Simultaneous formation of sorbitol and gluconic acid from cellobiose using carbon-supported ruthenium catalysts

Tasuku Komanoya [a,b], Hirokazu Kobayashi [a,b], Kenji Hara [a,b], Wang-Jae Chun [c], Atsushi Fukuoka [a,b]*

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

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

[c] Division of Arts and Sciences, International Christian University, 3-10-2 Osawa, Mitaka, Tokyo 181-8585, Japan

Abstract

A carbon-supported Ru catalyst, Ru/BP2000, is able to simultaneously convert cellobiose into sorbitol and gluconic acid. This reaction occurs as the result of hydrolytic disproportionation in water at 393 K under an Ar atmosphere, without the use of bases or sacrificial reagents. In-situ XANES measurements suggest that the active Ru species involved is composed of partially oxidized Ru metal.

Keywords

cellobiose; supported ruthenium catalyst; hydrolysis; disproportionation.

*Corresponding Author. Tel: +81-11-7069140; Fax: +81-11-7069139; E-mail: fukuoka@cat.hokudai.ac.jp.

1. Introduction

The catalytic conversion of biomass into renewable chemicals is of great importance given the current situation in which the cost of oil is climbing while its supply is simultaneously dwindling [1]. Cellulose, a polymer of glucose, is an abundant, non-food biomass resource produced via photosynthesis powered by energy from the sun. The conversion of cellulose to useful chemicals such as glucose, sorbitol and gluconic acid

has attracted significant attention in the field of biorefining [2,3].

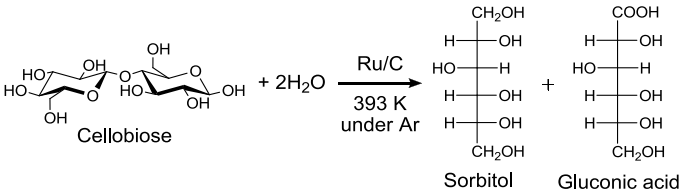
The reduction and oxidation of glucose produce sorbitol and gluconic acid, respectively, and these are both useful feedstock chemicals for a variety of foods, pharmaceuticals, medicines and polymers [2,3]. The simultaneous production of sorbitol and gluconic acid from glucose in electro-catalytic reactions has been reported [4], in which an external voltage and a mediator ($CaBr_2$) were necessary. Enzymes [5] and supported metal catalysts such as Pt/C or Rh/C [6] also produced sorbitol and gluconic acid, but these reactions required a stoichiometric amount of fructose as an acceptor of electrons from glucose as well as the addition of a base for the oxidation of glucose to gluconate. We anticipate, however, that the disproportionation of glucose ($C_6H_{12}O_6$) to sorbitol ($C_6H_{14}O_6$) and gluconic acid ($C_6H_{12}O_7$) should be possible via the hydrolysis of gluconolactone ($C_6H_{10}O_6$) (Eqs. 1,2), without the need for any sacrificial reagents or external power supplies. This could be accomplished by making use of suitable redox catalysts (resulting in favorable reaction thermodynamics such that ΔG = ca. 0 kJ mol^{-1}) [7] as well as a large excess of water. Sorbitol and gluconic acid thus formed can be isolated from the reaction mixture by a combination of an electrodialysis [8] and an ion exchange resin.

$$2\ C_6H_{12}O_6 \rightarrow C_6H_{14}O_6 + C_6H_{10}O_6 \quad (1)$$

$$C_6H_{10}O_6 + H_2O \leftrightarrow C_6H_{12}O_7 \quad (2)$$

We recently found that Ru/C catalysts promote the hydrolytic transfer hydrogenation of cellulose into sorbitol, in the presence of 2-propanol but without any added base [9], which implied that these same catalysts might accelerate both of the redox reactions in Eq. 1, via metal hydride intermediates. Carbon supports are known to be suitable for the conversion of sugars, since they are exceptionally stable in the presence of acids and water and also have very high surface areas. Moreover, Ru catalysts are able to hydrolyze β-1,4-glycosidic bonds [10], thus indicating their potential applicability to the conversion of polysaccharides. In this work, we investigated the one-pot production of sorbitol and gluconic acid from cellobiose, using Ru/C catalysts in water under Ar (Scheme 1). To our knowledge, this is the first report of the catalytic conversion of cellobiose or glucose to sorbitol and gluconic acid without the use of bases or sacrificial

reagents or the application of an electric current.



Scheme 1. Catalytic, hydrolytic disproportionation of cellobiose to sorbitol and gluconic acid.

2. Experimental

Supported metal catalysts (2 wt%) were prepared from metal chlorides by a conventional impregnation method [10]. The conversion of cellobiose was performed in a high-pressure PEEK reactor (internal volume of 3.5 cm^3) covered with a metal frame (SUS304) equipped with small windows to allow in-situ XAFS measurements (Fig. S1). Cellobiose (205 mg, 0.6 mmol), catalyst (150 mg) and water (2.5 mL) were transferred into the reactor, which was then purged with Ar and heated to 393 K for varying lengths of time by two cartridge heaters. The reaction mixture was subsequently combined with 7.5 mL of water, after which the solid catalyst was removed by filtration. The reaction products absorbed on the catalyst were recovered by Soxhlet extraction with 50 mL water/ethanol solution (50:50 vol/vol). Water-soluble products were analyzed by HPLC to determine their carbon-based yields and the conversion of cellobiose, using Eqs. 3 and 4.

$$\text{Yield (\%C)} = (\text{moles of carbon in product})/(\text{moles of carbon in added cellobiose}) \times 100 \quad (3)$$

$$\text{Conversion (\%)} = \{1 - (\text{moles of recovered cellobiose})/(\text{moles of added cellobiose})\} \times 100 \quad (4)$$

Transmission electron microscopy (TEM, JEOL JEM-2100F) and scanning electron microscopy (SEM, JEOL JSM-6360LA) were measured with an acceleration voltage of 200 kV and 25 kV, respectively. In-situ Ru K-edge QXAFS spectra of the Ru catalysts were recorded at the NW10A beam line on KEK-PF (Proposal No. 2010G591) using the reactor described above. Ru metal powder and $RuO_2 \cdot 2H_2O$ were used as reference standards.

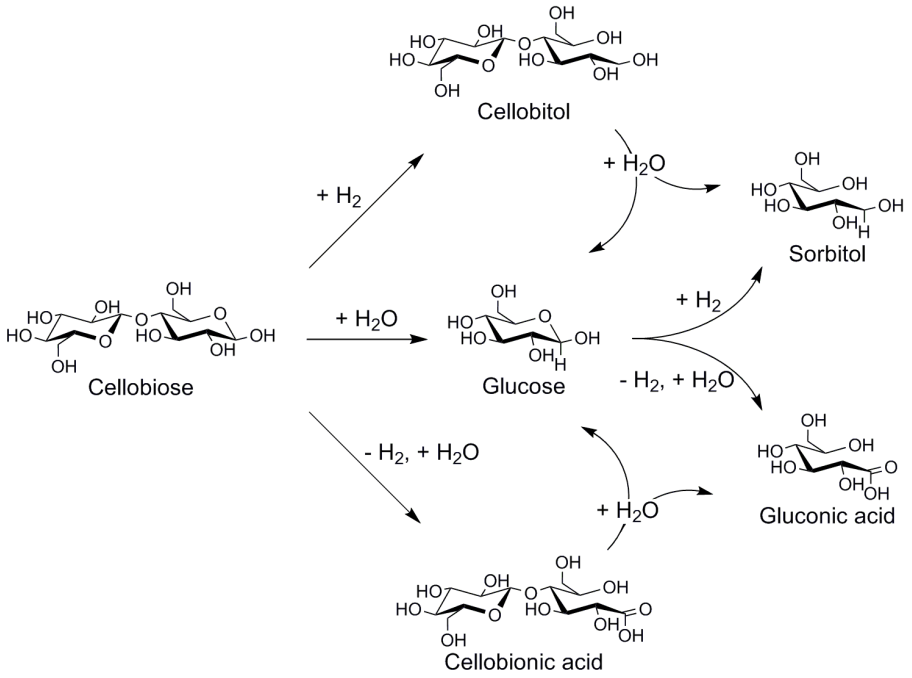
3. Results and discussions

As a test case, we initially studied the conversion of glucose using a Ru/BP2000 catalyst, heating the reaction mixture at 393 K for 4 h. The conversion of glucose under these conditions was 38%, with yields of 13% for sorbitol and 19% for gluconic acid based on carbon (Table 1, entry 10). These results illustrate that, as expected, the Ru catalyst is active for the redox reaction of glucose. This same process was subsequently applied to the conversion of cellobiose (Scheme 2). As shown in Table 1, the use of Ru/BP2000 resulted in 80% conversion of cellobiose, and the formation of sugar alcohols such as sorbitol (9.8% yield), mannitol (0.3%) and cellobitol (7.0%) (entry 1). Gluconic acid (14%) and cellobionic acid (15%), both oxidation products, were also obtained at slightly higher yields. Other products were glucose (27%), mannose (0.4%) and levoglucosan (0.3%). In contrast, the use of BP2000 without a metal did not produce any reduced or oxidized sugars, and gave only a low 2.3% glucose yield (entry 6). Other supported Ru catalysts were less active than Ru/BP2000 (entries 2-5). In addition, Rh, Ir, and Pt supported on BP2000 gave only 0.6-2.2% yields of sugar alcohols (entries 7-9). Average particle size of Ru on BP2000 was 1.5 nm by a transmission electron microscopy (Fig. S2) and almost the same as those of Ru/CMK-3 (1.1 nm) and Ru/AC(N) (1.4 nm). One possible reason for the better performance of Ru/BP2000 catalyst is a smaller primary particle size of BP2000 support (50 nm) than those of XC 72 (70 nm), CMK-3 (1 μm), and AC(N) (> 1 μm) estimated by SEM in Fig S3. Thus, the substrates can easily access active Ru sites on BP2000 even under the unstirred conditions. Based on these results, we used Ru/BP2000 as the sole catalyst for the remainder of the study.

Table 1. Conversion of cellobiose to sorbitol and gluconic acid by supported metal catalysts.[a]

Entry	Catalyst	Yield (%C)[b]								Conv. (%)
		Glu	Sor	Man	Col	Gla	Cac	Byp[c]	Total	
1	Ru/BP2000[d]	27	9.8	0.3	7.0	14	15	0.6	74	80
2	Ru/XC72[e]	25	3.3	0.2	8.3	3.7	12	0.5	53	52
3	Ru/CMK-3	25	4.0	0.2	9.1	5.8	19	0.4	63	64
4	Ru/AC(N)[f]	13	1.4	0.1	6.2	3.3	16	0.3	39	45
5	Ru/γ-Al_2O_3	14	1.1	0.1	4.8	1.4	6.3	3.5	31	44
6	BP2000	2.3	0.0	0.0	0.0	0.0	0.0	0.3	2.6	< 1
7	Rh/BP2000	29	0.1	0.0	0.5	2.7	8.9	0.7	42	46
8	Ir/BP2000	30	0.7	0.0	1.5	4.1	10	0.7	47	53
9	Pt/BP2000	31	0.3	0.0	0.9	4.1	16	0.6	52	61
10[g]	Ru/BP2000	–	13	0.4	–	19	–	1.3	34	38

[a] Cellobiose (205 mg), catalyst (2 wt%, 150 mg), water (2.5 mL), 393 K, 4 h, 0.1MPa Ar. [b] Glu: glucose; Sor: sorbitol; Man: mannitol; Col: cellobitol; Gla: gluconic acid (equilibrium mixture with gluconolactone); Cac: cellobionic acid. [c] Total amount of mannose, fructose and levoglucosan. [d] Carbon black Black Pearls 2000 (Cabot). [e] Carbon black VULCAN XC72 (Cabot). [f] Activated carbon Norit SX Ultra (Aldrich). [g] Glucose (218 mg) was used as a substrate.



Scheme 2. Reaction pathway for the conversion of cellobiose to sorbitol and gluconic acid.

The course of cellobiose conversion over time when using the Ru/BP2000 catalyst is shown in Fig. 1, in which minor products (< 1% yield) such as mannitol, mannose, fructose and levoglucosan are omitted. The cellobiose concentration gradually decreases with reaction time, reaching a minimum of 2.1% after 16 h. The initial products are glucose, cellobitol and cellobionic acid, demonstrating that the cellobiose also undergoes a parallel reaction involving the hydrolysis of glycosidic bonds and oxidation/reduction of the reducing terminal groups. The yields of the disaccharide products reach a maximum after 2 h and then gradually decrease, while the glucose yield reaches an apex of 33% after 8 h and then declines to 25% at 16 h, indicating that these three products are intermediates in this reaction. In contrast, yields of sorbitol and gluconic acid, which are the products of two-step hydrolysis/redox reactions, initially display an induction period of 2 h, then continuously increase to 23% and 35% (for a total yield of 58%), respectively, at the 16 h mark. The proportionately higher yield of oxidized sugars suggests that a portion of the hydrogen derived from the dehydrogenation of glucose is consumed in forming H_2 and in reducing the Ru catalyst, as discussed below.

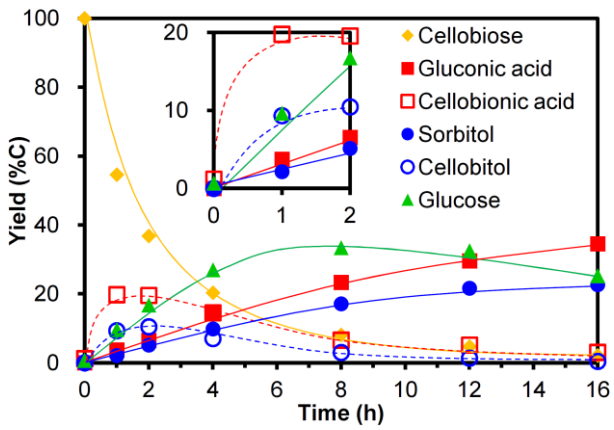


Figure 1. Cellobiose conversion over time using a Ru/BP2000 catalyst at 393 K.

The reuse experiments of Ru/BP2000 for the cellobiose conversion were carried out at 393 K for 16 h to investigate the catalyst durability (Table S1). Although the yields of sorbitol and gluconic acid were decreased in the second run, the catalytic activity was kept similar after that. Turnover numbers for the formation of sorbitol based on bulk Ru were 5-10 and those of gluconic acid were 9-15 in the three runs, indicating that Ru

worked as a catalyst. The decline of the initial activity might be due to the strong adsorption of by-products on Ru and/or the sintering of Ru species.

To determine the actual Ru species present during the cellobiose conversion, in-situ Ru K-edge XANES measurements of the Ru/BP2000 catalyst were performed at 393 K, as shown in Fig. 2. In the early stages of the reaction, the edge energy of Ru on BP2000 was 22,124 eV, which is similar to that determined for $RuO_2 \cdot 2H_2O$ (22,126 eV) but higher than that for Ru metal (22,117 eV). It is thus indicated that Ru is oxidized to $RuO_2 \cdot 2H_2O$ following H_2 reduction at 673 K and passivation in air at room temperature during synthesis of the catalyst [9]. The edge energy of Ru/BP2000 quickly shifts to 22,119 eV after 3.5 min with a simultaneous decrease of the peak at 22,147 eV and an increase of the peak at 22,165 eV. The resulting spectrum is similar to that of Ru metal, although the edge energy is still 2 eV higher. Subsequent to this, no changes were observed up to 150 min (not shown), suggesting that the Ru species in its working state is in the form of partially oxidized Ru metal. It is known that some supported metals convert glucose to hydrogen species and gluconolactone, following which the lactone rapidly achieves chemical equilibrium with gluconic acid in water [3,11,12]. In our system, these hydrogen species are not only responsible for the formation of sorbitol but also for the reduction of the Ru precursor species to its active form. Accordingly, we conclude that this partially oxidized Ru metal catalyzes the hydrolytic disproportionation of cellobiose and glucose into sorbitol and gluconic acid (Scheme 3).

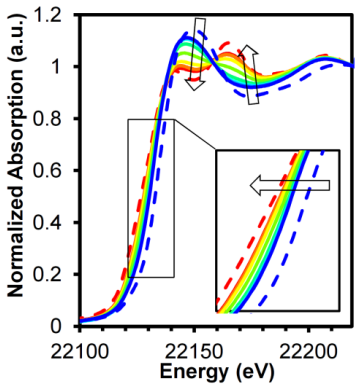
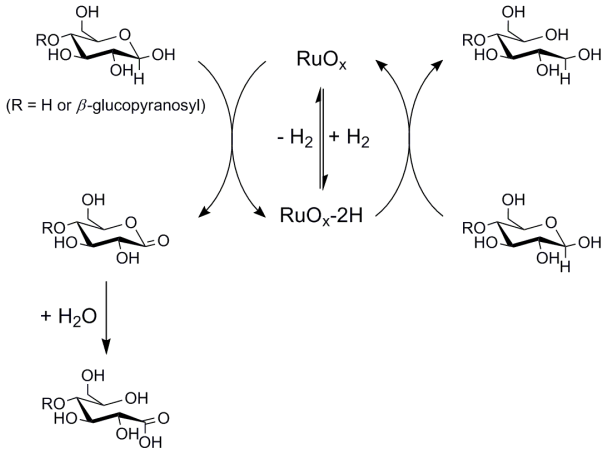


Figure 2. In-situ Ru K-edge XANES spectra of the Ru/BP2000 catalyst for cellobiose conversion (blue to red solid line), Ru metal (red dashed line) and $RuO_2 \cdot 2H_2O$ (blue dashed line) at 393 K. In-situ spectra were recorded from 0 to 3.5 min at 0.5 min intervals.



Scheme 3. Plausible mechanism for the disproportionation of cellobiose and glucose by Ru/BP2000 catalyst via transfer hydrogenation.

4. Conclusions

A Ru/BP2000 catalyst demonstrated the highest degree of activity for the conversion of cellobiose to sorbitol and gluconic acid among the catalysts tested. By monitoring the course of the reaction over time, we determined that sorbitol and gluconic acid were simultaneously formed by hydrolysis of glycosidic bonds and, in parallel, redox reactions of reducing terminal groups. XANES measurements have revealed that the active Ru species during the reaction are composed of partially oxidized Ru metal. Although further study is necessary to clarify the reaction mechanism, this work clearly shows that the catalytic disproportionation of glucose and polysaccharides is possible via the application of carbon-supported Ru catalysts.

Acknowledgments

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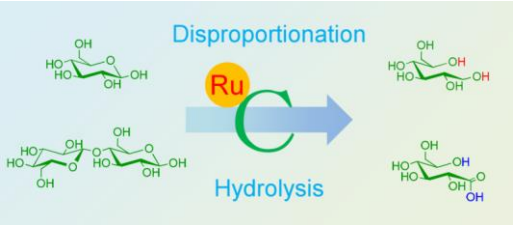
Graphic abstract



A green and energy-saving process was developed for the hydrolytic disproportionation of cellobiose to sorbitol and gluconic acid in water under Ar. Carbon-supported ruthenium catalyzes this reaction via the hydrolysis and hydrogen transfer.