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

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Cellulose is converted into sorbitol and related sugar compounds over water-tolerant and durable carbon-supported Pt catalysts under aqueous hydrogenation conditions. Pre-treatment of cellulose
 10 with ball-milling effectively reduces the crystallinity and particle size of cellulose, which results in high conversion of cellulose to sorbitol and mannitol. The selectivity of sorbitol increases by using Cl-free metal precursors in the catalyst preparation as residual Cl on the catalysts promotes the side-reactions. The transformation of cellulose to sorbitol consists of the hydrolysis of cellulose to glucose via water-soluble oligosaccharides and the successive hydrogenation of glucose to sorbitol.
 15 The hydrolysis of cellulose is the rate-determining step, and the Pt catalysts promote both the hydrolysis and the hydrogenation steps.

Introduction

Catalytic conversion of biomass to fuels and chemicals has attracted great attention as one of the future technologies for
 20 inhibiting the global warming and for building up the low-carbon society.¹⁻³ In the photosynthesis reaction, huge amount of carbohydrates and oxygen are produced from carbon dioxide and water in plants using sunlight, and the plant biomass is a potentially abundant and renewable resource.
 25 Recently, the use of edible biomass for producing bioethanol has resulted in a competition between food and fuel, and this lesson has given us a consensus that we should use nonfood biomass as a precursor to fuels and chemicals. A typical nonfood biomass is lignocellulose in cell walls of plants.
 30 Lignocellulose is composed of cellulose, hemicellulose and lignin, in which cellulose is a main component in woods.⁴ Therefore, the first target among nonfood biomass is cellulose.⁵

Cellulose is a polymer of D-glucose, and starch is also a
 35 polymer of glucose. They have different properties derived from the contrastive configuration of C–O bonding in polymer chains. In amylose of starch, glucose units are linked by α -1,4-glycosidic bonds, while in cellulose they are joined together through β -1,4-glycosidic bonds (Fig. 1). Although
 40 both polymers form crystalline structures with extensive intra- and inter-molecular hydrogen bonds, those of amylose are relatively weak, and amylose is gelatinised in hot water. On the other hand, those of cellulose are remarkably more rigid and impenetrable even by hot-compressed water at <590 K.^{5,6}
 45 As a result, cellulose is greatly more resistant to depolymerisation than starch.

An extensive number of works have been devoted to the degradation of cellulose using enzymes, mineral acids and supercritical water,^{4, 7-9} but these methods have drawbacks
 50 such as slow reaction rate, difficult separation of products and catalysts, corrosion hazards, harsh conditions and generation

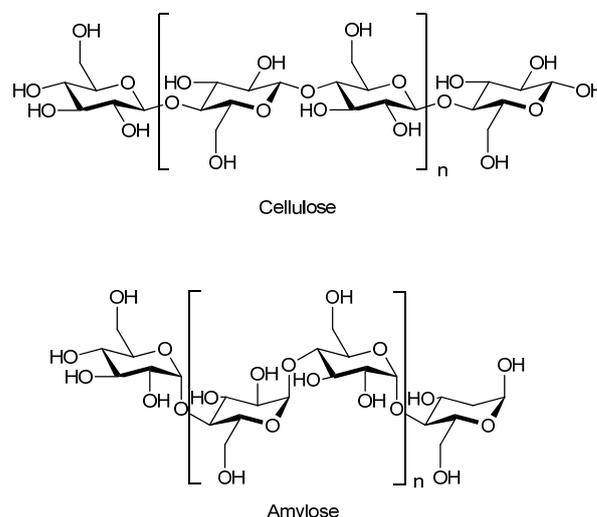


Fig. 1 Structures of cellulose and amylose.

of large amount of neutralisation waste. Heterogeneous
 55 catalysis has advantages to overcome these drawbacks. We reported the first catalytic degradation of cellulose into sugar alcohols such as sorbitol and mannitol by supported metal catalysts under hydrogenolysis conditions.¹⁰ The sugar alcohols are useful precursors for the production of plastics
 60 and pharmaceuticals. Since then the cellulose conversion by heterogeneous catalysis has rapidly developed for the synthesis of sugar alcohols,¹¹ ethylene glycol¹² and glucose.¹³ The hydrogenolysis reaction using supported metal catalysts has also been investigated on the conversion of lignin and its
 65 model compounds.¹⁴ However, there still remains a need to improve the productivity in the synthesis of sugar alcohols. In this work, we studied the several factors controlling the reactivity of cellulose and the catalytic activity to discuss the detail of the reaction mechanism.

Experimental

Catalyst preparation

Catalyst supports used in this study were as follows: carbon blacks BP2000 (Black Pearls 2000) and VULCAN XC72 were supplied from Cabot. Activated carbon denoted as AC (Norit SX Ultra) was purchased from Aldrich. Al_2O_3 (JRC-ALO-2) and ZrO_2 (JRC-ZRO-2) were obtained from Catalysis Society of Japan, and TiO_2 (P-25) from Degussa.

The supported metal catalysts prepared from $\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2$, $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$, H_2PtCl_6 , $\text{Ru}(\text{NO})(\text{NO}_3)_3$ and RuCl_3 were denoted as $\text{Pt}_{(\text{N})}$, $\text{Pt}_{(\text{Cl}, \text{N})}$, $\text{Pt}_{(\text{Cl})}$, $\text{Ru}_{(\text{N})}$ and $\text{Ru}_{(\text{Cl})}$, respectively. Other metal precursors used in this study were $\text{Rh}(\text{NO}_3)_3$, $\text{Ir}(\text{acac})_3$ and $\text{Pd}(\text{NO}_3)_2$. The typical catalyst, $\text{Pt}_{(\text{N})}/\text{BP2000}$ (Pt metal loading 2 wt%) was prepared by a conventional impregnation method as follows: $\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2$ aq. (0.202 mmol in 5 mL of water) was dropped into a mixture of carbon black BP2000 and water (20 mL), and the mixture was stirred for 16 h. After drying *in vacuo*, the solid was reduced with H_2 (30 mL min^{-1}) at 673 K for 2 h. In the preparation using oxide supports, the catalyst precursors were calcined in O_2 flow (30 mL min^{-1}) at 673 K before the H_2 -reduction, and in the impregnation of $\text{Ir}(\text{acac})_3$, CH_2Cl_2 was used as the solvent. The catalyst was analysed by using energy dispersive X-ray spectroscopy (EDX; Shimadzu EDX-720), X-ray diffraction (XRD; Rigaku Miniflex, Cu $\text{K}\alpha$ radiation) and CO adsorption measurement (Quantachrome, ChemBET-3000).

Pre-treatment of cellulose

Cellulose was pre-treated using a ball-mill (Nitto Kagaku, ANZ-51S). Cellulose (Merck, Avicel microcrystalline, 10 g) was charged in a rotary ceramic container with ZrO_2 balls (1 kg, 1 cm diameter).¹⁵ The container was rotated at a speed of 60 rpm for 2 days (48 h) or 4 days (96 h). The ball-milled cellulose was characterised by XRD, cross polarisation/magic angle spinning nuclear magnetic resonance (CP/MAS NMR; Bruker MSL-400, ^{13}C 100.6 MHz, rotation rate 4 kHz, external standard: glycine), optical microscope (Keyence VHX-1000) and laser diffraction (Nikkiso Microtrac MT3300EXII). The amount of physisorbed water was determined by using a total organic carbon analyser (TOC; Shimadzu SSM-5000A) and weight loss in vacuum drying at 373 K, and both experiments indicated that the water content was 5.0 ± 1.0 wt% in the cellulose ball-milled for 2 days.

Hydrogenation of cellulose

The conversion of cellulose under H_2 pressure, denoted as hydrogenation of cellulose, was conducted 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 5.0 wt% physisorbed water), a supported Pt catalyst (195 mg, Pt 20 μg -atom) and water (40 mL) were charged in the reactor (molar ratio of glucose unit/Pt = 95), and then pressurised with H_2 of 5.0 MPa. The reactor was heated to 463 K and maintained at the temperature for 24 h with stirring at 600 rpm. Products were separated by centrifugation and decantation, and water-soluble products

were analysed by high-performance liquid chromatography (HPLC; Shimadzu LC10-ATVP, refractive index detector). The columns used in this work were a Phenomenex Rezex RPM-Monosaccharide Pb⁺⁺ column ($\phi 7.8 \times 300$ mm, mobile phase: water 0.6 mL min^{-1} , 353 K) and a Shodex Sugar SH-1011 column ($\phi 8 \times 300$ mm, mobile phase: water 0.5 mL min^{-1} , 323 K).

Results and discussion

Pre-treatment of cellulose

Cellulose has crystalline and amorphous parts in its structure. It is known that the amorphous region is first attacked by acids in the hydrolysis reaction¹⁶ as cellulose I_α crystal, which is a typical crystal phase of natural cellulose, has 8 hydrogen bonds for each glucose unit, while the number of those in amorphous cellulose is 5.3.¹⁷ Likewise, it has been reported that amorphous cellulose is hydrolysed more rapidly than crystalline one by enzyme mixtures,¹⁸ although different cellulase enzymes have different preferential reaction sites on cellulose.¹⁹ The conversion of crystalline region into amorphous one gives higher reactivity to cellulose. Various methods have been reported for the pre-treatment of cellulose

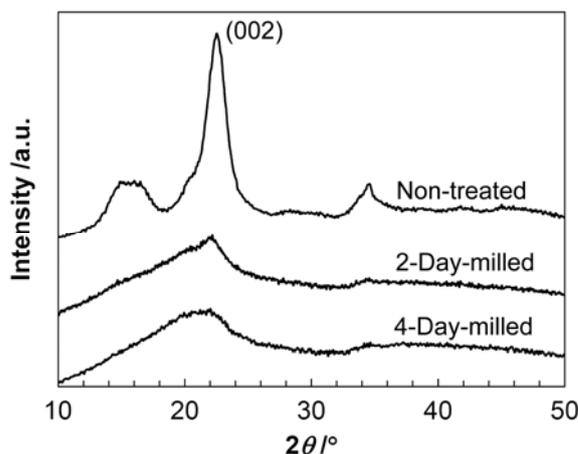


Fig. 2 XRD patterns of ball-milled cellulose.

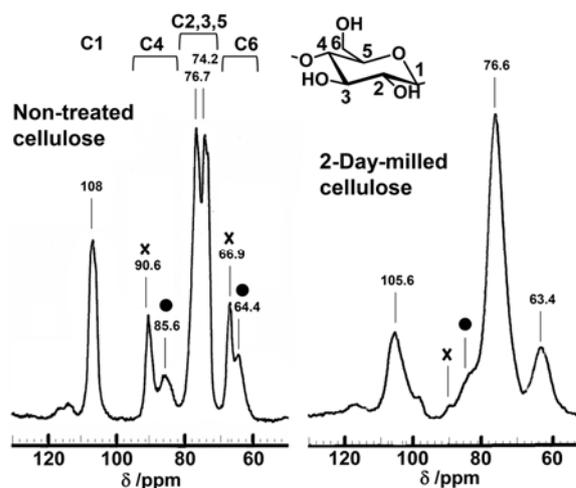


Fig. 3 CP/MAS ^{13}C NMR of cellulose with or without the pre-treatment. X: crystalline part, filled circles: amorphous part.

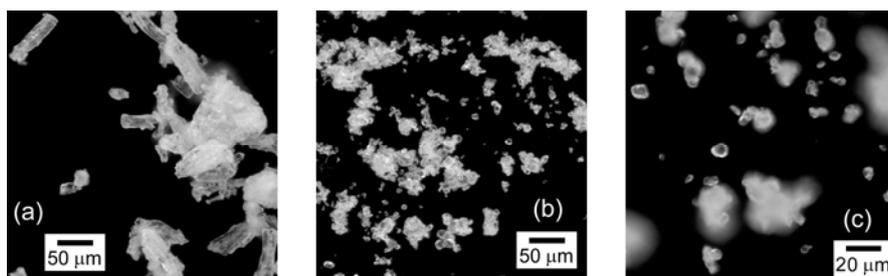


Fig. 4 Optical microscope images of (a) non-treated cellulose and (b, c) cellulose ball-milled for 2 days.

to reduce the crystallinity, and in our study ball-milling was selected for this purpose. Fig. 2 depicts the change of XRD diffractions of the cellulose after the pre-treatment. The intensity of (002) diffraction at 22.5° clearly decreased by the treatment. The crystallinity index (CrI) of each cellulose was 81% (non-treated), 22% (2-day-milled) and 14% (4-day-milled), estimated from the intensity difference of the (002) diffraction and that of amorphous part.^{7a,20} The CrI of cellulose significantly lowered during the pre-treatment for 2 days, but further milling gave no improvement. Thus, we compared the non-treated and 2-day-milled cellulose in the further characterisation.

The CrI can also be estimated by solid-state NMR. Fig. 3 exhibits CP/MAS ^{13}C NMR spectra of non-treated and 2-day-milled cellulose. C1-C6 carbons of pyranose ring resonate at 60-110 ppm, and the peaks at 82-92 ppm are assigned to C4. The C4-peak is allowed to be divided into two parts; the lower-field peak is assigned to crystalline part and the higher-field one is derived from amorphous part.²¹ The CrI calculated from the area ratio of the two peaks were 65% for the non-treated cellulose and 10% for the 2-day-milled cellulose. These CrI values are similar to those determined by XRD. Accordingly, we confirmed that the crystallinity is effectively decreased by the ball-milling treatment.

Non-treated cellulose had various shapes as shown in Fig. 4(a). A typical dimension of needle-type one was ca. $20 \times 50 \mu\text{m}$ and some parts were aggregated to make large secondary particles. After the ball-milling for 2 days, cellulose turned smaller particles and their major part was aggregated [Fig.

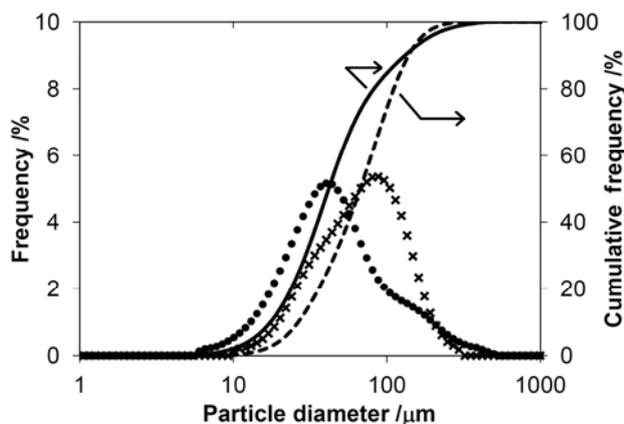


Fig. 5 Distribution of the particle diameter of cellulose in water. \times and dashed line: non-treated cellulose. Circles and solid line: 2-day-milled cellulose.

4(b)]. The primary particles with spherical or ellipsoidal structures in the range of $2\text{-}10 \mu\text{m}$ were observed in a higher magnification image [Fig. 4(c)]. The ball-milling treatment changes both the particle size and the morphology.

Fig. 5 shows the distribution of the secondary particle diameter of cellulose in water. We assume that this analysis reflects the valid specific surface area of cellulose to be contacted with bulk solid catalysts. The diameter range of the non-treated cellulose was $10\text{-}300 \mu\text{m}$ and the median diameter (the diameter that the cumulative frequency is 50%) was $67 \mu\text{m}$, which conforms to the particle diameter observed by the microscope. The distribution shifted lower and the median diameter diminished to $42 \mu\text{m}$ by the pre-treatment for 2 days. Although the ball-milled cellulose is rather aggregated in water as the secondary particles are one-order of magnitude larger than the primary particles, the size is still smaller than that of non-treated cellulose.

From these results, it is demonstrated that the ball-milling treatment decreases the CrI and the particle size of cellulose, thus enabling us to expect the improvement of the reactivity of cellulose.

Catalytic conversion of cellulose

Effect of the cellulose pre-treatment. The reactivity of cellulose with or without the pre-treatment was compared in the hydrogenation reaction. For this purpose, we used $\text{Pt}_{(N)}/\text{BP2000}$ catalyst in this experiment because of the highest activity and good durability among the catalysts used in this work (see **Optimisation of catalysts**). Table 1 summarises the results of the hydrogenation under pressurised H_2 conditions at 463 K. The major products were sugar alcohols (sorbitol 39% and mannitol 4%, total 43%, entry 7) and turnover number (TON) based on bulk Pt for the production of the sugar alcohols was 42. The conversion of the non-treated cellulose, determined by the weight loss in the reaction, was 66%. Therefore, the selectivity for the sugar alcohols based on the converted cellulose was 66%. Other identified products were 1,4-sorbitan, ethylene glycol, propylene glycol and glycerine. By ball-milling cellulose for 2 days, the conversion of cellulose was raised from 66% to 82%, and the total yield of the sugar alcohols reached 58% with 70% selectivity and 54 TON of Pt (entry 8). From these results, it is clearly shown that the reduction of the CrI and the particle size of cellulose by the ball-milling treatment enhances the reactivity of cellulose. No further improvement was observed for the 4-day-milled cellulose (60% yield, entry 11) as suggested in the XRD measurement shown in Fig. 2.

Table 1 Degradation of cellulose with H₂ by supported metal catalysts.^a

Entry	Catalyst	Yield based on carbon /%					Cellulose conversion ^c /%	
		Sorbitol	Mannitol	Sum of sorbitol and mannitol	1,4-Sorbitan	C ₂ -C ₃ polyols ^b		Glucose
1	Pt _(Cl) /Al ₂ O ₃	31.6	6.6	38.2 (43)	15.8	8.3	N.d.	89.2
2	Pt _(Cl, N) /Al ₂ O ₃	36.7	7.7	44.4	7.3	9.2	N.d.	N.d.
3	Pt _(N) /Al ₂ O ₃	46.0	4.8	50.8 (70)	3.0	0.8	0.2	72.3
4 ^d	Pt _(N) /Al ₂ O ₃	35.2	8.2	43.4 (55)	1.2	0.6	0.5	78.9
5 ^d	Pt _(N) /Al ₂ O ₃	45.1	8.1	53.2 (53)	1.5	2.0	0.7	101
6 ^e	Pt _(N) /Al ₂ O ₃	37.6	9.6	47.2 (48)	13.6	3.7	0.7	98.0
7 ^f	Pt _(N) /BP2000	38.8	4.3	43.1 (66)	5.3	0.9	0	65.6
8	Pt _(N) /BP2000	48.7	9.0	57.7 (70)	1.9	1.5	0.1	81.9
9 ^d	Pt _(N) /BP2000	52.5	11.0	63.5 (63)	2.2	1.8	0.1	101
10 ^d	Pt _(N) /BP2000	52.7	12.1	64.8 (64)	3.0	2.0	0.1	101
11 ^g	Pt _(N) /BP2000	53.4	6.3	59.7 (65)	10.4	1.0	0	92.3
12	Pt _(N) /XC72	44.3	11.1	55.4 (63)	1.9	1.4	0	87.8
13 ^d	Pt _(N) /XC72	41.9	9.7	51.6 (59)	1.3	1.7	0	86.9
14	Pt _(N) /AC	16.8	5.3	22.1 (29)	0	4.3	0.2	75.3
15	Pt _(N) /TiO ₂	20.0	6.2	26.2 (33)	1.3	1.6	0	78.8
16	Pt _(N) /ZrO ₂	35.7	10.0	45.7 (62)	2.7	1.7	0	74.1
17 ^d	Pt _(N) /ZrO ₂	36.1	9.1	45.2 (56)	1.9	0.7	0.2	80.6
18	Ru _(Cl) /Al ₂ O ₃	32.5	5.4	37.9 (40)	15.9	7.8	N.d.	95.5
19	Ru _(N) /Al ₂ O ₃	53.2	4.1	57.3 (71)	3.2	0.5	0.1	81.1
20	Ru _(N) /BP2000	36.9	12.7	49.6 (57)	1.9	0.5	0.1	86.4
21	Rh/BP2000	5.2	3.2	8.4 (10)	0.3	6.2	0.5	86.8
22	Ir/BP2000	20.7	2.3	23.0 (30)	0.9	8.9	0.3	77.3
23	Pd/BP2000	0.3	0.2	0.5 (1)	0.1	2.2	0.3	76.6

^a Reaction conditions; cellulose 324 mg (ball-milled for 2 days), catalyst 20 μg-atom-metal (metal 2 wt%), water 40 mL, reaction time 24 h, T=463 K, P(H₂)=5.0 MPa at r.t. Selectivity based on the substrate conversion is shown in parenthesis. ^b Sum of glycerine, propylene glycol and ethylene glycol. ^c Based on the loss of weight during the reaction. ^d The reuse experiment using the residue of the experiment of the previous entry number and fresh cellulose of 324 mg. The conversion and yields are based on the fresh cellulose. ^e HCl of 59 μmol was added. ^f Cellulose was used without the pre-treatment. ^g 4-Day-milled cellulose was used.

Accordingly, we conclude that the 2-day-ball-milling is effective for the pre-treatment of cellulose under our catalytic conditions, and hereafter this pre-treatment is used as the standard method.

Optimisation of catalysts. In the previous report, we used Pt_(Cl)/Al₂O₃ and Ru_(Cl)/Al₂O₃ catalysts for the hydrogenation of non-treated cellulose; however, the yields of the sugar alcohols (sorbitol 25%, mannitol 6%) need to be improved.¹⁰ It is known that a small amount of Cl on supported metal catalysts may affect the hydrogenation activity,²² which prompted us to study the effect of Cl in catalyst precursors on the conversion of the pre-treated cellulose. In this work, we used a Cl-free alumina support (JRC-ALO-2). Pt_(Cl)/Al₂O₃ gave sorbitol of 32% and mannitol of 6.6%, and the conversion of cellulose was 89% (Table 1, entry 1). The selectivity for the sugar alcohols based on the conversion was 43%. Large amounts of 1,4-sorbitan and C–C and/or C–O dissociated compounds such as ethylene glycol and propylene glycol were also generated (total 50% yield). The yield of the sugar alcohols was improved to 44% by using a less Cl-containing precursor [Pt(NH₃)₄Cl₂, entry 2] and to 51% by a Cl-free precursor [Pt(NH₃)₂(NO₂)₂, entry 3]. In the latter case, 1,4-sorbitan and other by-products significantly decreased, thereby raising the selectivity for the sugar alcohols up to 70% (entry 3). Ru catalysts also showed the same tendency; Ru_(Cl)/Al₂O₃ prepared from RuCl₃ produced the sugar alcohols in 38% yield and 40% selectivity (entry 18), whereas Ru_(N)/Al₂O₃ provided 57% yield and 71% selectivity (entry 19). These results indicate that Cl-free precursors are suitable

for the transformation of cellulose to sugar alcohols.

We performed EDX analysis of the Pt catalysts to determine the content of Cl (Fig. S1). Residual Cl in Pt_(Cl)/Al₂O₃ was 1.1 wt%, but Cl in Pt_(N)/Al₂O₃ was less than 0.01 wt%. Fig. 6(b, c) shows the XRD patterns of these catalysts, and both catalysts showed the diffraction lines of γ-Al₂O₃ with no distinct peaks of Pt, indicating that Pt is highly dispersed. The mean diameters of Pt particles, determined from CO-uptake, were 3.3 nm for Pt_(N)/Al₂O₃ and 4.5 nm for Pt_(Cl)/Al₂O₃, respectively, which represents that the structural properties of the catalysts are analogous. Therefore, a clear difference is the content of Cl, and the residual Cl may adsorb on the metal surface to cause the C–C and C–O cleavage reactions by inhibiting the selective hydrogenation sites and/or promoting the hydrogenolysis reactions. In addition, since the yield of 1,4-sorbitan, which is generated by the cyclodehydration of sorbitol, increased with the Cl-content in the catalyst precursors, another possible function of Cl is to accelerate acid-catalysed reactions by the formation of HCl or AlCl_x species. In fact, the addition of HCl (Cl 1.1 wt%) to Pt_(N)/Al₂O₃, which corresponded to the same Cl amount as that contained in Pt_(Cl)/Al₂O₃ (entry 1), reduced the selectivity for the sugar alcohols (48%) and increased the formation of by-products like 1,4-sorbitan (entry 6). It is thus shown that the use of Cl-free precursors is one of the key factors to gain higher yields of sugar alcohols.

The durability of Pt_(N)/Al₂O₃ catalyst was tested in reuse experiments; the catalyst was reused after drying at 383 K by adding fresh cellulose of 324 mg, where the yields and the conversion were calculated based on the fresh cellulose. Total

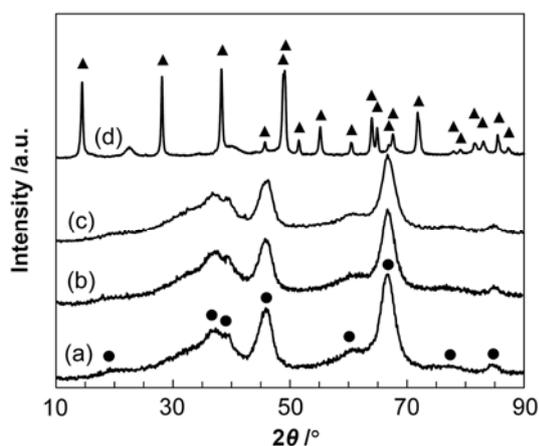


Fig. 6 XRD patterns of (a) Al₂O₃, (b) Pt_(N)/Al₂O₃, (c) Pt_(Cl)/Al₂O₃, and (d) Pt_(N)/Al₂O₃ after the hydrogenation of cellulose. Circles: γ-Al₂O₃, triangles: boehmite.

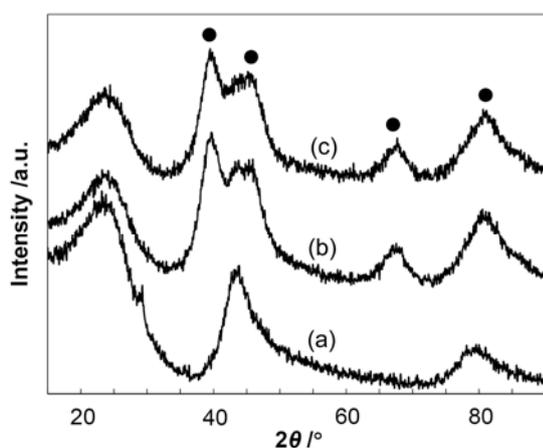


Fig. 7 XRD patterns of (a) BP2000, (b) Pt_(N)/BP2000 catalyst before the hydrogenation of cellulose, and (c) Pt_(N)/BP2000 after the reaction. Circles: Pt metal.

yields of the sugar alcohols in the reuse experiments were 43% (2nd run, entry 4) and 53% (3rd run, entry 5), which were comparable to that in the first run (51%). The conversion of cellulose increased from 72% to 101% in the reuses because of the consumption of remaining cellulose in the previous runs. Therefore, the selectivity for the sugar alcohols decreased from 70% to 53%, indicating the reduction of the hydrogenation activity of the catalyst. In the XRD measurement of the spent catalyst after the first reaction, diffraction patterns of γ-Al₂O₃ completely disappeared, and sharp peaks of AlO(OH) (boehmite) were observed [Fig. 6(d)]. The reduction of the catalytic activity is raised by the hydration of the support, perhaps causing burial of some Pt particles by the morphology change.

We carried out the screening of water-tolerant supports such as carbons, TiO₂ and ZrO₂ (entries 8-10, 12-17). Among these supports, a carbon black BP2000 was found to provide the highest catalytic activity and good durability; the yields of the sugar alcohols in the reuse tests were 58%, 64% and 65%, respectively, and the total TON of Pt was 175 (entries 8-10). Furthermore, no change was seen for the XRD patterns of Pt_(N)/BP2000 catalyst before and after the reaction [Fig. 7(b),

c)], and the mean Pt diameters calculated with Scherrer's equation were both 2.6 nm. These results indicate the water-tolerant property of this catalyst. Other supports, XC72 and ZrO₂ were less effective than BP2000, and AC and TiO₂ were not suitable as the support (entries 12-17). It is therefore concluded that BP2000 is a useful support for Pt to produce the sugar alcohols in water. BP2000-supported Ru, Rh, Ir and Pd catalysts were prepared from Cl-free precursors, but they were less active than the Pt catalyst (entries 20-23). This finding led us to choose Pt_(N)/BP2000 as the typical catalyst to study the kinetics of this reaction.

Mechanistic study using Pt_(N)/BP2000 catalyst. Fig. 8(a) shows the time course of the hydrogenation of cellulose using Pt_(N)/BP2000 catalyst. The "reaction time" denotes the duration time at 463 K with excluding the heating and the cooling time (Fig. S2), thereby showing that the reaction slightly proceeded even at 0 h. The amount of cellulose gradually decreased with the reaction time and reached 14% at 16 h. Although the conversion rate of cellulose is not expressed by a simple kinetic equation, we applied the first-order approximation in Eq. 1 to evaluate the reaction rate, where k_C is the pseudo first-order rate constant.²³ Eq. 1 is transformed to an integral form as Eq. 2, where X is the conversion of cellulose. The plot showed good linearity in the first 6 h (7-76% conversion), and k_C was determined to be 0.21 h⁻¹ [Fig. 8(b)].

$$d[\text{Cellulose}]/dt = -k_C[\text{Cellulose}] \quad (1)$$

$$\ln([\text{Cellulose}]/[\text{Cellulose}]_0) = \ln(1-X) = -k_C t \quad (2)$$

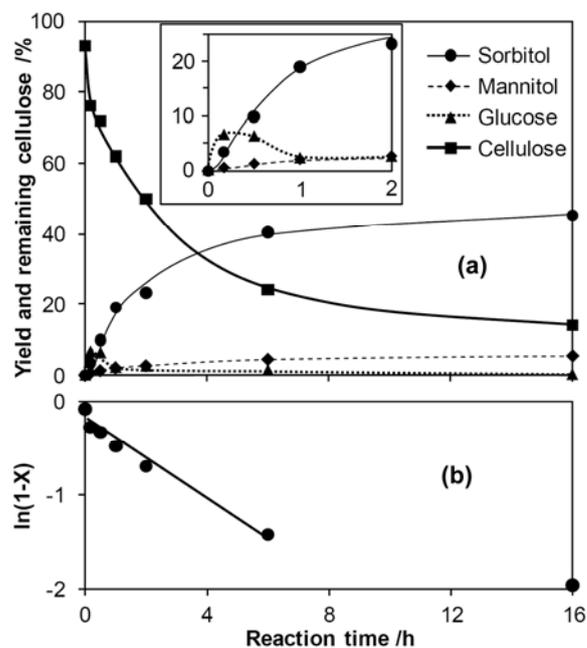
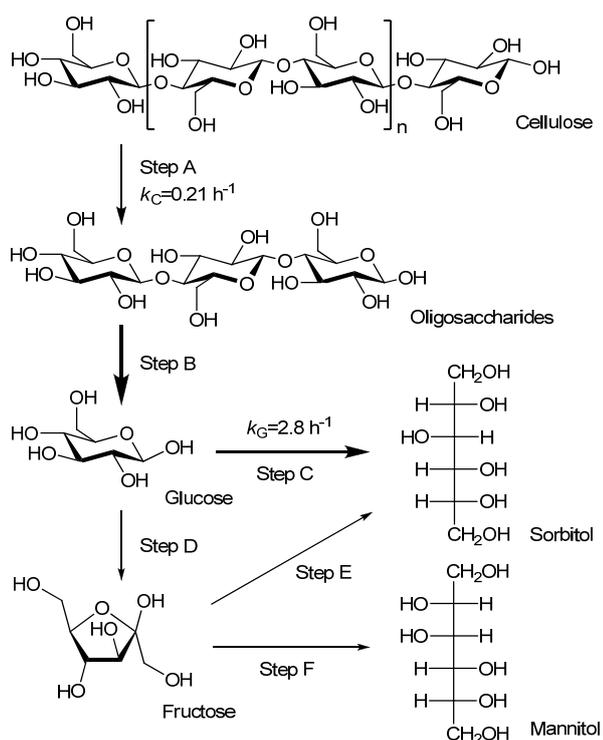


Fig. 8 (a) Time course of the hydrogenation of cellulose by Pt_(N)/BP2000 catalyst and (b) the first-order plot of the remaining cellulose. The inset shows the initial period of 2 h. Reaction conditions: cellulose 324 mg (1.9 mmol, 2-day-milled), Pt_(N)/BP2000 195 mg (Pt 20 μg-atom), water 40 mL, P(H₂) 5.0 MPa at r.t., T=463 K. Each plot is the result of each batch reaction with different reaction times.

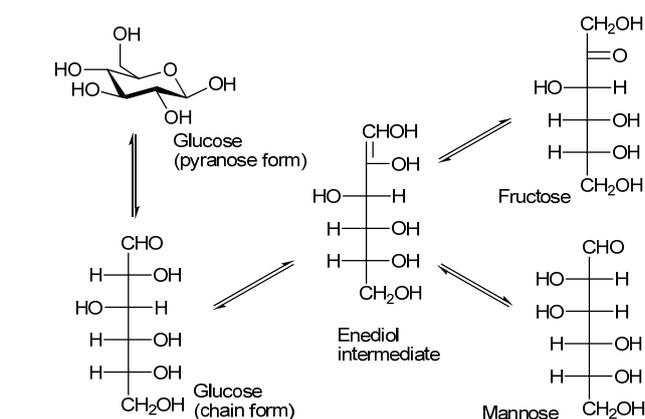


Scheme 1 Reaction pathway of the hydrogenation of cellulose using $\text{Pt}_{(\text{N})}/\text{BP2000}$ catalyst.

In focusing on the products, glucose was formed in 6.7% yield at 0.2 h as a major product [Fig. 8(a) inset], whereas water-soluble oligosaccharides were negligible (less than 1% yield in total, data not shown). The yield of glucose decreased to 0.4% at 16 h, while that of sorbitol smoothly increased after a short induction period and reached 45% at 16 h. These facts show that the conversion of cellulose to sorbitol consists of the hydrolysis of cellulose to glucose via water-soluble oligosaccharides, which is quickly hydrolysed to glucose, and the hydrogenation of glucose to sorbitol (Scheme 1 steps A-C). The maximum yield of glucose was only 6.7%, indicating that the hydrogenation of glucose is faster than the formation of glucose. To discuss the reaction rates of these steps quantitatively, we estimated the hydrogenation rate by using following hypothesis: glucose is hydrogenated by the Langmuir-Hinshelwood mechanism with the adsorption of glucose and the dissociative adsorption of H_2 .²⁴ Assuming a pseudo first-order reaction (Eq. 3) because of the sufficiently low concentration of glucose ($< 4 \text{ mM}$) and the large excess amount of H_2 , the rate constant (k_G) was calculated to be 2.8 h^{-1} by the curve fitting using the experimental results (Fig. S3), which is 13 times higher than that of the hydrolysis step (0.21 h^{-1}). From these results, it is concluded that the rate-determining step is the hydrolysis of cellulose as expected.

$$d[\text{Sorbitol}]/dt = k_G[\text{Glucose}] \quad (3)$$

A small amount of mannitol formed along with sorbitol. We also investigated the formation route of mannitol by assuming two possible pathways: (1) the hydrogenation of fructose and/or mannose and (2) the isomerisation of sorbitol.



Scheme 2 Lobry de Bruyn and van Ekenstein transformation of glucose.

Regarding the first hypothesis, small amounts of fructose (0.4%) and mannose (0.3%) were detected at 0.5 h which were generated from glucose by Lobry de Bruyn and van Ekenstein transformation²⁵ (Scheme 2), but they decreased with reaction time. In our experiments, the hydrogenation of fructose proceeded 2.2 times more rapidly than that of mannose, determined by an initial rate method, and produced sorbitol and mannitol in a ratio of 1:1 by using $\text{Pt}_{(\text{N})}/\text{BP2000}$ catalyst (Scheme 1 steps E, F, Table S1). As to the second hypothesis, if the isomerisation of sorbitol to mannitol is the major pathway, the formation rate of mannitol is correlated with the concentration of sorbitol, but it is not the case in our reactions as shown in Fig. 8(a). Therefore, the main intermediate for mannitol formation can be ascribed to fructose (steps D, F).

Fig. 9(a) represents the time course of the cellulose degradation with no catalyst under H_2 pressure. The amount of cellulose smoothly decreased with the reaction time and the

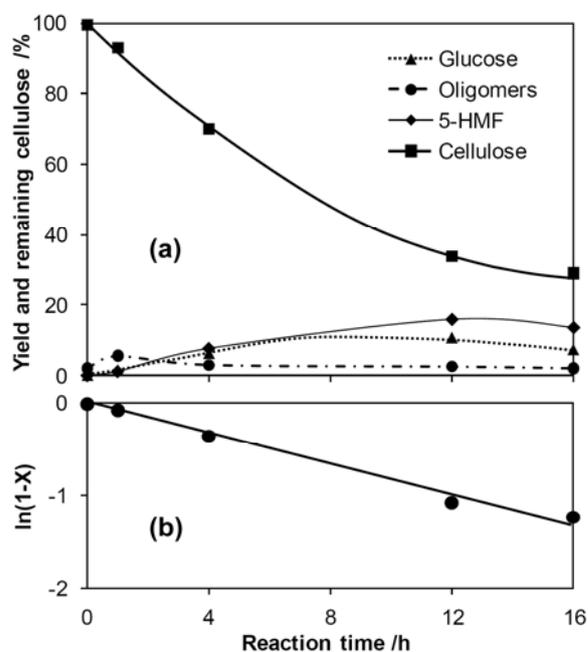


Fig. 9 (a) Time course of the degradation of cellulose under H_2 pressure by no catalysts and (b) the first-order plot of the remaining cellulose. Reaction conditions: cellulose 324 mg (1.9 mmol, 4-day-milled), water 40 mL, $P(\text{H}_2)$ 5.0 MPa at r.t., $T=463 \text{ K}$. Each plot is the result of each batch reaction with different reaction times.

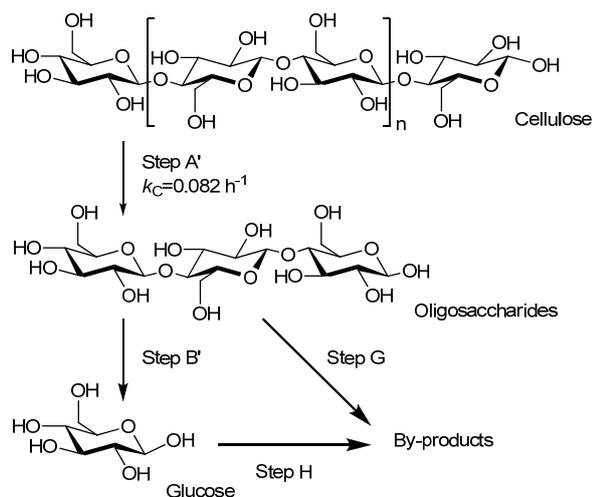
Table 2 Hydrolysis of cellulose under aerial conditions by Pt_(N)/BP2000 catalyst.^a

Entry	Catalyst	Yield based on carbon /%		Cellulose conv. ^c /%
		Glucose	Oligosaccharides ^b	
24	No catalyst	4.6	14.1	24.2
25	BP2000	4.7	12.3	18.5
26	Pt _(N) /BP2000	12.9	12.1	38.0

^a Reaction conditions; cellulose 324 mg (ball-milled for 4 days), catalyst 50 mg, water 40 mL, $T=503$ K, reaction time <1 min^{13e}, under air. ^b Dimer-octamer. ^c Based on the loss of weight during the reaction.

unreacted quantity was 29% at 16 h. It is proposed that H_3O^+ from water catalyses the hydrolysis of cellulose under these reaction conditions,^{11a,11c,26} because the ionic product of water (pK_w) decreases with the temperature from 14.0 (298 K) to 11.3 (463 K) as shown in Fig. S2.²⁷ Therefore, higher temperatures have an advantage to accelerate the hydrolysis of cellulose in the reaction without catalysts in terms of the concentration of H_3O^+ . The first-order plot of the remaining cellulose showed a linear line with a gradient of 0.082 h⁻¹ [Fig. 9(b)], which was lower than the rate constant of the reaction using the Pt catalyst (0.21 h⁻¹) in the conversion range of 10-70% (Fig. 8). These results suggest that Pt_(N)/BP2000 enhances the hydrolysis of cellulose; *i.e.*, the supported Pt catalyst could hydrolyse the glycosidic bonds, and other possibility might be that Pt generates protons by the heterolysis of H_2 .^{10,11c} As shown in Table 2, Pt_(N)/BP2000 catalyst gave a higher yield of glucose (13%) than BP2000 (5% yield) and no catalyst (5% yield) in the hydrolysis of cellulose without H_2 pressure under a rapid heating and cooling conditions at 503 K.²⁸ This result also indicates that Pt_(N)/BP2000 itself has the hydrolysis activity.

The reaction mixture without catalysts turned brownish with the reaction time, and black solids precipitated at ≥ 16 h, which is in contrast to the colourless solution in the reactions using the Pt catalyst. In the HPLC analysis of the solution, oligosaccharides were found as the principal products in the initial stage [Fig. 9(a), Scheme 3 Step A'], which is different from the reaction using the Pt catalyst. This result also



Scheme 3 Reaction pathway of the degradation of cellulose without catalysts.

supports that the Pt catalyst hydrolyses the glycosidic bonds. After the formation of the oligosaccharides, glucose was generated with large amounts of various isomerisation and dehydration by-products such as fructose, mannose, 5-hydroxymethylfurfural (5-HMF), furfural, levoglucosan and organic acids, whose detail is shown in Table S2, because of high chemical reactivity of glucose and the reducing terminals of the oligosaccharides (steps B', G, H). Among the by-products, 5-HMF was obtained as a major component after passing 4 h in Fig. 9. No formation of the hydrogenated products shows that supported metal catalysts are essential for the reduction reactions.

Conclusions

To achieve the effective production of sorbitol and mannitol from cellulose, we studied the pre-treatment of cellulose and developed new catalysts for the hydrogenation of cellulose. The reduction of the *CrI* and the particle size of cellulose by ball-milling treatment for 2 days increased the reactivity and gave higher yields of the sugar alcohols with keeping the selectivity. Secondly, we found that Pt_(N) supported on a carbon black BP2000 is a selective and durable catalyst, compared to the previous Pt catalysts such as Pt_(Cl)/Al₂O₃. A key point is the Cl-free catalyst precursors as residual Cl on the catalysts derived from precursors induces side-reactions such as the C-C cleavage and the dehydration. Another point is the water-tolerant supports which allow the reuse with good durability. The hydrogenation of cellulose consists of the hydrolysis of cellulose to glucose via oligosaccharides and hydrogenation of glucose to sorbitol. The kinetic constant of each reaction was determined, which demonstrated that the Pt catalyst promotes both the hydrolysis and the hydrogenation steps and that the rate-determining step is the hydrolysis step.

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