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SYNTHESIS OF MESOPOROUS CARBONS FROM HYDROLYSABLE TANNINS

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Introduction

Condensed tannins from Mimosa, Quebracho or Pine trees are able to undergo the same kinds of chemical reactions as phenol or resorcinol for preparing commercial resins and, for this reason, are highly valuable raw products. Tara (*Caesalpinia spinosa*) is a spiny tree or shrub native to Peru and cultivated as a source of tannins in America and in North Africa. Tara tannins (TT) are hydrolysable tannins, rich in pyrogallic acid, and require aldehydes as crosslinkers to form resin. They are generally used to treat leather, but other higher added-value applications are possible, as shown here.
In this study, we used TT as precursor of mesoporous materials by mixing with Pluronic F127 and various aldehydes, which increased the carbon yield but reduced the textural characteristics of the resultant carbons. However, blending Tara tannin together with Mimosa tannin, Pluronic F127 and water allowed obtained highly microporous-mesoporous materials without using any aldehyde.

Materials and Methods

Commercial Mimosa and Tara tannins, MT and TT, respectively, both provided by SilvaTeam (Italy) were used as carbon precursors. We followed three approaches for the synthesis of mesoporous carbons:

- In the first set of experiments, we mixed TT, Pluronic F127 (P) and 37.1 wt. % formaldehyde (F) solution were mechanically mixed in a PM100 (RESTCH) planetary ball miller for 1h with different P/TT and F/TT weight ratios.
- In the second set of experiments, we used different aldehydes instead of using F in order to have a greener synthesis approach: 97 wt. % furfural (Fur), 40 wt. % glyoxal (G) or 50 wt. % glutaraldehyde (GA) solutions. Mechanical mixing was applied as described above.
- In the third set of experiments, we mixed TT with MT, in different weight ratios, and with P and water (W). The total amount of tannin (T) was kept to 2 g, whereas P and W were set to 0.75 and 1.75 g, respectively. Mechanical mixing was applied as described above.

Nitrogen adsorption isotherms at -196°C, and carbon dioxide isotherms at 0°C, were obtained using Micromeritics ASAP 2020 and ASAP 2420 adsorption devices, respectively. The specific surface areas were determined from N_2 isotherms by applying the BET equation to obtain A_{BET} on the one hand, and from both N_2 and CO_2 isotherms by applying the 2D-NLDFT HS model to obtain S_{NLDFT} and the pore size distributions (PSDs) on the other hand. The total pore volume, $V_{T,\ NLDFT}$, was obtained from both isotherms by applying the NLDFT method, and the micropore volume was also calculated by applying the Dubinin-Radushkevich model to the nitrogen and carbon dioxide isotherms, independently, to obtain $V_{\mu\text{-}DR,N2}$ and $V_{\mu\text{-}DR,CO2}$, respectively. The mesopore volume, V_{mes}, was calculated as the difference between $V_{T,\ NLDFT}$ and $V_{\mu\text{-}NLDFT}$. PSDs, in the mesopore range, were also determined by application of the BJH method to the desorption branch of the N_2 isotherms.

Results and Discussion

Table 1 shows the textural parameters of the carbon materials produced by mixing TT, P and F. TT directly submitted to pyrolysis was purely microporous while those materials including P and F were micro-mesoporous. F addition improved the mesostructuration but reduced A_{BET}. F addition also increased the carbon yield from 20 (0 g) to 45% (2g). P addition increased the mesoporous and total pore volumes while microporous volumes remaining unchanged. The mesoporous carbons hadd A_{BET} values ranging from 212 to 536 m^2/g and some of them presented unimodal PSDs centered on 4.0-4.6 nm.

Table 1. Textural characteristics of mesoporous carbons produced by mixing TT (2 g), P and F.

P/TT (wt.)	F/TT (wt.)	A_{BET} (m^2/g)	S_{NLDFT} (m^2/g)	$V_{\mu\text{-DR, N2}}$ (cm^3/g)	$V_{\mu\text{-DR,CO2}}$ (cm^3/g)	$V_{\mu\text{-NLDFT}}$ (cm^3/g)	$V_{T,\text{ NLDFT}}$ (cm^3/g)	V_{mes} (cm^3/g)
0.00	0.00	111	334	0.05	0.22	0.07	0.07	0.02 (0.0%)
0.25	0.00	461	738	0.18	0.25	0.17	0.30	0.13 (44.5%)
0.25	0.25	402	630	0.15	0.18	0.14	0.26	0.12 (46.0%)
0.25	0.50	273	476	0.10	0.16	0.09	0.18	0.09 (48.2%)
0.25	1.00	212	364	0.08	0.11	0.07	0.14	0.07 (49.6%)
0.50	0.00	523	799	0.20	0.22	0.17	0.42	0.25 (59.3%)
0.50	0.25	405	597	0.15	0.15	0.11	0.34	0.22 (65.9%)
0.50	0.50	362	543	0.14	0.15	0.10	0.31	0.21 (68.8%)
0.50	1.00	330	512	0.12	0.15	0.09	0.28	0.19 (67.9%)
1.00	0.00	455	699	0.17	0.20	0.13	0.57	0.45 (77.7%)
1.00	0.25	424	612	0.16	0.16	0.10	0.57	0.47 (81.7%)
1.00	0.50	363	518	0.14	0.13	0.08	0.56	0.48 (85.4%)
1.00	1.00	305	441	0.11	0.12	0.06	0.51	0.45 (87.5%)

Figure 1 shows the nitrogen adsorption-desorption isotherms (a) and the PSDs in the mesopore range (b) of the carbon materials synthesized with the four aldehydes tested: F, Fur, G and Ga. These figures also include an ordered mesoporous carbon produced from MT (MS_MT 0.75:2:1.75W) for the sake of comparison [1]. All the materials had a micro-mesoporous texture as that obtained from MT, but the PSDs obtained by TT-derived carbon were broader, especially with G and Fur, and disordered. When using TT with GA, Fur or G, higher A_{BET} than that determined when using F were obtained, but the carbon yields were also lower that those obtained with F. A good compromise was obtained with Fur, which led to A_{BET} of 836 m^2/g and to a carbon yield of 20.6 %, compared to 362 m^2/g and 40.1 %, respectively, when using F.

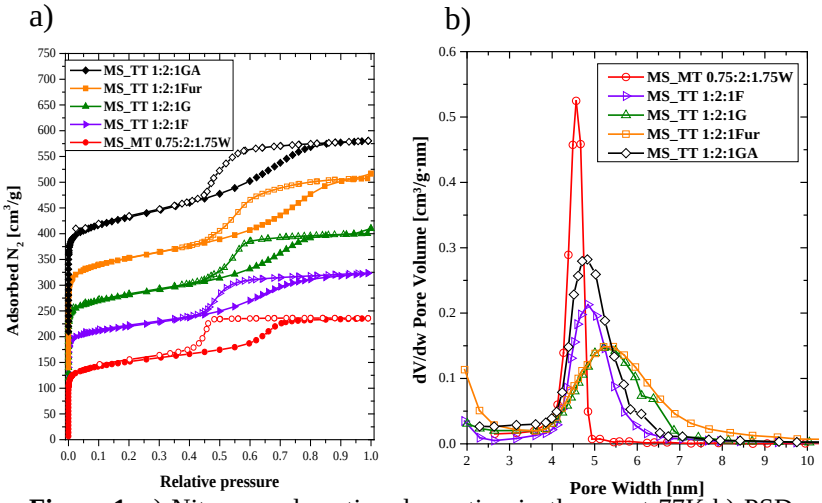

Figure 1. a) Nitrogen adsorption-desorption isotherms at 77K b) PSDs, in the mesoporous range of the carbons prepared by addition of F, Fur, G and Ga. MS_MT 0.5:2:1.75W is given for the sake of comparison.

Figure 2 shows the carbon yield based on the total amount of tannins (TT + MT) when varying the amount of TT in the initial formulation. When TT was set to 0 g, the formulation corresponded to that leading to perfectly ordered mesoporous carbons [1]. Carbon yield, based on total tannin, linearly decreased, from 50.3 to 22.2% with the addition of TT, indicating that there is no interaction between TT and MT. Adding TT also induced disorder but the mesopore volume progressively increased to a maximum obtained for equal amounts of TT and MT, 1 g of each. This approach is the greenest of the three presented here because it allowed mesostructuration of the final carbon material without using any aldehyde.

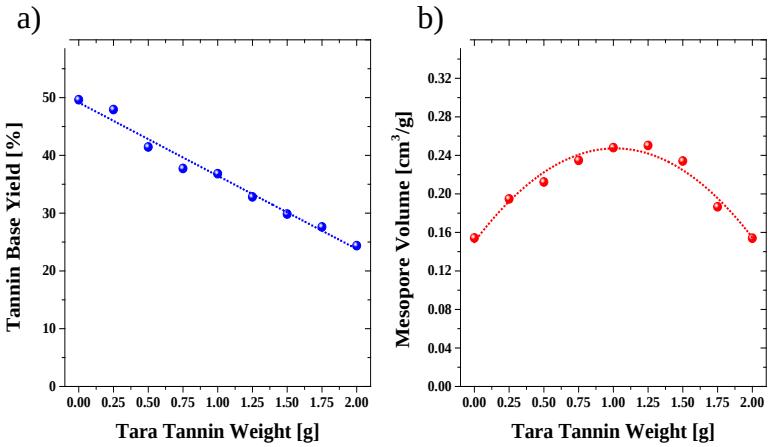

Figure 2. Effect of the addition of TT in the a) carbon yield (in tannin base) and b) mesopore volume (total amount of T being 2g).

Conclusion

Tara tannin (TT) is a new and cheap precursor for preparing mesoporous carbons. When reacting with Pluronic F127 and formaldehyde, carbon yields higher than 45% were obtained although A_{BET} were always lower than 425 m^2/g. The use of greener but less effective crosslinkers such as furfural, glyoxal or glutaraldehyde solutions allowed obtaining materials with much more developed porosity, with A_{BET} as high as 836 m^2/g, but with lower carbon yields. When combining mimosa (MT) tannin with TT, no crosslinker was needed, and an optimum of mesoporosity was found by mixing identical amounts of MT and TT.

Acknowledgments

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References

[1] J. Castro-Gutiérrez, A. Sanchez-Sanchez, J. Ghanbaja, N. Díez, M. Sevilla, A. Celzard, V. Fierro, Synthesis of perfectly ordered mesoporous carbons by water-assisted mechanochemical self-assembly of tannin, Green Chem. (2018). doi:10.1039/C8GC02295J.