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(Article begins on next page)



## UNIVERSITÀ DEGLI STUDI DI TORINO

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## Preparation and adsorption properties of activated porous carbons obtained using volatile zinc templating phases.

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**Abstract:** High-surface-area activated micro/mesoporous carbons ( $S_{\text{BET}} \cong 700\text{-}1900\text{m}^2/\text{g}$ ) were obtained by a simple synthesis method, consisting in the  $\text{ZnCl}_2$ -catalyzed polymerization of furfuryl alcohol followed by the polymer pyrolysis. The  $\text{ZnCl}_2$  salt, whose quantity exceeds that necessary for the polymerisation reaction, acts both as template and as activating agent during the thermal treatment. Depending on the precursor quantities, carbons with prevailing micro- or meso-porous nature were obtained. The peculiar porosities make these materials suitable for testing the adsorption of molecules of different size (methylene blue and Cy-5 cyanine), which can constitute an easy method to qualitatively identify the micro/mesoporous nature of carbon materials.

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High surface area activated carbons find specific use in many application fields, ranging from the removal of water pollutants to the energy storage, due to the large capacity of carbons in adsorbing chemicals from fluids [1-3]. Moreover, carbon molecular sieves with peculiar porosities are crucial in recent specific needs, such as in the segregation of  $\text{CO}_2$  [4] and in the  $\text{H}_2$  storage [5]. Porous carbons with tunable structures, textures and ordered porosity have been successfully obtained by the template carbonization methods, via the infiltration of carbonaceous liquid/gas sources in porous inorganic frameworks (e.g. zeolites, porous silica, anodic aluminium oxide), which is called *hard*-template synthesis. Another method, called *soft*-template synthesis, is based on the self assembly of organic molecules (e.g. CTAB, polymer beds, block copolymers) that can retain the porosity upon the thermal treatment. Among the advantages of both techniques, there is the potential replica of the sacrificial scaffold and the generation of peculiar porosities. However, the use of this synthesis techniques for large scale production suffers of some limitations for the employment of a strong chemistry (i.e. HF or concentrated NaOH), for the complexity of the processes or for the limited number of the organic materials that can retain the nanostructure during the decomposition [6].

Another route to obtain porous carbon materials with anisotropic high-porosity, is based on the pyrolysis/activation of carbon-based material (petroleum residues, carbon fibres, biomasses, carbohydrates, or polymers) [7-11] in presence of chemical activators (e.g. KOH, NaOH,  $\text{H}_3\text{PO}_4$  or  $\text{ZnCl}_2$ ), which can be used as templating phases as well, thus preventing the contraction of the material during the carbonization [12, 13].

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Among the chemical activators, it is widely recognized that  $\text{ZnCl}_2$ , a Lewis acid, acts as dehydration agent up to  $\approx 500\text{ }^\circ\text{C}$  [1, 12, 13], later than primary carbonization takes place. At higher temperatures  $\text{ZnCl}_2$  does not give rise to any further reaction because both molten anhydrous  $\text{ZnCl}_2$  and the derived metal zinc obtained by reduction leaves the carbon phase upon thermal treatment [1, 14]. Furfuryl alcohol (FA) is a polymer precursor suitable for infiltrating porous frameworks working as sacrificial scaffolds for preparing furfuryl alcohol polymers (PFA) [15, 16] and composites [17, 18] by means of acid-catalyzed polymerisation reactions.

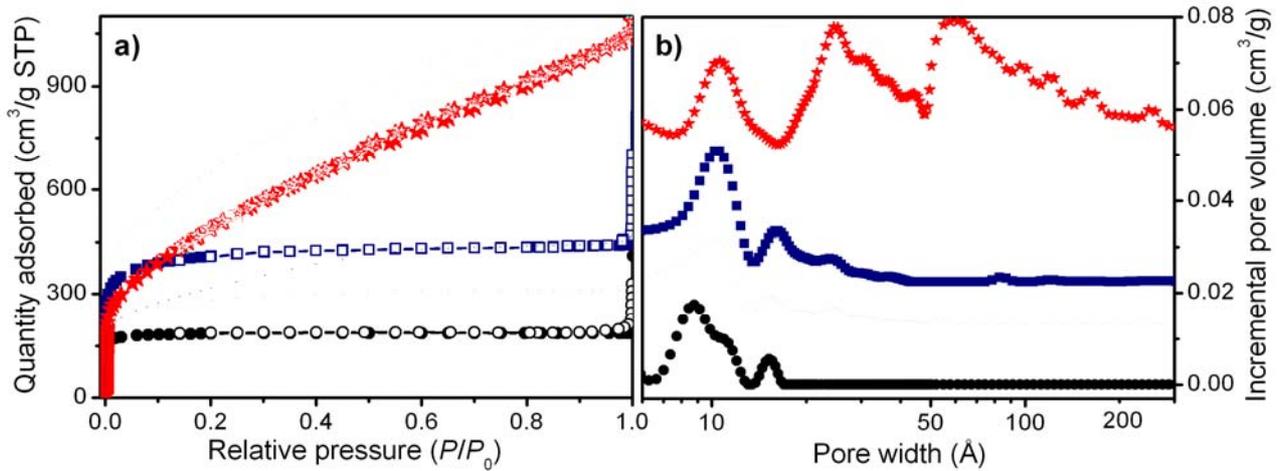
In a previous work, microporous carbon monoliths were obtained by means of thermal treatments of polymer composites obtained from the Lewis acid-catalysed reaction of furfuryl alcohol by using low quantities of  $\text{ZnCl}_2$  (1-17%wt) [14]. Due to the low solubility of the salt in FA under the adopted experimental conditions, a slow polymerization was obtained at RT ( $\geq 12\text{h}$ ) with the consequent medium-low surface area of the final samples ( $S_{\text{BET}} = 70\text{-}400\text{ m}^2/\text{g}$ ).

In this work, porous carbon materials having surface area as high as  $\approx 700\text{-}1900\text{ m}^2/\text{g}$  and peculiar micro or mesoporosity have been obtained. This was possible by a quick polymerization (30-120") of the FA occurring in presence of high amounts of  $\text{ZnCl}_2$  (33-90%wt). Besides the catalytic effects, the excess of  $\text{ZnCl}_2$  works as a sacrificial scaffold for the polymer assembly (primary templating process) and upon the thermal treatment, thus preserving the contraction of porosity (secondary templating process). The final aim of the work, is to verify an easy method for determining the adsorptive properties of materials with peculiar porosity (micro e mesoporosities) towards molecules of different size.

Owing to the synthesis, the process was constituted by two steps. First, furfuryl alcohol (FA) polymer composites have been obtained via a Lewis acid-catalyzed polymerization process, by mixing FA (liquid) with selected quantities of dried and grounded  $\text{ZnCl}_2$  powders (33%wt, 50%wt, 67%wt, 80%wt and 90%wt), labelled as C- $\text{ZnCl}_2$ 33%, C- $\text{ZnCl}_2$ 50%, C- $\text{ZnCl}_2$ 67%, C- $\text{ZnCl}_2$ 80% and C- $\text{ZnCl}_2$ 90%, respectively. Then,  $\text{ZnCl}_2$ /polymer composites were inserted into a horizontal quartz tube furnace and treated (heating rate of  $5^\circ\text{C}/\text{min}$ ) at  $800\text{ }^\circ\text{C}$  for 5 h under  $\text{N}_2$  flow in order to obtain carbon materials.

All the obtained materials are constituted by fully amorphous carbon phase (see XRD data, Supplementary Material) [19-21]. The absence of ZnO phase signals evidences that, upon  $800^\circ\text{C}$  thermal treatments, the carbon material is the sole product from  $\text{ZnCl}_2 \leq 80\%$ wt, although ZnO phase has been detected for  $\text{ZnCl}_2$  90%wt. Due to the minor properties (surface area and porosity), the sample obtained from the highest  $\text{ZnCl}_2$  composition has been excluded here for further discussion.

$\text{N}_2$ -adsorption/desorption isotherms and pore size distributions (PSDs) of carbon samples are shown in Figure 1a,b. Surface area/pore volume properties are summarized in Table 1, in comparison with those of materials prepared from low quantities of  $\text{ZnCl}_2$ , as described in [14].



**Figure 1.** a) Volumetric N<sub>2</sub> adsorption/desorption isotherms obtained at 77 K and b) pore size distributions of: C-ZnCl<sub>2</sub> 33% (circles), C-ZnCl<sub>2</sub> 67% (squares) and C-ZnCl<sub>2</sub> 80% (stars), respectively. Filled and empty scatters of a) refer to adsorption and desorption branches, respectively.

**Table 1.** Area (m<sup>2</sup>/g) and pore volume (cm<sup>3</sup>/g) values of carbon materials as function of the ZnCl<sub>2</sub> concentration used in the synthesis.

ZnCl <sub>2</sub> (%wt)	S <sub>BET</sub> <sup>a</sup> (m <sup>2</sup> /g)	S <sub>Langmuir</sub> <sup>a</sup> (m <sup>2</sup> /g)	V <sub>Tot</sub> <sup>b</sup> (cm <sup>3</sup> /g)	V <sub>Micro</sub> <sup>c</sup> (cm <sup>3</sup> /g)	V <sub>Meso</sub> <sup>d</sup> (cm <sup>3</sup> /g)	V <sub>Meso</sub> <sup>d</sup> (%)	S <sub>DR</sub> <sup>c</sup> (m <sup>2</sup> /g)	Ref.
1	65	81	0.030	0.030	–	–	83	[14]
9	175	317	0.113	0.113	–	–	319	[14]
17	379	522	0.179	0.179	–	–	530	[14]
33	704	817	0.288	0.288	–	–	816	
50	1050	1286	0.479	0.459	0.013	4	1290	
67	1544	1855	0.679	0.662	0.051	3	1863	
80	1875	2514	1.553	0.855	1.330	45	2514	

<sup>a</sup> Total area evaluated in the 0.05 < P/P<sub>0</sub> < 0.1 pressure range for ZnCl<sub>2</sub> ≤ 67%wt and in the 0.1 < P/P<sub>0</sub> < 0.2 pressure range for ZnCl<sub>2</sub>=80%wt, respectively;

<sup>b</sup> Total pore volume (V<sub>Tot</sub>) calculated as volume of the liquid at P/P<sub>0</sub> ≈ 0.95;

<sup>c</sup> V<sub>Micro</sub> and S<sub>micro</sub> calculated by the Dubinin-Radushkevich method (P/P<sub>0</sub> ≤ 0.2).

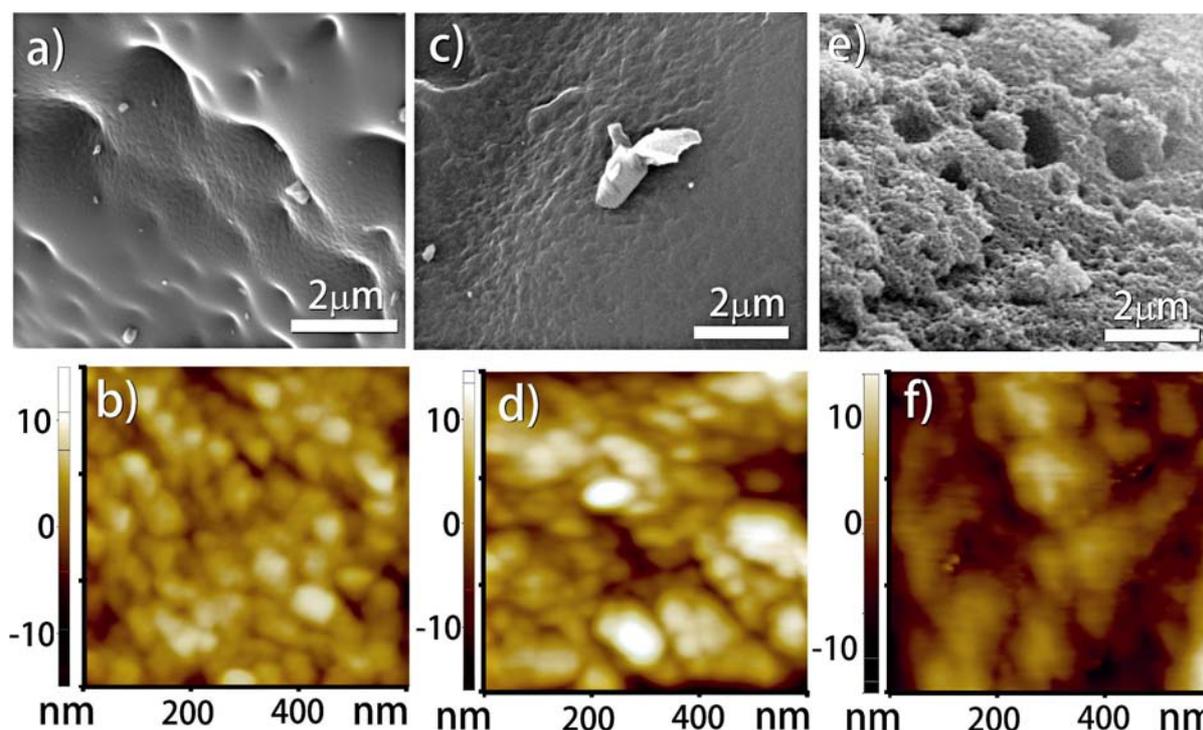
<sup>d</sup> V<sub>Meso</sub> = V<sub>Tot</sub> - V<sub>Micro</sub>;

From N<sub>2</sub> isotherms (Figure 1a), it is evident that the ZnCl<sub>2</sub> percentage in the 33-67%wt range does not affect the isotherm shape: in all cases a isotherm of type I was obtained with a well defined

plateau, which is encountered for microporous materials having relatively small external surface. Conversely, isotherms of the sample obtained from  $\text{ZnCl}_2$  in proportion as high as 80%wt, does not show a distinct plateau even at high relative pressure, thus indicating the presence of an extended mesoporosity as well. Hence, the content of the  $\text{ZnCl}_2$  precursor has a drastic effect on the apparent surface area ( $S_{\text{BET}}$ ) in the 1-80%wt range by a second order polynomial dependence, essentially ascribed to the increment in porosity (see Figure S2, Supplementary Material) and in the pore size. A similar dependence of  $\text{ZnCl}_2$  contents on the changes in porosity and on the widening of the micropores has been already observed for other activated carbons [12, 13].

By applying a Density Functional Theory (DFT) model with a non-negative least squares fitting on the adsorption isotherm data, pore size distributions (PSDs) of the samples have been obtained (Figure 1b). In this figure, it can be seen that the C- $\text{ZnCl}_2$ 33-67% samples basically show one family of pores in the 6-12 Å interval. A minor fraction is represented by pores of about 15-20 Å. In addition, the C- $\text{ZnCl}_2$ 67% exhibits a not null mesoporous component, although still minority (3% in volume). The DFT analysis of the C- $\text{ZnCl}_2$ 80% isotherm indicates a broad pore-size heterogeneity. More in details, the increase of the mesoporosity (45%), characterized by a bimodal distribution for pores larger than 20Å interval, is evidenced (see Figure 1b).

In order to get some information on the exposed porosity and on the surface morphology, the samples have been investigated by SEM and AFM microscopies (Figure 2).

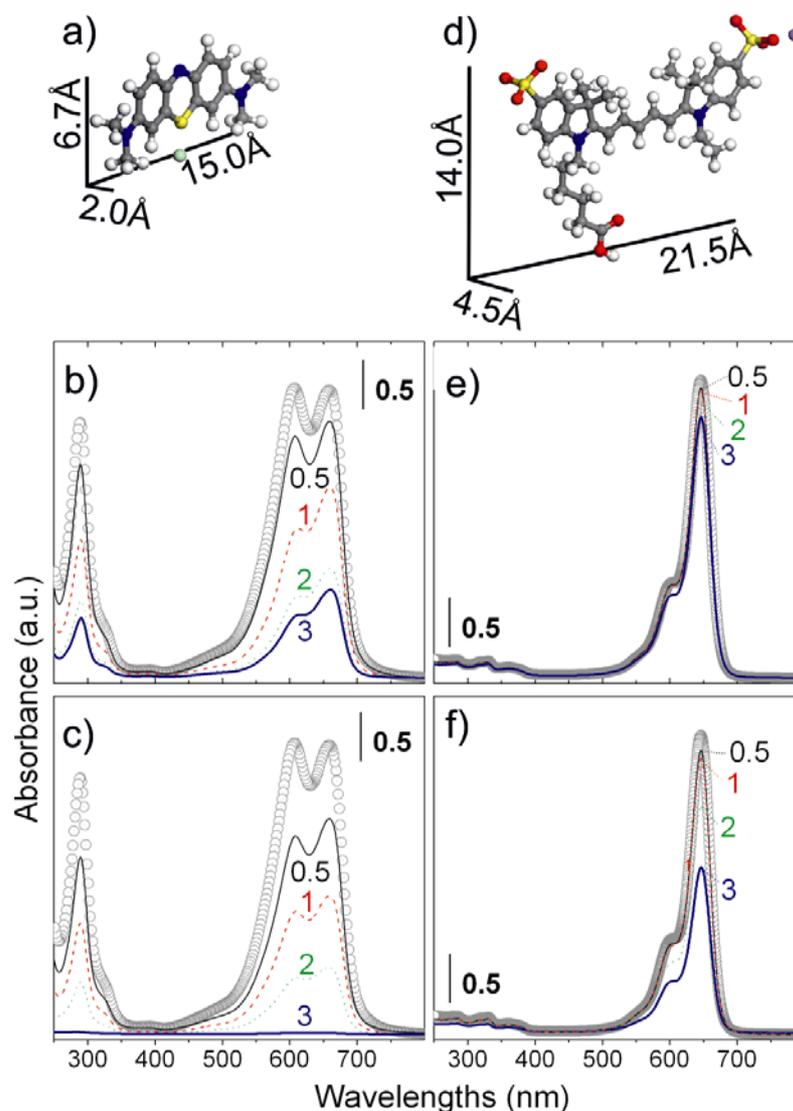


**Figure 2.** SEM and nc-AFM images of carbon materials obtained from: a,b)  $\text{ZnCl}_2$  33%wt; c,d)  $\text{ZnCl}_2$  67%wt; e,f)  $\text{ZnCl}_2$  80%wt, respectively.

The SEM image of C- $\text{ZnCl}_2$ 33% shows folds in the 0.5-2 μm range size and a quite rough surface (Figure 2a). At higher resolution, the AFM image depicts rounded nanodomains of 5-20nm in size, as obtained from the AFM height profile (50-60 nm as lateral size, due to the AFM tip-size effect), whose boundaries are responsible for the microporosity (Figure 2b). A similar surface texture is clearly in evidence for the other microporous sample (C- $\text{ZnCl}_2$ 67%) shown in Figure 2c,d. On the

other hand, the mesoporous sample (C-ZnCl<sub>2</sub>80%) has a totally different morphology (Figure 2e,f) because evidences exposed open cavities in the 40-100 nm range and  $\leq 2 \mu\text{m}$  sizes (detected by AFM and SEM), which are responsible for the major mesoporosity ( $\geq 20 \text{ nm}$ ) of the sample. As the two morphological textures are fully consistent with properties evidenced by the porosity analysis, C-ZnCl<sub>2</sub>67% and C-ZnCl<sub>2</sub>80% carbon materials look ideal samples for testing the adsorption of molecules with different size and an easy comparative investigation of their adsorption properties to determine the major porosity of samples has been developed.

To this end, methylene blue (MB) and (N-(5-carboxypentynyl) - N' - ethyl - 3,3,3',3' tetramethyl - 5,5' disulfonate - indodicarbocyanine potassium salt (Cy-5), have been selected. The MB is widely used as pigment, while the Cy-5 is suitable for labelling proteins and nucleic acids. They can penetrate and diffuse into pores of different sizes, hence enhancing the differences in porosity. The limit dimensions of MB and Cy-5 along the three independent perpendicular directions (obtained as nucleus-nucleus distances) are reported in Figure 3a) and d), respectively. These distances have been measured by considering the molecular structures of MB and Cy-5 as obtained by quantum mechanical calculations performed at the CAM-B3LYP/6-31G level (for further details, please refer to the Supplementary Material). From the comparison of the dimensions of MB and Cy-5, it is evident as Cy-5 is almost double in size with respect to MB. The adsorption of MB by activated carbons, whose detailed description is beyond the scope of this paper, is well known [2, 22-24]. Both the dye solutions can be investigated by the UV-Vis spectroscopy.



**Figure 3.** Structures of: a) methylene blue (MB) and d) N-(5-carboxypentynyl) - N'-ethyl - 3,3,3',3' tetramethyl - 5,5' disulfonate - indodicarbocyanine potassium salt (Cy-5) used in the adsorption experiments reported in b-c) and e-f), respectively. The size of the molecules in the three independent perpendicular directions are reported as nucleus-nucleus distances. UV-Vis spectra of centrifuged water solutions of MB (left panels) and of Cy-5 (right panels) after being contacted for 24h with: C-ZnCl<sub>2</sub>67% b,e), C-ZnCl<sub>2</sub>80% c,f), respectively. The different lines refer to the content of the porous carbon materials: 0.5mg (solid thin lines), 1mg (dashed lines), 2mg (dotted lines) and 3mg (solid thick lines). The spectra of pure 25 mg/l MB and 18 mg/l Cy-5 water solutions are also shown for comparison (grey dotted line).

The UV-Vis spectra of the MB solutions (25 ml) after being contacted for 24h with crescent portions (0.5, 1, 2, or 3g, respectively) of the two selected carbon materials (C-ZnCl<sub>2</sub>67% and C-ZnCl<sub>2</sub>80%), are shown in Figure 3b,c. In this figure, the decrease of the two main absorption bands of MB, assigned to monomeric and aggregated species [25, 26], with the quantity of carbon (increasing from 0.5 to 3 mg) is shown. The detailed assignment of these bands is outside the scope of this work and can be found in ref. [25]. By comparing the intensity decrease of monomer band at

≈660 nm, it can be inferred that the two carbon materials do not show any specific selectivity in absorbing MB. This is due the fact that MB molecule is sufficiently small to enter in almost all the pores of the carbon materials. The situation is clearly different when the adsorption of Cy-5 is investigated. The UV-Vis spectra of the Cy-5 solutions after having contacted crescent portions of the two selected carbon materials (0.5, 1, 2, and 3g, respectively) for 24h, are shown in Figure 3e,f. The two absorption bands with maxima at ≈ 603 and 646 nm are assigned to  $\pi \rightarrow \pi^*$  transitions with a partial character of charge transfer [27].

By comparing the Cy-5 band evolutions of the two different carbon materials a distinct size selectivity upon porosity is observed, despite the low quantities of the dyes used as adsorbate. More in detail, the Cy-5 molecules cannot easily enter into the pores of C-ZnCl<sub>2</sub>67%wt, which are too small to allow the penetration and diffusion. This result confirms that this method can provide a comparative method to easily determine the adsorptive properties of micro- mesoporous carbons.

In conclusion, high micro/mesoporous activated carbons ( $700 < S_{\text{BET}} < 1900 \text{ m}^2/\text{g}$ ) can be obtained through a very simple process from furfuryl alcohol and ZnCl<sub>2</sub> precursors by a two steps method, where the acid catalyzed polymerisation of FA (Step 1) is followed by the high temperature (800°C) carbonization/activation of the intermediate carbonaceous composite (Step 2). It was demonstrated that the pore structure of the synthesized material can be easily controlled and tailored by changing ZnCl<sub>2</sub> percentage. Adsorption experiments of two dyes of different shape (methylene blue and N-(5-carboxypentynyl) - N' - ethyl - 3,3,3',3' tetramethyl - 5,5' disulfonate - indodicarbocyanine potassium salt water solutions) provide a method for an easy evaluation of the porosity properties and demonstrate that the adopted synthesis method allows a fine control of the pores size.

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