Electronic Supplementary Information

Synthesis of sugar alcohols by hydrolytic hydrogenation of cellulose over supported metal catalysts

Hirokazu Kobayashi,[a] Yukiko Ito,[a] Tasuku Komanoya,[ab] Yuto Hosaka,[ab]

Paresh L. Dhepe,[a‡] Koji Kasai,[a] Kenji Hara[a] and Atsushi Fukuoka*[a]

[a] Catalysis Research Centre, Hokkaido University, Kita 21 Nishi 10, Kita-ku, Sapporo 001-0021, Japan

[b] Graduate School of Chemical Sciences and Engineering, Kita 13 Nishi 8, Kita-ku, Sapporo 060-8628, Japan

‡ Present address: National Chemical Laboratory, Pune 411008, India.

* E-mail: fukuoka@cat.hokudai.ac.jp, Fax: +81 11 706 9139

Table S1. Hydrogenation rate of sugars by $Pt_{(N)}$/BP2000 catalyst at 373 K.[a]

Entry	Substrate	Initial formation rate[b] /mM h^{-1} (Yield at 0.5 h)	
		Sorbitol	Mannitol
S1	Glucose	2.7 (5.4%)	0.0 (0.0%)
S2	Fructose	5.3 (10.5%)	4.4 (8.8%)
S3	Mannose	0.0 (0.0%)	4.4 (8.7%)

[a] Reaction conditions; sugar 180 mg (25 mM), $Pt_{(N)}$/BP2000 195 mg, water 40 mL, T=373 K, $P(H_2)$=5.0 MPa. [b] The average rate in the short reaction (0.5 h).

Table S2. Degradation of cellulose without catalysts at 463 K.[a]

Reaction time /h	Yield based on carbon /%								Cellulose conv.[b] /%
	Glucose	Oligo-saccharides	Fructose	Mannose	Levo-glucosan	5-Hydroxy-methylfurfural	Furfural	Others	
0	0.1	1.6	0	0	0	0	0	<0.5	0.5
1	1.5	5.6	0.4	0.3	0.1	1.1	0.6	<0.5	7.0
4	6.3	3.0	0.6	0.3	0.7	7.6	1.9	9.4[c]	29.8
12	10.8	2.5	N.d.[d]	N.d.[d]	0.8	15.8	3.0	33.2	66.1
16	7.4	2.0	N.d.[d]	N.d.[d]	0.4	13.5	3.6	44.1	71.0

[a] The detail of products analysis in Fig. 9. Sorbitol and mannitol were not found at all reaction times. [b] Based on the loss of weight during the reaction. [c] Formic acid 0.6%, glycolic acid 0.8% and lactic acid 0.9% were detected by HPLC with a UV detector (210 nm) using a Synergi 4μ Hydro-RP column (ø4.6×250 mm, mobile phase: 20 mM phosphate buffer pH 2.9, 0.7 mL min^{-1}, 298 K). [d] Not determined because of overlapping of unidentified products.
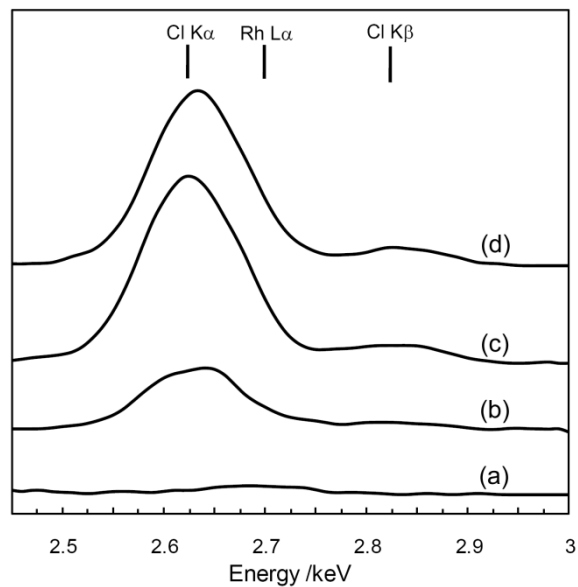
Fig. S1. EDX measurements of (a) $Pt_{(N)}/Al_2O_3$, (b) $Pt_{(Cl, N)}/Al_2O_3$, (c) $Pt_{(Cl)}/Al_2O_3$ and (d) 1 wt% Cl/Al_2O_3. Trace Rh Lα line is from the target of X-ray tube.
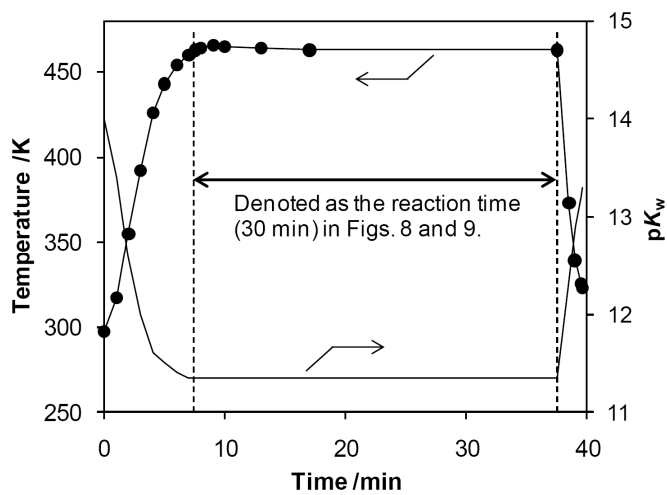

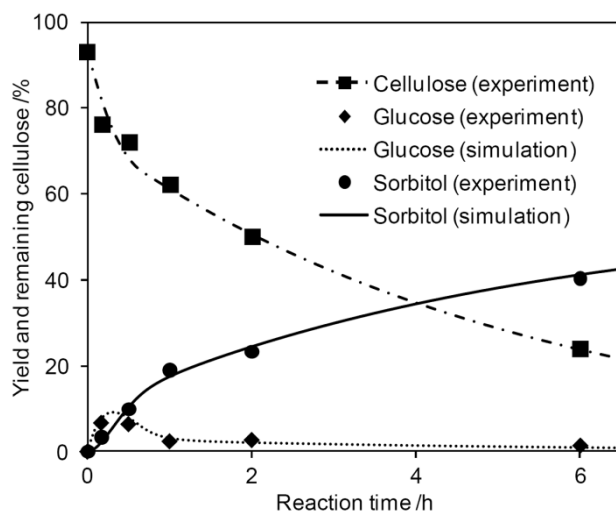Fig. S2. Profiles of the reaction temperature and pK_w of water in the conversion of cellulose for 40 min.

Fig. S3. Curve fitting of the time course of glucose and sorbitol (Fig. 8) using Eq. 2 and k_G=2.8 h^{-1}. The initial distribution of products at 0 h and the conversion curve of cellulose in the simulation were from those in the actual experiments. The selectivity for sorbitol in the experiment was 59% at 24 h (Table 1 entry 8), and therefore the rate constant of side-reactions from glucose was assumed as 1.9 h^{-1} [k_G×(100%–59%)/59%] in the simulation.