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Supplementary Online Materials

Hydrolysis of cellulose by cellulase-mimetic solid catalyst

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Experimental

Materials

Chemical reagents used in this study were purchased from Fisher Scientific (Pittsburgh, PA) or Sigma-Aldrich (St. Louis, MO) and used as received. Chloromethyl polystyrene (100 mesh) with 3.5~4.5 mmol chlorine per gram resin and Amberlyst-15 (100 mesh) with 4.5 mmol -SO_3H per gram resin was dried at 105ºC overnight prior to use.

Synthesis of sulfonated chloromethyl polystyrene resin (CP-SO_3H)

The synthesis of CP-SO_3H is schematically shown in Figure S1. The oven-dried CP resin (3 g) and DMF (50 mL) were added into a 100-mL flask and stirred at 120 ºC for 30 min in an oil bath. Then 2 g of sulfanilic acid was added into the flask and reacted with the resin at 120 ºC for 48 h. After the reaction, the resin was recovered by filtration (with 10 μm nylon membrane) followed by washing with 100 mL ethanol and 200 mL water sequentially. The resultant resin was green powder when dried at 105 ºC overnight.

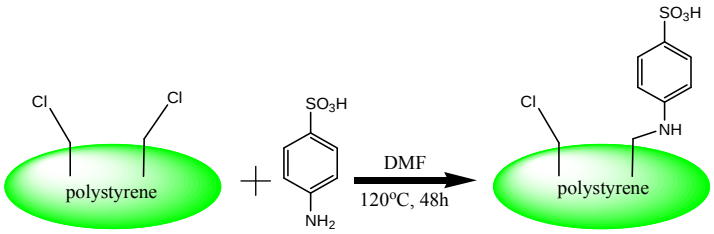


Figure S1. Synthesis of CP-SO_3H

Hydrolysis of cellobiose, starch and Avicel with CP-SO_3H or sulfuric acid

The proposed mechanism of CP-SO_3H-catalyzed hydrolysis of the glycosidic bond is shown in Figure S2. A predetermined amount of CP-SO_3H or sulfuric acid was mixed with 100 mg substrate (cellobiose, starch, or Avicel), respectively, into 1 mL water in 20-mL glass vials and mixed well. Hydrolysis was conducted in oil bath at 120 ºC for varied duration (as presented in Table 3, Figures S6 and S7). Supernatant samples were taken at 30, 60, 90 and 120 min to detect glucose yield.

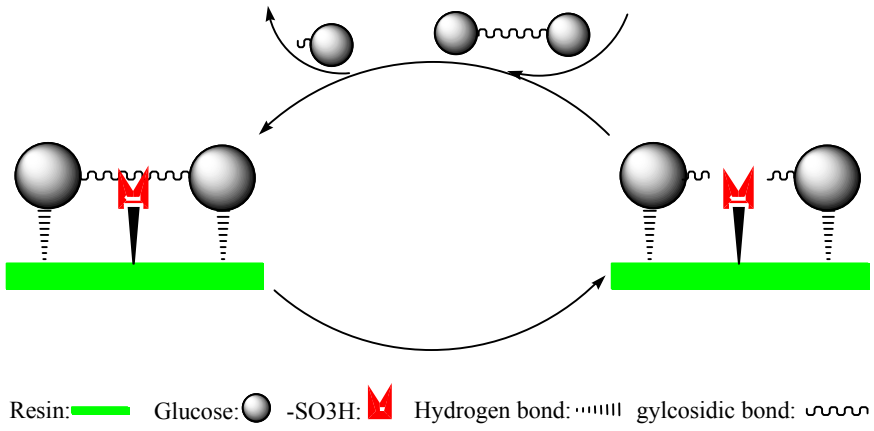


Figure S2. Hydrolysis of glycosidic bond catalyzed by CP-SO_3H resin

Adsorption of glucose and cellobiose on CP-SO_3H

CP-SO_3H (600 mg) was added into 12 mL water and vortexed. The mixture was divided into 12 equal portions in microtubes. Then 100 mg glucose and 90 mg cellobiose was respectively loaded into each microtube and mixed well. All microtubes were kept at room temperature and vortex every 5 min. One microtube was taken and centrifuged at the time of 10, 20, 30, 60, 90, and 120 min, respectively. Glucose and cellobiose in the supernatant was determined with high performance ion chromatograph, as described below, to calculate the adsorption capacity of CP-SO_3H. Competitive adsorption of glucose and cellobiose on CP-SO_3H was investigated under same conditions for 2 hours. More specifically, 50 mg glucose, 45 mg cellobiose and 50 mg CP-SO_3H was mixed in 1 mL water for 2 hours with occasional stirring.

Determination of glucose

Sugar analysis was conducted using a Dionex high performance ion charomatograph system (ICS-3000) equipped with an integrated amperometric detector and Carbopac™ PA1 guard and analytical columns at 20°C. Eluent was provided at a rate of 0.7 ml/min, according to the following gradient: 0~25 min, 100% water; 25.1~35 min, 30% water and 70% 0.1 M NaOH; 35.1~40 min, 100% water. To provide a stable baseline and detector sensitivity, 0.5 M NaOH at a rate of 0.3 ml/min was used as post-column eluent.

FTIR spectra of CP and CP-SO_3H

Fourier transform infrared (FT-IR) spectra were recorded on a PerkinElmer Spectrum 100 FT-IR spectrophotometer with universal attenuated- total-reflection (ATR)

sampling accessory (Waltham, MA). ATR allows samples to be examined directly in the solid state without further treatment.

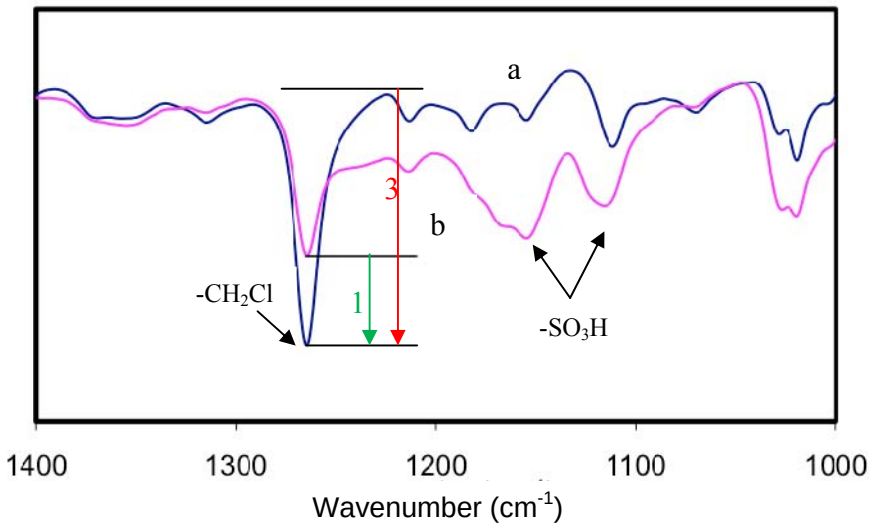


Figure S3. FTIR spectra of (a) CP resin and (b) CP-SO_3H resin

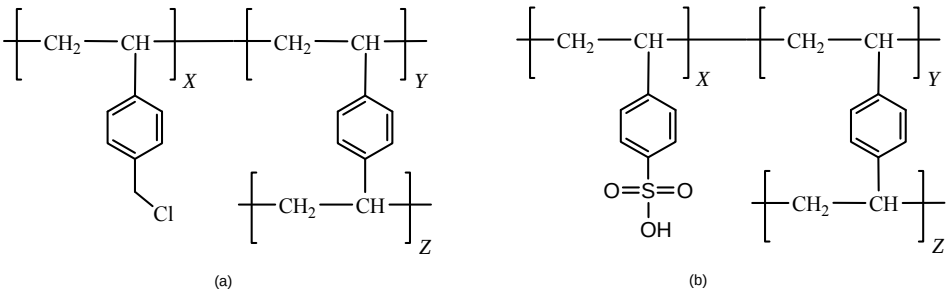


Figure S4. Chemical structures of (a) CP resin and (b) PS-SO_3H

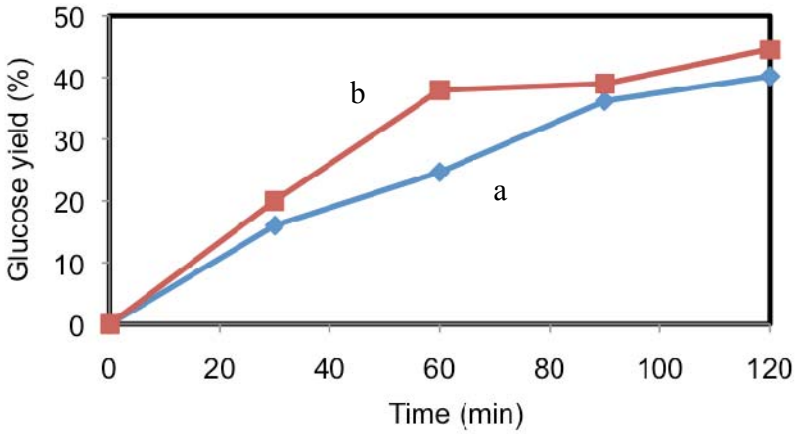
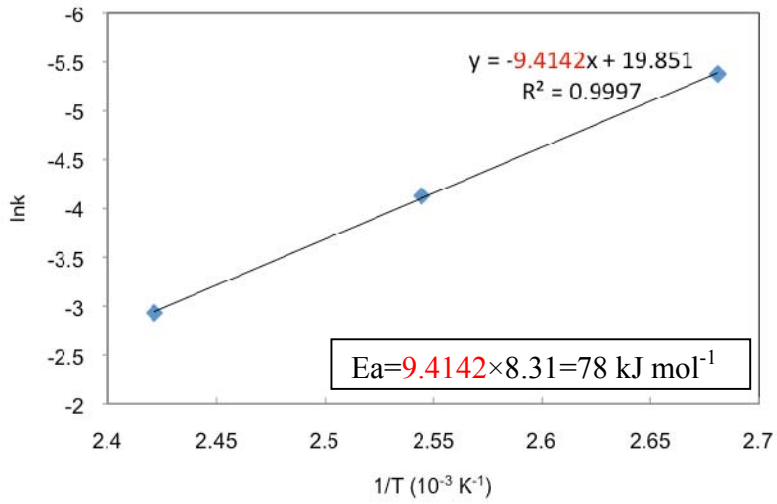


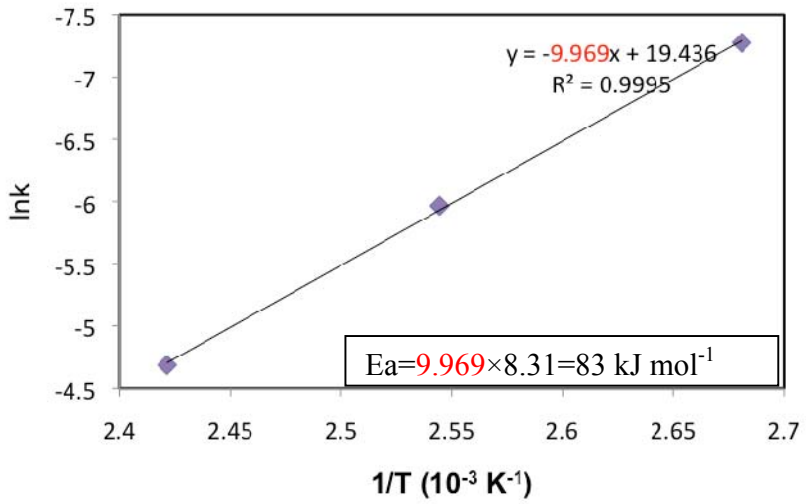
Figure S5. Comparison of cellobiose hydrolysis catalyzed by (a) CP-SO_3H and (b) PS-SO_3H (note: 500 mg resins, 100 mg cellobiose, 100ºC, 1 mL water, 2 hours)

Estimation of the activation energy of glycosidic bond cleavage with CP-SO_3H

The activation energy of cellobiose hydrolysis on two types of synthesized resins 2 ($t_{1/2}$ is half-life time). Half-life time at different temperatures was recorded for plotting, as shown in Figure S6.



(a)



(b)

Figure S6. Arrhenius plot of hydrolysis reactions of (a) cellobiose; (b) crystalline cellulose on CP-SO_3H.

Table S1. Activation energy of various solid acid catalysts

Catalyst	Activation energy (kJ/mol)	
	Cellobiose	Crystalline cellulose
Sulfuric acid	133[1]	170[2]
Carbon-SO_3H	/	110[2]
CP-SO_3H	78	83
Cellulase	3~50[3-4]	3~50[3-4]

Table S2. Diluted acid hydrolysis of cellulose

Concentration* (w/w)	Substrate	Time (hour)	Temperature (°C)	Yield (%)
0.5%	cellobiose	10	120	97
0.5%	Avicel cellulose	2	175	18
5%	Avicel cellulose	2	120	11
5%	Avicel cellulose	10	120	52
5%	Avicel cellulose	2	175	76**

Note: reaction conditions: 100 mg substrate, 1 ml aqueous solution. *: Acid concentration of aqueous solution; **: No cellulose solid left, but HMF was detected with a yield of 15% (molar yield on initial cellulose).

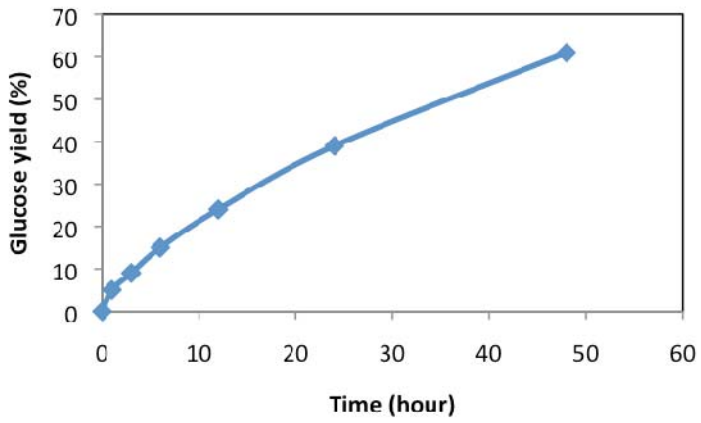


Figure S7. Enzymatic hydrolysis of Avicel cellulose (acetic acid buffer, pH=4.8, 50°C, 200 rmp，5 FPU cellulase/g cellulose, 15 CBU glucosidase/g cellulose, substrate concentration: 1 g/50 mL)

References

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