Supporting information

Selective conversion of concentrated microcrystalline cellulose to isosorbide over Ru/C catalyst

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1. Experimental

1.1 Conversion of cellulose

Ru/C, Pd/C, Pt/C (Wako, 5 wt%), microcrystalline cellulose (Alfa Aesar, relative crystallinity of about 74%) were used as received, H_2SO_4 (96%, GR), HCl (37%, GR) were purchased from Beijing Chemical. In a typical reaction, microcrystalline cellulose, mineral acids, supported catalysts and water were loaded in a 50 ml teflon-lined stainless steel autoclave. The reactors was flushed with N_2 for three times and then pressurized with 6 MPa H_2 (RT), the reactor was preheated in oil bath to the desired temperature with stirring at a low agitating rate. Then the reaction was started with stirring at a rate of 1300 rpm. After reaction the reactor was cooled to room temperature and the products were filtrated to separate the remaining solid, the solid was dried at 353 K overnight and weighed. The conversion was calculated by weight difference of solid before and after reaction. The products were analyzed and identified by using HPLC and GC-MS. The yield of each product was calculated as follows: yield (%) = (moles of each product)/(moles of anhydraglucose in cellulose)×100%.

In a cycle test, since cellulose was completely converted at the reaction conditions, the remaining solid catalyst was centrifuged and washed by dilute hydrochloric acid solution for three times and dried at 323 K for 8 h, used for the next run.

1.2 Conversion of sorbitol

0.2 g sorbitol (AR, Aladdin), 20 mg Ru/C catalyst, 10 ml dilute acid solution ($[H^+]$=0.10 M) were loaded in the reactor. The reactor was pressured to 6 MPa (RT) by hydrogen. The experiments were conducted at the identical conditions as used for cellulose.

1.3 Products analysis

The products were acetylated firstly and then analyzed by GC/MS (Agilent 5975/6890N) with a HP-5 column (30 m×0.25 um×0.25 mm i.d). The products were also identified by using ^{13}C NMR (Bruker Avance 300 MHz NMR Spectrometer). The product mixture was dried in a vacuum oven and then dissolved in D_2O solution as the sample for analysis. The liquid phase was measured with HPLC system (Shimadzu LC-20AB) with RI detector (Shimadzu RID-10A), and a Aminex HPX-87H column (Bio-Rad, 300×7.8 mm), using 0.5 mM H_2SO_4 as eluent at a flow rate of 0.7 ml/min at 323 K.

Table S1. Results for the conversion of sorbitol over Ru/C catalyst[a]

			Yield (%)			
Entry	T/K	Conversion (%)	Sorbitol	1,4-sorbitan + 3,6-sorbitan	2,5-mannitan + 2,5-iditan	isosorbide
1	468	79.4	20.6	52.4	8.2	8.8
2	478	91.7	8.3	67.3	9.1	20.6
3	498	95.0	5.0	21.4	11.7	47.5
4	508	94.7	5.3	7.4	10.0	56.9
5	518	95.1	4.9	3.9	6.2	56.0

[a] Reaction conditions: sorbitol 0.2 g, Ru/C 20 mg, H_2O 10 ml, HCl 0.10 M, H_2 6.0 MPa (RT), 1h.

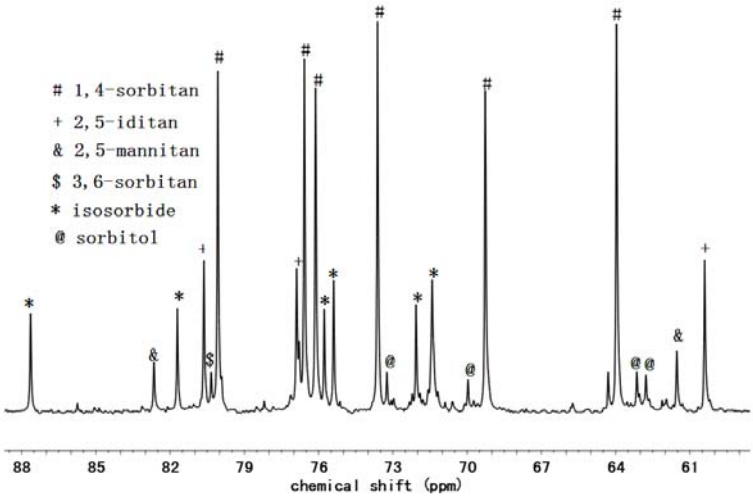

Figure S1 ^{13}C NMR spectra of product mixture in D_2O solution.

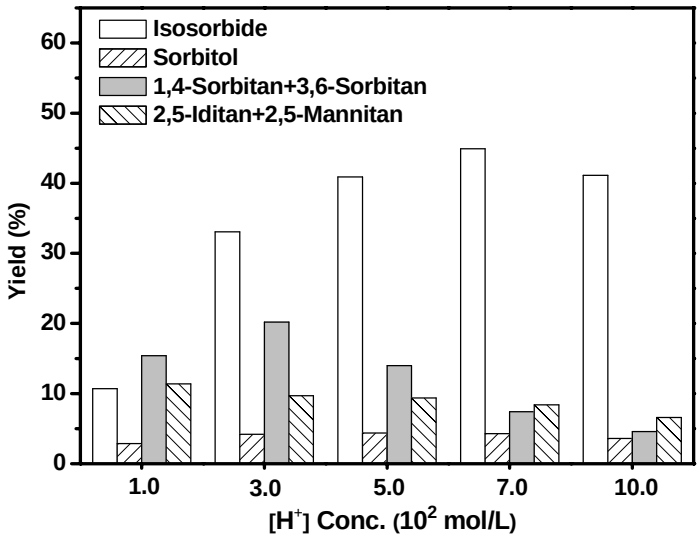

Figure S2 Effect of H^+ concentration on product distribution of cellulose conversion. Reaction conditions: cellulose 0.2 g, Ru/C 20 mg, H_2O 10 ml, HCl 0.10 M, 508 K ,60 min H_2 6.0 MPa (RT)

2 Characterization

2.1 XRD

The powder X-ray diffraction (XRD) was used to characterized the microcrystalline cellulose with a Bruker D8 Focus X-ray diffractometer using $Cu_{k\alpha}$ radiation (λ = 0.154 nm) , in a 2θ range of 10-50°.

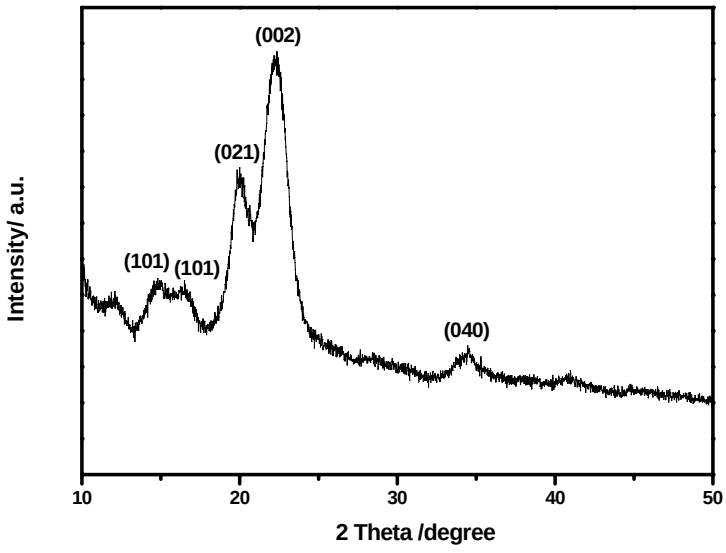

Figure S3 XRD pattern of microcrystalline cellulose

2.1 TEM

TEM micrographs were obtained on a PEI Tecnai F20 transmission electron microscope operating at 200 keV.

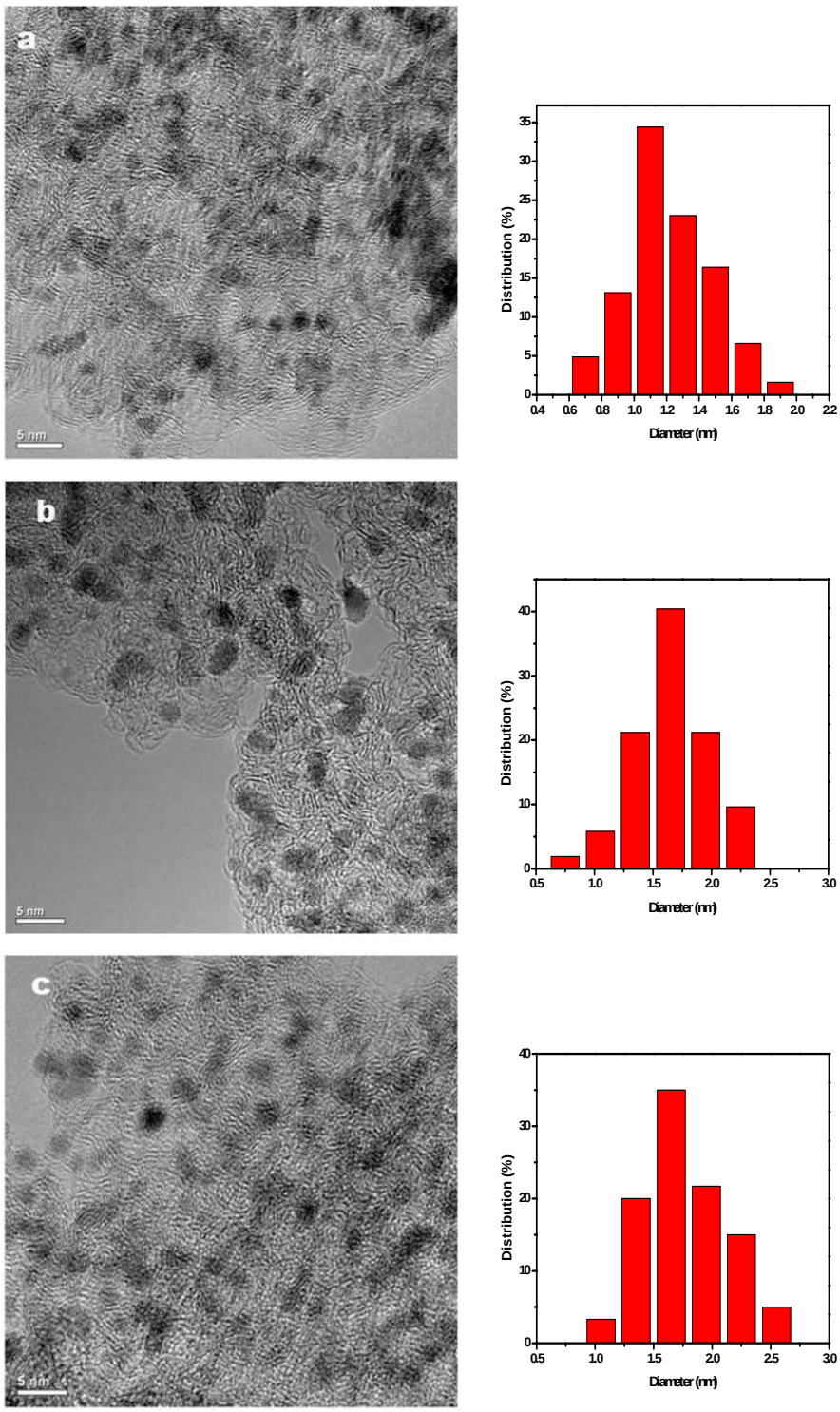

Figure S4 TEM images and histograms of Ru particle size distribution for the Ru/C catalysts (a) fresh, (b) after the first run, and (c) after the fourth run.