

## **Hydrolysis of cellulose into glucose over carbons sulfonated at elevated temperatures**

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## Supplemental Materials

### 1. Carbon materials

Active carbon (AC) was provided by NORIT Company. Acetylene carbon black (denoted as ACB) was provided by Lihujin Company, Tianjin, China. Multi-walled carbon nanotube (MWCNT) was supplied from Chengdu Organic Chemical Company. Coconut shell active carbon (refers to CSAC) was supplied by Jianxin Active Carbon Company, Tangshan, China.

CMK-3 was synthesized by a nanocasting method with SBA-15 as the hard template, according to Ryoo et. al (J. Am. Chem. Soc. 2000, **122**, 10712). In detail, 1 g of SBA-15 was impregnated with 1.25 g of sucrose, 0.14 g of concentrated H<sub>2</sub>SO<sub>4</sub>, and 5 g H<sub>2</sub>O, and the resultant mixture was left at ambient temperature overnight, and dried at 100 °C for 6 h and 160 °C for 6 h. The above impregnation procedure was repeated once again with 80% amount of the sucrose and concentrated sulfuric acid that was used in the first impregnation. The final solid was carbonized at 900 °C in N<sub>2</sub> for 6 h. The SBA-15 was removed by 5 wt% HF etching for 3 times. After filtration, washing, and drying at 100 °C overnight, the CMK-3 was obtained.

Cell-Carbon was prepared by carbonization of microcrystalline cellulose powder (Avicel) under N<sub>2</sub> flow at 400 °C for 5 h, according to the procedure reported by Hara et al. (J. Am. Chem. Soc. 2008, **130**, 12787).

Resin-Carbon was prepared by carbonization of a mesoporous resin, as we reported previously (Chem. Mater., 2008, **20**, 1881). In detail, 1.65 g (0.015 mol) of resorcinol was dissolved in a solution composed of 2.5 g of F127 (EO<sub>106</sub>PO<sub>70</sub>EO<sub>106</sub>) and 20 g of

ethanol/water (1/1 vol%) under stirring. When a light brown solution was formed, 0.2 g of HCl (37 wt%) was added as a catalyst. After stirring for 2 h, 2.5 g (0.030 mol, R/F = 1/2) of formaldehyde (37 wt%) was dropped into the above solution. Followed by an additional hour of stirring, the mixture was kept standing until it turned cloudy and began to separate into two layers. This two phase mixture was further kept aging for 96 h. Subsequently, the upper layer was discarded while the lower polymer-rich phase was stirred overnight until a sticky monolith was formed. Finally, the monolith was cured at 85 °C for 48 h and carbonized under a N<sub>2</sub> atmosphere at 800 °C for 3 h at a ramping rate of 1 °C/min.

## 2. Sulfonation of carbons

The sulfonation of carbons is described as following, with AC as an example. 2 g AC was added to 30 ml of concentrated sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, 98%) in a glass tube, and then was heated under the protection of nitrogen flow (10 ml/min) at 250 °C for 24 h (Note: other sulfonation temperatures were also investigated, such as 150, 200, 280, 300 °C, as shown in Table 1). After cooling and filtration, the solid was washed thoroughly with plenty of hot water (80 °C) until no SO<sub>4</sub><sup>2-</sup> was detected in the filtrate. Finally, the sulfonated carbon was heated at 200 °C in N<sub>2</sub> for 2 h, followed by filtration and washing with hot water.

## 3. Characterization methods

The X-ray diffraction (XRD) patterns of cellulose were obtained with an X'pert (PANalytical) diffractometer operated at 40 kV and 40 mA, using Ni-filtered Cu-K $\alpha$  radiation. The specific surface areas of the sulfonated carbons were measured by

nitrogen adsorption at  $-196\text{ }^{\circ}\text{C}$  on a Micromeritics ASAP 2010 instrument. The Brunauer-Emmett-Teller (BET) method was used to calculate the specific surface areas.

The saturated water uptakes of sulfonated carbon were determined by a static adsorption method. Prior to the adsorption, about 0.1 g of sulfonated carbon was dried at  $60\text{ }^{\circ}\text{C}$  in vacuum ( $1.0 \times 10^3\text{ Pa}$ ) until a constant weight ( $W_0$ ). For water adsorption measurement, the sample was placed in a desiccator containing an aqueous solution saturated with sodium chloride (NaCl) and maintained at  $35\text{ }^{\circ}\text{C}$  for 48 h until a constant value ( $W_1$ ). The saturated water uptake was calculated as  $(W_1 - W_0)/W_0 \times 100\%$ .

The acid densities of the sulfonated carbons were determined by two different methods: titration method and  $\text{NH}_3$ -adsorption method. For the titration method, 0.05 g of a carbon sample was added into an aqueous solution of sodium hydroxide ( $0.01\text{ mol L}^{-1}$ , 20 mL). Then, the suspension was dispersed uniformly in an ultrasonic bath at room temperature for 60 min. After centrifugal separation, the supernatant solution was titrated by an aqueous solution of hydrochloric acid ( $0.01\text{ mol L}^{-1}$ ) using phenolphthalein as an indicative. The  $\text{NH}_3$ -adsorption experiments were performed on a Micromeritics Autochem 2910 instrument. Typically, 0.1 g of a carbon sample was loaded into a quartz reactor and pretreated in He at  $200\text{ }^{\circ}\text{C}$  for 2 h. After the sample was cooled to  $100\text{ }^{\circ}\text{C}$  in He stream, pulses of  $\text{NH}_3$  were dosed in until saturation. The uptakes of  $\text{NH}_3$  were auto-calculated accordingly.

The density of  $\text{SO}_3\text{H}$  groups, as well as the leaching of  $\text{SO}_3\text{H}$  groups during the

reaction, was determined by elemental analysis of S, using ICP-AES (Inductively coupled plasma atomic emission spectroscopy) on an IRIS Intrepid II XSP instrument (Thermo Electron Corporation).

#### 4. Reaction tests

Prior to the hydrolysis reaction, the microcrystalline cellulose (Avicel) was pretreated by ball-milling at room temperature for 48 h, with ZrO<sub>2</sub> balls and a speed of 500 rpm (PM 100, RETSCH ball mills, 50 ml).

The hydrolysis of cellulose was carried out in a stainless-steel autoclave with autogenous pressure. For each reaction, 0.27 g of cellulose, 0.3 g of catalyst and 27 ml of water were put into the reactor and stirred at a rate of 100 rpm. The reaction proceeded at 150 °C for 24 h. After the reaction, the mixture was centrifuged to separate the solid (containing the catalyst and the unreacted cellulose) and liquid phases. The liquid phase was analyzed by HPLC equipped with a column of Shodex Sugar SC 1011. The total organic carbon in the liquid phase was determined by TOC analyzer (Elementar). The carbon content in the cellulose was determined by a CHNS analyzer. The yield of glucose was calculated from the equation:  $Y_{\text{glu}} (\text{C}\%) = (\text{moles of glucose in the liquid phase} \times 6) / (\text{moles of carbon in cellulose fed into the reactor}) \times 100\%$ . The conversion of cellulose was calculated as:  $\text{Conv.}(\text{C}\%) = (\text{moles of total organic carbon in the liquid phase}) / (\text{moles of carbon in cellulose fed into the reactor}) \times 100\%$ . Yield of water soluble by-products was calculated by the difference between the cellulose conversion and the glucose yield.

#### 5. Results

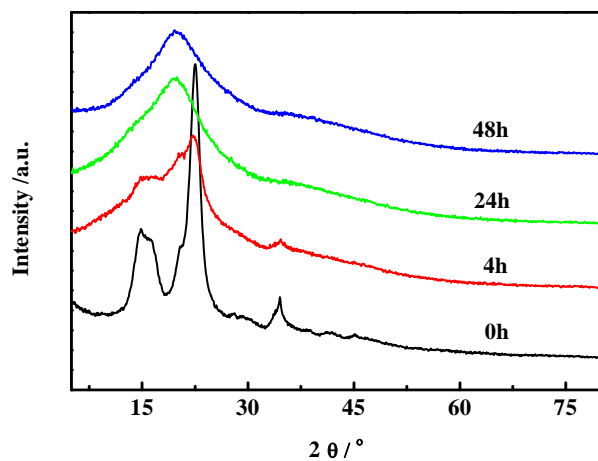


Figure S1. XRD patterns of microcrystalline cellulose pretreated by ball-milling for different time.

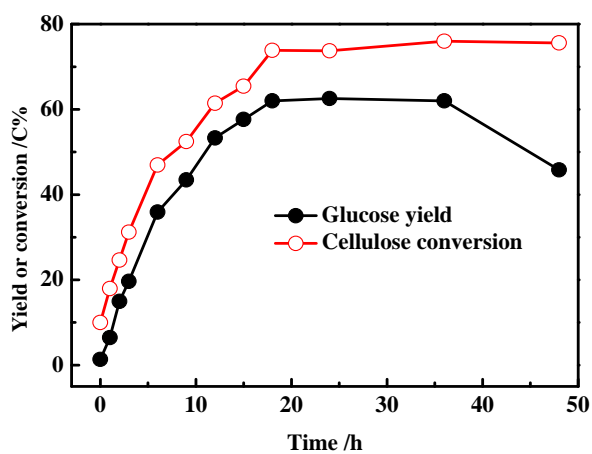


Figure S2. Glucose yield and cellulose conversion as a function of the reaction time.

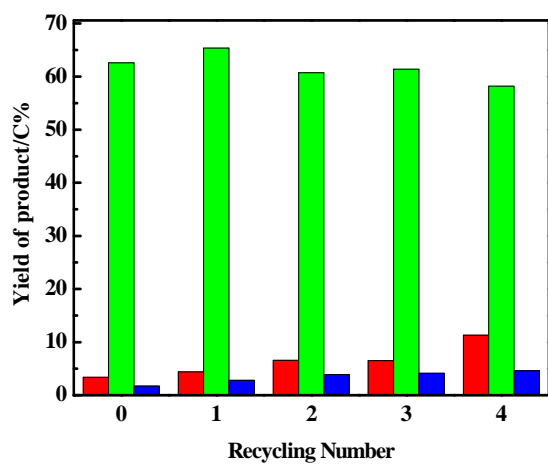


Figure S3. Tests for the reusability of AC-N-SO<sub>3</sub>H-250 catalyst. Red for cellobiose, green for glucose and blue for fructose.

Table S1. The -SO<sub>3</sub>H contents and acid densities of catalysts before and after recycling tests.

Catalyst	-SO <sub>3</sub> H <sup>a</sup> /mmolg <sup>-1</sup>	Acid density <sup>b</sup> /mmolg <sup>-1</sup>	S in solution /ppm
Fresh AC-N-SO <sub>3</sub> H-250	0.44	2.23	---
AC-N-S-250 after the 4 <sup>th</sup> recycling test	0.42	2.22	n.d. <sup>c</sup>

<sup>a</sup> The content of -SO<sub>3</sub>H was measured by ICP. <sup>b</sup> The acid density was determined by titration method. <sup>c</sup> The S leached in solution was too low to be detected by ICP-AES.