Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting information for

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

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General information

Unless otherwise stated, all reaction and manipulations were performed under nitrogen using standard Schlenk techniques. DOWEX 50WX2 – 100 strong cation-exchange resins (50 – 100 mesh, 276 ± 2 μm bead size, H^+ form, 2% cross-linked, gel-type, 4.8 meq g^{-1} exchange capacity) were obtained from Aldrich. The commercial resins were washed prior of use to remove all incidental impurities. Thus, 20 g of cation exchange resin were washed with refluxing deionised water for 2 h and with refluxing methanol for 1 h using a Soxhlet apparatus. After cooling down to room temperature, the resin was washed sequentially with dichloromethane (3 x 100 ml), methanol (3 x 100 ml) and diethyl ether (3 x 100 ml). The resin was dried in a stream of nitrogen and stored under nitrogen. The $R\text{-}SO_3^-H^+$ resin obtained as yellowish beads was stored under nitrogen. D-(+)-Glucose (BioXtra, ≥ 99.5 %), D-(+)-xylose (BioXtra, ≥ 99 %), D-sorbitol (BioUltra, ≥ 99.5%), xylitol (> 99%) D- lyxose and 1,4-sorbitan were obtained from Aldrich. Isosorbide (98%) and 1,4-anhydro-D-xylitol were obtained from abcr and Carbosynth, respectively. All other reagents were commercial products and were used as received without further purifications.

ESEM (Environmental Scanning Electron Microscopy) measurements were performed on a FEI Quanta 200 microscope operating at 25 KeV accelerating voltage in the low-vacuum mode (1 torr) and equipped with an EDAX Energy Dispersive X-ray Spectrometer (EDS). X-ray maps were acquired on the same instrument using a 512 x 400 matrix, 100 μs dwell time and 25 KeV accelerating voltage. TEM (Transmission Electron Microscopy) analyses were performed using a M12 PHILIPS instrument at 120 KeV accelerating voltage. The sample preparation was carried out by dispersing the grinded resin into about 1 ml of ethanol and treating the solution in an ultrasonic bath for 30 min. Successively, a drop of solution was deposited onto a carbon coated Cu TEM grid and the solvent left to evaporate. Statistical nanoparticle size distribution analysis was typically carried out on 300-400 particles. XRD (X-ray Diffraction) spectra were recorded on a PANanalytical XPERT PRO powder diffractometer, employing CuKα radiation (λ=1.54187 Å), a parabolic MPD-mirror and a solid state detector (PIXcel). The samples were prepared on a silicon wafer (zero background) that was rotating (0.5 rotations per second) during spectra acquisition. All XRD spectra were acquired at room temperature in a 2θ range from 4 to 95°, applying a step size of 0.0263° and a counting time of 77.5 seconds. $^{13}C\{^1H\}$ NMR spectra were recorded at 100.613 MHz on a Bruker Avance DRX-400 spectrometer, using a coaxial insert filled with D_2O and DEPT-135 pulse sequences. Chemical shift in ppm are relative to tetramethylsilane as external reference. The metal content both in the supported catalyst and leached in the catalytic reaction solutions was determined by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-OES) with a Varian 720ES instrument. The detection limit for Ru was 0.006 ppm. The solid samples (50-100 mg) were treated in a microwave-heated digestion bomb (Milestone, MLS-200, 20 min.@ 220 °C) with concentrated HNO_3 (1.5 mL), 98% H_2SO_4 (2 mL), and 0.5 mL of H_2O_2 30%. After filtration, the solutions were analysed .The solutions were analysed directly after 1:5 dilution in 0.1 M hydrochloric acid. GC-analyses were performed on a Shimadzu GC 2010 Plus gas chromatograph equipped with flame ionization detector and both VF-WAXms (30 m, 0.25 mm ID, 0.25 µm FT) and Nukol (30 m, 0.32 mm ID, 0.25 µm FT) fused silica capillary column. GC-MS analyses were performed on a Shimadzu QP5000 apparatus equipped with the same capillary columns. HPLC (High Pressure Liquid Chromatography) analyses were performed on a UFLC-Shimadzu apparatus equipped with a refraction index detector (RID) and either a Grace

Alltech OA-1000 Organic Acid column (300 mm x 6.5 mm), using 0.005 M sulphuric acid as eluent (flow 0.7 ml min^{-1} at 50 ºC) or a Rezex RPM Monosaccharides-Pb2+ column (300 x 7.8 mm) using H_2O as eluent (0.6 ml min^{-1} at 80 °C). Reactions under batch conditions were carried out using a stainless steel autoclave (25 mL internal volume) constructed at Istituto di Chimica dei Composti OrganoMetallici-CNR (Firenze, Italy) and equipped with a magnetic stirrer, a Teflon ® inset and a pressure controller.

Synthesis of the Ru@Dowex-H catalyst

600 mg of dry ion-exchange resin Dowex 50WX2–100 (2.88 meq SO_3H) were added to a degassed solution of ruthenium(III) nitrosyl nitrate (107 µl of $Ru(NO)(NO_3)_x(OH)_y$ nitric solution 2.55 wt % Ru, 0.029 mmol Ru, mol ratio SO_3H/Ru = 99) in deionised water (11.0 ml). The mixture was degassed with 3 cycles vacuum/nitrogen and stirred at room temperature for 4 h using an orbital stirrer (150 rpm). The solid material, initially light orange, became slowly brown. After that time, the solid material was decanted and washed with degassed, deionised water (4 x 50 ml). Degassed water (13.3 ml) and an excess of solid $NaBH_4$ (33.0 mg, 0.87 mmol, $NaBH_4$: Ru = 30 : 1) were then added in the order under nitrogen. After orbital stirring (150 rpm) at room temperature for 18h, the solid was decanted and was washed with degassed water (4 x 50 ml). The resulting black solid was treated three times for 30 min. each with a degassed solution of CF_3SO_3H in water (0.5 M, 58 ml, 28.8 mmol H^+) under orbital stirring (150 rpm). The resin was then decanted, washed with degassed portions of H_2O until neutral pH, methanol (3 x 50 ml) and diethyl ether (3 x 50 ml). I was collected on a sintered glass frit and dried in a stream of N_2 overnight. The product, obtained as black beads was stored under nitrogen. ICP-OES analysis showed the catalyst to contain a bulk 0.20 wt % Ru loading, corresponding to ca. 50% ruthenium uptake. A 6.8 ± 0.2 nm ruthenium particle aggregates size was obtained from TEM analysis. The sodium content in the final Ru@Dowex-H material was lower than 0.2 wt % by ICP-OES analysis.

Catalytic conversion of sugars under batch conditions

In a typical experiment, Ru@Dowex-H (104 mg, 0.2 wt % Ru, 0.002 mmol of ruthenium), was loaded into a metal-free autoclave under nitrogen. A degassed solution of sugar (0.1 M) in deionized water (10 ml) was transferred under nitrogen via a Teflon tube into the autoclave. Nitrogen was replaced by hydrogen with three cycles pressurization/depressurization. The autoclave was finally charged with the desired pressure of hydrogen, stirred at 150 rpm using a mechanical stirrer and heated up to the selected temperature using an oil bath. After the desired time, the reactor was cooled down to room temperature and depressurized and the clear solution obtained was removed under a stream of hydrogen using a gas-tight syringe. A sample of this solution was used for GC and HPLC (product yield), GC-MS, $^{13}C\{^1H\}$ NMR (product identification) and ICP-OES analysis (metal and sulphur leaching). After use in catalysis, the solid catalyst was washed with deionized water (3 x 10 ml), methanol (3 x 10 ml) and diethyl ether (3 x 10 ml), dried in a stream of nitrogen and stored under nitrogen for later characterization. .A sample of the recovered solid catalyst was analysed by ICP-OES (Ru loading) and TEM (particle size). For recycling experiments, a fresh solution of sugar was transferred under hydrogen via a gas-tight syringe into the reactor containing the recovered supported catalyst. The autoclave was then charged with hydrogen, stirred at 150 rpm and heated up. After the desired time, the mixture was treated as described above. The same recycling procedure was used in the subsequent hydrogenation cycles. 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.

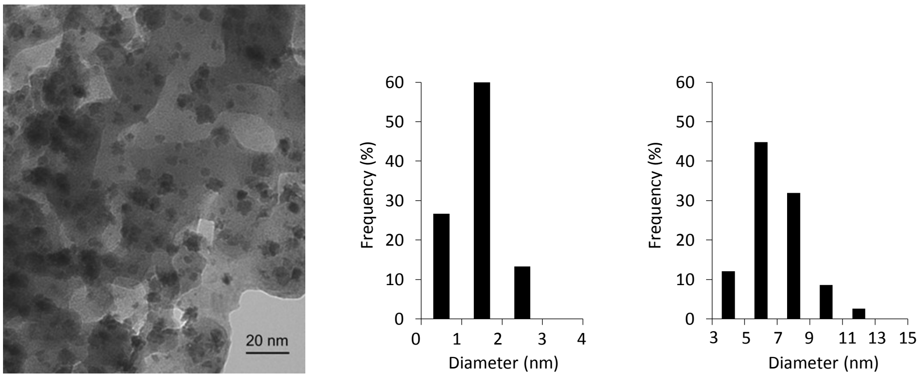

Fig. S1 Representative TEM image (left) and size distribution of Ru particles (centre) and aggregates (right) in 0.2% (w/w) Ru@Dowex-H.

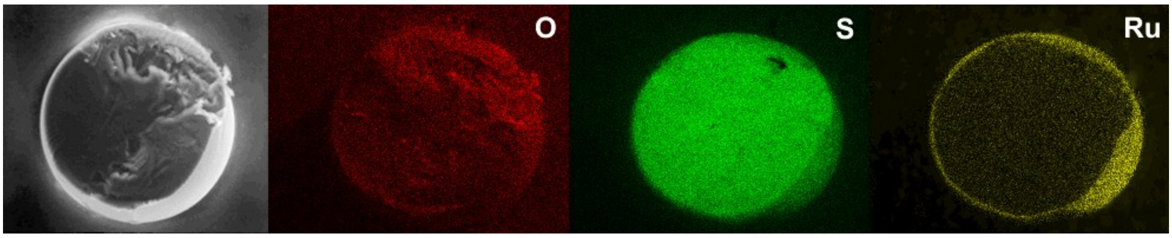

Fig. S2 ESEM image (left, backscattered electrons) and EDS oxygen (O Kα1), sulphur (S Kα1) and ruthenium (Ru Lα1) maps of an equatorial section of 0.2% (w/w) Ru@Dowex-H bead (25 KeV, 785 magnifications).

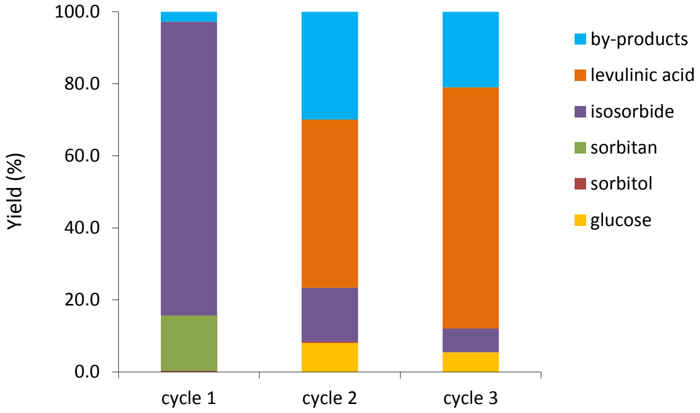

Fig. S3 Recycle of Ru@Dowex-H in the batch, direct conversion reaction of glucose. Reaction conditions: water, 30 bar H_2, 24 h, 190 °C, 0.2% Ru. Data from HPLC analysis.

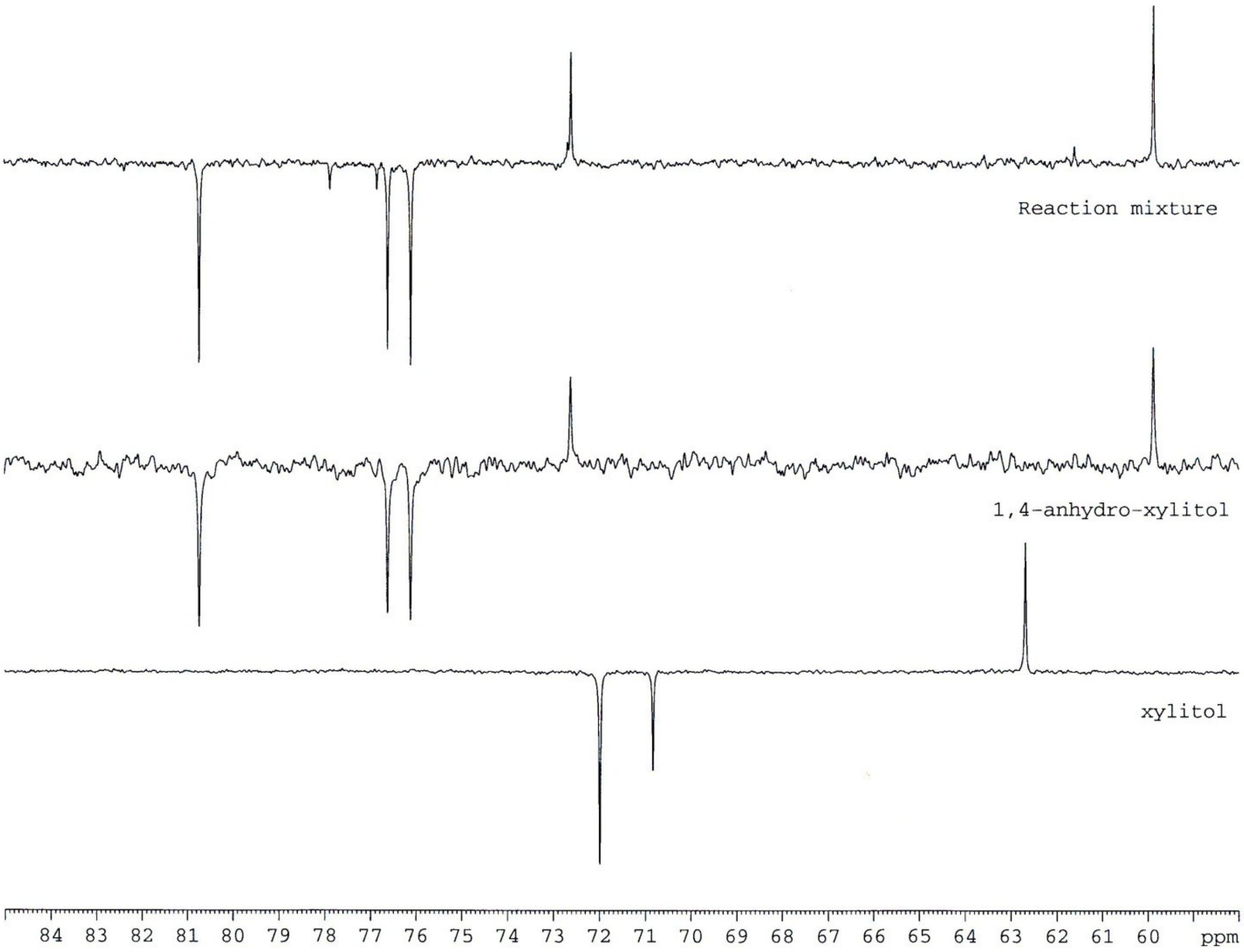

Fig. S4 $^{13}C\{^1H\}$ NMR DEPT spectra of xylitol (bottom) and 1,4-anhydro-xylitol (middle) reference standards, and the reaction mixture of xylose conversion using the Ru@Dowex-H catalyst (reaction conditions: water, 30 bar H_2, 6 h, 190 °C, 0.2% Ru).

Table S1 Representative 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]								Selectivity (%)	
1	glucose	190	30	63	100.0	sorbitol	0.7	sorbitan	10.8	isosorbide	86.4	by-prod.[c]	2.1	isosorbide	86.0
2				48	100.0		0.9		10.2		84.9		4.0		84.9
3				24	100.0		0.7		15.3		79.5		4.5		79.5
4			15	24	100.0		0.8		7.4		10.6		81.2		10.6
5		170	30	24	100.0		0.4		44.4		53.0		2.1		53.0
6		120	30	24	100.0		95.6		0.0		4.0		0.4	sorbitol	95.6
7				7	100.0		99.9		0.0		0.0		0.1		99.9
8	xylose	190	30	24	100.0	xylitol	0.0	lyxose	0.0	anhydroxylitol	90.9	by-prod.[c]	9.1	anhydroxylitol	90.9
9				6	100.0		0.0		0.0		94.9		5.1		94.9
10				3	100.0		31.8		0.0		57.9		10.3		57.9
11			5	24	88.4		0.0		0.0		45.9		42.5[d]		51.9
12		150	30	6	100.0		82.4		0.0		17.6		0.0	xylitol	82.4
13		120	30	7	99.7		99.3		0.0		0.0		0.4		99.6
14				6	95.3		95.3		0.0		0.0		0.0		100.0

[a] Ruthenium 0.2% (w/w), sugar 0.1 M in water. [b] Data from HPLC analysis. [c] Unidentified soluble products. [d] Levulinic acid 18.5 %.

Table S2 Catalytic hydrogenation of glucose to sorbitol by various catalysts

Entry	Catalyst	T (°C)	H_2 (bar)	Conversion (%)	Selectivity (%)	Ref.
1	Ru@Dowex-H [a]	120	30	100.0	99.9	this work
2	1.8% Ru/C	100	80	100.0	99.2	1
3	3.1% Ru-B/SiO_2	100	40	100.0	> 99	2
4	Ru-Cr-B	80	40	99.7	> 99	3
5	4.1% Ru/ZSM-5-TF	120	40	99.6	99.2	4
6	2.8% Ru/HPS	140	40	99.3	99.0	5
7	Ru/Al_2O_3	150	250	100.0	98	6
8	1% Ru/SiO_2	90	100	100.0	> 99.5	7
9	2.2% Ru/CNT	130	20	91.4	98.2	8

[a] 0.2 % w/w Ru.

Table S3 Catalytic hydrogenation of xylose to xylitol by various catalysts

Entry	Catalyst	T (°C)	H_2 (bar)	Conversion (%)	Selectivity (%)	Ref.
1	Ru@Dowex-H [a]	120	30	99.7	99.6	this work
2	5% Ru/C + Amberlyst-15	165	25	78	88.9	9
3	1% Ru/NiO-TiO_2	120	55	99.9	99.8	10
4	1% Ru/TiO_2	120	55	97.1	99.0	10
5	1% Ru/C	120	55	96.5	97.5	10
6	Raney Ni	120	55	96.9	96.7	10
7	PtSn/Al_2O_3	130	16	98	92	11

[a] 0.2 % w/w Ru.

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