



*Dedicated to the memory of
Professor Eugen Segal (1933-2013)*

SURFACE CHEMISTRY – THE KEY-PROPERTY OF TEMPLATED MESOPOROUS CARBONS FOR SORPTION

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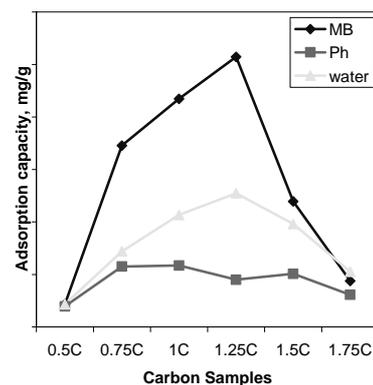
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Mesoporous carbons are applied in many fields as adsorbents, nanoreactors, catalyst supports and electrode materials. As the hydrophobic nature of highly mesoporous carbons is disadvantageous with respect to the access of water molecules, their surface chemistry became a key-property in many below mentioned applications. The surface chemistry of glycerol-derived mesoporous carbons, with a hexagonal packing, have been investigated in the present paper. This study reports the EPMA, FT-IR Spectroscopy, Boehm titration results, and some sorption measurements on the carbons resulted from templating siliceous nanoreactors. The obtained results showed that their surface is rich in surface functional groups that are responsible for sorption process of various substrates. A great ability for methylene blue removal (677 mg/g for 1.25C sample) and a moderate adsorption capacity for phenol (58 mg/g for 1C sample) have been obtained, without any chemical functionalization. Various carbon precursor/silica ratios in the carbon synthesis were used and investigated from this point of view.



INTRODUCTION

Recently, the preparation of a new series of ordered mesoporous carbons has been reported via the nanocasting technique using mesoporous silica as templates.¹ Compared with the typical porous carbons such as activated carbon, these types of carbon are complex and heterogeneous materials with unique adsorptive characteristics mainly influenced by the porous structure, surface area and chemical composition of the surface. Mesoporous carbons with high surface area, tunable pore size and modifiable surface functional

groups are of great interest in various applications such as adsorption, catalysis, biomolecular separation and electrode materials.² Moreover, their pore structure can be controlled by the nature of the carbon source, silica template and the silica/carbon precursor ratio. Depending on their chemical surface, porous carbons can be successfully applied as adsorbents for aqueous solutions of dyes and other contaminants in wastewater treatment processes. The sorption abilities in liquid phase are one of the most significant features required for these type of materials when applied in the manufacturing of

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medical dressings.³ Moreover, water vapour adsorption on carbons is important for adsorption processes, like the removal of contaminants from humid gas streams.⁴ Adsorption is probably the most widely employed method for separations, waste effluents treatment, refrigeration, heterogeneous catalysis as well as environmental control and life support systems in spacecrafts, etc.⁵

Because of the introduction of rigorous environmental regulations and the development of new applications, the demand for porous carbons increased progressively. Many researches on mesoporous carbon focus on its wettability and adsorption properties, which depend on the chemical composition and geometrical structure of the solid surface.⁶ The hydrophilic or hydrophobic quality of the surface is determined by its chemical make-up, enhanced by the roughness of the surface⁷ and the size of the pores. The process of water retention on carbons is known to be strongly affected by the presence and density of oxygenated groups on the carbon surface.⁸ As is clear from the above, the surface chemistry in mesoporous carbons plays a crucial role. However, there is no successful combination of ordered mesostructured materials and hydrophobic/hydrophilic properties, especially for ordered mesoporous carbons. But, because of its hydrophobic nature, post-treatment is often needed to enhance the surface hydrophilicity.

Recently we have developed a new cheap and sustainable carbon precursor to synthesize mesoporous carbons – glycerol.⁹ Here we study the benefit of using glycerol as a precursor in the template synthesis method as a way to generate in-situ more hydrophilic surface properties directly during the synthesis. The main objective of this study is to explore the possibility of using such mesoporous carbon as adsorbent for the removal of organic pollutants from aqueous solutions (*e.g.* phenol-Ph, methylene blue-MB). Moreover, the relation of the glycerol concentration and the surface chemistry to the adsorption behaviour is studied.

RESULTS AND DISCUSSION

Chemical composition and surface chemistry of the synthesized mesoporous carbons

In order to determine their elemental composition, the mesoporous carbon materials were analyzed by

electron probe microanalysis (EPMA), and the composition of the samples was found to consist in C as the major element, but also O as the secondary element have been found. This is probably due to the nature of the carbon precursor used in the synthesis, some oxygen atoms still remaining being incorporated in the carbon structure.

The qualitative characterization of their surface chemistry is given by FTIR measurements (Fig. 1). As could be observed, the first strong characteristic peak at 3440 cm^{-1} is attributed to the stretching vibration of the O-H bond.¹⁰ In the spectra of the synthesized (“wet”) samples (Fig. 1a) it is clear that more than one peak is visible in the OH region indicating that different types of surface hydroxide groups are present. Moreover, their relative ratio changes as a function of the used glycerol/silica ratio. The small peaks at 2920 and 2850 cm^{-1} originate from the stretching vibration of the C–H bond positions and depend on the structure.¹¹ The stretching vibrations of the saturated CH_2/CH_3 bonds are located at 1384 cm^{-1} , while the peaks centered at 1582 cm^{-1} and 1710 cm^{-1} are finger prints of carbonyl groups^{12,13} and, respectively, characterize C=O bonds¹² of carboxylic groups. Therefore, it is clear that there are present functional groups on the surface of the synthesized (“wet”) carbon samples. In order to study the origin of the O-H bonds and to evaluate the accessibility of these sites, the carbon samples were analyzed a second time after drying (denoted as “dry”, Fig. 1b). It must be noted that with respect to the “wet” carbons, the spectra of “dry” carbons do not exhibit any strong absorption in the $3600\text{--}3200\text{ cm}^{-1}$ region, meaning that this O-H bonds are originating from the environmentally retained water molecules rather than framework water or intra-material hydrogen bonds. This also indicates that these OH-groups are accessible to at the minimum small molecules.

Surface groups containing heteroatoms are responsible for the acid-base character of the carbon material in aqueous solutions. Therefore, the equilibrium Boehm titration was employed to characterize the chemical surface nature. The results reveal that the surface character of the analyzed carbons is acidic, while the basic character has a 1/5 contribution to the total acid/base character (Table 1).

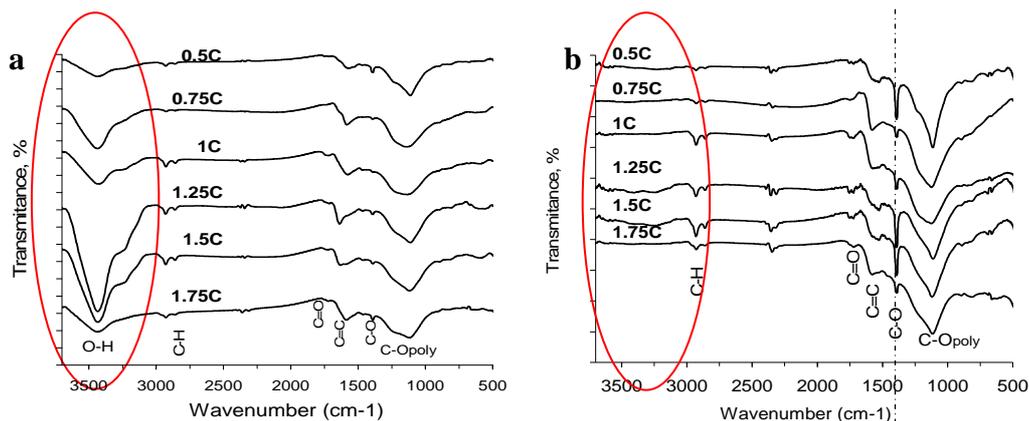


Fig. 1 – Transmission IR-spectra of: (a) “wet”, and (b) “dried” carbon materials.

Table 1

The acid/base characterization of the commercial AC and synthesized mesoporous carbons

Carbon	Total acidity, mmol/g	Total basicity, mmol/g	% of the acidic	% of the basic	Acidic/basic
AC	3.2	0.9	77.5	22.5	3.5
0.5C	2.7	0.6	81.8	18.2	4.5
1C	3.1	0.9	77.2	22.8	3.4
1.75C	3.7	0.9	79.8	20.2	3.9

AC = Norit SX 2 from Sigma Aldrich

Sorption properties

Nitrogen sorption. The pore structures and surface areas of ordered mesoporous carbon materials were investigated by N_2 adsorption-desorption. The isotherms are of type IV with a sharp capillary condensation step at high relative pressures, exhibiting a hysteresis loop near relative pressures of 0.60 in the desorption branch indicates the presence of mesopores. The measured results reveal that the obtained carbons are abundant in mesopores (3.7 nm) and a full description of their porosity has been recently related in Ref.9.

Water vapour sorption. Generally, the adsorption capacity of the carbon depends on the porosity as well as the chemical reactivity of functional groups at the surface. Knowledge on surface functional groups gives insight to the adsorption capability of the obtained carbons which have a high degree of porosity and a functionalized surface, both of which are useful in applications like fluid separation/purification. Selective adsorption with such materials can be achieved physically; by tailoring the pore size molecules are separated according to size, and also are chemically adsorbed by specific interactions with functional groups within the pore structure. As demonstrated, our carbon has already a functionalized surface, and water adsorption

isotherms were obtained (Fig. 2). All isotherms have a sharp adsorption uptake accompanied by a clear uptake occurring over a medium to higher relative pressure range. McBain *et al.*¹⁴ associated this noticeable uptake with the capillary condensation, while Dubinin *et al.*¹⁵ presumed the cluster growth of water on the hydrophilic sites and the coalescence of these clusters as the pressure increases. According to IUPAC classification, the isotherms are of type V characteristic to porous carbon,¹⁶ with the starting uptake at $P/P_0 \sim 0.2$. Knowing that the associated oxygen influences the adsorption of water vapours at relative pressures lower than $0.5 P/P_0$, and the porosity of the carbon is predominantly responsible for adsorption at higher relative pressures,¹⁷ the synthesised mesoporous carbons can be characterized from both viewpoints. Thus it seems that not only the porosity, but also the interaction of the water molecules with the surface plays an important role. The isotherms are S shaped with the uptake at high relative pressures.¹⁸

The wetting properties and the mesostructure together allow controlling the surface behaviour of mesoporous carbons and further extend their applications. Taking into account the affinity of water molecules to porous carbon surface, the synthesised carbons are candidates for adsorption of various organic molecules from aqueous solutions.

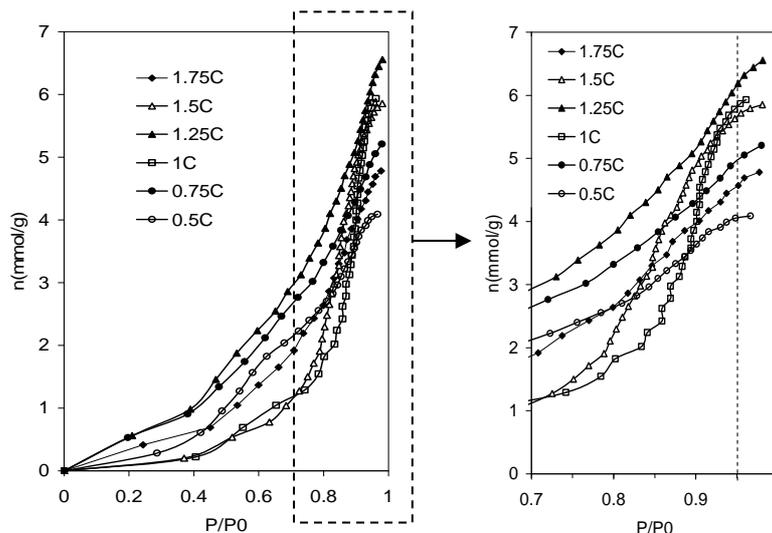


Fig. 2 – Water vapours adsorption isotherms of synthesized mesoporous carbon materials taken at 22 °C after degassing at 200 °C for 17 hours.

Table 2

Water, Ph and MB adsorption capacities from aqueous systems of obtained mesoporous carbons

Sample	Adsorbed water, mmol/g	Adsorbed Ph, mg/g	Adsorbed MB, mg/g	Reference
0.5C	4.1	42	583	This work
0.75C	4.9	58	644	This work
1C	5.8	58	661	This work
1.25C	6.2	53	677	This work
1.5C	5.7	55	622	This work
1.75C	4.5	47	592	This work
AC		18, 97	410, 590, 580	²²

Phenol adsorption. As well known, phenols are similar in structure to many herbicides and pesticides that are resistant to biodegradation. To date, the adsorption of phenolic compounds on carbons and the effect of surface oxygen complexes on phenol uptake have been subject of many researches.¹⁹ Phenol access micropores and the remainder free-oxygen functionalized surface,²⁰ its adsorption being competitive with water molecules²¹. Actually, the surface hydrophobicity enhances the affinity towards phenol, and the maximum phenol adsorption capacity of the synthesized carbons was found to be of 58 mg/g (Table 3). This seems to be a relative high value and its adsorption capacity is comparable with many available carbons in current use.

Methylene Blue adsorption. The adsorption of MB has long been applied for the evaluation of adsorption properties of carbons. Because MB is a cationic dye, it has strong interactions with carbons that have negatively-charged sites when placed in aqueous solutions. As the obtained carbon surfaces have acidic groups that ionize in water producing negative COO⁻ sites, high amount of acidic groups

will result in larger adsorption of MB (Table 2). Compare to other carbon sorbents related in literature, the MB adsorption capacity of the obtained mesoporous carbons exceeds 580 mg/g.

EXPERIMENTAL

Materials and method: Tetraethyl orthosilicate and Glycerol anhydrous were obtained from Aldrich. Tri-block copolymer poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (Pluronic P123, molecular weight = 5800, EO₂₀PO₇₀EO₂₀) was obtained from Acros Organics.

Mesoporous carbon materials were prepared by using a mesoporous silica as template and various loading amounts of anhydrous glycerol as carbon source⁹ and described elsewhere. The typical synthesis of mesoporous carbon consists of impregnating silica with a glycerol aqueous solution, then pyrolyzing it at high temperature in a inert atmosphere. By leaching silica template, a set of six carbon samples was obtained and labelled as xC where x represents the glycerol volume to silica weight ratios – 0.5, 0.75, 1, 1.25, 1.5, 1.75.

Characterization: The textural properties of were investigated by sorption measurements with a Quadrasorb SI (Quantachrome) automated gas adsorption system using nitrogen as adsorbate at -196 °C. The elemental composition was determined using the electron probe microanalysis (EPMA) performed on a JEOL JXA 733 apparatus. The

surface chemistry of the obtained materials was investigated by FTIR performed on a Nicolet Nexus spectrometer equipped with a MCT/B detector, collecting the transmission spectra from compressed pellets made by mixing a very small quantity of sample with KBr. The prepared carbons were assessed by the Boehm titration method²⁰ for the determination of acidic (with NaOH) and basic (with HCl) functional groups. Water adsorption isotherm were collected with a home-built volumetric sorption system equipped with a rotary vane pump, a turbo molecular pump and pressure transducers in the range of 1–1000 mbar (resolution 0.1 mbar). Prior to measurements, samples were outgassed for 16 h at 200°C. The water was frozen with liquid nitrogen, degassed and heated to room temperature again, prior to the measurements. Ph and MB adsorption were carried out in a set of Erlenmeyer flasks (100 ml). Solutions of Ph and MB with different initial concentrations were prepared from corresponding fresh stock solutions. To 20 mL of the Ph and MB solutions, a fixed mass of 0.01 g of the synthesized carbon was added and stirred at room temperature. After equilibration (2 hours for both MB and phenol), the solutions were centrifuged and analyzed using a Nicolet evolution 500 UV-Visible spectrophotometer (661 nm for MB and 270 nm for Ph).

CONCLUSIONS

The benefit of using glycerol as carbon precursor for functionalized carbon has been demonstrated. This material generates in-situ surface properties directly during the synthesis process, being an advantage and playing a key role in the performance of the organics adsorption. It has been demonstrated that the carbons obtained by this way contain on their surface acidic and basic sites at the same time, being a excellent candidate sorbent for both phenol and methylene blue from aqueous solutions. It was illustrated that the adsorption properties of obtained carbons with a high surface area, pore volume and functionalized surface were improved compare to the carbons reported in the literature. Further testing on the adsorption capacity of prepared mesoporous carbon would confirm the feasibility on the production of qualitative mesoporous carbon from glycerol, which would promote re-usage of waste glycerol protecting the environment.

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