POLYMER-BASED MESOPOROUS CARBONS:
SOFT-TEMPLATING SYNTHESIS, ADSORPTION AND
STRUCTURAL PROPERTIES

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by

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DEDICATION

I dedicate this dissertation to the memory of my mother
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CHAPTER 1

INTRODUCTION

Nanoporous carbons include a broad spectrum of carbons ranging from highly microporous active carbons to carbon nanotubes and ordered mesoporous carbons. The properties of each group of nanoporous carbons reflected by their porous structure and surface chemistry are influenced by both the nature of carbon precursors and the methods of carbonization and activation. For most applications such as fuel cells, supercapacitors and catalysis, the most desired properties include active carbons, graphitic carbons and carbon nanotubes. Graphitic carbons found applications in Li-ion batteries, double layer capacitors and heat-resistant composites used, for instance, for insulation in aircrafts and space shuttles. On the other hand, active carbons offer high specific surface area (up to 3000m$^2$/g) due to the presence of tiny pores, usually smaller than 2nm, called micropores. High porosity allows using carbon materials as fillers and sorbents, but at the same time it can limit their applications in fields such as catalysis due to poor mass transfer in micropores. Intensive efforts have been made to control the size of pores and simultaneously to avoid a significant reduction of the specific surface area.

Ordered mesoporous carbons (OMCs) possessing pores in the range from 2 to 50nm can combine all the most desirable features including high surface area, tunable structure and geometry of pores, and also, by selecting proper carbon precursors, it is possible to introduce graphitic domains into the structure of OMCs.
1.1 OVERVIEW OF THE METHODS USED FOR SYNTHESIS OF ORDERED MESOPOROUS CARBONS

The discovery of ordered mesoporous carbons (OMCs) in 1999 [1] has opened a new chapter in the synthesis of ordered mesoporous materials and initiated one of the most popular synthesis routes in the preparation of OMCs called hard-templating method (see Scheme 1A) [2-4]. The first step in this method involves the preparation of ordered mesoporous silica (OMS) followed by filling the pores of the template with suitable carbon precursor, carbonization and silica template removal. The resulting carbon materials are inverse replicas of the template and exhibit high surface area, large pore volume and ordered mesopores. The adsorption properties of these materials can be easily tuned by using different silica mesostructures as templates.

Another method, which is more appropriate for the preparation of mesoporous carbon materials, involves colloidal silica particles [5-7] or colloidal crystals as templates [8, 9]. In this case a broad variety of commercially available silica colloids creates tremendous possibilities to design the size of mesopores in carbons. This synthesis strategy employs mixing of colloidal silica particles with carbon precursor to obtain the silica-carbon composite, which is subjected to the carbonization and silica dissolution. The resulting carbon possesses disordered but interconnected and uniform mesopores that resemble the size of silica nanoparticles used [5-7]. In contrast, the colloidal crystal templating method affords ordered carbons [8, 9].

Even though these methods became very popular due to their simplicity, they have crucial disadvantages too. The need of preparing the OMS or colloidal crystals and
dissolving them increases the number of preparation steps and the total cost of the synthesis. Additionally, the use of hazardous sodium hydroxide or hydrofluoric acid solutions to remove the silica template is not very safe from the environmental point of view. Therefore, the environmental aspect and the high-cost make the hard-templating method unfeasible for up-scaling.

**Scheme 1.** Comparison of hard-templating (A) and soft-templating methods (B)

Most recently, ordered and disordered carbons prepared by the self-assembly of organic carbon precursors and triblock copolymers (soft templates) have been reported [10, 11]. This new strategy takes advantage of the favorable organic-organic interactions between some thermosetting polymers and thermally-decomposable surfactants to form ordered polymer-polymer nanocomposites (see Scheme 1B). During the initial heating of the latter,
the thermally unstable block copolymer used as a soft template is removed (decomposed), whereas the thermosetting polymer is carbonized by heating at higher temperatures in order to form the carbon pore walls. The development of such carbons from polymeric precursors represents a major step in materials science, since fewer steps are required and the block copolymers used are biodegradable and can be recovered, making this synthesis more environmentally friendly.

1.2 SOFT-TEMPLATING SYNTHESIS OF MESOPOROUS CARBONS

The first successful work on the soft-templating synthesis of ordered mesoporous carbon films has been reported in 2004 by Liang et al. [12] by using polystyrene-block-poly(4-vinylpyridine) (PS-P4VP) as a structure directing agent. Later, two independent groups [13, 14] proposed the use of poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) triblock copolymers (PEO-PPO-PEO) as structure forming agents (which are commonly employed in the synthesis of ordered mesoporous silicas such as SBA-15 and SBA-16) for the synthesis of OMCs. Besides that these groups developed two alternative synthesis routes leading to the ordered carbons not only in the form of thin films but also in the form of fibers and monoliths. Zhao’s strategy [14] is based on the pre-polymerization of a carbon precursor called resol, which is a low-molecular-weight copolymer of phenol and formaldehyde prepared in the presence of sodium hydroxide as a catalyst (see Scheme 2A). Next, as-made resol after neutralization interacts with surfactant to assemble into a polymeric mesostructure. In contrast, the procedure proposed by Dai and coworkers [13] involves phloroglucinol and formaldehyde as a carbon-yielding component (Scheme 2B).
Under acidic conditions, the phloroglucinol-formaldehyde mixture self-assembles in the presence of the block copolymer to form a polymeric composite, which after curing is transformed into the final carbon material. This one-pot synthesis has a major advantage of avoiding a pre-polymerization and pH adjustment required for the synthesis in an alkaline medium.

Scheme 2. Comparison of alkaline (Panel A) vs. acidic (Panel B) routes of the soft-templating synthesis

Some attempts were undertaken to modify the aforementioned recipes, which can be divided into two groups: i) searching for new materials to be used as soft templates and ii) new carbon precursors. To the first category belong the studies, which are focused on the
use of copolymers with a different ratio of PEO/PPO blocks (F108, P123 and other) [14, 15]. These studies showed the possibility of obtaining a whole sequence of mesostructures from lamellar to bicontinuous cubic, hexagonal and body centered cubic by increasing the PEO-to-PPO ratio. Moreover, the use of reverse amphiphilic triblock copolymer PPO$_{53}$-PEO$_{136}$-PPO$_{53}$ [16] led to the formation of mesoporous carbons with a face centered cubic structure and a bimodal pore size distribution. Zhao et al. [17] reported thick wall mesoporous carbons prepared by utilizing a weakly hydrophobic poly(ethylene oxide)-b-poly(methyl methacrylate) (PEO-b-PMMA) diblock copolymer. In this case the ester groups from PMMA block interact stronger with hydrophilic phenolic carbon precursor facilitating the formation of thick carbon walls. As regards to the carbon precursors most reports employ phenol, resorcinol, phloroglucinol or even mixtures of these [18] mostly but not only due to effectiveness in hydrogen bonds formation between the soft template and carbon precursors. Other important factors, which favor phenolic resin over any other carbon precursors are their ability for thermosetting, high carbon yield after carbonization and good miscibility with copolymers used as templates. Tanaka et al. [19] reported the use of triethyl orthoacetate (EOA) together with resorcinol-formaldehyde as co-precursors for the carbon synthesis. The resulting carbon films exhibited an enhanced periodicity proved by both XRD and TEM measurements. Another group reported the preparation of ordered and disordered carbons from resorcinol-furfural oligomers [20] and showed that the degree of polymerization and molecular architecture determines the self-assembly and the quality of the final product. Recently, also other polymeric precursors such as melamine [21], urea-formaldehyde [22], and even novolac resins [23] were also considered as an alternative for
the originally used phenolic resins. The advantage of using carbon precursors containing heteroatoms is the possibility of tailoring the surface chemistry of the resulting products according to the specific applications. For instance, the N-containing ordered mesoporous polymers obtained from urea-phenol-formaldehyde resin [22] are claimed to be more efficient adsorbents towards heavy metal ions due to greatly improved hydrophilic properties of the polymer surface and higher affinity toward metal ions. The aforementioned features can be utilized in catalysis, proton conducting membranes, adsorbents for CO$_2$ capture or in “reactive templates” for the preparation of nanostructured metal nitrides. It has been shown that the highest nitrogen content of ~3wt% could be obtained for the sample prepared with 1:1 molar ratio of urea to phenol. The amount of nitrogen can be easily augmented by using nitrogen rich precursor such as hexamethoxymethylmelamine (HMMM) [21]. HMMM usually used as an additive to melamine/formaldehyde system to prevent the self-condensation of the latter, here was used as a single carbon precursor, which in the presence of Pluronic F127 under acidic conditions condensed into N-rich mesoporous framework. The resulting polymers exhibited much bigger mesopores than those obtained from urea-phenol-formaldehyde system (7.8nm vs. 3.5nm, respectively). In spite of differences in mesoporosity, the nitrogen containing precursors altered the strength of the hydrogen bond formed between the carbon precursor and the soft template, which governs the self assembly. There is another popular type of phenolic resin called novolac, possessing the abundance of hydroxyl groups, which could be successfully utilized in the soft-templating synthesis of carbons; however, its linear structure and thermoplastic properties make it unstable at high
temperatures required for carbonization. To overcome this problem the new method has been recently proposed involving the addition of proper curing agent, which can promote the cross-linking of the linear novolac resins leading to the formation of stable, thermosetting polymeric frameworks [23].

Many practical applications demand not only well-defined porous structure but also specific macroscopic morphologies. Unlike other materials, which after synthesis can be shaped and processed, in the case of soft-templated carbons the mesostructure formation and morphology growth occur simultaneously, meaning the synthesis conditions need to be planned ahead to address both issues. It was demonstrated that the polymer solution obtained after phase separation can be easily used for the preparation of carbons in the form of monoliths, fibers and films [12, 13, 24] utilizing the popular processing techniques such as spin-coating or fiber extrusion. Regarding the preparation of monolithic carbons, the most commonly used evaporation induced self-assembly (EISA) method [12-15, 19, 25] affords carbons with different shapes and sizes depending on the mold used, however, the extensive material shrinkage and microcracks appearance considerably lowers the quality of materials considerably. To avoid the aforementioned problems, a series of extended low temperature treatments is performed prior to carbonization. This procedure called a low-temperature autoclaving (LTA) route [26] led to the crack-free mesoporous carbons with macroscopic dimensions and highly ordered \textit{p6mm} mesostructure. The carbon films are usually prepared by spin coating or dip coating [13] on a substrate with the polymeric solution containing a carbon precursor and a template. Both methods result in nicely ordered carbon films, where the film thickness can be controlled to some extent by
adjusting the density of polymeric solution spread on the substrate. A more effective way to substantially reduce film thickness without loosing good quality of the material is the stepwise assembly approach [12]. In the first part, the solution containing block copolymer and resorcinol is deposited on a substrate, which then is exposed to the formaldehyde gas for *in situ* polymerization and cross-linking. A similar strategy was recently demonstrated for the preparation of 15nm thin films from benzyl alcohol [27]. Except monoliths, fibers and films, other interesting carbon morphologies have been synthesized such as membranes [14], spheres [28], rods [29] and single-crystals [30, 31]. These can be achieved by either changing the solvent system from water-ethanol [13-19] to entirely aqueous [29-31] or ethanol solution [15], or by varying the PEO/PPO ratio and the concentration of triblock copolymer. Interestingly, the addition of reverse triblock copolymer 25R4 [32, 33] as an intercalating soft matter resulted in “plasticine”, easily shaped organic-organic hybrid mesostructures, which retain their shape and mesoporosity after carbonization.

1.3 ORGANIC-INORGANIC NANOCOMPOSITES OBTAINED BY SOFT-TEMPLATING

Adsorption, catalysis, separations and energy-related applications require often mesoporous carbons with incorporated inorganic species or carbon-inorganic nanocomposites. Inorganic species can be incorporated into mesoporous carbons during their synthesis or by post-synthesis infiltration [34, 35]. The latter strategy, although it is often used, has several shortcomings due to the limited loading of inorganic species, difficulties in controlling their size and distribution and possible pore blocking; however,
the aforementioned limitations do not appear when inorganic species are incorporated during carbon synthesis. Therefore, several attempts have been made to incorporate inorganic species during hard templating [36] and soft templating [37-42] synthesis of mesoporous carbons.

The colloidal templating is well suited for the incorporation of inorganic nanoparticles into carbons because these particles can be easily co-assembled with silica colloids to form a hard template [34]. In contrast to the post-synthesis modification of carbons, which does not allow for an easy control of the size and amount of the nanoparticles formed, the colloidal templating permits incorporation of a large amount of inorganic nanoparticles of desired size and shape without affecting the pore size of the resulting carbon composites; the latter is determined by the size of silica colloids only. A shortcoming of this approach is its limitation to nanoparticles, which can survive the removal of siliceous template.

In comparison to hard templating, the soft-templating synthesis is better suited for the incorporation of inorganic nanoparticles as well as for their formation from suitable inorganic precursors. It was shown previously that a direct addition of metal salts into synthesis mixture represents a convenient way for the formation of well-dispersed nanoparticles in the carbon matrix, but at the same time, it is difficult to control the size of these particles as well as the formation of carbon mesostructure, which often becomes microporous [43, 44]. Thus, application of the latter type of carbons may be limited in catalysis due to the poor mass transfer in micropores. In spite of the aforementioned shortcomings the recently presented [39, 40] idea of using block copolymers as soft templates for the carbon structure formation in the presence of metal salts that undergo
transformations into nanoparticles is a very promising approach for the design of nanostructured carbon-based catalysts.

In some of the first reports, it was shown in [36-38] that tetraethyl orthosilicate (TEOS) can easily participate in the self-assembly of organic species used for the synthesis of mesoporous carbons. The removal of silica (by dissolving it in HF or NaOH solution) and carbon (by burning it out) resulted in ordered mesoporous carbon and silica, respectively, which is an indication of uniform distribution of all species in the silica-carbon composites.

The addition of other inorganic components (e.g., iridium, titanium and nickel components) during self-assembly synthesis of carbons resulted in the formation of ordered mesostructures with inorganic nanoparticles [39-42, 50]. The titania containing mesostructures were synthesized with the use of pre-hydrolyzed TiCl₄ as an inorganic precursor [39, 45, 46]. In contrast to silica, titania easily nucleates leading to TiO₂ nanocrystals embedded in the pore walls of ordered mesoporous carbons. The uniform distribution of titania nanocrystals proved the formation of interpenetrating hybrid framework during co-assembly process. The same group recently modified this approach to obtain crystalline C-TiO₂ composites [45]. It was shown the use of acid-base pair (TiCl₄ and Ti(OC₄H₇)₄) as titania precursors instead of single source can greatly improve the titania content in the sample even up to 87wt%. Moreover, the mesostructured composites still exhibit good adsorption properties such as a relatively high specific surface area of ~200m²/g and relatively large pore volume.

The soft-templated mesoporous carbons containing iridium particles have been reported too [40]. It was found that the factors such as aging time of the gel and the molar ratio of
resorcinol to formaldehyde, which usually affect the structural ordering, also govern the size of the nanoparticles formed. In this case, small (∼2 nm) and highly dispersed iridium particles were obtained. Importantly, the Ir-OMC catalysts proved their good performance for the hydrazine decomposition.

OMCs with magnetic properties are of great interest due to their possible applications, e.g., magnetic storage media [47]. Since the discovery of soft-templating synthesis of mesoporous carbons, this easy and cost effective approach seems to be a good alternative for the quite laborious hard-templating method. In one of the recent reports [48, 49] the “one-pot” synthesis of γ-Fe₂O₃-containing mesoporous carbons obtained by the co-assembly of block-copolymer with resol and ferric citrate was demonstrated [48]. It was shown that the samples with low γ-Fe₂O₃ content (such as 9.0 wt %) possessed an ordered 2D hexagonal (p6mm) structure, uniform mesopores (∼4.0 nm), high surface areas (up to 590 m²/g) and pore volumes (up to 0.48 cm³/g). All maghemite/carbon nanocomposites exhibited excellent magnetic properties, where the saturation magnetization strength was easily tuned by increasing the γ-Fe₂O₃ loading. However, the latter also lowered the values of the BET surface area and pore volume.

The ferromagnetic properties of the Ni-OMC composites, especially the fact of being self-protected against acid leaching, make them attractive materials for magnetic separations [41]. Also, for the first time the metal-containing carbons with a cubic structure of I₄m3m symmetry have been reported. Different synthesis conditions required for the formation of cages instead of channels also affect the growth of Ni nanocrystals, which showed nearly the same size (∼20nm) regardless of the amount of Ni salt used in the
synthesis. In contrast, the work reported by Wang and Dai [51] shows that the average size of Ni particles increased with the metal loading. There is some evidence that the nanoparticles are formed in the carbon matrix and on the outer surface of hexagonally ordered carbons as well. Besides that, the resulting Ni-carbon composites exhibited good structural properties such as large and uniform mesopores (~7 nm), total pore volume (0.46-0.68 cm$^3$/g) and high BET surface area (up to 660 m$^2$/g).

The idea of using metal salt for the generation of nanoparticles in OMCs and tetraethyl orthosilicate (TEOS) as a mesostructure reinforcing agent was reported by Zhou et al. [42]. Depending on the NiCl$_2$ concentration, the Ni-C composite obtained after silica dissolution exhibited high specific surface area (1220 m$^2$/g). The as-prepared Ni-C samples served as supports for Pt nanoparticles formed under microwave conditions. The resulting binary catalyst (consisted of metallic Ni and Pt nanoparticles) has shown to be catalytically active in the methanol electro-oxidation reaction. Also, the concept of using TEOS to reinforce the mesostructure formation and to improve the overall structural parameters of the samples was employed to obtain carbon-supported ruthenium catalyst for benzene hydrogenation [52].

The fact that the addition of foreign species into the mixture of block copolymer and carbon precursor does not disintegrate the self-assembly process, provides a great opportunity for the one-pot synthesis of organic-inorganic composites. Previously, the methods such as surface functionalization [53, 54], filling the pores of mesoporous silicas with organic moieties [55, 56] or direct synthesis of periodic organosilicas (PMOs) [57, 58] were used to achieve ordered mesoporous organic-silica nanocomposites but with moderate
success. The risk of non-uniform distribution, pore blockage and also the use of rather expensive organosilanes largely limited the preparation of that type of materials. The soft-templating approach helps to overcome the aforementioned drawbacks. One of the first reports in this area employed tetraethyl orthosilicate (TEOS) \[36\] in the self-assembly of phenol and formaldehyde under basic conditions. Not only ordered polymer-silica and carbon-silica composites were obtained but also mesoporous silicas and carbons due to the dual-functionality of these composites. The pore sizes of the final products could be easily tuned by using different block copolymers (L64 or Brij76); however, in this case only disordered phases were obtained \[38\].

Recently, the same group reported an interesting approach to the synthesis of ordered mesoporous poly(furfuryl alcohol) PFA-silica nanocomposites \[59\]. The use of furfuryl alcohol (FA) as a carbon precursor requires usage of a special alkoxysilane as a linker between PFA/TEOS and a soft-template in order to improve the assembly of PFA/TEOS in hydrophilic domains of block copolymers. The resulting composites possessed high organic content even up to 60wt\%, although the structural and adsorption properties slowly deteriorated with the increasing amount of PFA in the samples. Also the hydrophilic/hydrophobic nature of PFA-silica nanocomposite was evaluated on the bases of water and toluene adsorption. Since PFA oligomers are hydrophobic, their larger loadings enhance affinity toward toluene molecules.

Although all examples of nanocomposites discussed above were obtained via one-pot synthesis, there are a few interesting post-synthesis modification methods involving soft-templated carbons. The simple bridging of the inorganic groups to the organic
frameworks was demonstrated to obtain \( \text{SO}_3 \text{H} \)-functionalized mesoporous polymers [60]. When carefully controlled, this facile sulfonation method allows the generation of substantial amount of Brønsted acid sites without loosing the structural ordering of the polymer framework. As-prepared material proved to be a stable and selective heterogeneous catalyst for the number of acid-catalyzed reactions such as Beckmann rearrangement of cyclohexanon oxime and condensation of ethylene glycol with aldehydes possessing different size characteristics. The strong oxidation conditions except creating carboxylic groups that allows for the grafting of many other functional groups on the surface, may easily cause structure deterioration. Because of that there is a need to explore other modification routes including the infiltration of mesoporous carbons with suitable precursors or surface modification. In the latter case so far two methods have been used. The first method involves chloromethylation of the aromatic moieties of the mesoporous polymers and subsequent amination with methyl amine, dimethylamine or ethylenediamine [61]. This two-step functionalization method allows the incorporation of amino or diamino groups into polymer framework to obtain a stable base catalyst with controllable basicity and mesostructure. The second method [62], Prato’s reaction, utilizes the 1,3 dipolar cycloaddition of azomethine ylides, which was successfully applied for the organic modification of carbon nanotubes, nanohorns and fullerenes. The thermal condensation of \( \alpha \)-amino acid with aldehyde generates azomethine ylides, which after cycloaddition reaction form pyrrolidines attached to the surface of ordered mesoporous carbons. The ylides addition led to the pore volume and surface area reduction, however the mesoporosity remained untouched. The same work
also shows that amorphous carbon has a preferential reactivity for ylide addition in contrast to graphitic carbon. Prato’s reaction also offers the possibility to integrate two different functional groups simultaneously, which could be a very simple method of preparing carbon-based cooperative catalysts. Another example of the post-synthesis modification of soft-templated carbons was based on the simple solution infiltration method [63, 64], where the carbon micropores were filled with elemental sulfur to obtain hierarchically structured sulfur-carbon nanocomposite and then tested as a novel cathode material for Li/S batteries [63]. For that kind of applications the hierarchical porosity seems to be crucial to achieve high utilization of sulfur. The micropores serve as micro-collectors of elemental sulfur, while high surface area provides enough contact to the insulating sulfur and carries high electrical conductivity to nanocomposite. The role of mesopores is to promote the Li ion transport and to accommodate the products of the electrochemical reactions. The electrochemical tests have revealed that the S/C composites possess high discharge capacitity at a much higher current density than the cathodes made of mesoporous carbon or microporous carbons.

### 1.4 METHODS FOR TAILORING MICRO- & MESOPOROSITY IN CARBONS

As mentioned in this overview, until recently the most of ordered mesoporous carbons (OMCs) have been obtained by using ordered mesoporous silicas (OMSs) [2,65] or colloidal silica crystals [66-68] as hard templates. In the former case the resulting carbons are inverse replicas of the OMS templates with pore widths determined by the silica wall thickness, which usually do not exceed 6nm. However, the use of colloidal silica crystals or
colloidal silica yields carbons with spherical pores of tailored sizes in the mesopore range from ~5-6 nm to 50 nm and macropore range (above 50 nm) due to availability of silica colloids in this range. Additionally, the broad variety of commercially available silica colloids reduces the total cost of the synthesis. Thus, the colloidal templating seems to be a very promising method for the preparation of ordered macroporous carbons [66-68] and polymers with large pores [69]. Initially, the colloid-templated carbons possessed a high specific surface area and a large mesopore volume [5] but at the same time a quite broad pore size distribution (PSD) due to aggregation of silica colloids. To prevent the latter, the addition of stabilizing surfactant has been used [6]. Although the strategy of using colloidal silica as a structure directing agent is straightforward, it is still a challenge to obtain uniform, spherical mesopores, which would accurately resemble the size of the silica colloids used [70]. This refers especially to the carbons obtained by the carbonization of polymeric precursors formed in the presence of colloidal silica, where templating can occur on the colloidal aggregates instead of single silica colloids, which results in a broad pore size distribution [5]. Initially, this difficulty was circumvented by using mesophase pitch particles as carbon precursor [71-73]. An effective control of interpenetration of silica colloids into mesophase pitch was achieved by the adjustment of heating, stabilization and carbonization conditions in order to assure a complete coverage of the surface of silica colloids with carbon precursor, which is the main requirement to obtain spherical mesopores reflecting the size of single colloids.

A complete filling of the template pores produces true inverse carbon replicas [68, 70]. Theoretical and experimental studies showed that the complete filling of pores of a
colloidal crystal template with carbon precursor yielded carbons with the pore volume of ~1.36 cm$^3$/g [74], whereas, the formation of a thin carbon film on the template surface afforded carbons with much larger pore volumes, e.g., it was shown that the formation of phenolic resin films just on the surface of colloidal silica afforded carbons with pore volumes as high as 9 cm$^3$/g [74, 75].

The use of colloidal silica facilitates the formation of carbon monoliths. The monolithic colloidal silica templates can be easily fabricated by evaporation of solvent from a colloidal silica solution and compressing dried silica into desired forms [34]. In the next step, the voids between colloids of the silica monolith are filled with carbon precursor, which creates a carbon monolith with uniform spherical mesopores after carbonization and silica dissolution.

In the case of the soft-templating approach the mesoporosity can be also tailored [76, 77] with silica colloids [78] especially if it is intended to obtain hierarchical porosity and to introduce distinct pore geometry into the system (spherical vs. cylindrical pores). The first implementation of this idea was presented by Deng et al. [78], who used silica colloidal crystals to prepare macro-mesoporous carbons. The resulting porous carbons have highly ordered macropores resembling the size of colloids used (230-430nm), which are interconnected through 30-65nm windows and smaller mesopores of ~11nm originated from soft-templating. The second method is analogous to these used for tuning the pore size of ordered mesoporous silicas and involves small organic molecules as pore expanders. The mesoporous carbons with ultra-large pores were synthesized by utilizing diblock copolymer PEO-$b$-PS as a template, homopolystyrene ($h$-PS) as a pore expander and resol
as a carbon precursor [79]. The addition of h-PS up to 20wt% relative to PEO-b-PS afforded highly uniform mesopores in the range from 26nm to 40nm, while higher loadings caused the multimodal pore size distributions.

Commonly, both hard- and soft-templating strategies produce most often carbons with ordered and uniform mesopores. However, numerous applications, especially gas storage, removal of pollutants of different sizes, heterogeneous catalysis, energy storage and conversion [80-83], require carbons with hierarchical structures that contain both micropores and mesopores [3, 4, 84-87]. Therefore, the creation of additional microporosity in mesoporous carbons without diminishing their mesoporosity is a very important task. In general, different strategies can be used for the development of microporosity in mesoporous carbons. One of these is the post-synthesis activation of soft- and hard-templated carbons with CO\textsubscript{2} or KOH in order to generate microporosity in the mesopore walls. Microporosity can be also created by one-pot soft-templating synthesis in the presence of tetraethyl orthosilicate (TEOS) followed by dissolution of TEOS-generated silica. Also, a combination of the latter approach with colloidal silica templating can be employed to obtain hierarchical carbons with micropores (formed after dissolution of the TEOS-generated silica) and two different types of mesopores created by soft-template and colloidal silica, which will be presented in this work.

So far, mesoporous carbons obtained by inverse replication of ordered mesoporous silicas such as SBA-15 were activated with CO\textsubscript{2} [88-91] and KOH [91, 92]. This activation resulted in a substantial increase of microporosity and a simultaneous reduction of mesoporosity [92]. The same was recently reported for mesoporous carbons fabricated by
using colloidal silica as a hard template [34]. Also, the soft-templated mesoporous carbons were activated by KOH [93-95] and CO$_2$ [96, 97]. In this case, the pH conditions for polymerization of carbon precursors and self-assembly seem to have a strong influence not only on the average mesopore size (4nm vs. 8nm in basic and acidic media, respectively), but also on the degree of cross-linking affecting the pore wall thickness and its stability [98, 14], which is especially important in post-synthesis activation. Carbons synthesized under acidic conditions possess exceptional resistance to a wide range of activating agents and temperatures, even graphitization [97-100] compared to those obtained by using basic synthesis route [96]. This was a quite unique finding, bearing in mind that for instance KOH activation is considered to be a harsh activation method compared to CO$_2$ or water vapor activation. Each of the activating agents used reacts with the carbon framework in a different way, which translates to different carbon burn-off and porosity development, however, the fully preserved mesoporosity is a common feature for this kind of carbons. Another example proving the exceptional stability of carbons prepared under acidic conditions involved the NH$_3$ activation at high temperatures [101, 102]. The latter except for creating micropores, which normally takes place during activation process, also induced the replacement reaction between oxygen-bearing species in carbon matrix and NH$_3$ resulting in nitrogen-doped carbons. Such as carbons meet requirements for oxygen reduction reaction catalysts not only because of their high activity and good stability but also due to a much higher resistance to CO poisoning than the commonly used Pt-based catalysts.
Another alternative of creating microporosity in mesoporous carbons involves the incorporation of TEOS during soft templating synthesis [36-38]. These works showed that a large amount of TEOS can be added during the formation of phenolic resin in the presence of block copolymer template. The resulting phenolic resin-TEOS-block copolymer composites were converted into mesoporous silica-carbon materials by controlled heating and carbonization under flowing inert gas. Dissolution of homogeneously distributed silica in these composite materials resulted in the creation of micropores in the mesopore walls.

1.5 RESEARCH OBJECTIVES AND SUMMARY

The discovery of ordered mesoporous carbons (OMCs) in 1999 [1] has opened a new chapter in the research of ordered mesoporous materials. The first OMCs were obtained by filling the pores of silica nanostructures (used as hard templates) with suitable carbon precursors followed by carbonization and dissolution of the template. The hard templating synthesis became a very popular way for the fabrication of OMCs, which in this case are inverse replicas of the silica templates used. Some disadvantages of this synthesis strategy relate to the need of preparing siliceous hard templates and dissolving those using hazardous hydrofluoric acid or sodium hydroxide solutions. The aforementioned environmental issue, multistep processing and higher costs make the hard templating synthesis less feasible for a large scale production of OMCs.

Recently, a simple and feasible way of preparing mesoporous carbons by self-assembly of appropriate polymerizing organics (carbon precursors) and triblock copolymers (soft
template) has been reported [10, 11]. A controlled thermal treatment of the as-synthesized polymeric nanocomposites results in the removal of triblock copolymer (soft template) leaving behind large and uniform mesopores and in the carbonization of the remaining polymer (carbon precursor) giving finally OMC. The development of soft-templated mesoporous carbons represents a major breakthrough in materials science because fewer steps are required for their preparation as well as the block copolymers used are commercially available and biodegradable, which makes this synthesis feasible from the industrial viewpoint.

The main objective of this dissertation research is to explore the soft-templating strategy for the preparation of well ordered mesoporous carbons by self-assembly of phenolic resins in the presence of triblock copolymers under acidic conditions and to monitor their adsorption and structural properties. Based on that, our goal is to develop an efficient synthesis route suitable for the design of a wide spectrum of carbon-based materials including carbons as well as carbon composites with incorporated inorganic nanoparticles, specific organic groups and heteroatoms. Assessment of adsorption, structural, and surface properties of these materials is based on nitrogen adsorption at -196°C, powder X-ray diffraction (XRD), high resolution thermogravimetry (TG), elemental analysis (EA), infrared and Raman spectroscopy.

In this dissertation the organic-organic self-assembly of phenolic resins and triblock copolymers under acidic conditions will be used to obtain ordered mesoporous carbons and carbon-based materials. The structure of this dissertation includes an introductory chapter (Chapter 1) dealing with ordered mesoporous carbon materials, particularly those prepared
by the soft-templating strategy. In addition, Chapter 2 covers a brief overview of the main techniques such as gas adsorption and powder X-ray diffraction used for the characterization of ordered mesoporous carbons, a list of materials and reagents used for the preparation of the aforementioned materials and the general experimental procedure.

Chapter 3 is focused on the optimization of the synthesis conditions for phenolic resin-based mesoporous carbons. Even though the main concept of the soft-templating synthesis seems to be well established for ordered mesoporous silicas, it is still in its initial stage in relation to carbon materials. A lot of reports follow the base-catalyzed procedure, while only a few of them deal with a synthesis in acidic media, which seems to be easier and more practical from the industrial point of view. It is shown that the adsorption and structural properties of these materials can be easily tuned by varying the synthesis parameters such as temperature, carbon precursor/copolymer ratio and acid concentration [98], which gives an insight into the self-assembly process under acidic conditions [103].

Next chapter (Chapter 4) is devoted to the organosilanes-assisted synthesis of mesoporous carbons using the soft-templating method [104]. The fact that the addition of foreign species into the mixture of block copolymer and carbon precursor does not disintegrate the self-assembly process provides a great opportunity for the one-pot synthesis of organic-inorganic composites. The main goal is to monitor the mesostructure formation as a function of the increasing amount of the organosilanes used. Moreover, two different organosilanes were studied to determine how the size of the organosilane introduced affects the self-assembly process and mesostructure formation. In the case of small organosilanes such as TEOS, it was possible to introduce up to 70wt% of TEOS
without significant structure deterioration. It is noteworthy that TEOS is mostly embedded in the carbon framework, which was proved by the remarkable increase in the micropore volume after silica dissolution. The same incorporation mechanism was also observed for much larger organosilanes, namely tris(3-trimethoxysilylpropyl) isocyanurate (ICS) possessing Si and N in the structure, which produced nanocomposites possessing groups resistant to carbonization.

Chapter 5 of this dissertation investigates the incorporation of inorganic species into carbon mesostructures. This can be achieved by employing suitable inorganic precursors, which after thermal treatment form nanoparticles [40, 51, 105] or by adding metal/metal oxide nanoparticles in the form of colloidal solutions to the synthesis mixture [106]. It was shown that the latter strategy is especially beneficial when potential applications require high loadings of nanoparticles embedded into a carbon matrix composed of large and uniform mesopores [107]. The inorganic species used for these studies include spherical silica and alumina nanoparticles of different sizes [106, 107] and also highly crystalline alumina nanosheets [108].

Since the soft-templated carbons possess mainly large and uniform mesopores, the last chapter (Chapter 6) of this dissertation discusses some methods aiming at the improvement of the specific surface area and microporosity [109] with simultaneous preservation of the mesoporous structure. One of the methods used is the post-synthesis KOH activation [110], that results in micro- and mesoporous carbons with a high surface area as well as a well-developed microporosity and mesoporosity; the latter is preserved when KOH activation is performed at a temperature of ~700ºC or higher. Moreover, it is shown that the temperature
of carbon pyrolysis prior to activation strongly affects not only the structural properties of the carbons but also their susceptibility to further activation and the simultaneous preservation of the mesoporous structure [111]. Also, physical activation of the soft-templated carbons [112], possessing two systems of mesopores, one originated from the block copolymer template used and another generated by dissolution of the silica nanoparticles added to the synthesis mixture, is performed. This strategy affords hierarchical carbons with greatly improved microporosity and specific surface area, and a very high total pore volume.

This dissertation is based on the following publications:


In addition, several articles closely related to those mentioned above have been published:


CHAPTER 2

EXPERIMENTAL SECTION

2.1 CHARACTERIZATION TECHNIQUES

2.1.1 NITROGEN ADSORPTION ANALYSIS

Since nitrogen adsorption is the primary characterization technique for the carbons and carbon composites, it will be discussed in greater details.

Gas adsorption analysis is commonly used to study surface and structural properties of porous solids. The latter include specific surface area, total pore volume and pore size distributions, which are crucial parameters determining materials quality application-wise. Moreover, the possibility to monitor changes in a surface hydrophilicity/ hydrophobicity alongside the changes in adsorption energy distribution (which often occur as a result of chemical/thermal treatment of an adsorbent) provides a global view of materials properties.

When gas molecules are adsorbed on a solid surface, the equilibrium at the gas-solid interface can be expressed by Equation 1:

\[ f(n, p, T) = 0 \]  \hspace{1cm} (1)

where, \( n \) is an amount of gas adsorbed on the clean solid surface (mol/g),

\( p \) is an equilibrium pressure,

\( T \) is a temperature.

At constant temperature, Equation 1 describes the adsorption isotherm:

\[ n = f(p)_T \]  \hspace{1cm} (2)
Regardless of the data obtaining method, the data are presented as the amount of gas adsorbed vs. pressure. According to Eq. 1 and 2 the quantity of gas adsorbed should be expressed in mol/g, however, the data recorded by gas sorption analyzers are usually given in cm$^3$STP/g, which is a volume of adsorbate at standard temperature and pressure and needs unit conversion to be used for further calculations. The pressure is usually expressed as relative pressure defined as equilibrium vapor pressure divided by saturation vapor pressure.

In general, adsorption depends on the size and shape of gas molecules and the roughness of solid surface (nonporous or porous). Among many standard gasses available, volumetric method most commonly utilizes nitrogen and argon, both at 77K, and argon at 87K. Since the adsorption mechanism depends on the size of pores, IUPAC classifies the latter into 3 regimes: very small pores below 2nm, pores between 2 and 50 nm and pores exceeding 50 nm called micropores, mesopores and macropores, respectively.

In the case of micropores, adsorption occurs in the entire accessible volume of pores and is referred to as a micropore filling, which is different from the formation of a monolayer and then multilayer of adsorbate on the walls of meso- and macropores. Another feature of mesopores is a capillary condensation/evaporation occurring if there is any empty space left after multilayer adsorption and it is usually associated with the presence of adsorption-desorption hysteresis.

Adsorption isotherms of most porous solids usually fall into one of six types of adsorption isotherms according to the IUPAC classification (Scheme 3) [113, 114].
In Type I, which is characteristic for microporous materials, the adsorption increases quite rapidly at relatively low pressures to reach a plateau after filling all pores with the adsorbate. This is indicative of monolayer formation, and is quite distinct from Type II and III, where multilayer formation is observed. While, both types of isotherms (II and III) are typical for macroporous or non-porous solids, the surface properties of a given adsorbent affect the beginning of the isotherm, which may be concave (type II) or convex (type III). The latter case refers to the adsorbate-adsorbate interactions greater than those between an adsorbate and a surface. The type VI adsorption isotherm exhibits layer-by-layer adsorption on energetically highly homogeneous surfaces (non-porous or macroporous).
Types IV and V of adsorption isotherms are the only ones featured with a hysteresis loop associated with a capillary condensation in mesopores. In type IV, the initial part of isotherm is analogous to that observed in type II and corresponds to the formation of a mono- and multilayer of adsorbate on a surface, which then is followed by instant capillary condensation in mesopores. Based on the relation between the radius of pores and the relative pressure at which the condensation step occurs (Kelvin–type equation), one can calculate the pore size distribution for a given adsorbent. Also the steepness and the height of the capillary condensation step give the information about the uniformity of mesopores and their overall contribution to the total pore volume. Type V is also characteristic for mesoporous materials, however due to weak adsorbate-adsorbent interactions is less common.

While the adsorption branch of the isotherms is used to determine all adsorption properties of porous materials, the desorption branch provides the data about pore geometry. Based on the shape, the hysteresis loops are classified into 4 types. The H1 type is typical of uniform cylindrical pore geometries, where the adsorption and desorption branches of the capillary condensation step are almost parallel to each other. The very steep desorption branch observed for H2 type of hysteresis is indicative of the channel-like pores with some constrictions or cage-like structure. Types H3 and H4 feature fairly narrow hysteresis loops, characteristic for slit-like pores, where H3 type corresponds to the aggregates of plate-like particles assembled into slit-like pores and H4 type is associated with highly microporous materials with slit-like pores.
All adsorption and structural parameters of the carbons studied were calculated from the nitrogen adsorption isotherms obtained at -196°C on ASAP 2010 and 2020 volumetric analyzers (Micromeritics, Inc., GA) over the interval of relative pressures ranging from $10^{-6}$ to 0.995. To ensure the accuracy of measurements, all samples were outgassed at the desired temperature (usually at 200°C) for at least 2 hrs prior to adsorption in order to remove traces of solvents or gasses adsorbed after synthesis.

**Specific surface area and pore volume**

The major method to evaluate the specific surface area is the Brunauer-Emmet-Teller (BET) [115]. The number of gas molecules adsorbed on the surface in a monolayer called monolayer capacity ($n_m$) is obtained by fitting the experimental data into the linear form of the BET equation:

$$\frac{p/p_o}{n (1-p/p_o)} = \frac{(C -1)}{n_mC} (p/p_o) + \frac{1}{n_mC}$$

(3)

where, $n$ is the amount adsorbed, and $C$ is the BET constant.

The obtained monolayer capacity, after unit conversion from [cm$^3$/STP/g] to [mol/g] can be used to calculate the specific surface area $S_{BET}$ (m$^2$/g):

$$S_{BET} = n_mN_0\omega_0$$

(4)

where, $N_0$ is the Avogadro constant and $\omega_0$ is the cross sectional area of the adsorbate molecule (0.162x10$^{-18}$ m$^2$/molecule for nitrogen).

The single point total pore volume is the amount adsorbed at 0.99 $p/p_o$, which is the cumulative volume of micro- and mesopores.
**Pore size distribution**

The pore size distributions (PSDs) were calculated according to the Kruk-Jaroniec-Sayari (KJS) method [116], which is based on the Barrett-Joyner-Halenda (BJH) algorithm [117] developed for the calculation of PSD from gas adsorption isotherms under the assumption of cylindrical pore geometry.

The concept of the BJH algorithm is based on the modified Kelvin equation (5), which links the pore width \( w \) (nm) to the relative condensation pressure:

\[
w = \frac{-4\gamma V_L}{RT \ln(p/p_o)} + 2t(p/p_o) + c
\]

where, \( \gamma \) is the surface tension (8.88x10^{-3} N/m for liquid nitrogen at -196°C), 
\( V_L \) is the molar volume of liquid adsorbate (34.68 cm³/mol for liquid nitrogen), 
\( R \) is the ideal gas constant (8.314 J/molK), 
\( T \) is the absolute temperature, 
\( t(p/p_o) \) is the statistical film thickness (nm), 
\( c \) is the empirical correction (nm)

The correct estimation of the pore sizes is possible if the statistical film thickness and the relation between the pore size and condensation pressure (Kelvin-type relation) are accurate. The nitrogen and argon adsorption data for a series of MCM-41 samples (OMSs with hexagonal arrangement of cylindrical mesopores) were used to obtain the aforementioned relations and employ them in the BJH algorithm. The resulting method of

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pore size analysis, known as the Kruk-Jaroniec-Sayari (KJS) method, was developed for siliceous materials with cylindrical mesopores [116, 118, 119]. Initially, the KJS method was calibrated for nitrogen at -196 °C in the mesopores range from about 2 to 7 nm [116]; this calibration has been recently extended up to 10 nm [118]. Also, the appropriate relations have been derived for argon adsorption at -196 °C [119]. For both nitrogen and argon at -196 °C the relation between the pore width \( w \) (nm) and the condensation relative pressure \( \frac{p}{p_0} \) in the range of mesopore diameters from about 2 to 10 nm can be approximated by the following Kelvin-type expression:

\[
w = -a \frac{\log(bp/p_0)}{2t} + c\]

(6)

where \( a, b \) and \( c \) are the best-fit parameters (see Table 1) estimated on the basis of argon and nitrogen adsorption isotherms at -196 °C measured for a series of hexagonally ordered mesoporous silicas of known pore diameters, and \( t \) is the statistical film thickness (nm).

**Table 1.** Parameters of eq 1 for argon and nitrogen at -196 °C estimated on the basis of adsorption data for a series of MCM-41 samples.$^a$

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>ref.</th>
<th>( a ) (nm)</th>
<th>( b )</th>
<th>( c ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Argon</td>
<td>[121]</td>
<td>1.079</td>
<td>0.826</td>
<td>0.69</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>[120]</td>
<td>1.149</td>
<td>0.875</td>
<td>0.27</td>
</tr>
</tbody>
</table>

$^a$Eq 6 with the parameters listed in this table can be used in the range of mesopores from 2 to about 12 nm.
Choma et al. [122] studied the applicability of the KJS pore size analysis method developed for siliceous materials with cylindrical mesopores to novel channel-like mesoporous carbons obtained by soft-templating synthesis. This study showed that a simple replacement of the statistical film thickness curves (t-curves) for argon and nitrogen on the silica surface at -196 °C by the corresponding t-curves on the carbon surface makes the KJS method applicable for pore size analysis of carbons with cylindrical mesopores. Moreover, the improved KJS method can be easily adopted for the pore size analysis of channel-like OMCs in the range of pore widths from 2 to 10 nm because for this range the relation (6) was calibrated by using hexagonally ordered silicas with cylindrical mesopores [118]. A comparative study of the KJS PSD curves with those obtained by the DFT method [118] demonstrated that the aforementioned range can be extended by about 1 nm in the direction of small pores and by about 2 nm in the direction of large pores, making the improved KJS method applicable for the pore range between 1 and 12 nm. The integration of the PSD peak up to 3-4 nm gives the volume of micropores and small mesopores, which are often called ascomplementary pores.

2.1.2 POWDER X-RAY DIFFRACTION (XRD)

The small angle X-ray diffraction measurements were performed to determine structural ordering of the samples studied. The wide angle XRD patterns were used to identify the presence of crystalline domains of inorganic species embedded into carbon framework. X-ray diffraction measurements were performed on a PANalytical X’Pert PRO MPD X-ray diffraction system using Cu Kα radiation (40 kV, 40mA). Small angle powder XRD
measurements were conducted in the range of $0.4^\circ \leq 2\theta \leq 3.5^\circ$, with a $0.01^\circ$ step size and a 20s step time, while wide angle patterns were recorded using $0.02^\circ$ step size and 4sec per step in the range of $5^\circ \leq 2\theta \leq 70^\circ$. All measurements were conducted at room temperature. Samples were manually ground and spread onto either a glass slide (small angle analysis) or an Al sample holder.

### 2.1.3 TRANSMISSION AND SCANNING ELECTRON MICROSCOPY (TEM AND SEM)

High-resolution transmission electron microscopy (HRTEM) was employed for imaging mesoporous carbon-$\alpha$-alumina nanosheets samples using field-emission gun energy-filtering high-resolution analytical scanning transmission electron microscope Tecnai F30 (FEI Company, Hillsboro, Oregon) with the acceleration voltage of 300 kV. Prior to the HRTEM analysis, fine-ground samples were dispersed by 5 min ultrasonication in alcohol and then transferred onto Cu grids, and dried under an IR heat lamp.

The morphology of the composites under study was examined using a scanning electron microscope (SEM, Model S-4500, Hitachi, Tokyo, Japan) at 5 kV accelerating voltage. Prior to the SEM analysis, the samples were ground into fine powder, attached to aluminium holders using a conductive carbon tape, and subsequently sputtered with a thin layer of palladium. These measurements were performed in collaboration with Dr. Suchanek from Sawyer Technical Materials, LLC.

The second laboratory where the TEM imaging was performed was at the Center for Nanophase Materials Sciences, which is sponsored by the Oak Ridge National Laboratory,
Division of Scientific User Facilities of the US Department of Energy. TEM images of the samples were taken on a Hitachi HD-2000 scanning and transmission electron microscope (STEM). The unit was operated at an accelerating voltage of 200 kV and an emission current at 30 mA.

2.1.4 THERMOGRAVIMETRIC ANALYSIS, CHNS ELEMENTAL ANALYSIS AND INFRARED SPECTROSCOPY

Thermogravimetric analysis was performed using a TA Instrument Hi-Res TGA 2950 Thermogravimetric Analyzer (New Castle, DE, USA) from 30 to 800ºC under nitrogen or air flow with a heating rate of 10 ºC/min. This instrument is equipped with an open platinum pan and an automatically programmed temperature controller. All TG data were recorded in the high-resolution mode, in which the heating mode is adjusted automatically to achieve the best resolution.

The elemental analysis of carbon, hydrogen and nitrogen was performed using a LECO CHNS-932 elemental analyzer (St. Joseph, MI).

FT-IR spectra were collected using a Bruker Vector 22 FT-IR Spectrometer in the frequency range of 4000-500 cm⁻¹ in order to confirm the presence of specific functionalities and species introduced into the final carbon materials.

2.2 MATERIALS AND REAGENTS

Poly(ethylene oxide) – poly(propylene oxide) – poly(ethylene oxide) triblock copolymer (EO₁₀₆PO₇₀EO₁₀₆; Pluronic F127) used as the soft-template was generously provided by
the BASF Corp. The carbon precursors: phloroglucinol, \((C_6H_3(OH)_3; 99\%)\), resorcinol \((C_6H_4(OH)_2; 98\%)\), and formaldehyde (HCHO) were purchased from Acros Organics. The organosilanes: tetraethyl orthosilicate (TEOS, 98\%) was acquired from Acros Organics, Tris(3-trimethoxysilylpropyl)isocyanurate (ICS, 95\%) from Gelest, Inc. Morrisville, PA. \(\text{Al}_2\text{O}_3\) nanoparticles suspension (50nm) was provided by Nyacol Nanotechnologies Inc., whereas silica nanoparticles (20nm and 50nm) by Precision Colloids, LLC. Solvents: HCl (35-38\%) from Fischer, ethanol (95\%) from Pharmco and HF (48-51\%) from Acros Organics. Deionized water was obtained using in-house Milipore Mili-Q water purification system. All chemicals were used as received without further purification.

2.3 GENERAL SYNTHESIS PROCEDURE TO OBTAIN THE SOFT-TEMPLTED CARBONS

For the synthesis of the materials studied two slightly different recipes were used [13, 98]. The main difference was the amount of hydrochloric acid added to the synthesis mixture, which was actually governed by the choice of carbon precursor used. In the case of phloroglucinol [13], which has trihydroxyl substituted benzene ring, 0.5M HCl was usually used to obtain an optimum polymerization rate, slow enough for good self-assembly and cross-linking, and fast enough to ensure a reasonable synthesis time. On the other hand, resorcinol [98] possessing two hydroxyl groups required more acidic conditions (3M HCl) to fulfill the aforementioned needs. In general, 1.25 g of phloroglucinol or resorcinol and 1.25 g of poly(ethylene oxide)–poly(propylene oxide)–
poly(ethylene oxide) triblock copolymer (Pluronic F127) were dissolved in 9.7 g of 10:9 weight ratio of ethanol and water solution and stirred vigorously at room temperature. After complete dissolution of copolymer 0.08 ml or 1.1ml of 37% HCl was added to the solution as a catalyst and stirred for additional half an hour until a light pink color appeared. Then, 1.25 ml of 37% formaldehyde was added to the synthesis mixture. The solution turned cloudy after 30 min and after additional 1–2 h it separated into two layers. The upper phase consisting mostly of water and ethanol, was removed while the bottom polymer-rich phase was transferred onto a Petri dish for solvent evaporation and then cured in the oven at 100ºC for 24 h. A thermal treatment and carbonization of the resulting carbon were performed in the tube furnace under nitrogen flow using the following heating profile: 2ºC/min up to 180ºC, holding at 180ºC for 5 h, again heating 2ºC/min in the range of 180–400ºC and 5ºC/min in the range of 400ºC to a desired final temperature (up to 1000ºC). After reaching the final temperature the sample was kept in flowing nitrogen for 2 h.

It was found that the slow heating rate up to 400ºC and thermosetting step (at 180ºC) are especially important for obtaining good quality materials.

Any other modifications done to the aforementioned recipes will be accounted for in each section separately.
CHAPTER 3

TAILORING PROPERTIES OF SOFT-TEMPLATED MESOPOROUS CARBONS†

Until now the research on the organic–organic self-assembly synthesis of OMCs under acidic conditions has been mostly focused on the introduction of new precursors [13], except the effect of acid concentration [98]. Therefore, some systematic studies were performed in order to gain better understanding of this process. As reported for ordered mesoporous silicas (OMSs) [123–126], the structure of the resulting materials can be easily modified by changing synthesis conditions. Therefore, in this work we investigated the impact of reaction temperature, block copolymer/carbon precursor ratio and acid concentration on the adsorption and structural properties of soft-templated OMCs. This study shows that an increase in temperature of the initial self-assembly process causes a decrease in the total pore volume and pore width. However, an increase in the copolymer/carbon precursor ratio results in a change of the structure from channel-like to cage-like. This change is more pronounced for the samples prepared at higher temperatures. In addition, the pore volume decreases as the polymer/carbon precursor ratio increases.

Triblock copolymer Pluronic F127, PEO$_{106}$-PPO$_{70}$-PEO$_{106}$ and phloroglucinol in amounts listed in Table 1, were dissolved in 5.95 mL of ethanol and 4.30 mL of water contained in a 60 mL polypropylene bottle under magnetic stirring at a specified

temperature, 15, 25, 40, or 55°C. The mixture was stirred until the entire solid was
dissolved, usually for 20 minutes. Next, 0.08 mL of 37% HCl was added to the mixture and
the sample was stirred until a pink color appeared, after 30 minutes and 2.5 hours. At that
point, 1.25 mL of formaldehyde was added to the solution and stirred until it became
cloudy. Once the sample became turbid, between one hour and up to no more than 24
hours, it was allowed for the phase separation; the aqueous layer was decanted off and the
remaining polymer layer was stirred overnight. In the next stage, the resulting sample was
transferred to an autoclave and kept in an oven at 100°C for 24 hours. Finally, the sample
was dried in a vacuum oven followed by carbonization in a tube furnace under the
following settings: 180°C for 5 hours, 2°C/min from 180°C-400°C, 5°C/min from 400°C-
850°C, and finally 850°C for 2 hours. The samples were labeled according to the formula
xC-y, where x stands for the reaction temperature (15, 25, 40 and 55°C, respectively) and y
denotes the block copolymer/carbon precursor ratio (see Table 1).

Also, a series of carbon samples was prepared by varying acid concentration, whereas
the reaction temperature was kept at 25°C and 1:1 block copolymer/carbon precursor ratio.
The latter samples were denoted as 25C-1:1-aM, where a refers to the acid concentration
(in moles).

<table>
<thead>
<tr>
<th>Block Copolymer/Carbon Precursor Ratio</th>
<th>Pluronic F127/g</th>
<th>Phloroglucinol/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>1.2500</td>
<td>1.2500</td>
</tr>
<tr>
<td>2:1</td>
<td>1.6700</td>
<td>0.8350</td>
</tr>
<tr>
<td>3:1</td>
<td>1.8500</td>
<td>0.6477</td>
</tr>
<tr>
<td>4:1</td>
<td>2.0000</td>
<td>0.5000</td>
</tr>
</tbody>
</table>
3.1 EFFECT OF TEMPERATURE

In the first part of this project all samples were prepared by varying synthesis temperature, while the copolymer to carbon precursor ratio remained the same (1:1). The nitrogen adsorption isotherms and the corresponding pore size distributions (PSDs) curves are shown in Figure 1. Adsorption isotherms measured on the carbons synthesized between 15°C and 40°C are of type IV with H1 hysteresis loops observed for cylindrical mesopores. The steep capillary condensation steps indicate that the corresponding PSD curves are narrow (see panel B on Figure 1). In contrast, the sample synthesized at 55°C exhibits much broader capillary condensation step as well as a stepwise desorption curve, which suggests the existence of pores with different openings. An increase in the synthesis temperature from 40°C to 55°C results in considerable structural changes. As can be seen from Table 2 all samples throughout the series possess the moderate BET surface areas of ~400-500 m²/g. The sample synthesized at 15°C exhibits quite a high total pore volume (0.78 cm³/g) with the main contribution coming from large mesopores (around 10.2 nm). A further increase in the temperature results in a gradual decrease in the surface area, pore volume and pore size. Even though the BET surface area for the sample prepared at 55°C is in good agreement with the results for the first three samples, the other structural properties suffer a significant loss. For this reason the latter temperature was excluded from further studies.
Table 3. Adsorption parameters for the phenolic resin-based carbons studied.\(^a\)

<table>
<thead>
<tr>
<th>Sample</th>
<th>(S_{\text{BET}}) ((\text{m}^2/\text{g}))</th>
<th>(V_t) ((\text{cm}^3/\text{g}))</th>
<th>(V_{\text{mi}}) ((\text{cm}^3/\text{g}))</th>
<th>(w_{\text{KJS}}) ((\text{nm}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>15C-1:1</td>
<td>455</td>
<td>0.78</td>
<td>0.02</td>
<td>10.2</td>
</tr>
<tr>
<td>15C-3:1</td>
<td>476</td>
<td>0.74</td>
<td>0.02</td>
<td>16.1</td>
</tr>
<tr>
<td>15C-4:1</td>
<td>486</td>
<td>0.59</td>
<td>0.05</td>
<td>12.1</td>
</tr>
<tr>
<td>25C-1:1</td>
<td>499</td>
<td>0.74</td>
<td>0.03</td>
<td>9.6</td>
</tr>
<tr>
<td>25C-3:1</td>
<td>428</td>
<td>0.65</td>
<td>0.04</td>
<td>13.6</td>
</tr>
<tr>
<td>25C-4:1</td>
<td>490</td>
<td>0.70</td>
<td>0.04</td>
<td>13.7</td>
</tr>
<tr>
<td>40C-1:1</td>
<td>466</td>
<td>0.71</td>
<td>0.03</td>
<td>9.6</td>
</tr>
<tr>
<td>40C-3:1</td>
<td>480</td>
<td>0.42</td>
<td>0.06</td>
<td>7.8</td>
</tr>
<tr>
<td>40C-4:1</td>
<td>423</td>
<td>0.30</td>
<td>0.07</td>
<td>6.2</td>
</tr>
<tr>
<td>55C-1:1</td>
<td>394</td>
<td>0.35</td>
<td>0.06</td>
<td>8.7</td>
</tr>
<tr>
<td>25C-1:1-0.5M</td>
<td>495</td>
<td>0.72</td>
<td>0.04</td>
<td>10.2</td>
</tr>
<tr>
<td>25C-1:1-1M</td>
<td>464</td>
<td>0.73</td>
<td>0.05</td>
<td>11.4</td>
</tr>
<tr>
<td>25C-1:1-3M</td>
<td>447</td>
<td>0.58</td>
<td>0.03</td>
<td>9.1</td>
</tr>
</tbody>
</table>

\(^a\) \(S_{\text{BET}}\) - BET surface area; \(V_t\) - single-point pore volume; \(V_{\text{mi}}\) - volume of micropores; \(w_{\text{KJS}}\) - mesopore width at the PSD maximum [118].

Figure 1. Nitrogen adsorption isotherms (A) and the corresponding pore size distributions (B) for soft-templated carbons synthesized at different temperatures by using 1:1 polymer-carbon precursors mass ratio.
3.2 EFFECT OF POLYMER-TO-CARBON PRECURSOR RATIO

Three series of samples were synthesized at different temperatures by varying the copolymer-to-carbon precursor ratio: 1:1, 3:1, and 4:1. All of the samples synthesized at 15°C (Figure 2A) exhibit type IV isotherms with H1 hysteresis loops which are characteristic for fully accessible channel-like mesopores. An increase in the copolymer/carbon precursor ratio caused a decrease in the total pore volume from 0.78 to 0.59 cm\(^3\)/g. The mesopore volume follows the same trend. The PSD curves show that the pore widths are shifted towards larger pores but at the same time the pore size distributions become much broader for the samples obtained with a higher copolymer/carbon ratio. The BET surface area was found to be in the range of 455-486 m\(^2\)/g. Even though the higher ratio facilitates the formation of micropores, the microporosity contributes as little as 10% to the total pore volume.

In the case of the samples synthesized at 25°C the corresponding nitrogen isotherms also indicate the presence of uniform, cylindrical pores. As shown in Figure 2B, these samples exhibited analogous changes in their structural properties to the previously discussed series, although these changes are less pronounced. An interesting feature of this series is that the samples prepared at 3:1 and 4:1 copolymer/carbon precursor ratios exhibited very similar structural properties. This suggests that after a certain ratio is reached, its further increase does not affect the structure much.
**Figure 2.** Nitrogen adsorption isotherms (A-C) and the corresponding pore size distributions (D-F) for the carbons synthesized by using different copolymer/carbon precursor ratios at 25°C.
Nitrogen adsorption isotherms measured for the carbon samples synthesized at 40°C feature significant changes with an increasing polymer/carbon ratio (Figure 2C). All isotherms can be classified as type IV but not all of them present the same type of the hysteresis loop. Analogously to the previous findings, the sample with 1:1 ratio exhibited the H1 hysteresis loop characteristic for channel-like structures. While the shapes of isotherms for the samples with a higher copolymer to carbon precursor ratio are close in appearance to the H2 hysteresis loops, which is typical for cage-like structures or porous structures with constrictions. This suggests a possible transition from a channel-like to a cage-like structure. The 3:1 sample can be considered as a transitional one. In the case of the 40C-4:1 sample, the absence of the sharp capillary condensation step suggests the formation of non-uniform pores, while a delay in desorption (which ends at the lower limit of hysteresis closure, i.e., at about 0.4 for nitrogen at -196°C) implies the existence of small pore openings below 5nm. Those results suggest two possibilities: the presence of cage-like structure with irregular cages or a channel-like structure with constrictions. The structure transformation seen through the series strongly affects the adsorption parameters; the total pore volume and mesopore volume are greatly reduced, the latter by as much as 4 times compared to the sample for 1:1 ratio. The same trend is observed for the corresponding pore size distributions (Figure 2D-F), which become broader and shift toward smaller pores. Even though the micropore fraction increased in the case of the 40C-3:1 and 40C-4:1 samples compared to 40C-1:1 carbon, the overall properties of this series are rather poor in contrast to the two previous sets of carbons.
3.3 EFFECT OF ACID CONCENTRATION

Finally, a series of samples was synthesized with different acid concentrations while the temperature and copolymer to carbon precursor ratio (25°C and 1:1, respectively) were kept constant. As shown in Figure 3, all isotherms measured for this series of carbons exhibit type IV with H1 hysteresis loop characteristic for channel-like mesoporous structures. The isotherms show that the total adsorption drops as acid concentration increases. Interestingly, there are no distinct changes in the low relative pressure range indicating that the acid concentration does not affect microporosity. The samples prepared with less concentrated acid exhibit a less steep capillary condensation step than the carbon synthesized with 3M HCl, which translates to broader pore size distributions. Besides that, the latter samples show mesopore peak maximum shifts towards smaller pores. TEM images presented in Fig. 4 revealed worm-like structure for all three samples prepared with different acid concentrations.
Figure 3. Nitrogen adsorption isotherms (A) and the corresponding pore size distributions (B) for carbons synthesized at different acid concentrations.

Figure 4. TEM images for 25C-1:1-0.5M (panel A), 25C-1:1-1M (panel B) and 25C-1:1-3M (panel C) carbons.
A few series of mesoporous carbons were synthesized at different temperatures by varying the block copolymer/carbon precursor ratio and acid concentration. It was shown that an increase in the synthesis temperature results in a decrease in the pore volume and the pore width. However, an increase in the copolymer/carbon precursor ratio causes a structural transformation from channel-like to cage-like. This change is more pronounced for the carbon samples synthesized at higher temperatures and higher copolymer/carbon precursor ratios. This transformation also leads to a decrease in the volume of mesopores. In addition, it was found that the acid concentration strongly affects the size and uniformity of mesopores created during the self-assembly process.
CHAPTER 4

ORGANOSILANE-ASSISTED SYNTHESIS OF MESOPOROUS CARBONS

The self-assembly of resorcinol, formaldehyde and block copolymer combined with polymerization and proper thermal treatment affords mesoporous polymers and carbons with a high surface area, large pore volume and a well-developed mesoporosity. The addition of organosilanes into this process opens new possibilities for tailoring adsorption, surface and framework properties of these materials as well as for expanding their porosity. It is shown that the use of heterocyclic organosilanes in the aforementioned soft-templating synthesis affords heteroatom-doped mesoporous carbons, the properties of which can be further modified by controlled dissolution of silica species that results in substantial microporosity in these materials.

In the first part of this study TEOS was employed in the preparation of these materials to examine how acidic polymerization conditions affect the TEOS incorporation into the carbon framework. Moreover, our goal was to show that the TEOS addition can be used to improve and easily tune microporosity in the final carbons. However, the main goal of this study was to introduce much larger organosilane than TEOS to obtain mesoporous polymers with functional groups. The use of organosilane such as tris(3-trimethoxysilylpropyl)isocyanurate (ICS) afforded mesoporous phenolic resins with high loadings of the ICS groups, which after carbonization became carbon mesostructures doped with Si and N atoms. A broad variety of commercially available organosilanes gives a lot

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of freedom in the design of mesoporous phenolic resins with various organic groups, which can be converted to heteroatom-doped carbon mesostructures with desired properties after carbonization, e.g., their hydrophilicity [127, 128] can be easily modified by controlled removal of silica from the pore walls [127].

Mesoporous carbons were synthesized according to a modified recipe of Wang et al. [98]. Approximately 1.25g of resorcinol and 1.25g of poly(ethylene oxide) – poly(propylene oxide) – poly(ethylene oxide) triblock copolymer (Pluronic F127) were dissolved in deionized water and ethanol. The weight ratio of water to ethanol was fixed to be 5.5:10. After stirring for about 10-15min, the reaction mixture was supplied with 1.1ml of 37%HCl and kept under stirring for an additional 30min. Subsequently, 1.25ml of formaldehyde and various amounts of TEOS were added to the synthesis mixture. When the resulting solution turned milky and after additional 30min of stirring the aqueous and solid phases were allowed to separate. The polymer-containing bottom layer obtained after separation was spread on a Petri dish and left under the fume hood overnight. Then, the sample was aged at 100ºC for 24h. Thermal treatment was performed under nitrogen atmosphere in the tube furnace using a heating rate of 2ºC/min up to 180ºC, keeping the sample at this temperature for 5hr, and resuming the heating at 2ºC/min up to 400ºC. Further thermal treatment was performed as follows: in the synthesis of porous polymers the samples were kept at 400ºC for 2hr, whereas, in the synthesis of carbons the samples were heated from 400ºC to 850ºC using the heating rate of 5ºC/min and kept at 850ºC for 2 hrs.
A second series of the samples was prepared using ICS instead of TEOS whereas the rest of synthesis route remained the same. In contrast to the previous series, ICS was added 20min after the addition of formaldehyde.

The resulting materials were labeled M-Sxt, where M indicates the type of material (P = polymer, C = carbon or S = silica), S refers to silane used (T = TEOS or I = ICS), x denotes to the weight percentage of silane in the sample and t indicates the post-synthesis treatment (HF = silica dissolution in 15%wt. HF or c = calcination in air at 550ºC for 2hr).

4.1 MESOSTRUCTURED MATERIALS PREPARED FROM PHENOLIC RESIN AND TEOS

Our goal was to obtain mesoporous carbon-silica composites and related materials using different carbon precursors and polymerization conditions than those proposed by Liu et al [36]. The latter report showed that the self assembly of phenol-formaldehyde and triblock copolymer in basic media affords carbons with relatively small mesopores (~3nm). The addition of the third component (TEOS) to the latter system caused a significant increase in the pore widths up to ~6nm.

On the other hand, it has been reported that the polymerization of resorcinol and formaldehyde is greatly enhanced under highly acidic conditions [98] leading to the materials with larger mesopores compared to those obtained in basic media (6.3nm vs. 2.9nm, respectively). Based on that, we had seen the need to investigate the co-assembly
of a resorcinol-formaldehyde/TEOS system under acidic conditions. An illustration of this organosilane-assisted synthesis is shown in Scheme 4.

Nitrogen adsorption isotherms and the corresponding pore size distributions (PSDs) for two representative sets of polymer-silica, carbon-silica and carbon materials prepared with TEOS content of 30 and 60wt.% are shown in Figure 5. All isotherms show type IV with H1-type of hysteresis loops, which clearly indicates the uniform and well-developed mesoporous structures. In both cases, the capillary condensation steps for polymer-silica composites are located at 0.7-0.8 p/p₀, which corresponds to quite large mesopores of ~ 8-10nm (see Table 3).

After carbonization at 850°C, the total adsorption of the carbon-silica samples is slightly reduced and the capillary condensation steps shifted towards smaller pores due to materials shrinkage at high temperatures. However, the biggest changes are observed for the samples treated with HF in order to remove silica. While the mesoporous structure is not altered much, there is a significant increase in adsorption at the lower range of relative pressures compared to the carbon-silica composites. Especially for the series with higher TEOS loading, the microporosity evolution can be clearly seen on the PSD curves in the range up to 4nm. The structural parameters listed in Table 3 suggest excellent adsorption properties of the samples studied. The high BET surface areas (range from 500 to 700m²/g) are characteristic for all polymer- and carbon-silica composites.
**Scheme 4.** Soft-templating strategy for the synthesis of mesoporous polymers and carbons involving polymerization of resorcinol and formaldehyde in the presence of block copolymer and organosilane (TEOS or ICS) under acidic conditions$^\text{a}$

$^\text{a}$ Initially, the polymeric mesostructure is formed, which after thermal treatment in flowing nitrogen at 400 °C gives mesoporous phenolic resin with incorporated organosilane (mesoporosity is formed due to the decomposition of block copolymer template) and after subsequent carbonization this resin transforms to mesoporous carbons doped with inorganic species depending on the organosilane used. Additional treatment of this carbon with HF or NaOH solutions removes silica species, which results in the creation of substantial microporosity.
Table 4. Adsorption parameters for mesoporous polymer and carbon samples obtained by co-assembly of resorcinol, formaldehyde and TEOS.\(^a\)

<table>
<thead>
<tr>
<th>Sample</th>
<th>(S_{\text{BET}}) (\text{m}^2/\text{g})</th>
<th>(V_t) (\text{cc/g})</th>
<th>(V_{\text{mi}}) (\text{cc/g})</th>
<th>(V_{\text{me}}) (\text{cc/g})</th>
<th>(w_{\text{KJS}}) (\text{nm})</th>
<th>(\text{SiO}_2) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-T30</td>
<td>651</td>
<td>0.70</td>
<td>0.12</td>
<td>0.54</td>
<td>8.2</td>
<td>8.9</td>
</tr>
<tr>
<td>C-T30</td>
<td>690</td>
<td>0.62</td>
<td>0.07</td>
<td>0.44</td>
<td>7.1</td>
<td>10.4</td>
</tr>
<tr>
<td>C-T30HF</td>
<td>854</td>
<td>0.74</td>
<td>0.13</td>
<td>0.51</td>
<td>6.8</td>
<td>2.9</td>
</tr>
<tr>
<td>P-T60</td>
<td>607</td>
<td>0.84</td>
<td>0.11</td>
<td>0.72</td>
<td>10.5</td>
<td>39.2</td>
</tr>
<tr>
<td>C-T60</td>
<td>497</td>
<td>0.66</td>
<td>0.04</td>
<td>0.57</td>
<td>9.9</td>
<td>42.8</td>
</tr>
<tr>
<td>C-T60HF</td>
<td>1462</td>
<td>1.42</td>
<td>0.47</td>
<td>0.97</td>
<td>9.6</td>
<td>6.0</td>
</tr>
</tbody>
</table>

\(^a\)Notation: \(S_{\text{BET}}\) – BET specific surface area; \(V_t\) – single-point pore volume; \(V_{\text{mi}}\) – volume of fine pores (mainly micropores) obtained by integration of PSD up to 4 nm; \(V_{\text{me}}\) – volume of mesopores obtained by integration of PSD from 4 nm to 20 nm; \(w_{\text{KJS}}\) – mesopore diameter at the maximum of the PSD curve obtained by the improved KJS method [118], \(\text{SiO}_2\)% – residue obtained from the TG curve recorded in air at 800°C.

Figure 5. Nitrogen adsorption isotherms (A) and the corresponding pore size distributions (B) for mesoporous polymers and carbons prepared using phenolic resin and TEOS. For clarity, the nitrogen adsorption isotherms denoted with triangles were offset by 375 \(\text{cm}^3\) STP/g, and the corresponding pore size distributions by 0.25 \(\text{cm}^3\)/g.nm.
The latter also displayed a relatively high total pore volume (0.62-0.84 cm$^3$/g) with the main contribution coming from the mesopores. Initially small amounts of micropores in the carbon-silica composites can be easily increased by silica dissolution, which proves that TEOS species were evenly incorporated into the carbon framework during the self-assembly process. Depending on the amount of TEOS added to the synthesis mixture not only microporosity can be increased but also other parameters such as the BET surface area, mesopore volume and the total volume of pores, can be enhanced. The development of mesoporosity in the resulting carbon samples is particularly interesting. It can be affected by a partial blockage of mesopores and by the accumulation of TEOS at the block copolymer and phenolic resin interface; note that an increase of TEOS from 30 to 60 wt.% caused an increase of the mesopore width from 6.8 to 9.6 nm (Table 3), whereas the BET surface area and pore volumes increased even more pronouncedly. Remarkably, the C-T60HF carbon exhibited a high specific surface area of 1462 m$^2$/g, the total pore volume of 1.42 cm$^3$/g and a more than 11 times larger volume of micropores in comparison to that for the corresponding carbon-silica composite.

An additional set of samples was synthesized to investigate the effect of gradually increasing amount of TEOS (from 10 to 70 wt.% ) on the structural properties of silica-carbon and carbon materials. Nitrogen adsorption isotherms of the carbon-silica composites (Fig.6) show that the capillary condensation steps shift progressively towards higher relative pressures, indicating an enlargement of mesopores with increasing TEOS content. However, this trend seems to be suppressed when TEOS loading is higher than 60 wt%. After silica etching, the resulting carbons exhibit much higher adsorption at
lower relative pressures, which is especially well pronounced for the C-T50HF, C-T60HF and C-T70HF carbons (Fig. 7). As can be seen from Table 4, all changes in physicochemical properties of the materials studied are consistent with the amount of the TEOS used. In general, the resorcinol-formaldehyde-TEOS co-assembly under acidic conditions results in the materials with much larger mesopores (up to 9.6nm) compared to the carbons synthesized from phenol-formaldehyde in the presence of TEOS under basic conditions, where the maximum pore widths achieved were ~6.7nm. The small angle XRD profiles for the entire series of carbon-silica composites (Fig 8) show some ordering of mesopores when the silica loading do not exceed 40%. For illustration, the mesoporous silicas obtained by burning off the carbon component in the carbon-silica composites with the highest TEOS loadings are shown in Fig. 9.
Table 5. Physicochemical properties of polymer, carbon and silica materials synthesized by polymerization of resorcinol and formaldehyde in the presence of TEOS and block copolymer under acidic conditions followed by controlled thermal treatment in flowing nitrogen.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{\text{BET}}$ m$^2$/g</th>
<th>$V_t$ cc/g</th>
<th>$V_{\text{mi}}$ cc/g</th>
<th>$V_{\text{me}}$ cc/g</th>
<th>$w_{\text{KJS}}$ nm</th>
<th>$\text{SiO}_2$ %</th>
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</thead>
<tbody>
<tr>
<td>C-T10</td>
<td>796</td>
<td>0.69</td>
<td>0.08</td>
<td>0.48</td>
<td>6.5</td>
<td>4.0</td>
</tr>
<tr>
<td>C-T20</td>
<td>810</td>
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<td>0.09</td>
<td>0.53</td>
<td>7.1</td>
<td>5.7</td>
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<tr>
<td>C-T30</td>
<td>690</td>
<td>0.62</td>
<td>0.07</td>
<td>0.44</td>
<td>7.1</td>
<td>10.4</td>
</tr>
<tr>
<td>C-T40</td>
<td>659</td>
<td>0.61</td>
<td>0.07</td>
<td>0.44</td>
<td>7.1</td>
<td>14.0</td>
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<td>0.05</td>
<td>0.55</td>
<td>8.7</td>
<td>29.8</td>
</tr>
<tr>
<td>C-T60</td>
<td>497</td>
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<td>0.57</td>
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<td>42.8</td>
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<tr>
<td>C-T70</td>
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<td>0.48</td>
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<tr>
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<td>1.9</td>
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<td>C-T30HF</td>
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<td>0.51</td>
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<td>C-T40HF</td>
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<td>6.0</td>
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<td>10.2</td>
</tr>
<tr>
<td>P-T30</td>
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<td>0.54</td>
<td>8.2</td>
<td>8.9</td>
</tr>
<tr>
<td>P-T60</td>
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<td>0.72</td>
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</tr>
<tr>
<td>S-T60c</td>
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<td>0.07</td>
<td>0.95</td>
<td>6.6</td>
<td>-</td>
</tr>
<tr>
<td>S-T70c</td>
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<td>0.94</td>
<td>0.08</td>
<td>0.87</td>
<td>8.1</td>
<td>-</td>
</tr>
</tbody>
</table>

*aNotation: $S_{\text{BET}}$ – BET specific surface area; $V_t$ – single-point pore volume; $V_{\text{mi}}$ – volume of fine pores (mainly micropores) obtained by integration of PSD up to 4 nm; $V_{\text{me}}$ – volume of mesopores obtained by integration of PSD from 4 nm to 20 nm; $w_{\text{KJS}}$ – mesopore diameter at the maximum of the PSD curve obtained by the improved KJS method [118]; $\text{SiO}_2$ % – residue obtained from the TG curve recorded in air at 800°C
Figure 6. Nitrogen adsorption isotherms and the corresponding pore size distributions for mesoporous carbon-silica composites prepared by co-assembly of resorcinol, formaldehyde and TEOS in the presence of block copolymer, Pluronic F127. For clarity, adsorption isotherms for C-T20, C-T30, C-T40, C-T50, C-T60 and C-T70 were offset by 150, 350, 500, 700, 900 and 1100 cm$^3$/g STP/g, respectively, while the each successive PSD curve for these samples was offset by using the same increment of 0.2 cm$^3$/g nm.
Figure 7. Nitrogen adsorption isotherms and the corresponding pore size distributions for mesoporous carbons obtained by dissolving silica with HF solution in the carbon-silica composites (see Fig. S1). For clarity, adsorption isotherms for C-T20HF, C-T30HF, C-T40HF, C-T50HF, C-T60HF and C-T70HF were offset by 150, 350, 500, 700, 900 and 1100 cm$^3$/g STP/g, respectively, while the each successive PSD curve for these samples was offset by using the same increment of 0.2 cm$^3$/g nm.
Figure 8. Small angle XRD patterns for mesoporous carbon-silica composites.

Figure 9. Nitrogen adsorption isotherms and the corresponding pore size distributions (inset) for mesoporous silicas obtained by burning off carbon component in the carbon-silica composites.
4.2 MESOPOROUS MATERIALS PREPARED USING PHENOLIC RESIN AND ISOCYANURATE ORGANOSILANE

In contrast to the materials prepared in the presence of TEOS, where it was possible to introduce high loadings of silica into the carbon matrix, the incorporation of tris(3-trimethoxysilyl-propyl)isocyanurate (ICS) is more challenging. This large molecule composed of an isocyanurate ring linked through flexible propyl chains with three trimethoxysilyls was used as a bridging group in the synthesis of periodic mesoporous organosilicas (PMOs) [129,130]. In general, the introduction of large bridging groups require much more effort to preserve a good structural ordering at higher concentrations of these groups than in the case of using small aliphatic or aromatic bridging groups [131,132]. The silica framework can accommodate up to 90% of ICS, however, the loading exceeding 30% resulted in disordered PMOs [129]. On the other hand, the introduction of ICS into phenolic resins can enhance the physicochemical properties of the resulting carbons due to the presence of N and Si atoms in the ICS molecule [127, 133-136]. It is well known that N-doped carbons exhibit an improved conductivity, while Si addition increases hydrophilicity of the carbon surface. Taking the above issues into account, the co-assembly of phenolic resins with organosilanes possessing different heteroatoms seems to be a promising strategy for the synthesis of new hybrid nanomaterials of desired framework and surface properties.

Nitrogen adsorption isotherms and the corresponding pore size distributions for the polymer-ICS composites are presented in Figure 10. Taking into account the large size of the ICS molecule we decided to introduce a maximum of 40wt% of ICS to the samples.
As can be seen from Fig.10, the observed capillary condensation steps are steep for all ICS-containing samples, reflecting a high uniformity of mesopores. As the ICS content increases in these materials, the total amount adsorbed successively drops, reaching a minimum for the P-I30 sample and suddenly increases by doubling it for the P-I40 sample. Another interesting feature of the latter sample is a much higher adsorption at low relative pressures compared to the remaining samples, which indicates that in the case of such high organosilane content and its fast co-condensation with phenolic precursors, the formation of micropores is greatly enhanced. The additional plot (open circles) presented in Fig.10 corresponds to the polymer obtained after silica dissolution (P-I30HF) and shows the reduced adsorption in the whole range of p/p₀ with still quite steep capillary condensation step. This indicates the reduction in both micro- and mesopore volumes, which is also visible on the PSD curves, where the maximum for mesopores is shifted toward smaller pore sizes in contrast to the remaining samples.

The physicochemical properties of the materials under investigation are listed in Table 5. The BET surface areas for polymers with ICS loading up to 30% were found to be ~550m²/g, as a consequence of having the same micropore volume. However, a very high specific surface area of 1018m²/g was obtained for the P-I40 sample due to high microporosity reaching a value of 0.28cm³/g.
Figure 10. Nitrogen adsorption isotherms (A) and the corresponding pore size distributions (B) for mesoporous polymers obtained in the presence of ICS.

Figure 11. Nitrogen adsorption isotherms (A) and the corresponding pore size distributions (B) for mesoporous carbons prepared from phenolic resin with different ISC loadings.
Table 6. Adsorption parameters for the polymer and carbon samples obtained in the presence of ICS.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{BET}$ m(^2)/g</th>
<th>$V_t$ cc/g</th>
<th>$V_{mi}$ cc/g</th>
<th>$V_{me}$ cc/g</th>
<th>$w_{KJS}$ nm</th>
<th>N%</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-I10</td>
<td>569</td>
<td>0.73</td>
<td>0.12</td>
<td>0.61</td>
<td>10.0</td>
<td>1.3</td>
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<tr>
<td>P-I20</td>
<td>509</td>
<td>0.64</td>
<td>0.12</td>
<td>0.52</td>
<td>10.2</td>
<td>2.7</td>
</tr>
<tr>
<td>P-I30</td>
<td>519</td>
<td>0.59</td>
<td>0.12</td>
<td>0.46</td>
<td>9.9</td>
<td>3.4</td>
</tr>
<tr>
<td>P-I30HF\textsuperscript{*}</td>
<td>211</td>
<td>0.29</td>
<td>0.05</td>
<td>0.28</td>
<td>7.9</td>
<td>2.0</td>
</tr>
<tr>
<td>P-I40</td>
<td>1018</td>
<td>1.17</td>
<td>0.28</td>
<td>0.87</td>
<td>10.6</td>
<td>4.4</td>
</tr>
<tr>
<td>C-I10</td>
<td>701</td>
<td>0.63</td>
<td>0.07</td>
<td>0.44</td>
<td>7.5</td>
<td>0.3</td>
</tr>
<tr>
<td>C-I20</td>
<td>553</td>
<td>0.53</td>
<td>0.06</td>
<td>0.38</td>
<td>8.4</td>
<td>0.4</td>
</tr>
<tr>
<td>C-I30</td>
<td>550</td>
<td>0.50</td>
<td>0.06</td>
<td>0.34</td>
<td>8.0</td>
<td>0.9</td>
</tr>
<tr>
<td>C-I30HF\textsuperscript{*}</td>
<td>1208</td>
<td>0.86</td>
<td>0.33</td>
<td>0.42</td>
<td>7.9</td>
<td>1.4</td>
</tr>
<tr>
<td>C-I40</td>
<td>460</td>
<td>0.40</td>
<td>0.07</td>
<td>0.25</td>
<td>8.0</td>
<td>0.8</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Notation: $S_{BET}$ – BET specific surface area; $V_t$ – single-point pore volume; $V_{mi}$ – volume of fine pores (mainly micropores) obtained by integration of PSD up to 4nm; $V_{me}$ – volume of mesopores obtained by integration of PSD from 4nm to 20nm; $w_{KJS}$ – mesopore diameter at the maximum of the PSD curve obtained by the improved KJS method [118]; N% – nitrogen elemental analysis data. Thermogravimetric analysis in air of the samples denoted with asterisk revealed the presence of residual silica of ~8 and 5% for P-I30HF and C-I30HF, respectively.
The mesopore volumes show a trend to decrease as the ICS content approaches 30%, while larger ICS loading results in an increased mesopore volume (0.87 cm$^3$/g). As can be seen from the PSD curves (Fig. 10), all ICS-containing polymers possess large mesopores ~10 nm. In the case of the P-I30HF sample, the dissolution of silica lowered all adsorption parameters implying a homogenous distribution of ICS in the polymer matrix.

Shown in Figure 11 are nitrogen adsorption isotherms and the corresponding PSD curves for the carbon-ICS composites. In general, a gradual introduction of ISC groups reduced the amount of nitrogen adsorbed. Also, the observed capillary condensation steps are shifted to lower p/p$_0$ values indicating some shrinkage of the framework due to carbonization. This translates to smaller mesopores, as can be seen in the PSD curves, which show maxima at about ~8 nm that are roughly 2 nm smaller than the mesopores found in the corresponding polymer-organosilica composites. Besides that, as more ICS is introduced the capillary condensation steps became less steep, which is also reflected in the flattening of the mesopore peaks on the PSD curves. In contrast to the ICS-polymer composite (P-I30-HF), where the silica removal resulted in structure deterioration mostly due to not fully condensed polymer framework, the ICS-carbon composite treated with HF (C-I30-HF) exhibited an enhanced adsorption properties; not only in terms of much higher microporosity, but also in an enhanced mesoporosity. This carbon possessed a very high BET surface area of 1208 m$^2$/g and the total pore volume equaling 0.86 cm$^3$/g with a significant contribution arising from micropores (0.33 cm$^3$/g). For the C-I samples, untreated with HF solution, the micropore volume does not change with the increasing amount of the ICS used in the synthesis, but the mesopore volume and the total pore
volume are gradually reduced (Table 2). The mesopore widths estimated at maxima of
the PSD curves are in the range of 7.5 to 8.4nm showing some framework shrinkage
(about 20-25%) in comparison to the corresponding polymer samples, which is larger
than that for the carbons prepared without ICS addition (~15%).

The ICS loading in the samples was monitored by recording thermogravimetric profiles for the polymer-ICS composites in flowing nitrogen. Shown in Figure 12 are the differential thermogravimetric (DTG) plots, where a single decomposition event occurring at ~460°C is usually associated with the decomposition of the ICS bridging group. The continuously increasing intensity of the DTG peak proves that the ICS incorporation can be precisely controlled. Also, the data obtained from elemental analysis are in good agreement with the TG data and show a gradual increase in the amount of nitrogen in the polymer-ICS composites with the increasing amount of the ICS used. Even after carbonization at 850°C all samples still possess nitrogen in the carbon framework.

Shown in Figure 13 is a comparison of the IR spectra for the sample with 30% of ICS in the polymer matrix before and after HF treatment (P-I30 and P-I30-HF, respectively). Both spectra exhibit characteristic band at 1694cm⁻¹, which can be easily assigned to C=O vibrations in isocyanurate rings [137]. Taking into account the relative intensities, one may say that the isocyanurate rings can be partially removed during the silica dissolution, which was also shown by elemental analysis.
Figure 12. Differential thermogravimetric plots for mesoporous polymer-ICS composites.

Figure 13. FTIR spectra for mesoporous polymer containing 30% ICS before and after silica dissolution.
The band found at 1605-1610 cm\(^{-1}\) is attributed to –OH groups, while the one at 1454-1462 cm\(^{-1}\) can be assigned to aliphatic –CH\(_2\) groups in the polymer [138,139]. A broad band observed at 1047 cm\(^{-1}\) with the tiny peak at 1224 cm\(^{-1}\) is typical for Si-OCH\(_3\) and Si-CH\(_2\) groups after removing silica splits, which is usually caused by the branching of the carbon atoms close to oxygen [139]. Out of several relatively small peaks found in the range from 675 to 900 cm\(^{-1}\), the one at 764 cm\(^{-1}\) is present in both samples and can be assigned to the C-H out of plane bending vibrations.

In conclusions, the soft-templated mesoporous polymers and carbons were successfully synthesized under acidic conditions in the presence of organosilane. The main goal was to monitor the mesostructure formation as a function of the increasing amount of the organosilane used. Moreover, two different organosilanes were studied to determine how their structure and size affects the self-assembly process and mesostructure formation. In the case of small organosilanes such as TEOS, we were able to introduce up to 70 wt% of TEOS without significant structure deterioration. Significantly, TEOS is mostly embedded in the carbon framework which was proved by the remarkable increase in microporosity after silica dissolution. An analogous incorporation mechanism took place in the case of the larger organosilanes used, such as ICS. The TGA and IR data clearly show the presence of isocyanurate rings in the polymer and possibly in carbon frameworks. All samples exhibited high surface area and high pore volumes. The well-developed mesopores with diameters of about 8-10 nm assure a good mass transfer in the polymer and carbon frameworks. This work shows that the soft-templating synthesis of mesoporous polymers and carbons can accommodate
high loadings of various organosilanes, such as large isocyanurate organosilane, which creates an effective way for tailoring surface and framework properties of these materials.
CHAPTER 5

INCORPORATION OF INORGANIC SPECIES INTO CARBON MESOSTRUCTURES

The incorporation of inorganic species into carbon mesostructures can be achieved directly during the organic-organic self-assembly process. The most common way involves the addition of inorganic precursors to the synthesis mixture containing a carbon precursor and a block copolymer. The thermal treatment of the resulting polymer-polymer nanocomposite containing metal ions results in the formation of metal nanoparticles incorporated throughout the carbon framework. So far, the mesoporous carbons with single metal/metal oxide nanoparticles were reported, including titania [39, 45, 46], irridium [40], nickel [41, 42, 51] and iron [48, 49]. However, the control of size of nanoparticles formed and their actual loadings can be considered as a potential drawback of this procedure [40, 51, 105]. An alternative method to the aforementioned one is based on the addition of metal/metal oxide nanoparticles in the form of colloidal solutions to the synthesis mixture [106, 107]. It was shown that the latter strategy is especially beneficial when potential applications require high loadings of nanoparticles embedded into the carbon matrix composed of large and uniform mesopores [107].

5.1 INCORPORATION OF SILICA AND ALUMINA COLLOIDS INTO MESOPOROUS CARBONS SYNTHESIZED BY SOFT TEMPLATING


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In this part the mesoporous carbon monoliths with embedded alumina and silica nanoparticles were synthesized using phloroglucinol and formaldehyde as carbon precursors and poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer as a soft template. While the carbon mesostructure was not significantly affected by embedding silica nanoparticles (~20 nm), this was not the case for the incorporation of alumina nanoparticles (~50 nm). The nanoparticles were found to be accessible and unprotected by a carbon shell. An additional advantage of these carbons is the presence of large and uniform mesopores (~10 nm) providing better mass transfer of reagents than the carbons that were reported previously (usually around 6 nm). Also, a broad variety of commercially available nanoparticles of different sizes and shapes makes this synthesis route even more attractive for the design of carbon-based materials, especially catalysts, with desired properties.

Mesoporous carbon samples were prepared according to a slightly modified recipe of Liang et al. [13]. In a typical synthesis, 1.25 g of phloroglucinol and 1.25 g of poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) triblock copolymer (Pluronic F127) were dissolved in 9.7 g of ethanol-water (10:9 wt. ratio) solution and stirred vigorously at room temperature. After complete copolymer dissolution, an aqueous suspension of alumina nanoparticles was introduced into the synthesis mixture. The amount of nanoparticles used (according to manufacturer specification) was calculated to be 10 and 20 wt% with respect to the carbon precursors. Then, 0.08 ml of 37% HCl was added to the solution as a catalyst. The resulting solution was stirred for an additional 30 min until a light pink color appeared. Subsequently, 1.25 ml of 37% formaldehyde was added to the synthesis mixture. The solution turned cloudy after 30 min and after an additional 1-2 hr separated into two layers. The
separation, drying and carbonization steps were performed as mentioned in the main experimental section.

Shown in Figure 14A are the TG profiles for the alumina-carbon nanocomposites revealing the total alumina content in each material after its thermal treatment in air. The TG residues were ~8% wt. and 15% wt. for the C-Al$_2$O$_3$-10 and C-Al$_2$O$_3$-20 samples, respectively. For comparison, the TG curves for the carbons containing silica nanoparticles were also recorded (Figure 14B). These results reveal similar weight percentages of silica nanoparticles to those obtained for the Al$_2$O$_3$-carbon materials, i.e., ~9% wt. and 16% wt. for the C-SiO$_2$-10 and C-SiO$_2$-20 samples, respectively.

All carbon samples exhibited similar thermal stability in air. Their oxidation occurred in the temperature range of 500-520°C for the samples containing either Al$_2$O$_3$ or SiO$_2$ nanoparticles. These results further indicate that the presence of alumina and silica nanoparticles did not affect significantly the thermal stability of the samples studied.
Table 7. Adsorption parameters for the carbon samples with incorporated alumina and silica nanoparticles.\(^a\)

<table>
<thead>
<tr>
<th>Sample</th>
<th>(S_{BET}) m(^2)/g</th>
<th>(V_t) cc/g</th>
<th>(V_{mi}) cc/g</th>
<th>(V_{me}) cc/g</th>
<th>(w_{KJS}) nm</th>
<th>R %</th>
<th>(D_t) °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-(\text{Al}_2\text{O}_3)-10</td>
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<td>0.56</td>
<td>10.6</td>
<td>8</td>
<td>512</td>
</tr>
<tr>
<td>C-(\text{Al}_2\text{O}_3)-20</td>
<td>360</td>
<td>0.36</td>
<td>0.05</td>
<td>0.26</td>
<td>9.2</td>
<td>15</td>
<td>520</td>
</tr>
<tr>
<td>C-(\text{SiO}_2)-10</td>
<td>441</td>
<td>0.71</td>
<td>0.03</td>
<td>0.65</td>
<td>10.6</td>
<td>9</td>
<td>517</td>
</tr>
<tr>
<td>C-(\text{SiO}_2)-20</td>
<td>416</td>
<td>0.69</td>
<td>0.02</td>
<td>0.63</td>
<td>10.9</td>
<td>16</td>
<td>512</td>
</tr>
<tr>
<td>C-(\text{SiO}_2)-20-HF</td>
<td>500</td>
<td>0.86</td>
<td>0.03</td>
<td>0.79*</td>
<td>10.6</td>
<td>1.5</td>
<td>515</td>
</tr>
</tbody>
</table>

\(^a\)Notation: \(S_{BET}\) – BET specific surface area; \(V_t\) – single-point pore volume; \(V_{mi}\) – volume of fine pores (mainly micropores) obtained by integration of PSD up to 3.5 nm; \(V_{me}\) – volume of mesopores obtained by integration of PSD from 3.5 nm to 16 nm (in the case of SiO\(_2\)-20-HF integration was done in the range of 3.5-20 nm); \(w_{KJS}\) – mesopore diameter at the maximum of the PSD curve obtained by the improved KJS method [118]; R – residue obtained from the TG curve recorded in air at 800°C; \(D_t\) – decomposition temperature.

Figure 14. TG profiles in air for the alumina-containing carbons (A) and silica-containing carbons (B).
Nitrogen adsorption isotherms measured at -196°C and the corresponding pore size distributions (PSDs) for the C-Al$_2$O$_3$-10 and C-Al$_2$O$_3$-20 samples are shown in Figure 15, while basic parameters evaluated by analysis of these isotherms are listed in Table 6. For all samples studied type IV nitrogen adsorption isotherms were recorded with steep condensation steps reflecting uniform mesopores. The condensation step for the C-Al$_2$O$_3$-10 sample is higher than that of C-Al$_2$O$_3$-20 reflecting its larger mesopore volume. While both samples exhibit similar microporosity (0.04-0.05cm$^3$/g), the mesopore volume of the C-Al$_2$O$_3$-20 sample is twice larger (see Table 6). Also, a decrease in the BET surface area is observed with the increasing loading of nanoparticles, i.e., from 438 m$^2$/g for C-Al$_2$O$_3$-10 to 360m$^2$/g for C-Al$_2$O$_3$-20. Since the pore size did not change much with the increasing loading of alumina nanoparticles (10.6 nm vs. 9.2 nm; see PSDs in Figure 3 inset), the observed significant reduction in the volume of mesopores cannot be explained only by the decrease of the carbon amount in the sample due to the presence of nanoparticles. In addition, it seems that high loadings of alumina nanoparticles reduce the amount of mesopores that are formed during the self-assembly process.

Another set of carbon samples was synthesized using silica nanoparticles instead of alumina. The nitrogen adsorption isotherms for these materials are presented in Fig 16. Regardless of the amount of nanoparticles introduced, both isotherms exhibited steep capillary condensation steps reflecting the high uniformity of mesopores. In contrast to the alumina-containing carbons, an increase in the loading of silica nanoparticles from 9 to 16% (values obtained by TGA; Figure 14B) did not cause any significant changes in the nitrogen adsorption isotherms and the resulting adsorption parameters. The BET surface area was found to be 441
m$^2$/g for C-SiO$_2$-10 and slightly smaller – 416 m$^2$/g for C-SiO$_2$-20. Both silica-carbon samples had higher total pore volumes in comparison to those for the alumina-carbon samples. Pore size distributions for C-SiO$_2$-10 and C-SiO$_2$-20, shown in the inset of Figure 16, are nearly identical.

A higher loading of silica nanoparticles caused only a slight decrease in the mesopore volume, which differs from the results obtained for the alumina-containing carbons. Note that the silica surface is more hydrophilic than alumina and most likely it does not disturb the mesostructure formation in the hydrophilic domains of the block copolymer template. Therefore, the whole system can adapt to a higher loading of silica nanoparticles more easily, undergoing only small structural changes. An experimental confirmation for the attraction of silica nanoparticles into hydrophilic domains of polymerizing carbon precursors is the easiness of the self-assembly of the latter precursors in the presence of tetraethyl orthosilicate (TEOS), which leads to the silica-carbon mesoporous composites [36, 38]. Also, the 2.5 times smaller size of silica nanoparticles in comparison to alumina particles improves silica incorporation into the carbon matrix without significant pore structure alteration.
Figure 15. Nitrogen adsorption isotherms and the corresponding pore size distributions (inset) for mesoporous carbons with embedded alumina nanoparticles.

Figure 16. Nitrogen adsorption isotherms and the corresponding pore size distributions (inset) for carbon samples with embedded silica nanoparticles. The plot with open circles refers to the C-SiO₂-20 sample treated with HF to remove the silica nanoparticles.
An additional plot shown in Figure 16 labeled as C-SiO$_2$-20-HF refers to the carbon sample obtained from C-SiO$_2$-20 after the removal of silica nanoparticles with HF solution. Nitrogen adsorption isotherm for this sample exhibits a steep condensation step at the same relative pressure as that for the untreated C-SiO$_2$-20 sample. The main difference between these two isotherms appears at the pressures close to the saturation pressure; namely, the isotherm curve for C-SiO$_2$-20-HF shows another step, which reflects the spherical pores created after the removal of silica nanoparticles. The HF etching increased the total pore volume from 0.69 to 0.86 m$^3$/g, which is visible in Figure 16 inset showing a comparison of the PSD curves. In addition to a small peak reflecting fine pores below 3 nm and the main peak located around 10 nm that represents uniform mesopores, there is an extra peak on the PSD curve located between 15 and 20 nm (see inset in Figure 16). The latter peak represents new mesopores created after removal (HF etching) of silica nanoparticles. Also, the BET surface area increased from 416 m$^2$/g for an untreated sample to 500 m$^2$/g for the HF treated silica-carbon composite. A successful etching of silica nanoparticles with HF, which is reflected the aforementioned extra peak on the PSD curve (Figure 16), proves that these nanoparticles are accessible for HF molecules.

The powder XRD measurements for the thermally treated nanocomposites at 850ºC were used to identify the presence of crystalline domains of the embedded nanoparticles. The XRD patterns of the alumina-containing carbons are presented in Figure 17. The diffraction patterns reveal the presence of some aluminum oxide phase and graphitic carbon in both C-Al$_2$O$_3$-10 and C-Al$_2$O$_3$-20 samples. The diffraction peaks referencing to the aluminum oxide phase are broad, which is characteristic for small crystallites. The latter feature of the XRD
pattern may indicate that alumina nanoparticles have been well dispersed in the carbon matrix; otherwise, their agglomeration could lead to larger aluminum oxide crystals. Furthermore, a few reflections can be assigned to graphitic carbon. The narrow and intense Al peaks originate from the sample holder used. Similarly, the wide angle XRD patterns recorded for the carbons with embedded silica nanoparticles (Figure 18) reveal some reflections that may correspond to graphitic carbon. Also, reflections from the sample holder corresponding to Al are present. However, there is no evidence for crystalline silica phases.
Figure 17. Wide angle XRD pattern for the alumina-containing carbons.

Figure 18. Wide angle XRD pattern for the silica-containing carbons.
The successful synthesis of mesoporous carbons with incorporated alumina and silica nanoparticles proves that the soft-templating synthesis represents a simple and effective way for the introduction of various inorganic nanoparticles into the carbon matrix. Regardless of the type of nanoparticles, smaller loadings yield mesoporous carbons with comparable adsorption properties. In the case of carbons with larger loadings of nanoparticles, the aforementioned properties depend on the chemistry and size of these particles. It is shown that the embedded particles in mesoporous carbons are accessible for other molecules, which was proved by a successful removal of silica with HF solution. Since the soft-templating synthesis of mesoporous carbons is a one-pot process involving commercially available block copolymers, phenol derivatives and formaldehyde, it is especially well suited for the addition of various inorganic nanoparticles.

5.2 SYNTHESIS AND PROPERTIES OF MESOPOROUS CARBONS WITH HIGH LOADINGS OF INORGANIC SPECIES**

A series of mesoporous carbons with high loading of silica has been synthesized by acid-catalyzed polymerization of resorcinol and formaldehyde in the presence of tetraethyl orthosilicate (TEOS), colloidal silica (silica source) and poly(ethylene oxide) – poly(propylene oxide) – poly(ethylene oxide) triblock copolymer (soft template) followed by carbonization. This synthesis route can be considered as a combination of soft-templating and hard-templating strategies and can be used to self-assemble block copolymer template and carbon precursors together with inorganic nanoparticles and TEOS (see Scheme 5) in order to obtain

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** Jaroniec M.; Górka J.; Choma J.; Zawislak A. Carbon, 2009, 47, 3034
nanoparticle-containing mesoporous silica-carbon composites. Dissolution of silica in the composite results in a high surface area carbon possessing uniform mesopores (created by thermal decomposition of block copolymer template), fine pores (obtained by dissolution of silica) improving pore accessibility and connectivity, and inorganic nanoparticles. To illustrate the feasibility of the aforementioned approach a series of mesoporous carbons has been synthesized by using colloidal silica and TEOS; colloidal silica was used to create spherical mesopores, and TEOS was employed to increase microporosity. It is shown that TEOS can be used to achieve a significant increase in the surface area and to improve pore connectivity and accessibility to inorganic nanoparticles.

Mesoporous carbons were synthesized according to a modified recipe proposed by Wang et al. [98]. Approximately 1.25g of resorcinol and 1.25g of poly(ethylene oxide) – poly(propylene oxide) – poly(ethylene oxide) triblock copolymer (PEO-PPO-PEO; Pluronic F127) were dissolved in deionized water and ethanol. The weight ratio of water to ethanol was fixed to be 5.5:10 keeping in mind the water content in the suspension of silica nanoparticles; the amount of the aforementioned suspension was introduced to the reaction mixture to achieve 25 and 50 wt% of silica with respect to the carbon precursors. After stirring for about 10-15min, the reaction mixture was supplied with 1.1ml of 37%HCl and kept under stirring for additional 30min. Subsequently, 1.25ml of formaldehyde and 1.87ml of TEOS were added to the synthesis mixture. The resulting solution turned milky after 2-3h and after additional 30min of stirring the aqueous and solid phases were allowed to separate.
**Scheme 5** – Illustration of soft-templating synthesis of mesoporous carbons in the presence of colloidal silica without (left side of scheme) and with (right side of scheme) tetraethyl orthosilicate (TEOS).

- **carbon precursor** + triblock copolymer + silica nanoparticles + TEOS → Template-containing polymer-silica
- Heating → Mesoporous polymer-silica
- Carbonization & silica removal → Mesoporous carbon
The polymer-containing bottom layer was spread on a Petri dish and left under the fume hood overnight. Then, the sample was aged at 100°C for 24h. Carbonization was performed under nitrogen atmosphere in the tube furnace using a heating rate of 2°C/min up to 180°C, keeping the sample at this temperature for 5hr, resuming heating at 2°C/min up to 400°C and with 5°C/min up to 850°C, and finally keeping the sample at 850°C for 2 hours. In order to remove silica, the resulting samples were etched with 15%wt HF, washed with deionized water and dried. The resulting materials were labeled $M$-$TxN$, where $M$ indicates the type of material ($CS =$ carbon-silica composite or $C =$ carbon), $T$ refers to TEOS and $x$ denotes to the weight percentage of silica nanoparticles (N) in the sample.

A second series of the samples was prepared using the same chemical composition and synthesis route except for the time of TEOS addition. In contrast to the previous series, TEOS was added 20min after formaldehyde. The resulting samples were labeled as $M$-$TxN^*$. Also, one sample analogous to CS-T50N (prepared with 20 nm colloidal silica) was synthesized by using 50nm colloidal silica (CS-T50N#); the corresponding carbon sample is denoted as $C$-T50N#.

For the purpose of comparison one silica-carbon composite (CS-T) was prepared with ~40%wt. of TEOS but without colloidal silica. Also, the corresponding carbon sample (C-T) was prepared from this composite by HF treatment.

The TG decomposition curves recorded in flowing air for the first series of samples are presented in Figure 19. These samples were prepared with high loadings of silica; ~25 or 50%wt. of silica nanoparticles and ~40%wt. of TEOS (these percentages were estimated in relation to the carbon precursors only). The TG analysis revealed that the total content of silica
introduced into the carbon framework was ~64% and ~77% for the CS-T25N and CS-T50N samples, respectively. These loadings are close to the expected values, indicating that the incorporation of TEOS-generated silica is enhanced in the presence of colloidal silica because much smaller amount of silica (~14%) was found in CS-T sample prepared with the same amount of TEOS as in the case of CS-T25N and CS-T50N but without colloidal silica (Table 7).

The higher oxidation temperatures (530-550°C) of the CS-T25N and CS-T50N samples in comparison to those for the HF treated samples are caused by the high silica content in the composite samples. It is noteworthy that even after treating the silica-carbon samples twice with an HF solution approximately 10% of silica remained proving that the latter was inaccessible to the acid. The thermal stability of the HF-treated samples is lower (~505°C) but still typical of phenolic resin-based carbons.
Figure 19. Thermogravimetric profiles for the silica-carbon composites studied and the corresponding carbons in air.

Figure 20. Nitrogen adsorption isotherms and the corresponding pore size distributions for the silica-carbon composites.
Nitrogen adsorption isotherms and corresponding pore size distributions (PSDs) for silica–carbon composites are shown in Figure 20 and the adsorption parameters are listed in Table 7. All samples exhibit type IV isotherm characteristic for mesoporous materials. The steep and high capillary condensation steps indicate uniform and well developed mesoporosity with a large mesopore volume. In the case of the CS-T50N sample the condensation step is shifted towards higher relative pressures suggesting increase in the pore diameter with higher loading of silica species. The specific surface area of this series of samples was found to be in the range of 200-300 m²/g with lower value corresponding to the sample with higher silica content. As can be seen from the PSD plots, these samples possess complementary (fine) pores up to 4nm and large mesopores with diameters in the range of 11-15nm. Because the volume of complementary pores is small in comparison to that of large mesopores it can be assumed that the latter reflects the major contribution to the total pore volume. Changing the time of TEOS addition (series with asterisks) did not affect much structural and adsorption properties of the composite materials significantly even though all of them show slightly lower volumes of mesopores and all pores.

Nitrogen adsorption isotherms and the corresponding PSD curves for the carbon samples obtained after silica removal are presented in Figure 21. All samples exhibit steep capillary condensation steps. In contrast to the silica-carbon composites, for which variation of the amount of silica nanoparticles did not cause a significant change in adsorption properties, the carbon samples obtained after dissolution of silica are very different. The first difference is in the large total pore volume for all carbons studied.
### Table 8. Adsorption parameters for the carbon samples with high loadings of inorganic species

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{BET}$ m$^2$/g</th>
<th>$V_t$ cc/g</th>
<th>$V_{mi}$ cc/g</th>
<th>$V_{me}$ cc/g</th>
<th>$w_{KJS}$ nm</th>
<th>SiO$_2$ %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CS-T</td>
<td>659</td>
<td>0.61</td>
<td>0.07</td>
<td>0.44</td>
<td>7.1</td>
<td>14</td>
</tr>
<tr>
<td>CS-T25N</td>
<td>304</td>
<td>0.47</td>
<td>0.013</td>
<td>0.40</td>
<td>11.9</td>
<td>64</td>
</tr>
<tr>
<td>CS-T25N*</td>
<td>301</td>
<td>0.45</td>
<td>0.012</td>
<td>0.38</td>
<td>10.9</td>
<td>64</td>
</tr>
<tr>
<td>CS-T50N</td>
<td>228</td>
<td>0.43</td>
<td>0.007</td>
<td>0.37</td>
<td>14.4</td>
<td>77</td>
</tr>
<tr>
<td>CS-T50N*</td>
<td>253</td>
<td>0.42</td>
<td>0.015</td>
<td>0.35</td>
<td>15.2</td>
<td>76</td>
</tr>
<tr>
<td>CS-T50N#</td>
<td>309</td>
<td>0.56</td>
<td>0.039</td>
<td>0.49</td>
<td>14.5</td>
<td>76</td>
</tr>
<tr>
<td>C-T</td>
<td>886</td>
<td>0.82</td>
<td>0.13</td>
<td>0.60</td>
<td>7.1</td>
<td>3</td>
</tr>
<tr>
<td>C-T25N</td>
<td>1246</td>
<td>1.91</td>
<td>0.25</td>
<td>1.57</td>
<td>12.8</td>
<td>7</td>
</tr>
<tr>
<td>C-T25N*</td>
<td>1364</td>
<td>1.92</td>
<td>0.29</td>
<td>1.52</td>
<td>12.0</td>
<td>6</td>
</tr>
<tr>
<td>C-T50N</td>
<td>1731</td>
<td>3.46</td>
<td>0.28</td>
<td>3.07</td>
<td>14.0</td>
<td>10</td>
</tr>
<tr>
<td>C-T50N*</td>
<td>1544</td>
<td>3.41</td>
<td>0.21</td>
<td>3.06</td>
<td>15.4</td>
<td>6</td>
</tr>
<tr>
<td>C-T50N#</td>
<td>1574</td>
<td>3.72</td>
<td>0.26</td>
<td>2.00</td>
<td>14.4*</td>
<td>5</td>
</tr>
</tbody>
</table>

Notation: $S_{BET}$ – BET specific surface area; $V_t$ – single-point pore volume; $V_{mi}$ – volume of fine pores (mainly micropores) obtained by integration of PSD up to 4 nm; $V_{me}$ – volume of mesopores obtained by integration of PSD from 4 nm to 20 nm; $w_{KJS}$ – mesopore diameter at the maximum of the PSD curve obtained by the modified KJS method [118]; * at the pore width value for C-T550N# indicates that in this case the PSD curve has another peak corresponding to large mesopores of ~50nm; %– SiO$_2$ residue obtained from the TG curve recorded in air at 800°C. Sample CS-T50N# has been prepared by using 50 nm colloidal silica; other samples with colloidal silica were prepared using 20nm particles.
Figure 21. Nitrogen adsorption isotherms and the corresponding pore size distributions for the carbon samples.
In particular, the total pore volume for C-T50N is impressive because it is nearly doubled in comparison to the C-T25N sample (3.46 cm$^3$/g vs. 1.91 cm$^3$/g). The same trend is observed for the mesopore volume, which is not surprising if one considers that C-T50N has as twice many silica nanoparticles in comparison to C-T25N.

Another interesting feature is a rather high microporosity in both samples, which was found to be 0.25-0.28 cm$^3$/g. These results indicate that the system already loaded with nanoparticles was still ready to host an additional portion of silica precursor without disturbing the mesostructure formation. The aforementioned data and the fact that the corresponding composites possessed an almost negligible amount of micropores lead us to the conclusion that almost entire microporosity was generated by removing silica formed from TEOS. The large amount of micropores is the main reason of the significant increase in the BET surface area up to 1730 m$^2$/g for the C-T50N sample. Note the unusual delay in desorption for the carbon obtained from the composite with 50% SiO$_2$ after HF treatment. The latter case shows that the silica removal causes some changes in the mesostructure. The PSD curves for these carbons show two systems of pores; the first one, very sharp with maximum at ~3 nm attributed to micropores and the second one with maxima at 12-13 nm and 14-15 nm (depending on the sample) assigned to the mesopores. Note that the second peak is quite broad (from ~5 to 25 nm) because it is a combination of two types of mesopores: (i) smaller mesopores (sizes of ~10 nm) formed during soft-templating synthesis, and (ii) larger mesopores (sizes of ~20 nm) caused by the dissolution of silica colloids. While the micropore volume for both groups of carbons was comparable (because the same amount of TEOS was employed), the mesopore volume greatly depended on the amount of the colloidal silica used. Also, the average size of
mesopores increased for the carbon prepared with larger amount of colloidal silica. The pore size enlargement in the system studied is quite complex and consists of at least three phenomena: (i) TEOS-induced enlargement of mesopores created during soft-templating process (columns A and B in Scheme 6), (ii) TEOS-induced enlargement of mesopores created during colloidal templating process (row C in Scheme 6), and (iii) possible colloidal silica-induced enlargement of mesopores formed during the self-assembly process (no TEOS addition). The reason of the first two types of enlargement (illustrated in Scheme 6) is favored interactions of the PEO blocks of the polymeric template with silica species (pre-hydrolyzed TEOS and colloidal silica). In (i) the pre-hydrolyzed TEOS species prefer to accumulate near PEO blocks, while in (ii) these species favorably interact with colloidal silica and PEO blocks, which in both cases leads to the enlargement of carbon mesopores formed during soft templating and colloidal templating processes, respectively. The case (iii) of mesopore enlargement is still unclear. It can be speculated that colloidal silica nanoparticles attract PEO blocks and enlarge hydrophobic domains of the polymeric template; further systematic studies are in progress in order to provide a more detailed explanation of the mesopore enlargement in the soft-templated carbons synthesized in the presence of TEOS and/or colloidal silica. For larger amounts of colloidal silica and TEOS the suggested mesopore enlargements are more pronounced due to the enhanced accumulation of pre-hydrolyzed TEOS species at PEO blocks and the enlarged total surface area of silica colloids able to attract PEO blocks. Therefore, for the same amount of TEOS used the mesopore width increased with the increasing amount of silica nanoparticles (see data in Table 8).
Scheme 6. Proposed pore size enlargement due to the TEOS accumulation at the PEO copolymer blocks (column B: system with TEOS) and colloidal silica nanoparticles (column C: system with TEOS and colloidal silica), respectively; column (A) shows the self-assembly process without TEOS and colloidal silica.
To show that the PSD peak at ~14-15nm in Figure 21 is a combination of two types of mesopores, created by soft templating and colloidal templating, one carbon sample (C-T50N\#) was prepared using 50 nm colloidal silica. The nitrogen adsorption isotherms and the PSD curves for the C-T50N\# carbon and the corresponding carbon-silica composite (CS-T50N\#) are shown in Figure 22. The isotherm curve for C-T50N\# shows a steep step at the relative pressures close to unity, which reflects the capillary condensation in colloid-templated pores. The inset in Figure 22 shows the PSD curves in the range up to 20nm with main peak located at ~14.5 nm, which is the same as for the samples synthesized by using 20 nm silica colloids. However, the PSD curve (Figure 23) for this sample plotted on the logarithmic scale of pore width (up to 100 nm) shows clearly three peaks reflecting micropores, primary channel-like mesopores (~14.5 nm), and secondary spherical mesopores (~50nm) formed by dissolution of TEOS-generated silica, block copolymer template and dissolution of colloidal silica, respectively. Note that the original BJH method [117] used to calculate the PSD curve for the C-T50N\# carbon in the range of 20-100 nm is applicable for large cylindrical mesopores, while colloid-templated mesopores are spherical; apparently, due to compensation effect associated with pore overestimation and structure shrinkage during carbonization the pore size estimation matched the size (~50 nm) of colloids used quite well.
Figure 22. A comparison of nitrogen adsorption isotherms and the corresponding pore size distributions for the silica-carbon composite obtained by using 50 nm silica colloids (left panel) and the corresponding carbon after dissolution of silica samples.

Figure 23. Pore size distribution plotted in the logarithmic scale of the pore width for the C-T50N# carbon obtained in the presence of TEOS using colloidal silica (~50 nm).
Figure 24 shows a comparison of nitrogen adsorption isotherms and the corresponding PSD curves for the silica-carbon composites obtained by using TEOS and carbon precursors with and without colloidal silica. Figure 25 shows an analogous comparison of adsorption isotherms and PSDs for the carbons obtained from the aforementioned silica-carbon composites by HF treatment. As can be seen from these figures and Table 7 a substantial increase in the surface area and pore volume was achieved after adding colloidal silica into synthesis gel, which shows clearly the advantage of using TEOS for the incorporation of inorganic nanoparticles during soft templating synthesis of mesoporous carbons.
Figure 24. A comparison of nitrogen adsorption isotherms and the corresponding pore size distributions for the silica-carbon composites obtained by using TEOS and carbon precursors with and without colloidal silica.

Figure 25. A comparison of nitrogen adsorption isotherms and the corresponding pore size distributions for the carbon samples obtained from the silica-carbon composites shown in Figure 24.
In conclusions, the mesoporous carbons with large surface area and total pore volume were synthesized by combining the hard templating method with the soft-templating approach. This study shows that the aforementioned combination of colloidal templating with soft templating is a simple and effective way to introduce large amount of silica into carbon mesostructure by using silica nanoparticles and TEOS. The total pore volume and mesopore volume of the carbons obtained after silica dissolution depend strongly on the amount of the silica nanoparticles, whereas the observed microporosity is formed due to the removal of the TEOS-generated silica. It is shown that the synthesis is reproducible even for the samples with high loadings of silica. In addition, this study shows a great potential of the TEOS-assisted incorporation of inorganic nanoparticles into carbon mesostructures, which affords high surface area microporous-mesoporous carbons with a high loading of inorganic nanoparticles. The TEOS-generated microporosity improves pore connectivity and accessibility of nanoparticles in adsorption and catalysis processes.

5.3 ORDERED MESOPOROUS CARBON/ α-AlUMINA NANOSHEETS COMPOSITE ††

In this part the use of α-alumina nanosheets for the preparation of alumina-carbon composites is reported for the first time, in which the latter component is a phenolic resin-based carbon with hexagonally ordered mesopores. As illustrated in Scheme 7, a unique feature of these composites is the surface-induced perpendicular orientation of ordered

mesopores of this carbon to the (001) facets of nonporous $\alpha$-alumina nanosheets accompanied by an enlargement of the diameter of these pores.

**Scheme 7.** Models of ordered mesoporous carbon-$\alpha$-alumina nanosheets composites

The $\alpha$-alumina nanosheets studied in this work were hydrothermally synthesized at Sawyer Technical Materials, LLC (Eastlake, OH) following the procedure reported elsewhere [140, 141]. The 20-35nm thick nonporous nanosheets with exposed (001) facets were identified as $\alpha$-alumina (corundum, $\alpha$-$\text{Al}_2\text{O}_3$) with high aspect ratio of 10-200.

The preparation of carbon-alumina nanocomposites was done by adding the desired amount of $\alpha$-alumina nanosheets during soft-templating synthesis of phenolic resin-based OMC. The latter was prepared according to a slightly modified recipe proposed by Wang et al. [98], which involves polymerization of carbon precursors, namely resorcinol and formaldehyde, in the presence of poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) triblock copolymer (Pluronic F127; used as soft template) under highly acidic conditions. The
resulting polymer-polymer mesostructure with incorporated α-alumina nanosheets was subjected to a series of thermal treatments to ensure thermopolymerization of carbon precursors, the removal of the soft template and carbonization of phenolic resin mesostructure. The final samples were labelled as C-xANS, where x indicates wt% of α-alumina nanosheets in the composite estimated by thermogravimetric analysis. The sample marked with an asterisk was carbonized at 1100°C in contrast to other two samples carbonized at 850°C. As can be seen from the wide angle XRD patterns (Fig. 26) α-alumina present in the alumina-carbon composite retains its phase composition and crystalinity after the carbonization process, while a characteristic peak at 20- 25° for carbon becomes clearly visible.

Due to the rather complex nature of agglomeration and orientations of the nanosheets in the composites, a range of microstructures was obtained, as shown in Scheme 7. The basic unit of the composite is a single α-alumina nanosheet covered with a layer of mesoporous carbon. In this basic unit, the mesopores are perpendicularly aligned to the surface of the α-alumina nanosheets, as shown schematically in Scheme 7 and confirmed by detailed HRTEM analysis (Figure 27). This surface-induced perpendicular orientation of mesopores to α-alumina nanosheets is the effect of interactions between distinct (001) facets of α-alumina and phenolic resin mesostructure. These basic units can form structures when several nanosheets are close to each other. Such α-alumina nanosheets are very rarely aligned in a parallel fashion; typically they are mutually oriented at various angles.
Figure 26. Wide-angle XRD patterns for alumina nanosheets (ANS) and carbon-alumina composite (C-30ANS).
Figure 27. TEM images of mesoporous carbon/α-alumina composite, C-30ANS.
The SEM images in Fig. 28 show the bulk of the synthesized $\alpha$-alumina/carbon composites, which consists of a relatively homogenously distributed $\alpha$-alumina nanosheets in the carbon mesostructure. The $\alpha$-alumina nanosheets form large agglomerates, in which the nanosheets are randomly oriented and covered with mesoporous carbon (Figure 28). The relatively thin layers of carbons are formed on individual nanosheets, but in the case of composites with a higher carbon/alumina ratio the separate domains of bulk mesoporous carbon can be formed. Under the conditions used in this study the bulk carbon shows hexagonally ordered mesopores, much smaller than those formed on the nanosheets, as illustrated in Figure 27 (bottom panels).
Figure 28. SEM images of mesoporous carbon/α-alumina composite, C-30ANS.
In our previous work [106] related to the incorporation of 50nm amorphous alumina nanoparticles into the phenolic resin-based carbon mesostructure a significant reduction in the pore volume was reported with an increasing loading of alumina nanoparticles. This led to the conclusion that the mesopore formation via the self-assembly process can be affected by differences in the surface properties of the nanoparticles used. In this work, the use of the single-crystal $\alpha$-alumina nanosheets with distinct (001) facets, which are much more energetically homogenous, resulted in weaker interactions between these facets and the phenolic resin interface. Consequently, a perpendicular orientation of phenolic resin-based carbon mesochannels on the $\alpha$-alumina (001) facets was favored instead of parallel alignment, which resulted in unique structure of the $\alpha$-alumina-OMC composites. This finding is not surprising in the light of numerous reports showing unique self-organization of block copolymers on various flat surfaces [142-147]. These reports demonstrate that the smooth, rigid and neutral surfaces promote the perpendicular orientation to the confining pore walls, which is thermodynamically favored even when the upper surface is removed. Also, the diameters of these channels are often larger than those observed in the bulk phases. The current study shows that the aforementioned mesostructures of block copolymers on the flat surfaces [142-147] can be used to prepare new composites because these mesostructures are not significantly disturbed by the incorporation of phenolic resin precursors. The thermosetting nature of phenolic resin permits the removal of block copolymer templates upon thermal treatment in an inert gas (e.g., argon or nitrogen) followed by carbonization process without destroying the ordered mesostructure formed on the $\alpha$-alumina nanosheets.
Nitrogen adsorption isotherms and the corresponding pore size distributions (PSDs) for the composites studied are presented in Figures 29 and 30, whereas the corresponding adsorption parameters such as the BET specific surface area, the pore volume and pore widths are listed in Table 9. All adsorption isotherms are of type IV according to the IUPAC classification, which is typical for materials with channel-like mesopores. The steep capillary condensation steps at relative pressure of ~0.6 for C (carbon without alumina), C-20ANS and C-30ANS suggest high uniformity of primary mesopores, which stays in a good agreement with data obtained from small angle XRD and TEM analysis (see Figures 31 and 27). Importantly, the isotherms for C-20ANS and C-30ANS show some evidence for the presence of larger mesopores as reflected by the increase of adsorption in the relative pressure range of 0.8-0.9. In order to explain this behavior, two samples (C-66ANS and C-70ANS) with a high loading of alumina nanosheets were prepared to eliminate or at least significantly reduce the amount of bulk OMC (not deposited on alumina nanosheets). As can be seen in Figures 29 and 30, the isotherm curves for C-66ANS and C-70ANS show the steps of capillary condensation at higher relative pressures, which confirms the formation of larger mesopores on alumina nanosheets than those present in the bulk carbon. In addition, these larger carbon mesopores are perpendicularly oriented on the (001) facets of α-alumina nanosheets (as shown in Figure 27 by HR TEM analysis). Thus, a substantial increase in the α-alumina loading resulted in the larger amount of the OMC formed on the (001) facets α-alumina nanosheets, which is reflected by the significant change in the PSD curves from one mesopore peak with a shoulder to a double mesopore peak (see the right panels of Figures 29 and 30). This suggests that larger polymeric micelles are formed on the (001) facets of α-alumina than those in the bulk aqueous phase.
Figure 29. Nitrogen adsorption isotherms and the corresponding pore size distributions for the OMC-alumina nanosheets composites studied (C-30ANS, C-30*ANS, C-66ANS) and phenolic resin-based carbon (C).

Figure 30. Nitrogen adsorption isotherms and the corresponding pore size distributions for C-20ANS and C-70ANS samples.
Figure 31. Small-angle XRD pattern for C-30ANS nanocomposite.

Table 9. Adsorption parameters for the carbon-alumina nanocomposites studied

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{BET}$ (m$^2$/g)</th>
<th>$V_t$ (cc/g)</th>
<th>$V_{mi}$ (cc/g)</th>
<th>$V_{me}$ (cc/g)</th>
<th>$w$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>813</td>
<td>0.70</td>
<td>0.08</td>
<td>0.50</td>
<td>6.5</td>
</tr>
<tr>
<td>C-20ANS</td>
<td>671</td>
<td>0.63</td>
<td>0.06</td>
<td>0.46</td>
<td>6.8</td>
</tr>
<tr>
<td>C-30ANS</td>
<td>650</td>
<td>0.60</td>
<td>0.07</td>
<td>0.44</td>
<td>6.5</td>
</tr>
<tr>
<td>C-30*ANS</td>
<td>685</td>
<td>0.64</td>
<td>0.08</td>
<td>0.47</td>
<td>6.4</td>
</tr>
<tr>
<td>C-66ANS</td>
<td>383</td>
<td>0.53</td>
<td>0.03</td>
<td>0.46</td>
<td>8.4/12.8</td>
</tr>
<tr>
<td>C-70ANS</td>
<td>312</td>
<td>0.49</td>
<td>0.02</td>
<td>0.42</td>
<td>13.6</td>
</tr>
</tbody>
</table>

*aNotation: $S_{BET}$ – BET specific surface area; $V_t$ – single-point pore volume; $V_{mi}$ – volume of fine pores (mainly micropores) obtained by integration of PSD up to 3nm; $V_{me}$ – volume of mesopores obtained by integration of PSD from 3nm to 20nm; $w_{KJS}$ – mesopore diameter at the maximum of the PSD curve obtained by the improved KJS method [118].
As mentioned above an analogous behavior was observed in the case of the block copolymer films formed on flat surfaces [142-147].

Also, the data listed in Table 9 show that an increase in the loading of $\alpha$-alumina nanosheets caused a decrease in the BET surface area and the total pore volume, which can be easily explained by a simultaneous reduction of the adsorbing carbon in the composite samples. The BET surface area, pore width, total, mesopore and micropore volumes for the samples with smaller loadings of $\alpha$-alumina nanosheets were found to be about 700m$^2$/g, 6.5nm, 0.60cm$^3$/g, 0.45cm$^3$/g and 0.06cm$^3$/g, respectively, which are typical values for phenolic resin-based carbons; however, the corresponding values for C-66ANS and C-77ANS are smaller. Since $\alpha$-alumina nanosheets can easily sustain high temperatures, one of the samples was carbonized in flowing nitrogen at 1100ºC (C-30*ANS) to prove the exceptional thermal stability of these materials. As can be seen from Fig. 29 and Table 9, the thermal treatment did not cause any structure deterioration, which can be very useful for high temperature applications.

Potential applications of such composites include catalysis, where a high surface area of thermally stable alumina and mesoporous carbon is desired [140, 141]. Strong faceting of the $\alpha$-alumina nanosheets is very important here, because it can have a tremendous impact on catalytic selectivity [148]. The $\alpha$-alumina nanosheets can also act as a reinforcement of mesoporous carbon thus increasing the mechanical strength of the material. The oriented mesopores could be used as hard templates for the synthesis of oxide nanofiber/$\alpha$-alumina nanosheets composites. This work shows the possibility of creating novel composite materials, the structural properties of which can be altered due to interfacial interactions,
which in this case resulted in the aforementioned orientation and enlargement of carbon mesopores.

In conclusion, a new type of OMC-alumina composites was successfully prepared by employing single-crystal $\alpha$-alumina nanosheets in the soft-templating synthesis of hexagonally ordered mesoporous carbons. These composites feature perpendicular orientation of mesochannels to the surface of highly crystalline $\alpha$-alumina nanosheets. The size of these channels is also significantly enlarged, which makes them promising materials for catalysis and energy-related applications.
CHAPTER 6

ENHANCEMENT OF SPECIFIC SURFACE AREA AND MICROPOROSITY

The presence of mesopores (i.e., pores having widths between 2 and 50 nm) is essential in microporous carbons to improve the transport of molecules within a porous network and to facilitate adsorption of larger molecules. This stimulated a great interest in the development of mesoporous carbons [149], which resulted in the discovery of carbons with ordered mesopores created by using various hard [1-2, 4] and soft [13, 29] templates. While the latter synthesis strategies are perfectly suited for the preparation of highly mesoporous carbons, the amount of intrinsic micropores (pores below 2 nm) in these carbons is often insufficient. Therefore, chemical or physical activation is additionally performed to increase the amount of micropores in the mesoporous carbons. Recently, mesoporous carbons obtained by inverse replication of a hexagonally ordered mesoporous silica, SBA-15, were activated with CO\textsubscript{2} [88] and KOH [92]. This activation resulted in a substantial increase of microporosity and a simultaneous reduction of mesoporosity [92]. The same was recently reported for mesoporous carbons fabricated by using colloidal silica as a hard template [34]. The aforementioned diminishment of mesoporosity in addition to the drawbacks of the hard-templating (HT) synthesis of carbons (the necessity of the silica template preparation and its removal), make the feasibility of activating the HT carbons without alteration of their mesoporosity a challenging task. In contrast, the recently reported soft-templating (ST) synthesis of mesoporous carbons is much simpler and easier to scale up [13, 29]. Moreover, the soft-
templated carbons exhibit great thermal stability, which allows for the extensive development of microporosity with a simultaneous preservation of mesopores during activation.

6.1 KOH ACTIVATION

Although phenolic resins were activated by using different agents, including KOH [150], the resulting carbons were entirely microporous. In this part of the dissertation it is shown that the KOH activation of soft-templated mesoporous carbons instead of resins results in a substantial increase of microporosity with a simultaneous preservation of mesoporous structure. The resulting micro- and mesoporous carbons possess a high surface area and a relatively large volume of mesopores, the latter is preserved when KOH activation is performed at ~700°C or higher temperature. Moreover, it is shown that the temperature of carbon pyrolysis prior to activation strongly affects not only the structural properties of the carbons but also their susceptibility to further activation and the simultaneous preservation of the mesoporous structure.

In a typical synthesis we followed a slightly modified Liang and Dai recipe [13]; namely, 1.25 g phloroglucinol and 1.25 g poly(ethylene oxide) – poly(propylene oxide) – poly(ethylene oxide) triblock copolymer (Pluronic F127) were dissolved in 9.7 g of 10:9 weight ratio of ethanol and water solution and stirred vigorously at room temperature. After complete copolymer dissolution 0.08 ml of 37% HCl was added to the solution as a catalyst and stirred for additional ½ hour until a light pink color appeared. Then, 1.25 ml of 37% formaldehyde was added to the synthesis mixture. The solution turned cloudy after 30 min and after an
additional 1-2 hr it separated into two layers. The polymer-rich bottom layer was kept under magnetic stirring overnight. Then the elastic, non-sticky monolith was transferred to an autoclave and cured in the oven at 100 °C for 24hr. The thermal treatment and carbonization of the resulting carbon were performed in a tube furnace under nitrogen flow using two different heating profiles: (i) heating up to 180 °C for 5 hr with a heating rate of 2 °C/min followed by the same heating cycle in the range of 180-400 °C and at 5 °C/min in the range of 400 °C to 850 °C (sample C1), and (ii) heating from 100 to 400°C at the rate of 1°C/min and from 400 to 850°C at the rate of 5°C/min (sample C2); finally, both samples were carbonized at 850°C for 2 hours in flowing nitrogen. Note that the above recipe afforded carbons with worm-like mesopores.

The post-synthesis activation was performed by impregnating 0.4 g of the carbon with a KOH solution (1.6 g KOH in 4 cm³ of water) followed by water evaporation at 100°C. This process was carried out in a tube furnace under flowing nitrogen by heating the sample at a rate of 10°C/min up to the desired temperature and holding at this temperature for 45 min. To ensure a complete removal of KOH, the resulting sample (after cooling in flowing nitrogen) was washed successively with 0.1 M HCl solution and deionized water. Finally, the activated carbon was dried at 105°C for 12 h. The resulting samples were labeled C1-T and C2-T, where T refers to the activation temperature.
6.1.1 DETERMINATION OF BEST ACTIVATION TEMPERATURE

As shown in Scheme 8 the synthesis of mesoporous carbon involves the polymerization of phloroglucinol and formaldehyde in the presence of a block copolymer template and subsequent thermal treatment and carbonization of the resulting nanocomposite followed by post-synthesis KOH activation.

The C1 carbon sample was used to find the optimal temperature for KOH activation. For this purpose the sample was divided into three parts that were activated at 550, 700 and 850°C; the resulting samples are denoted C1-550, C1-700 and C1-850, respectively. Shown in Figure 32 are nitrogen adsorption isotherms and the corresponding pore size distributions (PSD) for these activated mesoporous carbons as well as for the same sample before activation process. The PSD curves were calculated by using the improved KJS-BJH method adapted to carbons with channel-like pores [122]. As can be seen from this figure the type IV isotherm, characteristic for mesoporous solids, was obtained for the C1 carbon. The sequence of initial parts of adsorption isotherms as well as the PSD curves (Figure 32) shows a gradual increase in the micropore volume (Table 9) with increasing activation temperature. The size and volume of mesopores did not change upon activation up to ~700°C; however, activation at temperature exceeding 700°C caused a partial deterioration of the mesoporous structure. Thus, an optimal activation temperature that does not cause a substantial deterioration of mesoporosity in phenolic resin-based carbons was found to be about 700°C.

‡‡ Górka J.; Zawislak A.; Choma J.; Jaroniec J. Carbon, 2008, 46, 1159-1174
Scheme 8. Illustration of soft-templating synthesis of mesoporous phenolic resin-based carbons subjected to the post-synthesis KOH activation.
Table 10. Adsorption parameters for the KOH activated mesoporous carbons.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Carbon</th>
<th>(S_{\text{BET}}) m(^2)/g</th>
<th>(V_t) cm(^3)/g</th>
<th>(V_{\text{mi}}) cm(^3)/g</th>
<th>(V_{\text{me}}) cm(^3)/g</th>
<th>(w_{\text{me}}) nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>377</td>
<td>0.36</td>
<td>0.05</td>
<td>0.31</td>
<td>8.0</td>
</tr>
<tr>
<td>C1-550</td>
<td>493</td>
<td>0.44</td>
<td>0.11</td>
<td>0.33</td>
<td>8.6</td>
</tr>
<tr>
<td>C1-700</td>
<td>748</td>
<td>0.53</td>
<td>0.23</td>
<td>0.30</td>
<td>8.6</td>
</tr>
<tr>
<td>C1-850</td>
<td>795</td>
<td>0.46</td>
<td>0.24</td>
<td>0.21</td>
<td>-</td>
</tr>
<tr>
<td>C2</td>
<td>497</td>
<td>0.70</td>
<td>0.04</td>
<td>0.66</td>
<td>9.7</td>
</tr>
<tr>
<td>C2-700</td>
<td>901</td>
<td>0.87</td>
<td>0.22</td>
<td>0.64</td>
<td>9.2</td>
</tr>
</tbody>
</table>

\textsuperscript{a}C1 and C2 – non-activated carbon samples; C1-T and C2-T – KOH activated samples at temperature T; \(S_{\text{BET}}\) – BET surface area; \(V_t\) – single-point pore volume; \(V_{\text{mi}}\) and \(V_{\text{me}}\) – volumes of micropores and mesopores, respectively; \(w_{\text{me}}\) – mesopore width at the PSD maximum.

Figure 32. Nitrogen adsorption isotherms and the corresponding pore size distributions (PSDs) for the C1 sample (mesoporous phenolic resin-based carbon prepared at 850\(^\circ\)C) before (filled circles) and after (open symbols) KOH activation 550, 700 and 850\(^\circ\)C, respectively.
Figure 33 shows another example of activation of mesoporous carbon carbonized at 850°C followed by KOH activation at 700°C. The weight loss associated with KOH activation of this sample is about 40%. As can be seen from this figure and Table 9 the KOH activation of the C2 carbon increased its microporosity from 0.04 to 0.22 cm³/g and did not change mesoporosity. The resulting activated mesoporous carbon showed a large volume of mesopores, which was not affected by KOH activation. A comparison of adsorption parameters for the C1 and C2 carbons shows that the microporosity of C2 is twice as high as that of C1. While the micropore volumes of both C1 and C2 samples before activation are similar, the BET surface area and the mesopore volume of C2 are significantly higher than the corresponding values for C1. It seems that the BET surface area and the mesopore volume of the initial carbon sample are essential for the KOH activation. For the C2 sample, which showed higher BET surface area and larger mesopore volume than those of C1, the KOH activation resulted in a significantly larger volume of micropores without any significant alteration of mesoporosity.
Figure 33. Nitrogen adsorption isotherms and the corresponding pore size distributions (PSDs) for the C2 sample (mesoporous phenolic resin-based carbon prepared at 850°C) before (filled circles) and after (open circles) KOH activation at 700°C.
In conclusion, this study shows that the microporosity of mesoporous phenolic resin-based carbons can be easily increased and tailored by KOH activation. The resulting micro- and mesoporous carbons have a high surface area as well as a well-developed microporosity and mesoporosity; the latter is preserved if KOH activation is performed at ~700°C.

6.1.2 EFFECT OF TEMPERATURE OF CARBONIZATION ON KOH ACTIVATION

This work is a continuation of our previous studies devoted to the synthesis of soft-templated mesoporous carbons under acidic conditions followed by their post-synthesis KOH activation. The main goal of this project was to determine the relationship between the pyrolysis temperature of carbons and their structural parameters after KOH activation. The carbonization was performed in the temperature range of 400-1000°C, while the KOH activation was done at 700°C and only for carbons pyrolyzed at 500, 600, 700 and 850°C. It is shown that the KOH activation affords carbons with a high surface area and large total pore volume. The preservation of mesoporosity is also possible if the aforementioned activation is carried out under specified conditions.

Nitrogen adsorption isotherms and the corresponding pore size distributions are shown in Figure 34. All isotherms are of type IV with steep and well-defined condensation steps and hysteresis loops characteristic for channel-like structures. The sample carbonized at 400°C shows the capillary condensation step placed at relative pressure of ~0.8, which corresponds to the mesopores size of ~12 nm. As the temperature of pyrolysis increases the condensation step

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is gradually shifted towards lower values of relative pressure to finally reach the minimum value of ~0.65 corresponding to mesopores of ~ 8nm. As can be seen from Table 10, the BET surface area was found to vary from 440 m$^2$/g for STC1-1000 to 623 m$^2$/g for STC1-600. The total pore volume and also the mesopore volume show the trend to decrease with an increase in pyrolysis temperature, whereas the micropore volume, which remains relatively small in the case of the STC1-400 sample is doubled and reached its maximum when carbonization temperature approaches 500-600ºC. Further temperature increase cause a slight reduction in the micropore volume. In general, the percentage of micropores in the carbon samples did not exceed 15%.
<table>
<thead>
<tr>
<th>Carbon</th>
<th>$S_{BET}$ $m^2/g$</th>
<th>$V_t$ $cm^3/g$</th>
<th>$V_{mi}^{\alpha}$ $cm^3/g$</th>
<th>$P_{mi}^{\alpha}$ %</th>
<th>$w_{KJSme}$ nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>STC1-400</td>
<td>491</td>
<td>0.89</td>
<td>0.06</td>
<td>6.7</td>
<td>12.6</td>
</tr>
<tr>
<td>STC1-500</td>
<td>594</td>
<td>0.90</td>
<td>0.13</td>
<td>14.5</td>
<td>11.4</td>
</tr>
<tr>
<td>STC1-600</td>
<td>623</td>
<td>0.85</td>
<td>0.12</td>
<td>14.1</td>
<td>10.4</td>
</tr>
<tr>
<td>STC1-700</td>
<td>542</td>
<td>0.80</td>
<td>0.09</td>
<td>11.2</td>
<td>10.5</td>
</tr>
<tr>
<td>STC1-750</td>
<td>551</td>
<td>0.77</td>
<td>0.10</td>
<td>13.0</td>
<td>9.7</td>
</tr>
<tr>
<td>STC1-800</td>
<td>535</td>
<td>0.72</td>
<td>0.08</td>
<td>11.2</td>
<td>9.4</td>
</tr>
<tr>
<td>STC1-850</td>
<td>547</td>
<td>0.72</td>
<td>0.09</td>
<td>12.5</td>
<td>9.1</td>
</tr>
<tr>
<td>STC1-900</td>
<td>464</td>
<td>0.72</td>
<td>0.05</td>
<td>7.0</td>
<td>9.6</td>
</tr>
<tr>
<td>STC1-1000</td>
<td>440</td>
<td>0.69</td>
<td>0</td>
<td>0</td>
<td>8.9</td>
</tr>
<tr>
<td>STC1-500-a</td>
<td>1874</td>
<td>0.87</td>
<td>0.78</td>
<td>89.6</td>
<td>-</td>
</tr>
<tr>
<td>STC1-600-a</td>
<td>2199</td>
<td>1.20</td>
<td>0.69</td>
<td>57.5</td>
<td>-</td>
</tr>
<tr>
<td>STC1-700-a</td>
<td>1443</td>
<td>1.14</td>
<td>0.40</td>
<td>35.1</td>
<td>9.6</td>
</tr>
<tr>
<td>STC1-850-a</td>
<td>847</td>
<td>0.99</td>
<td>0.20</td>
<td>20.2</td>
<td>10.2</td>
</tr>
<tr>
<td>STC2-400</td>
<td>438</td>
<td>0.80</td>
<td>0.06</td>
<td>7.5</td>
<td>12.1</td>
</tr>
<tr>
<td>STC2-500</td>
<td>573</td>
<td>0.88</td>
<td>0.10</td>
<td>11.4</td>
<td>11.3</td>
</tr>
<tr>
<td>STC2-600</td>
<td>615</td>
<td>0.90</td>
<td>0.11</td>
<td>12.2</td>
<td>10.8</td>
</tr>
<tr>
<td>STC2-700</td>
<td>753</td>
<td>0.93</td>
<td>0.10</td>
<td>10.7</td>
<td>9.2</td>
</tr>
<tr>
<td>STC2-850</td>
<td>490</td>
<td>0.70</td>
<td>0.08</td>
<td>11.4</td>
<td>9.8</td>
</tr>
<tr>
<td>STC2-400-a</td>
<td>898</td>
<td>0.52</td>
<td>0.33</td>
<td>63.5</td>
<td>-</td>
</tr>
<tr>
<td>STC2-500-a</td>
<td>2364</td>
<td>1.10</td>
<td>0.95</td>
<td>86.4</td>
<td>-</td>
</tr>
<tr>
<td>STC2-600-a</td>
<td>1696</td>
<td>0.98</td>
<td>0.58</td>
<td>59.2</td>
<td>-</td>
</tr>
<tr>
<td>STC2-700-a</td>
<td>1240</td>
<td>0.95</td>
<td>0.35</td>
<td>36.8</td>
<td>8.2</td>
</tr>
<tr>
<td>STC2-850-a</td>
<td>882</td>
<td>0.87</td>
<td>0.22</td>
<td>25.3</td>
<td>9.2</td>
</tr>
</tbody>
</table>

$^a$ $S_{BET}$ - BET surface area; $V_t$ - single-point pore volume; $V_{mi}^{\alpha}$ - volume of micropores obtained by $\alpha_s$-method; $P_{mi}^{\alpha}$ - percentage of micropores; $w_{KJSme}$ - mesopore width at the PSD maximum obtained by the KJS method [118]
Figure 34. Nitrogen adsorption isotherms and corresponding pore size distributions for soft-templated carbons carbonized at different temperatures. For clarity the amount adsorbed values were shifted by 250 cm$^3$/g STP, while the PSD values were shifted by 0.15 cm$^3$/g nm.
Figures 35 & 36 present nitrogen adsorption isotherms and the PSD plots for the KOH activated carbons. As can be seen from these graphs, the KOH activation of the sample carbonized at 500°C gives purely microporous material analogous to the previously reported carbons obtained by activation of phenolic resins [150]. The BET surface area was found to be 1874 m$^2$/g, which is three times more than that of the initial sample. Note that the micropores contribute about 90% of the total pore volume, while the mesoporous structure suffers a significant loss. However, the isotherm for the next sample (STC1-600-a) shows some evidence for a partial preservation of mesopores. The PSD plot also proves the existence of mesopores, although it is difficult to determine the maximum of the peak. Moreover, this sample possesses a remarkable specific surface area of 2199 m$^2$/g and total pore volume of 1.20 cm$^3$/g. The relatively high microporosity generated during activation accounts for about 60% of total pore volume, which is lower than in the case of the STC1-500-a sample. A further increase in the temperature of pyrolysis prior to activation results in clearly micro- and mesoporous materials (samples denoted as STC1-700-a and STC1-850-a). Both isotherms show well-defined hysteresis loops, although the shape of the condensation step of the STC1-700-a sample suggests a slightly broader pore size distribution than that for STC1-850-a. In comparison to the really high parameters of the BET surface area and the total pore volume characteristic for the STC1-600-a sample, the corresponding parameters for STC1-700-a and STC1-850-a are lower but still very high. Notably, the micropores created by activation are about 1.8nm (estimated by the KJS method [118]) for the entire series regardless of the temperature of carbonization. Even though the contributions of micropores and mesopores to the total pore volume are nearly equal for the STC1-600-a sample (57% vs. 43%, respectively),
the STC1-700-a carbon seems to be more promising material for many applications due to its well-preserved mesopores, high microporosity (~35%) and high surface area.

For the purpose of comparison the same preparation, carbonization and activation procedures were used to prepare a new batch of phenolic resin samples carbonized in the range from 400°C to 850°C (STC2-T) and subjected to the KOH activation (STC2-T-a). Adsorption parameters for these samples (Table 10) are in a good agreement with the first series of the carbon samples proving reliable reproducibility of the proposed method for the preparation of activated soft-templated mesoporous carbons.
Figure 35. Nitrogen adsorption isotherms for activated carbon samples.

Figure 36. Pore size distributions for activated carbon materials.
This study shows that the post-synthesis KOH activation of mesoporous phenolic resin-based carbons can be effectively used not only to increase microporosity but also to tune mesoporosity. The resulting micro- and mesoporous carbons have high surface area as well as a well-developed microporosity and mesoporosity; the latter is preserved if KOH activation is performed at ~700°C on the phenolic resin samples carbonized at ~700-850°C. The temperature of carbon pyrolysis prior to activation strongly affects not only the structural properties of the resulting carbons but also their susceptibility to further activation and simultaneous preservation of the mesoporous structure. The higher carbonization temperatures (above 600°C) facilitate consolidation of the carbonaceous framework, resulting in a more rigid structure, which withstands the KOH activation process.

6. 2 HIERARCHICALLY POROUS PHENOLIC RESIN-BASED CARBONS OBTAINED BY BLOCK COPOLYMER-COLLOIDAL SILICA TEMPLATING AND POST SYNTHESIS ACTIVATION WITH CARBON DIOXIDE AND WATER VAPOR***

Physical activation of the soft-templated carbons, possessing two systems of mesopores, one originated from the block copolymer template used and another generated by dissolution of the silica nanoparticles added to the synthesis mixture, were performed. This strategy affords hierarchical carbons with greatly improved microporosity and specific surface area, and a very high total pore volume.

*** Górka J.; Jaroniec M. Carbon, 2011, 49, 154-160
**Scheme 9.** Schematic illustration of a combined soft- and hard-templating synthesis of mesoporous carbons followed by post-synthesis activation with CO$_2$ or H$_2$O. Triblock copolymer Pluronic F127 is used as a soft template and colloidal silica is used a hard template to form two types of mesopores, while the TEOS-generated silica template is used to create fine pores, micropores. The network of fine pores is further developed by post-synthesis activation with CO$_2$ or H$_2$O.

Hierarchical carbons were prepared according to the synthesis recipe for the high loading of inorganic species (see section 5.2 for details).

For activation, the samples were heated in a tube furnace under nitrogen atmosphere with heating rate of 5ºC/min up to 850. After reaching this temperature the activating gas was introduced to the tube furnace (80cm$^3$/min) for 3-5hr and then switched back to nitrogen to prevent further activation during the cool down.
The resulting materials were labeled $M$-$a$-$t$, where $M$ indicates the type of material (CS = carbon-silica composite or $C$ = carbon), $a$ refers to the activating agent used ($cd$= CO$_2$ or $v$= water vapor) and $t$ denotes the activation time. The samples marked with (*) were prepared by using 20nm silica nanoparticles, while those indicated by (#) were synthesized with 50nm silica colloids.

To show how TEOS addition affects structural parameters, two samples were prepared just with silica colloids and without TEOS (ntC* and ntC#, respectively) and then activated with CO$_2$ for 4hrs.

The goal of this work was to study the structural changes of carbons obtained by the combination of soft- and hard-templating methods upon CO$_2$ or water vapor activations. A schematic illustration of the synthesis strategy followed by post-synthesis activation is illustrated in Scheme 6. In the first part, the time of the exposition of as-prepared carbons to the activating agent was varied to determine the material stability at high temperatures and during long activation time. Nitrogen adsorption isotherms and the corresponding pore size distributions are presented in Figure 37. All carbons show adsorption isotherms of type IV, indicating the presence of a well-developed mesoporous structure. The capillary condensation steps are almost perpendicular to the relative pressure axis, suggesting a high uniformity of mesopores. The initial carbon material (C*) exhibits a very high nitrogen uptake, ~2200 cm$^3$/g, which can be easily improved by post-synthesis activation, and even doubled when the latter is performed for 4-5hrs. However, there seems to be an optimal activation time at which the carbon reaches its maximum adsorption, and longer activation does not increase it any more.
Table 12. Adsorption parameters for the phenolic resin-based carbons activated with CO$_2$ and H$_2$O

<table>
<thead>
<tr>
<th>Sample</th>
<th>S$_{BET}$ $m^2$/g</th>
<th>$V_t$ cc/g</th>
<th>$V_{mi}$ cc/g</th>
<th>$V_{me}$ cc/g</th>
<th>$V_{me}$* cc/g</th>
<th>$w_{KJS}$ nm</th>
<th>SiO$_2$ %</th>
<th>Burn-off %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CS*</td>
<td>244</td>
<td>0.42</td>
<td>0.01</td>
<td>0.34</td>
<td>-</td>
<td>13.8</td>
<td>78</td>
<td>-</td>
</tr>
<tr>
<td>C*</td>
<td>1434</td>
<td>3.29</td>
<td>0.14</td>
<td>3.02</td>
<td>-</td>
<td>14.3</td>
<td>5</td>
<td>-</td>
</tr>
<tr>
<td>C*-cd-3h</td>
<td>1857</td>
<td>3.94</td>
<td>0.13</td>
<td>3.66</td>
<td>-</td>
<td>13.8</td>
<td>5</td>
<td>33</td>
</tr>
<tr>
<td>C*-cd-4h</td>
<td>2700</td>
<td>5.83</td>
<td>0.22</td>
<td>4.96</td>
<td>-</td>
<td>12.4</td>
<td>6</td>
<td>63</td>
</tr>
<tr>
<td>C*-cd-5h</td>
<td>2793</td>
<td>6.00</td>
<td>0.20</td>
<td>5.40</td>
<td>-</td>
<td>11.4</td>
<td>6</td>
<td>75</td>
</tr>
<tr>
<td>C*-v-3h</td>
<td>2370</td>
<td>5.02</td>
<td>0.18</td>
<td>4.73</td>
<td>-</td>
<td>13.3</td>
<td>6</td>
<td>56</td>
</tr>
<tr>
<td>C*-v-4h</td>
<td>2475</td>
<td>5.09</td>
<td>0.19</td>
<td>4.73</td>
<td>-</td>
<td>12.3</td>
<td>8</td>
<td>57</td>
</tr>
<tr>
<td>ntC*</td>
<td>958</td>
<td>1.50</td>
<td>0.09</td>
<td>1.22</td>
<td>-</td>
<td>16.4</td>
<td>5</td>
<td>-</td>
</tr>
<tr>
<td>ntC*-cd-4h</td>
<td>1669</td>
<td>2.50</td>
<td>0.21</td>
<td>1.97</td>
<td>-</td>
<td>16.4</td>
<td>6</td>
<td>30</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>S$_{BET}$ $m^2$/g</th>
<th>$V_t$ cc/g</th>
<th>$V_{mi}$ cc/g</th>
<th>$V_{me}$ cc/g</th>
<th>$V_{me}$* cc/g</th>
<th>$w_{KJS}$ nm</th>
<th>SiO$_2$ %</th>
<th>Burn-off %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CS#</td>
<td>239</td>
<td>0.49</td>
<td>0.01</td>
<td>0.46</td>
<td>-</td>
<td>14.3</td>
<td>77</td>
<td>-</td>
</tr>
<tr>
<td>C#</td>
<td>1577</td>
<td>3.84</td>
<td>0.17</td>
<td>2.75</td>
<td>3.60</td>
<td>14.3</td>
<td>4</td>
<td>-</td>
</tr>
<tr>
<td>C#-cd-3h</td>
<td>1685</td>
<td>4.44</td>
<td>0.15</td>
<td>2.47</td>
<td>4.15</td>
<td>15.2</td>
<td>6</td>
<td>32</td>
</tr>
<tr>
<td>C#-cd-4h</td>
<td>1873</td>
<td>4.59</td>
<td>0.19</td>
<td>2.81</td>
<td>4.34</td>
<td>14.5</td>
<td>6</td>
<td>35</td>
</tr>
<tr>
<td>C#-v-3h</td>
<td>2195</td>
<td>5.62</td>
<td>0.22</td>
<td>3.29</td>
<td>5.28</td>
<td>14.4</td>
<td>7</td>
<td>46</td>
</tr>
<tr>
<td>C#-v-4h</td>
<td>2213</td>
<td>5.72</td>
<td>0.22</td>
<td>3.36</td>
<td>5.46</td>
<td>14.3</td>
<td>7</td>
<td>46</td>
</tr>
<tr>
<td>ntC#</td>
<td>844</td>
<td>1.86</td>
<td>0.06</td>
<td>0.89</td>
<td>1.72</td>
<td>13.0</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>ntC#-cd-4h</td>
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<td>0.14</td>
<td>1.16</td>
<td>2.21</td>
<td>13.2</td>
<td>7</td>
<td>31</td>
</tr>
</tbody>
</table>

Notation: S$_{BET}$ – BET specific surface area; $V_t$ – single-point pore volume; $V_{mi}$ – volume of fine pores (mainly micropores) obtained by integration of PSD up to 4 nm; $V_{me}$ – volume of mesopores obtained by integration of PSD from 4 nm to 20 nm; $V_{me}$* - volume of mesopores calculated from the whole range of mesopores; $w_{KJS}$ – mesopore diameter at the maximum of the PSD curve obtained by the modified KJS method [118]; %– SiO$_2$ residue obtained from the TG curve recorded in air at 800ºC. Samples (*) have been prepared by using 50 nm colloidal silica; samples (**) were prepared using 20nm silica particles.
Figure 37. Nitrogen adsorption isotherms and the corresponding pore size distributions for the carbons prepared with 20nm silica colloids and activated with CO$_2$. 
Additionally, the capillary condensation step became slightly broader, implying some minor deterioration of the mesopore structure. The structural parameters for all materials under examination are listed in Table 12.

As mentioned above, all samples possess impressive specific surface areas, ranging from 1434 m$^2$/g for starting carbon material to almost 2800 m$^2$/g for C*-cd-5h sample. Interestingly, the activation conducted for 3hrs did not significantly improve the BET surface area or microporosity, when compared to the parent carbon sample. In contrast, longer CO$_2$ activation definitely alters both kinds of pores, which is reflected by the high surface area and total pore volume. This can be seen from the PSD plots: as the time of activation is prolonged, the peak maxima corresponding to mesopores are shifted towards smaller pores and peaks become wider, which is especially evident in the range of 5nm to 10nm.

Figure 38 shows two sets of adsorption isotherms related to the carbons synthesized with 20nm (panel A) and 50nm silica colloids (panel B), and then activated in CO$_2$ and water vapor. All isotherms are classified as type IV; however, there are some differences in the shapes of capillary hysteresis loops. The carbons obtained after dissolving 20nm silica nanoparticles (see panel A) exhibit comparable adsorption isotherms to those presented in Figure 37, where the single capillary condensation step is located at ~0.85p/$p_o$. In contrast, the carbons prepared with 50nm silica colloids show two distinct steps on each adsorption branch of the isotherms, one appearing also at 0.85-0.90p/$p_o$ and the second placed close to unity, which confirms the presence of mesopores with two distinct and uniform pore widths. This is also clearly shown on the PSD plots, where one can easily distinguish one system of pores of about 12nm (C* series) and in the case of C# series, an additional system of pores of about 50nm, resembling
the size of the silica nanoparticles used. A comparison of CO$_2$ and water vapor activations of
the samples within the C* series shows that there are noticeable differences, especially in the
case of CO$_2$ activation, where just one hour longer activation results in greatly enhanced
structural properties. It is noteworthy that the samples (after CO$_2$ activation) from the second
series exhibit very similar total adsorption; however, the height of the first capillary
condensation step demonstrates the generation of some small mesopores, which were found to
be between 5nm and 12nm from the PSD curves. In contrast, the water vapor seems to create
approximately the same amount of porosity regardless of the time of the activation. The same
behavior was observed for C#-v-3h and C#-v-4h (see Panel B), where both isotherms almost
overlapped. The adsorption properties listed in the Table 12 reflect all structural changes
discussed above. In general, the specific surface areas for C* carbons were found to be higher
and/or more diverse than those for the C# carbons. The reverse trend is observed for total pore
volumes, though one needs to remember that all parameters are the function of the carbon
burn-off, which changes within both series. The mesopore widths calculated by integration of
the PSD peaks are shifted towards smaller values, which could be a sign of a material
shrinkage under extended high temperature treatment. The changes in the micropore and
mesopore volumes will be discussed in more detail in the next section.
Figure 38. A comparison of nitrogen adsorption isotherms and the corresponding pore size distributions for the carbons prepared with 20nm (panel A) and 50nm (panel B) silica colloids and activated with CO$_2$ and water vapor.
The aim of the next stage of this project was to determine how much the TEOS addition, or rather, the microporosity created after its dissolution prior to activation, helps in obtaining high surface areas and pore volumes. In order to answer this question, the two new samples with just colloidal silica alone (no TEOS) were synthesized and then activated in CO$_2$ for 4hrs. A comparison of nitrogen isotherms and the corresponding PSDs for the carbons prepared with and without TEOS before and after activation are shown in Figure 39.

In both series, the lowest nitrogen adsorption is exhibited by non-activated carbons prepared without TEOS; then, as a result of activation, their structural parameters were enhanced but still show lower values compared with the non-activated carbons fabricated with the use of a double silica source. Based on that, there is not doubt that the microporosity generated by dissolving TEOS intensifies the effect of activation, which is especially pronounced in the case of C*-cd-4h carbon. There are some differences between the carbons from C* and C# series, but the general trend toward significantly increased micro- and mesoporosity stays the same.
Figure 39. A comparison of nitrogen adsorption isotherms and the corresponding pore size distributions for the carbons prepared with and without TEOS addition before and after CO$_2$ activation (panel A-20nm silica colloids and panel B- 50nm silica colloids).
For years the hard-templating synthesis was utilized for the preparation of carbons with hierarchical porosity [79, 151-152]. In terms of scaling up and lowering the cost of carbon preparation the soft-templating method seems to be a better alternative. In particular, the acidic route affords carbons with better-developed mesopore structure (usually showing steep and high condensation steps at higher p/p_{o}, proving the presence of larger and uniform mesopores) than the carbons prepared under basic conditions. In the latter case, not only the mesopores obtained are smaller, but the materials themselves also show extensive framework shrinkage and some structure deterioration at higher carbonization temperatures [100, 14]. In relation to the post-synthesis activation, it was found that the carbons obtained under lower pH tolerate more extreme activation conditions and even graphitization at 2600ºC without significant changes in the mesopore structure. The highest values of the BET surface area and total pore volumes reported to date for the activated soft-templated carbons oscillate about 2400m^{2}/g [110] and 2.8cm^{3}/g [95], respectively. However, the samples possessing such high parameters exhibit either extensively developed microporosity with a small amount of mesopores [110] or small primary mesopores accompanied by secondary mesoporosity [95], and cannot be really considered as true hierarchical carbons. The fact that the activation results depend on the degree of carbon burn-off does not leave much room for further improvement, unless some modifications/additions will be made at the synthesis stage. Our group showed that soft-templating synthesis has a great potential to accommodate large loadings of various organic and inorganic species during the mesophase formation without causing major disruption to the latter [106, 107]. This feature was employed to obtain highly micro- & mesoporous carbons by combining the colloidal templating and soft-templating methods [107]. The double silica
source (silica nanoparticles and TEOS) provides spherical mesopores, and additional micropores created by the removal of the TEOS-generated silica along with the cylindrical mesopores obtained by decomposition of the polymeric soft template. Carbon materials prepared according to this synthesis route exhibit high surface area and total pore volume that can be further enhanced by post-synthesis activation.

Physical activation is based on the controlled gasification of a char with an oxidant gas (usually CO$_2$ or steam) at a high temperature. In general, it proceeds towards gradual pore enlargement, where ultramicropores become supermicropores, reflected by higher micropore volume; next, the resulting pore widening causes the drop in microporosity along with a small increase in mesoporosity [153]. Many reports show that regardless of the activation medium, activated carbons usually possess comparable specific surface area and total pore volume [154]; however CO$_2$ and water vapor tune porosity in a different way, resulting in a slightly different distribution of micro- and mesopores. In the case of water vapor activation, two phenomena have been observed: (i) the increase in all adsorption parameters, with respect to the parent sample, is much higher than that observed for CO$_2$ activation, and (ii) the changes in the micro- and mesopore volumes with increasing time of activation are regular. This can be explained by the difference in size of CO$_2$ and H$_2$O molecules [153]. The smaller size of H$_2$O facilitates its penetration into the carbon framework and causes an enlargement in both micro- and total pore volumes. However, the activation with water vapor seems to be more difficult to control, taking into account the fact that longer activation time do not improve structural parameters of the carbon studied and almost showed the same burn-off percentage.
In the case of CO$_2$, the results are more diverse. The carbons prepared with 20nm silica colloids (C* series) seem to follow the general activation scenario in which the micropores became larger and their contribution slightly drops in favor to mesopores, thus longer activation results in the gradual increase in both parameters. This suggests that, initially, CO$_2$ molecules cannot fully access and penetrate the framework. However, after a sufficient amount of micropores is created the activation proceeds rapidly, which is clearly displayed by the degree of the framework burn-off. To confirm these findings, two samples without TEOS were synthesized and then activated. The results clearly show that the additional microporosity created prior to activation enhances the latter effect quite markedly. A comparison of C* and C# series of carbons lends some insight into how activation affects mesopores. However, this is difficult to estimate based only on the C* series of carbons, where the peak for mesopores obtained by etching 20nm silica nanoparticles and the peak corresponding to mesopores created by soft templating overlap with each other. While the changes in the micropore volume for C# carbons follow the same trend as in the case of C* series, the initial decrease in the mesopore volume corresponding to the pores of about 14nm indicates that some part of the carbon between silica nanoparticles might have thinner pore walls, which are partially destroyed during activation. Pores created in this way contribute to 50nm mesopores.

Based on the burn-off percentage, lower surface areas, and total pore volumes, the C# carbons seem to be less susceptible to activation. The activating gas seems to go through large spherical pores without causing much change in the structure as activation time increases. As the reason for this is unclear, more research is needed; specifically into the problem of
adjusting the flow of the gas and/or extending activation time since the burn-off is still below 50%.

Recently, carbons with hierarchical porosity became the nanomaterials of interest, not only from the standpoint of adsorption/separation, but also catalysis and energy storage. The synthesis strategy presented in this work combines the best features of soft- and colloidal templating methods. The latter is a well-known method for obtaining high pore volume carbons with uniform spherical mesopores. The soft-templating method, under acidic conditions, delivers cylindrical mesopores with diameters of about 10nm. In the light of the recent work by Wu et al. [155] showing a synergistic effect of 2-D channel-like structure of OMCs and 3-D network of carbon aerogels on electrochemical performance, it is expected that our carbons will exhibit similar electrochemical properties. Moreover, the activation step employed to improve the BET surface area and microporosity should additionally enhance material capacitance. The fact that, in the case of soft-templated carbons, a complete silica etching is difficult may help to reduce the capacity fading after prolonged charging-discharging cycles as reported by Shon et al. [156]. From the catalysis viewpoint, the good access to micropores gives the advantage of fast adsorption/desorption, which, when combined with the acidic sites created by the post-synthesis oxidative treatment makes the materials appealing for specific applications.

This work shows that hierarchical carbons with two distinct pore geometries (cylindrical and spherical) and sizes can be synthesized via combined soft- and hard-templating strategies. Triblock copolymer Pluronic F127 was used under acidic conditions as a soft template to form a network of hexagonally arranged cylindrical mesopores (~12 nm), while
colloidal silica (20-50 nm) was embedded into this network to create larger spherical mesopores. This one-pot synthesis was carried out in the presence of TEOS that was employed for the generation of micropores. The latter was additionally enhanced by post-synthesis activation with CO$_2$ and water vapor. All carbons studied exhibited a high surface area and large pore volume. Regardless of the activating medium used, there was no indication of structural deterioration for activations carried out below 4hrs, showing the exceptional thermal stability of these carbons. A comparison of CO$_2$ and water vapor activation indicates that the latter is more effective for the enhancement of micro- and mesoporosity. Interestingly, the use of TEOS in this synthesis generated additional microporosity in the original carbon, which enhanced post-synthesis activation with CO$_2$ and water vapor.
CHAPTER 7

CONCLUSIONS

A comparison of hard- and soft-templating synthesis showed that the latter is more feasible for the preparation of ordered mesoporous carbons and carbon–based materials. Not only reduced number of preparation steps and greener synthesis route but also bigger freedom in the design of the structural properties of the final material make the soft-templating synthesis very appealing for both industry and academia.

This dissertation is primarily focused on the development of effective synthesis routes to prepare ordered mesoporous carbons using phenolic resins as carbon precursors and triblock copolymers as soft templates under acidic conditions. Some systematic studies were performed to improve the understanding of this process. It was shown that an increase in the synthesis temperature causes a decrease in the pore volume and pore diameter. Subsequently, there is a possibility to change the pore symmetry from channel-like to cage-like by increasing a copolymer/carbon precursor ratio. This effect is even more pronounced for the samples prepared at higher temperatures and higher copolymer/carbon precursor ratios. Another feature of the aforementioned structure transformation is a reduction in the volume of mesopores. In addition, it was found that the size and ordering of mesopores depends strongly on acid concentration. All these findings provide a foundation for expanding the use of soft-templating to the preparation of other carbon-based materials.
The first class of the aforementioned materials was prepared in the presence of organosilanes to determine how the typical reaction mixture adjusts itself to accommodate the increasing loading of these molecules and how this affects the mesostructure formation. In the first part of the study small organosilane such as TEOS was successfully introduced into a carbon framework in amount up to 70wt% with respect to carbon precursors. The high loading of TEOS resulted in a significant increase of microporosity achieved by the dissolution of TEOS-generated silica and in a gradual enlargement of mesopores, suggesting that TEOS is mostly embedded in the carbon framework but also at higher concentrations interacts with hydrophilic domains of micelles causing a pore enlargement. For the larger organosilanes used such as ICS, the incorporation mechanism seems to follow the same trend as in the case of TEOS. The TGA data clearly show a progressive incorporation of isocyanurate groups into the polymer matrix, the presence of which was additionally confirmed by FTIR analysis. Even after carbonization at 850°C all samples still possess nitrogen in the carbon matrix. Regardless of the organosilane used all polymer and carbon materials exhibit large and uniform mesopores ~8-10nm, high surface area and pore volume. Thus, the organosilane-assisted synthesis represents an effective way of tailoring surface and framework properties of soft-templated carbons. Also the possibility of introducing large amounts of organosilanes possessing different functional groups and their large variety on the market creates enormous opportunities for the development of novel carbon-based materials for various applications.

The flexibility of the soft-templating system observed for organosilane-assisted synthesis was an inspiration to fabricate the organic-inorganic nanocomposites by direct addition of metal oxide nanoparticles to the synthesis mixture. The carbons with 10wt% and 20wt% of
alumina and silica nanoparticles were prepared. In the case of the lower loadings of nanoparticles the resulting materials are almost identical in terms of adsorption properties; however, when the content of nanoparticles increased, the chemistry and size of these particles seemed to affect more the structural properties of the final materials. The uniform and large mesopores provide good access to the nanoparticles embedded in the carbon matrix, which was proved by a successful removal of silica by using aqueous solutions of HF or NaOH.

In the next set of experiments, it was decided to increase the loading of silica nanoparticles even more up to 50wt%. At this point the whole procedure can be considered as a combination of the colloidal- and soft-templating and allows introducing mesopores with a spherical geometry in controlled manner by simply controlling the size and the amount of the silica nanoparticles used. Moreover, the whole system seems to be capable of accommodating even more of silica species as it was found by supplying TEOS to the synthesis mixture. It was shown that double silica source (silica nanoparticles and TEOS) can be used to easily tune both meso- and microporosity leading to greatly improved total pore volume and specific surface area. The synthesis procedure appeared to be very reproducible even for high loadings of silica species. Also, this TEOS-assisted incorporation of nanoparticles holds great promise for the development of nanomaterials for specific adsorption and catalysis applications, where both the porosity of carbon support and the incorporation of active species can be simultaneously adjusted during one-step synthesis.

Up to this point all composite carbon materials were synthesized with the use of spherical nanoparticles mostly due to their availability in a wide range of sizes but also the possibility to create additional mesoporosity with known geometry after their dissolution. In recent years, a
new class of nanomaterials called nanosheets attracted a lot of attention because of their possible applications in catalysis, energy and gas storage, sensors and electronics design. The features such as 2-dimensional morphology, high crystallinity, well-defined composition, and most importantly, the presence of large-area crystallographic facets make these layered materials the attractive components for fabrication of nanostructured composites. In our studies we used 20-35nm thick nonporous α-alumina nanosheets with exposed (001) facets, which seem to be responsible for the surface-induced perpendicular orientation of ordered mesopores in carbon and the enlargement of the diameter of these pores. To the best of our knowledge this is the first report showing such as unique pore orientation in the carbons obtained by soft-templating.

Another important part of this dissertation was devoted to the elaboration of the efficient ways to improve the BET surface area and micropore volume in the soft-templated carbons. The general synthesis procedure results in mostly mesoporous carbons, having microporosity below 15% of the total pore volume. First, the post-synthesis KOH activation of mesoporous phenolic resin-based carbons was proposed to enhance the microporosity. This strategy afforded micro- and mesoporous carbons featuring high surface area as well as a well-developed microporosity and mesoporosity. The latter was preserved if KOH activation was performed at ~700°C on the phenolic resin samples carbonized at ~700-850°C. It was shown that the susceptibility of phenolic resin-based carbons to further activation that does not cause a significant alteration in the mesopore structure, depends strongly on the temperature of carbon pyrolysis prior to activation.
Also, a physical activation of the soft-templated carbons, possessing two systems of mesopores, one originated from the block copolymer template used and another generated by dissolution of the silica nanoparticles added to the synthesis mixture, was performed. When this combined soft- and hard-templating synthesis was performed in the presence of TEOS, hierarchical carbons with two distinct pore geometries, cylindrical and spherical, and with an extra microporosity generated by removal of the TEOS-generated silica, were obtained. The porosity of these hierarchical carbons was further improved by post-synthesis activation with CO$_2$ and water vapor. Interestingly, it was found that the TEOS-generated microporosity greatly enhances the post-synthesis CO$_2$ and water vapor activation of the aforementioned hierarchical structures, resulting in the carbons with very high surface areas and total pore volumes approaching 2800 m$^2$/g and 6 cm$^3$/g, respectively. Furthermore, the fact that this relatively long post-synthesis activation did not cause a noticeable structure deterioration proves their exceptional thermal stability under neutral atmosphere. A comparison of CO$_2$ and water vapor activations indicate that the latter is more effective for the enhancement of micro- and mesoporosity.

Every year brings a larger number of publications in the area of soft-templated carbons, indicating a growing interest in this simpler, greener and less expensive synthesis of ordered mesoporous carbons. The existing literature in this relatively new research area shows an enormous potential in the development of soft-templated OMCs and OMC-based composites for advanced applications ranging from adsorption and catalysis to environmental processes, energy storage and conversion.
References


