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An efficient and selective conversion of sorbitol in ionic liquids: use of ion exchange resin as a solid acid catalyst

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ABSTRACT

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1. Introduction

Conversion of biomass to valuable chemicals is of interest to develop sustainable chemistry.¹ Sorbitol is a biomass-derived chemicals and its conversion to isosorbide is an important reaction for this purpose.² The conversion is usually achieved by heating sorbitol by the presence or absence of an appropriate catalyst. However, the reaction usually requires high temperature conditions and long reaction time, the energy consumption of the process becomes a considerable problem. It is desired to shorten the reaction time as well as efficient energy delivery to the reaction pot is required. Ionic liquids are regarded as a novel reaction solvent for chemical conversions because they have very unique properties that were never observed in any other solvent. The ionic liquids are recyclable and regarded as a green solvent in the chemical reaction. We recently developed a new use of ionic liquids for feedstock recycling chemistry and achieved efficient depolymerization of polyamides and unsaturated polyesters.⁴ We also achieved an efficient chemical conversion of cellulose to glucose.⁵ We employed hydrophobic ionic liquids for these purposes because of high iconicity⁶ that enhanced the reactivity of the reaction and ready separation of products and ionic liquids by simple extraction manipulation. For example, glucose without contamination of ionic liquids was readily isolated by our procedure.' This is a point that our methodology was superior to other methodologies that usually use hydrophilic ionic liquids. To improve the methodology, we thought that use of insoluble acid would give simple separation of acid catalyst. There are many types of ion exchange resin that have been used in organic synthesis. In this paper we report use of ion exchange resin for the conversion of sorbitol to isosorbide. We found

Sorbitol was readily converted by heating in hydrophobic ionic liquids by the presence of ion exchange resins. Chemoseletivity of the dehydration depended on the choice of ion exchange resin; Nafion selectively produced isosorbide while Amberlite gave 1,5-anhydrosorbitol along with unreacted sorbitol. Ionic liquids used in the reaction were readily recovered by simple extraction procedure. With these procedures, we succeeded to prepare isosorbide in pure form, not contaminated with either ionic liquids or acid catalyst, by simple experimental procedure.

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chemoselectivity of the reaction depended on the use of the type of resin, and achieved selective formation of isosorbide or 1,5anhydrosorbitol.

2. Results and discussion

We used three types of acidic ion exchange resins, Nafion, Dowex, and Amberlite, which were readily available commercially. We first examined Nafion as the catalyst. The conversion was performed in [TMPA][NTf₂] (trimethylpropylammmonium bis(trifluoromethylsulfonyl)imide, Me₃NPr⁺ Tf₂N⁻), a hydrophobic ionic liquid, by the presence of 20 wt% Nafion NR50 (Scheme 1). The results are summarized in Table 1.



Scheme 1

1 able 1. Conversion of sorbitol 1 by the presence of Nation	Table	1.	Conversion	of	sorbitol	1 t	by the	presence	of Naf	ion.	
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entry	temp (°C)	time (min)	2 ; yield (%) ^{a,b}	3 ; Yield (%) ^a
1	180	10	$65^{c}(9)$	0
2	150	10	30 (28)	23
3	200	10	41 (7)	3
4	230	10	34 (8)	2
5	180	20	53 (5)	0

a. Determined by HPLC analyses. b. Recovery of the starting material **1** is in parentheses. c. Isolated yield.

Sorbitol was smoothly converted into isosorbide **2** in 65% yield by treatment with $[TMPA][NTf_2]$ in the presence of 20 wt% of Nafion, although small amounts of sorbitol **1** remaining was detected after the reaction (entry 1).⁸ The reaction progressed very fast under these conditions and was almost complete within 10 minutes. When the reaction temperature was set to 150 °C, the reaction rate was decelerated and the yield of isosorbide **2** decreased to 30% along with 28% of remaining sorbitol **1**. Note that the formation of 1,5-anhydrosorbitol **3** increased to 23% (entry 2). Higher reaction temperature did not change the results very much and isosorbide 2 was formed in slightly lower yields (entries 3 and 4). This is probably due to the decomposition of isosorbide during the reaction because of too high temperature conditions. To consume all of sorbitol we exposed the reaction mixture for 20 minutes, but the results were not very different.

Isolation and purification of isosorbide **2** was very simple. The reaction mixture was diluted with water and then filtered to remove resin catalyst. The filtrate was then extracted with organic solvent to remove the ionic liquids. The recovery of ionic liquids reached 98% after drying and evaporation of the organic solvent. ¹³C NMR spectrum of the recovered ionic liquids indicated a sharp quartet signal coming from the NTf₂ group. This result clearly suggested that the group survived during the manipulation and its amounts was maintained in almost the same level of the virgin ionic liquids. Finally concentration of the remaining water phase in vacuo afforded desired isosorbide **2** in almost pure form.

We then examined DOWEX HCR W-2 and Amberlite IR-120B for the reaction (Scheme 2). The results are summarized in Table 2.

OH OH HO UH OH Sorbitol 1	DOWEX HCR W-2 (20 wt%) or Amberlite IR-120B (20 wt%) [TMPA][NTf ₂] 180 °C, 10 min microwave irradiation	H OH or HO H or isosorbide 2	OH HO OH OH
Scheme 2			

Table 2. Conversion of sorbitol **1** by the presence of DOWEX or Amberlite.

entry	resin	pre-	2 ; Yield	3; Yield
		treatment	$(\%)^{a,b}$	$(\%)^{a}$
1	DOWEX	-	0 (100)	0
2	Amberlite	-	0 (100)	0
3	DOWEX	6M HCl	50(1)	18
4	DOWEX	AcOH	0 (100)	0
5	Amberlite	1M HCl	5 (32)	62

a. Determined by HPLC analyses. b. Recovery of the starting material 1 is in parentheses.

We firstly examined the both resin for the reaction, but no formation of isosorbide was observed (entries 1 and 2). This was probably because their capability as an acid catalysis was not sufficient to promote the reaction progress. To enhance the activity as the acid catalysis, we pretreated the resins with acid. Treatment of DOWEX with HCl enhanced the catalytic activity to consume sorbitol 1 quickly and desired isosorbide 2 was obtained in 50% along with the formation of 1,5-anhydrosorbitol 3 in 18% yield (entry 3). On the other hand pretreatment with acetic acid did not enhance the catalytic activity and no reaction occurred under the same conditions (entry 4). Pretreatment of Amberlite with HCl also improved the activity, however, 1,5anhydrosorbitol 3 was formed as the major product in this reaction although starting sorbitol 1 remained in 32% (entry 5). It was interesting that changing the resin catalyst controlled the chemoselectivity of the reaction. We are not sure the exact reason

of the change of the selectivity, but 1,5-anhydrosorbitol tends to become the major products when sorbitol 1 was treated less acidic or much milder conditions. For example, simple heating conditions conducted compound 3 as the kinetic product. Treatment of sorbitol 1 at lower temperature also formed 3 as a side product (Table 1, entry 2). We assume that the selective formation of 3 occurred because Amberlite is less acidic catalyst than Nafion and offers much milder conditions.

In the end, we examined reuse of the ionic liquids and the resin catalyst (Scheme 3).



Scheme 3

Unfortunately the recovered ionic liquids provided sluggish progress of the reaction and isosorbide 2 was obtained only 38% yield. Note that we observed the formation of 1,5anhydrosorbitol in 38% yield. We are not sure the reason why the recovered ionic liquids did not work well for the conversion although the recovered ionic liquids showed almost complete spectra in 13C NMR. The reuse of the resin catalyst was not effective because the reaction did not progressed well and most of sorbitol **1** remained in the reaction mixture. This is probably because Nafion was decomposed during the first reaction and the catalytic activity as an acid was spoiled. Or the cation exchange between [TMPA] cation and proton could progress in the resin surface, and this exchange spoiled the reactivity of recovered Nafion. So we concluded that recycling use of ionic liquids is not really effective and the acid resin tolerates only one-time use. Even so, we feel the present modification is effective because almost pure isosorbide was obtained by simple extraction and filtration manipulation.

In conclusion, we examined effective conversion of sorbitol to isosorbide, an important reaction of biomass conversion, under various conditions. Ionic exchange resin, especially Nafion, serves as an effective catalyst for the conversion and almost pure isosorbide was isolated in 65% by simple manipulation. The present methodology avoids contamination of acid catalysis such as TsOH in the product. Less acidic resin prefers to form 1,5anhydrosorbitol selectively. This information will give important information for further improvement of the reaction.

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- Conversion of sorbitol to isosorbide. Typical experimental 8. procedure (Table 1, entry 1): A mixture of sorbitol 1 (200.0 mg, 1.01 mmol) and Nafion NR-50 (44.1 mg) in [TMPA][NTf2] (2.689 g) was stirred and heated to 180 °C by microwave irradiation for 10 min. The residue was dissolved in MeOH (10 mL) and the MeOH solution was combined with the filtrate. The resulting organic solution was concentrated in vacuo. The filtrate was concentrated and water (30 mL) was added. The water solution was extracted with CH_2Cl_2 (10 × 30 mL). The organic phase was dried over Na₂SO₄. Filtration and concentration gave [TMPA][NTf₂] in 98% recovery (2.622 g). The water phase was concentrated in vacuo. The residue was subjected to flash chromatography (silica gel/EtOAc-MeOH 20:1 v/v) to give sorbitol 2 in 65% yield (98.4 mg). ¹H NMR (500 MHz, D_2O) δ 4.51 (t, J = 4.6 Hz, 1H), 4.36 (d, J = 4.2 Hz, 1H), 4.27 (td, J = 6.9, 5.0 Hz, 1H), 4.20 (d, J = 2.8 Hz, 1H), 3.84 – 3.77 (m, 2H), 3.74 (dd, J = 10.5, 3.2 Hz, 3H), 3.36 (dd, J = 9.0, 7.5 Hz, 1H); NMR (126 MHz, D₂O) δ 87.3, 81.4, 75.5, 75.1, 71.8, 71.1. Quantification of product 2 and 3 by HPLC was carried out by the following method. Fluctose (201.3 mg) as the internal standard was added to the residue of concentrated water phase and the mixture was dissolved by water (10 mL). This solution was analyzed by HPLC column (Waters X-bridgeAmide, 3.5 m, 4.6 mm id × 100 mm, CH₃CN-water 70:30, 0.6 mL/min, detected by JASCO RI2031plus RI detector).

- Efficient conversion of sorbitol to isosorbide in

hydrophobic ionic liquids.

- Microwave heating achieved very rapid conversion.

- perfect separation of product from ionic liquids Acception and catalyst was accomplished by simple extraction manipulation.