[Regular Paper]

One-pot Conversion from Lignocellulosic Biomass to Isosorbide

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(Received March 7, 2016)

Isosorbide and its derivatives are important monomers in the polymer industry and valuable intermediates in the pharmaceutical industry. Recently, one-pot conversion of cellulose into isosorbide has been reported using supported metal catalysts and acid catalysts. The present study investigated one-pot conversion of lignocellulosic biomass into isosorbide using supported metal catalyst and ion-exchange resin Amberlyst 70. Isosorbide could be obtained from one-pot conversion of Japanese cedar with 25.4 % yield using supported ruthenium catalyst and Amberlyst 70 at 463 K. Isosorbide yields from one-pot conversion of eucalyptus and bagasse were 8.3 % and 12.8 %, respectively. One-pot conversion has the potential to be a powerful method to convert lignocellulosic biomass to useful chemicals.

Keywords

Biomass conversion, Lignocellulose, Cellulose, Isosorbide, Sugar alcohol, Ruthenium catalyst

1. Introduction

Utilization of lignocellulosic biomass as a feedstock for the production of useful chemicals is expected to be extremely important for the future sustainable society^{1)–3)}. Currently, cellulose is the most promising component of lignocellulosic biomass because of its abundance and easy conversion *via* the intermediate sorbitol into valuable chemicals^{4),5)}. Sorbitol can be produced by one-step cracking of cellulose using a platinum catalyst and hydrogen in water^{6),7)}. Direct conversion of cellulose into sorbitol has been reported by hydrogenolysis using supported metal catalysts with hydrogen^{6)–14)}.

Isosorbide, which can be obtained by dehydration of sorbitol^{15)–18)}, has a rigid structure and two functional hydroxyl groups, so isosorbide can increase the glass transition temperatures of polyesters compared with ethylene glycol in poly(ethylene terephthalate) (PET)^{15),19),20)}. Isosorbide and its derivatives are not only prospective monomers in the polymer industry but also valuable intermediates in the pharmaceutical industry²⁰⁾. Recently, one-pot conversion of cellulose into isosorbide has been reported using supported metal catalysts and acid catalysts (**Scheme 1**)^{21)–25)}. Cellulose

could be converted into isosorbide with a yield of 56.7 % using ruthenium supported on niobium phosphate and hydrogen²¹⁾. We reported that isosorbide could be obtained from cellulose with a yield of 55.8 % using ruthenium supported on carbon, ion-exchange resin, and hydrogen²²⁾.

Cellulose is incorporated into the hemicellulose-lignin matrix in lignocellulosic biomass, and pure cellulose is generally produced from lignocellulosic biomass using a strong base and strong acid catalyst to remove the lignin and hemicellulose components completely. Conversion of cellulose into chemicals has been an active area of research, but conversion of lignocellulosic biomass into chemicals has not been extensively investigated. One-pot conversion of lignocellulosic biomass into isosorbide was reported with yields of isosorbide of 4 % and 7 % from softwood and hardwood, respectively, using supported ruthenium catalyst and tungstosilicic acid at 483 K²³⁾.

The present study describes the one-pot conversion of lignocellulosic biomass such as softwood, hardwood, and herbaceous biomass into isosorbide using supported metal catalyst and ion-exchange resin, Amberlyst 70, (**Scheme 1**) to increase the yield of isosorbide from lignocellulosic biomass.

2. Experimental

Ruthenium and platinum catalysts (Ru/C and Pt/C)

DOI: dx.doi.org/10.1627/jpi.59.155

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Scheme 1 One-pot Conversion of Lignocellulosic Biomass into Isosorbide

supported on carbon were prepared by an impregnation method using carbon black BP2000 (Cabot Corp.) and aqueous solutions of RuCl_3 or $\text{cis}[\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2]$ as follows^{26,27}. The aqueous solution of ruthenium or platinum and carbon black were stirred for 12 h at ambient temperature and evaporated to dryness at 323 K under reduced pressure using a rotary evaporator, so that the amount of metal in the catalyst was 4 wt%. Then the samples were dried for 10 h at 373 K in an oven, followed by treatment at 673 K for 2 h under flowing hydrogen.

Japanese cedar, eucalyptus, and bagasse chips were used as the lignocellulosic biomass, which were obtained by cutting or crushing, then pulverized with a ball mill at 60 rpm for 48 h. Analysis to measure the components such as cellulose, hemicellulose, and lignin in the biomass was carried out according to the literature²⁸.

One-pot conversion of lignocellulosic biomass into isosorbide by hydrogenolysis was carried out in a batch reactor with inner volume of 100 cm³^{6,26}. The lignocellulosic biomass (0.324 g), supported metal catalyst (0.2–0.3 g), Amberlyst 70 (2.0–3.0 g) and water (40 g) were loaded into the reactor, then hydrogen gas (5 MPa) was introduced into the reactor at ambient temperature. The reactor was heated to 453–463 K and maintained at that temperature for the reaction time (16 h) with screw stirring. After the reaction, the resultant mixture of liquid and solid was filtered to separate the solid materials from the liquid fraction. Quantitative analysis of the water-soluble products in the liquid fraction was conducted by high performance liquid chromatography (HPLC). The yield of each product was calculated based on the hexose content in the reactant chips as follows:

Yield of each product (%) = (each product of C6 (mol)) / (hexose in reactant chips (mol)) $\times$ 100.

Conversion of lignocellulosic biomass into sugar alcohols was also carried out without Amberlyst 70 as reference experiments. The lignocellulosic biomass (0.324 g), supported metal catalyst (0.2–0.3 g) and water (40 g) were loaded into the reactor, then hydrogen gas (5 MPa) was introduced into the reactor at ambient temperature. The analysis procedure was as described above.

Sorbitol dehydration reaction was also carried out in a batch reactor. The sorbitol aqueous solution (0.05 mol dm⁻³, 40 cm³) and Amberlyst 70 1 g or 3 g were loaded into the reactor, the reactor was purged with helium gas, and then the reactor was heated to 463 K and maintained at that temperature for 16 h.

3. Results and Discussion

Table 1 shows the component and sugar contents of the Japanese cedar, eucalyptus, and bagasse used as substrates in this study²⁷. Cellulose contents in the used lignocellulosic biomass were about 40 wt%. Cellulose is a polymer of glucose and hemicellulose is a polymer of several types of sugars including glucose. Therefore, the glucose contents in the biomass were higher than the cellulose contents by the difference of glucose contained in the hemicellulose.

Direct conversion of cellulose into sorbitol by hydrogenolysis has been achieved using supported platinum catalysts^{6,7,11,29,30} and supported ruthenium catalysts^{8,11,13,29,31,32}. Removal of lignin and hemicellulose by chemical treatment is required to obtain pure cellulose from lignocellulosic biomass. We previously reported the direct conversion of lignocellulosic biomass into sugar alcohols using Pt/C and Ru/C without pretreatment for the removal of lignin and hemicellulose^{26,27}. Sorbitol could be obtained from Japanese cedar over Pt/C and Ru/C catalysts under

Table 1 Analyses of Component and Sugar Content for Japanese Cedar, Eucalyptus, and Bagasse

Biomass	Component [wt%]		Hexose content [wt%]		
	Cellulose	Hemicellulose	Glucose	Mannose	Galactose
Japanese cedar	40.9	24.8	46.5	8.8	1.8
Eucalyptus	39.8	35.4	40.1	7.6	3.9
Bagasse	37.0	31.4	45.9	0	0

Table 2 Hexitol Yield from Conversion of Japanese Cedar over Supported Metal Catalysts under 5 MPa H₂ for 16 h (Japanese cedar 0.324 g)

Catalyst	Sorbitol [%]	Mannitol [%]	Galactitol [%]	Total [%]
Pt/C, 0.2 g	39.5	12.0	0.0	51.5
Pt/C, 0.3 g	40.4	14.1	2.6	57.1
Ru/C, 0.2 g	26.7	12.4	0.0	39.1

Table 3 Product Yields of Sorbitol Dehydration Using Amberlyst 70 (0.05 mol dm⁻³ sorbitol aqueous solution 40 cm³, 16 h)

Temperature [K]	Amount of Amberlyst 70 [g]	Yield [%]	
		Isosorbide	1,4-AHSO
453	1.0	45.6	42.7
453	3.0	64.6	10.8
463	1.0	62.9	23.9
463	3.0	78.8	0

Table 4 Product Yields Obtained from Conversion of Japanese Cedar Using Supported Metal Catalyst and Amberlyst 70 under 5 MPa H₂ (Japanese cedar 0.324 g, Amberlyst 70 3.0 g, Pt/C 0.3 g or Ru/C 0.2 g, 16 h)

Catalyst	Temperature [K]	Yield [%]				
		Isosorbide	1,4-AHSO	Sorbitol	Isomannide	Mannitol
Pt/C	453	1.8	7.1	2.4	0.0	2.4
Pt/C	463	2.0	5.3	0.6	0.0	1.9
Ru/C	453	22.6	14.2	0.0	0.1	0.0
Ru/C	463	25.4	12.4	0.0	0.1	0.0

5 MPa H₂ at 463 K for 16 h (**Table 2**)²⁷. The yield of sorbitol was about 40 % with Pt/C catalyst, higher than the 26.7 % obtained with Ru/C catalyst.

Sorbitol can be dehydrated into 1,4-anhydrosorbitol (1,4-AHSO) and 1,4-AHSO can be dehydrated into isosorbide using acid catalysts such as sulfuric acid¹⁹, sulfated zirconia³³, and zeolite³⁴. Amberlyst 70 is an ion-exchange resin, which can also catalyze sorbitol dehydration as a solid acid (**Table 3**). Isosorbide yield increased with higher amount of Amberlyst 70 and higher reaction temperature. We reported that cellulose could be converted into isosorbide using Pt/C (isosorbide yield 29.9 % at 453 K) and Ru/C (isosorbide yield 55.8 % at 463 K) with Amberlyst 70²².

In this study, we carried out one-pot conversion of Japanese cedar into isosorbide using Pt/C and Ru/C catalysts with Amberlyst 70 (**Table 4**). Isosorbide was obtained with 25.4 % yield using Ru/C and Amberlyst 70 at 463 K, which was much higher than the reported isosorbide yield (7 %) from lignocellulosic biomass²³. Therefore, this reaction method will allow conversion of lignocellulosic biomass into useful chemicals using

supported metal catalysts in a one-step procedure. On the other hand, isomannide, a dehydration product of mannitol, could not be obtained (**Table 4**) even if the isosorbide yield was more than 25 %. Sorbitol can be dehydrated into isosorbide, but mannitol is dehydrated into isomannide with only 20 % yield in high temperature liquid water¹⁸, indicating that mannitol dehydration into isomannide is not a major dehydration pathway.

Conversion of lignocellulosic biomass into isosorbide consists of four steps: removal of lignin and hemicellulose, cellulose hydrolysis, glucose hydrogenation, and sorbitol dehydration (**Scheme 1**). For conversion of biomass into sorbitol, the Pt/C catalyst (40.4 % sorbitol yield) was more active than the Ru/C catalyst (26.7 %) (**Table 2**). On the other hand, the isosorbide yield obtained by the one-pot reaction with Amberlyst 70 using Pt/C (2.0 %) at 463 K was much lower than the yield (25.4 %) using Ru/C (**Table 4**). Previously, we found that the Ru/C catalyst was more active than the Pt/C catalyst for direct cellulose conversion to isosorbide with Amberlyst 70²². Ru/C was also reported

Table 5 Product Yields Obtained from Conversion of Japanese Cedar Using Supported Ruthenium Catalyst and Amberlyst 70 under 5 MPa H₂ (biomass 0.324 g, Amberlyst 70 3.0 g, Ru/C 0.2 g, 463 K, 16 h)

Biomass	Yield [%]				
	Isosorbide	1,4-AHSO	Sorbitol	Isomannide	Mannitol
Japanese cedar	25.4	12.4	0.0	0.1	0.0
Eucalyptus	8.3	21.9	0.0	0.0	0.0
Bagasse	12.8	42.7	0.0	0.0	0.0

as more active than Pt/C for one-pot conversion cellulose to isosorbide with hydrochloric acid or sulfuric acid²⁴).

The most effective reaction condition for the one-pot conversion of Japanese cedar (softwood) was applied to the direct conversion of eucalyptus (hardwood) and bagasse (herbaceous biomass) (Table 5). The isosorbide yields from eucalyptus and bagasse were 8.3 % and 12.8 %, respectively, indicating that the effectiveness of one-pot conversion into isosorbide depended on the type of biomass. The reasons for the changes in isosorbide yield with the reactant are unknown. One possible reason is that other components, such as lignin and inorganic components, reduced the activity of the catalysts. The yields of isosorbide from eucalyptus and bagasse were lower than that from Japanese cedar (Table 5), whereas the yields of 1,4-AHSO from eucalyptus and bagasse were higher than that from Japanese cedar, indicating that dehydration of 1,4-AHSO did not proceed well in the case of eucalyptus and bagasse. Lignin or inorganic components, as mentioned before, would suppress the acidity of Amberlyst 70, resulting in higher yield of 1,4-AHSO and lower yield of isosorbide.

Our present study succeeded in one-pot conversion of lignocellulosic biomass into isosorbide using supported ruthenium catalyst with Amberlyst 70. Isosorbide could be obtained from one-pot conversion of Japanese cedar with 25.4 % yield using Ru/C and Amberlyst 70, which was about three times higher than the reported isosorbide yield (7 %) from lignocellulosic biomass²³). This technique has considerable potential for one-pot conversion of lignocellulosic biomass into isosorbide.

4. Conclusions

One-pot conversion of lignocellulosic biomass into isosorbide was investigated using supported metal catalysts and ion-exchange resin Amberlyst 70. Isosorbide could be obtained from one-pot conversion of Japanese cedar with 25.4 % yield using Ru/C and Amberlyst 70 at 463 K. Isosorbide yields from similar one-pot conversion of eucalyptus and bagasse were 8.3 % and 12.8 %, respectively. One-pot conversion has the potential to be a powerful method to convert lignocellulosic biomass to useful chemicals.

Acknowledgment

Dr. Takashi Endo and Dr. Tatsuo Yagishita of National Institute of Advanced Industrial Science and Technology (AIST) kindly provided lignocellulosic biomass and we appreciate their helpful technical support about the component and sugar analysis of the biomass. We also acknowledge Prof. Atsushi Fukuoka and Prof. Hirokazu Kobayashi of Hokkaido University for helpful technical discussions about experimental setup and catalyst preparation.

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要 旨

リグノセルロース系バイオマスからイソソルビドのワンポット合成

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イソソルビドおよびその派生物は、高分子産業で有望な単量体であるだけでなく、医薬品産業における重要な中間体である。近年、担持金属触媒と酸触媒を利用して、セルロースからワンポットでイソソルビドへの変換が報告されているが、リグノセルロース系バイオマスからワンポットでイソソルビドへの変換は、ほとんど報告されていない。本稿では、担持金属触媒とイオン交換樹脂 Amberlyst 70を用いてリグノセルロース系バイオ

マスからイソソルビドへのワンポット変換を検討した。463 Kで担持ルテニウム触媒と Amberlyst 70を用い、スギから収率25.4 %でイソソルビドにワンポットで変換することに成功した。ユーカリおよびバガスを用いたワンポット変換反応では、それぞれ収率が8.3 % および12.8 %でイソソルビドが得られた。リグノセルロース系バイオマスから有用化学物質へのワンポット変換反応が有望であることが示された。