation with H1 in the H2BC experiment. The presence of a cross-peak at δ_H 4.98, δ_C 74.1, in the HSQC-TOCSY experiment and at δ_H 3.55, δ_C 74.1 in the HSQC spectrum further supported the assignment of C2. C3 (75.6 ppm) was assigned by observing a cross peak at δ_H 3.79 (H3), δ_C 75.6 in the HSQC spectrum. This assignment was further supported by the presence of cross-peaks at δ_H 4.98, δ_C 75.6 in the HSQC-TOCSY and the HMBC spectra. The carbon cross peak at δ_H 4.98, δ_C 72.3 in the HSQC-TOCSY spectrum did not appear in the HMBC spectrum. This identified the carbon as being greater than 3-bonds from H1 and therefore the carbon peak at 72.3 ppm was assigned as C4. Remaining carbon peaks in the HSQC-TOCSY were in the range of 73.9 – 74.65 ppm. It was not possible to accurately identify C5 for the major component from this cluster. However these shifts are similar to those for C5 of iso-maltose (δ_c 74.4). C6 (63.2 ppm) was easily assigned as it was the only carbon-correlated signal to δ_H 4.98 in the HSQC-TOCSY spectrum which was identifiable in the multiplicity-edited HSQC as a CH_2 group (crosspeak 180° phase different from CH crosspeaks).

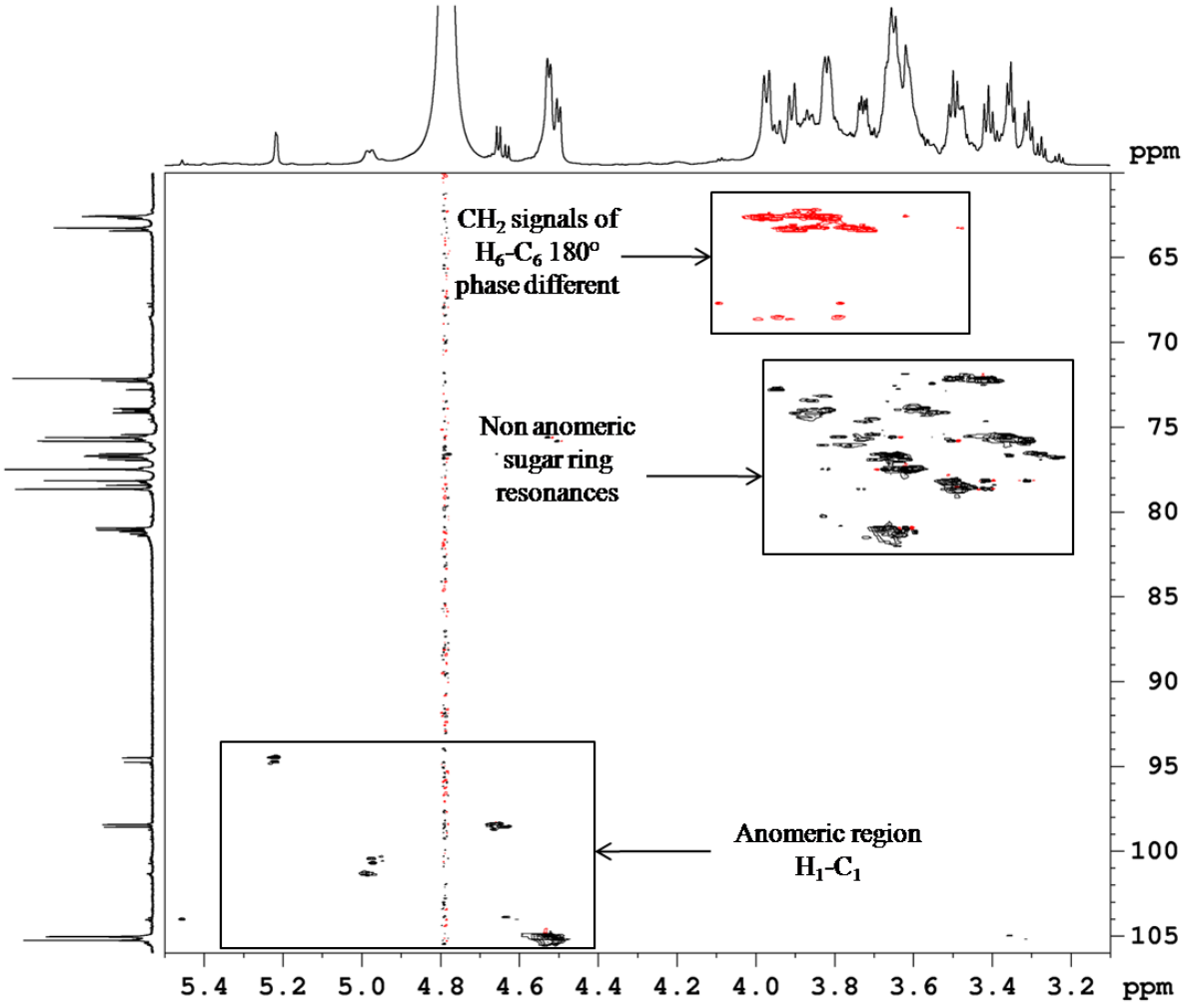

Fig. S3 Multiplicity-edited HSQC spectrum of C- 0.25/10 (30mg/ml) in D_2O at 298 K (^{13}C shifts – vertical axis, ^{1}H shifts – horizontal axis)

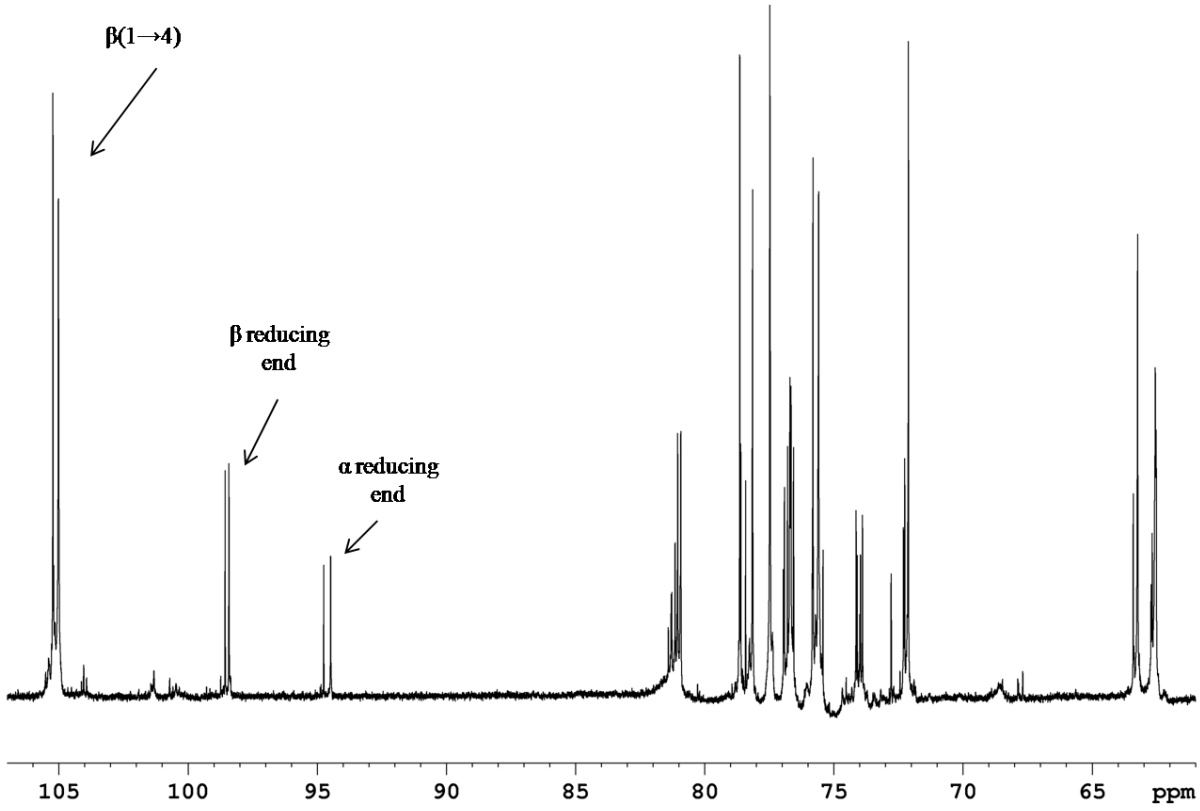

Fig. S4 ^{13}C spectrum of C-0.25/10 (30 mg/mL) in D_2O at 298 K