Supporting Information

Transfer hydrogenation of cellulose to sugar alcohols over supported ruthenium catalysts

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Reaction Procedure

Cellulose (Merck, Avicel) was milled using ZrO_2 balls at 60 rpm for 4 days as the pre-treatment. Transfer hydrogenation of cellulose was carried out in a stainless steel (SUS316) high-pressure reactor (OM Lab-Tech MMJ-100, 100 mL). The milled cellulose (324 mg, 1.90 mmol glucose units, containing 4.8 wt% physisorbed water), supported Ru catalyst (50 mg), water (30 mL) and 2-propanol (10 mL) were charged in the reactor (glucose unit/Ru = 190), and then purged with 1 atm of N_2 or He. The mixture was heated to 463 K and maintained at this temperature for 18 h with stirring at 600 rpm.

Analysis methods of products

The products were separated by centrifugation and decantation, and the water-soluble products were analysed by high-performance liquid chromatography (HPLC; Shimadzu LC10-AT*VP*, refractive index detector). The columns used in this work were a Phenomenex Rezex RPM-Monosaccharide Pb++ column (ø7.8 × 300 mm, mobile phase: water 0.6 mL min^{-1}, 353 K) and a Shodex Sugar SH-1011 column (ø8 × 300 mm, mobile phase: water 0.5 mL min^{-1}, 323 K). A typical example is shown in Fig. S1.

Characterisation of Ru catalysts

X-ray diffraction (XRD; Rigaku Miniflex) measurements were conducted using Cu Kα radiation and energy dispersive X-ray spectroscopy (EDX; Shimadzu EDX-720) was carried out using Rh target. The electron binding energy of Ru $3p_{3/2}$ was determined by X-ray photoelectron spectroscopy (XPS; JEOL JPC-9010MC). H_2-temperature programmed reduction (H_2-TPR) was performed by using Quantachrome CHEMBET-3000 (detector: TCD).

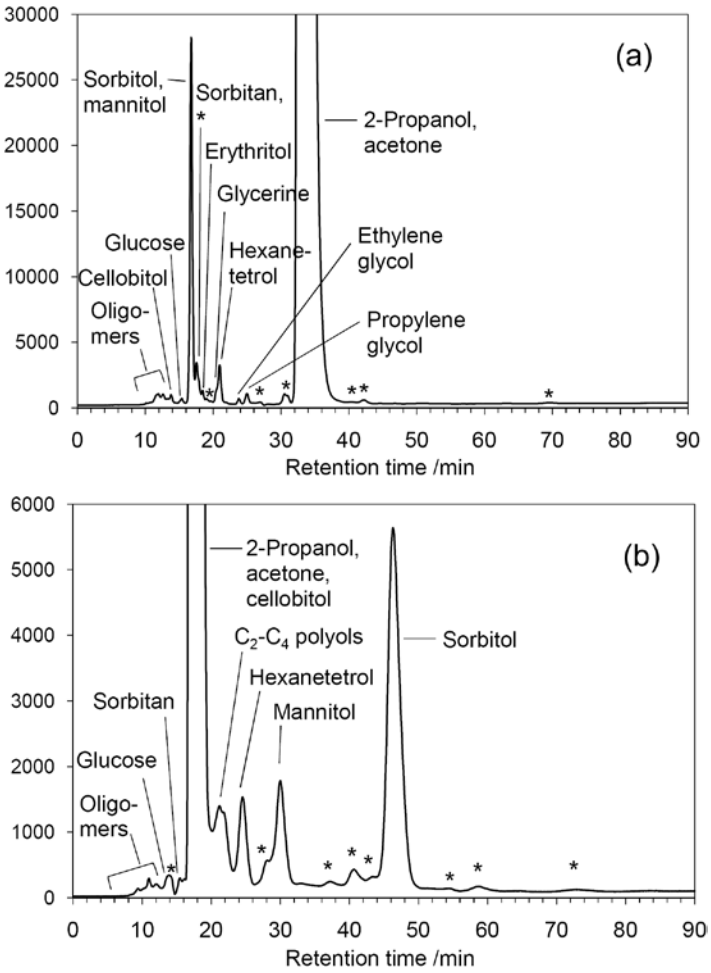

Fig. S1 HPLC analysis for the reaction by Ru/AC(N) catalyst shown in Table 1 entry 3 with (a) a Sugar SH-1011 column and (b) a Rezex RPM-monosaccharide Pb++ column. The asterisks indicate unidentified products. Cellobitol: 4-*O*-*β*-glucopyranosyl-D-glucitol.

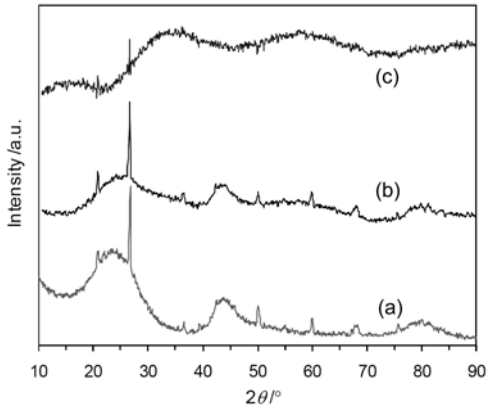

Fig. S2 XRD patterns of (a) AC(N), (b) 10 wt% Ru/AC(N) and (c) the differential pattern of (b)–(a).

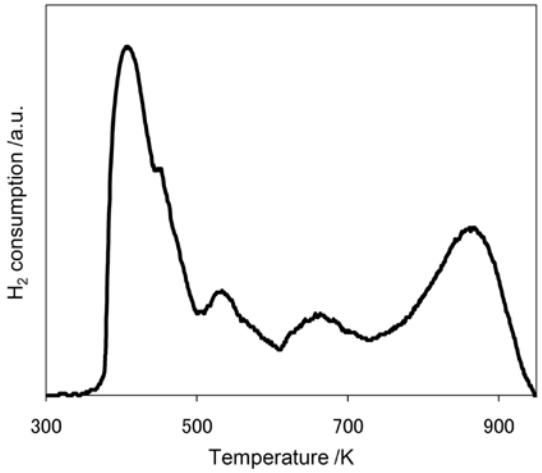

Fig. S3 H_2-TPR of Ru/AC(N).

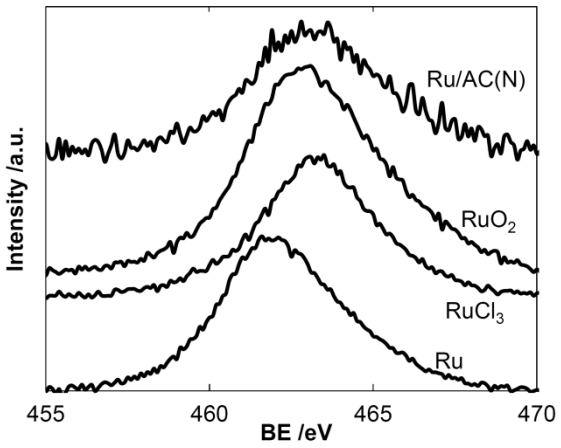

Fig. S4 Ru $3p_{3/2}$ XPS of Ru/AC(N) and standard compounds.

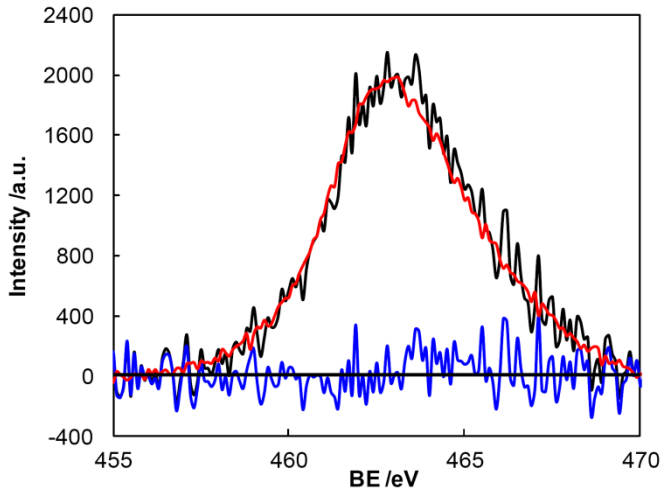

Fig. S5 Curve fitting of Ru $3p_{3/2}$ XPS for Ru/AC(N) using the data of reference compounds. Black line: Ru/AC(N), red line: the fitting curve (sum of 99.7% RuO_2 and 0.3% Ru metal), blue line: the difference between Ru/AC(N) and the fitting curve.

Table S1 Effect of the concentration of 2-propanol on the transfer hydrogenation of cellulose by Ru/AC(N) catalyst.[a]

Entry	Concentration of 2-propanol /vol%	Yield based on carbon /%								Cellulose conv.[e] /%	Yield of acetone /%
		Sorbitol	Mannitol	Sum of sorbitol and mannitol	Sorbitan	C_2-C_4 polyols[b]	Glucose	5-HMF[c]	Others[d]		
21	0	0	0	0	0	0	1.6	8.8	64	74	–
22	5	3.1	1.0	4.1	0	0	1.5	2.9	71	79	12 (40)[f]
23	13	31	6.5	38	1.2	5.7	0.7	0	30	76	22 (20)[f]
24	20	33	9.6	43	1.5	4.3	0.8	0	27	77	16 (20)[f]
3	25	34	9.0	43	0.6	6.1	0.9	0	23	74	15 (24)[f]
25	38	24	10	34	0.5	4.3	0.6	0	32	71	10 (30)[f]
26	50	21	10	31	0.5	0	1.1	0	31	64	8.0 (35)[f]
27	75	12	8.5	21	0.3	0	0	0	38	59	8.3 (81)[f]
28	100	0	0	0	0	0.4	0	0	22	22	5.6

[a] Cellulose 324 mg (1.90 mmol), catalyst 50 mg (metal 2 wt%), water + 2-propanol 40 mL, 463 K, 18 h. [b] Sum of erythritol, glycerine, propylene glycol and ethylene glycol. [c] 5-Hydroxymethyl furfural. [d] Others include soluble sugar compounds and unidentified ones. [e] Based on the carbon balance calculated from the weight difference after the reaction. [f] Ratio of acetone yield against the sugar alcohols yield (mol/mol).

Table S2 Screening tests of alcohols on the transfer hydrogenation of cellulose by Ru/AC(N) catalyst.[a]

Entry	Alcohol	Yield based on carbon /%								Cellulose conv.[e] /%	Yield of aldehyde or ketone /%
		Sorbitol	Mannitol	Sum of sorbitol and mannitol	Sorbitan	C_2-C_4 polyols[b]	Glucose	5-HMF[c]	Others[d]		
29	Ethanol	0	0	0	0	0	0.2	0	70	70	N.d.
3	2-Propanol	34	9.0	43	0.6	6.1	0.9	0	23	74	15 (24)[f]
30	Glycerine	0.7	0	0.7	0	0	1.0	3.2	69	74	N.d.
31	2-Butanol	3.0	1.5	4.5	0	5.6	1.6	0	58	70	24 (300)[f]

[a] Cellulose 324 mg (1.90 mmol), catalyst 50 mg (metal 2 wt%), water 30 mL, alcohol 10 mL, 463 K, 18 h. N.d.: Not determined. [b] Sum of erythritol, glycerine, propylene glycol and ethylene glycol. [c] 5-Hydroxymethyl furfural. [d] Others include soluble sugar compounds and unidentified ones. [e] Based on the carbon balance calculated from the weight difference after the reaction. [f] Ratio of the ketone yield against the sugar alcohols yield (mol/mol).