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Short communication

One-pot conversion of cellulose to isosorbide using supported metal catalysts and ion-exchange resin



Aritomo Yamaguchi ^{a,b,*}, Osamu Sato ^a, Naoki Mimura ^a, Masayuki Shirai ^c

^a Research Center for Compact Chemical System, National Institute of Advanced Industrial Science and Technology (AIST), 4-2-1 Nigatake, Miyagino, Sendai 983-8551, Japan

^b JST, PRESTO, 4-2-1 Nigatake, Miyagino, Sendai 983-8551, Japan

^c Department of Chemistry and Bioengineering, Faculty of Engineering, Iwate University, Ueda 4-3-5, Morioka 020-8551, Japan

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ABSTRACT

One-pot conversion of cellulose to isosorbide was investigated by supported metal catalysts and ion-exchange resin in water. The maximum isosorbide yield using supported platinum catalysts and Amberlyst 70 was less than 30%. The isosorbide yield drastically increased with supported ruthenium catalysts instead of supported platinum catalysts and it also increased with the loading of ruthenium on carbon support. One-pot conversion of cellulose to isosorbide by 4 wt.% ruthenium catalyst and Amberlyst 70 proceeded with isosorbide yield of 55.8%.

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1. Introduction

Conversion of lignocellulosic biomass to fuels and chemicals has greatly attracted attention for establishing the sustainable society because of the abundance and renewability of the lignocellulose [1-3]. Cellulose, a polymer of D-glucose, is the most abundant component of biomass; thus, valorization of cellulose is an issue of great interest. Recently, cellulose conversion to sorbitol has been reported by some research groups (Scheme 1) [4-12]. Subsequently, dehydration of sorbitol can provide valuable chemicals: both anhydrosorbitol (sorbitan) and isosorbide (Scheme 1) [13-19]. Anhydrosorbitol is a key material for producing sorbitan fatty acid esters, which are used as naturallyderived surfactants or nontoxic food additives. Isosorbide is a drug medicine used as osmotic diuretics and blood-pressure-lowering drugs. Also, isosorbide has attracted a great deal of attention because poly (ethylene terephthalate) (PET) containing isosorbide has higher glass transition temperatures than pure PET [13,20-22], broadening the applications of polyesters. Consequently, the cellulose valorization can be realized by conversion of cellulose to isosorbide or anhydrosorbitol. One-pot conversion of cellulose to isosorbide has been reported using a combination of supported metal catalyst and homogeneous acid such as sulfuric acid [23], hydrochloric acid [24], and heteropoly acid [25,26]. In these processes, however, neutralization procedure is essential to remove homogeneous acid catalysts and also separation processes of products from the salt solutions are required. Thus, the usage of heterogeneous acid catalyst is desirable for easy separation of the products. Li et al. reported that ruthenium supported on niobium phosphate showed high activity for cellulose conversion to isosorbide (maximum yield 52%) [27]. Further improvement of catalyst system such as combination of supported metal catalyst and solid acid is required for the higher isosorbide yield. In this work, we found that the combination of supported ruthenium catalysts and ion-exchange resin, Amberlyst 70, was effective for one-pot conversion of cellulose to isosorbide (Scheme 1). Recently, Shrotri et al. reported transfer hydrogenation of cellulose-based oligomers to sorbitol in a fixed-bed reactor [28], leading to the technique for the direct conversion of cellulose into isosorbide using a flow reactor.

2. Experimental

2.1. Catalyst preparation

The supported platinum catalysts were prepared by an impregnation method using a carbon black BP2000 (Cabot Corporation) and a nitric acid aqueous solution of cis-[Pt(NH₃)₂(NO₂)₂] (Furuya Metal Co., Ltd.) as follows. The aqueous solution of platinum precursor and the carbon black were stirred for 12 h at ambient temperature and evaporated to dryness at 323 K under reduced pressure by a rotary evaporator. Then the samples were dried for 10 h at 373 K in an oven, followed by

^{*} Corresponding author at: Research Center for Compact Chemical System, National Institute of Advanced Industrial Science and Technology (AIST), 4-2-1 Nigatake, Miyagino, Sendai 983-8551, Japan.

E-mail address: a.yamaguchi@aist.go.jp (A. Yamaguchi).



Scheme 1. One-pot conversion of cellulose to isosorbide.

treatment at 673 K for 2 h under flowing hydrogen. The amounts of platinum in the catalysts were 2 and 4 wt.%, of which the catalysts were represented as 2%Pt/C and 4%Pt/C, respectively.

The supported ruthenium catalysts were also prepared by an impregnation method using BP2000 and an aqueous solution of RuCl₃ (Wako Pure Chemical Industries, Ltd.). The preparation process of supported ruthenium catalysts (2%Ru/C and 4%Ru/C) was same as that of platinum catalysts.

The ion-exchange resin, Amberlyst 70, was purchased from The Dow Chemical Company and used without further purification.

2.2. Reaction procedure

Cellulose (Merck KGaA) was pulverized with a ball mill at 60 rpm for 48 h. The conversion of cellulose was carried out in a batch reactor (OM Lab-Tech, MMJ-100), of which inner volume was 100 cm³ [4,29]. The cellulose (0.324 g), the supported metal catalyst (0.1-0.4 g), Amberlyst 70 (0.5-3 g), and water (40 g) were loaded in the reactor and the reactor was purged with hydrogen gas, and then hydrogen gas (5 MPa) was loaded in the reactor at ambient temperature. The reactor was heated to 443-463 K and maintained at the reaction temperature for the reaction time (16 h) with screw stirring at 600 rpm. After the reaction, a mixture of liquid and solid was recovered and filtered to separate the solid materials from the liquid fraction. The quantitative analvsis of water-soluble products in the liquid fraction was conducted by high-performance liquid chromatography (Shimadzu, HPLC) with a refractive index detector (Shimadzu, RID-10A) and a UV-Vis detector (Shimadzu, SPD-20AV) equipped with a Rezex RPM-Monosaccharide Pb + 2 (8%) (Phenomenex) and a SUGAR SC1211 column (Shodex). Amount of total organic carbon (TOC) in the liquid fraction was determined using a total organic carbon analyzer (Shimadzu, TOC-V_{CSN}). The other water-soluble (WS) products defined in this manuscript were calculated from the amount of total organic carbon in the liquid fraction other than the amount of total carbon detected by HPLC. The product yield was calculated based on glucose unit in the reactant cellulose.

Some of the recovered solid fractions by filtration after the reaction were loaded in the reactor again to investigate the reusability of the catalysts, and then 0.324 g of fresh cellulose was also loaded in the reactor. The reaction was carried out in the same method as identified above.

Sorbitol dehydration reaction was also carried out in a batch reactor (OM Lab-Tech, MMJ-100). The sorbitol aqueous solution $(0.05 \text{ mol } \text{dm}^{-3}, 40 \text{ cm}^3)$ and Amberlyst 70 1 g were loaded in the reactor and the reactor was purged with helium gas, and then the reactor was heated to 463 K and maintained at the temperature for 16 h with screw stirring at 600 rpm.

3. Results and discussion

Sorbitol was obtained from cellulose by hydrogenolysis, combination of hydrolysis and hydrogenation, using supported platinum catalyst (2%Pt/C) and hydrogen (5 MPa) in water at 463 K for 16 h with a vield of sorbitol 60.2% (Table S1 and characterization result of the Pt/C catalyst are shown in ESI) [4,29,30]. Also, isosorbide could be obtained from sorbitol by dehydration using ion-exchange resin Amberlyst 70 1 g at 463 K for 16 h with a yield of isosorbide 62.9% (Table S2), where the maximum operating temperature of Amberlyst 70 was 463 K, as shown in its instructions. Accordingly, we carried out onepot conversion of cellulose to isosorbide using the Pt/C catalyst and Amberlyst 70 at 463 K for 16 h, resulting in 8.4% of isosorbide yield (Table 1). The isosorbide yield obtained by the one-pot reaction (8.4%) was much lower than the expected yield (38%) from stepwise reactions (first step 60.2% and second step 62.9%). The conversion of cellulose to isosorbide consists of cellulose hydrolysis, glucose hydrogenation, and sorbitol dehydration (Scheme 1). The acid catalyst Amberlyst 70 can enhance not only sorbitol dehydration but also cellulose hydrolysis; thus, it enables lower reaction temperature than 463 K. The isosorbide yield increased to 9.3% at 453 K (Table 1); however, it decreased to 6.5% at 443 K where the yield of sorbitol increased with decreasing reaction temperature, indicating that sorbitol dehydration was slow at lower temperature. Next, we changed the amount of the acid catalyst to accelerate the sorbitol dehydration. The isosorbide yield increased with increasing the amount of Amberlyst 70 and it reached 16.1% in the case of 3 g of Amberlyst 70 at 453 K (Table 2). Pt loadings and catalyst amounts were also investigated for the enhancement of the isosorbide yield from the cellulose (Table 3). The sizes of metal particle in 2%Pt/C and 4%Pt/C were 1.7 nm and 1.9 nm from hydrogen adsorption, respectively [30]. The isosorbide yield was increased from 16.1%

Table 1

Product yields obtained from conversion of milled cellulose using 2%Pt/C and Amberlyst 70 with 5 MPa H_2 for 16 h (milled cellulose 0.324 g, 2%Pt/C 0.2 g, Amberlyst 70 1.0 g).

$T^{a}(K)$	Yield (%)							
	IS ^b	1,4-AHSO ^c	SO ^d	IM ^e	MA ^f	Other WS ^g		
443	6.5	2.9	24.2	0.5	3.2	20.2		
453	9.3	0.3	12.4	0.5	1.1	21.5		
463	8.4	0.2	0.8	0.4	0.0	18.2		

^a Reaction temperature.

^b Isosorbide. 1.4-Anhydrosorbitol.

Ы Sorbitol.

Isomannide f

Mannitol.

g Other water-soluble products.

Table 2

Product yields obtained from conversion of milled cellulose using 2%Pt/C and Amberlyst 70 at 453 K with 5 MPa H₂ for 16 h (milled cellulose 0.324 g, 2%Pt/C 0.2 g).

Resin ^a (g)	Yield (%)				
	IS ^b	1,4-AHSO ^c	SO ^d	IM ^e	MA^{f}	Other WS ^g
0.5	7.0	2.7	20.1	0.2	3.4	19.7
1.0 ^h	9.3	0.3	12.4	0.5	1.1	21.5
3.0	16.1	9.2	2.2	0.7	0.2	8.9

^a Amount of Amberlyst 70.

^b Isosorbide.

^c 1,4-Anhydrosorbitol.

^d Sorbitol.

^e Isomannide.

^f Mannitol.

^g Other water-soluble products.

^h Same data in Table 1.

to 24.7% by an increase of 2%Pt/C catalyst amount from 0.2 to 0.3 g. On the other hand, the isosorbide yield over 0.1 g of 4%Pt/C (16.8%) was almost the same as that over 0.2 g of 2%Pt/C (16.1%) when the amounts of Pt surface atoms were almost the same. The isosorbide yield over 4%Pt/C increased with increasing catalyst amount and reached 29.9% using 0.3 g of 4%Pt/C; however, the obtained yield of isosorbide was still lower than the expected yield in the case of Pt/C catalysts.

The supported ruthenium catalysts were also reported to be active for the cellulose hydrogenolysis to sorbitol [5-7,11,29,31]. The sorbitol yield from cellulose was 51.2% at 463 K for 16 h, using supported ruthenium catalyst (4%Ru/C) and hydrogen (5 MPa) (Table S3 and characterization result of the Ru/C catalyst are shown in ESI). The Ru/C catalyst was comparably active to the Pt/C catalyst for the cellulose hydrolysis to sorbitol (Tables S1 and S3) in agreement with the previous reports [29,31]. We carried out one-pot conversion of cellulose to isosorbide using 4%Ru/C catalyst and Amberlyst 70 for 16 h (Table 4). The isosorbide yields using Ru/C were much higher than those using Pt/C catalysts. The total yield of sorbitol-derived materials, which were sorbitol, 1,4-anhydrosorbitol, and isosorbide, decreased with increasing reaction temperature. On the other hand, the isosorbide yield was higher at higher reaction temperature, indicating that the dehydration of sorbitol to isosorbide proceeded at high reaction temperature and at the same time side reaction also proceeded slightly. The isosorbide yield (55.8%) over 4%Ru/C and Amberlyst 70 was higher than the expected yield (32%) from stepwise reactions (first step 51.2% and second step 62.9%). We found that the Ru/C catalyst was more active than the Pt/C catalyst for the direct cellulose conversion to isosorbide with Amberlyst 70. The activity for cellulose into sorbitol using Ru/C was almost the same as that using Pt/C; however, the activity for cellulose into isosorbide using Ru/C and Amberlyst 70 was higher than that using Pt/C and Amberlyst 70. The activity of platinum was

Table 3

Product yields obtained from conversion of milled cellulose using Pt/C and Amberlyst 70 at 453 K with 5 MPa H_2 for 16 h (milled cellulose 0.324 g, Amberlyst 70 3.0 g).

Cat ^a	Yield (%)						
	IS ^b	1,4-AHSO ^c	SO ^d	IM ^e	$MA^{\mathbf{f}}$	Other WS ^g	
2%Pt/C, 0.2 g ^h	16.1	9.2	2.2	0.7	0.2	8.9	
2%Pt/C, 0.3 g	24.7	13.2	0.5	0.8	0.1	5.5	
4%Pt/C, 0.1 g	16.8	9.9	7.7	0.8	0.3	16.7	
4%Pt/C, 0.2 g	27.3	16.9	2.8	1.0	0.3	8.6	
4%Pt/C, 0.3 g	29.9	16.8	0.7	1.1	0.1	5.4	

^a Catalysts.

^b Isosorbide.

^c 1,4-Anhydrosorbitol.

^d Sorbitol.

^e Isomannide.

^f Mannitol.

^g Other water-soluble products.

^h Same data in Table 2.

Table 4

Product yields obtained from conversion of milled cellulose using 4%Ru/C and Amberlyst 70 with 5 MPa H₂ for 16 h (milled cellulose 0.324 g, 4%Ru/C 0.2 g, Amberlyst 70 3.0 g).

$T^{a}(K)$	Yield (?	%)				
	IS ^b	1,4-AHSO ^c	SO ^d	IM ^e	$MA^{\mathbf{f}}$	Other WS ^g
443	31.8	42.5	3.2	1.8	0.1	5.0
453	39.6	35.4	0.8	2.0	0.0	1.2
463	55.8	16.1	0.0	3.3	0.0	2.3

^a Reaction temperature.
^b Isosorbide

¹1,4-Anhydrosorbitol.

^d Sorbitol.

^e Isomannide.

^f Mannitol.

^g Other water-soluble products.

inhibited by Amberlyst 70; on the other hand, the Ru/C catalyst worked well for cellulose hydrogenolysis even with Amberlyst 70. Zhao et al. also reported the similar results that Ru/C was more active for cellulose conversion to isosorbide with hydrochloric acid or sulfuric acid [24]. The reported maximum isosorbide yield from one-pot conversion of cellulose was 52% using Ru/C and heteropoly acid [26] and Ru/niobium phosphate [27]. The one-pot conversion of cellulose to isosorbide consists of cellulose hydrolysis, glucose hydrogenation, and sorbitol dehydration. 5-Hydroxymethylfurfural (HMF) is also reported as one of the promising chemicals from cellulosic biomass, which is reviewed in some articles [32,33]. HMF can be obtained by cellulose hydrolysis, glucose isomerization, and fructose dehydration. These reactions also proceed using acid catalysts; however, the HMF yield is not so high (ca. 30%) unless ionic liquid or organic solvent was used [32,33]. In this study, we obtained isosorbide (yield 55.8%) and a trace amount of HMF can be obtained, indicating that glucose hydrogenation into sorbitol was faster than glucose isomerization to fructose under the reaction condition with acid catalyst, supported metal catalyst, and high-pressure hydrogen. We also investigated the effects of Ru loadings and catalyst amounts on the isosorbide yield from the cellulose (Table 5). The isosorbide yields using 4%Ru/C 0.1 g (29.4%) or 0.3 g (42.1%) were lower than that using 4%Ru/C 0.2 g (55.8%), indicating that optimum amount of 4%Ru/C was 0.2 g. In the case of 0.1 g of 4%Ru/C, the yield of the other water-soluble products was higher than those using 0.2 or 0.3 g, implying that the hydrogenation of glucose was slow because of less number of ruthenium metal sites. Interestingly, the isosorbide vield using 2%Ru/C 0.4 g (24.1%) was much lower than that using 4%Ru/C 0.2 g (55.8%) despite the same amount of Ru atoms on these catalysts. The metal dispersion of 2%Ru/C catalyst was 50.7% (Ru metal size 2.6 nm), which was twice larger than that of 4%Ru/C (25.0%, Ru metal size 5.3 nm); thus, the number of surface Ru atoms in 4%Ru/C 0.2 g (isosorbide yield 55.8%) was almost the same as that in 2%Ru/C 0.2 g

Table 5

Product yields obtained from conversion of milled cellulose using Ru/C and Amberlyst 70 at 463 K with 5 MPa H_2 for 16 h (milled cellulose 0.324 g, Amberlyst 70 3.0 g).

Cat ^a	Yield (%)						
	IS ^b	1,4-AHSO ^c	SOd	IM ^e	$MA^{\mathbf{f}}$	Other WS ^g	
2%Ru/C, 0.2 g	13.2	3.5	0.1	0.5	0.4	14.2	
2%Ru/C, 0.4 g	24.1	15.7	0.6	0.5	0.0	6.4	
4%Ru/C, 0.1 g	29.4	18.6	0.6	0.4	0.6	15.6	
4%Ru/C, 0.2 g ^h	55.8	16.1	0.0	3.3	0.0	2.3	
4%Ru/C, 0.3 g	42.1	24.4	0.6	2.4	0.0	3.1	

^a Catalysts.

^b Isosorbide.

^c 1,4-Anhydrosorbitol. ^d Sorbitol.

^e Isomannide.

^f Mannitol.

^g Other water-soluble products.

^h Same data in Table 4.



Fig. 1. Recycling results for the one-pot conversion of cellulose to isosorbide using 4%Ru/C and Amberlyst 70 at (a) 463, (b) 453, and (c) 443 K with 5 MPa H₂ for 16 h (milled cellulose 0.324 g, 4%Ru/C 0.2 g, Amberlyst 70 3.0 g). IS: isosorbide, 1,4-AHSO: 1,4-anhydrosorbitol, SO: sorbitol.

(isosorbide yield 13.2%). These results indicated that the active ruthenium species were formed in 4%Ru/C. Li et al. investigated the size effect of ruthenium metal particles on cellulose conversion to isosorbide [27] and showed that Ru metal particles with 5.5 nm showed the highest isosorbide yield. In this study, we also showed that 4%Ru/C with 5.3 nm of Ru metal particles provided the higher isosorbide yield than 2%Ru/C with 2.6 nm of Ru metal particles. We have succeeded in one-pot conversion of cellulose to isosorbide (yield 55.8%) by supported ruthenium catalysts and ion-exchange resin, Amberlyst 70, in water without homogeneous acid catalysts.

The reusability of the catalysts, 4%Ru/C and Amberlyst 70, was investigated by using them three times. These catalysts were recovered by filtration after the reaction and used without any treatment three times. The fresh cellulose was added each time and the yields were calculated based on the amount of fresh cellulose. The isosorbide yield at 463 K decreased from 55.8% (1st run) to 10.6% (2nd run) where the 1,4-AHSO also decreased from 16.1% to 4.2% (Fig. 1), indicating that the Ru/C catalyst deactivated and glucose hydrogenation did not proceed effectively. We confirmed that ruthenium species were not detected in water-soluble fraction after the reaction by ICP measurement, indicating that ruthenium species remained on the carbon support. The reason of the catalyst deactivation might be carbon precipitation on the ruthenium surface after the 1st run of the reaction. The reusability of the catalysts at lower reaction temperature became better. At 443 K, the yields of isosorbide and 1,4-anhydrosorbitol decreased from 31.8% and 42.5% (1st run) to 20.3% and 29.9% (2nd run), respectively. At low temperature, the side reactions such as polymerization might be slow and carbon precipitation might be less adsorbed on the metal surface; thus, the activity of ruthenium catalyst could be kept relatively. The isosorbide yield at the 3rd run became only 4.8% even at 443 K. The catalyst life time and regeneration method should be developed, which we must consider next.

4. Conclusions

We have succeeded in converting cellulose into isosorbide directly with 55.8% yield by a supported ruthenium catalyst and Amberlyst 70 in water. It has been demonstrated that the direct catalytic conversion of cellulose into useful chemicals is a powerful technique for the use of lignocellulosic biomass.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx. doi.org/10.1016/j.catcom.2015.04.009.

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