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Selective conversion of concentrated microcrystalline cellulose to isosorbide over Ru/C catalyst†Guanfeng Liang,^{a,b} Chaoyong Wu,^{a,b} Limin He,^{a,b} Jun Ming,^{a,b} Haiyang Cheng,^a Linhai Zhuo^a and Fengyu Zhao^{*a}

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Highly concentrated microcrystalline cellulose was directly converted to isosorbide with yields of 35–50%, providing a new approach for producing important fine chemicals from biomass.

Isosorbide is a promising biomass platform molecule having very important applications in many fields, for example, as additive to enhance the strength and rigidity of polymers, as a pharmaceutical intermediate, and as a monomer for biodegradable polymers.^{1,2} It is industrially produced by dehydration of sorbitol using a strong acid catalyst.³ Very recently, the feasibility of converting cellulose into isosorbide in a ZnCl₂ molten hydrate medium was investigated.⁴ In this work, we show for the first time that concentrated cellulose in the aqueous phase can be converted directly to isosorbide, a compound that is rarely obtained from cellulose. Therefore, this work is a new potential application of biomass to produce important chemicals.

Cellulose is one of the most abundant biomass materials on earth – the conversion of cellulose to fine chemicals is an important issue, and a great challenge in the research fields of energy and the environment.⁵ The efficient utilization of renewable biomass to produce fuels and chemicals is a promising way to solve the energy crisis and environmental issues by reducing the consumption of fossil fuels.⁶ Recently, many studies regarding the direct catalytic conversion of cellulose into polyols have been reported. For example, Fukuoka *et al.* investigated the conversion of cellulose over a supported noble metal catalyst (Pt/Al₂O₃), producing hexitols with 31% yield under optimum conditions.⁷ Subsequent research mainly focused on the design of hydrogenation catalysts for obtaining hexitols in high yield.⁸ Notably, tungsten carbide was reported to be effective in converting cellulose into ethylene glycol with a high yield.⁹

However, although some progress has been achieved, there is an inevitable conflict between fast cellulose hydrolysis and efficient carbon utilization when using a single hydrogenation catalyst. Cellulose hydrolysis is catalyzed by the H⁺ from water or the acid sites on the surface of catalyst, followed by hydrogenation over a metal catalyst, and cellulose hydrolysis is the rate-determining step. Elevated temperatures (>498 K) were usually used, which also make the hydrogenolysis step easier. In addition, combining acids with a supported metal catalyst was proven to be a feasible way of carrying out cellulose conversion, as the rate of cellulose hydrolysis could be enhanced by the acid catalyst under moderate conditions.¹⁰

Although researchers have already reported that polyols (a mixture of sorbitol, mannitol and other small molecular alcohols) could be obtained in the aqueous phase, the selectivity for sorbitol from the hydrogenation of glucose was not considered in those studies. Furthermore, the amount of catalyst used was usually quite high, with a substrate/catalyst ratio of 20–200/1 (w/w), which is not suitable for practical applications. In the current work, isosorbide was obtained directly by conversion of microcrystalline cellulose over Ru/C catalyst with dilute hydrochloric acid in superheated water. Concentrated cellulose produced isosorbide with 35–50% yield, by balancing the fast acid hydrolysis of cellulose and the selective hydrogenation of glucose using a much lower catalyst loading than previously – the cellulose/catalyst ratio of 800/1 (w/w) is 4–40 times lower than in the literature.^{8–10}

Initially, the activities of the supported noble metal catalysts were examined at the relatively low temperature of 448 K, using 6.0 MPa hydrogen pressure in the presence of mineral acids, with Ru/C showing the highest activity. Previous studies reported that hexitols and sorbitan were the main products over Ru/C.¹⁰ Intriguingly, in our present system isosorbide was produced as the main product in the presence of HCl at relatively high temperatures. Table 1 shows that Ru/C showed excellent selectivity for producing isosorbide compared with the other two catalysts, and that HCl was more effective than H₂SO₄. In contrast, when Pt/C or Pd/C were used, isosorbide was produced in much lower quantity (<4% yield) with levulinic acid and other degradation products being the main products.

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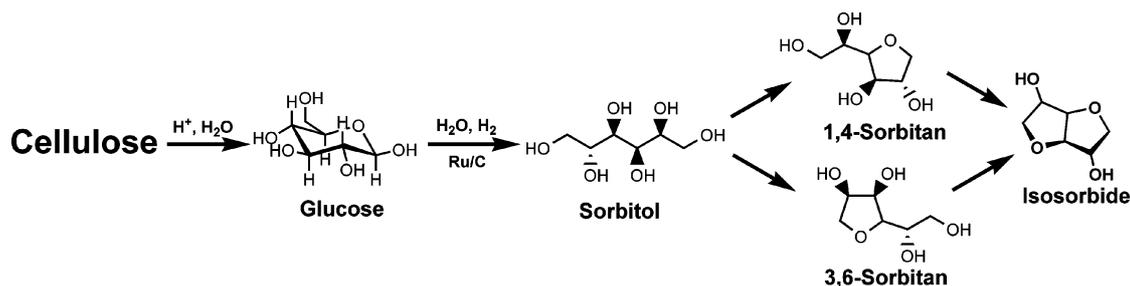


Fig. 1 Reaction pathway for cellulose conversion into isosorbide.

Table 1 Conversion of microcrystalline cellulose over supported metal catalysts^a

Entry	Catalyst ^b	Acid	Conversion (%)	Isosorbide (%)
1	Ru/C	HCl	100	41.1
2	Ru/C	H ₂ SO ₄	100	14.0
3	Pt/C	HCl	100	2.1
4	Pt/C	H ₂ SO ₄	100	1.6
5	Pd/C	HCl	100	3.5
6	Pd/C	H ₂ SO ₄	100	1.2

^a Reaction conditions: 0.2 g cellulose, 508 K, 60 min, 10 ml H₂O, 20 mg catalyst, [H⁺] = 0.10 M. ^b Metal loading = 5 wt%.

As shown in Table 2, quantitative conversion of cellulose was readily achieved at temperatures above 478 K within 30 min, indicating that cellulose was rapidly hydrolyzed to glucose under the standard conditions. At 468 K, the overall selectivity of sorbitol and its cyclodehydration products was 92%, and the degradation products of glucose were not detected. Hence it was proposed that the generated glucose was immediately hydrogenated into sorbitol over Ru/C at a relatively low temperature. Interestingly, sorbitol and its cyclodehydration products were the major products in the liquid phase (see Fig. S1†), while mannitol and its cyclodehydration products (1,4-mannitan and isomannide) were not detected. However, mannitol, an isomer of sorbitol, was often produced in the one-pot conversion of cellulose.⁷ In addition, the direct conversion of sorbitol (initial reactant) under identical conditions showed a similar

product distribution as in the conversion of cellulose (Table S1†). Glucose could be isomerized to fructose and mannose by enolization in neutral aqueous solution, followed by subsequent hydrogenation to mannitol. In the present work, we propose that glucose is selectively hydrogenated to sorbitol (because the isomerization of glucose to fructose and mannose is inhibited in the presence of HCl), producing a high yield of isosorbide under the reaction conditions used.

As deduced from the product distribution, the conversion of cellulose is proposed to proceed by the reaction pathway shown in Fig. 1. Cellulose is first hydrolyzed to glucose under the acid catalysis, and then glucose is selectively hydrogenated to sorbitol; this is then converted to several compounds by dehydration. For example: the conversion of sorbitol into isosorbide proceeds through two steps, sorbitol is cyclodehydrated to 1,4-sorbitan and 3,6-sorbitan, and then dehydrated to isosorbide. Additionally, several other dehydration products including 2,5-iditan and 2,5-mannitan (in addition to minor amounts of ethylene glycol and xylitol) were also detected by GC-MS.

Reaction temperature has a significant effect on the product distribution. At relatively low temperatures, the conversion of cellulose mainly produced sorbitol, 1,4-sorbitan and 3,6-sorbitan within a short reaction time in the liquid phase. At elevated temperatures, the cyclodehydration of 1,4-sorbitan and 3,6-sorbitan was accelerated, producing isosorbide in high yield after an extended reaction time, but simultaneously the selectivity of C₆ products was lowered (Fig. 2). Isosorbide was obtained with a maximum yield of 49.5% after reaction for 6 h

Table 2 The results for the conversion of cellulose at different temperatures^a

Entry	T/K	Conv. (%) ^b	E _{C₆} (%) ^c	Yield (%) ^d				
				Glucose	Sorbitol	1,4-Sorbitan + 3,6-sorbitan	2,5-Iditan + 2,5-maninitan	Isosorbide
1	468	75.4	92	2.2	36.9	21.9	4.8	3.7
2	478	98.3	83	0.8	24.5	39.9	9.4	7.0
3	488	99.4	80	0.1	5.8	46.2	10.8	16.8
4	498	100	73	0.1	3.9	34.6	9.1	25.7
5	508	100	58	0.0	3.5	13.9	5.2	35.6
6	518	100	53	0.0	3.4	3.6	6.4	39.6
7 ^e	488	100	62	0.0	4.0	3.1	5.3	49.5
8 ^f	488	100	46	0.0	3.4	2.2	4.4	35.5
9 ^g	488	100	63	0.0	4.2	4.0	6.7	47.9

^a Reaction conditions: 0.2 g cellulose, 20 mg Ru/C, 10 ml H₂O, 0.10 M HCl, 6.0 MPa H₂ (RT), 30 min. ^b Conversion was calculated with the initial weight of cellulose divided by the residual solid weight after reaction. ^c Efficiency of C₆ products = (yield of glucose, sorbitol and its cyclodehydration products)/cellulose conversion. ^d Yield (%) = (moles of each product)/(moles of anhydroglucose units in cellulose). ^e 0.2 g cellulose, 6 h. ^f 0.8 g cellulose, 6 h. ^g 2.0 g cellulose, 200 mg Ru/C, 6 h.

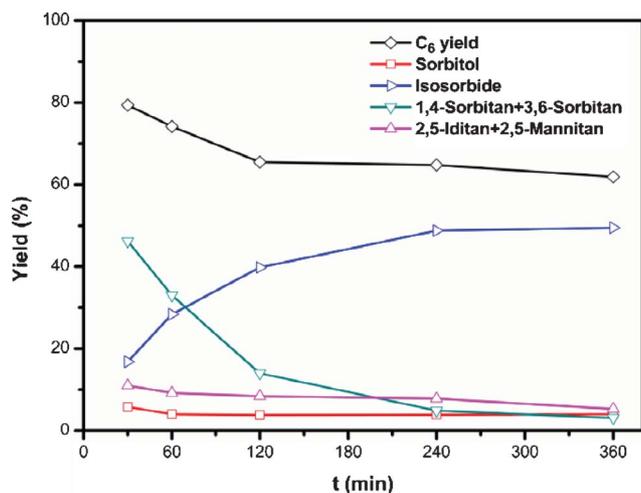


Fig. 2 Cellulose conversion over Ru/C and hydrochloric acid at 488 K. Reaction conditions: 0.2 g cellulose, 20 mg Ru/C, 10 ml H₂O, 0.1 M HCl, 6.0 MPa H₂ (RT).

at 488 K, 6.0 MPa H₂ and 0.10 M HCl, with the total yield of C₆ products reaching 61.9% (Table 2, entry 7).

H⁺ can efficiently accelerate cellulose hydrolysis, increase the selectivity of glucose hydrogenation and catalyze the cyclodehydration of sorbitol. For the effect of H⁺ concentration on product distribution, see Fig. S2†. Interestingly, mannitol and its cyclodehydration products (1,4-mannitan and isomannide) were detected at the quite low H⁺ concentration of 0.01 M, and disappeared at 0.05 M. H⁺ could therefore favor the formation of isosorbide by accelerating the dehydration of sorbitol. Very recently, Kobayashi *et al.* reported that the residual Cl on catalysts could induce the C–C cleavage and dehydration of hexitols to 1,4-sorbitan,¹¹ which may explain the higher yields of isosorbide obtained in the presence of HCl, as shown in Table 1. Also, Palkovits *et al.* recently discussed the influence of acid strength and concentration on the product distribution in the conversion of cellulose over Ru/C. C₄–C₆ sugar alcohols were produced as the main products during the reaction, and isosorbide was detected with increasing acid concentration in the presence of H₄[Si(W₃O₁₀)₄] and H₃[P(W₃O₁₀)₄].¹²

It is notable that complete conversion of cellulose with a comparable yield of isosorbide could be achieved at 16.7 wt% cellulose (Table 2, entry 9). Upon increasing the cellulose/Ru ratio (w/w) from 200/1 to 800/1, the yield of isosorbide and total C₆ products showed a slight decrease. Satisfactorily, >35% yield of isosorbide at a quantitative conversion of cellulose was attained even at a ratio of 800/1. This suggested that the capacity and stability of the Ru/C catalyst is predictable, therefore the recycling of the Ru/C catalyst was tested. The results in Fig. 3 show that the yield of isosorbide was 47.4% for the first reaction run, decreasing to 33.5% for the second run (1st recycling), but then changing very slightly in subsequent runs. It is therefore feasible to recycle the Ru/C catalyst under the present reaction conditions. There are two likely reasons for the decrease after the first run – leaching of the active Ru species due to the acidity of the system, and catalyst loss in the recycling procedure (washing, centrifuging *etc.*). The loss of catalyst during the recycling stage is not unusual, but it is surprising that no leaching of Ru could be

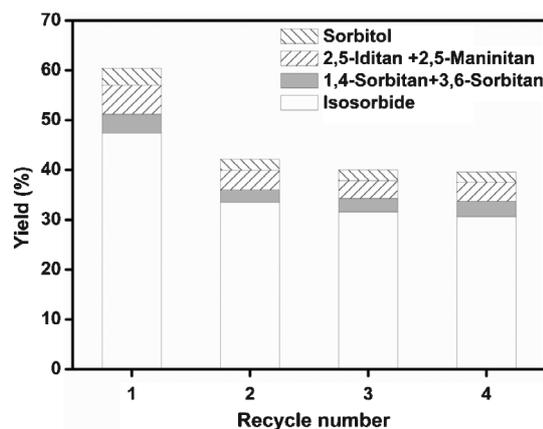


Fig. 3 Results for the recycling of Ru/C catalyst in the conversion of cellulose. Reaction conditions: 0.2 g cellulose, 20 mg Ru/C, 6.0 MPa H₂ (RT), [H⁺] = 0.10 M, 10 ml H₂O, 488 K, 4 h.

detected by ICP in the reaction solution after the first run. The TEM images of the Ru/C catalyst after the first reaction showed that the average size of Ru particles had increased from 1.2 to 1.7 nm, and remained around 1.7 nm in subsequent runs (see Fig. S3†); this increase could therefore be one of the reasons for the decrease in activity. This is the first report that the conversion of concentrated cellulose can produce isosorbide with such a good yield. We ascribe this to the unique reaction system – namely, a balance between the fast hydrolysis of cellulose and the excellent hydrogenation activity due to the combination of hydrochloric acid and Ru/C catalyst.

In summary, we have presented an efficient approach for converting concentrated cellulose to isosorbide. The reaction conditions are important factors for controlling the reaction rate and product distribution, and in particular the active metal species is a key factor for converting cellulose to isosorbide. This work reveals a new and promising prospect of cellulosic biomass conversion, and opens up prospects for producing fine chemicals, such as high-value intermediates for pharmaceuticals and polymers, from biomass.

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