Metal/Acid bifunctional catalyst for the one-pot conversion of sugars into high-added value chemicals

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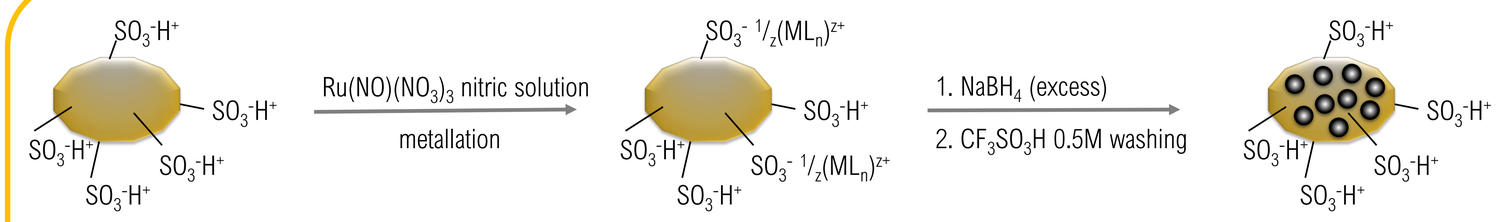
Introduction

The depletion of fossil resources has compelled the scientific community to search alternative raw materials for the production of platform and high-added value molecules. In this sense, lignocellulosic biomass, due to their large non-edible portion, is replacing petrochemical sources in the last years. Several methods have been developed, which often entail complex reaction sequences (reduction and acid-mediated catalytic steps), harsh reaction conditions or modest yields, with significant drawbacks in terms of cost, waste emission, efficiency, space and energy. A potential solution for the optimization of these methodologies may be the use of bifunctional catalyst, that is, a single catalytic body showing both acidic and metallic functions and being able of working under the same reaction conditions. In the present work, we report the selective, direct conversion of aqueous solutions of glucose and xylose into fine chemicals using a novel resin-supported bifunctional ruthenium catalyst Ru@Dowex-H

The key element — BIFUNCTIONAL METAL/ACID CATALYST



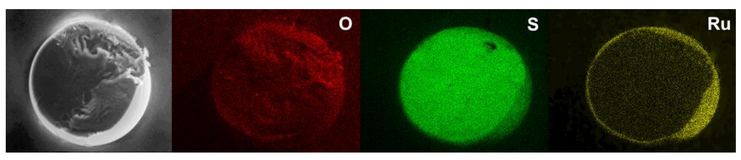


Fig 1. ESEM image (left, backscattered electrons) and EDS oxygen (O Kα1), sulphur (S Kα1) and ruthenium (Ru Lα1) maps of an equatorial section

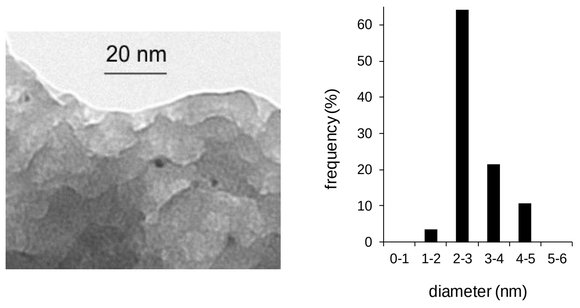
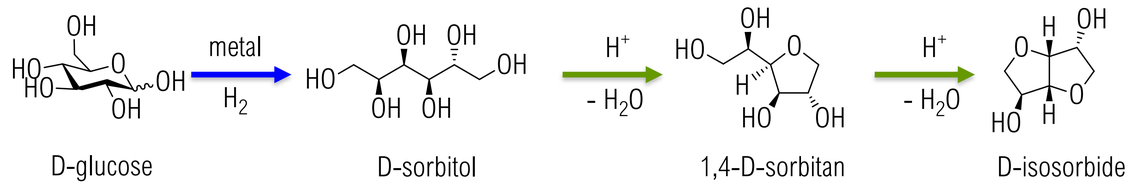


Fig. 2. TEM image (left), RuNPs size distribution (right)

- ✓ 2-steps synthesis: metallation and formation of RuNPs.
- ✓ 1 catalyst able to perform acid and hydrogenation reactions in one-pot.
- ✓ Double role of the commercial ion-exchange resin; solid support stabilizing RuNPs of small dimension and acid catalyst
- ✓ Egg shell distribution of the metal within the bead
- ✓ 0,2 wt% Ru loading

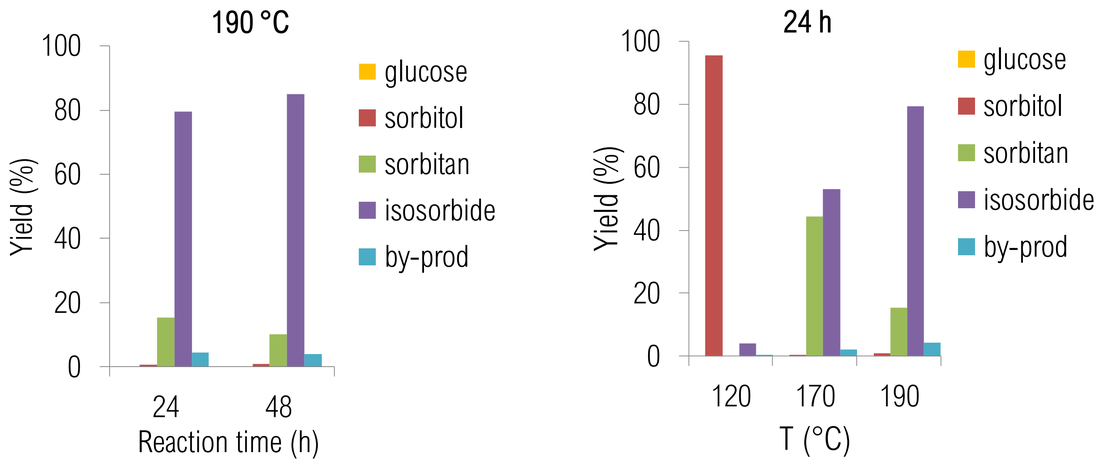
One-pot conversion of glucose into isosorbide



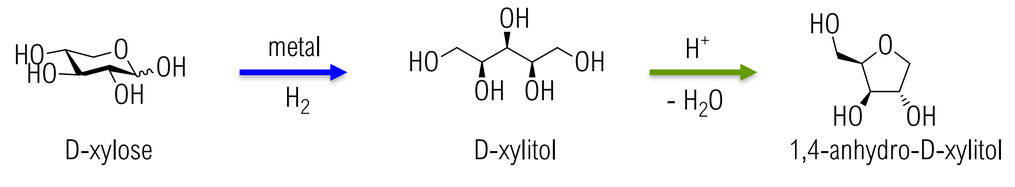
Direct catalytic conversion of glucose by Ru@Dowex-H under batch conditions [a]

Entry	T (°C)	H_2 (bar)	Time (h)	Conv (%)	Product yield (%) [b] sorbitol	sorbitan	isosorbide	by-prod.[c]	Selectivity (%) isosorbide	sorbitol
1	190	30	24	100	0.7	15.3	79.5	4.5	79.5	0.7
2	190	30	48	100	0.9	10.2	84.9	4.0	84.9	0.9
3	170	30	24	100	0.4	44.4	53.0	2.1	53.0	0.4
4	120	30	24	100	95.6	0.0	4.0	0.4	4.0	95.6
5	120	30	7	100	99.9	0.0	0.0	0.1	0.0	99.9

[a] 0.2 wt% Ru, glucose 0.1 M in water. [b] Data from HPLC analysis. [c] Unidentified soluble products.



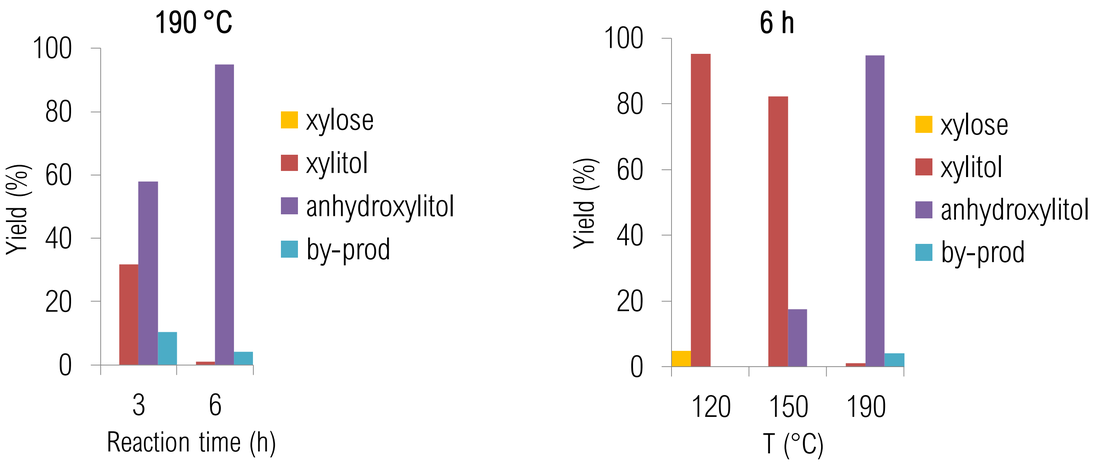
One-pot conversion of xylose into 1,4-anhydroxilitol



Direct catalytic conversion of xylose by Ru@Dowex-H under batch conditions [a]

Entry	T (°C)	H_2 (bar)	Time (h)	Conv (%)	Product yield (%) [b] xylitol	anhydroxylitol	by-prod.[c]	Selectivity (%) anhydroxylitol	xylitol
1	190	30	6	100	0.0	94.9	5.1	94.9	0.0
2	190	30	3	100	31.8	57.9	10.3	57.9	31.8
3	150	30	6	100	82.4	17.6	0.0	17.6	82.4
4	120	30	6	95.3	95.3	0.0	0.0	0.0	100.0

[a] 0.2 wt% Ru, sugar 0.1 M in water. [b] Data from HPLC analysis. [c] Unidentified soluble products.



Conclusions

- ✓ truly bifunctional, heterogeneous catalysts for one-pot conversions
- ✓ simple catalyst design
- ✓ commercial, low cost materials
- ✓ green solvent
- ✓ no acidic additives
- ✓ no metal contamination
- ✓ selection of the desired product by tuning the reaction conditions

References

- C.Moreno-Marrodan, P.Barbaro, *Green Chem.*, **2014**, 16, 3434.
- P. Barbaro, F. Liguori, C. Moreno-Marrodan, Green. Chem. 2016, 18, 2935

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