**Hydrothermal carbon materials for energy and biomass conversion**

Natalia Rey-Raap1, Lucília S. Ribeiro1, Rafael G. Morais1, José J.M. Órfão1, José L. Figueiredo1, M. Fernando R. Pereira1*\**

*1 Laboratory of Separation and Reaction Engineering - Laboratory of Catalysis and Materials (LSRE-LCM), Department of Chemical Engineering, Faculty of Engineering of the University of Porto, Rua Dr. Roberto Frias s/n, 4200-465 Porto, Portugal*

*\* Corresponding author:* *fpereira@fe.up.pt*

**Highlights**

* The properties of hydrothermal carbons can be easily controlled.
* Well-developed microporosity results in materials with higher electrocatalytic activity.
* Total conversion of cellulose and a sorbitol yield of 59 % is attained after 3 h.

**1. Introduction**

Energy and biomass conversion are two of the most important issues to achieve a sustainable society. Fuel cells are one of the most efficient technologies for energy conversion. The performance of a fuel cell is mainly controlled by the oxygen reduction reaction (ORR) that takes place at the cathode. The most efficient electrocatalysts for ORR are based on platinum (Pt/C), which is costly and scarce, and hence, replacing platinum by materials with lower cost and broader availability has become a major challenge. A sustainable society is also focused on the direct conversion of biomass into valuable chemicals, being sorbitol one of the most promising platform molecules. Ruthenium catalysts supported on carbon materials have shown to be very effective supports for the direct conversion of cellulose to sorbitol. However, the best results to date are obtained using long reaction times, high metal loadings or expensive carbon supports. Thus, further research needs to be carried out in an attempt to match or surpass the results obtained to date by using cheaper carbon supports. In this context, the perspective of processing waste biomass into valuable carbonaceous materials has gained an increasing interest in the field of materials science. Carbon-based materials are highly promising catalysts for several applications, due to their high catalytic activity, cost-effectiveness, and durability. The optimization of the catalytic activity of carbon-based catalysts lies in the appropriate design of the materials’ properties. To this end, it is essential to understand the influence of the textural and chemical properties on the performance of carbon-based catalysts. Accordingly, this work aims to prepare glucose-derived carbons with tailored textural properties via hydrothermal carbonization and subsequent physical activation, in order to study the effect of porosity and chemical composition on the performance of the catalysts in two different applications related to energy and biomass conversion.

**2. Methods**

Glucose-based carbon materials were prepared by hydrothermal carbonization (HTC). The solid/water ratio (w/v) was fixed at 1:5 and the HTC process was performed at 180 ºC for 12 h. The materials were then carbonized at 700 ºC under N2 for 2 h (CG) or physically activated at 900 ºC under CO2 atmosphere for 4 and 6 h (AG4h and AG6h). The prepared materials were then directly used for the ORR testes, which were performed in a three-electrode cell by cyclic and linear sweep voltammetry measurements. For the biomass conversion, ruthenium catalysts were prepared by incipient wetness impregnation of Ru (0.4 wt.%) on the prepared carbon supports and the one-pot hydrolytic hydrogenation of cellulose into sorbitol was performed in a reactor at 205 ºC for 5 h. All materials were characterized by nitrogen adsorption, microscopy (SEM and TEM), elemental analysis, TGA, TPD, XRD, XPS and ICP.

**3. Results and discussion**

All the prepared materials display a type I isotherm, which is characteristic of microporous solids. In addition, the microporosity increases due to the rise in the temperature and time of activation applied. The electrochemical results show two main differences: i) the onset potential shifts to more positive values by increasing the time of activation, which can be related to the more graphitic structure that is generated during activation; and ii) the value of the limiting current density increases with microporosity, which can be related to the more developed porous structure [1]. On the other hand, the prepared Ru catalysts were highly efficient for the one-pot reaction, yielding 100 % cellulose conversion after just 3 h. The conversion rate seemed to increase for the materials with the most developed porous structure. Moreover, the production of sorbitol increases with the surface area (Table 1), probably due to the faster access to the metal, favoring the hydrogenation of glucose into sorbitol [2].

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| **Table 1. Textural properties and catalytic results** | | | | | | |
|  | Supports | | |  | Ru catalysts | |
| Sample | *S*BET (m2 g-1) | *V*DR (cm3 g-1) | Eonset (V) |  | Yield of sorbitol (%, 3 h) | Conversion (%, 3 h) |
| CG | 573 | 0.22 | 0.683 |  | 33 | 100 |
| AG4h | 936 | 0.38 | 0.751 |  | 53 | 100 |
| AG6h | 1984 | 0.85 | 0.782 |  | 59 | 100 |

**4. Conclusions**

The appropriate combination of activation conditions during the polymerization of glucose led to the most efficient catalyst for both the oxygen reduction reaction (onset potential 100 mV higher) and the production of sorbitol (59 % of sorbitol was achieved after just 3 h of reaction).

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**References**

[1] R.G. Morais, N. Rey-Raap, J.L. Figueiredo, M.F.R. Pereira, Beilstein J. Nanotech. 10 (2019) 1089-1102.

[2] N. Rey-Raap, L.S. Ribeiro, J.J.M. Órfão, J.L. Figueiredo, M.F.R. Pereira, Appl. Catal. B 256 (2019).