



Title	Production of sugar alcohols from real biomass by supported platinum catalyst
Author(s)	Kobayashi, Hirokazu; Yamakoshi, Yukiyasu; Hosaka, Yuto; Yabushita, Mizuho; Fukuoka, Atsushi
Citation	Catalysis today, 226, 204-209 https://doi.org/10.1016/j.cattod.2013.09.057
Issue Date	2014
Doc URL	http://hdl.handle.net/2115/56609
Type	article (author version)
File Information	CatalToday_226_204.pdf



[Instructions for use](#)

Production of sugar alcohols from real biomass by supported platinum catalyst

Hirokazu Kobayashi^a, Yukiyasu Yamakoshi^b, Yuto Hosaka^{a,c}, Mizuho Yabushita^{a,c},
Atsushi Fukuoka^{a,*}

^aCatalysis Research Center, Hokkaido University, Kita 21 Nishi 10, Kita-ku, Sapporo, Hokkaido 001-0021, Japan.

^bIndustrial Research Institute, Hokkaido Research Organization, Kita 19 Nishi 11, Kita-ku, Sapporo, Hokkaido 060-0819, Japan.

^cGraduate School of Chemical Sciences and Engineering, Hokkaido University, Kita 13 Nishi 8, Kita-ku, Sapporo, Hokkaido 060-8628, Japan.

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

Abstract

The influence of lignin and inorganic salts on the catalytic activity was studied in the hydrolytic hydrogenation of real biomass by a supported Pt catalyst. The direct conversion of raw silver grass by Pt/carbon catalyst under H₂ pressure produced small amounts of sorbitol (2.8 wt%), xylitol (7.3 wt%), and other sugar alcohols. It has been suggested that lignin reduces the reactivity of cellulose, as lignin exists together with cellulose in the biomass and both compounds are insoluble in water. Moreover, even weak bases drastically change the product distribution with more by-products such as EG and PG. Bases enhance the decomposition of sugar intermediates and sorbitol. The removal of lignin and inorganic salts by alkali-explosion and neutralization raises the contents of cellulose and hemicellulose, thus increasing the yields of sorbitol (13 wt%) and xylitol (14 wt%) in the hydrolytic hydrogenation reactions.

Keywords: biomass, cellulose, hemicellulose, sorbitol, supported platinum catalyst, xylitol

1. Introduction

Catalytic conversion of lignocellulosic biomass has attracted great interest for the production of renewable chemicals and fuels, since this abundant material has been largely wasted [1, 2]. Furthermore, the use of lignocellulose in chemical industry does not compete with food production,

which is contrastive to current biorefinery using starch and molasses. Lignocellulose consists of cellulose, hemicellulose, and lignin, in which cellulose is a polymer of glucose and hemicellulose is a copolymer of various C₅ and C₆ sugars. Thus, the hydrolytic hydrogenation of the sugar polymers produces hexitols and pentitols (Figure 1), and these sugar alcohols are practically used as precursors to plastics, surfactants, and medicines as well as low-calorie and non-cariogenic sweeteners [2]. The annual productions of sorbitol and xylitol have already been 6.5×10⁵ and 2-4×10⁴ tons per year, respectively, although the current feedstock of sorbitol is starch. Hence, the hydrolytic hydrogenation of lignocellulosic biomass is an attractive issue for the next-generation biorefinery.

Cellulose conversion by heterogeneous catalysts has been intensively studied in the last several years [2], and it has been known that pure cellulose can be converted into sugar alcohols in good yields in one-pot by various supported metal catalysts under H₂ pressure [3-27]. In the mechanism of this reaction, it has been found that the hydrolysis step is promoted by some supported metal catalysts [6, 7] in addition to effect of hot-compressed water [28], and the hydrogenation is catalyzed by transition metals. In contrast, only a few reports have addressed the one-pot conversion of raw or less-treated biomass; arabitol [29] and xylitol [30, 31] have been synthesized from beet fiber and bleached birch kraft pulp, respectively. Furthermore, influence of various ingredients such as lignin and ionic compounds on this catalytic reaction has not yet been evaluated. Both acid and reduction catalysis can be affected by these components, and hydrolysis rate of cellulose is indeed declined by sulfate ions [32]. In this study, we conducted the conversion of real biomass and crystalline cellulose by a supported Pt catalyst (Pt/BP2000) to evaluate the effects of lignin and salts. **Pt/BP2000 is one of the most active and durable catalysts for the conversion of pure cellulose [7].** Silver grass was mainly used as a substrate because this plant survives in cold climate unsuitable to food crops. Furthermore, silver grass moves nutrients such as K and P from the plant body to rhizomes before winter [33], and hence loss of the elements in soil by collecting the plant for biorefinery is small.

2. Material and methods

2.1 Biomass materials

Silver grass-1 is silver grass (*Miscanthus sinensis*) collected in summer in Kochi, and **silver**

grass-2 is that mowed in winter in Nakashibetsu (Hokkaido). Other biomass used in this study was Amur silver grass (*Miscanthus sacchariflorus*) sampled in Nakashibetsu (Hokkaido) and wheat straw (*Triticum aestivum*) in Memuro (Hokkaido). These samples were coarsely ground using a cutter mill with a 3 mm screen (Horai MAC-0.75kW). Microcrystalline cellulose (Avicel, 1.02331.0500) was purchased from Merck.

2.2 Pretreatment of biomass

Five pretreatment methods were used in this study [34]; **silver grass-1** was boiled in water at 373 K for 3 h (**silver grass-1W**), treated by the Soxhlet extraction using water for 3 days (**silver grass-1S**), or washed with 10 wt% HCl aq. at 298 K for 3 h (**silver grass-1H**). **Silver grass-2** was immersed in 1.4 wt% NaOH at 298 K for 24 h, and exploded after keeping the temperature at 463 K for 2 min (**silver grass-2A**). **Silver grass-2A** was neutralized with HCl at room temperature to adjust its pH to 3, and washed with water (**silver grass-2AN**). This set of alkali-explosion and neutralization is expressed as AN treatment hereafter, and also used for Amur silver grass and wheat straw (**Amur silver grass-AN** and **wheat straw-AN**, respectively).

2.2. Composition analysis of biomass

Elemental analysis of biomass was performed using energy dispersive X-ray spectroscopy (EDX; Shimadzu, EDX-720). The content of each sugar fraction in biomass was analyzed according to the literature (NREL, TP-510-42618 [35]). Biomass (300 mg) was stirred in 72% H₂SO₄ aq. (3.0 mL) for 1 h at 303 K. Water of 84 mL was added to the solution, and then agitated at 394 K for 1 h in a high-pressure reactor. The mixture was filtrated and the aqueous phase was analyzed by a high-performance liquid chromatography (HPLC; Shimadzu, LC10-AT/VP, refractive index detector) equipped with a Shodex Sugar SH-1011 column (ø8×300 mm, mobile phase: water 0.5 mL min⁻¹, 323 K) after neutralizing with CaCO₃ to pH 6. The amount of acid-insoluble lignin was determined from the weight difference before and after the combustion of solid residue at 848 K. Crystallinity of biomass was analyzed by X-ray diffraction (XRD; Rigaku, MiniFlex, Cu K α).

2.3. Preparation of catalysts

Pt(NH₃)₂(NO₂)₂ nitric acid solution (Tanaka Kikinzoku Kogyo, 138 μmol) was dropped into a mixture of carbon black BP2000 (Cabot, Black Pearls 2000, 2.0 g) and water (20 mL), and the mixture was stirred for 16 h. After drying in vacuo, the solid was treated with H₂ (30 mL min⁻¹) at 673 K for 2 h. The prepared catalyst is denoted as 1.3 wt% Pt/BP2000.

2.4. Hydrolytic hydrogenation of biomass

Biomass (324 mg), Pt/BP2000 catalyst (200 mg, Pt 14 μg-atom), and water (40 mL) were transferred into a stainless steel high-pressure reactor (OM Lab-Tech, MMJ-100), and 5 MPa of H₂ was charged at room temperature. The reactor was heated to 463 K and kept at this temperature for 24 h with stirring at 600 rpm. Products were separated by centrifugation and decantation, and water-soluble products were analyzed by HPLC. 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, 343 K) and a Shodex Sugar SH-1011 column (ø8×300 mm, mobile phase: water 0.5 mL min⁻¹, 323 K). Product assignment was also checked by LC/MS (Thermo Fisher Scientific, LCQ-Fleet, APCI). The conversion of cellulose was determined by liquid-phase total organic carbon analysis (TOC; Shimadzu, TOC-V CSN) when we performed the model reactions using pure cellulose and salts. The formation of small amounts of gaseous products was excluded in this estimation.

3. Results and discussion

3.1. Analysis of treated silver grasses

Elemental compositions of silver grasses were analyzed by EDX as shown in Table 1. Si of 3.7 wt% was detected in **silver grass-1** as gramineous plants use silica for their frameworks (entry 1) [36]. Other ingredients were K (1.0 wt%), Ca (0.14), P (0.13), S (0.09), Fe (0.03), and Cl (0.02). K, P, and Cl were almost completely removed by boiling in water, and the amounts of Si and S decreased by half (**silver grass-1W**, entry 2). However, the contents of Ca and Fe were unchanged. The Soxhlet extraction reduced Ca to 0.03 wt% in addition to the effect of boiling water (**silver grass-1S**,

entry 3). The HCl treatment provided a similar result to that of the Soxhlet extraction, but Si remained unchanged at 3.4 wt% (**silver grass-1H**, entry 4). The amounts of K (0.08) and P (0.01) in **silver grass-2**, collected in winter, were significantly lower than those in **silver grass-1** (entry 5) mowed in summer. The AN treatment for **silver grass-2** (entry 6) had a similar effect to that of the Soxhlet extraction (entry 3). It is thus shown that K and P are eliminated completely and the S content is declined in these four treatments.

The NREL/TP-510-42618 method [35] was used to determine the contents of sugar polymers and lignin. **Silver grass-1** had cellulose (34 wt%), hemicellulose (19 wt%), and lignin (26 wt%) (Table 2, entry 7), and the hemicellulose consisted of xylan 16 wt%, arabinan 2.6 wt%, and negligible amounts of other sugar residues. The boiling treatment slightly increased cellulose (42 wt%) and hemicellulose (24 wt%), whereas lignin was reduced (18 wt%) (Table 2, entry 8). The alkali-explosion for **silver grass-2** (entries 9, 10) gave a similar effect to that by the boiling for **silver grass-1** (entries 7, 8), and combination with neutralization using HCl, the AN treatment, obviously decreased the amount of lignin from 21 to 11 wt% in addition to the increase of cellulose content (38 to 58 wt%) (entries 9, 11). Hence, the AN treatment is more effective than the boiling and the single alkali-explosion to remove useless ingredients. Although the loss of carbohydrates during pretreatments sometimes comes to an issue, 87 wt% of carbohydrates (> 95 wt% of cellulose, 74 wt% of hemicellulose) remained in the AN treatment of **silver grass-2** (not shown in Table 2). The constituents of **Amur silver grass-AN** and **wheat straw-AN** were similar to those of **silver grass-2AN** (entries 12, 13).

XRD patterns of **silver grass-1**, **2**, and **2AN** are shown in Figure 2. All of them provided similar diffraction peaks of cellulose I at 16°, 23°, and 35°, and the crystallinity indexes were 55-60% for the samples. Accordingly, cellulose I crystals was stable even in the AN treatment at 463 K. Although it is known that NaOH aq. (> 8 wt%) transforms cellulose I to cellulose II [37], the concentration of NaOH used in the AN treatment in this work was too low (1.4 wt%) to cause it.

3.2. Hydrolytic hydrogenation of biomass

Pristine and pretreated silver grass powders were subjected to the hydrolytic hydrogenation by

1.3 wt% Pt/BP2000 catalyst at 463 K for 24 h. **Silver grass-1** gave sorbitol in 2.8 wt% yield based on the weight of the substrate and xylitol in 7.3 wt% yield (Table 3, entry 14), and identified major by-products were ethylene glycol (EG; 2.0 wt%) and propylene glycol (PG; 4.0 wt%). Conversions of cellulose and hemicellulose were not determined in this case, as the substrate consists of many ingredients. The dissolution amount of the sample was 57 wt%, containing both the conversion of carbohydrates and the dissolution of any components. **Silver grass-1W**, the boiled sample, afforded xylitol and arabitol in 16 wt% and 4 wt%, respectively, and the total yield of the pentitols corresponds to 72 %C based on containing hemicellulose (entry 15). The yield of sorbitol almost did not change (4.0 wt%; 8.6 %C based on containing cellulose), and those of EG (1.3 wt%) and PG (2.1 wt%) decreased similarly. The Soxhlet extraction and HCl pretreatments also increased the yield of xylitol (entries 16, 17), suggesting that xylitol was produced in good yields by reducing the amounts of metal cations, P, and S. Phosphorus and sulfur compounds are typical poisons to hydrogenation catalysts. It is not probable that metal cations directly inhibit the hydrolytic hydrogenation, but counter anions may promote side-reactions or slow down the hydrolysis step as shown in section 3.3. Meanwhile, the catalyst was tolerant to a small amount of SiO₂ as the yield of xylitol was independent of the content of Si in the range of 1.5-3.4 wt%. The yields of sorbitol were only 3.5-4.8 wt% also in these cases. A control experiment using pure crystalline cellulose provided a significantly higher yield of sorbitol [39 wt% (35 %C)] under the same reaction conditions (Table 4 entry 24), indicating the presence of inhibitors for the reaction of cellulose in the silver grass. Since cellulose is almost insoluble even in hot-compressed water at < 590 K [38], a presumable reason would be coexistence of lignin (18 wt% in **silver grass-1W**) that prevents the depolymerization of cellulose.

A prospective strategy to convert cellulose in real biomass is the removal of lignin. Therefore, **silver grass-2AN** was subjected to the hydrolytic hydrogenation as this substance had a less amount of lignin (11 wt%). **Silver grass-2AN** afforded the highest yield of sorbitol (13 wt%, corresponding to 20 %C based on cellulose, entry 19) among treated silver grasses, implying that the removal of lignin made cellulose reactive. The yield of xylitol was improved (14 wt%, 45 %C) and those of EG and PG were kept low (0.9 wt%, 1.5 wt%, respectively) by the AN pretreatment. **Silver grass-2A**

was also tested in the hydrolytic hydrogenation, but negligible amounts of sorbitol and xylitol were formed (entry 18). Instead, EG of 4.5 wt% and PG of 4.7 wt% were produced due to the contamination of base, the detailed effect of which is discussed in section 3.3. Thus, **silver grass-2AN** was chosen to study the time course of this reaction (Figure 3). The amount of sorbitol smoothly increased to 13 wt% (20 %C) over 24 h, whereas that of xylitol was maximized at 4 h (19 wt%, 60 %C) and gradually decreased. The quicker formation of xylitol is due to higher reactivity of hemicellulose, as the rate-determining step is the hydrolysis of sugar polymers [7]. Reuse experiments of Pt/BP2000 were performed in the reaction of **silver grass-2AN** (Table 3, entries 19-21), in which the yields of sorbitol and xylitol obviously dropped in the second run (entry 20). Since Pt/BP2000 is reusable in the reaction of pure cellulose [7], the reduction of yield may be ascribed to some ingredients such as lignin (7 wt%), sulfur (0.03 wt%), or remaining basic compounds. This problem has not been overcome by changing catalyst components. Although the active metals for the hydrolytic hydrogenation are Ru and Ni in addition to Pt, it is known that Ru is very sensitive to sulfides [39]. A Ni/KB catalyst working for the reaction of pure cellulose did not give a good yield of xylitol even in the reaction of purified hemicellulose (Table 4, entries 31, 32). In addition, carbon is the best support in terms of tolerance to hot water and selectivity for sugar alcohols [7].

The AN treatment was applied to other biomass; the yields of sorbitol and xylitol were 17 wt% (25 %C) and 16 wt% (50 %C), respectively, in the reaction of **Amur silver grass-AN** (entry 22). Likewise, **wheat straw-AN** gave 12 wt% (20 %C) yield of sorbitol and 15 wt% (49 %C) yield of xylitol (entry 23). The AN pretreatment is useful to increase the yield of sorbitol in the hydrolytic hydrogenation of real biomass.

3.3. Influences of salts estimated in model reactions

We have observed that washing of biomass to remove inorganic salts is effective to increase the yields of sugar alcohols. Thus, model reactions using microcrystalline cellulose were conducted to clearly evaluate the effects of inorganic salts (Table 4). Pt/BP2000 catalyst transformed cellulose to sorbitol (35 %C yield) and mannitol (3.7 %C), and the formation of EG (0.4 %C) and PG (0.4 %C)

were suppressed (entry 24). Other products were sorbitan (2.7 %C), hexanetetrol (0.3 %C), erythritol (1.0 %C), glycerol (0.5 %C), and unidentified ones (6 %C). The yield of sorbitol dramatically reduced (0.3 %C) by the addition of CaCO₃ regardless of fair conversion of cellulose (38%) (entry 25). Note that hydrolysis of cellulose still takes place in the absence of protons by adding the base. Even in the non-catalytic reaction, water molecules may directly attack glycosidic bonds at high temperatures [28]. In contrast, the yields of EG and PG increased to 4.3 %C and 5.2 %C, respectively. The reaction of cellulose catalyzed by Ru/BP2000 also showed almost the same effect by adding CaCO₃ (entries 29, 30), suggesting that the drastic change of product distribution commonly happens by the salt. In the presence of CaSO₄, the yield of sorbitol given by Pt/BP2000 was as high as 25 %C, but neither EG nor PG increased (entry 26). In this case, the conversion of cellulose (33%) was lower than that (50%) in the absence of the salt due to the deceleration of hydrolysis by SO₄²⁻ [32]. A similar phenomenon was observed by adding NaHCO₃ and Na₂SO₄. NaHCO₃ reduced the yield of sorbitol to 1.0 %C but increased EG and PG to 14 %C in total (entry 27), whereas Na₂SO₄ just decreased the conversion of cellulose to 28% (entry 28). These results suggest that the basic anions (CO₃²⁻, HCO₃⁻) drastically shift the products distribution from sorbitol to by-products. It has been reported that Ni catalysts supported on basic supports convert cellulose to EG and PG [40, 41]. The reaction of raw **silver grass-1** gave low yields of sugar alcohols, but the amounts of EG and PG were larger than those in the reaction of the pretreated samples (Table 3, entries 14-17). The reason for this difference might be due to the presence of basic compounds in the raw biomass. Consequently, even weak bases such as NaHCO₃ need to be removed for the production of sorbitol.

We propose that bases enhance both the side-reactions of sugar intermediates in the reaction of cellulose and promote the decomposition of sorbitol [42] (Figure 4). For the former point, it is known that bases catalyze the isomerization and retro-aldol reactions of glucose. For the latter, control experiments for the degradation of sorbitol were performed with Pt/BP2000 or CaCO₃ catalysts. Pt/BP2000 decomposed sorbitol under the reaction conditions (37% conversion, entry 33), but neither EG nor PG were formed (total 0.4 %C yield). By adding CaCO₃ to this system, conversion of sorbitol increased to 95%, and yields of EG and PG were remarkably raised (total

30 %C, entry 34). In contrast, CaCO₃ did not transform sorbitol in the absence of Pt catalyst (entry 35), showing that metal and base catalysts synergistically decompose sorbitol. Thus, we speculate that metal catalysts cause both dehydrogenation of sorbitol and hydrogenation of sugars in a chemical equilibrium, and that the sugars undergo base-catalyzed reactions. A similar mechanism has been proposed for the conversion of xylitol to EG and PG [42]. Pt also degrades sugars [43], but bases are significantly more active as even weak bases drastically change the product selectivity.

4. Conclusions

The direct conversion of raw silver grass by a carbon-supported Pt catalyst under H₂ pressure produced small amounts of sorbitol (2.8 wt%), xylitol (7.3 wt%), and other sugar alcohols. It has been suggested that lignin reduces the reactivity of cellulose, as lignin presents together with cellulose and both compounds are insoluble in water. Moreover, even weak bases drastically changes the main products from sugar alcohols to by-products such as EG and PG. The major effect of bases is the decomposition of sugar intermediates and sorbitol. The removal of these ingredients by alkali-explosion and neutralization, condensing cellulose and hemicellulose at the same time, increased the yields of sorbitol (13 wt%) and xylitol (14 wt%). Simple boiling treatment is not suitable for the synthesis of sorbitol, but effective for the production of xylitol, as lignin largely remains.

Acknowledgements

We would like to thank Prof. Toshihiko Yamada for supplying **silver grass-1**. This work was supported by a Grant-in-Aid for Scientific Research (KAKENHI, 20226016).

References

- [1] C.O. Tuck, E. Pérez, I.T. Horváth, R.A. Sheldon, M. Poliakoff, *Science* 337 (2012) 695-699.
- [2] H. Kobayashi, A. Fukuoka, *Green Chem.* 15 (2013) 1740-1763.
- [3] A. Fukuoka, P.L. Dhepe, *Angew. Chem. Int. Ed.* 45 (2006) 5161-5163.
- [4] C. Luo, S. Wang, H. Liu, *Angew. Chem. Int. Ed.* 46 (2007) 7636-7639.

- [5] W. Deng, X. Tan, W. Fang, Q. Zhang, Y. Wang, *Catal. Lett.* 133 (2009) 167-174.
- [6] V. Jollet, F. Chambon, F. Rataboul, A. Cabiac, C. Pinel, E. Guillon, N. Essayem, *Green Chem.* 11 (2009) 2052-2060.
- [7] H. Kobayashi, Y. Ito, T. Komanoya, Y. Hosaka, P. L. Dhepe, K. Kasai, K. Hara, A. Fukuoka, *Green Chem.* 13 (2011) 326-333.
- [8] R.M. Ravenelle, F.Z. Diallo, J.C. Crittenden, C. Sievers, *ChemCatChem* 4 (2012) 492-494.
- [9] J. Geboers, S. Van de Vyver, K. Carpentier, P. Jacobs, B. Sels, *Green Chem.* 13 (2011) 2167-2174.
- [10] M. Liu, W. Deng, Q. Zhang, Y. Wang, Y. Wang, *Chem. Commun.* 47 (2011) 9717-9719.
- [11] H. Kobayashi, H. Matsuhashi, T. Komanoya, K. Hara, A. Fukuoka, *Chem. Commun.* 47 (2011) 2366-2368.
- [12] J. Pang, A. Wang, M. Zheng, Y. Zhang, Y. Huang, X. Chen, T. Zhang, *Green Chem.* 14 (2012) 614-617.
- [13] T. Deng, H. Liu, *Green Chem.* 15 (2013) 116-124.
- [14] J.W. Han, H. Lee, *Catal. Commun.* 19 (2012) 115-118.
- [15] D. Reyes-Luyanda, J. Flores-Cruz, P.J. Morales-Pérez, L.G. Encarnación-Gómez, F. Shi, P.M. Voyles, N. Cardona-Martínez, *Top. Catal.* 55 (2012) 148-161.
- [16] L.-N. Ding, A.-Q. Wang, M.-Y. Zheng, T. Zhang, *ChemSusChem* 3 (2010) 818-821.
- [17] P. Yang, H. Kobayashi, K. Hara, A. Fukuoka, *ChemSusChem* 5 (2012) 920-926.
- [18] S. Van de Vyver, J. Geboers, M. Dusselier, H. Schepers, T. Vosch, L. Zhang, G. Van Tendeloo, P.A. Jacobs, B.F. Sels, *ChemSusChem* 3 (2010) 698-701.
- [19] S. Van de Vyver, J. Geboers, W. Schutyser, M. Dusselier, P. Eloy, E. Dornez, J.W. Seo, C.M. Courtin, E.M. Gaigneaux, P.A. Jacobs, B.F. Sels, *ChemSusChem* 5 (2012) 1549-1558.
- [20] G. Liang, H. Cheng, W. Li, L. He, Y. Yu, F. Zhao, *Green Chem.* 14 (2012) 2146-2149.
- [21] J. Geboers, S. Van de Vyver, K. Carpentier, K. de Blochouse, P. Jacobs, B. Sels, *Chem. Commun.* 46 (2010) 3577-3579.
- [22] R. Palkovits, K. Tajvidi, A.M. Ruppert, J. Procelewska, *Chem. Commun.* 47 (2011) 576-578.
- [23] Y. Zhu, Z.N. Kong, L.P. Stubbs, H. Lin, S. Shen, E.V. Anslyn, J.A. Maguire, *ChemSusChem* 3

- (2010) 67-70.
- [24] I.A. Ignatyev, C. Van Doorslaer, P.G.N. Mertens, K. Binnemans, D.E. De Vos, *ChemSusChem* 3 (2010) 91-96.
- [25] J. Geboers, S. Van de Vyver, K. Carpentier, P. Jacobs, B. Sels, *Chem. Commun.* 47 (2011) 5590-5592.
- [26] Y. Ogasawara, S. Itagaki, K. Yamaguchi, N. Mizuno, *ChemSusChem* 4 (2011) 519-525.
- [27] J. Hilgert, N. Meine, R. Rinaldi, F. Schüth, *Energy Environ. Sci.* 6 (2013) 92-96.
- [28] O. Bobleter, *Prog. Polym. Sci.* 19 (1994) 797-841.
- [29] S.K. Guha, H. Kobayashi, K. Hara, H. Kikuchi, T. Aritsuka, A. Fukuoka, *Catal. Commun.* 12 (2011) 980-983.
- [30] M. Kåldström, N. Kumar, D.Y. Murzin, *Catal. Today* 167 (2011) 91-95.
- [31] M. Kåldström, N. Kumar, M. Tenho, M.V. Mokeev, Y.E. Moskalenko, D.Y. Murzin, *ACS Catal.* 2 (2012) 1381-1393.
- [32] H. Kobayashi, M. Yabushita, T. Komanoya, K. Hara, I. Fujita, A. Fukuoka, *ACS Catal.* 3 (2013) 581-587.
- [33] M. Himken, J. Lammel, D. Neukirchen, U. Czipionka-Krause, H.-W. Olf, *Plant Soil* 189 (1997) 117-126.
- [34] M.J. Taherzadeh, K. Karimi, *Int. J. Mol. Sci.* 9 (2008) 1621-1651.
- [35] A. Sluiter, B. Hames, R. Ruiz, C. Scarlata, J. Sluiter, D. Templeton, D. Crocker, NREL/TP-510-42618 (2011). <http://www.nrel.gov/biomass/pdfs/42618.pdf>.
- [36] J.F. Ma, N. Yamaji, *Trends Plant Sci.* 11 (2006) 392-397.
- [37] E. Dinand, M. Vignon, H. Chanzy, L. Heux, *Cellulose* 9 (2002) 7-18.
- [38] S. Deguchi, K. Tsujii, K. Horikoshi, *Chem. Commun.* (2006) 3293-3295.
- [39] C.H. Bartholomew, *Appl. Catal. A: Gen.* 212 (2001) 16-60.
- [40] X. Wang, L. Meng, F. Wu, Y. Jiang, L. Wang, X. Mu, *Green Chem.* 14 (2012) 758-765.
- [41] X. Wang, F. Wu, S. Yao, Y. Jiang, J. Guan, X. Mu, *Chem. Lett.* 41 (2012) 476-478.
- [42] J. Sun, H. Liu, *Green Chem.* 13 (2011) 135-142.
- [43] Y. Kanie, K. Akiyama, M. Iwamoto, *Catal. Today* 178 (2011) 58-63.

Tables

Table 1 EDX analysis of biomass.

Entry	Biomass	Element /wt%						
		K	Ca	Fe	Si	P	S	Cl
1	Silver grass-1	1.0	0.14	0.03	3.7	0.13	0.09	0.02
2	Silver grass-1W	0.04	0.15	0.02	1.7	0.01	0.05	n.d. ^a
3	Silver grass-1S	n.d. ^a	0.03	0.03	1.5	n.d. ^a	0.04	n.d. ^a
4	Silver grass-1H	n.d. ^a	n.d. ^a	0.02	3.4	n.d. ^a	0.04	0.01
5	Silver grass-2	0.08	0.21	0.01	7.7	0.01	0.04	0.03
6	Silver grass-2AN	n.d. ^a	0.03	0.01	2.2	n.d. ^a	0.03	0.10

^a Not detected.

Table 2 Dry-basis composition of biomass.

Entry	Biomass	Ingredient /wt%			
		Glucan (cellulose)	C ₅ sugar polymers (hemicellulose)	Acid-insoluble lignin	Others
7	Silver grass-1	34	19	26	21
8	Silver grass-1W	42	24	18	16
9	Silver grass-2	38	24	21	17
10	Silver grass-2A	50	25	17	8
11	Silver grass-2AN	58	27	11	4
12	Amur silver grass-AN	62	27	7	4
13	Wheat straw-AN	55	27	14	4

Table 3 Hydrolytic hydrogenation of biomass over Pt/BP2000 catalyst.

Entry	Substrate	Yield ^a /wt% based on dried substrate					
		Sor	Man	Xyl	Ara	EG	PG
14	Silver grass-1	2.8(7.4) ^b	0 (0) ^b	7.3 (33) ^c	3.9 (18) ^c	2.0	4.0
15	Silver grass-1W	4.0(8.6) ^b	0 (0) ^b	16 (57) ^c	4.0 (15) ^c	1.3	2.1
16	Silver grass-1S	4.8	0	15	3.5	1.3	2.4
17	Silver grass-1H	3.5	0	13	3.5	1.1	2.6
18	Silver grass-2A	0.4(0.7) ^b	0 (0) ^b	1.4 (4.9) ^c	0.9 (3.1) ^c	4.5	4.7
19	Silver grass-2AN	13 (20) ^b	1.9 (2.9) ^b	14 (45) ^c	2.0 (6.2) ^c	0.9	1.5
20 ^d	Silver grass-2AN	4.6(6.9) ^b	2.0 (3.0) ^b	6.1 (28) ^c	0 (0) ^c	2.9	5.4
21 ^d	Silver grass-2AN	2.6(3.9) ^b	1.6 (2.4) ^b	5.7 (27) ^c	0 (0) ^c	3.0	5.7
22	Amur silver grass-AN	17 (25) ^b	2.5 (4.0) ^b	16 (50) ^c	2.6 (8.2) ^c	1.1	1.8
23	Wheat straw-AN	12 (20) ^b	2.0 (3.2) ^b	15 (49) ^c	2.0 (6.4) ^c	0.8	1.3

Reaction conditions: 1.3 wt% Pt/BP2000 200 mg, substrate 320 mg (dry basis), water 40 mL, $p(\text{H}_2)$ 5 MPa, 463 K, 24 h. ^a Sor: sorbitol; Man: mannitol; Xyl: xylitol; Ara: arabitol; EG: ethylene glycol; PG: propylene glycol. ^b %C based on containing cellulose. ^c %C based on containing hemicellulose. ^d A reuse experiment using the residue of the experiment of the previous entry number and fresh substrate of 320 mg.

Table 4 Control experiments for hydrolytic hydrogenation.

Entry	Catalyst	Additive	Substrate	Conv. /%	Yield ^a /%C							
					Sor	Man	Xyl	Ara	EG	PG	Others	
24	Pt/BP2000	None	Cellulose ^d	50	35	3.7	–	–	0.4	0.4	11	
25	Pt/BP2000	CaCO ₃	Cellulose ^d	38	0.3	0.3	–	–	4.3	5.2	28	
26	Pt/BP2000	CaSO ₄ ·0.5H ₂ O	Cellulose ^d	33	25	2.6	–	–	0.4	0.3	5	
27	Pt/BP2000	NaHCO ₃	Cellulose ^d	42	1.0	0.4	–	–	5.5	8.5	27	
28	Pt/BP2000	Na ₂ SO ₄	Cellulose ^d	29	16	2.8	–	–	0.5	0.4	9	
29	Ru/BP2000	None	Cellulose ^d	47	18	2.7	–	–	1.1	2.7	23	
30	Ru/BP2000	CaCO ₃	Cellulose ^d	48	0.1	0	–	–	6.2	6.1	36	
31 ^b	Pt/BP2000	None	Hemicellulose ^e	–	–	–	96 ^h	61 ⁱ	0.4	1.6	–	
32 ^b	Ni/KB ^c	None	Hemicellulose ^e	–	–	–	30 ^h	46 ⁱ	1.9	10	–	
33	Pt/BP2000	None	Sorbitol ^f	37 ^g	–	2.5	–	–	0.1	0.3	34	
34	Pt/BP2000	CaCO ₃	Sorbitol ^f	95 ^g	–	1.3	–	–	12	18	64	
35	None	CaCO ₃	Sorbitol ^f	1 ^g	–	0.6	–	–	0	0	0	

Reaction conditions: 1.3 wt% M/BP2000 (M: 14 μ g-atom), additive 8.5 mM based on cation, water 40 mL, $p(\text{H}_2)$ 5 MPa, 463 K, 24 h. ^a Sor: sorbitol; Man: mannitol; Xyl: xylitol; Ara: arabitol; EG: ethylene glycol; PG: propylene glycol; Others: glycerol, erythritol, hexanetetrol, sorbitan, and unidentified products containing undetected ones. ^b 433 K. ^c 70 wt% Ni/Ketjenblack EC600JD 50 mg. This catalyst is active for the conversion of cellulose. ^d Microcrystalline cellulose 320 mg. ^e Arabinoxylan 324 mg. ^f Sorbitol 180 mg. ^g Determined by HPLC analysis. ^h Based on xylan content. ⁱ Based on arabinan content.

Figure captions

Figure 1. Hydrolytic hydrogenation of cellulose and hemicellulose.

Figure 2. XRD patterns of silver grass samples.

Figure 3. Time course of the hydrolytic hydrogenation of **silver grass-2AN**.

Figure 4. Reaction pathways for the catalytic conversion of cellulose.

Figures

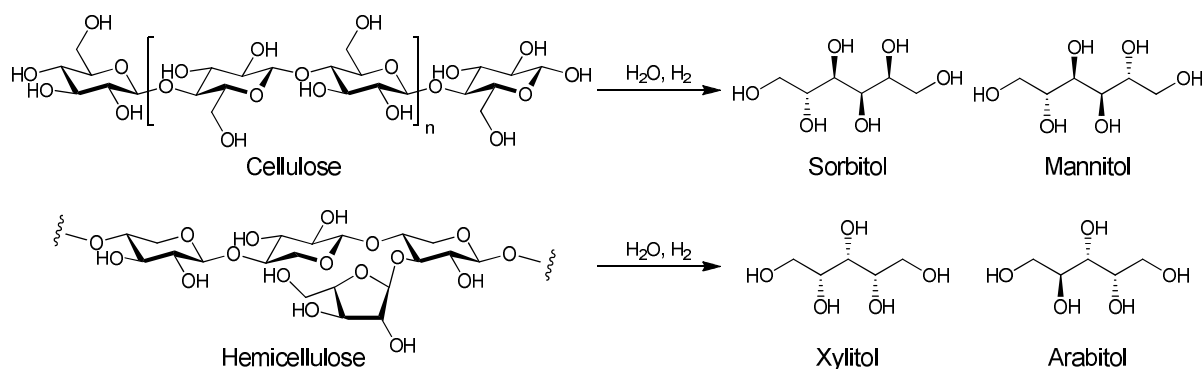


Figure 1. Hydrolytic hydrogenation of cellulose and hemicellulose.

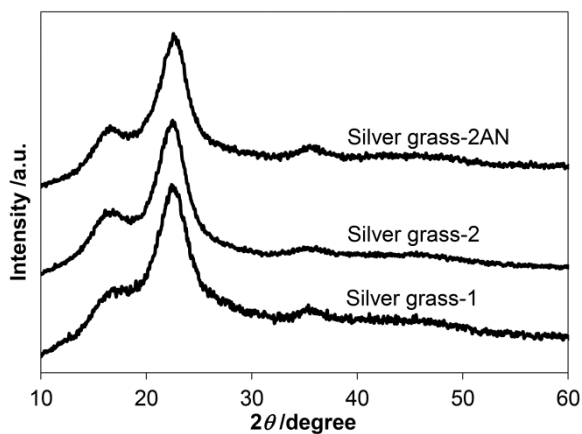


Figure 2. XRD patterns of silver grass samples.

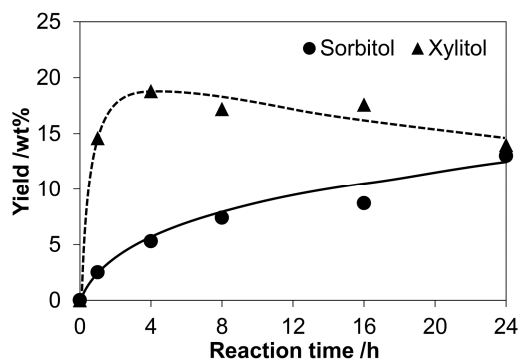


Figure 3. Time course of the hydrolytic hydrogenation of silver grass-2AN.

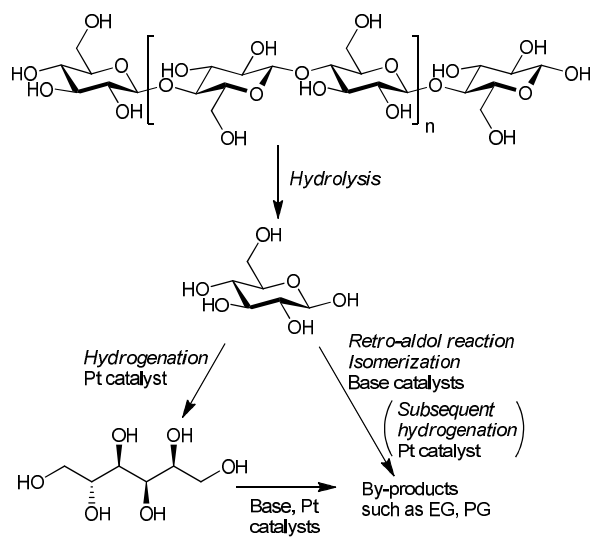


Figure 4. Reaction pathways for the catalytic conversion of cellulose.

Production of sugar alcohols from real biomass by supported platinum catalyst

Highlights

Hydrolytic hydrogenation of real biomass

Production of sorbitol and xylitol

Reduction of cellulose reactivity by lignin

Base catalysis for side-reactions of sugar compounds

Alkali-explosion for removal of lignin and inorganic salts

