PhD Open Days

SUGAR DERIVED CARBON SPHERES AS ESTERIFICATION CATALYSTS

PHD CATSUS Programm

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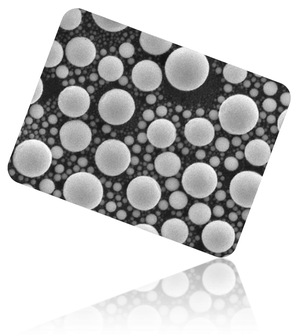
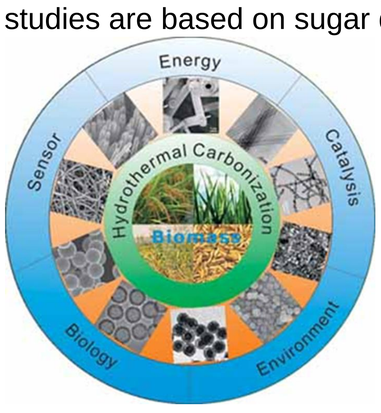
Introduction



Carbon spheres have been used in different research fields, namely as supercapacitors, adsorbents, catalyst supports, and also as catalysts. [1] The most common synthesis strategy involves hydrothermal treatments, and as carbon precursors, although various renewable biomasses have been explored, a great number of studies are based on sugar derived materials. [2].



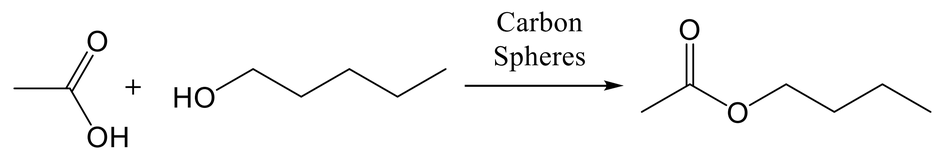
In the studies that are being developed, glucose, fructose and sucrose derived carbon spheres obtained by hydrothermal treatment at 190 ºC were tested as catalysts for the esterification of acetic acid with 1-butanol. The materials have acidic surface properties, demonstrated by the presence of carboxylic acids and alcohols, estimated by the Bohem titration.

The introduction of sulfonic groups has a positive effect on the reaction yield which in the more favorable case reaches 95 % after 6 h of reaction. The results obtained so far point out the potentialities of these materials as alternatives to the commonly used strong inorganic acids.

Carbon Spheres Synthetic Procedure:
Different ratios between the quantities of acrylic acid: 0 and 10 wt % regarding sucrose (S) and glucose (G) concentration was prepared. The solutions were then sealed into the Teflon inlet in an autoclave and hydrothermally treated at 190 ºC for 5 or 16 hours for the case of sucrose solutions, and 16 hours for glucose mixture. The materials were washed several times with water and acetone and dried overnight at 100 ºC .
Samples nomenclature: sugar acrylic acid(%)_hydrothermal time(h).

S-Dopped Carbon Spheres Synthesis:
The synthetized carbon spheres were then treated with concentrated sulfuric acid (20 ml H_2SO_4/g solid) at 100 ºC for 4h. The sulfonated sample was then washed thoroughly with hot distilled water and dried overnight at 100 ºC.
Samples nomenclature: sugar acrylic acid(%) S_acid treatment time(h).

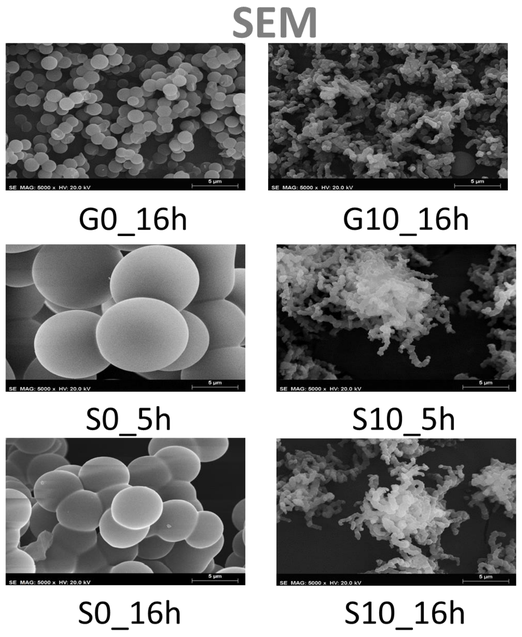
Catalytic Procedure:
The mixture of acetic acid (5 mmol), butanol (1.5 mL) and catalyst (30 mg) was stirred at 80 ºC. The reaction was monitored by GC analysis of the small aliquots withdrawn. Octane was used as internal standard.



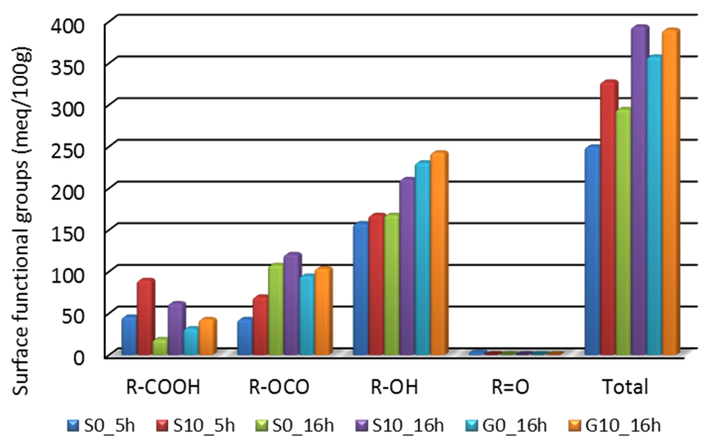
Characterization of Carbon Spheres:

Carbon	Yield (%)	pH_{pzc}
S0_5h	35	2.4
S10_5h	33	2.1
S0_16h	40	2.0
S10_16h	32	1.9
G0_16h	36	3.0
G10_16h	31	2.3

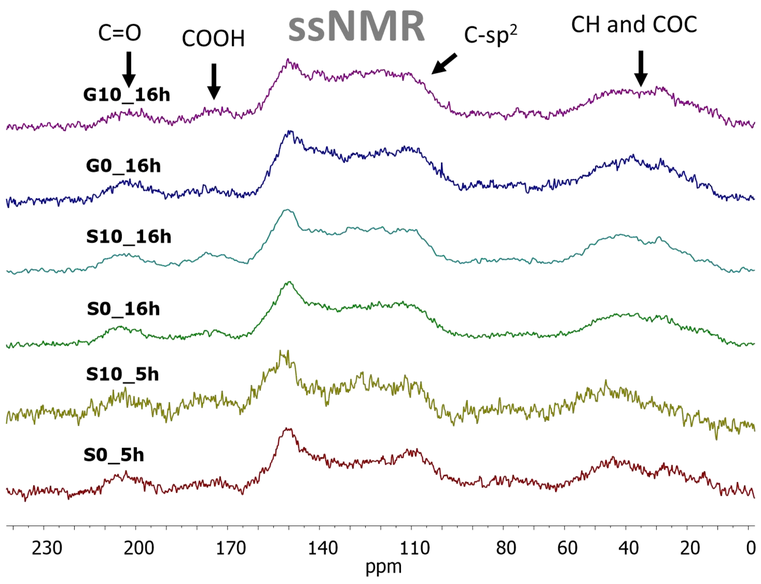
SEM



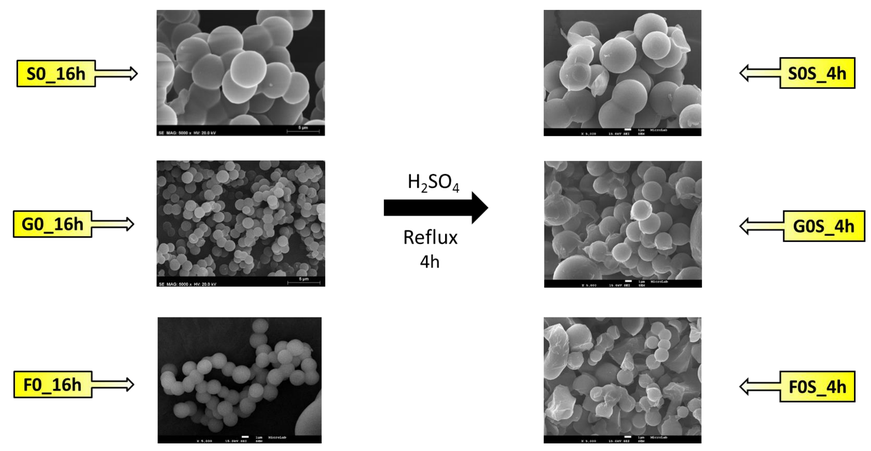
Boehm Titration



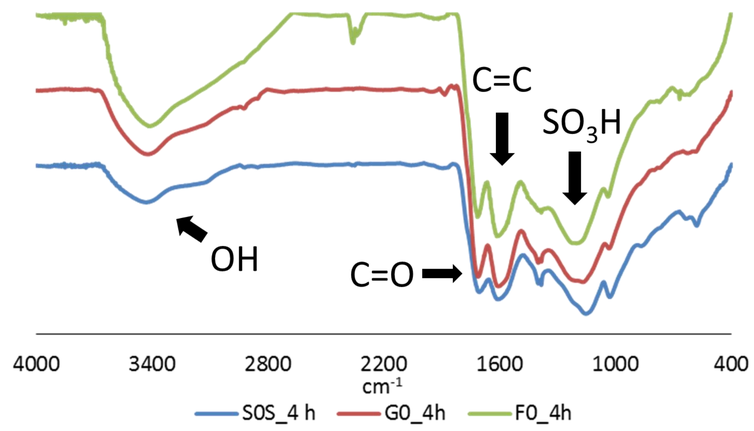
ssNMR



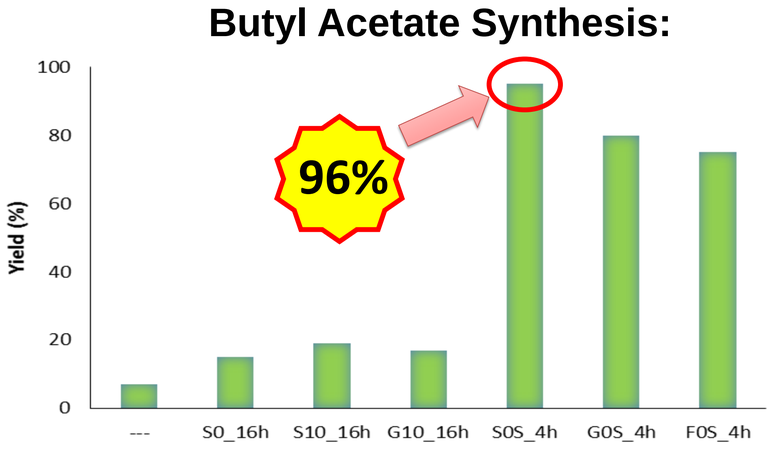
Characterization of S-Dopped Carbon Spheres:



Carbon	Acidicity (mmolH⁺/g)
S0S_4h	1.86
G0S_4h	1.25
F0S_4h	0.98



Butyl Acetate Synthesis:



Conclusions:

Carbon Spheres Synthesis:
The increase of the acrylic acid amount lead to:
- ✓ Significant decrease of the spheres size;
- ✓ Small increase of surface acid groups.

Catalytic tests:
- ✓ Slight increase of esterification reaction yield as a consequence of the increase in acrylic acid amount.
- ✓ High yields are obtained with sulfuric acid treated hydrochars.

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References: [1] M. Wu, Y. Wang, D. Wang, M. Tan, P. Li, W. Wu, N. Tsubaki, J. Porous Mater., 2016, 23, 263. [2] R. Demir-Cakan, N. Baccile, M. Antonietti, M.M. Titirici, Chem. Mater.,2009, 21, 484.

TÉCNICO LISBOA

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