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## Highly microporous biomass-derived carbon supports for the direct conversion of cellulose to sorbitol

### AUTHORS

Lucília RIBEIRO / LA LSRE-LCM, DR. ROBERTO FRIAS S/N, PORTO

Natalia REY-RAAP / LA LSRE-LCM, RUA DR. ROBERTO FRIAS, S/N, PORTO

José J.M. ÓRFÃO / LA LSRE-LCM, RUA DR. ROBERTO FRIAS, S/N, PORTO

José L. FIGUEIREDO / LA LSRE-LCM, RUA DR. ROBERTO FRIAS, S/N, PORTO

M. Fernando R. PEREIRA / LA LSRE-LCM, RUA DR. ROBERTO FRIAS, S/N, PORTO

### PURPOSE OF THE ABSTRACT

One of the most efficient pathways for a future sustainable society dependent on cellulosic biomass is the one-pot hydrolytic hydrogenation of cellulose into valuable chemicals, especially sorbitol [1]. Sorbitol is one of the most promising platform molecules included in the list of the twelve base products of maximum potential derived from biomass [2]. Ruthenium supported on carbon-based supports, such as carbon nanotubes and activated carbon, are the catalysts typically used. Although carbon nanotubes are the most promising [3,4], it is necessary to match or surpass them using cheaper carbon supports. Accordingly, the aim of the present work is to use glucose, one of the main compounds derived from biomass, as precursor of the carbon supports. As a result, the costs can be reduced, and lignocellulosic biomass can be valorised, since glucose is used for the preparation of the catalyst and cellulose is the substrate for the reaction.

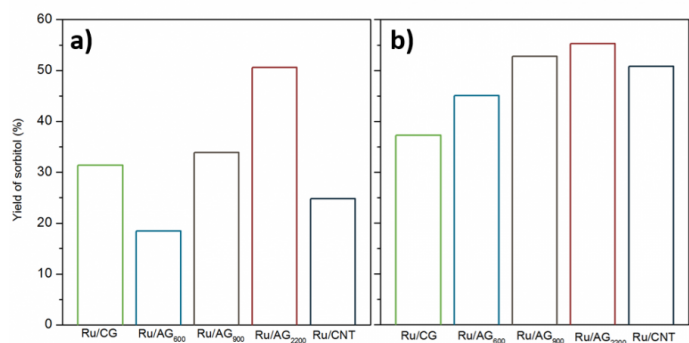
Four carbon supports with different surface areas were prepared by hydrothermal polymerization of glucose and subsequent carbonization at 700 °C under N<sub>2</sub> for 2 h (CG) or subsequent physical activation at 900 °C under CO<sub>2</sub> atmosphere for 2, 4 and 6 h (AG). Ruthenium monometallic catalysts were then prepared by incipient wetness impregnation of Ru (0.4 wt.%) on these carbon supports. Catalysts were then heat treated under nitrogen flow at 250 °C for 3 h and subsequently reduced under hydrogen flow at 250 °C for 3 h. The catalysts were denoted as Ru/CG or Ru/AG in reference to carbonized or activated glucose, respectively, in this last case also followed by the value of the surface area determined by nitrogen adsorption. The synthesized supports and catalysts were characterized by different techniques, such as nitrogen adsorption, microscopy, elemental analysis, TG, TPD and XPS. The different catalysts were then tested in the one-pot hydrolytic hydrogenation of cellulose into sorbitol. In standard tests, 300 mL of water, 750 mg of ball-milled cellulose and 300 mg of catalyst were introduced into a 1000 mL stainless steel Parr reactor. After heating under N<sub>2</sub> to 205 °C, the reaction was initiated by switching to H<sub>2</sub> (50 bar). The conversion and products distribution were analysed by HPLC and TOC.

The supports presented type I isotherms, characteristic of microporous materials. As expected, higher microporosity was obtained with the increase of the activation time (Table 1). The prepared Ru catalysts were then tested for the one-pot reaction and were in general highly efficient, with 100 % cellulose conversions after just 3 h. The production of sorbitol was favoured by the microporosity of the materials (Figure 1). Moreover, Ru/CG and Ru/AG600 exhibited similar microporosity but led to different behaviour during the reaction, which could be assigned to the differences on the oxygen functionalities (see Table 1). In addition, Ru/AG2200 allowed to attain 50 % sorbitol yield within the first hour of reaction, which could be due to its higher surface area, along with its higher basic character. Furthermore, Ru/AG900 and Ru/AG2200 enabled reaching higher cellulose conversions and sorbitol yields than those of the reference catalyst Ru/CNT, indicating that CNT can be successfully replaced by low-cost supports derived from biomass.

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## FIGURES



**FIGURE 1**

Figure 1

Sorbitol yields obtained after a) 3 h and b) 5 h of reaction.

Sample	S <sub>BET</sub> (m <sup>2</sup> ·g <sup>-1</sup> )	CO/CO <sub>2</sub> [a]
CNT	282	4.5
CG	573	4.0
AG <sub>600</sub>	569	5.1
AG <sub>900</sub>	936	6.5
AG <sub>2200</sub>	2214	7.2

[a] Ratio between the amounts of CO and CO<sub>2</sub> released, obtained by integration of the areas under TPD profiles.

**FIGURE 2**

Table 1

Textural and chemical properties of the supports.

## KEYWORDS

Cellulose conversion | hydrolytic hydrogenation | glucose-based materials | sorbitol

## BIBLIOGRAPHY

- [1] D.M. Alonso, S.G. Wettstein, J.A. Dumesic, Chem. Soc. Rev., 2012, 41, 7965-8216.
- [2] A.M. Ruppert, K. Weinberg, R. Palkovits, Angew. Chem. Int. J. Ed., 2012, 51, 2564-2601.
- [3] L.S. Ribeiro, J.J. Delgado, J.J.M. Órfão, M.F.R. Pereira, Catal. Today, 2017, 279, 244-251.
- [4] L.S. Ribeiro, J.J. Delgado, J.J.M. Órfão, M.F.R. Pereira, ChemCatChem, 2017, 9, 888-896.