Supporting Information

Selective terminal C-C scission of C5-carbohydrates

Frits van der Klis, Linda Gootjes, Jacco van Haveren, Daan S. van Es and Johannes H. Bitter



Fig. S1. Representative GC-FID for product mixtures obtained after reaction. A = glycerol, B = diphenylmethane (internal standard), C = erythritol, D = threitol, E = arabitol, F = xylitol, G = adonitol. (Reaction conditions: D-xylose, 10 bar H₂ pressure, 140 °C, 2 h).

Table S1	Overview	of reaction	conditions	favouring	chain	scission	reactions i	n carbohyd	rates
				0				2	

Reaction type	Typical temp. range (°C)	Typical pressure and atmosphere	Additional conditions			
Retro-aldol	200-240	60-100 bar H ₂	Alkaline environment			
Retro-Claisen	Exact reaction conditions unclear, enolate chemistry (base or acid needed)					
Decarbonylation (homogeneous)	140-180	Inert atmosphere	Complex solvent			
Decarbonylation (heterogeneous)*	130-150	6-10 bar H ₂	Absence of base			

*This investigation

Background on hydrogenation and isomerization of carbohydrates:

Scheme S1 shows the hydrogenation and isomerization of xylose as an example for these types of reactions. First xylose can be hydrogenated to xylitol, an alditol which still has the same stereo configuration as the parent sugar. Hydrogenation of carbohydrates to the corresponding alditols is a well-known reaction and proceeds in general fast.¹⁻³ Next, dehydrogenation of one of the (chiral) alcohol functionalities in the chain will lead to the formation of a (pro-chiral) carbonyl group. When this group is re-hydrogenated to an alcohol, the stereochemistry can be different compared to the original configuration, leading to the formation of another sugar(alcohol). So, starting from xylose or xylitol, two other sugar alcohols can be formed, namely arabitol and adonitol. All these reactions are equilibria, and this can also occur for the lower sugar alcohols of our interest: erythritol and threitol. Effectively the hydrogenation/dehydrogenation steps result in isomerization of the OH groups, no chain scission occurs in these cases.



Scheme S1 Hydrogenation and isomerization of xylose via (de)hydrogenation reactions of the sugar alcohol-groups.

Design of Experiment (DOE):

A Central Composite Design (CCD) was chosen in order to optimize the process variables. Reactions were performed in 6x 75 mL parallel pressure reactors, using 1g of xylose in 25 mL water and 5% Ru/C (2.2mol% Ru) for 24h. Products were quantified by GC-FID using an internal standard, after removal of the catalyst by filtration and evaporation of the water. Mild reaction conditions (140 °C, 10 bar H₂) were chosen as the center point of the design. For the two variables the following range of values was chosen: Temperature 120-160 °C, initial H₂ pressure 7-13 bar. For the two variables (n = 2) the total number of experiments was 12, determined by the equation: $2^n (2^2 = 4 \text{ factorial points}) + 2n (2 \times 2 = 4 \text{ axial points}) + 4 \text{ center points}$. In order to minimize the effects of unexpected variability, the experiments were randomized (see Table S2).

The reaction mixtures contained only a very limited number of compounds, i.e, only C5-C2 polyols (see Fig. S1). Note that the C5-products are not the starting aldose (xylose) but the reduced products (the C5-alditols). Therefore the response for the combination of variables was chosen as the yield of C5-C2 polyols.

Based on the results, a linear regression model was fit:

$$Y = b_0 + b_1 x_1 + b_2 x_1^2 + b_3 x_2 + b_4 x_2^2 + b_5 x_1 x_2$$
(1)

where Y is the response (yields C5-C2), x_1 the variable H₂ pressure and x_2 the variable temperature and b_0 - b_5 the regression coefficients determining the estimated response surface. The best model was chosen with an all-subset selection (GenStat).

Good fits were obtained for the C5-C3 products. C2-products could not be adequately fitted probably because C2 could be further converted to gaseous products which we could not detect (see chapter on gas phase analysis in main article). The results for the other variables (C5-C3) are shown in Table S3. The evolution of the C5-C4 fraction could be well described (R^{2} >0.93) while description of the evolution of the C3 fraction is satisfactory (R^{2} >0.8).

		Variables R		esponse vield in mol%)			
Design points	Point type	x ₁ Pressure (bar H ₂)	x ₂ Temp (°C)	C5	C4	C3	C2
1	Center	10	140	16	20	9	2
2	Axial	10	112	58	17	3	0
3	Factorial	13	120	28	19	7	0
4	Axial	10	168	6	10	7	2
5	Factorial	7	160	24	18	7	2
6	Center	10	140	18	20	11	3
7	Axial	6	140	42	24	6	0
8	Axial	14	140	9	16	12	2
9	Factorial	7	120	54	21	5	0
10	Center	10	140	22	23	11	3
11	Factorial	13	160	4	11	9	2
12	Center	10	140	20	19	9	0

Table S2. Central Composite Design and observed responses (C5-C2 yields) for the conversion of D-xylose with 5% Ru/C after 24h.^a

^aReaction conditions (75 mL pressure reactor): D-xylose (1.00 g, 6.7 mmol), supported metal catalyst (2.2 mol % metal relative to xylose), 25 mL deoxygenated demineralized water, 24 h.

Fig. S2 is a graphical representation of the results in Table S3, showing the individual product fractions (C3, C4 and C5). The figure shows the yield (in colour) of the individual polyol fractions as a function of temperature (x-axis) and initial hydrogen pressure (y-axis). The black dots represent the design points (1-12 in table 1), corresponding to the conditions where the actual experiments were performed to fill the model.

The C5-polyols yield (bottom graph, the sum of xylitol, arabitol and adonitol) clearly increases with decreasing temperatures. The effect of the initial hydrogen pressure on the yield is less pronounced. The decreasing C5 selectivity at higher temperatures and H_2 pressures is in line with the expectation that under these conditions C-C splitting becomes more predominant, thereby lowering the final yield of C5-alditols. Furthermore it is known from literature that Ru-catalysts are extremely active in dehydrogenation/hydrogenation reactions, even at low temperatures.⁴⁻⁸

Parameter	C5	C4	C3
Constant (b_0)	500.88	-141.225	-124.611
Pressure (b_1)	-10.5967	1.85671	1.76005
Pressure ² (b_2)	0.337988	*	-0.0607768
Temp (b_3)	-5.06595	2.37105	1.7007
$\operatorname{Temp}^2(b_4)$	0.0152732	-0.00825655	-0.00587557
Temp.Pressure (b_5)	*	-0.0192362	*
Adjusted R ²	0.964	0.936	0.80

Table S3. Estimated regression coefficients and adjusted R².

*Not included in the model.

The yield of the desired C4 alditols (middle graph, sum of erythritol and threitol) increases at lower hydrogen pressures. Furthermore, a clear optimal temperature region is found between 128-146 °C.

According to the model the highest yield (24%) lies around 138 °C and the lowest tested H₂ pressure (6 bar). The maximum calculated yield lies close to the calculated yield of 21% at our centre point, 10 bar H₂, 140 °C.

The yield of C3 (top graph, glycerol yield) increases with increasing pressure, and shows an optimal temperature around 140 $^{\circ}$ C. This result is in line with the literature focussing on ethylene and propylene production from sugars via hydrogenolysis reactions,^{9,10} where high pressures are applied to achieve maximal C-C splitting.

The DOE results showed that, in agreement with our hypothesis, higher C4 yields can indeed be achieved when applying lower hydrogen pressures and temperatures. To the best of our knowledge, it is the first time that a tetritol yield of 24% was achieved using a heterogeneous catalyst system. Furthermore, the GC analysis showed a rather remarkable product distribution, since no dehydration products (such as propylene glycol) were found (see Fig. S1).



Fig. S2 Counter plot for C3, C4 and C5 products depending on initial H_2 pressure and reaction temperature.

Catalyst characterization:

Nitrogen physisorption:

 N_2 adsorption/desorption isotherms at -196 °C was measured using a Micromeritics TriStar II Plus. The (water wet) sample was pre-dried at 100 °C for 60 min, and 0.0487 g of sample was used for the measurement. The sample was outgassed for 21 h under vacuum (< 0.1 mbar) at 200 °C prior to measurement. The linear part of the BET equation (relative pressure between 0.05 and 0.30) was used for the determination of the specific surface area. The microporous pore volume was determined using the *t*-plot method. The pore size distribution was calculated from the adsorption branch of the N₂ physisorption isotherms and the Barret–Joyner–Halenda (BJH) formula from BET (4V/A). The results are shown in Table S4.

Hydrogen chemisorption:

Metal dispersion was analysed by H2 chemisorption using a Micromeritics ASAP 2020. The (water wet) moist sample was pre-dried at 105 °C for 60 min to remove most of the water. The sample (0.1 g) was place between plug of quartz wool in a u-shaped quarts tube. First the sample was evacuated at 100 °C for 10 min to remove ambient gases. Then, the sample was reduced in a hydrogen flow at a temperature of 150 °C (ramped at 10 °C/min.) for 1 h. Next the sample was evacuated at 300 °C for 4 h and cooled to 35 °C at 10 °C/min. to remove residual hydrogen. After a leak test followed by evacuation for 30 min. the analysis was performed at 35 °C. Two isotherm measurements were performed and the monolayer uptake was obtained by fitting the linear part of the first isotherm (200-600 mbar) and extrapolation to zero pressure. The metal surface area was calculated assuming a H/Ru ratio of 1, an atomic cross-sectional area of 0.0614 nm2, a ruthenium density of 12.410 cm3/g and a metal loading of 5.000% Ru as provided by the manufacturer. The results are summarized in Table S4.

Table S4. N₂ physisorption and H₂ chemisorption of 5% Ru/C (Escat 4401)

Surface area (m ² /g) ^a	Pore volume (cm ³ /g)	Average pore size (Å) ^c	Average metal particle size (nm) ^d	Metal Dispersion (%) ^e
930	0.25	63	3.5	38

^aCalculated from N₂ physisorption using the BET equation. ^bCalculated from N₂ physisorption using the *t*-plot method. ^cCalculated from N₂ physisorption using the BJH formula using 4V/A from BET. ^dAverage crystallite size calculated from H₂ chemisorption. ^eRuthenium dispersion calculated from H₂ chemisorption.

Transmission Electron Microscopy (TEM) and High-Angle Annular Dark-Field Imaging (HAADF):

TEM / HAADF measurements were performed with a Philips Tecnai 20 FEG instrument, operating at 200 kV. The H_2 chemisorption sample was used without further treatment, dispersed in ethanol followed by deposition on a carbon coated copper grid. The particle size distribution was determined by measuring the dimensions of 578 particles using Image-J software.

Fig. S3 shows an overview of the TEM/HAADF images of the sample after H_2 chemisorption. All images that were taken showed a homogeneous distribution of metal particles over the support. The particles size varied between 1-6 nm, with only a few bigger particles. The corresponding histogram of the particle size distribution is shown in Fig. S4, showing an average particle size of ~3nm.

X-ray Diffraction (XRD):

The X-ray diffraction patterns were recorded using a Philips PC-APD diffractometer with a Cu K α 1 anode operating at 50 mA and 30 kV, and a 15 mm Ni foil monochromator. The patterns were recorded between 20 and 80 °2 Θ using a step-size of 0.05 °2 Θ and a counting time of 25 s. The XRD pattern of fresh 5% Ru/C (Escat 4401) after drying (105 °C, 1h) is shown in Fig. S5.

The XRD showed no clear ruthenium(oxide) diffractions, which indicates small crystallite sizes in accordance with H_2 chemisorption and TEM/HAADF.



Fig. S3 TEM images (A1, B1 and C1) and corresponding HAADF images (A2, B2 and C2) of 5% Ru/C (Escat 4401) after H_2 chemisorption.



Fig. S4 Histogram of the particle size distribution of 5% Ru/C (Escat 4401) after H₂ chemisorption.



Fig. S5 XRD of fresh 5% Ru/C (Escat 4401) after drying (105 °C, 1h).

Catalyst screening:

A screening of various commercial catalysts was performed under standard reaction conditions (see comment under Table S5) in order to compare the performance.

The following catalysts were used as received: 5% Pd/C (5% Palladium on activated wood carbon, reduced, 50% water wet paste, Escat 1421, %H₂O 53.63, STREM), 5% Pt/C (5% Platinum on activated wood carbon, reduced, 50% water wet paste, Escat 2421, %H₂O 54.19, STREM), 1% Ir/C (1.01% Iridium on activated carbon powder, reduced, nominally 50% water wet, STREM), 5% Au/C (up to 5% Au on activated carbon, waterwet, Evonik), 5% Rh/C (4.59 wt% Rhodium (dry) on carbon, wet, DeGussa-type G106NB/W, 67.48% moisture, Aldrich), 64% Ni/SiO₂ (64% Nickel powder on silica, reduced and stabilized (Ni-5249P), 65% Ni, reduced value rate = 0.37, STREM), 0.5% Ru/C (0.5% Ruthenium on activated carbon, reduced, 50% water wet paste, Escat 4401, %H₂O 53.96, STREM), 5% Ru/Al₂O₃ (5% Ruthenium on alumina, STREM).

Under the applied conditions, the blank reaction and the reaction with activated carbon support already showed ~ 50% conversion of xylose (Table S5, entry 1-2), but none of the desired sugar alcohols were detected. Although GC analysis showed no other quantifiable products than starting material and C5-C2 polyols, furfural and humins can be expected as by-products.^{11,12}

The desired C4 alditols were formed in small amounts for most of the supported metal catalysts, except in the case of 5% Au/C (Table S5, entry 6) and 0.5% Ru/Al₂O₃ (Table S5, entry 10). In general however, the Ru-catalysts showed the highest selectivity towards C4 alditols (Table S5, entry 8-9,11). An industrial Ni/SiO₂ catalyst turned out to be unstable under the applied conditions, as was apparent by the complete dissolution of the catalyst.

Entry	Catalyst	Conv. mol% ^b	C5 mol% ^c	C4 mol% ^c	C3 mol% ^c	C2 mol% ^c	Mass balance mol% ^d
1	Blank	47	0	0	0	0	53
2	Activated Carbon	50	0	0	0	0	50
3	5% Pd/C	80	13	0	0	0	34
4	5% Pt/C	95	26	2	0	0	34
5	5% Rh/C	94	5	1	0	0	11
6	5% Au/C	69	0	0	0	0	31
7	1% Ir/C	100	8	1	1	7	18
8	0.5% Ru/C	100	39	10	4	2	54
9	5% Ru/C	100	18	20	11	3	52
10	$0.5\%~Ru/Al_2O_3$	100	4	0	1	0	5
11	5% Ru/Al ₂ O ₃	100	32	16	5	1	55
12	64% Ni/SiO ₂	95	23	1	0	0	28

Table S5. Catalyst screening for the decarbonylation of D-xylose^a

^aReaction conditions (75 mL pressure reactor): D-xylose (1.00 g, 6.7 mmol), supported metal catalyst (2.2 mol % metal relative to xylose), 25 mL deoxygenated demineralized water, 10 bar H₂ (initial pressure) 140 °C, 24 h. ^bConversion of xylose determined by GC-FID. ^cPolyol (sugar alcohol) product yield determined by GC-FID after acetylation. C5 and C4 products are the sum of stereoisomers. ^dSum of starting material and C5-C2 polyols.

References:

- 1 H.M. Baudel, C. A. M. de Abreu, C. Z. Zaror, J. Chem. Technol. Biotechnol. 2005, 80, 230.
- 2 J. Wisniak, M. Herskow, R. Leibowit, S. Stein, Ind. Eng. Chem. Prod. Res. Dev. 1974, 13, 75.
- 3 V. A. Sifontes Herrera, O. Oladele, K. Kordás, K. Eränen, J. -P. Mikkola, D. Y. Murzin, T. Salmi, *J. Chem. Technol. Biotechnol.* 2011, **86**, 658.
- 4 J. Sun, H. Liu, *Green Chem.* 2011, **13**, 135.
- 5 H. Kobayashi, H. Matsuhashi, T. Komanoya, K. Hara, A. Fukuoka, *Chem. Commun.* 2011, 47, 2366.
- J. Le Notre, J. van Haveren, D.S. van Es, *ChemSusChem*, 2013, 6, 1.
- P. Gallezot. N. Nicolaus, G. Flèche, P. Fuertes, A. Perrard, J. Catal. 1998, 180, 51.
- 8 L. Wright, L. Hartmann, J. Org. Chem. 1961, 26, 1588.
- 9 D. K. Sohounloue, C. Montassier, J. Barbier, *React. Kinet. Catal. Lett.* 1983, 22, 391.
- 10 L. Zhao, J. H. Zhou, Z. J. Sui, X. G. Zhou, Chem. Eng. Sci. 2010, 65, 30.
- 11 S. B. Kim, S. J. You, Y. T. Kim, S.M. Lee, H. Lee, K. Park, E. D. Park, *Korean J. Chem. Eng.* 2011, 28, 710.
- 12 C. Liu, C. E. Wyman, *Carbohydr. Res.* 2006, **341**, 2550.
- 13 Z. Kowalczyk, S. Jodzis, W. Raróg, J. Zielinski, J. Pielaszek, A. Presz, Appl. Catal., A 1999, 184, 95.
- 14 T. Kawaguchi, W. Sugimoto, Y. Murakami, Y. Takasu, J. Catal. 2005, 229, 176.