Green Chemistry

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: P. Barbaro, F. liguori and C. M. Marrodan, *Green Chem.*, 2016, DOI: 10.1039/C6GC00128A.

View Article Online
DOI: 10.1039/C6GC00128A

Green Chemistry

COMMUNICATION

Selective direct conversion of C_5 and C_6 sugars to high added-value chemicals by a bifunctional, single catalytic body

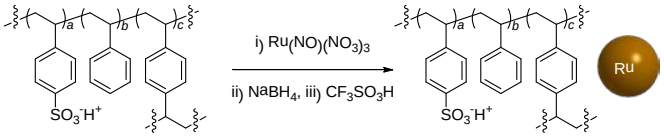
Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Pierluigi Barbaro,* Francesca Liguori and Carmen Moreno-Marrodan

The selective multi-step conversion of lignocellulose-derived monosaccharides to fine-chemicals has been achieved in one-pot, one-stage by a readily available heterogeneous bifunctional catalyst comprising 0.2% (w/w) ruthenium onto a Brønsted acid solid support. The anhydro-sugar alcohols of glucose and xylose were obtained in 86 % and in 95 % yield , respectively.



Scheme 1 Sketch of Ru@Dowex-H synthesis and microstructure.

In order to reduce the dependence from petrochemical sources, several chemical methods to convert lignocellulosic biomass derivatives into high added value products have been developed. These methods often entail complex reaction sequences of two or more consecutive reduction and acid-mediated catalytic steps.[1] However, the achievement moderate yields of desired product usually requires multiple reactor units, strong mineral acids, harsh conditions, organic solvents, homogeneous catalysts or troublesome purifications procedures. This involve significant drawbacks in terms of cost, efficiency, waste emissions, space and energy inputs.[2] The challenge is to attain 100% selectivity at high conversion in one-pot, one-stage under the mildest possible reaction conditions.[3] A potential solution is to use a combination of well-defined supported acid and metal sites acting under the same conditions,[4] notably metal catalysts onto solid acids, hereinafter referred as *truly bifunctional catalysts*.[5]

In the present work we report the selective, direct conversion of concentrated aqueous solutions of C_5 and C_6 sugars to fine chemicals[6] using a novel resin-supported bifunctional ruthenium catalyst (Ru@Dowex-H). Thus, ruthenium nanoparticles of 1.3 ± 0.5 nm, mostly gathered into 6.8 ± 0.2 nm size aggregates (TEM, XRD) (Fig. S1),[7] were immobilized onto the commercial, gel-type acidic Dowex 50WX2 resin (4.8 meq/g proton density)[8] by ion-exchange with ruthenium(III) nitrosyl nitrate, followed by reduction with an excess of sodium borohydride and washing with trifluoromethane sulfonic acid in one-pot (Scheme 1). The procedure resulted in a 0.2% (w/w) bulk ruthenium content (ICP- OES) and an egg-shell type metal distribution within the support beads (EDS, Fig. S2)[9].

The as prepared material was tested in the heterogeneous-phase catalytic conversion of glucose and xylose under various temperatures and H_2 pressures. In a typical experiment, a mixture of monosaccharide, catalyst and water was loaded into a Teflon-lined reactor together with the selected hydrogen pressure. After stirring at the desired temperature and time, the resin was decanted and the resulting clear solution analysed without further treatments by a combination of chromatographic, mass spectrometry and NMR techniques. Representative results are reported in Table 1.

Motivations for choice of glucose are multiple. Glucose is the most abundant monosaccharide found in lignocellulosic biomass and it is the unique component of cellulose, from which it can be obtained by depolymerisation.[10] Glucose can be used to produce several important market compounds,[11] including isosorbide, a versatile platform chemical for the cosmetic and pharmaceutical industriy, as well as a monomer for the manufacture of bio-based plastics, namely poly-(ethylene-*co*-isosorbide) terephthalate (PEIT), poly(isosorbide carbonate) (PIC) and poly(isosorbide oxalate).[12] Isosorbide demand for PEIT was estimated at 3,586.9 tons in 2012, while the global isosorbide market is expected to be 324.6 million by 2020.[13] Conventional catalytic route to isosorbide synthesis involves a sequence of metal hydrogenation of glucose to sorbitol,[14] followed by a twofold acid dehydration of sorbitol *via* 1,4-sorbitan (Scheme 2).[15] The latter steps are known to proceed slowly in presence of water, requiring much higher reaction temperatures in that case.[16] Isosorbide is industrially produced in 10^4 ton/year scale by a three stages process comprising enzymatic depolymerisation of starch feedstock,

Consiglio Nazionale delle Ricerche , Istituto di Chimica dei Composti Organo Metallici, Via Madonna del Piano 10, 50019 Sesto Fiorentino, Firenze, Italy. E-mail: pierluigi.barbaro@iccom.cnr.it.

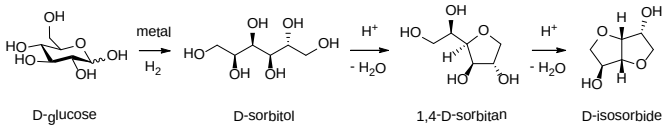
† Electronic Supplementary Information (ESI) available: Details of equipment, experimental procedures, characterization data, full catalytic results table (S1). See DOI: 10.1039/x0xx00000x

View Article Online
DOI: 10.1039/C6GC00128A

Table 1 Selected results for the direct catalytic conversion of sugars by Ru@Dowex-H under batch conditions [a]

Entry	Sugar	T (°C)	H_2 (bar)	Time (h)	Conv. (%)	Product, yield (%) [b]							
1	glucose	190	30	48	100.0	sorbitol	0.9	sorbitan	10.2	isosorbide	84.9	by-prod.[c]	4.0
2		120	30	7	100.0		99.9		0.0		0.0		0.1
3	xylose	190	30	6	100.0	xylitol	0.0	lyxose	0.0	anhydroxylitol	94.9	by-prod.[c]	5.1
4		120	30	7	99.7		99.3		0.0		0.0		0.4

[a] Ruthenium 0.2% (w/w), sugar 0.1 M in water. [b] Data from HPLC analysis. [c] Unidentified soluble products.



Scheme 2 Pathway for the catalytic conversion of glucose to isosorbide.

hydrogenation over Ni catalyst and H_2SO_4 catalysed dehydration. High purity isosorbide is obtained in *ca.* 60% yield based on sorbitol,[17] however a complicated downstream processing is required because of the formation of stained by-products.[18] On the other hand, the intermediate sorbitol is largely used in the food and pharmaceutical industries as low calorie sweetener, laxative, humectant, precursor for vitamin C and for the preparation of several other chemicals besides isosorbide.[19] As a consequence, sorbitol holds the biggest market share among sugar alcohols with an expected demand of 2,148.9 kilo tons in 2018.[20]

In the case in our hands, Ru@Dowex-H showed to catalyse the quantitative conversion of glucose at temperatures above 100 °C and H_2 pressures above 15 bar. Under 30 bar H_2 and 190 °C the conversion reaction gave directly isosorbide with 85% selectivity at full conversion after 48 h, the only other products identified are sorbitol (1%) and 1,4-sorbitan (10%) (Table 1, entry 1). Higher quantities of intermediate products were obtained for shorter reaction times. The composition of the reaction mixture over the time is graphically reported in Fig. 1, a. Use of lower temperatures had a dramatic effect on the progression of the conversion, since the amount of dehydrated products 1,4-sorbitan and isosorbide was drastically reduced. The composition of the mixture after 24 h reaction time at 120, 170 and 190 °C, respectively, is reported for comparison in Fig. 1, b. As a matter of fact, sorbitol could be obtained in 99.9% selectivity at full conversion, after 7 h at 120 °C (Table 1, entry 2). Irrespective of the temperature (up to 190 °C) and the H_2 pressure (up to 40 bar) neither traces of hydrocarbons nor shorter chain glycol products were detected.[21] The above results point out to a low-temperature conversion kinetic involving fast glucose hydrogenation, followed by slow sorbitol dehydration and a slower sorbitan dehydration step, in agreement with what previously reported for comparable aqueous phase dehydration systems.[22]

Considerably lower amounts of 1,4-sorbitan and isosorbide products were observed using the parent sodiated catalyst

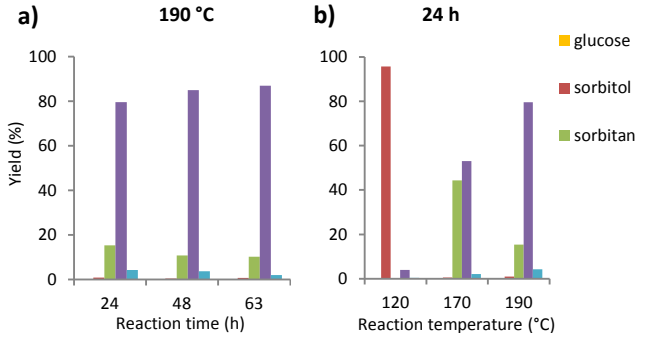


Fig. 1 Catalytic conversion of glucose by Ru@Dowex-H (0.2% Ru, water, 30 bar H_2): a) effect of reaction time at 190 °C, b) effect of temperature at 24 h reaction time.

Ru@Dowex-Na,[23] thus confirming the role of Brønsted sites in sorbitol dehydration.[15b] A black solid and a deep yellow solution containing traces of furanic derivatives were instead obtained by contacting glucose or xylose (*vide infra*) with the metal-free Dowex-H catalyst under analogous reaction conditions. This can be ascribed to the formation of humins arising from the condensation of sugars with furanics, as a consequence of acid-catalysed glucose dehydration,[24] as reported for the liquid-phase acid treatment of monosaccharides.[25] This indicates a significant stabilisation effect of the metal on the catalytic system.

To the best of our knowledge, *Ru-Dowex-H is the first example reported for the direct, catalytic conversion of glucose to isosorbide in high yield*. Systems have been described for the production of isosorbide from cellulose, yet in modest yields. Yields in the range 6 - 52% (selectivity 9 - 70%), have been achieved in a single stage either using a combination of Ru/C and strong soluble acids (HCl,[26] H_2SO_4,[27] heteropoly acids[28]), with severe drawbacks in terms of neutralization waste formation and product separation, a Ru@mesoporous niobium phosphate bifunctional catalyst,[29] or a mixture of molten $ZnCl_2$, Ru/C and HCl in a two-stages process.[30] Best results have been obtained in one-pot by a 15 : 1 (w/w) Amberlyst-70 + 4% Ru/C mechanical mixture (55.8% yield, 190°C, 50 bar H_2).[31]

It must be pointed out that Ru@Dowex-H selectivity in hydrogenation of glucose to sorbitol well compares with that of the best catalytic systems reported for this reaction (Table S2).

The Ru@Dowex-H catalyst could be reused by simple decantation showing marginal conversion loss (5%) over three consecutive runs at 190 °C and 30 bar H_2, however with

View Article Online
DOI: 10.1039/C6GC00128A

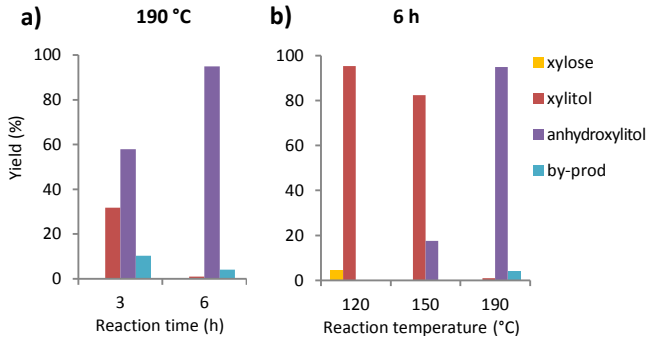


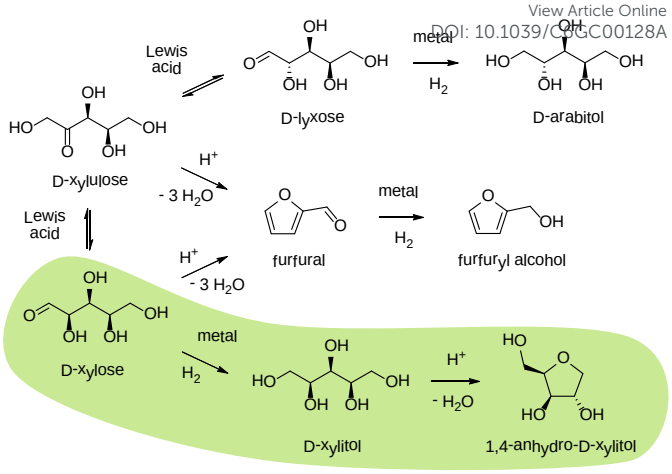
Fig. 2 Catalytic conversion of xylose by Ru@Dowex-H (0.2% Ru, water, 30 bar H_2): a) effect of reaction time at 190 °C, b) effect of temperature at 6 h reaction time.

significant changes in the reaction mixture composition (Fig. S3). Previously reported reuse of catalysts for isosorbide production from cellulose was practically unsuccessful, which was attributed either to metal fouling by insoluble by-products,[28,31,] metal particle sintering,[26] metal leaching or loss of solid acid catalyst.[32] In our case, no significant changes of Ru particle size after use in catalysis (TEM) nor significant Ru leaching in solution (< 0.5%, ICP-OES) were detected, whereas ca. 15% sulphur leaching was observed in each cycle (ICP-OES), consistently with the upper temperature operational limit of the sulfonated resin (150 °C).[33] Thus, change of product distribution upon Ru@Dowex-H catalyst reuse can be tentatively attributed to desulfurization leading to unbalance of Lewis / Brønsted acidic sites (see below) and to the degradation of residual isosorbide in the reaction mixture.

The conversion of xylose catalysed by Ru@Dowex-H was similar to that of glucose, albeit with some significant variations. Xylose is the main component of hemicellulose xylan, the second most abundant component of biomass after cellulose.[34] Under 120 °C, 30 bar H_2 and 7 h, xylose was quantitatively hydrogenated to xylitol, with no formation of dehydration products observed, because of the low temperature (Table 1, entry 4). Increasing of the temperature to 190 °C resulted in the formation of 1,4-anhydro-xylitol in 94.9% yield after 6 h, together with some unidentified soluble compounds (5.1%) (Table 1, entry 3). The composition of the reaction mixture as a function of reaction time and temperature is graphically reported in Fig. 2 a and b, respectively. As for glucose, the above findings indicate that the one-stage catalytic conversion of xylose proceeds through a fast hydrogenation of xylose to xylitol,[35] followed by the selective dehydration of the latter (Scheme 3).

Few systems have been described for the preparation of 1,4-anhydro-D-xylitol in moderate yields, and invariably by dehydration of xylitol, either using H_2SO_4,[36] Amberlyst-36[37], zeolites[38] or $H_4SiW_{12}O_{40}$[22a] catalysts. To the best of our knowledge, Ru@Dowex-H *is the first catalyst reported for the synthesis of 1,4-anhydro-D-xylitol from xylose in one-stage, one-pot.* No large-scale production methods for 1,4-anhydro-D-xylitol have been described to date, even though its use as non-toxic cosmetic ingredient has been demonstrated.[39]

Xylitol is widely used as sweetener and refreshing agent in foods and in toothpastes because of its low caloric value, glycemic



Scheme 3 Preferred pathway (green) for the catalytic conversion of xylose over Ru@Dowex-H catalyst under H_2.

index and anti-cariogenicity.[40] It is currently manufactured in 10^4 ton/year through the catalytic hydrogenation of xylose over Raney nickel.[41] Several supported-noble metal catalysts have been proposed for this reaction that, however, show lower selectivity compared to that of Ru@Dowex-H (Table S3). Usual by-products include xylulose, arabitol and minor amounts of dehydration and hydrogenolysis derivatives.[42] Formation of xylulose and arabitol can be ascribed to the Lewis acid sites-catalysed isomerisation of xylose to xylulose at temperatures above 100 °C, followed by epimerization to lyxose,[43] which then undergoes hydrogenation to arabitol (Scheme 3). Thus, the high xylitol selectivity of Ru@Dowex-H can be safely attributed to the low Lewis acid character of the catalyst.[44] Accordingly, no arabitol nor lyxose were detected in the reaction mixture.

In addition, no significant amounts of furfural derivatives[45] were whatsoever observed in the conversion of xylose using Ru@Dowex-H at H_2 pressures above 15 bar. This indicates that, under these conditions, the rate of xylose hydrogenation is higher than that of its dehydration (Scheme 3). An analogous result was previously reported using a 25 : 1 (w/w) Amberlyst-15 + 5% Ru/C mechanical mixture under similar conditions.[46] These evidences clearly show that that xylose hydrogenation is kinetically favoured over competitive dehydration using dual catalysts comprising Ru(0) and solid Brønsted acid sites, at least under medium H_2 pressures. Attainment of the reverse order is possible, although using different catalytic systems. For example, furfuryl alcohol was the main product obtained from xylose in one-stage using a Pt/SiO_2 + sulfated zirconia mixture under hydrogen transfer conditions (H_2O / 2-propanol, 30 bar H_2, 170 °C) (Scheme 3).[47] Preference of Ru@Dowex-H for hydrogenation *versus* xylose dehydration can be explained in terms of both the low Lewis acidy of the catalyst, which would favour the formation of furfural *via* isomerization-dehydration route,[48] and the high activation barrier of xylose dehydration by Brønsted acid type catalysts.[49,50] A check experiment carried out under 5 bar H_2 and 190 °C resulted in the formation of a coloured solution containing significant amounts

of furfural derivatives and other by-products, thus revealing that hydrogenation and dehydration of xylose over Ru@Dowex-H attain comparable kinetic at low hydrogen pressures.

Conclusions

Methods for fine-chemicals production from not-critical, renewable raw materials are of increasing relevance in the current process industry. Lignocellulosic biomass, hence the sugars thereof, is central to this because of its large non-edible portion and its potential to be obtained from wastes or from alternative farming, e.g. algae,[51] thus to have limited competition with the food industry. It has been estimated that only 3-4% of the total carbohydrates produced are currently used for food, so there is an abundant untapped supply of biomass sugars.[52] However, processing of lignocellulosic derivatives usually involves multistep reaction sequences, with corrosion and neutralization issues often associated, wherein a multitude of compounds can be generated. The development of alternative methods for the catalytic conversion of lignocellulosic materials that comply with sustainability criteria are thus highly desirable.[53]

Herein we described the one-pot, one-stage conversion of C_5 and C_6 sugars to expensive and/or rare anhydro sugar alcohols in high yields, using an heterogeneous single catalytic body comprising immobilized metal sites for hydrogenation and acid sites for dehydration onto the same support. Anhydroxylitol and isosorbide were selectively obtained with no need of organic solvents, high metal loadings, strong soluble acid additives or purification steps, from xylose and glucose, respectively.[54] The solid catalyst could be easily and quantitatively recovered, showing no significant metal leaching in solution. The superior selectivity of Ru@Dowex-H has to be related to the high selectivity in both the hydrogenation and dehydration steps. While hydrogenation selectivity by gel-type resin supported-metal catalyst was previously attributed to the favourable combination of the microporous structure of the support with the narrow size distribution of immobilized metal particles,[55] selectivity in dehydration can be ascribed to the proper balance of density and strength of Brønsted acid sites. It is also clear that whenever a bifunctional hydrogenation / acid catalyst is employed, selectivity toward a defined reaction path is ruled by the relative rate of competitive hydrogenation and dehydration reactions, which, in turn, is controlled by the ratio of Brønsted to Lewis acid sites.[56] In the case of Ru@Dowex-H, the low Lewis acidity character favours an hydrogenation $\rightarrow$ dehydration sequence and minimize the occurrence of isomerisation side-reactions. It is also worth mentioning the switchability of Ru@Dowex-H: the simple change of the reaction temperature allows to drive the catalyst selectivity to different products, i.e. sugar alcohol or anhydrosugar alcohol, to get the desired material with high purity in any case.

In conclusion, we have shown that a very simple catalyst design using commercial materials allows for the conversion of sugars to take place selectively and in a flexible way, without intermediate processing stages. The proof of concept provided by this study may serve as basis for the engineering of novel, improved bifunctional catalysts for selective biomass conversion.

Experimental

Synthesis of the catalyst

All reactions were performed under nitrogen. 600 mg of dry ion-exchange resin Dowex 50WX2–100 (2.88 meq SO_3H) were added to a solution of ruthenium(III) nitrosyl nitrate (107 μl of $Ru(NO)(NO_3)_3$ nitric solution 2.55 wt % Ru, 0.029 mmol Ru) in deionised water (11.0 ml). The mixture was stirred at room temperature for 4 h. After that time, the solution was decanted and the solid material washed with deionised water (4 x 50 ml). Water (13.3 ml) and solid $NaBH_4$ (33.0 mg, 0.87 mmol, $NaBH_4$: Ru = 30 : 1) were then added. After stirring at room temperature for 18h, the solid was decanted and washed with water (4 x 50 ml). The resulting black material was treated three times for 30 min. each with a solution of CF_3SO_3H in water (0.5 M, 58 ml, 28.8 mmol H^+) under stirring. The solid was then decanted, washed with H_2O until neutral pH, methanol (3 x 50 ml), diethyl ether (3 x 50 ml) and dried in a stream of N_2 overnight. Ru loading 0.20 wt % (ICP-OES).

Catalytic reactions

In a typical experiment, Ru@Dowex-H (104 mg, 0.20 wt% Ru), was loaded into a metal-free autoclave under nitrogen. A degassed solution of sugar in deionized water (0.1 M) was added under nitrogen via a Teflon tube. Nitrogen was replaced by hydrogen with three cycles pressurization /depressurization. The autoclave was then charged with the desired pressure of hydrogen, stirred and heated up to the selected temperature using an oil bath. After the desired time, the reaction solution was removed and analysed. The reaction products were unequivocally identified by comparison of the GC and HPLC retention times, mass spectra and $^{13}C\{^1H\}$ NMR resonances with those of authentic specimens. Quantitative analysis of the reaction products was carried out via HPLC based on calibration curves of the pure compounds.

Acknowledgements

Thanks are due to Centro Microscopie Elettroniche (CNR, Firenze) for technical support.

Notes and references

1 (*a*) P. J. Deuss, K. Barta and J. G. de Vries, *Catal. Sci. Technol.*, 2014, **4**, 1174; (*b*) M. J. Climent, A. Corma and S. Iborra, *Green Chem.*, 2014, **16**, 516; (*c*) R. A. Sheldon, *Green Chem.*, 2014, **16**, 950.

2 S. M. Sen, D. M. Alonso, S. G. Wettstein, E. I. Gürbüz, C. A. Henao, J. A. Dumesic and C. T. Maravelias, *Energy Environ. Sci.*, 2012, **5**, 9690.

3 P. Gallezot, *Chem. Soc. Rev.*, 2012, **41**, 1538.

4 (*a*) F. Liguori, C. Moreno-Marrodan and P. Barbaro, *ACS Catal.*, 2015, **5**, 1882; (*b*) W. Luo, U. Deka, A. M. Beale, E. R. H. van Eck, P. C. A. Bruijnincx and B. M. Weckhuysen, *J. Catal.*, 2013, **301**, 175.

5 (*a*) S. Sartipi, M. Makkee, F. Kapteijn and J. Gascon, *Catal. Sci. Technol.*, 2014, **4**, 893; (*b*) P. Barbaro, F. Liguori, N. Linares and C. Moreno-Marrodan, *Eur. J. Inorg. Chem*., 2012, 3807; (*c*) M. J. Climent, A. Corma and S. Iborra, *Chem. Rev*., 2011, **111**, 1072.
6 See: P. Pollak, *Fine Chemicals: The Industry and the Business*, Wiley-Interscience, Hoboken, 2007.
7 XRD data were in line with TEM results. Physisorption experiments were hampered by the limited accessibility of gas reactants to gel-type resin in the dry state, see: A. Biffis, H. Landes, K. Jeřábek and B. Corain, *J. Mol. Catal. A: Chem*., 2000, **151**, 283.
8 The Dow Chemical Company, Form No. 177-01509-904. ICP-OES analysis revealed that less than 5% proton sites were exchanged with sodium in the final catayst.
9 This is attributed to higher rate of Ru^{III} migration within the solid beads compared to the rate of Ru^{III} reduction, see: B. Corain and M. Králik, J. *Mol. Cat. A: Chem*., 2001, **173**, 99.
10 G. W. Huber, S. Iborra and A. Corma, *Chem. Rev*., 2006, **106**, 4044.
11 (*a*) M. J. Climent, A. Corma and S. Iborra, *Green Chem*., 2011, **13**, 520; (*b*) S. Van de Vyver, J. Geboers, P. A. Jacobs and B. F. Sels, *ChemCatChem*, 2011, **3**, 82.
12 (*a*) M. Rose and R. Palkovits, *ChemSusChem*, 2012, **5**, 167; (*b*) G. Fleche and M. Fuchette, *Starch*, 1986, **38**, 26.
13 *Isosorbide market analysis by application and segment forecasts to 2020*, http://www.grandviewresearch.com /industry-analysis/isosorbide-industry (accessed October 2015).
14 B. Kamm, M. Kamm, M. Schmidt, T. Hirth and M. Schulze, in *Biorefineries - Industrial Processes and Products*, ed. B. Kamm, P. R. Gruber and M. Kamm, Wiley-VCH, Weinheim, 2010, ch. 3, vol. 2, pp. 97.
15 (*a*) H. Kobayashi, H. Yokoyama, B. Feng and A. Fukuoka, *Green Chem*., 2015, **17**, 2732; (*b*) A. A. Dabbawala, D. K. Mishra, G. W. Huber and J. S. Hwang, *Appl. Catal. A: Gen*., 2015, **492**, 252 and references therein.
16 (*a*) J. Xia, D. Yu, Y. Hu, B. Zou, P. Sun, H. Li and H. Huang, *Catal. Commun*., 2011, **12**, 544; (*b*) P. Sun, D. Yu, Y. Hu, Z. Tang, J. Xia, H. Li and H. Huang, *Korean J. Chem. Eng*., 2011, **28**, 99
17 (*a*) *Additives for Polymers*, 2015, issue 6, p. 8; (*b*) P. Fuertes, *US* 213439A1, 2008; (*c*) K. M. Moore and A. J. Sanborn, *US* 152907A1, 2004.
18 (*a*) C. G. Moyers, J. K. Withrom and J. L. Stephens, *US* 259056A1, 2009; (*b*) N. Fujihana, Y. Tategami and M. Mihashi, *JP* 316025(A), 2006; (*c*) G. Fleche, P. Fuertes, R. Tamion and H. Wyart, *US* 110969A1, 2004.
19 J. Zhang, J. B. Li, S. B. Wu and Y. Liu, *Ind. Eng. Chem. Res*., 2013, **52**, 11799.
20 http://www.transparencymarketresearch.com/sorbitol-market.html (accessed October 2015).
21 L. Vilcocq, A. Cabiac, C. Especel, S. Lacombe and D, Duprez *Catal. Today*, 2015, **242**, 91.
22 (*a*) J. U. Oltmanns, S. Palkovits and R. Palkovits, *Appl. Catal. A: Gen*., 2013, **456**, 168; (*b*) A. Yamaguchi, N. Hiyoshi, O.Sato and M. Shirai, *Green Chem*., 2011, **13**, 873.
23 C. Moreno-Marrodan and P. Barbaro, *Green Chem*., 2014, **16**, 3434.
24 See. e.g.: G. Morales, J. A. Melero, M. Paniagua, J. Iglesias, B. Hernández and M. Sanz, *Chinese J. Catal*., 2014, **35**, 644.
25 X. Hu, C. Lievens and C. Z. Li, *ChemSusChem* 2012, **5**, 1427.
26 G. Liang, C. Wu, L. He, J. Ming, H. Cheng, L. Zhuoa and F. Zhao, *Green Chem*., 2011, **13**, 839.
27 R. Palkovits, K. Tajvidi, J. Procelewska, R. Rinaldi and A. Ruppert, *Green Chem*., 2010, **12**, 972.
28 B. Op de Beeck, J. Geboers, S. Van de Vyver, J. Van Lishout, J. Snelders, W.J. J. Huijgen, C. M. Courtin, P. A. Jacobs and B.F. Sels, *ChemSusChem*, 2013, **6**, 199.
29 P. Sun, X. Long, H. He, C. Xia and F. Li, *ChemSusChem*, 2013, **6**, 2190.
30 R. M. de Almeida, J. Li, C. Nederlof, P. O'Connor, M. Makkee and J.A. Moulijn, *ChemSusChem*, 2010, **3**, 325.
31 A.Yamaguchi, O. Sato, N. Mimura and M. Shirai, *Catal. Commun*., 2015, **67**, 59.
32 I. Sádaba, M. López Granados, A. Riisagerc and E. Taarning, *Green Chem*., 2015, **17**, 4133.
33 Y. Román-Leshkov, J. N. Chheda and J. A. Dumesic, *Science*, 2006, **312**, 1933.
34 *Polysaccharides: Structural Diversity and Functional Versatility*, ed. S. Dumitriu, Marcel Dekker, New York 2005.
35 J. P. Mikkola, H. Vainio, T. Salmi, R. Sjöholm, T. Ollonqvist and J. Väyrynen, *Appl. Catal. A: Ge*n., 2000, **196**, 143.
36 (*a*) J. M. Robinson, A. M. Wadle, M. D. Reno, R. Kidd, S. R. Barrett Hinsz and J. Urquieta, *Energy Fuels*, 2015, **29**, 6529; (*b*) S. Selifonov, F. Jing and N. Zhou, *WO* 138842A1, 2010; (*c*) J. F. Carson and W.D. Maclay, *J. Am. Chem. Soc*., 1945, **67**, 1808.
37 E. F. Sousa-Aguiar, L. G. Appel, P. C. Zonetti, A. do Couto Fraga, A. A. Bicudo and I. Fonsecad, *Catal. Today*, 2014, **234**, 13.
38 M. Kurszewska, E. Skorupowa, J. Madaj and A. Wiśniewski, *J. Carbohyd. Chem*., 2004 , **23**, 169.
39 V. R. Leite e Silva, M. A. Schulman, C. Ferelli, J. M. Gimenis, G. W.Ruas, A. R. Baby, M. V. R. Velasco, M. E. Taqueda, and T. M. Kaneko, *J. Cosmet. Dermatol*.,2009, **8**, 32.
40 *D-Xylitol - Fermentative Production, Application and Commercialization*, ed. S. Silvério da Silva and A. K. Chandel, Springer-Verlag, Heidelberg 2012.
41 (*a*) T. Granstrom, K. Izumori and M. Leisola, *Appl. Microbiol. Biotechnol*., 2007, **74**, 273; (*b*) M. Herskowitz, *Chem. Eng. Sci*., 1985, **40**, 1309.
42 A. P. Tathod and P. L. Dhepe, *Green Chem*., 2014, **16**, 4944.
43 (*a*) V. Choudhary, S. Caratzoulas and D. G. Vlachos, *Carbohyd. Res.*, 2013, **368**, 89; (*b*) M. S. Holm, Y. J. Pagán-Torres, S. Saravanamurugan, A. Riisager, J. A. Dumesic and E. Taarning, *Green Chem*., 2012, **14**, 702.
44 A residual Lewis acidity in Ru@Dowex-H can be ascribed to the ruthenium sites, see: N. Scotti, M. Dangate, A. Gervasini, C. Evangelisti, N.Ravasio and F. Zaccheria, *ACS Catal.*, 2014, **4**, 2818.
45 (*a*) M. M. Antunes, S. Lima, A. Fernandes, M. Pillinger, M. F. Ribeiro and A. A. Valente, *Appl. Catal. A: Ge*n., 2012, **417-418**, 243, and references therein; (*b*) J. Serrano-Ruiz, R. Luque and A. Sepúlveda-Escribano, *Chem. Soc. Rev*., 2011, **40**, 5266.
46 V.V. Ordomsky, J.C. Schouten, J. van der Schaaf and T.A. Nijhuis, *Appl. Catal. A: Ge*n., 2013, **451**, 6.
47 R. F. Perez and M. A. Fraga, *Green Chem*., 2014, **16**, 3942.
48 (*a*) C. Aellig, D. Scholz, P. Y. Dapsens, C. Mondelli and J. Pérez-Ramírez, *Catal. Sci. Technol*., 2015, **5**, 142; (*b*) S. Dutta, S. De, B. Saha and Md. I. Alam, *Catal. Sci. Technol*., 2012, **2**, 2025; (*c*) V. Choudhary, A. B. Pinar, S. I. Sandler, D. G. Vlachos and R.F. Lobo, *ACS Catal*. 2011, **1**, 1724.
49 (*a*) M. B. Fusaro, V. Chagnault and D. Postel, *Carbohyd. Res.*, 2015, **409**, 9; (*b*) I. Agirrezabal-Telleria, A. Larreategui, J. Requies, M.B. Güemez and P.L. Arias, *Bioresource Technol*., 2011, **102**, 7478.
50 Effective xylose dehydrogenation by Brønsted sites requires soluble mineral acids or strong solids acids, e.g. ZSM-5 zeolite in H^+ form, see: R. O'Neill, M. Najeeb Ahmad, L. Vanoye and F. Aiouache, *Ind. Eng. Chem. Res*., 2009, **48**, 4300.
51 C. Y. Chen, X. Q. Zhao, H. W. Yen, S. H. Ho, C. L. Cheng, D. J. Lee, F. W. Bai and J. S. Chang, *Biochem. Eng. J*., 2013, **78**, 1.
52 W. H. Gong, *US* 7385081B1, 2008.
53 (*a*) H. Kobayashi and A. Fukuoka, *Green Chem*., 2013, **15**, 1740; (*b*) G. Centi, P. Lanzafame and S. Perathoner, *Catal. Today*, 2011, **167**, 14.
54 *Top Value Added Chemicals from Biomass*, ed. T. Werpy and G. Petersen, U.S. Department of Energy , Volume I, 2004.
55 F. Liguori, C. Moreno-Marrodan and P. Barbaro, *Chinese J. Catal*., 2015, **36**, 1157.

56 R. Weingarten, G. Tompsett, W. Conner Jr. and G. Huber, *J. Catal.*, 2011, **279**, 174.

View Article Online
DOI: 10.1039/C6GC00128A

View Article Online
DOI: 10.1039/C6GC00128A

The selective multi-step conversion of monosaccharides to anhydro-sugar alcohols was achieved in one-pot, one-stage by a bifunctional Ru catalyst