

Efficient catalytic conversion of concentrated cellulose feeds to hexitols with heteropoly acids and Ru on carbon†

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A combination of heteropolyacids and Ru on carbon catalyzes the conversion of concentrated cellulose feeds into hexitols under H₂ pressure. Quantitative conversion of ball-milled cellulose was observed with remarkable hexitol volume productivity.

Limited supply of fossil fuels and the emission of greenhouse gases associated with their consumption has prompted renewed research and industrial interest in biomass as a sustainable source of fuels and chemicals.¹ Cellulose is the most abundant source of biomass. Unlike starch, it is insoluble in water and not digestible by humans because of the semicrystalline structure composed of β -1,4-glycoside bonded glucose monomers. One of the most promising routes for cellulose valorisation is inspired by reactions on starch, and relies on the one-pot dual catalytic conversion of cellulose into useful chemicals.² Herein, cellulose is hydrolysed under the action of an acid catalyst, followed by a fast metal-catalyzed hydrogenation of the formed glucose to hexitols. Hexitols, *viz.* sorbitol, mannitol and sorbitan, are important platform molecules³ for renewable chemicals and fuels.⁴ A main advantage of the bifunctional catalytic approach is the fast removal of unstable glucose avoiding its degradation into caramel, tars, *etc.* Since the formed hexitols have a higher thermal stability than the corresponding hexoses, higher process temperatures and cellulose concentrations are feasible than in classic cellulose hydrolysis.

Several authors have recently reported on the bifunctional catalytic conversion of cellulose diluted in water (0.8–2 wt%) using catalyst loadings of 0.2 to 0.4 wt%,^{2,5} achieving hexitol yields in the range of 30–73%, typically within 24 h. However, the need remains for a catalytic system that is capable of more rapidly and selectively transforming more concentrated cellulose feeds into hexitols in high yields. We report here the catalytic conversion of highly concentrated microcrystalline and ball-milled cellulose into hexitols by combining a heteropoly acid (HPA) and Ru on carbon (Ru/C).

A preliminary screening of the hydrolysis of cellobiose, a β -1,4-glycoside bonded disaccharide, over several mineral acids, HPAs and solid acids, *viz.* USY zeolites, demonstrated

the highest activity and hexose selectivity for commercially available H₃PW₁₂O₄₀ and H₄SiW₁₂O₄₀ HPAs (see ESI†). Notably, the HPAs performed much better than an equinormal aq. H₂SO₄ solution, an industrial standard for cellulose hydrolysis. This was recently also reported by Shimizu *et al.*⁶

A comparison of the performance of the combined hydrolysis and hydrogenation catalysts, *viz.* H₄SiW₁₂O₄₀ and Ru/C against H₂SO₄ and Ru/C, in the conversion of microcrystalline cellulose to hexitols at 463 K and 5 MPa H₂ is presented in Fig. 1. The experiments were performed in a 100 ml stainless steel autoclave, the product mixture being analysed after derivatisation on a HP 5890 GC equipped with a HP 7673 autosampler, a 50 m CP-Sil-5CB column and a FID (see ESI†). The conversion of cellulose was determined by measuring the soluble carbon content in the reaction mixture using TOC. The H₄SiW₁₂O₄₀-Ru/C combination is clearly effective and selective in producing hexitols with 82% cellulose conversion (*vs.* 56% for H₂SO₄-Ru/C) after 24 h, and a maximum hexitol yield of 49% (*vs.* 28% for H₂SO₄-Ru/C).

Within the fraction of hexitols, the sugar alcohols, *viz.* sorbitol and mannitol, are the main products, followed by sorbitan, the 1,4-isomer being analyzed most abundantly. These cyclic polyols result from a HPA-catalyzed dehydration of the sugar alcohols. Other minor byproducts include ethylene glycol, 1,2-propanediol, glycerol, and C₄ and C₅ polyol isomers. This second family of by-products results from the Ru/C catalyzed hydrogenolysis of the primary hexitols, as reported

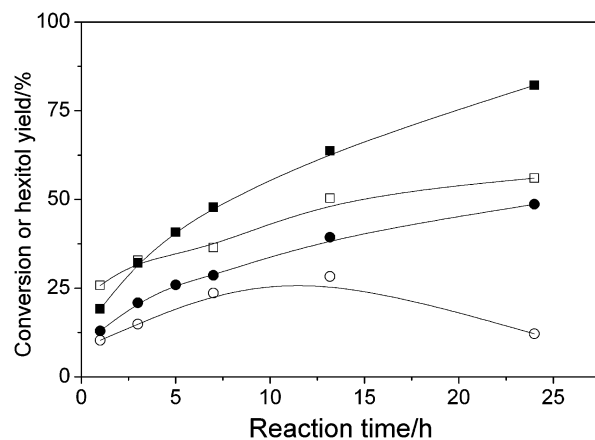


Fig. 1 Conversion of microcrystalline cellulose by H₄SiW₁₂O₄₀ & Ru/C (filled) and H₂SO₄ & Ru/C (open); (square) conversion, (circle) hexitol yield. Reaction conditions: cellulose 1 g, [H⁺] = 1.22 × 10⁻² M, Ru/C 0.25 g, water 50 ml, H₂ 5 MPa, 463 K.

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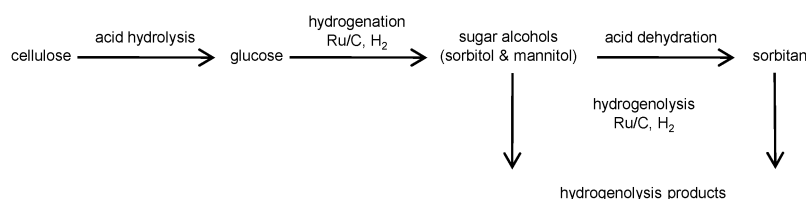


Fig. 2 Reaction scheme for cellulose conversion to hexitols.

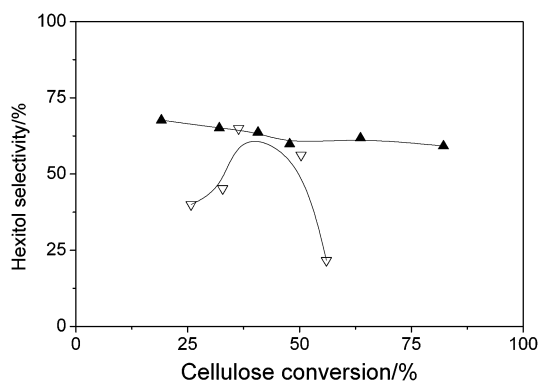


Fig. 3 Hexitol selectivity vs. cellulose conversion for (▲) H₄SiW₁₂O₄₀ & Ru/C and (▼) H₂SO₄ & Ru/C. Reaction conditions as in Fig. 1.

e.g. in ref. 7. An overall reaction scheme for the HPA–Ru/C system is advanced in Fig. 2.

Taking a closer look at the catalytic data further reveals a selectivity maximum (of 68%) at intermediate cellulose conversion in the H₂SO₄ experiment, while the hexitol selectivity remains high and around 65% at very high cellulose conversion with HPA and Ru/C (Fig. 3).

The drop in hexitol selectivity for high cellulose conversion in the H₂SO₄ experiment is attributed to a slow formation of glucose at longer contact times. As both hydrogenation and hydrogenolysis are competitive surface reactions on Ru, hydrogenolysis of the hexitol fraction will dominate if glucose is offered too slowly. In contrast, contacting cellulose with the HPA–Ru/C catalytic system provides a more balanced reaction network in favor of hexitol formation. For clarity, the low hexitol selectivity at low cellulose conversion for the experiment with H₂SO₄–Ru/C is due to the formation of large quantities of oligosaccharides, as measured by HPLC analysis. Intriguingly, no such high amounts of oligomers were analyzed with HPA–Ru/C, suggesting a selective hydrolysis mechanism, in which glucose-by-glucose units are released from cellulose.

Chemical or mechanical lowering of the cellulose crystallinity is known to improve its degradability.^{6,8,9} To allow

shorter reaction times, thereby suppressing the Ru-catalyzed cracking reaction while maintaining high cellulose conversion and hexitol yield, we used a 24 h ball-milling pretreatment (see ESI†) to reduce cellulose crystallinity before reaction (Table 1). It is important to emphasize here that the present catalytic concept is also applicable with cellulose obtained from decrystallisation procedures, perhaps more practical than ball-milling. It follows that compared to untreated cellulose, the ball-milled form is fully converted after 1 h, while conversion of microcrystalline cellulose is still incomplete, even after 24 h (compare entry 1 and 4, Table 1).

As a result of the shorter contact time with mechanically treated cellulose, very high hexitol selectivities, up to 87%, were obtained at full conversion. The reaction temperature had no effect on the hexitol selectivity. For instance, an increase from 453 to 463 K shows an enhanced cellulose conversion rate (higher conversion or shorter time to reach about 100% conversion) without changing the hexitol selectivity at isoconversion (entries 1 and 2, Table 1). Only after contacting the hexitol fraction for 24 h in the reaction conditions at 463 K, can a significant decrease in yield be noticed, thus pointing to a high stability of the hexitols in this reaction medium. At 443 K, the hexitol fraction is stable far beyond the 24 h reaction time, but we noticed an incomplete cellulose conversion at the lower temperature even after prolonged reaction times. Possibly, to the hydrolysis power of the HPA catalyst, that of overheated water⁴ should be added.

As the presence of glucose is negligible in the reaction medium of the various entries in Table 1, the hydrogenation activity of the Ru/C catalyst is sufficiently high compared to the hydrolysis rate of the acid catalyst. Thus, the subtle balance of the catalytic functions, viz. hydrolysis and hydrogenation needed for high yield of hexitols seems to be optimal in the HPA–Ru/C, except for the small deficit in selectivity (~15%) due to hydrogenolysis.

In an attempt to suppress such C–C cracking reaction, while retaining the high hexitol yields and fast cellulose conversion obtained at higher temperatures, the influence of the H₂

Table 1 Temperature dependence of ball-milled cellulose conversion in presence of H₄SiW₁₂O₄₀ and Ru/C catalysts^a

Entry	Reaction T/K	Reaction time/h	Conversion/%	Hexitol selectivity/% ^b	Hexitol yield/%		
					Sugar alcohol yield/%	Sorbitan yield/%	Glucose yield/%
1	463	1	99	87 (72)	68	19	1
2	453	2	99	86 (82)	68	17	1
3	443	6	83	84	57	11	1
4 ^c	463	24	83	59	32	17	<0.5

^a Reaction conditions: Ball-milled cellulose 1 g, [H⁺] = 1.22 × 10⁻² M (assuming full dissociation of acid catalyst), Ru/C 0.25 g, water 50 ml, H₂ 5 Mpa. ^b Values in parentheses refer to a reaction time of 24 h. ^c Untreated cellulose.

Table 2 Influence of H₂ pressure and water concentration on cellulose conversion by H₄SiW₁₂O₄₀ and Ru/C catalysts

Entry	Substrate	Pressure/ MPa	Reaction time/h	Conversion/ %	Productivity/ g L ⁻¹ h ^{-1d}	Hexitol selectivity/%	Hexitol yield/%		
							Sugar alcohol yield/%	Sorbitan yield/%	Glucose yield/%
1	Ball-milled cellulose ^a	9.5	1	100	19	100	85	15	<0.5
2	Microcrystalline cellulose ^a	9.5	5	77	2	72	36	19	1
3	Ball-milled cellulose ^b	5	0.33	96	279	95	65	27	<0.5
4	Microcrystalline cellulose ^b	5	4	79	15	80	27	34	<0.5
5	Microcrystalline cellulose ^c	5	1.5	65	83	91	38	22	<0.5

^a Reaction conditions: substrate 1 g, [H⁺] = 1.22 × 10⁻² M, Ru/C 0.25 g, water 50 ml, 463 K. ^b Reaction conditions: substrate 5 g, [H⁺] = 6.1 × 10⁻² M, Ru/C 1.25 g, water 50 ml, 463 K. ^c Reaction conditions: substrate 10 g, [H⁺] = 12.2 × 10⁻² M, Ru/C 2.5 g, water 50 ml, 463 K. ^d Calculated at the given reaction time.

pressure was investigated. Hydrogenolysis reactions are usually negative order in H₂ concentration, which is attributed to competitive adsorption between H₂ and the substrate, *viz.* hexitol. An increase of H₂ pressure from 5 to 9.5 MPa eliminates hydrogenolysis, resulting in an unprecedented *quantitative* conversion of cellulose into hexitols. A similar pressure effect was noticed with microcrystalline cellulose (compare Fig. 1 with Table 2, entry 2).

Next to the high hexitol yield, we here communicate fast cellulose conversion and excellent hexitol volume productivities (in g L⁻¹ h⁻¹) with the HPA–Ru/C catalytic system (Table 2). Yamaguchi *et al.*⁹ recently proposed that the rate of cellulose hydrolysis over a solid acid is dependent on the water concentration. As cellulose hydrolysis in the present study is rate limiting, more concentrated cellulose feeds were examined, while maintaining the cellulose/catalyst ratio (Table 2, entries 3 & 4). The data on both ball-milled (compare Table 2, entry 3 with Table 1, entry 1) and microcrystalline cellulose (compare Table 2, entry 4 with Fig. 1) indeed show significantly faster reactions. For instance, a hexitol yield of 92% was reached within 20 min using 10 wt% ball-milled cellulose, corresponding to a record volume productivity of 279 g of hexitol fraction per liter liquid phase in one hour (Table 2, entry 3). Catalytic conversion of 20 wt% microcrystalline cellulose with HPA–Ru/C gives an hexitol volume productivity of 83 g L⁻¹ h⁻¹ with a hexitol selectivity of 91% (Table 2, entry 5).

In summary, the commercial heteropoly acids H₃PW₁₂O₄₀ and H₄SiW₁₂O₄₀ were demonstrated to be very effective acid catalysts in combination with Ru/C to directly produce hexitols from cellulose. The strength of HPAs seems the fast and selective hydrolysis of cellulose to glucose. Immediate hydrogenation of glucose at elevated H₂ pressure with Ru/C provides (almost) quantitative amounts of hexitols when ball-milled cellulose is used. Record volume productivities were presented for concentrated treated and untreated cellulose feeds. As the recovery of heteropoly acid catalysts from aqueous solutions has been reported *via* recrystallisation⁶ or ether extraction,¹⁰ the development of recyclable H₃PW₁₂O₄₀–Ru/C and H₄SiW₁₂O₄₀–Ru/C systems is within reach.

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