

Catalytic conversion of cellulose using carbon nanostructures

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Objectives and Novelty

Developing effective strategies for the selective conversion of cellulose is one of the first subjects for an eventual realization of bio-based industries. In this framework, this Thesis applied modern trends in the catalyst design based on carbon nanostructures for cellulose transformation through various processing options: acid carbons for the hydrolysis reaction into glucose and metal supported catalysts for the synthesis of sorbitol via hydrolytic hydrogenation (*one-pot* conversion).

The study was divided into three main blocks. The first part of the work aims to provide a fundamental understanding on how the structure and surface composition of the catalyst impact on their hydrolyzing activity. To this end, *fishbone* carbon nanofibers (CNF) were used as the starting material to modify their structural and chemical features as per the reaction requirements. Optimization of reaction conditions was conducted under alternative heating sources: conventional and microwave (MW) radiation.

In a second approach, a series of Ni-based catalysts supported on carbon nanofibers were assessed for direct transformation of cellulose into sugar alcohols. In this system, the role of carbon is the metal dispersion onto a large surface area, whereas the acid species involved in the hydrolysis stage are *in situ* generated from water under hydrothermal conditions. A quantitative description on the influence of catalyst design details (metal composition, mass fraction and crystallite size), process severity (temperature and time) and structural features of cellulose on catalytic results (cellulose conversion and products distribution) was outlined. A significant advance in this field was the substitution of noble metals to earth abundant metals, bringing down the catalyst costs.

Lastly, an example of comprehensive use of biomass was depicted using almond hulls as raw material. Herein, a process for extracting nanocellulose from almond hulls was used as the reference to evaluate different waste management possibilities. For this purpose, a broad set of soluble products was recovered from the spent liquors and further upgraded via catalytic hydrogenation reactions.

Results

Controlling the surface chemistry of CNF becomes essential for defining their reactivity. Pristine CNF are inert and hydrophobic in nature. The surface modification with different oxygenated and acid moieties turns the graphitic material into a catalyst potentially active towards the hydrolysis of cellulose (*carbocatalysis*). Initially, various oxidative treatments were explored to unravel the nature of the active sites

and modulate their acid density and strength. These included the immersion in nitric acid (HNO₃) and the chemical treatment with KMnO₄ and HNO₃ in H₂SO₄ according to a modified Hummer's method. This last treatment allowed for the extensive functionalisation of CNF, giving rise to a material denoted as graphene oxide nanofibers (GONF). Structurally, GONF reserves the filamentous morphology of CNF but showing an expansion on the interlayer distance (0.81 vs 0.33 nm) to accommodate the large variety of O- and S- functionalities (-OH, -COOH, -SO₃H), accounting to 45.6 wt. % and 1.9 wt. % of the bulk composition. This results in the surface overlay of multiple chemical groups with various pK_a, whose relative abundance can be subsequently adjusted through a hydrothermal treatment (180 °C, 6h). Noteworthy, a further level of control on these functionalities in terms of chemical nature, distribution and density could be attained through the fine tune of the layered structure, planar size and edges-to-basal planes ratio. Thus, an obvious increase on the oxidation degree was noted for their exfoliated and dimensionless counterparts: 47.2% of O for sheets of few layers (FLGO) and 54.7 % from zero-dimensional domains based on graphene quantum dots (GOQD). Sulphur percentage was also much higher on these morphologies (2.1 and 6.1 % on FLGO and GOQD, respectively).

The interest of tailoring the graphene domain size at nanometric scale not only arises as a neoteric strategy for surface modification but also may help to suppress mass transfer limitations. From a holistic perspective, the catalytic activity of different GO-derivatives was compared. Zero-dimensional GOQD, featuring the smallest size and the highest content in surface functionalities showed the best catalytic activity. However, its behaviour was still dependent on the crystalline properties of the starting cellulose and the substrate-to-catalyst interaction degree. Thus, only 17.8 % of raw cellulose was depolymerized into sugars after 24 h at 135 °C, which rose to 60.1 % upon enhancing its reactivity by ball-milling (8h, 600 rpm). Moreover, a simple mix-milling of the cellulose with the catalyst for 10 min enabled an effective solid-solid contact, rendering complete conversion and 83.5 % of glucose. In comparison, 71.3% and 60.4 % of glucose was obtained from their sister counterparts: FLGO and GOQD, respectively (Figure 1) [1].

Seeking to harness the good dielectric properties of carbon materials, a follow-up study explored the benefits of MW radiation on the GO-catalyzed hydrolysis of amorphous cellulose. Experimental results revealed that similar glucose yields can be attained from both heating sources once the

operational conditions are optimized for each technology. Thus, whereas conventional heating requires soft conditions (135 °C) and high dilution ratios (inlet solution of 0.25 wt. % of cellulose), shorter time runs in MW-systems (20-120 min) become compatible with higher processing temperatures (150-165 °C) and cellulose loading (2.0 wt. %), which is a significant contribution towards the process intensification. The maximum productivity of glucose, in the range of 60.1- 63.7 %, was assessed over GOQD. The most highlighted influence of the GO morphology was noticed during the first reaction interval, with an activation energy that ranked in the following decreasing order: 171.6 KJ/mol (GONF) > 148.9 KJ/mol (FLGO) > 135.2 KJ/mol (GOQD). However, all GO morphologies underwent a gradual decay on their hydrolysis performance over time, which likely prevented from a better glucose production.

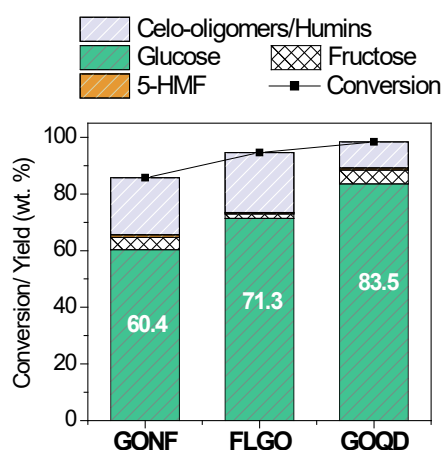


Figure 1. Catalytic activity of different graphene oxide mix-milled with cellulose for 10 min. Reaction conditions: 135 °C, 24h [1].

Direct synthesis of sorbitol from cellulose (*one-pot* conversion) is another promising route to limit the sugars reactivity under hydrothermal conditions. The rational control of product distribution, however, requires for a detailed understanding of the operational conditions, catalyst compositions and mass transport limitations (primarily determined by the cellulose crystallinity and H₂ gas pressure). All these aspects can be individually studied by starting from feedstocks with different polymerization degree and crystalline ordering. Correlations between Ni metal loading (3-14 wt. %) and particle size (2.1-20.4 nm) were established using the *one-pot* conversion of cellobiose as the hydrogenation test (190 °C, 3h, 4.0 MPa H₂). An optimum yield of sorbitol (81.2 wt. %) was found from catalyst prepared by dry impregnation (10.7 wt. % of Ni, mean diameter of 11.3 nm). The ease oxidation of Ni at smaller particle sizes impeded the use of low-loaded catalysts with high metal dispersion. This tendency could be somewhat reverted upon doping it with small quantities of noble metals (Ni:noble metal=3:0.5 wt. %). A remarkable synergetic effect was noted for the Ni-Pt/CNF and Ni-Pd/CNF combinations, since the yield to hydrogenations products (sum of cellobiose and sorbitol) exceeded the sum of activity of their pure constituents. In turn, the Ru/CNF catalyst enabled the

practically total hydrogenation of cellobiose, making unnecessary the Ni-Ru alloy formation [2].

To extent the conversion of cellulose, a further parametric optimization was mandatory. The interplay between reaction temperature (190-230 °C) and time (3-26 h) and cellulose crystallinity (0-80 %) was studied following a Box Wilson Face Centered (CCF) Design of Experiments at a fixed pressure of 4.0 MPa H₂. The highest productivity to polyols (49.7%; 37.6 % of hexitols) could be obtained after treating amorphous cellulose for 26 h at 190°C. This value improved up to 61.5 % (77.0 % of total sugar alcohols) upon including an additional mix-milling stage of 30 min and increasing the hydrogen pressure from 4.0 to 8.0 MPa (RT) to overcome plausible gas internal diffusion resistances.

Finally, this Thesis demonstrates the feasibility of a biorefinery concept based on the nanocellulose extraction from almond hulls using the aforementioned hydrogenation technologies for downstream processing. For instance, sugars from hemicellulose appear as an intermediate stream that can be catalytically hydrogenated to sugar alcohols (sorbitol and xylitol) with relatively high yield (47.4 %) after 3h at 165 °C and 5.0 MPa H₂ in contact with a Ru/CNF loaded at 0.5 wt. %. A best suited valorisation approach for the MW-hydrolysate stream was to combine solvent extraction with mild hydrothermal treatment. By this means, an organic oil product rich in bioactive molecules based on 3-hydroxypyridines was directly extracted from this effluent. The oligomeric portion of this phase was chemically stabilized through a catalytic hydrothermal treatment (230 °C, 60 min, 4.0 MPa H₂, Ru/CNF) to produce additional chemicals (diethyl succinic acid) and fuel intermediates. As compared with the early scheme based on a single production of nanocellulose, this multi-product layout introduces an enhancement on the resource recovery from 21.8 to 37.8 wt. %.

Conclusions

Carbon nanostructures offer a great potential in biomass conversion reactions. In this Thesis, several catalysts based on carbon nanofibers were prepared, characterized and tested for the conversion of cellulose into high-value added products (glucose and sorbitol). Further advances in understanding interrelationships between cellulose reactivity, catalyst properties and process conditions allowed for the rational control of products distribution and a better reaction efficiency.

Related Publications

[1] E. Frecha, D. Torres, I. Suelves, J.L. Pinilla, Custom-sized graphene oxide for the hydrolysis of cellulose, *Carbon* 175 (2021) 429-439.

[2] E. Frecha, D. Torres, A. Pueyo, I. Suelves, J.L. Pinilla, Scanning different Ni-noble metal (Pt, Pd, Ru) bimetallic nanoparticles supported on carbon nanofibers for one-pot cellobiose conversion, *Applied Catalysis A: General* 585 (2019) 117182.

Full thesis can be downloaded from Digital.CSIC at <http://hdl.handle.net/10261/266635>.