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## **Supporting Information**

## **Reaction Engineering Implications of Cellulose Crystallinity and Water-Promoted Recrystallization**

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Figure S1. Mass balance closure for acid (red squares) and hot liquid water (blue diamonds) treated ball-milled cellulose samples.



**Figure S2.** X-ray diffractograms of a) MCC-BM50, b) MCC-BM50 washed with acetone and dried at 65 °C, c) MCC-BM50 washed with water and dried.



**Figure S3.** X-ray diffractograms of progressively ball-milled cellulose samples after liquid hot water treatment at 150 °C for 1 hour: a) Avicel-PH101, b) MCC-BM10-HLW, c) MCC-BM20-LHW, d) MCC-BM30- HLW, e) MCC-BM40-HLW, f) MCC-BM50-HLW.



**Figure S4**. X-ray diffractograms of progressively ball-milled cellulose samples after sample preparation simulated conditions: a) Avicel-PH101, b) MCC-BM10-SP, c) MCC-BM20-SP, d) MCC-BM30-SP, e) MCC-BM40-SP, f) MCC-BM50-SP.



**Figure S5.** Raman spectra of progressively ball-milled cellulose samples: a) Avicel-PH101, b) MCC-BM10, c) MCC-BM20, d) MCC-BM30, e) MCC-BM40, f) MCC-BM50.



**Figure S6.** Raman spectra of progressively ball-milled cellulose samples after 0.1 M HCl acid treatment at 150 °C for 1 hour: a) Avicel-PH101, b) MCC-BM10-AC, c) MCC-BM20-AC d) MCC-BM30-AC, e) MCC-BM40-AC, f) MCC-BM50-AC.



**Figure S7.** Raman spectra of progressively ball-milled cellulose samples after liquid hot water treatment at 150 °C for 1 hour: a) Avicel-PH101, b) MCC-BM10- HLW, c) MCC-BM20- HLW, d) MCC-BM30- HLW, e) MCC-BM40- HLW, f) MCC-BM50- HLW.



**Figure S8.** Raman spectra of progressively ball-milled cellulose samples after samples after sample preparation simulated conditions: a) Avicel-PH101, b) MCC-BM10-SP, c) MCC-BM20-SP, d) MCC-BM30-SP, e) MCC-BM40-SP, f) MCC-BM50-SP.



**Figure S9.** Expanded region of the X-ray diffractograms of progressively ball-milled cellulose samples after sample preparation simulated conditions: a) Avicel-PH101, b) MCC-BM10-SP, c) MCC-BM20-SP, d) MCC-BM30-SP, e) MCC-BM40-SP, f) MCC-BM50-SP. The peak at approximately 12.2° is identified as cellulose II.



Ball milling time (min)

**Figure S10.** Full-width-halfmax (FHWM) of 200 diffraction peak plotted versus ball milling time for ball-milled cellulose samples recrystallized by sample preparation and heat up treatment.



**Figure S11.** X-ray diffractograms of selected samples: a) MCC-BM50 and b) MCC-B50 after treatment in ethanol (130 °C, 1 hour).



**Figure S12.** X-ray diffractograms after ethanolysis of selected cellulose samples: a) MCC, b) MCC-BM50-HLW, and c) MCC-BM50.