METAL DOPED CARBON GELS
PhD THESIS

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1. Preface

In 1989 R.W. Pekala reported first the synthesis of organic aerogels [Pekala 1989]. Most often these materials are prepared by drying resorcinol – formaldehyde (RF) polymer gels, but several other monomers can also be used for this purpose. The organic aerogels are much harder than inorganic ones, and due to their extremely high thermal resistance (what is six times larger than that of the fiberglass) they are very promising insulator materials. Their notability is in the high specific surface area and controllable pore structure. Owing to the sol – gel preparation method, the gel can be prepared in various forms: from microspheres to relatively large monoliths (columns of tens of centimetres in length) (Figure 1).

![Figure 1. Monolithic type organic and carbon gels](image)

Carbonizing the organic aerogels carbon aerogels can be prepared that maintain the pore structure of the dry organic gels. In addition they become electrically conductive materials. This unique feature allows them to be used for various electrochemical applications in electrical capacitors [Babić 2004, Frackowiak 2001, Hrubesh 1998, Kibi 1996, Li 2008, Zhu 2007], lithium-ion batteries [Chao 2008, Yuan 2007], capacitive deionization (CDI) processes [Jung 2007], solar cells [Kim 2004], electrochemical water treatment systems [Rana 2004].

Today these carbon gels are among the most suitable materials for gas separation purposes [Yamamoto 2004]. Due to their favourable properties they can also be used for packing in chromatography columns or as adsorbents [Hrubesh 1998, Kim 2006]. Different heteroatoms (e.g. metals) can be introduced into the structure during the preparation
process, which allows these materials to be used as catalysts [Moreno-Castilla 1999, Moreno-Castilla 2005] or catalyst supports [Job 2006 (1)]. Figure 2 summarizes the different types of utilization of the carbon aerogels.

Figure 2. Carbon gel applications
2. Background

2.1. Preparation of RF hydrogels

The first published organic aerogel was prepared from resorcinol (R) and formaldehyde (F), with Na$_2$CO$_3$ as a catalyst (C) in aqueous medium [Pekala 1989]. After one week of curing at 85 °C the initial resorcinol – formaldehyde sol became an RF hydrogel. The mechanism of the polymerization involves aromatic electrophilic subtraction, followed by condensation reactions that lead to cross-linking. The reaction starts when R is deprotonated by the base catalyst, and then the phenoxide attacks the F in ortho- or para-positions, leading to a hydroximethylated R (Figure 3).

![Polycondensation reaction between resorcinol and formaldehyde](image)

**Figure 3.** Polycondensation reaction between resorcinol and formaldehyde [Lin 1997]
The rate of both steps depends strongly on the synthesis conditions such as the pH of the initial solution, the synthesis temperature, the overall concentration, and the molar ratios (R/F, R/C). Since the two steps take place simultaneously, the final texture of the wet RF gel is influenced by the ratio of the addition and condensation rates. When the addition step is fast, many methylol derivatives are formed before gelation actually takes place, which leads to the formation of small primary clusters, small polymer structures and small pores, probably through a phase demixing phenomenon. When the condensation step is fast, each methylol derivative reacts quickly with another one, which leads to large primary clusters, large polymeric structures and large pores [Job 2006 (2)].

![Structure formation model of RF hydrogel](image)

**Figure 4.** Structure formation model of RF hydrogel [Tamon 1998]

In a structural study of sol–gel transition of RF solutions with real-time SAXS measurements it was found that in the initial stage of the hydrogel formation, small clusters of branched polymer species are formed that display mass fractal behaviour [Tamon 1998]. The
change in the shape of the response curves showed that the particle size increases with the time, and becomes constant after the gelation point that is identified by the steep increase of viscosity. Hence, the growth of particle stops at the gelation point because the gel structure is fixed. SAXS was also used to obtain information about the structure of polymeric species during the sol–gel transition through the power law behaviour of the response curve. Tamon et al. proposed a model for the structure formation of RF hydrogels during the sol–gel transition (Figure 4). At the initial stage, small clusters consisting of branched polymeric species form, showing mass fractal behaviour (Figure 4a). Later the clusters aggregate and form particles, and they became surface fractals (Figure 4b). When the RF solution is gelled, the structure is fixed and a hydrogel is obtained (Figure 4c). Finally the surface becomes smooth upon aging (Figure 4d).

The gelation process of resorcinol and formaldehyde was intensively studied by dynamic light scattering (DLS) [Martin 1988, Stauffer 1982]. It was observed by this method of the polymerisation reaction with Na2CO3 at 25 °C [Yamamoto 2002 (2)], that the decay time spectrum changes during the sol–gel transition. At the beginning the spectra are unimodal, and the peak value increases as the sol–gel transition proceeds. After a critical time the spectrum becomes bimodal. The peak corresponding to the larger decay time shifts to larger decay time ranges until complete gelation indicates the formation of a network structure composed of colloidal particles. The size of the colloidal particles gradually increases at the early stage of the sol–gel transition, followed by a relatively steeper increase as the transition proceeds. It is assumed that the gradual increase corresponds to the growth of individual colloidal particles, and the steeper increase to aggregation of the colloidal particles. Before the critical time, colloidal particles behave as Brownian particles and their diffusion constant is simply determined by the thermal fluctuation of solvent molecules. At longer time intervals, colloidal particles form a network structure that is still not percolated, and their dynamics are also governed by concentration fluctuations associated with the translational motion of the network, in addition to the thermal fluctuation of solvent molecules. Fluctuation of the network structure is considered to show a much longer relaxation time compared to that of solvent molecules. Thus, the occurrence of the bimodal mode in the decay time spectra reflects the formation of a network structure of colloidal particles.

Nevertheless, gelation does not mean that the polymerization reaction is over. Aging is in all cases necessary to complete the polymer formation so that the solid network can withstand the surface tension due to the liquid–gas interfaces during the drying treatment. Just after gelation, the gel looks like jelly and only hardens with time. To enhance the
polymerization reaction, and improve the stability of the gel, after the one week curing period Pekala applied a washing step with trifluor-acetic acid [Pekala 1989]. To avoid this final treatment, and to shorten the reaction time Lin et al. found that setting the pH of the initial solution with dilute HNO₃ leads to appropriate resorcinol – formaldehyde gels [Lin 1997].

The pore structure of the gels can be also be modified by adding surfactant to the initial RF solution [Matos 2006, Wu 2006 (2)]. The surfactant concentration has an important role on pore size distribution and shape. Gels prepared with anionic surfactant exhibit mesopores of different shapes and larger sizes than those prepared with non-ionic and cationic ones. The effect of non-ionic surfactants was not relevant in the textural modification of the original RF gel.

2.1.1. Effect of the molar ratios

The applied molar ratios in the initial reaction mixture found to have a strong influence on the structure of the forming gel. Therefore the effect of these parameters is widely studied. The R/C ratio can be varied between 50 and 2000 [Lin 1997, Li 2008, Job 2006 (2)]. The micropore volume of the samples can be slightly increased by increasing the resorcinol/formaldehyde (R/F) ratio [Maldonado-Hódar 1999], but this effect is marginal. This is the reason why all the preparation processes employ the R/F = 0.5 ratio.

Dynamic light scattering (DLS) studies were performed by Yamamoto et al. to examine the effects of the different molar ratios to the polymerisation reaction using Na₂CO₃ as catalyst [Yamamoto 2002 (2)]. It was found that the growth rate of the size of the colloidalical particles becomes larger on decreasing the resorcinol/water (R/W) or increasing the resorcinol/catalyst (R/C) ratios. Furthermore, size of the final clusters shows the same tendency. In contrast, the time that is needed for gelation at a given temperature is higher if the R/C value is increased [Job 2007]. But this effect found to be weaker that the effect of the temperature of the gelation. At high R/C ratio (e.g., R/C = 500), the addition rate is probably very large compared to the condensation rate. Since the polymer probably passes through phase demixing before gelation, it is likely that the temperature affects less the final texture than the R/C ratio itself [Job 2006 (2)].

Li et al. found that the particle size of carbon aerogels increases with the increase of R/C ratio from 500 to 1500 [Li 2008]. In order to compare the effects of different R/C ratios on the morphology of the carbon aerogels, a direct morphology observation was conducted by
scanning electron microscopy (SEM). When the R/C ratio was equal to 500 or 1000 the carbonized samples exhibited a compact network structure, the particles agglomerated together. The carbon aerogel particles become bigger with increasing R/C ratio. When the R/C ratio reached 1500, spherical morphology of the particles can be clearly seen, the particle size was mainly less than 1000 Å. This structure was typical for acid-catalyzed carbon aerogels. The apparent surface area and the micropore volume do not change significantly with the R/C ratio. The meso- and macroporous character of the carbon gels develops as R/C increases.

It has also been found that decreasing the R/C ratio makes the structure of the dry gels mainly microporous, while increasing this ratio results in increased cluster size and essentially meso/macroporous character [Li 2008]. The concentration of the catalyst also determines the size of the clusters and the morphology of the structure of the dried RF gels. During the first stage of the polymerization each cluster grows individually, and their number is determined by the amount of catalyst. Subsequently they aggregate to form an interconnected structure. If the concentration of the catalyst is high (low R/C) the density of nucleation centres is high, and the size of the clusters is therefore small [Yamamoto 2001 (2)]. Following the same idea, it can be also concluded that the average pore size of the aerogels increases on increasing R/C or on decreasing R/W [Tamon 1999, Yamamoto 2001 (2)]. The R/C ratio has no significant influence on the apparent surface area and the micropore volume [Mathieu 1997].

2.1.2. Effect of the catalyst

Systematic studies of various catalysts, including several acids (perchloric acid, nitric acid, acetic acid), showed that the catalyst can strongly affect the structure of the developing RF gel [Berthon 2001, Farién-Jiménez 2006]. Almost all the structural properties derived from Na₂CO₃-catalyzed RF aerogels could be reproduced with acetic acid catalyst simply by changing the concentration. Nevertheless, in some of the acidic cases, connectivity among the primary particles is exceptionally high [Farién-Jiménez 2006].

The nature of the alkaline carbonate affects the development of the porosity in the final carbon aerogel [Tamon 2000]. This effect might be related to the different polarizing power of e.g. Na⁺ and K⁺ ions due to their different size [Farién-Jiménez 2006]. The pore characteristics of the RF carbon aerogels vary with the catalyst species. A characteristic difference was found in the mesopore size distribution of the RF carbon aerogels, which was
caused by the RF gelation process of the RF hydrogels [Horikawa 2004 (2)]. The amount of adsorbed N₂ at p/p₀→1, in the cases of the RF carbon aerogels synthesized with KHCO₃ and NaHCO₃ catalysts, was found to be larger than for K₂CO₃ and Na₂CO₃ catalyzed systems. The specific surface area values of all the RF carbon aerogels were about the same and only a small difference was found in the micropore volumes for different catalyst species. The mesopore volumes were significantly higher for the hydrocarbonate-catalyzed systems, and the mean pore radius was 30% higher for these samples. Comparing the two alkali metals, it was found that in the case of K⁺ the pore volumes and the mean pore radius were higher than in the case of Na⁺. Following the gelation by small angle X-Ray scattering (SAXS) measurements it was found that the scattering intensity becomes larger with the progress of duration time, and the SAXS curves became unchanged beyond a certain time that was characteristic of the catalyst used. This time for the hydrocarbonate-catalyzed systems was twice as long as for Na₂CO₃ and K₂CO₃. The sizes of the primary particles of spherical shape were different with the different catalysts (K₂CO₃, KHCO₃, Na₂CO₃ and NaHCO₃), and it became constant after a large time period. A longer time was needed for this in the Na⁺ containing systems.

In the experiments of Tamon et al. [Tamon 2000] three different basic catalysts (NaOH, NH₃ and NaHCO₃) were compared in aqueous media. It was found that alkali metals are indispensable to gelation. When NH₃ was used, the RF solution became milk-white and muddy and did not gel.

Berthon et al. [Berthon 2001] followed the reaction catalyzed by either basic (in water as solvent) or acidic catalyst (in acetone as solvent) by dynamic light scattering (DLS) measurements. The results showed that the gelation mechanisms are fundamentally different. In the acid catalyzed series, at least not too far above from the critical concentration, chemical gelation is governed by percolation. As soon as the hydroxymethyl is created (slow kinetics owing to acid catalysis and low water content), this molecule immediately combines with a neighbouring cluster. In contrast, gelation in base-catalyzed systems is comparable to aggregation in dense colloidal solutions. In this case the kinetics of formation of hydroxymethyl is fast and the sol is composed of small highly reactive clusters. Clusters grow by draining matter from their immediate neighbourhood, creating depletion layers and yielding spatial ordering when the reaction proceeds with large sticking probability.

A catalyst is said to be a substance that initiates or accelerates a chemical reaction without itself being affected. Therefore the concentration of the catalyst should not affect the reaction, and thus the resulting product. From this point of view the polycondensation reaction
between resorcinol and formaldehyde is irregular. In this case the catalyst also acts as nucleation agent, and thus highly affects the morphology of the hydrogel (Figure 5). It was found that the maximum of the pore size distribution definitely depends on the catalyst concentration. At high catalyst/water (C/W) ratios the average pore size is relatively small, but on increasing the C/W ratio it increases significantly [Yamamoto 2001 (2)].

![Figure 5](image.png)

**Figure 5.** Gelation at low (a) and high (b) catalyst concentration [Yamamoto 2001 (2)]

By ultrasonic irradiation together with suitable catalyst concentrations, interesting improvement in mesoporosity of resorcinol–formaldehyde carbon gels can be observed especially when the catalyst concentration (C/W) or pH is high [Tonanon 2005]. The gelation time is also greatly shortened.

### 2.1.3. Effect of the initial pH and synthesis temperature

Different studies proved that the pH of the initial solution plays a determining role in textural properties of the forming gel [Lin 1997, Job 2004 (1), Job 2006 (2)], since the pH strongly affects the reaction route of the polymerization. If there is no additional base or acid in the system, the initial pH of the solution simply depends on the amount of the catalyst.
At high (> 6) and low (< 4) pH values the appearance of methylol derivatives is favoured, either via the deprotonation of resorcinol (the resorcinolate anion is more sensitive to formaldehyde addition than resorcinol) or through the protonation of formaldehyde (protonated formaldehyde is more reactive with regard to molecular formaldehyde).

Figure 6. Gelation time ($t_g$) at 90 °C (◇), 85 °C (□) 70 °C (■) and 50 °C (▲) as a function of the pH of the precursors solution measured at 25 °C [Job 2006 (2)]

At high pH values, the condensation step is probably induced by phase separation, while at low pH values H$_3$O$^+$ catalyzes the condensation reaction. It was observed that the gelation time passes through a maximum as the pH of the starting mixture increases from 2 to 8 (Figure 6). The location of the maximum of the curve depends on the synthesis temperature. The polymerization mechanism suggests that small pores are favoured when the condensation reaction is slow and is induced by phase separation (high pH), and that the pore size increases when the condensation fastens (low pH). It was found that both the pore size and the polymer nodule size decrease with temperature, which indicates that increasing the temperature favours the addition reaction more than the condensation reaction, which is certainly due to the increase of the addition reaction rate constant with the temperature. The concentration of both H$_3$O$^+$ and OH$^-$ increases with temperature, due to the increase of the water dissociation constant. The H$_2$CO$_3$/HCO$_3^-$/CO$_3^{2-}$ equilibriums are affected in the same way. Moreover, the dissociation constant of resorcinol is larger at higher temperature too. This promotes the addition reaction step, and decreases the polymer nodule size. At low pH the addition mechanism occurs through the formation of protonated formaldehyde. Protonated formaldehyde reacts then with resorcinol to produce the methylol derivatives whose
condensation is catalyzed by H⁺. However, increasing the temperature cannot favour the formation of protonated formaldehyde: the dissociation constant increases with temperature. Therefore, it is probable that the effect of temperature on the pore texture is not the same at low and high pH values. Since the polycondensation mechanism shifts progressively from one (basic mechanism) to another (acidic mechanism) when the pH decreases, it is possible that the pore size decrease observed at high temperature will not be observed anymore when the addition reaction occurring via resorcinolate anions is hindered, i.e. when the pH is too low. At this case the reaction should occur mainly through the formation of protonated formaldehyde.

It was found that increasing the temperature of the polymerization leads to a significant reduction of the gelation time [Job 2007]. The transition from the sol to the gel corresponds to the development of connected structures above a critical threshold, i.e., the gel point, either by weak interactions for reversible gels, or strong interactions for permanent gels made of cross-linked polymer chains that lose their translational mobility during gelation or by cluster–cluster aggregation. The activation energy of the gelation was estimated from measurements performed at temperatures between 50 and 90 °C. The overall activation energy was found to be close to 80 kJ/mol and independent of the R/C ratio.

Since the size and number of RF clusters generated during polymerization depend on the pH of the initial solution, this parameter ultimately controls the pore structure of the carbon aerogels. Lin et al. [Lin 1997] examined the effect of the pH to the structure of the polymer and carbon aerogels. All the parameters of the synthesis (molar ratios, temperature and time of the polymerization) were fixed, and the pH of the initial solution was set by adding diluted HNO₃ to the reaction mixture.

The effect of pH on the surface area and total pore volume of the carbon aerogels is shown in Figure 7. It appears that carbon aerogels synthesized with an initial pH between 7.0 and 7.5 were non-porous. As the pH decreased, both the surface area and the pore volume increased. However, the effect of pH on the surface area was different from that on the pore volume. As the pH decreased from 7.0 to 6.5, the surface area increased sharply from 0 to 600 m²/g, then remained constant over the pH range from 6.5 to 5.5.
In contrast, the pore volume increased almost linearly as the pH decreased between 7.0 and 5.7, and then remained constant at around 0.8 cm$^3$/g. These results indicate that the increase in the pore volume that occurred on decreasing the pH from 6.5 to 5.5 corresponded to the creation of larger pores, which did not contribute much to the surface area. Furthermore, it was observed that during synthesis, the RF gels prepared using an initial pH higher than 7.0 were sticky and very difficult to filter, while the gels prepared using an initial pH lower than 6.8 were slippery and very easy to handle. The higher pH yielded gels with a weak pore structure because fewer structure-forming condensation reactions occurred. These gels could not withstand the harsh drying and pyrolysis conditions, which apparently caused the nanostructure to collapse, leading to carbon aerogels with no appreciable surface area and pore volume. On the other hand, the lower pH promoted the condensation reaction, thereby forming a highly cross-linked and thus very strong structure, where the majority of the pores remained intact even after the high temperature treatment.

The morphology of the aerogels also depends on the synthesis temperature [Job 2006 (2)], which could be explained from the addition and condensation reaction rates. The pore size tends to decrease when the synthesis temperature increases, but this can be counterbalanced by increasing the R/C ratio (see Chapter 2.1.1). Another important point is that at high temperature (e.g., 90 °C), bubbles very often appear in the gel: in the case of large monoliths, 70 °C is preferable, even though decreasing the temperature leads to longer aging periods when R/C is high.
2.1.4. Effect of the solvent

The mechanism of polymerization and cross-linking of resorcinol with formaldehyde is also affected by the applied media [Berthon-Fabry 2004]. In water the catalyst (sodium carbonate) dissociates. The anion, stabilized by water, contributes to the formation of the phenolate by abstracting one of the two alcoholic protons of resorcinol. By conjugation effect, the 2, 4, or 6 ring positions possess a strong electrophilic character. Formaldehyde exhibits most of the general chemical properties of the aldehydes, but it is generally more reactive. It participates in electrophilic substitution reactions with aromatic compounds. Gels that are synthesized in water, which is a protic solvent, favour ionic stability. The high solubility of the basic catalyst enhances stable phenolate formation, which allows fast formation of hydroxymethyl groups. The sol is then made of small and highly reactive clusters. The probability that every collision induces a link is high (high sticking probability). For these systems, gelation process can be described as an aggregation in dense colloidal solution in which reorganization yielding cluster interpenetration and, therefore, a large density, is almost unlikely. Because clusters grow by draining matter from their immediate neighbourhood, they leave depletion domains, eventually yielding spatial ordering.

When acetone, which is not protic, is used as a solvent, the solubility of sodium carbonate is poor (it is only soluble in the water coming from the formaldehyde solution, which is used for the synthesis). Therefore, the phenolate intermediate form is not stable and the formation of hydroxymethyl groups is slow. Collision probability is low and every collision does not lead to a chemical link (low sticking probability). Surface reaction, rather than diffusion, limits the reaction. In order to form bonds, clusters need to interpenetrate each other, making the clusters more compact. The gelation time in acetone is also much longer than in water because of the solubility problems mentioned above and also because the gelation temperature is lower (50 °C in acetone instead of 85 °C in water).

2.1.5. Monomers other than resorcinol and formaldehyde

Besides resorcinol and formaldehyde there are other monomers that can be used to obtain organic aerogels. Similarly to phenolics other nucleophiles can be employed in reaction with formaldehyde, such as melamine and urea, which can be used as nitrogen containing precursors for sol – gel polycondensation. The possibilities are summarized in Table 1.
Table 1. Monomers and synthesis parameters of organic aerogels

<table>
<thead>
<tr>
<th>Monomers</th>
<th>Special parameters</th>
<th>Authors</th>
</tr>
</thead>
<tbody>
<tr>
<td>resorcinol + formaldehyde</td>
<td>Constant temperature gradient during freeze-drying</td>
<td>Nishihara 2004</td>
</tr>
<tr>
<td></td>
<td>Polystyrene sphere templated polymerization</td>
<td>Baumann 2004</td>
</tr>
<tr>
<td></td>
<td>RF gel film with extremely high R/C ratio</td>
<td>Shen 2004</td>
</tr>
<tr>
<td></td>
<td>RF gel film with extremely high R/C ratio</td>
<td>Shen 2004</td>
</tr>
<tr>
<td></td>
<td>Template directed polymerization in diluted polymethyl-methacrylate microemulsion latex</td>
<td>Guo 2007</td>
</tr>
<tr>
<td>phenol + furfural</td>
<td>KOH catalyst</td>
<td>Zhu 2007</td>
</tr>
<tr>
<td>phenol + formaldehyde</td>
<td>Alcoholic medium</td>
<td>Pekala 1995</td>
</tr>
<tr>
<td></td>
<td>two-step polymerization</td>
<td>Wu 2006</td>
</tr>
<tr>
<td>resorcinol + furfural</td>
<td>Post-etching with KOH</td>
<td>Teng 2001</td>
</tr>
<tr>
<td>cresol + formaldehyde</td>
<td>Alcoholic medium</td>
<td>Wu 2004</td>
</tr>
<tr>
<td>cresol + resorcinol + formaldehyde</td>
<td>Alcoholic medium</td>
<td>Li 2000 and 2001</td>
</tr>
<tr>
<td>melamine + formaldehyde + cresol + phenolic resin</td>
<td>Alcoholic medium</td>
<td>Li 2002</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Zhang 2002</td>
</tr>
</tbody>
</table>

2.1.6. Organic and carbon aerogels in different shapes

As mentioned in the Preface, one of the major advantages of these polymer based carbons is that owing to the sol – gel preparation method, they can be prepared in various forms. Following the simple preparation method the shape of the vial used for the curing period determines the shape of the hydrogel. Since the drying and carbonizing process can be performed without destroying the macroscopic appearance of the samples, with careful drying the form of the hydrogel can be conserved.

Spherical RF gels can be prepared by emulsion polymerization [Horikawa 2004 (1), Horikawa 2004 (3), Yamamoto 2002 (1), Yamamoto 2004]. In this method the initial RF solution is suspended and stabilized in an organic non-polar solvent with the help of a surfactant. The emulsion droplets act as microreactors during the gelation (Figure 8).
2.2. Drying methods

Three kinds of drying techniques are used to convert the hydrogel to a solid RF gel. The applied technique influences the morphology of the dry RF gel so strongly that the names of the different solid gels are different. The first method which can be used is drying in an inert atmosphere, which gives a RF xerogel [Lin 1997]. A second method is freeze-drying, which yields a RF cryogel [Tamon 1999]. The third technique is the supercritical extraction with carbon dioxide, which results in a RF aerogel [Pekala 1989].

The pore structure and the surface area of the final carbon gel depend not only on the initial conditions of synthesis but also on the drying and carbonizing techniques [Lin 1997, Pekala 1989, Tamon 1999]. With this technology, carbons with high surface area and controlled pore structure can be prepared.

Of the three drying methods outlined above, drying in an inert atmosphere (generally in N₂) is the simplest way to convert the RF hydrogel into a solid gel, but the surface area, pore volume and mean pore diameter of the xerogel are smaller than those of the aerogel or the cryogel [Lin 1997]. Most often the gels are dried for 10 hours (5 h at 65 °C and 5 h at 110 °C), with a continuous N₂ flow. The drying method used in the gel preparation therefore exerts a strong influence on the adsorption properties of the final carbon gel.

With freeze-drying, which is also an effective way of preparing high surface area carbons with controlled pore structure, the drying step is much less expensive than supercritical CO₂ extraction [Yamamoto 2001 (1)]. During the process the gel with pores filled with solvent is frozen and by decreasing the pressure the frozen solvent evaporates from the system. The surface area, the pore volume and the mean pore diameter are largest for RF cryogels [Tamon 1999]. Shrinkage of these gels during the drying procedure is also the lowest.
As to the third method, supercritical drying is the most useful for obtaining mesoporous RF gels since this method avoids the evolution of the capillary pressure, thus the original gel structure remains largely preserved. Most often the solvent exchange is performed with CO₂, which is not harmful to the environment, and its critical point (31 °C, 73.8 bar) can be easily achieved technically. At this case the solvent in the pores of the gel is first exchanged to liquid CO₂ at elevated pressure (most often at 80 bar) and room temperature. Than the CO₂ is converted to supercritical state, by increasing the temperature above 31 °C, which is its the critical temperature. Finally the pressure is gradually lowered to atmospheric. The disadvantage of this method is the extremely high cost.

![Figure 9. Macroscopic look of the different RF gels (a) hydrogel (b) xerogel (c) cryogel (d) aerogel (scalebar = 1 cm) [Czakkel 2005]](/image)

The dry polymer gels are hard and brittle. The gel may shrink during the drying process, but the degree of shrinkage depends on the drying protocol (Figure 9) [Czakkel 2005]. The diameter of the RF xerogel rods is about 50% of that of the original hydrogel, while the RF cryogel rods hardly change in diameter during the drying process.

RF aerogels have a sharper pore size distribution than the cryogels. The mesopore volume of the cryogels is about 40% of the mesopore volume of the aerogels, and this ratio is 57% in case of macropores. Xerogels have the highest micropore content.

While in the case of monolithic RF gels porous structure can be obtained by any of the three drying methods, it has been reported that porous spherical RF gels cannot be obtained by drying the hydrogel with heat treatment in an inert atmosphere [Horikawa 2004 (1)].
2.2.1. Solvent exchange

The gels are most often synthesized in aqueous medium. The presence of water, owing to its polarity, high boiling point and relatively low vapour pressure, is disadvantageous in any of the drying processes. Therefore a solvent exchange step is advised before drying.

With heat treatment in an inert atmosphere, the boiling point of the solvent is the most determining property. For supercritical drying the most commonly used solvent is CO₂. Since supercritical carbon dioxide (scCO₂) is non-polar, it is not miscible with water. Both for heat treatment and CO₂ extraction acetone is appropriate for solvent exchange prior to drying.

For freeze-drying, in addition to the vapour pressure of the solvent, the expansion rate during freezing is also critical, in order to preserve the structure of the hydrogel. For this method t-butanol was found to be the appropriate solvent (Table 2).

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\Delta \rho$ (g/cm$^3$)</th>
<th>$p_0$ (0 °C) Pa</th>
<th>$F_p$ °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>7.5·10$^{-2}$</td>
<td>61</td>
<td>0</td>
</tr>
<tr>
<td>t-butanol</td>
<td>3.4·10$^{-4}$</td>
<td>821</td>
<td>−24</td>
</tr>
<tr>
<td>Acetone</td>
<td>7.8·10$^{-2}$</td>
<td>9226</td>
<td>−76</td>
</tr>
</tbody>
</table>

$\Delta \rho$: density change during the freezing, $p_0$: vapour pressure, $F_p$: freezing point

To shorten the preparation process it is possible to prepare RF gels in acetonic [Barbieri 2001, Berthon-Fabry 2004] or alcoholic [Qin 2001] media. The structure of the alco- or acetogels is similar to the structure of the hydrogels.

2.3. Preparation of carbon gels

Carbon aerogels can be prepared by carbonizing the dry RF gels (xerogels, cryogels, aerogels). This heat treatment process is carried out in inert atmosphere, most often in nitrogen. The pyrolysis can be performed either in a rotating quartz reactor [Czakkel 2005], conventional furnace [Tamon 2000] or in an oven [Job 2005]. Under a continuous flow of N₂, the samples are heated slowly to the target temperature. This can be varied from 700 to 1050 °C [Job 2005]. In most cases the carbonization is performed in one step. Tamon et al.
[Tamon 2000] performed the pyrolysis in two consecutive steps: first they kept the samples at 250 °C for 2 h, then increased the temperature up to 1000 °C, and maintained there for 4 h. The average pyrolysis time is 1–2 hours, but some authors applied much shorter (30 min [Horikawa 2004 (2)]) or longer (5 h [Rojas-Cervantes 2004]) times.

The final texture of the carbon gels can also be modified in the carbonization step, by changing the temperature and/or the duration of the treatment [Czakkel 2005]. It was found that the yield of the carbonization strongly depends on the applied temperature and time. Increasing either the temperature from 900 °C to 1000 °C, or the time from 1 h to 2 h, results in a decrease in the yield. Both parameters affect mainly the micropore region: the higher the temperature, or the longer the treatment, the higher micropore content can be achieved. In a correspondence with this observation the specific surface area of the samples behaves in the same way.

2.4. **Metal doped RF and carbon gels**

This synthesis route has the advantage that metal ions can easily be introduced either in the sol–gel process or by impregnation of the network, before or after the carbonization step. When sodium carbonate is replaced by other metal salts with basic character (e.g. K⁺, Mg²⁺, Zr⁴⁺), carbon with highly dispersed metal oxide particles can be produced. In this way, the porous texture of the carbonaceous component can be combined with the basic properties of the oxides. Zr-containing carbon aerogels obtained by copolymerisation of organic and inorganic (zirconium(IV)-propoxide) precursors displayed a more uniform distribution of the metal in the carbon matrix than supported catalysts prepared by other methods [Rojas-Cervantes 2004]. Addition of Ce³⁺ and Zr⁴⁺ to the initial RF solution enhanced the means of controlling the porosity in the micropore region. Depending on the initial pH of the solution, materials with different morphology and porosity were prepared. The structure of doped carbon aerogels synthesized at pH = 7 was mesoporous, while when the initial pH of the solution was low (pH = 3) they exhibit mainly microporous morphology [Bekyarova 2000].

Pd²⁺, Fe²⁺, Co²⁺, Cu²⁺ or Ni²⁺ salts can also be added to the resorcinol – formaldehyde aqueous solution. For Pd²⁺, Ni²⁺, Cu²⁺, Fe²⁺, a complexing agent (hydroxyethylethylene-diaminetriacetic acid (HEDTA) or diethylenetriamine-pentaacetic acid (DTPA)) was required to keep the metal in solution. Texture analysis showed that the complexant modified the
microporous texture of the samples and the presence of metal salt affected the mesopore range. Ni^{2+}, Fe^{2+} and Pd^{2+} were found in the metallic state after drying, indicating that the metal complexes did not remain stable throughout the polymerisation reaction [Job 2004 (2)]. It was found by Fu et al. [Fu 2003 (2)] that during the carbonization process, metal loaded samples became partially graphitized in the case of the Fe^{2+}, Co^{2+} and Ni^{2+}-doping. All the metals had an oxidation state of zero except iron, which was a mixture of Fe_{2}O_{3} and Fe^{0}, i.e., reduction of the metallic species is typical in the carbonization step. Formation of interconnected carbon nanoparticles was observed in cobalt-doped aerogels, provided they were not heated above 500 °C. At higher temperature cobalt nanoparticles were obtained. Their size can be adjusted by the temperature of the carbonization. The type of doping metal also affects the morphology of the samples: Fe^{2+} and Cu^{2+}-doped samples have significantly higher surface area and more developed porosity [Maldonado-Hódar 2004].

When resorcinol is replaced by the K^{+} salt of 2,4-dihydroxybenzoic acid in the sol–gel process, Cu^{2+}-doped carbon aerogels can be obtained in an ion-exchange process performed in the hydrogel state [Baumann 2002]. The surface area of these materials is higher than that of the K^{+}-doped carbon aerogel owing to the presence of the Cu^{0} nanoparticles, which provide a large surface area. With XPS measurements it was found that the metal species are uniformly incorporated into the framework of the carbon aerogel [Fu 2002].

When the usual catalyst is replaced by various metal salts at the outset of the preparation process, the metal salt becomes trapped within the gel structure and the metal ions may be chelated by the functional groups of the polymer matrix. They can also affect the morphology and the pore texture of the organic aerogel [Moreno-Castilla 2003]. A study of the formation of carbon aerogels doped with Fe^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} concluded that the morphology and textural characteristics of the network are determined mainly by the pH, which is defined by the chemical character of the metal ion [Moreno-Castilla 2003, Maldonado-Hódar 2004]. Pt^{2+}, Pd^{2+}, Ag^{+} and Ti^{4+} were also found to exert a strong influence on the aerogel architecture [Fu 2003, Maldonado-Hódar 1999, Moreno-Castilla 2002]. From nitrogen adsorption measurements it was concluded that transition metal-containing RF gels are generally both meso- and macroporous, except Fe and Cu, which yield mainly macroporous aerogels. The influence of the anions has not been addressed.
3. **Aim of the work**

Although the importance of the method of drying is widely recognized, comparative studies of the effects of drying remain incomplete. In this thesis a systematic investigation has been undertaken into the influence of the drying method on the pore structure and the surface area of the RF gels.

Supercritical drying is a commonly used technique for obtaining mesoporous RF gels. However, the conditions of this procedure have not been explored. The supercritical extraction referred to in the literature involves extraction step with liquid CO$_2$ (liqCO$_2$). Carbon dioxide is then transformed to the supercritical state (scCO$_2$) just before the final, depressurizing step. As the extraction capacity of scCO$_2$ is generally superior to that of liqCO$_2$, my intention was to examine real supercritical conditions. A detailed study was performed on various parameters that may influence the process.

The polymer gels were converted to carbon by single step carbonization in an inert atmosphere. The morphology of the resulting carbon xero-, cryo- and aerogels were compared.

The effect of Cu$^{2+}$ and Ti$^{4+}$ salts was investigated. These metal ions were introduced at three different stages of the preparation process: i) during the polymerization reaction; ii) by impregnation of the metal-free dry RF gels from aqueous solutions followed by carbonization; iii) by impregnation of the metal-free carbon gel. The polymerization reaction was monitored and the resulting RF and carbon gels were characterized. A combination of different characterization techniques (scanning electron microscopy, SEM; low temperature N$_2$ adsorption/desorption, small/wide angle X-Ray scattering measurements, SAXS/WAXS) was employed to determine structural differences. The effect of Cu$^{2+}$ on the polymerization reaction was followed by dynamic light scattering (DLS).

Copper doping is expected to improve the gas separation properties of the carbon. Titanium-doped carbon aerogels were tested for photocatalytic activity.
4. Materials and Methods

4.1. Materials

4.1.1. Preparation of resorcinol – formaldehyde gels

The preparation of the monolithic RF hydrogels was based on the method of Lin et al. [Lin 1997]. Aqueous solution of resorcinol (Merck, extra pure), formaldehyde (37% aqueous solution, stabilized with ca. 10% methanol, for synthesis, Merck) and sodium carbonate (Merck), was prepared in such a way that the solid material was 5% (wt/v) of the total volume. The molar ratios of resorcinol/formaldehyde (R/F) and resorcinol/sodium carbonate (R/C) were fixed at 1 : 2 and 50 : 1, respectively. In practice, 1.599 g resorcinol, 2.10 ml formaldehyde solution, 0.0308 g Na$_2$CO$_3$ and 48 ml distilled water were mixed for one batch. The initial pH of the solution was adjusted to pH 6.0 with dilute HNO$_3$. The solution was magnetically stirred in a beaker for 30 min at room temperature. The RF solution was poured into glass vials with an inner diameter of 4 mm, and length of ca. 10 cm, and sealed. This procedure was followed by a thermal treatment at 85 °C for a week.

4.1.2. Drying methods

The opaque brown – orange hydrogels were transferred to excess acetone or t-butanol (three times their own volume, both extra pure, Merck) for 3 days, and the solvent renewed every day.

4.1.2.1. Heat treatment in inert atmosphere

The soft gel rods were filtered from acetone before drying, then placed in an oven flushed with high purity nitrogen (99.996% from Linde, 50 ml/min) to ensure the inert atmosphere during the process. The temperature was raised to 65 °C (2 °C/min) and maintained for 5 h. The temperature was then increased to 100 °C (2 °C/min) for another 5 h.
4.1.2.2. **Freeze drying**

Prior to freeze drying a pre-freezing period is necessary. The gel rods together with the excess t-butanol were pre-cooled to –20 °C for 2 h. Then the frozen gel rods were transferred into the freeze-drying apparatus, where the temperature was reduced to –45 °C. At this temperature the pressure was slowly reduced to 1 mbar to sublimate the frozen solvent. The whole procedure took 1 day.

4.1.2.3. **Extraction with supercritical CO$_2$**

Parameters of the supercritical CO$_2$ (scCO$_2$) extraction were chosen from Pekala et al. [Pekala 1989]. The extraction itself was performed with liquid CO$_2$. The gels were transferred to the reactor, which was then filled with liquid carbon dioxide at 80 bar and room temperature. The solvent exchange was performed by a batch-type extraction, changing the solvent in the extractor for three times. The gel rods were kept under liquid CO$_2$ (liqCO$_2$) during the whole procedure. To avoid the destructive effect of solvent evaporation, prior to the final step the temperature of the system was raised to 45 °C (critical point of CO$_2$ is 31 °C and 73.8 bar), which was followed by a slow depressurization.

Extraction with scCO$_2$ with a continuous solvent flow of 1.2 ml/min was also performed. The pressure was varied between 100–300 bar. The applied temperature range was 33–53 °C. The effect of the drying time was modified in the 50–250 min range.

4.1.3. **Carbonization**

The carbonization was performed in a rotary quartz reactor at 900 °C for 1 h in a 25 ml/min high purity (99.996%, Linde) nitrogen flow.
4.1.4. Metal impregnation

4.1.4.1. Metal doped vinyl-pyridine-divinylbenzene co-polymer based spherical carbons

Spherical microporous carbon beads (SC and SCOX) of different surface chemistry were used for the pre-experiments.

Oxidized carbon sample (SCOX) was prepared by treating SC with aqueous HNO₃ (ccHNO₃ : water = 1 : 1 by volume) in a Soxhlet apparatus, for one cycle. The beads were thoroughly washed with water, than dried.

Cu²⁺ impregnated samples with were prepared by soaking SC or SCOX in aqueous solutions of the metal salts. The chemicals used were copper(II)-acetate (analytical grade, Reanal), copper(II)-nitrate (analytical grade, Merck), copper(II)-sulphate (analytical grade, Merck). Impregnation was performed for 24 h at room temperature, with 0.3–0.52 mol/l metal salt solutions. The amount of aqueous solution used varied between 4.1–16 ml/g carbon. The pH was not controlled.

4.1.4.2. Metal doped RF gels

4.1.4.2.1. Heteroatom as catalyst

Copper-containing samples were prepared by adding copper(II)-acetate (analytical grade, Reanal) to the sol–gel reaction mixture described in Chapter 4.1.1. The total R/C molar ratio and the concentration of the initial reaction mixture were 25 and 5.2 wt/v%, respectively. The pH was limited to 5.3 by the solubility of CuAc₂.

Ti-doped RF gels were prepared by the method of Maldonado-Hódar et al. [Maldonado-Hódar 2000]. After dissolving the resorcinol, and the formaldehyde in distilled water, the solution was heated to 60 °C. The allotted amount of titanium-isopropoxide (TIP, Fluka) was added drop by drop, while the solution was continuously stirred. Then the mixture was aged for 4 h at 60 °C. The R/F and R/W molar ratios were the same as described in Chapter 4.1.1, while the R/TIP molar ratio was 1. After filtration the formed precipitate was washed with acetone for three days to prepare for the drying procedure.
4.1.4.2.2. *Post-impregnation*

Cu-impregnated RF and carbon gels were prepared by soaking either the dry RF aerogels or carbon gels for 24 h at room temperature in 0.02 or 0.04 mol/l copper(II)-acetate (analytical grade, Reanal) aqueous solution. 75 ml solution was used for 1 g gel. The melting and the boiling point of CuAc$_2$ is 115 °C and 240 °C, respectively.

Ti-impregnated RF and carbon gels were prepared by soaking either the dried RF aerogels or carbon gels for 24 h at room temperature in 0.02 or 0.04 mol/l titanium-isopropoxide (Fluka) solution. The solvent used was acetone (extra pure, Merck). 75 ml solution was used for 1 g gel.
4.1.5. Nomenclature of the samples

Table 3 summarizes the labels and the descriptions of the prepared samples.

<table>
<thead>
<tr>
<th>Label</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>PX</td>
<td>RF xerogel, RF gel dried with heat treatment in N\textsubscript{2} atmosphere</td>
</tr>
<tr>
<td>PC</td>
<td>RF cryogel, RF gel dried with freeze-drying</td>
</tr>
<tr>
<td>PA</td>
<td>RF aerogel, RF gel dried with liquid CO\textsubscript{2} extraction</td>
</tr>
<tr>
<td>CGX</td>
<td>PX, carbonized</td>
</tr>
<tr>
<td>CGC</td>
<td>PC, carbonized</td>
</tr>
<tr>
<td>CGA</td>
<td>PA, carbonized</td>
</tr>
<tr>
<td>P</td>
<td>RF aerogel, RF gel dried with supercritical CO\textsubscript{2} extraction</td>
</tr>
<tr>
<td>CuP</td>
<td>P synthesized in the presence of CuAc\textsubscript{2}</td>
</tr>
<tr>
<td>TiP</td>
<td>P synthesized in the presence of Ti</td>
</tr>
<tr>
<td>P/Cu L</td>
<td>P, post-impregnated with low concentration CuAc\textsubscript{2}</td>
</tr>
<tr>
<td>P/Cu H</td>
<td>P, post-impregnated with high concentration CuAc\textsubscript{2}</td>
</tr>
<tr>
<td>P/Ti L</td>
<td>P, post-impregnated with low concentration Ti</td>
</tr>
<tr>
<td>P/Ti H</td>
<td>P, post-impregnated with high concentration Ti</td>
</tr>
<tr>
<td>CG</td>
<td>P, carbonized</td>
</tr>
<tr>
<td>CuP carb</td>
<td>CuP, carbonized</td>
</tr>
<tr>
<td>TiP carb</td>
<td>TiP, carbonized</td>
</tr>
<tr>
<td>P/Cu H carb</td>
<td>P/Cu H carbonized</td>
</tr>
<tr>
<td>P/Ti L carb</td>
<td>P/Ti L carbonized</td>
</tr>
<tr>
<td>P/Ti H carb</td>
<td>P/Ti H carbonized</td>
</tr>
<tr>
<td>CG/Cu L</td>
<td>CG, post-impregnated with low concentration CuAc\textsubscript{2}</td>
</tr>
<tr>
<td>CG/Cu H</td>
<td>CG, post-impregnated with high concentration CuAc\textsubscript{2}</td>
</tr>
<tr>
<td>CG/Ti L</td>
<td>P, post-impregnated with low concentration Ti</td>
</tr>
<tr>
<td>CG/Ti H</td>
<td>P, post-impregnated with high concentration Ti</td>
</tr>
</tbody>
</table>

4.2. Methods

4.2.1. Dynamic light scattering (DLS)

DLS measurements were made in the sol–gel reaction bath, using an ALV goniometer (ALV, Langen, Germany). The light source was a HeNe laser working at 632.8 nm. The correlator was an ALV 5000E multi-tau instrument. Samples were contained in glass NMR sample tubes of 9 mm internal diameter, and observations were made in the scattering angle range $30^\circ \leq \theta \leq 150^\circ$. For measurements with a short optical path, X-ray
capillary tubes of diameter 1 and 2 mm were used, at $\theta = 90^\circ$. The sample tubes were placed in a refractive index matching toluene bath and measurements were performed at 30, 35, 40 and 50 °C.

4.2.2. Morphological characterization

4.2.2.1. Scanning electron microscopy (SEM)

Surface morphological investigations were made on a JEOL 5500 (JEOL, Japan) electron microscope in high vacuum mode with a secondary electron detector. The accelerating voltage was 20 kV and the working distance varied between 5 and 27 mm. Samples were fastened to a copper sample holder by adhesive carbon tape. The polymer samples were coated with Au/Pd to prevent charging.

4.2.2.2. Small/wide angle X-Ray scattering (SAXS/WAXS)

SAXS/WAXS measurements of the dry and carbonized samples were made on the BM2 small angle camera in the European Synchrotron Radiation Facility (ESRF), Grenoble, France. The transfer wave vector range explored was $0.0019 < q < 5.7 \text{ Å}^{-1}$, where

$$q = \frac{4\pi \sin(\theta/2)}{\lambda}$$

and $\lambda$ is the wavelength of the incident radiation. An indirect illumination CCD detector (Princeton Instruments) with effective pixel size 50 µm was used. Intensity curves, $I(q)$, obtained by azimuthal averaging, were corrected for grid distortion, dark current, sample transmission and also for background scattering.

The powdered samples were placed in glass capillary tubes of diameter 1.5 mm. Intensities were normalised with respect to a standard sample (lupolen), assuming an effective sample thickness of 1 mm to account approximately for the filling factor of the powder. The resulting error in the stated absolute values of the intensity is expected to be no greater than 25%.
4.2.2.3. Low temperature nitrogen adsorption/desorption

Nitrogen adsorption/desorption isotherms were measured at –196 °C with an Autosorb-1 (Quantachrome, USA) computer controlled volumetric gas adsorption apparatus. Pre-treatment of the samples was performed at 20 °C and p < 3·10^{-4} mbar, for 24 h.

4.2.3. Energy Dispersive X-ray Spectroscopy (EDS)

Elemental analyses were performed on the metal doped RF and carbon gels by the Kα lines of the elements, using a JEOL 5500 electron microscope (JEOL, Japan) in high vacuum mode. The applied magnification was 5000x, and the average metal concentrations were calculated from at least six different measurements.

4.2.4. Boehm titration

As the carbon surfaces are decorated only with O-containing heteroatoms, the functional groups of different pKa range were determined by Boehm titration [Boehm 1966]. 1 g of the carbons was stirred with 35 ml of 0.05 mol/l HCl or NaOH solution for three days. The equilibrium concentration of the solutions was titrated with 0.1 mol/l HCl or NaOH solutions.

4.2.5. Application test
4.2.5.1. Decomposition of methylene blue

5 ml methylene blue solution (20 mg/l) was added to 5 ml, 0.1 wt/v% aqueous suspension of the carbon gels. The measurements were performed in a Solarbox (Figure 10) containing six lamps (λ ≥ 310 nm; 6x25 W). The distance between the sample and the light source was 10 cm. Prior to the UV irradiation an adsorption time of 10 minutes was applied. The suspension was continuously stirred during the 12 minutes test, and the concentration of the methylene blue was determined by UV spectrophotometry in every 2 minutes.
4.2.5.2. Decomposition of phenol

The decomposition of phenol was investigated in a cylindrical, double walled photoreactor (Figure 11). The applied light source was a mercury vapour lamp (350 W). The sample suspension (20 mM/l phenolic solution + 0.05 wt/v% carbon aerogel suspension) was continuously stirred, and cooled, in order to decrease the warming effect in system (the initial temperature 20 °C increased to 35 °C). During the 120 min irradiation continuous airflow was applied, because the presence of O₂ is necessary for the photodegradation process. The change of phenol concentration of the suspension was measured by a liquid chromatography system equipped with a UV detector in every 20 minutes.
5. Results and Discussion

5.1. Characterization of the dry RF gels

5.1.1. Effect of the drying method on the morphology of the polymer gels

Three drying methods were compared: heat treatment in N$_2$ atmosphere, freeze drying and supercritical extraction (batch-type extraction with liquid CO$_2$).

Drying the hydrogels with any of the methods yielded hard and brittle RF gels. The gel rods shrank differentially during the drying processes, depending on the method employed. The micrograph of the sample dried at high temperature in nitrogen (polymer xerogel, $PX$, Figure 12a) reveals a somewhat compact structure, consisting of more or less uniform microspheres of diameter about 0.1 µm. Figure 12b shows the structure of the freeze-dried RF gel (polymer cryogel, $PC$), which is very loose. This is the finest of all three samples. It consists of small spheres of diameter approximately 300 Å, arranged in a filament like structure to form a three-dimensional matrix. The network appears to be very fragile. The sample obtained by supercritical extraction (polymer aerogel, $PA$) exhibits also a compact structure as can be seen in Figure 12c, but the individual microspheres are smaller than in $PX$ (Figure 12a).

![Figure 12. SEM images of the RF gels (a) $PX$ (b) $PC$ (c) $PA$ (scalebar = 1µm)](image)

Low temperature nitrogen adsorption/desorption isotherms of all the three RF gels, shown in Figure 13, belong to Type IIb [Rouquerol 1999]. This type of isotherm is identified with unrestricted monolayer – multilayer adsorption, and is characteristic of nonporous or macroporous adsorbents. The abrupt upturn in the isotherms at high relative pressures is the signature of strong capillary condensation. For the cases of $PC$ and $PA$, the isotherms exhibit a narrow hysteresis loop, indicating thermodynamically irreversible adsorption.
The hysteresis loops are of Type B, which are usually given by samples containing slit-shaped pores [Rouquerol 1999].

Figure 13. Low temperature nitrogen adsorption/desorption isotherms of the $PX$ (◇), $PC$ (□), and $PA$ (△)

To quantify the difference in the structure of the samples several parameters were deduced from the adsorption/desorption isotherms (Table 4). With gas adsorption only the micropore ($d < 20$ Å) and part of the mesopore ($20$ Å $< d < 300$ Å) range can be examined. The upper limit of the calculations is due to the exponential nature of the $d = f(p/p_0)$ relationship [Gregg 1982]. In certain samples, owing to capillary condensation, the total pore volume can be estimated from the $p/p_0 \to 1$ region of the isotherms only with high uncertainty. For this reason, the pore volume ($V_{0.90}$) was derived from the amount of vapour adsorbed at relative pressure 0.90, assuming that the pores are then filled with liquid adsorbate, which corresponds to pores with $d < 210$ Å. The volume of the adsorbed gas ($V_{\text{ads}}$) can be transformed into liquid nitrogen volume ($V_{\text{liq}}$) by the following equation:

$$V_{\text{liq}} = \frac{pV_{\text{ads}}V_m}{RT}$$

where $p$ is the pressure, $V_m$ is the molar volume of liquid nitrogen (34.7 cm$^3$/mol), $R$ is the universal gas constant (8.314 J/molK) and $T$ is the absolute temperature. The apparent surface area ($S_{\text{BET}}$) was calculated using the Brunauer–Emmett–Teller (BET) model [Brunauer 1938].
The micropore volume \((W_0)\) and micropore width \((w)\) were derived by the Dubinin–Radushkevich (DR) method, the \(\beta\) parameter was 0.391.

### Table 4. Porosity data of RF gels from \(N_2\) adsorption measurements

<table>
<thead>
<tr>
<th>Sample</th>
<th>(S_{\text{BET}}) m(^2)/g</th>
<th>(V_{0.90}) cm(^3)/g</th>
<th>(W_0) cm(^3)/g</th>
<th>(w) Å</th>
<th>(\frac{W_0}{V_{\text{TOT}}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(PX)</td>
<td>110</td>
<td>0.13</td>
<td>0.04</td>
<td>12.9</td>
<td>0.31</td>
</tr>
<tr>
<td>(PC)</td>
<td>570</td>
<td>0.76</td>
<td>0.22</td>
<td>13.3</td>
<td>0.29</td>
</tr>
<tr>
<td>(PA)</td>
<td>270</td>
<td>0.36</td>
<td>0.09</td>
<td>13.0</td>
<td>0.25</td>
</tr>
</tbody>
</table>

\(S_{\text{BET}}\): specific surface area from BET method; \(V_{0.90}\): total volume of pores read at \(p/p_0 = 0.90\); \(W_0\): micropore volume; \(w\): micropore width

Results in Table 4 show that the freeze-dried RF cryogel \((PC)\) has the highest surface area. The trend in the values of \(V_{0.90}\) as well as the shape of the isotherms above \(p/p_0 \sim 0.1\) reflects the relative openness of the structures, which is also visible in the SEM micrographs.

The pore size distribution in the micropore region (Figure 14) was computed from nonlinear density function theory (NLDFT) [Evans 1986, Gelb 1999, Gubbins 1997, Ravikovitch 1998]. The micropore size distributions of all the three RF gels were found to be very similar. They show a wide peak in the 12–22 Å region, but less intense shoulders on both sides of the maxima can also be identified.

![Figure 14. Pore size distribution of \(PX\) (◇), \(PC\) (□), and \(PA\) (△) by NLDFT method](image-url)
5.1.2. Drying from CO$_2$ medium

Most often CO$_2$ is used to obtain dry RF gels. Although a great number of papers has been published on RF gels [Fairén-Jiménez 2006, Horikawa 2004 (2), Job 2005, Pekala 1989], no systematic studies on supercritical CO$_2$ drying have been reported. In fact, in these studies the so-called supercritical extraction means an extraction step with liqCO$_2$, and carbon dioxide is transferred into supercritical state just before the final, depressurizing step.

Since the extraction capacity of scCO$_2$ is generally better than liqCO$_2$, a detailed study was performed on the various parameters that may influence the structure under real supercritical conditions. I developed an instrumental setup with controllable pressure and temperature. Unlike in reported methods instead of a batch-type reactor constant flow of scCO$_2$ was applied. Figure 15. shows the scheme of the apparatus.

![Figure 15. Scheme of the apparatus used for scCO$_2$ extraction](image)

(1: extractor, 2: depressurizing tank)

5.1.2.1. Effect of the pressure and temperature

Three different pressures and temperatures were chosen, above the critical point of CO$_2$. The detailed parameters of the $2^2$ experimental plan are listed in Table 5.

The drying process consists of three parts: (i) pressurization (ii) extraction at constant pressure with a fixed flow rate of CO$_2$, (iii) depressurization. The temperature is constant (and above the critical temperature of CO$_2$) during the whole procedure. The crucial point of the process is the third step: when the rate of the pressure change is high, the samples may become damaged. From preliminary measurements it was concluded that the (iii) step is safe if the depressurizing rate does not exceed 5 bar/min.
Table 5. Parameters of supercritical drying for examining the effect of the applied pressure and temperature

<table>
<thead>
<tr>
<th>Sample</th>
<th>p bar</th>
<th>T °C</th>
<th>CO₂ volume ml</th>
<th>Extraction time min</th>
<th>Total drying time min</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>100</td>
<td>33</td>
<td>118</td>
<td>95</td>
<td>150</td>
</tr>
<tr>
<td>P2</td>
<td>200</td>
<td>43</td>
<td>163</td>
<td>134</td>
<td>245</td>
</tr>
<tr>
<td>P3</td>
<td>300</td>
<td>33</td>
<td>112</td>
<td>94</td>
<td>250</td>
</tr>
<tr>
<td>P4</td>
<td>100</td>
<td>53</td>
<td>197</td>
<td>164</td>
<td>225</td>
</tr>
<tr>
<td>P5</td>
<td>300</td>
<td>53</td>
<td>123</td>
<td>103</td>
<td>235</td>
</tr>
</tbody>
</table>

Figure 16. (a) Low temperature N₂ adsorption/desorption isotherms (insert shows the p/p₀ > 0.8 region) and pore size distributions by (b) NLDFT and (c) BJH (from desorption) methods of RF aerogels (P1: □, P2: ○, P3: △, P4: ◇, P5: +)

All the yielded RF gels were hard and brittle. After drying in samples P1 and P2 moderate acetone odour was detected, which indicated that the solvent exchange was not perfect. The shrinkage of the samples was not significant, with the diameter of the gel rods hardly changing.
The adsorption/desorption isotherms of the RF gels (Figure 16a) belong to Type IIb [Rouquerol 1999]. Basically the isotherms are very similar to each other, but the higher relative pressure region ($p/p_0 > 0.9$) shows significant differences. Analysis of the N$_2$ adsorption/desorption isotherms (Table 6) shows that the specific surface area of the RF gels differs only by about 10% from each other. The micro- and mesopore volumes (Table 6), as well as the pore size distributions in the micropore region (Figure 16b), are very similar to each other.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{BET}$ m$^2$/g</th>
<th>$V_{TOT}$ cm$^3$/g</th>
<th>$V_{0.94}$ cm$^3$/g</th>
<th>$W_0$ cm$^3$/g</th>
<th>$V_{meso}$ cm$^3$/g</th>
<th>$V_{macro}$ cm$^3$/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P1$</td>
<td>578</td>
<td>2.83</td>
<td>0.72</td>
<td>0.22</td>
<td>0.50</td>
<td>2.11</td>
</tr>
<tr>
<td>$P2$</td>
<td>533</td>
<td>3.62</td>
<td>0.72</td>
<td>0.20</td>
<td>0.52</td>
<td>2.90</td>
</tr>
<tr>
<td>$P3$</td>
<td>577</td>
<td>5.70</td>
<td>0.77</td>
<td>0.21</td>
<td>0.56</td>
<td>4.93</td>
</tr>
<tr>
<td>$P4$</td>
<td>541</td>
<td>1.72</td>
<td>0.71</td>
<td>0.21</td>
<td>0.50</td>
<td>1.01</td>
</tr>
<tr>
<td>$P5$</td>
<td>562</td>
<td>4.42</td>
<td>0.75</td>
<td>0.21</td>
<td>0.54</td>
<td>3.67</td>
</tr>
</tbody>
</table>

$S_{BET}$: apparent surface area, $V_{TOT}$: total pore volume at $p/p_0 \to 1$, $V_{0.94}$: pore volume derived from adsorbed volume at $p/p_0 = 0.94$, $W_0$: micropore volume from DR analysis,

$V_{meso} / V_{TOT} = (V_{0.94} - W_0) / V_{TOT}$, $V_{macro} / V_{TOT} = (V_{TOT} - V_{0.94}) / V_{TOT}$

The size distribution of the mesopores was calculated by the method of Barrett, Joyner and Halenda [Barrett 1951] from the desorption branch. This method was used for pores of $d > 200$ Å assuming cylindrical pore shape. In the lower mesopore region of the samples are very similar to each other, but a significant difference can be observed only at the wider mesopore region ($d > 200$ Å) (Figure 16c). The final steep part of the isotherms reflects macroporosity. Although the N$_2$ adsorption method itself is not appropriate for quantitatively determining macropores, a large porosity ($V_{macro}$, Table 6) can be assumed from the $p/p_0 \to 1$ part of the isotherms (Figure 17). From these values it can be concluded that all the samples are basically macroporous and this behaviour is affected by the parameters of the scCO$_2$ drying. Figure 17 also shows that the micro- and mesopore volumes are independent of either the drying temperature or pressure, while $V_{macro}$ and $V_{TOT}$ show a linearly increasing trend with increasing pressure.

SAXS and WAXS measurements on selected samples ($P1$, $P2$, $P3$) revealed that basically the structure of the different samples is very similar to each other.
Figure 17. Variation of pore volumes ($V_{TOT}$, $V_{macro}$, $V_{meso}$, $W_0$) with the applied pressure and temperature during supercritical CO$_2$ extraction.

In summary it can be concluded that the temperature and the pressure of the extraction step modify the macropore content of the samples, and higher pressure and lower temperature favour a higher porosity.

5.1.2.2. Effect of the drying time

The effect of the drying time was investigated at 100 bar and 43 °C. The rate of the pressure change was constant, 5 bar/min. Table 7 summarizes the parameters in detail.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Extraction time min</th>
<th>Depressurizing time min</th>
<th>Total drying time min</th>
<th>CO$_2$ volume ml</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P6$</td>
<td>50</td>
<td>20</td>
<td>98</td>
<td>60</td>
</tr>
<tr>
<td>$P7$</td>
<td>200</td>
<td>30</td>
<td>258</td>
<td>238</td>
</tr>
<tr>
<td>$P8$</td>
<td>100</td>
<td>40</td>
<td>184</td>
<td>119</td>
</tr>
<tr>
<td>$P9$</td>
<td>100</td>
<td>20</td>
<td>142</td>
<td>126</td>
</tr>
<tr>
<td>$P10$</td>
<td>100</td>
<td>40</td>
<td>167</td>
<td>115</td>
</tr>
<tr>
<td>$P11$</td>
<td>100</td>
<td>40</td>
<td>157</td>
<td>120</td>
</tr>
</tbody>
</table>

All the RF gel rods were hard and brittle, and a slight acetone odour could be detected at samples $P6$ and $P9$. The shrinkage of the samples was negligible. N$_2$ adsorption/desorption
results (Figure 18) were similar to the cases of temperature and pressure dependence. Basically the shape of the isotherms was almost identical, significant differences appeared only in the high pressure region (Figure 18a). The size distribution of the micropores shows slight differences for samples P6 and P9 (Figure 18b). The mesopore size distribution functions are practically parallel to each other (Figure 18c). The porosity data are summarized in Table 8. The drying time (i.e. the amount of scCO$_2$) has an effect on the total pore volume, which means that the macropore region is affected by changing the parameters of the supercritical extraction (Figure 19). The SAXS/WAXS spectra of the samples confirmed the structural similarities on the length scale of the micropores.

Figure 18. (a) Low temperature N$_2$ adsorption/desorption isotherms (insert shows the p/p$_0$ > 0.8 region) and pore size distributions by (b) NLDFT and (c) BJH methods of RF aerogels (P6: ○, P7: ▽, P8: ×, P9: △, P10: △, P11: □)
Table 8. Porosity data of aerogels dried under different, supercritical conditions from N₂ adsorption measurements

<table>
<thead>
<tr>
<th>Sample</th>
<th>(S_{\text{BET}}) m²/g</th>
<th>(V_{\text{TOT}}) cm³/g</th>
<th>(V_{0.94}) cm³/g</th>
<th>(W_0) cm³/g</th>
<th>(V_{\text{meso}}) cm³/g</th>
<th>(V_{\text{macro}}) cm³/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>(P6)</td>
<td>663</td>
<td>1.59</td>
<td>0.93</td>
<td>0.20</td>
<td>0.73</td>
<td>0.66</td>
</tr>
<tr>
<td>(P7)</td>
<td>580</td>
<td>2.99</td>
<td>0.84</td>
<td>0.18</td>
<td>0.66</td>
<td>2.15</td>
</tr>
<tr>
<td>(P8)</td>
<td>591</td>
<td>1.65</td>
<td>0.85</td>
<td>0.19</td>
<td>0.66</td>
<td>0.80</td>
</tr>
<tr>
<td>(P9)</td>
<td>660</td>
<td>2.17</td>
<td>0.87</td>
<td>0.21</td>
<td>0.66</td>
<td>1.30</td>
</tr>
<tr>
<td>(P10)</td>
<td>607</td>
<td>1.97</td>
<td>0.87</td>
<td>0.19</td>
<td>0.68</td>
<td>1.10</td>
</tr>
<tr>
<td>(P11)</td>
<td>568</td>
<td>1.69</td>
<td>0.78</td>
<td>0.18</td>
<td>0.60</td>
<td>0.91</td>
</tr>
</tbody>
</table>

\(S_{\text{BET}}\): apparent surface area, \(V_{\text{TOT}}\): total pore volume at \(p/p_0 \rightarrow 1\), \(V_{0.94}\): pore volume derived from adsorbed volume at \(p/p_0 = 0.94\), \(W_0\): micropore volume from DR analysis, \(V_{\text{meso}}(\%) = (V_{0.94} - W_0) / V_{\text{TOT}} \cdot 100\), \(V_{\text{macro}}(\%) = (V_{\text{TOT}} - V_{0.94}) / V_{\text{TOT}} \cdot 100\)

Figure 19. Dependence of pore volumes (\(V_{\text{macro}}\): ■, \(V_{\text{meso}}\): ▲, \(W_0\): ○) on the amount of scCO₂ during supercritical CO₂ extraction

5.1.2.3. Supercritical vs. liquid carbon dioxide extraction

RF aerogels dried with liqCO₂ extraction and supercritical CO₂ extraction were compared. With the liquid carbon dioxide method a batch-type extraction was performed at 80 bar, at room temperature. Before the depressurizing step the temperature of the reactor was increased to 45 °C, in order to get above the critical point of CO₂. The true supercritical extraction was performed at 100 bar and 43 °C with a continuous flow of 1.2 ml/min of CO₂.
Figure 20. Influence of the drying method on the diameter of the RF gels (a) RF hydrogel (b) aerogel dried with liquid CO₂ (c) aerogel dried with supercritical CO₂ (scalebar = 1 cm)

When the extraction step was performed with liqCO₂, the gel rods shrank during the drying process (Figure 20b). In contrast, when the acetone from the pores of the gel was extracted with scCO₂ the diameter of the gels remained practically the same (Figure 20c).

The presence of the spherical building units is conserved after both kinds of extraction drying (Figure 21), although liquid CO₂ extraction results in a more compact structure.

Figure 21. SEM images aerogels dried with (a) liquid and (b) supercritical CO₂ extraction (scalebar = 1 µm)

The low temperature N₂ adsorption isotherms (Figure 22) are again of Type IIb [Rouquerol 1999]. The derived data (Table 9) show that in the supercritical case, the looser structure resulted in a remarkably higher surface area, which is comparable with the gel dried by freeze-drying (PC, Table 4). The higher pore volumes in all categories also reflect the looser structure.
Table 9. Porosity data of aerogels from N\textsubscript{2} adsorption measurements

<table>
<thead>
<tr>
<th>Extraction medium</th>
<th>(S_{\text{BET}}) m\textsuperscript{2}/g</th>
<th>(V_{\text{TOT}}) cm\textsuperscript{3}/g</th>
<th>(V_{0.94}) cm\textsuperscript{3}/g</th>
<th>(W_0) cm\textsuperscript{3}/g</th>
<th>(V_{\text{meso}}) cm\textsuperscript{3}/g</th>
<th>(V_{\text{macro}}) cm\textsuperscript{3}/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>liqCO\textsubscript{2}</td>
<td>270</td>
<td>1.00</td>
<td>0.47</td>
<td>0.01</td>
<td>0.46</td>
<td>0.53</td>
</tr>
<tr>
<td>scCO\textsubscript{2}</td>
<td>582</td>
<td>1.77</td>
<td>0.78</td>
<td>0.21</td>
<td>0.57</td>
<td>0.99</td>
</tr>
</tbody>
</table>

\(S_{\text{BET}}\): apparent surface area, \(V_{\text{TOT}}\): total pore volume at \(p/p_0\to1\), \(V_{0.94}\): pore volume derived from adsorbed volume at \(p/p_0 = 0.94\), \(W_0\): micropore volume from DR analysis, \(V_{\text{meso}} = V_{0.94} - W_0\), \(V_{\text{macro}} = V_{\text{TOT}} - V_{0.94}\)

Figure 22. Low temperature \(N\textsubscript{2}\) adsorption/desorption isotherms of aerogels dried with liquid (\(\triangle\)) and supercritical (\(\triangle\)) CO\textsubscript{2} extraction

Figure 23. Pore size distributions by (a) NLDFT and (b) BJH (from desorption isotherms) methods of aerogels dried with liquid (\(\triangle\)) and supercritical (\(\triangle\)) CO\textsubscript{2} extraction
The low $q$ region of the SAXS curves reveals differences in the large scale structure of the samples (Figure 24). While the response curve of supercritically extracted sample shows interconnected particles, which form a linear arrangement, at the case of the liqCO$_2$ extraction the elementary units are branched together, and form large objects. The slopes of the curves in the $q \approx 0.1$ region are similar to each other (slope $= -4$ at both cases), which is due to scattering from smooth surfaces. To quantify the differences in scattering response, the elementary cluster units composing the networks were assimilated with independent uniform solid spheres of external radius $R$ [Rayleigh 1911]. Thus the scattering intensity is defined by the structure factor of a single sphere,

$$S_{\text{sphere}}(q) \propto \left[3\left(\sin qR - qR \cos qR\right) / (qR)^3\right]^2.$$  \hspace{1cm} (3)

At large $q$, this function exhibits the $q^{-4}$ power law behaviour characteristic of smooth surfaces. The plot of $S_{\text{sphere}}(q)q^4$ vs. $q$ is a characteristic oscillatory function with its first maximum at $qR = 2.74$ and first minimum at 4.49 (Figure 24b).

**Figure 24.** SAXS response curves (a) and the initial part of the SAXS spectrum (b) of aerogels dried with liquid (△) and supercritical (△) CO$_2$

In this representation, for a measured scattering intensity $I(q)$, the intensity of the maxima is proportional to $(4\pi R^3/3)^2NS_{\text{sphere}}(q) \cdot q^4$, where $N$ is the number of spheres per unit volume. Since $S_{\text{sphere}}(q)$ is a function of $qR$ only, for otherwise identical samples having the same total concentration
but composed of spheres of different radii $R$, the intensity of the maxima is inversely proportional to $R$, i.e.,

$$I(q) \propto \frac{1}{R^4}.$$  \hspace{1cm} (5)

Using this approximation the size of the elementary beads in the samples was found to be 3.5 times bigger than in the case of the liquid CO$_2$ extraction (Figure 24b).

Summarizing the results from the investigation of the supercritical extraction, it can be concluded that applying real supercritical conditions instead of using liqCO$_2$ during the extraction step ensures better conservation of the loose structure of the RF gels, and thus results in enhanced porosity. The drying parameters (temperature, pressure and time) have a strong effect on the large porosity of the samples, while the micropore and mesopore region is practically independent of them.

5.2. Conversion of the polymer gels to carbon gels

The dry RF gels were converted to carbon gels with a yield of 40–50% (Table 10). The CG derived from the xerogel (CGX) preserved the compact structure and uniform character of the constituent spheres during the pyrolysis (Figure 25a). The carbon cryogel (CGC), for which the change in structure is the most pronounced (Figure 25b), exhibits very fine structure, although the spheres no longer form individual chains, but rather two-dimensional ribbons, which constitute a loose 3D gel. The aerogel (Figure 25c) also conserves its compact structure during carbonization, but the basic microspheres are significantly larger (ca. 2000 Å) than in the starting RF gel (< 0.1 µm, Figure 12c).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Drying method</th>
<th>Yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CGX</td>
<td>Heat treatment in N$_2$ atmosphere</td>
<td>50.5</td>
</tr>
<tr>
<td>CGC</td>
<td>Freeze-drying</td>
<td>40.7</td>
</tr>
<tr>
<td>CGA</td>
<td>Extraction with liqCO$_2$</td>
<td>46.6</td>
</tr>
</tbody>
</table>

Table 10. Yield of the carbonization
The shape of their adsorption isotherms (Figure 26a) is similar to that of the corresponding precursor RF gel, but in each case the initial part reflects the development of microporosity. This is most pronounced in the CGC sample. In the carbonization process, thermal degradation of the RF gels is combined with self-activation. The O-containing volatile degradation products may work as activating agents, since the oxygen content (derived from the stoichiometric composition) of the polymer gel is about 35%. Microporous structure develops during pyrolysis. Microporosity is especially high in the CGX sample,
where it approaches 80% (Table 11). Similarly to the RF xerogel, absence of the hysteresis loop in the CGX sample can be observed.

Table 11. Porosity data of carbon gels from nitrogen adsorption measurements

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{BET}$ m$^2$/g</th>
<th>$V_{0.90}$ cm$^3$/g</th>
<th>$W_0$ cm$^3$/g</th>
<th>$w$ Å</th>
<th>$W_0$/$V_{0.90}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CGX</td>
<td>891</td>
<td>0.44</td>
<td>0.34</td>
<td>5.4</td>
<td>0.77</td>
</tr>
<tr>
<td>CGC</td>
<td>2650</td>
<td>2.05</td>
<td>1.05</td>
<td>7.0</td>
<td>0.51</td>
</tr>
<tr>
<td>CGA</td>
<td>1010</td>
<td>0.79</td>
<td>0.40</td>
<td>7.5</td>
<td>0.57</td>
</tr>
</tbody>
</table>

$S_{BET}$: apparent surface area, $V_{0.90}$: pore volume derived from adsorbed volume at $p/p_0 = 0.90$, $W_0$: micropore volume from DR analysis; $w$: micropore width from DR analysis

The increase of microporosity during carbonization is also reflected in the micropore size distribution (Figure 26b). Carbonization mainly influences the < 10 Å region. The distribution curves are sharper and the peak maxima are shifted towards slightly smaller values. Significant porosity below 6.0 Å develops in the cryogel. The apparent surface area $S_{BET}$ of the carbon gels (Table 11) is some 3–9 times larger than that of precursors (Table 4). Like the RF gel, the carbon cryogel exhibits the largest value of $S_{BET}$ and pore volume ($V_{0.90}$).

The $q$-range of the SAXS measurements spans a higher spatial resolution scale than that covered by the SEM images. For this reason, structures larger than about 500 Å were not detected. The SAXS curves for the three sets of RF and carbon samples are shown in Figure 27. The RF gels (open circles) display an extended range in which the intensity follows power law behaviour, where the slope is −4. This property is characteristic of scattering from smooth surfaces with a sharp boundary [Porod 1983]. At the high-$q$ end of the SAXS response, the RF samples exhibit a peak, at $q_{max} \approx 1.18$ Å$^{-1}$, corresponding to an effective repeat distance $2\pi/q_{max} \approx 5.3$ Å between molecular units in the RF gel, i.e., close to the size of the resorcinol monomer. When the molecular units are reduced to carbon, the repeat distance scale shrinks and the peak migrates to higher $q$ values beyond the observed SAXS range. The cluster sizes of RF cryogel in both the uncarbonised and carbonised forms are smaller than in the aerogel (112 and 72 Å, respectively) while the surface area of the carbonised form is higher. The latter result is surprising, since supercritical drying in CO$_2$ is expected to occur in conditions close to a spinodal decomposition, where polymer-solvent interfacial tension disappears, thus favouring the formation of high surface area filament structures on drying. In this case, however, lyophilisation is more successful in reducing both cluster and micropore size and hence in increasing surface area because t-butanol is a better
solvent than liquid carbon dioxide. The surface area of the carbonised form of xerogel (891 m²/g) is the lowest of the three. As is to be expected, direct drying in nitrogen is the least successful in keeping the polymer strands separate.

Figure 27. SAXS response of the polymer (open symbols) and carbon (closed symbols) (a) xerogels (b) cryogels and (c) aerogels

The deviation from power law behaviour visible at the low $q$ end of the spectra in Figure 27 is the signature of large scale clustering. This feature is more clearly revealed in a
representation that masks surface scattering, i.e., by plotting $Iq^4$ vs. $q$. **Figure 28** shows the oscillations in $I(q)$ for the aerogel sample, both in the RF and the carbon gel. In a monodisperse distribution of spheres for the RF and the carbon aerogel the apparent values of $R$ are equal to $270 \pm 40$ and $80 \pm 10$ Å, respectively. However, as the position of the first maximum is sensitive to size polydispersity, and as the attenuated oscillations in **Figure 28** indicate that the cluster size distribution is broad, a more reliable estimate of the radius of gyration ($R_G$) is obtained using the Guinier representation. The Guinier equation is

$$I(q) \propto \exp\left[-\left(qR_G\right)^2 / 3\right]$$

if $qR_G \leq 1$. For a uniform sphere, this gives

$$R_G^2 = (3/5)R^2. \quad (7)$$

In this approximation plotting ln$I(q)$ vs. $q^2$, the radius of gyration ($R_G$) can be determined from the slope. **Table 12** lists the values of $R_G$ obtained in this way for the different samples.

To compare these sizes with those found from the SEM micrographs, it is reasonable to assume, first, that the spheres are uniform in density, which gives for their diameter

$$d = 2R_G\sqrt{\frac{5}{3}}. \quad (8)$$

Second, over a wide range of values of polydispersity the apparent value of $R_G$ remains approximately 80% of the median value.
Table 12. Data obtained from SAXS measurements for aerogel, cryogel, xerogel, and the corresponding carbon derivates

<table>
<thead>
<tr>
<th>Sample</th>
<th>$R$</th>
<th>$R_G$</th>
<th>$S_X^a$</th>
<th>$S_{BET}^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Å</td>
<td>Å</td>
<td>m$^2$/g</td>
<td>m$^2$/g</td>
</tr>
<tr>
<td>$PA$</td>
<td>270</td>
<td>230</td>
<td>71</td>
<td>270</td>
</tr>
<tr>
<td>$PC$</td>
<td>130</td>
<td>100</td>
<td>260</td>
<td>570</td>
</tr>
<tr>
<td>$PX$</td>
<td>95</td>
<td>84</td>
<td>92</td>
<td>110</td>
</tr>
<tr>
<td>$CGA$</td>
<td>79</td>
<td>67</td>
<td>1690</td>
<td>1010</td>
</tr>
<tr>
<td>$CGC$</td>
<td>72</td>
<td>65</td>
<td>1760</td>
<td>1160$^b$</td>
</tr>
<tr>
<td>$CGX$</td>
<td>220</td>
<td>190</td>
<td>910</td>
<td>890</td>
</tr>
</tbody>
</table>

$^a$where $\rho_{He} = 1.86$ g/cm$^3$ for the carbon and $\rho_{He} = 1.3$ g/cm$^3$ for the polymer [Delhaès 1981]

$^b$measurement performed 18 months after the preparation

Comparisons with the SEM micrographs may thus plausibly be made by multiplying the values of $R_G$ listed in Table 12 by a factor of roughly 3.1. Table 13 summarizes the results. Given that estimates of $d$ from visual observations of SEM images are probably accurate to no more than one significant figure, the agreement between the two sets of observations is acceptable in all cases, with the notable exception of the polymer xerogel and carbon aerogel. In $PX$ there is a higher order of association in which the elementary cluster units coalesce into larger clusters. $PA$ sample displays a two-level change during carbonisation: the SAXS results show that the radius of the clusters shrinks by more than a factor of 3, while the SEM results indicate that on the contrary they swell by about the same factor.

Table 13. Approximate cluster sizes from SEM and SAXS observations for different polymer gels

<table>
<thead>
<tr>
<th>Sample</th>
<th>RF diameter</th>
<th>Carbon diameter</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SEM</td>
<td>SAXS</td>
</tr>
<tr>
<td></td>
<td>Å</td>
<td>Å</td>
</tr>
<tr>
<td>$PX$</td>
<td>1000$^a$</td>
<td>260</td>
</tr>
<tr>
<td>$PC$</td>
<td>300$^a$</td>
<td>300</td>
</tr>
<tr>
<td>$PA$</td>
<td>500$^a$</td>
<td>700</td>
</tr>
</tbody>
</table>

$^a \pm 100$ Å

As there is no reason to reject the evidence either of the SEM or the SAXS results, the two observations imply that a second level of clustering occurs during carbonization of the aerogel: shrunken carbon beads of diameter ca. 200 Å aggregate into units that are an order of magnitude larger. Such large clusters lie outside the detection window of the present SAXS observations. It is interesting to note that the cryogel and the xerogel display no such
instability during carbonisation: their submicron-scale structures are preserved. By contrast, on scales larger than a micron the structure does evolve substantially, as can be seen in Figures 12 and 25. The specific surface area $S_x$ (Table 12) of the gels is derived from the X-ray measurements using the Porod approach [Porod 1983]. As mentioned earlier, this method assumes that the adsorbing surfaces are flat on the length scale of the measurement, and have a sharp discontinuity in density at the interface between the uniform substrate and the outside medium. In practice, at the short length scales relevant to the systems investigated here, the substrate structure is far from regular. A region of the response is therefore sought where the intensity varies as

$$I(q) = Kq^{-4} + b$$

(9)

where $K$ is the final (Porod) slope and $b$ is the scattering from atomic disorder in the sample [Luzzati 1965]. The surface area of the large clusters, which, as already seen, yields this type of scattering behaviour at low $q$, is too small to contribute significantly to the total internal surface area of the gels. The region of the spectrum that could give rise to significant adsorption is to be found above 0.3 Å$^{-1}$. The specific surface area can be determined from the expression [Porod 1983]

$$S_x = \frac{V_{tot} \pi K}{1 + V_{tot} \rho_{He} Q}$$

(10)

where $\rho_{He}$ is the true density of the sample, and $Q$ is given by

$$Q = \int_0^\infty [I(q) - b]q^2 dq .$$

(11)

The low-$q$ behaviour of the integral was determined by extrapolating the intensity to $q = 0$ in a Guinier plot, $(\ln I(q))$ vs. $q^2$. The helium density of the carbon gels was found to be $\rho_{He} = 1.86$ g/cm$^3$, while that for the RF gels, $\rho_{He} = 1.3$ g/cm$^3$, was taken from the literature [Delhaës 1981]. For the carbon gels $S_X$ is appreciably larger than $S_{BET}$, except for the cryogel, where $S_{BET}$ was found to decrease with time. It is not uncommon that $S_X$ is greater than $S_{BET}$, since X-rays detect all internal surfaces including those from which the gas molecules are excluded. The most striking result in Table 12, however, is that in the RF gels the measured value of $S_X$ is substantially smaller than $S_{BET}$. This finding contrasts with other SAXS measurements on RF gels [Berthon 2001, Brandt 2004, Schaefer 1995] in which acceptable agreement is reported between the results of the two techniques. It has been argued that inclusion of long-range correlations can lead to an overestimate in the value of the integral $Q$ [Schaefer 1995], which, if true, would lead to $S_X$ being underestimated. Exclusion of long
range correlation, however, is normally associated with crystalline order, which is clearly absent from the present system. Among the samples investigated here, the one for which the existence of longer range order seems most plausible is the carbon aerogel, as it displays two levels of organisation. In this sample, however, $S_X$ is substantially greater than $S_{BET}$, which does not favour this argument. More specifically, the contribution to $Q$ coming from the $q$-range below 0.01 Å$^{-1}$ in the RF samples is much too small to account for the observed discrepancy.

5.3. **Metal doped adsorbents**

5.3.1. **Preliminary study on the effect of metal doping of porous polymer based carbons**

Microporous spherical carbons with two different surface chemical properties but similar morphology were used for the systematic study of the after-doping parameters. The surface of microporous, vinyl-pyridine-divinylbenzene co-polymer based spherical carbon was modified by Cu$^{2+}$ impregnation. The effect of the doping was investigated in different conditions. The surface chemistry of the carbon was modified by nitric acid treatment prior to impregnation. The concentration of the Cu$^{2+}$ salt in the impregnation solution, as well as the effect of the anion of the Cu$^{2+}$ salt was examined.

5.3.1.1. **Morphological characterization of the undoped carbons**

To examine the effect of the surface chemistry of the carbon to the metal adsorption, the pristine carbon (SC) was oxidized with dilute HNO$_3$ in a Soxhlet apparatus (SCOX). The acidic treatment strongly eroded the surface of the carbon. The practically reversible low temperature nitrogen isotherms of Type I in the IUPAC classification (Figure 29) reveal the microporous character of the SC carbon, which was also retained during the oxidative treatment. The earlier mentioned models were used to evaluate the N$_2$ adsorption isotherms. In the cases of samples with higher metal content, however it should be kept in mind that the local interactions might be significantly different. Parameters deduced from the adsorption/desorption isotherms are listed in Table 14.
Table 14. Porosity data of microporous carbons from N2 adsorption measurements

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{BET}$ ($m^2/g$)</th>
<th>$V_{TOT}$ ($cm^3/g$)</th>
<th>$d_{ave}$ ($Å$)</th>
<th>$W_0$ ($cm^3/g$)</th>
<th>$w$ ($Å$)</th>
<th>$\frac{W_0}{V_{TOT}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SC</td>
<td>1457</td>
<td>0.69</td>
<td>9.47</td>
<td>0.58</td>
<td>9.1</td>
<td>0.84</td>
</tr>
<tr>
<td>SCOX</td>
<td>1176</td>
<td>0.55</td>
<td>9.35</td>
<td>0.46</td>
<td>7.8</td>
<td>0.84</td>
</tr>
</tbody>
</table>

$S_{BET}$: apparent surface area, $V_{TOT}$: pore volume derived from adsorbed volume at $p/p_0 \rightarrow 1$, $d_{ave}$: average pore width, $W_0$: micropore volume from DR analysis; $w$: micropore width from DR analysis

Figure 29. N2 adsorption/desorption isotherms of the SC (●), SCOX (●) carbons

Figure 30. PSD of SC (●) and SCOX (●) samples by NLDFT method
The pore size distributions (PSD) of the two samples found to be very similar in the micropore range. Figure 30 reveals a broad distribution with maxima at 7, 11, 15 and 18.5 Å. The oxidative treatment affects only the microporous region of the SC carbon.

The SAXS response of the SC and SCOX samples at low wave vector $q$ exhibits power law behaviour, the slope of which is characteristic of scattering from a rough surface [Hasmy 1994]. A pronounced shoulder can be found for both carbons at $q \approx 0.1$ Å$^{-1}$, which is the result of the microporous structure. By plotting the data in a Guinier representation ($\log(I(q))$ vs. $q^2$), the radius of gyration of the micropores were found to be 10.9 and 12.3 Å for SC and SCOX respectively. Comparison of the surface area (1560 and 1390 m$^2$/g, respectively), calculated by the method of Porod, with the nitrogen adsorption data reveals only limited inaccessible porosity [László 2005].

In spite of the presence of nitrogen, the acid treatment significantly reduces the pH of the carbon (Table 15), and leads to an elevated surface heteroatom concentration, as presented by the data from the Boehm titration method (Table 15).

| Table 15. Surface chemical properties of SC and SCOX in aqueous phase |
|---------------------------------|------|------|
|                                  | SC   | SCOX |
| pH                              | 7.9  | 3.4  |
| Acidic functional groups (µequiv/g) | 273  | 838  |
| Basic functional groups (µequiv/g) | 538  | 223  |

5.3.1.2. Effect of the surface chemistry to the post-impregnation

In order to study the influence of the surface chemistry and the metal cations, Cu$^{2+}$ adsorption isotherms were measured for SC and SCOX from aqueous solutions of Cu(CH$_3$COO)$_2$. The isotherms, which belong to type L in the Giles classification [Giles 1960], were evaluated from the linear Langmuir plot (Table 16).

The cation exchange capacity of SC and SCOX (Table 15), measured by Boehm titration [Boehm 1966], was found to be about an order of magnitude smaller than the corresponding copper uptake. This may be explained by the nitrogen-containing functional groups present, which may react as complexing agents and increase the copper adsorption.
Table 16. Parameters of the Langmuir equation for SC and SCOX

<table>
<thead>
<tr>
<th>Sample</th>
<th>$n_m$ mg/g</th>
<th>$K$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SC</td>
<td>139.7</td>
<td>14.5</td>
<td>0.9511</td>
</tr>
<tr>
<td>SCOX</td>
<td>133.4</td>
<td>18.8</td>
<td>0.9578</td>
</tr>
</tbody>
</table>

$n_m$: monolayer capacity, $K$: interaction parameter, $R$: regression coefficient of the fit

5.3.1.3. Carbons with different metal loadings

Metal loading was studied on SCOX carbon with Cu$^{2+}$ post-impregnation. For metal loading below the saturation capacity of SCOX ($n_m$, Table 16), the monotonic decrease in the N$_2$ adsorption/desorption isotherms (Figure 31a) and in pores of size smaller than 14 Å visible in Figure 31b is accompanied by a corresponding reduction in both the surface area and the pore volume that becomes more pronounced with increasing loading.

Figure 31. N$_2$ adsorption/desorption isotherms (a) and pore size distribution curves by the NLDFT method (b) of metal-free SCOX (○) compared to SCOX after loading with 0.62 (▼), 1.43 (△) and 2.24 (+) mmol/g copper.
Table 17. Structural parameters from low temperature N₂ adsorption measurements for the SCOX carbons with different loading

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cu²⁺ loading mg/g</th>
<th>(S_{\text{BET}}) m²/g</th>
<th>(V_{\text{TOT}}) cm³/g</th>
<th>(d_{\text{ave}}) Å</th>
<th>(W_0) cm³/g</th>
<th>(w) Å</th>
<th>(W_0/V_{\text{TOT}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCOX</td>
<td>-</td>
<td>1176</td>
<td>0.55</td>
<td>9.4</td>
<td>0.46</td>
<td>7.8</td>
<td>0.84</td>
</tr>
<tr>
<td>SCOX/Cu</td>
<td>39.4</td>
<td>956</td>
<td>0.47</td>
<td>20</td>
<td>0.39</td>
<td>9.5</td>
<td>0.83</td>
</tr>
<tr>
<td>SCOX/Cu</td>
<td>90.8</td>
<td>734</td>
<td>0.38</td>
<td>21</td>
<td>0.30</td>
<td>10.5</td>
<td>0.79</td>
</tr>
<tr>
<td>SCOX/Cu</td>
<td>142.2</td>
<td>128</td>
<td>0.12</td>
<td>38</td>
<td>0.06</td>
<td>15.9</td>
<td>0.50</td>
</tr>
</tbody>
</table>

\(S_{\text{BET}}\): apparent surface area, \(V_{\text{TOT}}\): total pore volume at \(p/p_0 \rightarrow 1\), \(d_{\text{ave}}\): average pore width, \(W_0\): micropore volume from DR analysis; \(w\): micropore width from DR analysis

The microporous character and the accessibility of the larger pores, however, are unaffected. When the loading exceeds 133.4 mg/g a dramatic change in the structural parameters occurs. The sensitivity of the small pores to metal impregnation is apparent upon comparing the porosity of SCOX carbons with different loadings (Figure 31, Table 17).

5.3.1.4. Effect of the anion

When SCOX was loaded from the 0.03 M aqueous solutions of copper salts, under unbuffered conditions (16.0 ml/g carbon) with various anions, at room temperature, different uptakes of copper ion were observed (Table 18).

Table 18. Structural parameters from low temperature N₂ adsorption measurements for the SCOX carbons loaded with different copper salts

<table>
<thead>
<tr>
<th>Anion</th>
<th>Cu²⁺ loading mg/g</th>
<th>(S_{\text{BET}}) m²/g</th>
<th>(V_{\text{TOT}}) cm³/g</th>
<th>(d_{\text{ave}}) Å</th>
<th>(W_0) cm³/g</th>
<th>(w) Å</th>
<th>(W_0/V_{\text{TOT}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>-</td>
<td>1176</td>
<td>0.55</td>
<td>9.4</td>
<td>0.46</td>
<td>7.8</td>
<td>0.84</td>
</tr>
<tr>
<td>CH₃COO⁻</td>
<td>39.4</td>
<td>956</td>
<td>0.47</td>
<td>20</td>
<td>0.39</td>
<td>9.5</td>
<td>0.83</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>9.54</td>
<td>971</td>
<td>0.48</td>
<td>20</td>
<td>0.39</td>
<td>9.9</td>
<td>0.81</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>7.62</td>
<td>1280</td>
<td>0.61</td>
<td>19</td>
<td>0.52</td>
<td>9.0</td>
<td>0.85</td>
</tr>
</tbody>
</table>

\(S_{\text{BET}}\): apparent surface area, \(V_{\text{TOT}}\): total pore volume at \(p/p_0 \rightarrow 1\), \(d_{\text{ave}}\): average pore width, \(W_0\): micropore volume from DR analysis; \(w\): micropore width from DR analysis

This finding indicates that the size and the charge of the anions and their different state of hydration may influence the sorption of the cations [Santafé-Moros 2007].
5.3.2. Metal doped RF and carbon aerogels

In order to find the most effective method of metal doping, taking advantage of the sol–gel method, metals were introduced into the systems at three different stages of the preparation process (Figure 32): adding them to the polymerisation mixture (1); by impregnating the dry polymer gels (2), and impregnation of the carbon gel (3). In protocols (2) and (3) the effect of the concentration (L for low concentration, H for high concentration in sample names) of the metal salt solution was also investigated. The nomenclature of the samples is given in Table 3.

![Figure 32. Preparation of metal doped aero- and carbon gels](image)

5.3.2.1. Cu-containing RF and carbon gels

5.3.2.1.1 Effect of Cu\(^{2+}\) to the sol–gel transition

The sol–gel reaction occurring in the aqueous resorcinol–formaldehyde solution was followed by DLS measurements. The main goal of these experiments was to reveal the influence of CuAc\(_2\) on the process.

Owing to the large refractive index difference between the forming polymer and the solvent, multiple scattering becomes significant at later stages of the reaction. As the polymerization reaction progresses, the scattered light intensity increases monotonically until multiple scattering attenuates the emerging light. The detected intensity then decreases until the gel transition is reached. At the gel point, indicated by G in Figure 33, slowly moving speckles generated by the network structure cause the scattered intensity to fluctuate randomly. It is notable that the gel point occurs at the same time delay (18 h) for both samples.
**Figure 33.** Time \( t \) dependence of scattered intensity at \( \theta = 90^\circ \) (detector count rate CR) from the reaction bath of the RF system at 40 °C, without (+) and with (x)CuAc₂

![Graph showing time dependence of scattered intensity](image)

**Figure 34.** Autocorrelation function \( g_2(\tau)-1 \) of RF systems measured at \( \theta = 90^\circ \), after 3 hrs at 40 °C (a) without CuAc₂ in 9 mm diameter cell (+) (b) with CuAc₂ in a 2 mm diameter cell (x); the continuous lines show the corresponding CONTIN Laplace transforms

![Graph showing autocorrelation functions](image)

The difference in structures is illustrated by the autocorrelation functions \( g_2(\tau)-1 \) of the two systems, displayed in **Figures 34a** and **b**, measured after the same incubation time of 3 hours. The distribution of the relaxation times, calculated from the Laplace transform

\[
a(t) = \int [g_2(\tau) - 1] \exp(-\tau/t)d\tau,
\]

(12)
using the CONTIN procedure [Provencher 1982], are also shown in the corresponding figures.

The correlation function of the copper-free system requires a broad range of relaxation times for its description. This type of relaxation response is characteristic of samples containing a wide distribution of cluster sizes, as is expected for the early stages of the sol–gel transition [Stauffer 1982, Del Gado 2004]. After eliminating the problem of multiple scattering, which was a major issue at the case of the copper containing sample, it is visible from Figure 34b that the polymerization reaction is faster in the presence of Cu$^{2+}$ ions, the size distribution of the forming clusters became shaper and are shifted to larger values after the same incubation time.

These measurements nevertheless enable us to estimate the effect of the catalyst on the average characteristic relaxation rate in the system: the mean hydrodynamic radius determined from Figure 34a by the method of cumulants [Koppel 1972] is $R_H = 100$ Å, while from Figure 34b, $R_H = 490$ Å. These results confirm that CuAc$_2$ does indeed increase the mean size of the clusters.

![Figure 35](image_url)

**Figure 35.** Reaction times in sol–gel transition by RF polycondensation without (+) and with (x)CuAc$_2$, expressed as a ratio with respect to the reaction time at 25 °C; straight lines shown are least squares fits through the data.

Measurement of the time required to reach the gel point as a function of the reaction bath temperature provides an estimate for the activation energy $E$ of the reaction (Figure 35). These observations yield for the reaction with Na$_2$CO$_3$ alone, $E = 75 \pm 4$ kJ/mol, while in the
presence of CuAc₂, \( E = 76 \pm 14 \text{ kJ/mol} \). Within experimental error, these values are in mutual agreement and are also consistent with the literature [Job 2007].

It can be concluded, that when adding copper salt to the initial reaction mixture of resorcinol and formaldehyde affects the kinetics of the polycondensation reaction, although, as it will be shown later (see Chapter 5.3.2.1.3) Cu²⁺ does not build in the polymer network. The polymer aerogel, which is synthesized in the presence of Cu²⁺ has outstandingly high (2000 m²/g) specific surface area.

5.3.2.1.2. Effect of Cu²⁺ on the morphology of the hydrogels

One of the obstacles that confronts small angle X-ray scattering in gels is radiation damage. In the vicinity of the sol – gel transition especially, the induced ionisation can substantially alter network development in the path of the beam. For this reason the SAXS measurements were performed only on the mature networks. The SAXS response of the wet gels is shown in Figure 36 as a function of the wave vector \( q \).

![Combined SAXS and WAXS spectra of RF hydrogels synthesized without (+) and with (×)CuAc₂ at (a) 40 °C (b) 85 °C](image)

**Figure 36.** Combined SAXS and WAXS spectra of RF hydrogels synthesized without (+) and with (×)CuAc₂ at (a) 40 °C (b) 85 °C

In these spectra, the signal from the bulk water has been subtracted out. In the high \( q \) region of Figures 36a and b, a residual feature appears that mimics that of bulk water, but its
main peak and shoulder are shifted, which shows that the wet polymer networks possess a hydration layer. In the region below 0.2 Å⁻¹ the spectra in Figure 36 display a steep increase of intensity as $q$ decreases, followed by a shoulder and power law region with weaker slope. The steep region can also be represented by a power law, where the slope of $-4$ is characteristic of surface scattering. The value found for $R_G$ in the gel synthesized at 40 °C in the presence of CuAc₂ (ca. 250 Å, Figure 36a) is appreciably larger than that with Na₂CO₃ alone (ca. 30 Å). These differences substantiate the finding from DLS that in the early reaction of the CuAc₂-containing system the cluster sizes are much larger than with Na₂CO₃.

At the lowest values of $q$ in Figure 36, the intensity continues to increase with a power law slope of about $-1.4$, indicating that the clusters are arranged in randomly branched linear arrays, as proposed by Tamon et al. [Tamon 1998]. The gel structure can thus be pictured as consisting of sequences of smooth beads, the radius of which depends on the conditions of catalysis. When the gels are synthesized at 85 °C (Figure 36b), however, the structures of the two systems are identical and closely similar to that of the Na₂CO₃ catalyst at 40 °C. The SAXS spectra reveal no indication of the very large clusters observed in the DLS measurements.

5.3.2.1.3. Copper doped RF aerogels

Copper containing RF aerogels were prepared by either introducing Cu²⁺ during the polymerization reaction of resorcinol and formaldehyde, or post-impregnation of the dry RF gel. The copper content of the polymer gels depends strongly on the synthesis protocol (Table 19). The low metal content of the CuP sample indicates that most of the copper is not incorporated into the gel structure. For the X-ray analysis, therefore, CuP can be taken as a simple binary system. The Cu-content of the post-impregnated samples is related to the concentration of the soaking solution.

<table>
<thead>
<tr>
<th>Table 19. Copper content of the polymer samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
</tr>
<tr>
<td>CuP</td>
</tr>
<tr>
<td>P/Cu L</td>
</tr>
<tr>
<td>P/Cu H</td>
</tr>
</tbody>
</table>

aData Determined by EDS measurements,
bDetermined from the mass balance
The low resolution SEM images of the polymer aerogels (Figure 37) reveal the striped surface of the sample P (Figure 37a), while P/Cu (Figure 37b) has a fractured surface. The vaguely striped structure becomes more pronounced after post-impregnating P with copper acetate (Figures 37c and d). The width of the elementary filaments depends on the amount of metal loading: P/Cu L is built up of finer filaments of width about 20 µm, while the filaments in P/Cu H are about 45 µm wide.

Figure 37. Low (a–d, x500, scalebar = 50 µm) and high resolution (e–h, x10000, scalebar = 1 µm) SEM images of the polymer aerogels
The influence of the metal ions is also apparent at higher resolution. The finer structure of the polymer aerogels also exhibits significant differences depending on the metal content and the synthesis route. While the parent RF aerogel \((P)\) possesses a three-dimensional filamentary architecture (Figure 37e), the presence of copper during the polymerization reaction resulted in a more finely packed structure (Figure 37f). Post-impregnation of the RF aerogel causes the loose filaments to cling together, forming a more compact surface morphology (Figures 37g and h).

![Figure 38. N\(_2\) adsorption/desorption isotherms of \(P\) (□), \(CuP\) (△), \(P/Cu L\) (○) and \(P/Cu H\) (▽) aerogels](image)

The difference in morphology is also reflected in the adsorption properties (Figure 38). The low temperature N\(_2\) adsorption/desorption isotherms of samples \(P\) and \(CuP\) are of Type IIb [Rouquerol 1999] and exhibit a wide hysteresis loop. This distorted Type A hysteresis reveals the presence of mesopores formed by interstices between spherical particles of different size [Gregg 1982]. The presence of Cu\(^{2+}\) during the polymerization reaction enhances the porosity in the case of the \(CuP\) sample. Post-impregnation of the \(P\) aerogel resulted in a reduced N\(_2\) adsorption. The isotherms are of Type IVb, which reflects partial blockage of the pores. The steep desorption branch depends on network-percolation effects.

Inclusion of CuAc\(_2\) during the synthesis results in a sample with outstandingly high micro- and mesopore volume. It increases the BET surface area by a factor of more than two
(Table 20), while the apparent surface area decreases inversely with the Cu-content introduced by post-impregnation. Both energy parameters (C from the BET and the slope from the DR model) indicate different interactions arising from the modified surface morphology and chemistry in the presence of copper. The two models show similar trends in the interactions. It is important to recall that the Kelvin equation used to deduce porosity in the mesopore regime is practically not applicable for pores wider than 300 Å [Gregg 1982], which means that values of the macroporosity are no more than estimates of the real content.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(S_{\text{BET}}) (\text{m}^2/\text{g})</th>
<th>(C)</th>
<th>(V_{\text{TOT}}) (\text{cm}^3/\text{g})</th>
<th>(V_{0.94}) (\text{cm}^3/\text{g})</th>
<th>(W_0) (\text{cm}^3/\text{g})</th>
<th>slope</th>
<th>(V_{\text{meso}}) (\text{cm}^3/\text{g})</th>
<th>(V_{\text{macro}}) (\text{cm}^3/\text{g})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(P)</td>
<td>846</td>
<td>168</td>
<td>3.16</td>
<td>0.98</td>
<td>0.27</td>
<td>−3.9</td>
<td>0.70</td>
<td>2.18</td>
</tr>
<tr>
<td>(CuP)</td>
<td>2000</td>
<td>361</td>
<td>10.1</td>
<td>3.22</td>
<td>0.64</td>
<td>−4.7</td>
<td>2.58</td>
<td>6.88</td>
</tr>
<tr>
<td>(P/Cu L)</td>
<td>519</td>
<td>160</td>
<td>0.79</td>
<td>0.77</td>
<td>0.16</td>
<td>−3.7</td>
<td>0.61</td>
<td>0.02</td>
</tr>
<tr>
<td>(P/Cu H)</td>
<td>250</td>
<td>61</td>
<td>0.52</td>
<td>0.51</td>
<td>0.08</td>
<td>−6.4</td>
<td>0.43</td>
<td>0.01</td>
</tr>
</tbody>
</table>

\(S_{\text{BET}}\): apparent surface area, \(C\): interaction parameter related to the net energy of adsorption, \(V_{\text{TOT}}\): total pore volume at \(p/p_0\rightarrow1\), \(V_{0.94}\): pore volume derived from adsorbed volume at \(p/p_0 = 0.94\), \(W_0\): micropore volume from DR analysis, slope: slope of the DR plot (~\(E^{-2}\), \(E\): characteristic adsorption potential); \(V_{\text{meso}} = V_{0.94} - W_0\), \(V_{\text{macro}} = V_{\text{TOT}} - V_{0.94}\)

Figure 39. PSD of \(P\) (\(\square\)), \(CuP\) (\(\triangle\)), \(P/Cu L\) (\(\bigcirc\)) and \(P/Cu H\) (\(\blacktriangledown\)) aerogels by NLDFT (a) and BJH (b) methods

The PSD of the \(P\) and \(Cu/P\) samples exhibits very similarly articulated curves in the micropore region (Figure 39). The influence of post-impregnation on the pore size distribution is related to the amount of salt deposited. Micropores become gradually blocked,
while the large pores get narrower. The increased mesoporosity comes from the partially plugged macropores originally not detected by gas adsorption. This results in an intense peak in the BJH distribution of P/Cu L at ~70 Å, which undergoes a change in shape and shifts to ~70 Å due to the combined filling of narrow and wider pores.

The SAXS response of the polymer gels in the low q region (Figure 40a) also reveals the difference in the large scale structure. Although the presence of Cu during polymerisation generates a remarkably different SAXS response, the SAXS and WAXS curves of the two post-impregnated samples were, within experimental error, identical. For this reason, only the H sample is discussed in this section. The parameters deduced from the SAXS data are listed in Table 21.

![Figure 40](image-url)

**Figure 40.** SAXS (a) and WAXS (b) response of P (□), CuP (△) and P/Cu H (▽) aerogels; vertical lines show the characteristic peaks of CuAc₂

<table>
<thead>
<tr>
<th>Sample</th>
<th>SAXS slope (^a)</th>
<th>R (Å)</th>
<th>R_G (Å)</th>
<th>(Iq(^4))(_{max}) (10^4) cm(^{-1})Å(^{-4})</th>
<th>S(\chi) m(^2)g(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>-3.6</td>
<td>71</td>
<td>67</td>
<td>4.7</td>
<td>450</td>
</tr>
<tr>
<td>CuP</td>
<td>-3.6</td>
<td>28</td>
<td>84</td>
<td>8.5</td>
<td>840</td>
</tr>
<tr>
<td>P/Cu H</td>
<td>-3.7</td>
<td>72</td>
<td>54</td>
<td>4.1</td>
<td>-</td>
</tr>
</tbody>
</table>

\(^a\)from the region q ≈ 0.1 Å\(^{-1}\)
Post-impregnation does not affect the radius $R$ of the elementary beads, while the presence of CuAc₂ during the polycondensation reaction results in smaller spherical units. The radius of gyration of the beads ($R_G$) was determined from the Guinier representation. For a uniform sphere the ratio of the two radii, $R_G/R$, is equal to $(3/5)^{1/2}$. For samples $P$ and $P/Cu H$ this relationship is approximately valid. For $CuP$, however, $R_G$ is larger than $R$, which indicates that the smaller spheres of radius 28 Å are clustered into larger secondary structures. The discrepancy between the two values of $(lq^4)_{\text{max}} R$ shows that sample $CuP$ is not a simple scaled replica of the undoped RF aerogel: the larger clusters in $CuP$ contain extra polymer material in addition to that composing the small spheres. Moreover, the values of $S_X$ derived from SAXS for $P$ and $CuP$ are substantially smaller than those from N₂ adsorption. This discrepancy is a consequence of the rough internal surfaces formed by the bulky polymer segments in the polymer aerogel. Although such surfaces appear smooth on a larger scale (low $q$), they harbour irregular sites that can accommodate small molecules during adsorption, thereby contributing to the BET surface area. The irregularity makes the surface difficult to evaluate by the X-ray technique.

At the molecular scale $P$ and $CuP$ are amorphous, as witnessed by the absence of Bragg peaks in WAXS region shown in Figure 40b. Sample $P/Cu H$, however, exhibits distinct crystallinity: the positions of the Bragg peaks correspond to those of copper(II)-acetate. In the sample $P/Cu$ impregnated with a lower concentration of CuAc₂, no crystallinity was detected. This observation implies that the copper salt may form clusters in the network rather than being uniformly distributed.

5.3.2.1.4. Copper doped carbon gels

The Cu²⁺ containing RF aerogels were converted into carbon gel forms by heat treatment in N₂ atmosphere. The structure-modifying effect of the post-impregnation was also investigated. Table 22 shows the macroscopic yields of the carbonization together with the results of the EDS analysis. From the comparison of the yield and the Cu-content of the $P/Cu H$ carb it can be concluded that the presence of the Cu does not influence the carbonization of the polymer matrix. This might be surprising, since the melting and boiling point of cupric acetate is relatively low, volatile Cu-substances may form during the carbonization [Van Niekerk 1953].
Table 22. Yield of carbonization and copper content of doped carbon gels from EDS

<table>
<thead>
<tr>
<th>Sample</th>
<th>Yield %</th>
<th>Cu concentration wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>CG</td>
<td>38</td>
<td>-</td>
</tr>
<tr>
<td>CuP carb</td>
<td>38</td>
<td>0.5 ± 0.3</td>
</tr>
<tr>
<td>P/Cu H carb</td>
<td>49</td>
<td>48.4 ± 8.3</td>
</tr>
<tr>
<td>CG/Cu L</td>
<td>-</td>
<td>2.3 ± 0.1</td>
</tr>
<tr>
<td>CG/Cu H</td>
<td>-</td>
<td>21.3 ± 0.6</td>
</tr>
</tbody>
</table>

High resolution SEM images in Figure 41 show that the porous structure of the samples is conserved in the pyrolysis process. The surface morphology of the two post-impregnated CG samples, particularly CG/Cu H, is spectacularly different from that of CG itself.

Figure 41. High resolution (x10000, scalebar = 1 µm) SEM images of (a) CG, (b) CuP carb, (c) P/Cu H carb, (d) CG/Cu L and (e) CG/Cu H carbon gels

The Cu-free gel retains the Type IIb isotherm shape [Rouquerol 1999], but displays a narrow H3-type (IUPAC) hysteresis loop in a relative pressure range extending down to the low pressure region. The isotherms of CuP carb, CG/Cu L and CG/Cu H are of Type IVa with a pronounced plateau at high p/p0. Their very narrow hysteresis loop (type H1) is typical of compacted spheroidal particles of fairly uniform size [Gregg 1982] (Figure 42). The shape of
the isotherms of the post-impregnated polymer gel samples, \(P/Cu \text{ H carb}\), as well as its low pressure hysteresis, is unchanged after the carbonization.

Both the micropore and mesopore volumes of the CuP sample decrease, while the BJH distribution of the mesopores is shifted to larger sizes (Table 23, Figure 43). The BET surface area and the total pore volume of \(P\) and its post-impregnated derivatives (\(P/Cu\)) increased during pyrolysis, which also increased the microporosity of these samples. While the change in the micropore region is negligible in the \(P/Cu\) sample, the sharp peak in the mesopore range shifts to 50–60 Å.

![Figure 42. N\(_2\) adsorption/desorption isotherms of CG (■), CuP carb (▲), CG/Cu L (♦), CG/Cu H (□), and P/Cu H carb (▼) carbon gels](image)

**Table 23. Morphology data of the carbonized samples from \(N_2\) adsorption measurements**

<table>
<thead>
<tr>
<th>Sample</th>
<th>(S_{BET}) cm(^2)/g</th>
<th>(C)</th>
<th>(V_{TOT}) cm(^3)/g</th>
<th>(V_{0.94}) cm(^3)/g</th>
<th>(W_0) cm(^3)/g</th>
<th>slope</th>
<th>(V_{meso}) cm(^3)/g</th>
<th>(V_{macro}) cm(^3)/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CG)</td>
<td>1990</td>
<td>652</td>
<td>6.15</td>
<td>2.10</td>
<td>0.78</td>
<td>–2.5</td>
<td>1.32</td>
<td>4.05</td>
</tr>
<tr>
<td>(CuP carb)</td>
<td>1328</td>
<td>651</td>
<td>4.47</td>
<td>3.30</td>
<td>0.53</td>
<td>–3.0</td>
<td>2.77</td>
<td>1.17</td>
</tr>
<tr>
<td>(P/Cu \text{ H carb})</td>
<td>376</td>
<td>134</td>
<td>0.65</td>
<td>0.63</td>
<td>0.12</td>
<td>–3.6</td>
<td>0.51</td>
<td>0.02</td>
</tr>
<tr>
<td>(CG/Cu L)</td>
<td>616</td>
<td>220</td>
<td>5.21</td>
<td>0.97</td>
<td>0.23</td>
<td>–3.7</td>
<td>0.74</td>
<td>4.24</td>
</tr>
<tr>
<td>(CG/Cu H)</td>
<td>263</td>
<td>106</td>
<td>2.84</td>
<td>0.63</td>
<td>0.07</td>
<td>–4.0</td>
<td>0.56</td>
<td>2.21</td>
</tr>
</tbody>
</table>

\(S_{BET}\): apparent surface area, \(C\): interaction parameter related to the net energy of adsorption, \(V_{TOT}\): total pore volume at \(p/p_0\rightarrow 1\), \(V_{0.94}\): pore volume derived from adsorbed volume at \(p/p_0 = 0.94\), \(W_0\): micropore volume from DR analysis, slope: slope of the DR plot (\(E^{-2}\), \(E\): characteristic adsorption potential); \(V_{meso} = V_{0.94} - W_0\), \(V_{macro} = V_{TOT} - V_{0.94}\)
Post-impregnation of \textit{CG} significantly reduced the porosity, however, as in the RF aerogels. The reduction in microporosity is more remarkable. The mechanism of the pore blocking/filling is similar to that described earlier for the impregnation of the polymer gels. (Table 23, Figure 43). While the Cu-containing carbon aerogels differ mainly in their micropore volume but not in the width of the distribution, their pore size window in the mesopore range is tuned by the Cu-adding protocol: \textit{P/Cu H carb} around 50–60 Å, \textit{CuP carb} 100–200 Å and \textit{CG/Cu H} at 300–400 Å.

![Figure 43](image1.png)

\textbf{Figure 43.} PSD of \textit{CG} (■), \textit{CuP carb} (▲), \textit{CG/Cu L} (●), \textit{CG/Cu H} (◇) and \textit{P/Cu H carb} (▼) carbon aerogels by NLDFT (a) and BJH (b) methods

![Figure 44](image2.png)

\textbf{Figure 44.} SAXS (a) and WAXS (b) response curves of \textit{CG} (■), \textit{CuP carb} (▲), \textit{P/Cu H carb} (▼) and \textit{CG/Cu H} (◇) carbon aerogels
The SAXS response curves of the carbonized samples reveal the differences in their morphology (Figure 44a). The post-impregnated CG samples (CG/Cu L and CG/Cu H) exhibit similar structures, i.e., the metal content does not significantly affect the signal. In the region of the curves below $q = 0.03 \, \text{Å}^{-1}$, the $q^{-1.4}$ dependence of the intensity is typical of interconnected chain-like structures. In the same low $q$ region of the post-impregnated polymer (P/Cu H carb), however, the power-law behaviour with slope $-4$ is the signature of scattering from smooth surfaces. The absence of deviation from power law behaviour at the lowest values of $q$ implies that the size of these structures is larger than the limit determined by the smallest value of $q$ explored ($R > 1000 \, \text{Å}$). For CuP carb the curve is horizontal in this $q$ region, implying that the structure may be uniform on larger spatial scales. Owing to the weakness of the shoulder feature in the other carbonized samples, the radius of gyration $R_G$ cannot be defined with certainty. Unlike the RF gels (Figure 40), in the $q$ range above the shoulder, the structure of the carbonized gels is more complex and simple power law behaviour is not observed.

The WAXS response can reveal crystallinity in the samples. In Figure 44b the essentially amorphous character of samples CG, CG/Cu H and CuP carb is demonstrated by the absence of Bragg peaks, with liquid-like ordering in the vicinity of $q \approx 1.7, 2$ and $3 \, \text{Å}^{-1}$, i.e., amorphous analogs of the (002), (100) and (101) crystallographic lines in graphite. For sample P/Cu H carb, however, distinct Bragg peaks occur at the positions characteristic of metallic copper. From the width of these peaks $\Delta q$ the approximate size $L$ of the copper particles can be estimated on the basis of the Scherrer equation [Patterson 1939],

$$\Delta q \approx 0.9 \cdot 4\pi / L,$$

which yields $L \approx 180 \, \text{Å}$.

As in the case of the RF aerogels, the radius $R$ of the elementary beads in the carbonized aerogel structures is deduced from the $Iq^4$ vs. $q$ plot shown in Figure 45. The values are listed in Table 24, together with other parameters calculated from the SAXS spectra. Comparison with Table 21 shows that carbonization causes $R$ to shrink in samples $P$ and P/Cu H (from 71 to 58 Å and from 72 to 52 Å, respectively), while in CuP and in CuP carb the smaller beads hardly change in size (28 to 30 Å). As with the RF aerogels, the intensity maximum of CuP carb is greater than that of CG, but in the present case the ratio is 1.16, which is in more acceptable agreement with the conservation principle of Eq. 5. This finding, together with the relatively well defined oscillations in Figure 45, indicates a narrow size distribution of the spherical beads in each of these carbonized samples.
The substantial increase of the surface area $S_X$ in the carbonized samples $CG$ and $CuP$ carb with respect to their polymer counterparts is a consequence of the small size of the carbon atoms compared to the precursor polymer segments, which favours the formation of more regular and identifiable pore structures.

### Table 24. Parameters from SAXS curves of the carbonized samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>$R$ (Å)</th>
<th>$R_G$ (Å)</th>
<th>$(Iq^4)_{max}\cdot10^4$ cm$^{-1}$Å$^{-4}$</th>
<th>$Q$ cm$^{-1}$Å$^{-2}$</th>
<th>$S_X$ m$^2$/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>$CG$</td>
<td>57</td>
<td>-</td>
<td>1.25</td>
<td>0.0100</td>
<td>2180</td>
</tr>
<tr>
<td>$CuP$ carb</td>
<td>30</td>
<td>68</td>
<td>2.04</td>
<td>0.0104</td>
<td>1550</td>
</tr>
<tr>
<td>$P/Cu H$ carb</td>
<td>52</td>
<td>-</td>
<td>0.89</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$CG/Cu H$</td>
<td>60</td>
<td>-</td>
<td>1.58</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

In common with other microporous carbons, $S_X$ is slightly greater than $S_{BET}$, a difference that is generally attributed to closed porosity or kinetic hindrance in the low temperature N$_2$ adsorption measurements [László 2005]. In the high-$q$ region of the SAXS curves simple power law behaviour is not recovered, owing to additional scattering contributions from other sources than the internal surfaces, notably from atomic disorder.

As a conclusion, it can be stated that the morphology of RF gels is influenced by the presence of CuAc$_2$. Although Cu$^{2+}$ greatly influences the polymerization reaction between resorcinol and formaldehyde, it has no effect on the gelpoint and on the activation energy of

---

**Figure 45.** $Iq^4$ vs. $q$ representation of the of $CG$ (▱), $CuP$ carb (▲), $P/Cu H$ carb (▼) and $CG/Cu H$ (◀) carbon aerogels
the process. The structure of the mature RF hydrogels showed significant differences, depending on the presence of Cu$^{2+}$ during the polymerization, at 40 °C. The Cu$^{2+}$-catalyzed RF aerogel has significantly enhanced porosity compared to the basic RF aerogel. The post-impregnation method strongly modified both the morphology and the copper-content of the samples. In the post-impregnated samples the copper is reduced during pyrolysis, and is found on the surface of P/Cu H carb in the form of large metallic clusters. No crystallinity was observed in the other carbonized samples.

5.3.2.2. Titanium containing RF and carbon gels

5.3.2.2.1. Titanium doped RF aerogels

Addition of titanium-isopropoxide to the aqueous reaction mixture of the resorcinol and formaldehyde promptly results in a thick, yellow precipitate. After drying the sample (TiP) is a high Ti-containing (67.7 ± 5.8 wt% from EDS) powder, unlike the other monolithic RF gels. Ti-containing monoliths therefore can not be obtained by this method. The SEM morphology of the Ti catalyzed sample (Figure 46b and f) is also highly different from the undoped polymer aerogel (Figure 46a and c). While P has a striped surface, the low resolution image of TiP samples reveals a fractured structure. The difference between the two samples is more pronounced in the high resolution images (Figure 46e and f). No filament-like order can be observed in the case of the Ti catalyzed system.

Post-impregnation with Ti resulted in a similar effect in the SEM image as Cu-impregnation, i.e. the fine structure becomes more compact, and a secondary filament-like pattern appears in smaller resolution. The effect depends on the concentration (Table 25).
Figure 46. Low (a–d, x500, scalebar = 50 μm) and high resolution (e–h, x10000, scalebar = 1 μm) SEM images of the RF aerogels

<table>
<thead>
<tr>
<th>Sample</th>
<th>wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>P/Ti L</td>
<td>22.7 ± 3.6</td>
</tr>
<tr>
<td>P/Ti H</td>
<td>37.9 ± 22.8</td>
</tr>
</tbody>
</table>
Figure 47. N\textsubscript{2} adsorption/desorption isotherms of $P$ ($\square$), TiP ($\triangle$), $P/Ti L$ ($\Diamond$) and $P/Ti H$ ($\triangledown$) aerogels

The difference in morphology is also reflected in the adsorption isotherms (Figure 47). TiP shows an isotherm of Type IIb, similarly to the undoped sample $P$, post-impregnation modifies the adsorption isotherms to Type IVb with a well defined plateau at $p/p_0 > 0.85$, as a consequence of pore blocking. All the doped samples show a reduced nitrogen adsorption. The deduced data from the adsorption isotherms are summarized in Table 26. The pore volumes in all categories are the lowest in the TiP precipitate. Post-impregnation eliminates macroporosity.

Table 26. Morphology data of Ti-doped polymer aerogels from nitrogen adsorption measurements

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{BET}$ m\textsuperscript{2}/g</th>
<th>$C$</th>
<th>$V_{TOT}$ cm\textsuperscript{3}/g</th>
<th>$V_{0.94}$ cm\textsuperscript{3}/g</th>
<th>$W_0$ cm\textsuperscript{3}/g</th>
<th>slope</th>
<th>$V_{meso}$ cm\textsuperscript{3}/g</th>
<th>$V_{macro}$ cm\textsuperscript{3}/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P$</td>
<td>846</td>
<td>168</td>
<td>3.16</td>
<td>0.87</td>
<td>0.27</td>
<td>−3.9</td>
<td>0.60</td>
<td>2.29</td>
</tr>
<tr>
<td>TiP</td>
<td>223</td>
<td>155</td>
<td>0.47</td>
<td>0.20</td>
<td>0.07</td>
<td>−3.6</td>
<td>0.13</td>
<td>0.27</td>
</tr>
<tr>
<td>$P/Ti L$</td>
<td>259</td>
<td>43</td>
<td>0.93</td>
<td>0.49</td>
<td>0.06</td>
<td>−6.3</td>
<td>0.43</td>
<td>0.44</td>
</tr>
<tr>
<td>$P/Ti H$</td>
<td>164</td>
<td>140</td>
<td>0.54</td>
<td>0.33</td>
<td>0.04</td>
<td>−5.8</td>
<td>0.29</td>
<td>0.21</td>
</tr>
</tbody>
</table>

$S_{BET}$: apparent surface area, $C$: interaction parameter related to the net energy of adsorption, $V_{TOT}$: total pore volume at $p/p_0 \rightarrow 1$, $V_{0.94}$: pore volume derived from adsorbed volume at $p/p_0 = 0.94$, $W_0$: micropore volume from DR analysis, slope: slope of the DR plot ($\sim E^{-2}$, $E$: characteristic adsorption potential); $V_{meso} = V_{0.94} - W_0$, $V_{macro} = V_{TOT} - V_{0.94}$
Due to the high Ti-content the DFT software can not be applied to deduce PSD and only qualitative trends were concluded also from the BJH model. The PSD (Figure 48) shows that the post-impregnation blocks the smaller pores. The Ti-compound narrow the width of the larger pores (the slope of the isotherm is 0 at \( p/p_0 \to 1 \)), this leads to the shift of the peak at 300 Å to smaller values in the BJH distribution curves (Figure 48b). In sample TiP the absence of wider pores \((d > 100 \text{ Å})\) in the BJH pore size distribution can be observed.

\[ \text{(a)} \quad \text{(b)} \]

**Figure 49.** SAXS (a) and WAXS (b) response of \( P (\square), \quad \text{TiP} (\triangle) \) and \( P/Ti \ H (\triangledown) \) aerogels
Figure 50. Plot of $Iq^4$ vs. $q$ for $P$ (□), $TiP$ ($\triangle$) and $P/Ti H$ (▽) aerogels

The shape of the SAXS curve (slope of $-4$ in the low $q$ region) indicates that this sample has secondary structure. The elemental clusters branched together, and form big aggregates resulting in surface scattering from large objects the size of which was beyond the $q$-limit of the measurement. The slope $-2.6$ in the higher $q$ range is typical for volume scattering, its value being typical of a branched structure. The size of the elementary beads could not be calculated from the $Iq^4$ vs. $q$ plot. The SAXS and WAXS curves of the two post-impregnated samples were identical within experimental error, for this reason only the H sample is discussed here (Figure 49). Post-impregnation of $P$ using titanium-isopropoxide in acetone did not affect the large scale structure, as indicated by the slopes of the SAXS responses in the region of $0.005 \leq q \leq 0.01$. The slope in the higher $q$ region ($-2.7$) show volume scattering in this aerogel, unlike in $P$. In the latter the slope of $-3.6$ corresponds to surface scattering. From the $Iq^4$ vs. $q$ representation (Figure 50), using the spherical model it was found that the size of the elementary beads in the post-impregnated sample is 100 Å, which is significantly larger than in the undoped $P$ sample (71 Å).

5.3.2.2. Titanium doped carbon gels

Ti-doped carbon gels were obtained either by the pyrolysis of the Ti-containing RF aerogel or by post-impregnating the carbon aerogel. The Ti-content of the samples, derived from EDS measurements, show significant differences (Table 27). The observed metal
content of the P/Ti gels is in good agreement with the Ti-content of the polymer aerogels, taking into account the yields of the carbonization. The post-doping of the carbon gel results in a smaller Ti-content, and also proportional to the concentration of the titanium-isopropoxide solution.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Yield %</th>
<th>Ti concentration wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>P/Ti L carb</td>
<td>46</td>
<td>52.8 ± 0.6</td>
</tr>
<tr>
<td>P/Ti H carb</td>
<td>48</td>
<td>72.4 ± 3.9</td>
</tr>
<tr>
<td>CG/Ti L</td>
<td>-</td>
<td>9.2 ± 0.2</td>
</tr>
<tr>
<td>CG/Ti H</td>
<td>-</td>
<td>14.5 ± 0.3</td>
</tr>
</tbody>
</table>

SEM images in Figure 51 show that the relatively smooth surface of TiP sample became also highly structured during the carbonization. The loose structure of the doped polymer samples is conserved in the pyrolysis process. The post-impregnation of the carbon gel with titanium does not affect significantly the visible size of the beads in the samples (Figure 51a, d and e), although the structure becomes slightly more compact after the doping.

Figure 51. High resolution (x10000, scalebar = 1 μm) SEM images of (a) CG, (b) TiP carb, (c) P/Ti H carb (d) CG/Ti L and (e) CG/Ti H carbon gels
The isotherm of the TiP carb sample (Figure 52) is very similar to that of the precursor. The enhanced adsorption is also reflected by the surface area which trebled during the carbonization (Table 28).

The isotherms of the pyrolysed impregnated polymers (P/Ti L carb and P/Ti H carb) are of Type IVa with a pronounced plateau at high p/p₀, which suggest the lack of macropores. Their narrow hysteresis loop (type H1) is typical of compacted spheroidal particles of fairly uniform size [Gregg 1982].

The isotherms of the post-impregnated carbon gels (CG/Ti L and CG/Ti H), similarly to the metal free carbon gel, are of Type II with a narrow H3-type hysteresis. This type of isotherm is characteristic to non-porous or macroporous systems [Rouquerol 1999]. The steep final sectors of the isotherms at p/p₀→1 are the sign of capillary condensation.

The surface area of the impregnated polymer aerogel samples (P/Ti L carb and P/Ti H carb) increased slightly during the pyrolysis, although the change is less significant than in the TiP carb sample (Table 28). The post-impregnation of CG drastically reduces the porosity, due to the pore blocking by titanium. The concentration of the impregnating solution has smaller effect than in the case of the Cu-doped samples. The pore blocking is also demonstrated by the BJH pore size distributions in the mesopore range (Figure 53).

The energetic parameters, C from the BET method and the slope of the DR plot (Table 28), show that the presence of titanium affects the adsorption interactions.
Table 28. Morphology data from N$_2$ adsorption measurements of CG and the Ti-doped derivates

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{BET}$ m$^2$/g</th>
<th>$C$</th>
<th>$V_{TOT}$ cm$^3$/g</th>
<th>$V_{0.94}$ cm$^3$/g</th>
<th>$W_0$ cm$^3$/g</th>
<th>$slope$</th>
<th>$V_{meso}$ cm$^3$/g</th>
<th>$V_{macro}$ cm$^3$/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>CG</td>
<td>1990</td>
<td>652</td>
<td>6.15</td>
<td>1.83</td>
<td>0.78</td>
<td>-2.5</td>
<td>1.05</td>
<td>4.32</td>
</tr>
<tr>
<td>TiP carb</td>
<td>718</td>
<td>435</td>
<td>0.77</td>
<td>0.50</td>
<td>0.25</td>
<td>-2.2</td>
<td>0.25</td>
<td>0.27</td>
</tr>
<tr>
<td>P/Ti L carb</td>
<td>330</td>
<td>169</td>
<td>0.71</td>
<td>0.56</td>
<td>0.11</td>
<td>-4.3</td>
<td>0.45</td>
<td>0.15</td>
</tr>
<tr>
<td>P/Ti H carb</td>
<td>306</td>
<td>226</td>
<td>0.54</td>
<td>0.47</td>
<td>0.10</td>
<td>-3.9</td>
<td>0.37</td>
<td>0.07</td>
</tr>
<tr>
<td>CG/Ti L</td>
<td>393</td>
<td>66</td>
<td>3.58</td>
<td>0.52</td>
<td>0.10</td>
<td>-4.9</td>
<td>0.42</td>
<td>3.06</td>
</tr>
<tr>
<td>CG/Ti H</td>
<td>301</td>
<td>95</td>
<td>3.98</td>
<td>0.37</td>
<td>0.09</td>
<td>-5.4</td>
<td>0.28</td>
<td>3.61</td>
</tr>
</tbody>
</table>

$S_{BET}$: apparent surface area, $C$: interaction parameter related to the net energy of adsorption, $V_{TOT}$: total pore volume at $p/p_0 \rightarrow 1$, $V_{0.94}$: pore volume derived from adsorbed volume at $p/p_0 = 0.94$, $W_0$: micropore volume from DR analysis, $slope$: slope of the DR plot ($-E^{-2}$, E: characteristic adsorption potential); $V_{meso} = V_{0.94} - W_0$, $V_{macro} = V_{TOT} - V_{0.94}$

Figure 53. PSD of CG (■), TiP carb (▲), P/Ti L carb (●), P/Ti H carb (▼), CG/Ti L (◆) and CG/Ti H (♦) carbon gels by BJH method

The SAXS response curves of the Ti-doped samples show only slight differences in the structures. The large scale structure of the samples, as revealed by SAXS, is basically identical. The spherical model was appropriate in all cases to estimate the size of the basic beads in the samples. From the $Iq^4$ vs. $q$ representation it was found that the elementary objects in the samples are different in size (Table 29). The carbonization reduces the size of the primary beads. In P/Ti H carb the radius of the beads are 20 Å, while this value is 70 Å for the post-impregnated carbon (CG/Ti H carb) sample. The characteristic size in TiP carb is slightly smaller ($R = 45$ Å) than in the pure carbon gel.
**Figure 54.** SAXS (a) and WAXS (b) response curves of CG ( ■), TiP carb ( ▲), P/Ti H carb ( ▼) and CG/Ti H ( ▷ ) carbon gels

**Table 29.** Data from SAXS curves of CG and the Ti-doped derivates

<table>
<thead>
<tr>
<th>Sample</th>
<th>$R$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CG</td>
<td>57</td>
</tr>
<tr>
<td>TiP carb</td>
<td>45</td>
</tr>
<tr>
<td>P/Ti H carb</td>
<td>20</td>
</tr>
<tr>
<td>CG/Ti H</td>
<td>70</td>
</tr>
</tbody>
</table>

In the WAXS response curves of the samples Bragg reflections can be observed (Figure 54b), when the heat treatment was performed after the introduction of titanium to the system (samples TiP carb and P/Ti H carb). The lack of the Bragg peaks in the CG/Ti H sample shows that the Ti-dopant is non-crystalline. The positions of the Bragg peaks correspond to TiO$_2$. It is very important to distinguish between the two forms of TiO$_2$ (i.e. anatase or rutile), since these two forms have different catalytic activity. Both samples contain a mixture of the anatase and rutile forms. The ratio of the two forms can be estimated, and it was found that the anatase content of the samples is not more than 10%, at each cases. It is worthwhile to note that TiO$_2$ can be transformed from rutile to anatase form. By heating the sample higher than 550 °C, the main part of anatase transforms to rutile [Moreno-Castilla 2002, Maldonado-Hódar 2000]. Since the carbonization step of sample TiP
and $P/Ti H$ was performed at 900 °C, it is not surprising that both Ti-doped carbon gels contain mainly rutile.

Titanium-doping in any stage reduces the surface area compared to the undoped carbon aerogel. The most pronounced this effect is in the post-impregnated carbon ($CG/Ti H$). In all cases, however, the surface area is significantly higher than in commercial Degussa P25 TiO$_2$ (49 m$^2$/g). The titanium withold by the matrix is much higher (from 9.2 wt% to 72.4 wt%) than in the case of the copper and also depends on the preparation protocol. No monolith can be obtained during the Ti-catalyzed polymerization. Carbons which were prepared by the impregnation of the dry polymer do not contain macropores detectable with N$_2$ adsorption. The form of titanium also depends on the synthesis protocol. Titanium was found in amorphous form in all cases if its introduction was not followed by a heat treatment. Pyrolysis converts the amorphous titanium to a crystalline mixture of anatase and rutile. The anatase/rutile ratio was found to be not higher than 1:9.

5.3.3. Application tests

Three Ti-containing carbon samples ($TiP carb$, $P/Ti H carb$ and $CG/Ti H$) were chosen to test their photocatalytic activity. The applied methods were developed to study photocatalytic activity of TiO$_2$ nanoparticles. The optimization of the method, as well as the investigation of the mechanism in detail are beyond the scope of the thesis.

5.3.3.1. Degradation of methylene blue

Figure 55 compares the catalytic activity of $P/Ti H$ carb sample to Degussa P25 TiO$_2$ (anatase : rutile = 3 : 1) particles. Due to their high adsorption capacity, $TiP carb$ and $CG/Ti H$ adsorbed the whole amount of the test material prior to the irradiation, which excluded them from photodegradation test measurements.

While commercial TiO$_2$ reduces the methylene blue (MEB) concentration by an exponential decay, the $P/Ti H$ carb sample exhibits a more complex time dependence. After promptly adsorbing 85% of MEB this sample possibly becomes a MEB-source. As MEB degrades the adsorption equilibrium – by desorbing MEB – is continuously re-established. The equilibrium between the decomposition and desorption resulted is an apparently constant
MEB concentration in the first 8 minutes of the experiment. After this period the degradation becomes the major effect. The total decomposition time is equal to that of the pure TiO$_2$, although the TiO$_2$ content is 74% of the aerogel only.

*Figure 55.* Removal of methylene blue without catalyst (○), with Degussa P25 TiO$_2$ (○) and P/Ti H carb (▼)

### 5.3.3.2 Degradation of phenol

The *Degussa P25 TiO$_2$* catalyst degraded the whole amount of the phenol exponentially within ca. 80 minutes (*Figure 56*). The Ti doped carbon aerogels adsorbed about 50% of the phenol from the solution, prior to the UV irradiation. The best performing sample was the *P/Ti H carb*, which reduced the phenol concentration in the solution to the 25% of the original value within the experimental error (*Figure 56*). Similarly to the decomposition of MEB, this sample the phenol adsorption/degradation processes may combine. The C and DR slope values of *TiP carb* in Table 28 show that this sample has a carbon-like surface character, i.e. the TiO$_2$ particles, although they are crystalline, are covered by carbon. This may explain the lack of catalytic activity as phenol has no access to TiO$_2$. The catalytic inactivity of *CG/Ti H* is a result of the amorphous character of TiO$_2$. 

---

83
Figure 56. Removal of phenol without catalyst (○), with Degussa P25 TiO$_2$ (○), TiP carb (▲), P/Ti H carb (▼) and CG/Ti H (▲)
6. Summary

Highly porous carbon gels (CG) most often prepared from resorcinol – formaldehyde (RF) based polymer hydrogels exhibit outstanding material properties (high specific surface area, well developed porosity, adjustable morphology, special combination of thermal resistance and electrical conductivity). Their properties can be further tailored by introducing metal into the matrix or on their surface.

The aim of my work was to prepare and characterize transition metal doped RF polymer and carbon gels. Copper and titanium salts were used for the impregnation.

The polymer hydrogels were obtained by the catalytic polycondensation of resorcinol and formaldehyde.

After comparing the possible drying technologies (heat treatment in inert atmosphere, freeze drying and supercritical CO2 extraction) which strongly influence the final morphology of the gels, the extraction with supercritical CO2 was investigated. It was found that the micro- and mesopore volumes are independent of either the drying temperature or pressure, while the macropore volume shows a linearly increasing trend with increasing pressure and the volume of supercritical CO2 used during the process.

Taking advantage of the sol – gel preparation process of the RF gels, the two transition metals (copper(II) and titanium(IV), both in their organic compound) were introduced in three different stages: during the polymerization, by impregnation of the dry polymer or the carbon gel itself.

Scanning electron microscopy (SEM), small and wide angle X-Ray scattering (SAXS/WAXS) and low temperature N2 adsorption/desorption measurements were used for the characterization. The distribution of the metal in the matrix was examined by energy dispersive X-Ray spectroscopy (EDS). Additional measurements were made by dynamic light scattering (DLS).

The presence of copper during the polymerization modifies the kinetics of the polymerization. It also highly affects the morphology leading to an RF monolith with a surface area as high as 2000 m²/g. The similar titanium-treatment does not result in a monolith, but a powder with a significantly smaller surface area.

Metal salts used as catalyst results in carbon aerogels with the lowest metal content. The surface area of these samples is relatively high, comparing to any of the post-impregnated ones.
Impregnation of the polymer aerogels leads to higher metal content after carbonization, than the post-impregnation of CG, even the conditions are identical. Impregnation in the RF stage reduces the volumes of both the micropores and the wider pores. Post-impregnation in the carbon aerogel stage reduces the porosity less dramatically. The loss is the greatest in the micropore range.

The chemical properties and the structure of the loaded metals are also affected by the synthesis protocol. The copper introduced in the polymer stage becomes crystalline Cu\(^0\) after the heat treatment, while the post-impregnation of the CG results in amorphous copper(II)-acetate in the matrix.

TiO\(_2\) is present in a mixture of anatase and rutile in all the cases, when the introduction of the Ti\(^{4+}\) precedes the heat treatment. The carbon gel obtained from the impregnated RF stage exhibited photocatalytic activity. Titania therefore is amorphous after the post-impregnation of CG.

As a conclusion, the way of the metal doping has a strong influence on the structure of the carbon gels. The two transition metals studied, namely copper and titanium behaves in different ways in the doping procedures.
7. Bibliography


8. New scientific results

1. Cu(II)-acetate in the polymerization stage modifies the cluster formation (pH = 5.3, R/C = 25, total initial concentration 5.2 wt/v%). The copper practically does not integrate into the gel structure, but affects the kinetics of the polycondensation reaction without changing the overall activation energy within the temperature range of 30–50 °C (E = 76 ± 14 kJ/mol). It also has a strong effect on the morphology and yields monoliths of specific surface area as high as 2000 m²/g. The size of the elementary beads is also strongly reduced (from to).[Czakkel et al, J. Coll. Int. Sci. accepted]

2. The parameters of ‘real’ supercritical CO₂ extraction were studied by a home-built controllable apparatus. Under conditions of ‘real’ scCO₂ extraction the polymer network shrinkage from acetone is small and comparable to that of lyophilization from t-butanol. The surface area is also high (580 m²/g) and comparable to that of the cryogel. Micro- and mesoporosity is insensitive to the conditions of temperature, time and pressure during the ‘real’ scCO₂ extraction process, but macroporosity is strongly affected. The lower temperature and higher pressure favours higher porosity. At constant scCO₂ flow rate the pore volume retained was found to be proportional to the contact time. Thus, the total pore volume can be tuned in the range 1.6–5.7 cm³/g. [Czakkel et al, Micropor. Mesopor. Mater. 2005, 86, 124; Székely et al., Olaj Szappan Kozmetika, 2009, Special Edition, 84]

3. Post-impregnation of the aerogels in both polymer and carbonized stages either with Cu²⁺ or Ti⁴⁺ results in reduced specific surface area and porosity. Pores bigger than d > 180 Å disappear from the systems. [Czakkel et al, J. Coll. Int. Sci. accepted, Czakkel et al, Micropor. Mesopor. Mater., submitted]

4. The metal uptake can be adjusted with the concentration of the impregnation solution (50–60 Å on impregnation in the polymer aerogel stage, 100–200 Å with Cu²⁺-acetate as a catalyst and 300–400 Å on impregnation of the carbon aerogels). This effect is less obvious in the Ti-containing carbon aerogels. [Czakkel et al, J. Coll. Int. Sci. accepted]
5. The response of the two metals on the heat treatment following the impregnation is different. Carbonization of the copper containing samples reduces Cu$^{2+}$ to Cu$^{0}$. The amorphous titania transforms into a mixture of anatase and rutile (the ratio of anatase is not more than 10%) during the heat treatment at 900 °C. [Czakkel et al, J. Coll. Int. Sci., accepted]
9. Appendix

Cu doped RF polymer and carbon aerogels
*Journal of Colloid and Interface Science*, accepted
(IF 2007: 2.309)

A2 **O. Czakkel**, E. Geissler, A. Moussaïd, B. Koczka, K. László
Copper-containing resorcinol – formaldehyde networks
*Microporous Mesoporous Materials*, submitted
(IF 2007: 2.21)

A3 E. Székely, **O. Czakkel**, B. Nagy, K. László, B. Simándi
Aerogélek szárítása
*Olaj Szappan Kozmetika* 2009, Special Edition, 84-87

A4 **O. Czakkel**, I. Szilágyi, E. Geissler, N. Kanellopoulos, K. László
Morphological characterization of oxidized and metal impregnated spherical carbons
*Progress in Colloid and Polymer Science* 2008, 135, 139-147
(IF 2007: 1.62)

A5 **O. Czakkel**, K. Marthi, E. Geissler, K. László
Influence of drying on the morphology of resorcinol – formaldehyde based carbon gels
*Microporous Mesoporous Materials* 2005, 86, 124-133
(IF 2005: 3.355; independent citations: 9)
Cu doped RF polymer and carbon aerogels

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\textsuperscript{3}Materials Structure and Modelling Research Group of the Hungarian Academy of Sciences, Budapest University of Technology and Economics, Department of Inorganic and Analytical Chemistry, H-1111 Budapest, Szt. Gellért tét 4., Hungary
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Abstract

Introduction of transition metal salt(s) onto the surface of porous carbons may increase the selectivity and/or efficiency of these adsorbents in catalysis or separation. Carbon aerogels with low pressure-drop are particularly suited for these applications. Moreover the sol-gel process used in the synthesis of the resorcinol-formaldehyde polymer gel (RF) precursors offers an extra opportunity for introducing metal ions. Salts of different metals modify both the macroscopic texture and the porosity, depending on the synthesis protocol. In this paper we show, by means of low temperature nitrogen adsorption measurements, SEM, as well as small and wide angle X-ray scattering (SAXS and WAXS), how the addition of copper acetate at three different stages influences not only the specific surface area but also the resulting overall structure over a wide range of length scales. Post-treatment in either the polymer or carbon aerogel stage provides a means of adjusting the copper content. While the Cu-containing carbon aerogels differ mainly in their micropore volume but not in the width of the distribution, their pore size window in the mesopore range can be tuned between 50 and 400 Å by the protocol of Cu-addition. The synthesis protocol also determines the chemical form of the copper.

Keywords: RF aerogel; carbon aerogel; SAXS/WAXS; gas adsorption; copper; doping


**Introduction**

The response characteristics of an adsorbent are a function not only of its total adsorption capacity, but also of its response rate. The design of exchange structures in biology, such as that of plants or of animal respiratory systems, serves to demonstrate that, in order to achieve a high response rate in a limited volume, the architecture must be optimized over a wide range of length scales. In many adsorption applications, therefore, a tailored combination of narrow porosity and open structures is called for.

In this respect, the simultaneous macro- and microporosity of carbon aerogels offers advantages over other forms of adsorbents for applications that require rapid access to the micropores. Meso- and macroporous carbons can be prepared from resorcinol and formaldehyde under controlled conditions. In aqueous solution, resorcinol and formaldehyde undergo a polycondensation reaction, most often catalyzed by sodium-carbonate, to yield a three-dimensional polymer matrix, the resorcinol-formaldehyde (RF) hydrogel. The morphology of the RF gels can be adjusted by modifying the concentration or the mixing ratio of the monomers and the catalyst in the precursor solution, as well as by changing the pH [1-8]. Most of these parameters act by controlling the mechanism and kinetics of the polycondensation process. In the subsequent drying step, the structure of the hydrogel can effectively be retained by careful removal of the solvent [9]. Water, however, owing to its physico-chemical properties, adversely affects the drying process, and consequently a solvent exchange step is often introduced before drying. Three kinds of drying technique are generally employed: (1) drying in an inert atmosphere [1, 10, 11], (2) freeze-drying [4, 5-7] or (3) extraction with supercritical CO\(_2\) [12-14]. The carbon aerogels are prepared by carbonizing the solvent-free RF gel, a process that basically maintains the primary structure of the dry gel. This treatment, however, results in a significant increase in the micropore volume.

This RF aerogel synthesis route has the advantage that metal ions can easily be introduced, either in the sol/gel process or by impregnation of the network, before or after the carbonization step. When sodium carbonate is replaced by other metal salts of basic character (e.g., K\(^+\), Mg\(^{2+}\), Zr\(^{4+}\)), carbon with highly dispersed metal oxide particles can be produced. In this way, the porous texture of the carbonaceous component can be combined with the basic properties of the oxides. Zr-containing carbon aerogels obtained by copolymerisation of organic and inorganic (zirconium(IV)-propoxide) precursors display a more uniform distribution of the metal in the carbon matrix than supported catalysts prepared by other
methods [15]. Addition of Ce$^{3+}$ and Zr$^{4+}$ to the resorcinol-formaldehyde solution enhances the means of controlling the porosity in the micropore region. Depending on the initial pH of the solution, materials with different morphology and porosity can be prepared. The structure of doped carbon aerogels synthesized at pH=7 is mesoporous, while when the initial pH of the solution is low (pH=3) they exhibit mainly microporous morphology [16].

Pd$^{2+}$, Fe$^{2+}$, Co$^{2+}$, Cu$^{2+}$ or Ni$^{2+}$ salts can also be added to the aqueous resorcinol-formaldehyde solution. For Pd, Ni$^{2+}$, Cu$^{2+}$, Fe$^{2+}$, a complexing agent (hydroxyethylethylenediaminetriacetic acid (HEDTA) or diethylenetriaminepentaacetic acid (DTPA)) was required to keep the metal in solution. Texture analysis showed that the complexant modified the microporous texture of the samples and the presence of metal salt affected the mesopore range. Ni$^{2+}$, Fe$^{2+}$ and Pd$^{2+}$ were found in the metallic state after drying, indicating that the metal complexes did not remain stable throughout the polymerisation reaction [11]. During the carbonization process, metal-loaded samples became partially graphitized in the case of the Fe$^{2+}$, Co$^{2+}$ and Ni$^{2+}$-doping [17]. The oxidation state of all the metals was zero, except for iron, which was a mixture of Fe$_2$O$_3$ and Fe$^0$, i.e., reduction of the metallic species is typical in the carbonization step. Formation of interconnected carbon nano-particles was observed in cobalt-doped aerogels, provided they were not heated above 500 °C. At higher temperature cobalt nano-particles were obtained, the size of which may be adjusted by the temperature of the carbonization. The type of the metal also affects the morphology of the samples: Fe and Cu-doped samples have significantly higher surface area and more developed porosity [18].

Cu$^{2+}$-doped carbon aerogels can be obtained by an ion-exchange process performed in the hydrogel state, when resorcinol is replaced by the K$^+$ salt of 2,4-dihydroxybenzoic acid in the sol-gel process [19]. The surface area of these materials is higher than that of the K$^+$-doped carbon aerogel owing to the presence of the Cu$^0$ nanoparticles, which provide a large surface area, and the metal species are uniformly incorporated into the framework of the carbon aerogel [20].

The aim of the present work is to compare the effect of various copper doping protocols both on the microscopic structure and on the macroscopic texture of the polymer and of the carbon aerogels. The morphology and adsorption properties of copper doped species were monitored by small and wide angle X-ray scattering (SAXS/WAXS), scanning electron microscopy (SEM/EDS) and by low temperature N$_2$ adsorption measurements.
**Experimental**

**Sample preparation**

Rod-shaped RF polymer gels were prepared following the method of Lin [1]. The detailed preparation of the pure RF hydrogel in the presence of copper(II) acetate (CuAc) is given elsewhere [21]. The Cu-free and Cu-containing gels were dried, after acetone-water exchange, by supercritical CO$_2$ (scCO$_2$) extraction at 100 bar and 43 °C in a unit of 40 ml inner volume. The treatment lasted for 70 minutes, with a constant 1.2 ml/min scCO$_2$ flow followed by slow depressurization.

Impregnated samples were prepared by soaking either the dried RF polymer (P) or carbon aerogel (CG) rods at room temperature in 0.02 M (L) or 0.04 M (H) aqueous solutions of CuAc for 24 h. The liquid/solid ratio was 75 ml/g dry gel. The dry RF gels were carbonized at 900 °C for 1 h in nitrogen atmosphere. **Table 1** summarizes the nomenclature of the different samples investigated.

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>Undoped RF aerogel</td>
</tr>
<tr>
<td>CuP</td>
<td>RF aerogel synthesized in the presence of CuAc</td>
</tr>
<tr>
<td>P/Cu</td>
<td>P, post-impregnated with CuAc</td>
</tr>
<tr>
<td>CG</td>
<td>P, carbonized</td>
</tr>
<tr>
<td>CuP carb</td>
<td>CuP, carbonized</td>
</tr>
<tr>
<td>P/Cu carb</td>
<td>P/Cu, carbonized</td>
</tr>
<tr>
<td>CG/Cu</td>
<td>C, post-impregnated with CuAc</td>
</tr>
</tbody>
</table>

**Methods**

**SEM/EDS**

Surface morphology and the elemental composition were studied by a SEM/EDS JEOL JSM-5500LV electron microscope in high vacuum mode with a secondary electron detector. The accelerating voltage was 25 kV and the working distance was varied between 5 and 27 mm. Samples were fastened to the copper sample holder by adhesive carbon tape. To prevent surface charging, the uncarbonized samples were coated with Au/Pd. Elemental analysis was performed using the Kα lines of the elements, at magnification 5000x, the average concentrations being calculated from at least six different measurements. The spatial distribution of copper was investigated by using the mapping function of the apparatus, with a resolution of $256 \times 256$ points. The measurement time for each point was 10 ms.
Nitrogen adsorption

Nitrogen adsorption/desorption isotherms were measured at 77 K in the relative pressure range $3 \cdot 10^{-3} \leq p/p_0 \leq 0.995$ with a computer controlled Quantachrome Autosorb-1 instrument. The apparent surface area ($S_{BET}$) and interaction parameter $C$ related to the net energy of adsorption were calculated using the Brunauer–Emmett–Teller (BET) model. The total pore volume ($V_{TOT}$) was derived from the amount of vapour adsorbed at relative pressure $p/p_0 \to 1$, assuming that the pores are then filled with liquid adsorbate. The micropore volume ($W_0$) was derived from the Dubinin–Radushkevich (DR) plot. The characteristic energy of adsorption $E$ could not be determined since the interaction parameter $\beta$ is not known for metal-doped carbon surfaces. For this reason the energy of adsorption was characterised by the slope of the DR plot. The quality of this fit to the data is very satisfactory. Furthermore, as the validity of the assumption in the DR model of a single Gaussian distribution for the adsorption energy is not ascertained for the present copper-containing systems, we also give the $W_0$ derived from the more general Dubinin-Astakov (DA) model.

The PSD in the mesopore range was deduced from the desorption branch using the Barret-Joyner-Halenda (BJH) method. This model combines the Kelvin equation for cylindrical pore geometry with a correction term for the layer thickness. The latter was estimated using de Boer’s empirical equation. The macropore and mesopore volumes ($V_{macro}$ and $V_{meso}$) were estimated using the cumulative BJH distribution. On account of the shape of the isotherms, pores with $d < 330$ Å ($p/p_0 = 0.94$) were considered to be mesopores. All the calculations were performed using the Quantachrome software.

Small and wide angle X-ray scattering (SAXS/WAXS)

SAXS/WAXS measurements of the solid samples were made at 15.3 keV on the BM2 small angle camera at the European Synchrotron Radiation Facility (ESRF), Grenoble, France. The $q$-range explored was $0.005 < q < 5.7 \text{ Å}^{-1}$ (where $q = (4\pi/\lambda)\sin(\theta/2)$ ), $\lambda$ being the wavelength of the incident radiation and $\theta$ the scattering angle). The powdered samples were placed in glass capillary tubes of diameter 1.5 mm. Scattering intensities $I(q)$ were normalised with respect to a standard (lupolen), assuming an effective sample thickness of 1 mm to account for the filling factor of the powder. To allow for small differences in the effective illuminated volume of the sample resulting from its granular nature, the intensities of the polymer samples were standardized with respect to the amorphous halo between 1 and 2 Å$^{-1}$. 


A similar procedure was used for the carbonized samples with the amorphous halo around 1.8 Å\(^{-1}\), which corresponds to the interlayer (002) reflection in graphite.

The specific surface areas \(S_X\) of the undoped polymer aerogel \(P\) and its counterpart \(CuP\) synthesized in the presence of CuAc, as well as of the corresponding carbonized networks \(CG\) and \(CuP\ carb\), were evaluated from the range 0.1<\(q\)<1 Å\(^{-1}\), where the \(Iq^4\) vs. \(q^4\) representation is linear (Porod scattering [22]). The second moment of the scattering curves, is

\[
Q = \int_0^\infty I(q)q^2dq.
\]  

(1)

\(Q\), which is a measure of the amount of material in the sample, was found by summing the recorded values of \(I(q)q^2\) between zero and the Porod region, and then by analytical integration to infinity. As detailed in reference [23], \(S_X\) is obtained from the expression, applicable to binary systems,

\[
S_X = \frac{\pi K}{Q} \cdot \frac{V_{TOT}}{1+V_{TOT}d_{He}}
\]

(2)

where \(V_{TOT}\) is the total pore volume found from low temperature nitrogen adsorption, \(d_{He}\) is the helium density of the material and \(K\) is the "final slope" of the intensity measured in the Porod region [22]. For the RF polymer, \(d_{He}\) was measured to be 1.36 g/cm\(^3\), in acceptable agreement with the literature [24]. For the carbonized aerogels the value of \(d_{He}\) was found to be 1.8 g/cm\(^3\). Eq. 2 is not applicable to samples containing significant amounts of copper, owing to the resulting ternary character of the air-carbon-copper system.

**Results**

**Polymer gels**

The low resolution SEM images of the polymer aerogels (**Figure 1**) reveal the striped surface of the sample \(P\) (**Figure 1a**), while \(P/Cu\) (**Figure 1b**) has a fractured surface. The vaguely striped structure becomes more pronounced after post-impregnating \(P\) with copper acetate (Figures 1c, d). The width of the elementary filaments depends on the amount of metal loading: \(P/Cu\ L\) is built up of finer filaments of width about 20 µm, while the filaments in \(P/Cu\ H\) are about 45 µm wide. The influence of the metal ions is also apparent at higher resolution. The finer structure of the polymer aerogels also exhibits significant differences depending on the metal content and the synthesis route. While the parent RF aerogel (\(P\)) possesses a three-dimensional filamentary architecture (**Figure 1e**), the presence of copper during the polymerization reaction resulted in a more finely packed structure (**Figure 1f**).
Post-impregnation of the RF aerogel causes the loose filaments to cling together, forming a more compact surface morphology (Figures 1g, h).

Figure 1. Low (a-d, x500, scale bar is 50 μm) and high resolution (e-h, x10,000, scale bar is 1 μm) SEM images of the polymer aerogels.

Table 2. Copper content of the polymer samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuP</td>
<td>0.7±0.1</td>
</tr>
<tr>
<td>P/Cu L</td>
<td>3.7**</td>
</tr>
<tr>
<td>P/Cu H</td>
<td>18**</td>
</tr>
</tbody>
</table>

* Determined by EDS measurements, ** Determined from the mass balance

The copper content of the polymer gels depends strongly on the synthesis protocol (Table 2). The low metal content of the CuP sample indicates that most of the copper is not incorporated into the gel structure. For the X-ray analysis, therefore, CuP can be taken as a simple binary system. The Cu-content of the post-impregnated samples is related to the concentration of the soaking solution. Owing to the limited amount of material no reliable estimate could be made of \( d_{He} \) for the copper impregnated samples. The residual mass fractions in the CuP and P aerogels after thermal analysis (not shown here) were practically identical, however, confirming the low copper content of CuP.

Figure 2. \( \text{N}_2 \) adsorption/desorption isotherms of \( P \) (□), CuP (△), P/Cu L (○) and P/Cu H (▼) aerogels. Inserts show the data from the pressure region \( p/p_0 \leq 0.1 \) in a logarithmic scale.

The difference in morphology is also reflected in the adsorption properties (Figure 2). The low temperature \( \text{N}_2 \) adsorption/desorption isotherms of samples P and CuP are of Type IIb [25] and exhibit a wide hysteresis loop. Post-impregnation of the P aerogel resulted in reduced \( \text{N}_2 \) adsorption. The isotherms are of Type IVb, which reflects partial blockage of the pores. The steep desorption branch depends on network-percolation effects.

Inclusion of CuAc during the synthesis (i.e., reducing the R/C ratio) results in a sample with outstandingly high micro- and mesopore volume. It increases the BET surface area by a factor of more than two (Table 3). By contrast, with post-impregnation, the apparent surface area decreases inversely with the Cu-content. In more dilute catalytic systems (R/C range: 500-1500) decreasing R/C ratio was found to reduce both the apparent surface area and the total pore volume [3]. Both energy parameters (C from the BET and the slope from the...
DR model) indicate different interactions arising from the modified surface morphology and chemistry in the presence of copper. The two models show similar trends in the interactions.

Table 3. Morphology data of the polymer gels from N\textsubscript{2} adsorption measurements.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$V_{TOT}$ cm\textsuperscript{3}/g</th>
<th>$V_{330}$ cm\textsuperscript{3}/g</th>
<th>$S_{BET}$ m\textsuperscript{2}/g</th>
<th>C</th>
<th>$W_{0,DR}$ cm\textsuperscript{3}/g</th>
<th>$W_{0,DA}$ cm\textsuperscript{3}/g</th>
<th>DR slope</th>
<th>$V_{meso}$ cm\textsuperscript{3}/g</th>
<th>$V_{macro}$ cm\textsuperscript{3}/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>3.16</td>
<td>0.98</td>
<td>846</td>
<td>168</td>
<td>0.27</td>
<td>0.35</td>
<td>-3.9</td>
<td>0.70</td>
<td>2.18</td>
</tr>
<tr>
<td>CuP</td>
<td>10.1</td>
<td>3.22</td>
<td>2000</td>
<td>361</td>
<td>1.04</td>
<td>1.64</td>
<td>-4.7</td>
<td>2.58</td>
<td>6.88</td>
</tr>
<tr>
<td>P/Cu L</td>
<td>0.79</td>
<td>0.77</td>
<td>519</td>
<td>160</td>
<td>0.16</td>
<td>0.23</td>
<td>-3.7</td>
<td>0.61</td>
<td>0.02</td>
</tr>
<tr>
<td>P/Cu H</td>
<td>0.52</td>
<td>0.51</td>
<td>250</td>
<td>61</td>
<td>0.08</td>
<td>0.06</td>
<td>-6.4</td>
<td>0.43</td>
<td>0.01</td>
</tr>
</tbody>
</table>

$V_{TOT}$: total pore volume at $p/p_0 \rightarrow 1$; $V_{330}$: pore volume of pores with volume at $d \leq 330$ Å; $S_{BET}$: apparent surface area; C: interaction parameter related to the net energy of adsorption; $W_{0,DR}$ and $W_{0,DA}$ micropore volume from DR and DA analyses, respectively; slope: slope of the DR plot; $V_{meso}=V_{330}-W_0$; $V_{macro}=V_{TOT}-V_{330}$

Figure 3. PSD of P (□), CuP (△), P/Cu L (○) and P/Cu H (◇) aerogels in the mesopore range

The influence of post-impregnation on the porosity is related to the amount of salt deposited. The values of $W_0$ in Table 3 indicate that micropores become progressively blocked. The increased mesoporosity comes from the partially plugged macropores originally not detected by gas adsorption. This results in an intense peak in the BJH distribution of P/Cu L at ~70 Å, which undergoes a change in shape and shifts to ~70 Å due to the combined filling of narrow and wider pores (Figure 3). While the $V_{TOT}$ of the copper-free and the CuP gels are remarkably different, the ratios of the different pore classes are closely similar (Table 3).

Figure 4. SAXS (a) and WAXS (b) response of polymer aerogels. The vertical lines in P/Cu H correspond to principal Bragg reflections of cupric acetate. No measurable Bragg reflections were found in sample P/Cu L.

The SAXS response of the polymer gels (Figure 4a) also reveals, in the low $q$ region, the difference in the large scale structure. Although the presence of Cu during polymerisation generates a markedly different SAXS response, the SAXS curves of the two post-impregnated samples were, within experimental error, identical. For this reason, only the H sample is discussed in this section. The WAXS responses of the same two samples, however, were different. The spectrum of P/Cu H displays clearly resolved Bragg peaks corresponding to crystalline CuAc (Figure 4b) [26], while that of P/Cu L was smooth, indicating that the CuAc was amorphous. To quantify the differences in SAXS response, we represent the elementary
cluster units composing the networks by independent uniform solid spheres of external radius $R$. The scattering intensity is thus defined by the structure factor of a single sphere,

$$S_{sphere}(q) \propto [3(sinR-qRcosq)/(qR^3)]^2.$$  \hfill (3)

**Figure 5.** Plot of $Iq^4$ vs $q$ for polymer aerogels.

At large $q$, this function exhibits the $q^{-4}$ power law behaviour characteristic of smooth surfaces. The plot of $S_{sphere}(q)q^4$ vs. $q$ is a characteristic oscillatory function with its first maximum at $qR = 2.74$ and first minimum at 4.49 (Figure 5). These features provide a means of evaluating the radius of the spheres (Table 4). In this representation, for a measured scattering intensity $I(q)$, the intensity of the maxima is proportional to $(4\pi R^3/3)^2NS_{sphere}(q)q^4$, where $N$ is the number of spheres per unit volume. Since $S_{sphere}(q)$ is a function of $qR$ only, for otherwise identical samples having the same total concentration $c=(4\pi R^3/3)N$ but composed of spheres of different radii $R$, the intensity of the maxima is inversely proportional to $R$, i.e.,

$$I(q)q^4 \propto 1/R.$$  \hfill (4)

**Table 4.** Parameters derived from SAXS measurements of the polymer gels

<table>
<thead>
<tr>
<th>Sample</th>
<th>SAXS slope*</th>
<th>$R$ Å</th>
<th>$R_G$ Å</th>
<th>$(Iq^4)_{max}\times10^4$ cm$^{-1}$Å$^{-4}$</th>
<th>$Q$ cm$^{-1}$Å$^{-2}$</th>
<th>$S_X$ m$^2$g$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P$</td>
<td>-3.6</td>
<td>71</td>
<td>67</td>
<td>4.7</td>
<td>0.0259</td>
<td>380</td>
</tr>
<tr>
<td>CuP</td>
<td>-3.6</td>
<td>28</td>
<td>84</td>
<td>8.5</td>
<td>0.0225</td>
<td>700</td>
</tr>
<tr>
<td>P/Cu H</td>
<td>-3.7</td>
<td>72</td>
<td>54</td>
<td>4.1</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

* from the region $q \approx 0.1$ Å$^{-1}$

The parameters deduced from the SAXS data are listed in Table 4, where the specific surface area $S_X$ are calculated as described in the experimental section (eqs 1 and 2).

Post-impregnation does not affect the radius $R$ of the elementary beads, while the presence of CuAc during the polycondensation reaction results in smaller spherical units. The latter is in agreement with the results of Li et al [3]. The radius of gyration of the beads ($R_G$) was determined from the Guinier representation ($lnI$ vs $q^2$, not shown here). For a uniform sphere the ratio of the two radii, $R_G/R$, is equal to $(3/5)^{1/2}$. In samples $P$ and $P/Cu H$ this relationship is approximately valid. For CuP, however, $R_G$ is larger than $R$, which indicates that the smaller spheres of radius 28 Å are clustered into larger secondary structures. For $P$ and CuP, which have almost identical compositions (the copper content of CuP being
negligible in the SAXS response), the proportionality relationship of Eq. 4 is not satisfied: 
\[(Iq^4)_{\text{max}} \cdot R\] is significantly smaller in CuP than in P. The discrepancy between the two values of \((Iq^4)_{\text{max}} \cdot R\) is greater than can be accounted for by differences in concentration and sample volume, represented by the second moment \(Q\), and, moreover, in view of the high electron density of the copper salt, is opposite in sign to what would be expected if CuAc were present. Sample CuP is therefore not a simple scaled replica of the undoped RF aerogel: the larger clusters in CuP contain extra polymer material in addition to that composing the small spheres. Moreover, the values of \(S_X\) derived from SAXS for P and CuP are substantially smaller than those from N\(_2\) adsorption. This discrepancy is a consequence of the rough internal surfaces formed by the bulky polymer segments in the aerogel, as corroborated by the values of the SAXS slopes in Table 4. These are intermediate between -4 and -3, indicating surface fractal roughness. Although such surfaces appear smooth on a larger scale (low \(q\)), they harbour irregular sites that can accommodate small molecules during adsorption, thereby contributing to the BET surface area. The irregularity makes the surface difficult to evaluate by the X-ray technique.

At the molecular scale P and CuP are amorphous, as witnessed by the absence of Bragg peaks in WAXS region shown in Figure 4b. Sample P/Cu H, however, exhibits distinct crystallinity: the positions of the Bragg peaks correspond to those of cupric acetate. In the sample P/Cu impregnated with a lower concentration of CuAc, no crystallinity was detected. This observation implies that the copper salt deposited at low concentration is essentially amorphous.

*Carbon gels*

Table 5 lists the macroscopic yields of the carbonization, together with the results of the EDS analysis. From the comparison of the yield and the Cu-content of P/Cu H carb we can conclude that the presence of the Cu does not influence the carbonization of the polymer matrix, a finding that is corroborated by thermal analysis (not shown here). This might be surprising, since, as the melting and boiling point of cupric acetate is relatively low (MP 115 °C, BP 240 °C), volatile Cu-compounds may form during the carbonization [27].
Table 5: Yield of carbonization and copper content from EDS

<table>
<thead>
<tr>
<th>Sample</th>
<th>Yield (%)</th>
<th>Cu concentration (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CG</td>
<td>38</td>
<td>-</td>
</tr>
<tr>
<td>CuP carb</td>
<td>38</td>
<td>0.5±0.3</td>
</tr>
<tr>
<td>P/Cu H carb</td>
<td>49</td>
<td>48.4±8.3</td>
</tr>
<tr>
<td>CG/Cu L</td>
<td>-</td>
<td>2.3±0.1</td>
</tr>
<tr>
<td>CG/Cu H</td>
<td>-</td>
<td>21.3±0.6</td>
</tr>
</tbody>
</table>

Figure 6: High resolution (x10.000, scale bar is 1 μm) SEM images of the carbon gels.

High resolution SEM images in Figure 6 show that the porous structure of the samples is conserved in the pyrolysis process. The surface morphology of the two post-impregnated CG samples, particularly CG/Cu H, is spectacularly different from that of CG itself.

The Cu-free gel retains the Type IIb isotherm shape [26], but displays a narrow H3-type (IUPAC) hysteresis loop in a relative pressure range extending down to the low pressure region. The isotherms of CuP carb, CG/Cu L and CG/Cu H are of Type IVa with a pronounced plateau at high \( p/p_0 \). Their very narrow hysteresis loop (type H1) is typical of compacted spheroidal particles of fairly uniform size [28] (Figure 7). The shape of the isotherms of the post-impregnated polymer gel samples, P/Cu H carb, as well as its low pressure hysteresis, is unchanged after the carbonization.

Figure 7: \( \text{N}_2 \) adsorption/desorption isotherms of CG (■), CuP carb (▲), CG/Cu L (◇), CG/Cu H (◆) and P/Cu H carb (▼) carbon gels. Inserts show the data from the pressure region \( p/p_0 \leq 0.1 \) in a logarithmic scale.

Figure 8: PSD of CG (■), CuP carb (▲), CG/Cu L (◇), CG/Cu H (◆) and P/Cu H carb (▼) carbon gels.

Both the micropore and mesopore volumes of the CuP sample are depleted (Figure 8). The BET surface area and the total pore volume of P and its post-impregnated derivatives (P/Cu) increased during pyrolysis, which also increased the microporosity of these samples. In the P/Cu sample, the sharp peak in the mesopore range shifts to 50-60 Å as a result of the heat treatment. Post-impregnation of CG significantly reduces the porosity, however, as in the RF aerogels. The reduction in microporosity is the most marked, by an order of magnitude. A pore blocking/filling mechanism occurs, similar to that described earlier for the impregnation of the polymer gels (Table 6). While the Cu-containing carbon aerogels differ mainly in their micropore volume but not in the width of the distribution, their pore size window in the
mesopore range is tuned by the Cu-adding protocol: P/Cu H carb around 50-60 Å, CuP carb 100-200 Å and CG/Cu H at 300-400 Å. While the un- and post-treated CG are mainly macroporous, the other three Cu-containing carbon aerogels contain mainly mesopores.

Table 6: Morphology data of the carbonized samples from N₂ adsorption measurements.

<table>
<thead>
<tr>
<th>sample</th>
<th>( V_{TOT} ) cm³/g</th>
<th>( V_{330} ) cm³/g</th>
<th>( S_{BET} ) m²/g</th>
<th>( C )</th>
<th>( W_{0,DR} ) cm³/g</th>
<th>( W_{0,DA} ) cm³/g</th>
<th>DR slope</th>
<th>( V_{meso} ) cm³/g</th>
<th>( V_{macro} ) cm³/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>CG</td>
<td>6.15</td>
<td>2.10</td>
<td>1990</td>
<td>652</td>
<td>0.78</td>
<td>0.86</td>
<td>-2.5</td>
<td>1.32</td>
<td>4.05</td>
</tr>
<tr>
<td>CuP carb</td>
<td>4.47</td>
<td>3.30</td>
<td>1328</td>
<td>651</td>
<td>0.53</td>
<td>0.49</td>
<td>-3.0</td>
<td>2.77</td>
<td>1.17</td>
</tr>
<tr>
<td>P/Cu H carb</td>
<td>0.65</td>
<td>0.63</td>
<td>376</td>
<td>134</td>
<td>0.12</td>
<td>0.19</td>
<td>-3.6</td>
<td>0.51</td>
<td>0.02</td>
</tr>
<tr>
<td>CG/Cu L</td>
<td>5.21</td>
<td>0.97</td>
<td>616</td>
<td>220</td>
<td>0.23</td>
<td>0.19</td>
<td>-3.7</td>
<td>0.74</td>
<td>4.24</td>
</tr>
<tr>
<td>CG/Cu H</td>
<td>2.84</td>
<td>0.63</td>
<td>263</td>
<td>106</td>
<td>0.07</td>
<td>0.06</td>
<td>-4.0</td>
<td>0.56</td>
<td>2.21</td>
</tr>
</tbody>
</table>

\( V_{TOT} \): total pore volume at \( p/p_0 \rightarrow 1 \); \( V_{330} \): pore volume of pores with volume at \( d \leq 330 \) Å; \( S_{BET} \): apparent surface area; \( C \): interaction parameter related to the net energy of adsorption; \( W_{0,DR} \) and \( W_{0,DA} \) micropore volume from DR and DA analyses, respectively; \( DR \) slope: slope of the DR plot; \( V_{meso}=V_{330}-W_0 \); \( V_{macro}=V_{TOT}-V_{330} \)

Figure 9: SAXS (a) and WAXS (b) response curves of carbon aerogels. In b) the curves have been shifted vertically for clarity.

The SAXS response curves of the carbonized samples reveal the differences in their morphology (Figure 9a). The post-impregnated CG samples (CG/Cu L and CG/Cu H) exhibit similar structures, i.e., the metal content does not significantly affect the signal. In the region of the curves below \( q = 0.03 \) Å⁻¹, the \( q^{-1.4} \) dependence of the intensity is typical of interconnected chain-like structures. In the same low \( q \) region of the post-impregnated polymer (P/CuH carb), however, the power-law behaviour with slope -4 is the signature of scattering from smooth surfaces. The absence of deviation from power law behaviour at the lowest values of \( q \) implies that the size of these structures is larger than the limit determined by the smallest value of \( q \) explored (\( R>1000 \) Å). For CuP carb the curve is horizontal in this \( q \) region, implying that the structure may be uniform at larger spatial scales. Owing to the weakness of the shoulder feature in the other carbonized samples, the radius of gyration \( R_G \) cannot be defined with certainty. Unlike the RF gels (Fig 4), in the \( q \) range above the shoulder, the structure of the carbonized gels is more complex and simple power law behaviour is not observed.

Figure 9

The WAXS response can reveal crystallinity present in the samples. In Figure 9b the essentially amorphous character of samples CG, CG/Cu H and CuP is demonstrated by the
absence of Bragg peaks, with liquid-like ordering in the vicinity of \( q \approx 1.7, 2 \) and 3 Å\(^{-1}\), i.e., amorphous analogs of the (002), (100) and (101) crystallographic lines in graphite. For sample \( P/Cu H \), however, distinct Bragg peaks occur at the positions characteristic of metallic copper. From the width of these peaks \( \Delta q \) the approximate size \( L \) of the copper particles can be estimated on the basis of the Scherrer equation [29],

\[
\Delta q \approx 0.9 \times 4\pi/L,
\]

which yields \( L \approx 180 \) Å.

As in the case of the RF aerogels, the radius \( R \) of the elementary beads in the carbonized aerogel structures is deduced from the \( Iq^4 \) vs \( q \) plot shown in Figure 10. The values are listed in Table 7, together with other parameters calculated from the SAXS spectra. Comparison with Table 4 shows that carbonization causes \( R \) to shrink in samples \( P \) and \( P/Cu H \) (from 71 to 58 Å and from 72 to 52 Å, respectively), while in \( CuP \) and in \( CuP carb \) the smaller beads hardly change in size (28 to 30 Å). As with the RF aerogels, the intensity maximum of \( CuP carb \) is greater than that of \( CG \), but in the present case the ratio \( (Iq^4_{max}R)_{CG}/(Iq^4_{max}R)_{CuP carb} = 1.16 \), is in more acceptable agreement with the conservation principle of eq 4. This finding, together with the relatively well defined oscillations in Figure 10, indicates a narrow size distribution of the spherical beads in each of these carbonized samples.

Figure 10. \( Iq^4 \) vs \( q \) representation of the carbon aerogels.

| Table 7. Parameters from SAXS curves of the carbonized samples. |
|------------------|------------------|------------------|------------------|------------------|
| \( R \) (Å) | \( R_G \) (Å) | \( (Iq^4)_{max} \times 10^4 \) cm\(^{-1}\)Å\(^{-4}\) | \( Q \) cm\(^{-2}\)Å\(^{-2}\) | \( S_X \) m\(^2\)g\(^{-1}\) |
| CG | 57 | - | 1.25 | 0.0100 | 2180 |
| CuP carb | 30 | 68 | 2.04 | 0.0104 | 1550 |
| P/Cu H carb | 52 | - | 0.89 | - | - |
| CG/Cu H | 60 | - | 1.58 | - | - |

The substantial increase of the surface area \( S_X \) in the carbonized samples \( CG \) and \( CuP carb \) with respect to their polymer counterparts is a consequence of the small size of the carbon atoms compared to the precursor polymer segments, which favours the formation of more regular and identifiable pore structures. In common with other microporous carbons, \( S_X \) is slightly greater than \( S_{BET} \), a difference that is generally attributed to closed porosity or kinetic hindrance in the low temperature \( N_2 \) adsorption measurements [23]. In the high-\( q \) region of the SAXS curves simple power law behaviour is not recovered, owing to additional
scattering contributions from other sources than the internal surfaces, notably from atomic disorder.

The stage at which the copper is introduced affects not only the morphology of the resultant copper doped aerogel but also the chemical form of the transition metal. When added to the precursor solution it behaves as a catalyst and remains only as a trace after solvent exchange. When the polymer aerogel is impregnated, the polymer and the copper salt are simultaneously exposed to the heat treatment, giving rise to a complex set of reactions. Pyrolytic degradation of the polymer matrix, starting above 200 ºC, involves loss of oxygen from the surface and leaves behind a reactive carbon surface, which in turn reduces the copper. A detailed analysis of these reactions, however, lies outside the scope of this study. The reduced copper is in the form of large metallic clusters. The post-impregnated carbon aerogels contain the copper in Cu$^{2+}$ form. No crystallinity was detected in these samples. The mapping EDS measurements of the carbonized samples (not shown here) indicate that the distribution of both forms of the copper on the surface is homogenous on the scale of the SEM micrographs.

Conclusions

Copper-containing RF-based carbon aerogels were synthesized by introducing a copper salt at different stages of the preparation. The morphological and structural changes were followed in a wide range of length scales. The presence of copper was found to modify not only the macroscopic texture of the carbon aerogels but also their microscopic structure. The synthesis protocol also determines the chemical form of the copper.

When copper acetate was added in the polymerization stage (CuP) the porosity was greatly enhanced, although the Cu-concentration obtained was low (< 1 wt%), as a result of the solvent extraction step. Post-impregnation, however, produced a substantial decrease in the porosity. Post-treatment in either the polymer or carbon aerogel stage provides a means of adjusting the copper content. Carbonization of the polymer matrix enriched the copper content, but the yield is not affected by the presence of the copper. If the post-treatment took place in the RF aerogel stage, carbonization of the post-impregnated samples reduced copper acetate completely to Cu$^0$ without influencing the pyrolysis of the supporting RF gel. The copper took the form of metallic clusters between 100 and 200 Å in size, and was also dispersed uniformly in the matrix. In contrast, post-treatment of the carbonized RF gel contained the copper distributed uniformly as a non-crystalline salt.
The Cu-containing carbon aerogels differed mainly in their micropore volume. In the mesopore range, however, the pore size window could be tuned by the Cu-adding protocol: \( P/\text{Cu H carb} \) around 50-60 Å, \( \text{CuP carb} \) 100-200 Å and \( \text{CG/Cu H} \) at 300-400 Å, as seen by nitrogen adsorption. \( P/\text{Cu H carb} \), by virtue of its narrower porosity, had a higher surface area, in spite of the higher Cu-content. The dominant macroporosity of the post-treated \( \text{CG} \) sample, on the other hand, may afford lower pressure-drop in dynamic applications, such as gas separation, personnel protection or selective adsorption. These findings are equally important for preparing metal doped porous carbons of sufficiently high porosity for biological applications that require adsorptive removal of contaminants of size much greater than small molecules.

**Acknowledgements**

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Figure 1. Low (a-d, x500, scale bar is 50 μm) and high resolution (e-h, x10,000, scale bar is 1 μm) SEM images of the polymer aerogels.
Figure 2. N\textsubscript{2} adsorption/desorption isotherms of P (□), CuP (△), P/Cu L (○) and P/Cu H (▽) aerogels. Inserts show the data from the pressure region p/p\textsubscript{0} ≤ 0.1 in a logarithmic scale.
Figure 3. PSD of \( P (\square) \), \( CuP (\triangle) \), \( P/Cu L (\bigcirc) \) and \( P/Cu H (\downarrow) \) aerogels in the mesopore range calculated from BJH model.
Figure 4. SAXS (a) and WAXS (b) response of polymer aerogels. The vertical lines in P/Cu $H$ correspond to principal Bragg reflections of cupric acetate. No measurable Bragg reflections were found in sample $P/Cu L$. 
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Figure 6: High resolution (x10,000, scale bar is 1 μm) SEM images of the carbon gels.
Figure 7: N$_2$ adsorption/desorption isotherms of CG (■), CuP carb (▲), CG/Cu L (◇), CG/Cu H (■), and P/Cu H carb (▼) carbon gels. Inserts show the data from the pressure region $p/p_0 \leq 0.1$ in a logarithmic scale.
Figure 8: PSD of CG (■), CuP carb (▲), CG/Cu L (◇), CG/Cu H (⊗) and P/Cu H carb (▼) carbon gels in the mesopore range.
Figure 9: SAXS (a) and WAXS (b) response curves of carbon aerogels. The curves have been shifted vertically for clarity.
Figure 10. $Iq^4$ vs $q$ representation of the carbon aerogels.
Copper-containing Resorcinol Formaldehyde Networks

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Abstract

The effect of copper ions on the polymerisation and the structure of resorcinol-formaldehyde (RF) hydrogels, and on the resulting aerogels, is studied by a range of different techniques. Although the activation energy of the RF reaction in the presence of copper acetate is the same as with sodium carbonate, measurements by dynamic light scattering, small angle X-ray scattering, scanning electron microscopy and nitrogen adsorption reveal appreciable differences in the microscale structure and porosity of aerogels that have been synthesized with or without CuAc, before they are dried supercritically. The presence of copper ions produces a much finer mesh size on the submicron scale and increases the BET surface area of the aerogels to 2000 m²/g, more than twice as much as those synthesized with sodium carbonate alone. The increase in the volume of wider pores detected by gas adsorption is even more striking. The observed effects can be attributed to the copper acetate.

Introduction

Among the adsorbents most widely used to combat pollution, high specific surface area activated carbons occupy a place of honour. The great advantage of these materials is their ability to separate gas mixtures at very low concentrations. When these solid adsorbents are doped with metals, notably with transition metal salts, their receptive capacity can increase, especially for gases having low molecular weight, low boiling point and appreciable polarizability.

High surface area carbons can be prepared from organic aerogels. The carbon aerogel precursors are typically synthesized in aqueous solution by polycondensation of resorcinol
(R) and formaldehyde (F) in the presence of a basic catalyst (C) (most often Na₂CO₃), followed, e.g., by supercritical drying [1]. Their applications are numerous, ranging from electrical capacitances, batteries, catalyst supports, to toxic gas protection devices [2]. The sol-gel method permits carbon gels to be prepared in various forms, from microspheres to monoliths up to several centimetres in size. The ease of preparation of metal doped derivatives, through the introduction of metal salts at various stages of the synthesis, makes the potential of these polymer-based carbons all the more promising.

The macroporous morphology of the resorcinol-formaldehyde (RF) gels, which offers easy access of target molecules to the micropores, can be adjusted by changing the concentration and the mixing ratio of the monomers as well as the pH in the precursor solution [3-10]. Most of these parameters act by controlling the kinetics of the polycondensation process.

Dynamic light scattering (DLS) investigations of the polymerisation reaction with Na₂CO₃ at 25 °C have shown that individual colloidal particles are generated first, which later form bigger aggregates. The growth rate of the primary colloidal particles is accelerated by increasing the molar ratio R/C or by decreasing R/W (water) [11]. In a study by small angle X-ray scattering (SAXS) of structure formation it was found that in the initial stage of the hydrogel formation, small clusters of branched polymer species are formed that display mass fractal behaviour [12]. Later in the reaction, the clusters aggregate into particles with surface fractal properties. At gelation, the hydrogel structure becomes fixed and the surface of the particles becomes smoother upon ageing.

Rheological measurements have shown that the gelation time becomes shorter with increasing reaction temperature and decreasing R/C ratio. The apparent activation energy determined in a R/F/Na₂CO₃/W system between 50 and 90 °C is approximately 80 kJ/mol, and is independent of the R/C ratio [4]. Since increasing the R/C ratio in such systems decreases the pH of the precursor solution, it follows that the activation energy is also independent of pH.

It has also been found that decreasing the R/C ratio makes the structure of the dry gels predominantly microporous, while increasing this ratio results in increased cluster size and essentially meso/macroporous character [5]. The concentration of the catalyst also determines the size of the clusters and the morphology of the structure of the dried RF gels. During the first stage of the polymerization each cluster grows individually, and their number is determined by the amount of catalyst. Subsequently they aggregate to form an interconnected structure. If the concentration of the catalyst is high (low R/C) the density of nucleation
centres is high, and the size of the clusters is therefore small [8]. Following the same idea it can be also concluded that the average pore size of the aerogels increases by increasing R/C or by decreasing R/W [7, 8]. The R/C ratio has no significant influence on the apparent surface area and the micropore volume [6].

Systematic studies of various catalysts, also including several acids (perchloric acid, nitric acid, acetic acid), have shown that the catalyst can strongly affect the structure of the developing RF gel [13, 14]. Almost all the structural properties derived from Na₂CO₃-catalyzed RF aerogels could be reproduced with acetic acid catalyst simply by changing the concentration. Nevertheless, in some of the acidic cases, connectivity among the primary particles is exceptionally high [14].

Performing the synthesis in acetone also influences the structure of the dried gel. Below the gel point, it was found that the formation of the RF aerogels prepared with an acidic catalyst in acetone or with a basic catalyst in water can be described in terms of diffusion of the primary clusters. Unlike with acidic catalysts, gelation in the aqueous basic catalyst system cannot be described by a percolation model, but more probably involves a nucleation and growth mechanism of colloidal particles that form the fully connected network as the gel ages. This case is similar to aggregation in dense colloidal solutions. The kinetics of the hydroxymethyl formation is fast and the sol is composed of small, highly reactive clusters.

When, at the start of the preparation process, the Na₂CO₃ is replaced by salts of various metals, the metal salt becomes trapped within the gel structure and the metal ions may be chelated by the functional groups of the polymer matrix. They can also affect the morphology and the pore texture of the organic aerogel [15]. A study of the formation of carbon aerogels doped with Fe(II), Co(II), Ni(II) and Cu(II) concluded that the morphology and the textural characteristics of the network are determined mainly by the pH, which is defined by the chemical character of the metal ion [15, 16]. Pt(II), Pd(II), Ag(I) and Ti(IV) were also found to exert a strong influence on the aerogel architecture [17-19]. Nitrogen adsorption measurements showed that transition metal-containing RF gels are generally both meso- and macroporous, except Fe- and Cu-, which yield mainly macroporous aerogels. The influence of the anions has not been addressed.

In this paper the effect of copper(II) ions on the kinetics of the polymerisation reaction and on the porosity of the organic aerogel is reported. The morphology and adsorption properties are probed by dynamic light scattering (DLS), small and wide angle X-ray scattering (SAXS/WAXS), scanning electron microscopy (SEM) and low temperature N₂ adsorption measurements.
**Experimental**

**Sample preparation**

RF polymer gels were prepared according to the method of Lin [3]. Resorcinol (Merck, extra pure), formaldehyde (37% aq. solution, Merck, synthesis grade) and the catalyst sodium carbonate (Reanal, analytical grade), were dissolved in distilled water. The R/C and R/F molar ratios were 50 and 0.5, respectively, and the overall concentration of the initial solution was 5 w/v %. The pH of the system was set to 6.0 with a few drops of dilute HNO₃. After thorough mixing, the solution was sealed into glass vials and cured at 85 °C for 7 days.

Copper-containing samples were prepared by adding additional copper(II)–acetate (CuAc, Reanal, analytical grade) to the same reaction mixture. The total R/C molar ratio and the concentration of the initial reaction mixture were 25 and 5.2 w/v %, respectively. The pH was limited to 5.3 by the solubility of CuAc.

After the 7-day curing period, the water in the hydrogels was exchanged for acetone (Merck, extra pure) and the gels were dried by supercritical carbon dioxide (scCO₂) extraction. The applied pressure and temperature were 100 bar and 43 °C, respectively. This treatment with a 1.2 ml/min scCO₂ flow lasted for 70 minutes.

**Methods**

**Dynamic light scattering (DLS)**

DLS measurements were made in the sol-gel reaction bath, using an ALV goniometer (ALV, Langen, Germany). The light source was a HeNe laser working at 632.8 nm. Samples were contained in glass NMR sample tubes of 9 mm internal diameter, and observations were made in the scattering angle range $30^\circ \leq \theta \leq 150^\circ$. For measurements with a short optical path, X-ray capillary tubes of diameter 1 and 2 mm were used, at $\theta = 90^\circ$. The sample tubes were placed in a refractive index matching toluene bath and measurements were performed at 30, 35, 40 and 50 °C.

**Small/wide angle X-ray scattering (SAXS/WAXS)**

SAXS/WAXS measurements of the solid samples were made at 16 keV on the BM2 small angle camera at the European Synchrotron Radiation Facility (ESRF), Grenoble, France. The transfer wave vector range explored was $0.0019 < q < 5.7$ Å⁻¹ (where $q = 4\pi \sin(\theta/2)/\lambda$ and $\lambda$ is the wavelength of the incident radiation). An indirect illumination CCD detector (Princeton Instruments) with effective pixel size 50 µm was used. Intensity curves $I(q)$, obtained by azimuthal averaging, were corrected for grid distortion, dark current, sample transmission and also for background scattering. The powdered samples were placed in glass
capillary tubes of diameter 1.5 mm. Intensities were normalised with respect to a standard sample (lupolen), assuming an effective sample thickness of 1 mm to account approximately for the filling factor of the powder. The resulting error in the stated absolute values of the intensity is expected to be no greater than 25%.

**Nitrogen adsorption**

Nitrogen adsorption/desorption isotherms were measured at -196 °C with a computer controlled Quantachrome Autosorb-1 instrument. Transformation of the primary adsorption data and the (micro)pore analysis were performed with the Quantachrome software. The apparent surface area ($S_{BET}$) and interaction parameter $C$ related to the net energy of adsorption were calculated using the Brunauer–Emmett–Teller (BET) model. The total pore volume ($V_{TOT}$) was derived from the amount of vapour adsorbed at $p/p_0 \rightarrow 1$, assuming that the pores are then filled with liquid adsorbate. Similarly, the pore volume was determined at $p/p_0 = 0.94$ ($V_{0.94}$), just before the sharp increase of the isotherms. The micropore volume ($W_0$) was derived from the Dubinin–Radushkevich (DR) plot. The characteristic energy of adsorption $E$ could not be determined, since the interaction parameter $\beta$ is not known for metal-doped surfaces. The energy of adsorption in the micropores was therefore characterised from the slope of the DR plot, which is proportional to $E^{-2}$. The mesopore volume, $V_{meso}$, was estimated using the pore volumes derived from the adsorbed nitrogen volumes at $p/p_0 = 0.94$ ($V_{meso}=V_{0.94}-W_0$), where $d = 330$ Å.

**SEM**

Surface morphological investigations were made on a JEOL 5500 JSM-5500LV scanning electron microscope in high vacuum mode with a secondary electron detector. The accelerating voltage was 20 kV and the working distance 20 mm. Samples were fastened to the copper sample holder by adhesive carbon tape. The samples were coated with Au/Pd to prevent charging.

**Results**

**The sol-gel transition**

DLS measurements were made in the reaction bath of the resorcinol/ formaldehyde (RF) system [20, 21]. Owing to the large refractive index difference between the polymer and the solvent, multiple scattering becomes significant at later stages of the reaction. As the polymerization reaction progresses, the scattered light intensity increases monotonically until multiple scattering attenuates the emerging light. The detected intensity then decreases until
the gel transition is reached. At the gel point, denoted by G in Figure 1, slowly moving speckles generated by the network structure cause the scattered intensity to fluctuate randomly.

Figure 1. Time dependence of scattered intensity at $\theta = 90^\circ$ (detector count rate CR) from the reaction bath of the RF system at 40 °C. Without CuAc (+, lower curve), and with CuAc ($\times$, upper curve). The gel point (arrow) occurs at approximately the same time delay (18 hrs) for both samples.

During the early part of the reaction the scattered intensity in the presence of CuAc is some three orders of magnitude greater than in the copper free sample, as seen in Fig. 1. The difference in structures is illustrated by the intensity correlation functions $g_2(\tau)-1$ of the two systems, displayed in Figure 2a and b, measured after the same incubation time of 3 hours. The principal relaxation times that describe these spectra, calculated from the Laplace transform

$$a(t) = \int [g_2(\tau) - 1] \exp(-\tau/t) d\tau,$$

(1)

using the CONTIN procedure [22], are shown in the corresponding figures. According to Fig. 2b, the correlation function of the CuAc-containing system appears to possess a single narrow
Figure 2. a) Intensity correlation function of RF system without CuAc at 40°C measured at θ=90° in 9 mm diameter cell after 3 hrs (+), and the CONTIN Laplace transform of the corresponding field correlation function (continuous line); b) $g_2(\tau)$-1 with CuAc ($\times$) in 9 mm diameter cell after 3 hrs at 40°C. The narrow decay time distribution in b) is centred at $t=2.6$ ms. c) $g_2(\tau)$-1 with CuAc at 40°C measured after 3 hrs at θ=90° in a 2 mm diameter cell ($\times$), with its CONTIN Laplace transform (continuous line).

Distribution of relaxation times $t$ centred at 2.6 ms, corresponding to an apparent hydrodynamic radius $R_H \approx 1500$ Å. By contrast, the correlation function of the copper-free system requires a broad range of relaxation times for its description. The latter type of relaxation response is characteristic of samples containing a wide distribution of cluster sizes, as is expected for the early stages of the sol-gel transition [21, 23].
Spectroscopic transmission measurements show that the increase in optical density of the Cu-containing sol is stronger and more precocious than in the copper-free sample. DLS measurements of the CuAc system at 40 °C were therefore repeated in a 2 mm diameter capillary tube. **Figure 2c** shows how the resulting $g_2(\tau)-1$ loses its single exponential character, with the multiple correlation times being recovered in the Laplace transform. This means that the single exponential character in Fig 2b is an artefact of multiple scattering, which intervenes early in the reaction. The measurements nevertheless enable us to estimate the effect of the catalyst on the average characteristic relaxation rate in the system: from Fig. 2a, the mean hydrodynamic radius, determined by the method of cumulants [24], is $R_H=100$ Å, while, from Fig. 2c, $R_H=490$ Å. These results confirm that CuAc does indeed increase the mean size of the clusters.

It is instructive to correlate the hydrodynamic radius $R_H$ of the growing clusters during the early stage of polymerization with that of the variation of the scattered intensity. **Figure 3** compares this dependence in the copper-free and the copper-containing systems. The measurements were both made in dilute conditions where the clusters do not overlap, and where multiple scattering is negligible. The power law behaviour that appears in the copper-free case can be interpreted in terms of the scattering intensity $I$, according to which, at small $q$ (i.e., $qR_H \ll 1$),

$$ I \propto NM^2, \quad (2) $$

where $N$ is the number of clusters per unit volume of solution and $M$ their average mass. $N$ depends on the concentration of catalyst, $C$. Assuming that the structure of the clusters can be described by a fractal dimension $d$, we have

$$ M \propto R_H^d \quad (3) $$
Figure 3. Dependence of the intensity of light scattered at 90° on the hydrodynamic radius $R_H$ of the clusters during polymerization, a) without CuAc, in 9 mm cylindrical cell at 30°C, 40°C and 50°C; b) with CuAc in 1 mm cylindrical cell at 40°C.

From the power law slope of 3.4 in Figure 3a it follows from eqs 2 and 3 that

$$d \leq 1.7 \quad (4)$$

The inequality in expression 4 applies if $N$ is an increasing function of time. In the present case it is reasonable to suppose that after the initial incubation period, the nucleation process is exhausted and $N$ is therefore constant, i.e.,

$$d = 1.7 \quad (5)$$

This value of $d$ is close to that expected for fractal aggregates.

Figure 3b shows that in the copper-containing sample the polymerization differs radically from the copper-free case. The addition of the copper salt increases the number of nucleation centres. Power-law behaviour is displayed only at the very beginning, with a much higher slope, approximately 8.8. A reasoning analogous to that above yields for the corresponding fractal dimensionality

$$d \leq 4.4 \quad (6)$$

In the early stage of polymerization $R_H$ is small enough to satisfy the Rayleigh scattering condition $qR_H \ll 1$, which means that surface scattering effects may be discounted. Consequently, the intensity in Figure 3b can be attributed to volume scattering and hence $d$ cannot exceed 3. It seems probable therefore that the high apparent value of $d$ in expression 6 results from a combination of dense clusters ($d \approx 3$) and a rapidly increasing nucleation
density \( N \). At longer times, however, \( N \) must tend to a constant as the nucleation rate slows. No clearly identifiable scaling regime develops at any later stage. The continuously decreasing slope in Figure 3b implies that the density of each cluster decreases as it grows in size: the mature clusters are therefore dense at their core and acquire a corona of gradually diminishing density with increasing distance from the centre.

Two remarks are relevant at this point. Firstly, the copper ions are mobile, since, as will be pointed out later, no significant amount of copper remains in the sample after washing and drying. It is likely therefore that during the reaction the copper ions remain mobile and hence they are not themselves the source of the intense initial scattering. Secondly, the two reactions, without and with copper, display different kinetics. The initial reaction rate with copper is very fast, but becomes slower as available resorcinol and formaldehyde become scarce. The \textit{a priori} surprising finding that the gelation times in the two systems are closely similar seems to be the consequence not only of the similar concentration of reactants, but also of the slightly higher pH of the copper-free sample.

In their pioneering light scattering investigation of the sol-gel transition in silica-methanol gels, Martin and Wilcoxon [20] observed that the intensity correlation function \( g_2(\tau) - 1 \) initially adopts a stretched exponential shape of the form \( \exp[-(\Gamma \tau)^m] \), where \( \Gamma \) is the relaxation rate of the concentration fluctuations and the exponent \( m \approx 0.65 \). As the gel point is

![Figure 4](image_url)

**Figure 4.** Light scattering intensity correlation functions (\( \theta = 90^\circ \)) from RF sol-gel transition without Cu in two different capillary sizes, at 40 °C; 1 mm sample: after 23.5 h; 9 mm sample: after 18.5 h.
Figure 5. Reaction times in sol-gel transition by RF polycondensation, expressed as a ratio with respect to the reaction time at 25 °C. Straight lines shown are least squares fits through the data.

approached, \( g_2(\tau)-1 \) transforms into a power law \( \tau^{-n} \), where \( n \approx 0.27 \). Those measurements, like those described here, were performed in the reaction bath. In the present observations, within experimental error this power law behaviour is indeed observed for both sodium- and copper-containing samples, provided the measurement is made in large diameter (9 mm) optical cells.

Although multiple scattering is negligible during the early stage of the copper-free system, it becomes a major issue close to the gel point. The Cu-free reaction was therefore performed in capillary tubes of diameter 1 mm. At the beginning of the reaction the resulting intensity correlation functions were found to be at first stretched exponentials, the exponent \( m \) of which gradually increased from about 0.65 up to a value of almost 1, then, as the gel point approached, \( m \) again fell 0.65±0.05. At the transition, power law behaviour appears, but the relevant exponent, \( n = 0.42 \), is higher than that reported in ref 20 (Figure 4). These results were found to be reproducible. While the physical cause of power law behaviour at the gel point is inescapable, the exact shape, and hence the power law slope, of the dynamic light scattering correlation function are sensitive to multiple scattering. Other workers have also reported values of \( n \) in excess of 0.27 [25-27], as have also Kroon et al., who, significantly, noted that \( n \) is a decreasing function of gel concentration [28]. It is reasonable to conclude from these observations that the lower values of the power law exponent \( n \) are a consequence of multiple scattering. It is also noteworthy that in the Cu-containing sample at 40 °C power
law behaviour at the gel point also prevails. Owing to overwhelming multiple scattering in this case, even in 1 mm diameter capillaries, however, only the weaker power-law exponent, \( n \approx 0.3 \), was observed. These findings illustrate the importance of precautions against multiple scattering in DLS measurements of gelation.

Measurement of the time required to reach the gel point as a function of the temperature provides an estimate for the overall activation energy \( E \) of the reaction (Figure 5). For the reaction with Na\(_2\)CO\(_3\) alone, \( E = 75 \pm 4 \) kJ/mol, while in the presence of CuAc, \( E = 76 \pm 14 \) kJ/mol. Since the chemical reaction is, in the pH range investigated, the same in the two cases, their activation energies are not expected to be different. Within experimental error, the values found for \( E \) are indeed both in mutual agreement and consistent with the literature [4].

**Morphology of the hydrogels**

One of the obstacles that confronts small angle X-ray scattering in gels is radiation damage. In the vicinity of the sol-gel transition especially, the induced ionisation can substantially alter network development in the path of the beam. For this reason the SAXS measurements were performed only on the mature networks. The SAXS response of the wet gels is shown in Figure 6 as a function of the wave vector \( q \). In these spectra, the signal from the bulk water, which constitutes about 90 % of the sample, has been subtracted out. In the high \( q \) region of Figs 6a and b, a residual feature appears that mimics that of bulk water, but its main peak and shoulder, at 2.04 Å\(^{-1}\) and 2.95 Å\(^{-1}\), are shifted with respect to those of bulk water (2.0 Å\(^{-1}\) and 2.8 Å\(^{-1}\) respectively). This residual signal shows that the wet polymer networks possess a hydration layer, the density of which is about 6 % greater than that of bulk water.

In the region below 0.2 Å\(^{-1}\) the spectra in Fig. 6 display a steep increase of intensity as \( q \) decreases, followed by a knee and power law region with weaker slope. The steep region can also be represented by a power law,

\[
I(q) \propto q^{-p},
\]

where the slope \( p \) (3.5 \( \leq p \leq 4.0 \)) is characteristic of surface scattering. The radius of gyration \( R_G \) of the polymer clusters that give rise to this surface scattering may also be estimated by plotting \( \log(I) \) vs \( q^2 \) (Guinier plot) in the region of the knee (not shown). The value found for \( R_G \) in the gel synthesized at 40 °C in the presence of CuAc (ca. 250 Å, Fig. 6a) is appreciably larger than that with Na\(_2\)CO\(_3\) alone (ca. 30 Å). These differences substantiate the finding from
DLS that in the early reaction of the CuAc-containing system the cluster sizes are much larger than with Na$_2$CO$_3$.

At the lowest values of $q$ in Fig 6, the intensity obeys a power law with a slope of about -1.4, indicating that the clusters are arranged in randomly branched linear arrays, as proposed by Maldonado-Hódar et al. [12]. In the mature gel, therefore, the power law behaviour of the cluster structure is slightly weaker than that prevailing before the gel point, in the early stages of polymerization, where the slope was found to be -1.7 (eq 5). The gel structure can thus be pictured as consisting of sequences of beads, the radius of which depends on the conditions of catalysis. When the gels are synthesized at 85 °C, however, the structures of the two systems are identical, and also closely similar to that obtained with Na$_2$CO$_3$ catalyst at 40 °C (Figure 6b). No indication of the very large clusters observed in the DLS measurements is visible in the SAXS spectra, but it should be recalled that the upper resolution range of these measurements does not exceed a few hundred angstrom units.

**Morphology of the aerogels**

Drying the gel can be expected to modify the structure of the network. Figure 7 shows the SAXS response of the aerogels derived from those of Figure 6b, i.e., that have been synthesized without and with CuAc at 85 °C, and then dried under supercritical conditions.
For comparison, Fig. 7 also shows the spectrum of the wet gel prepared with CuAc at the same temperature. In the high $q$ region of the two aerogels, as is to be expected, the signal from water is absent. Only a broad amorphous signal survives in the vicinity of 1.2 Å$^{-1}$, which is due to the local disorder of the polymer subunits. At the larger spatial scales probed in the lower $q$ range of the spectrum, however, substantial differences between these two aerogel structures emerge. In view of the almost identical network structure of the parent networks synthesized at 85 °C (Figure 6b), the influence of the Cu on the resulting aerogel structure is remarkable.

To quantify the differences in scattering response of the aerogels in Fig. 7, we approximate the basic cluster units in the network by uniform spheres of external radius $R$. The scattering intensity of a uniform sphere may be expressed as

$$I_{\text{sphere}}(q) \propto [3(\sin qR - qR \cos qR)/(qR)^3]^2.$$  \hspace{1cm} (8)

At large $q$, this function exhibits the $q^{-4}$ behaviour characteristic of smooth surfaces. When expression (8) is multiplied by $q^4$, a characteristic oscillatory function is obtained, the first maximum being located at $qR = 2.742$ and the first minimum at $qR = 4.493$. These

![SAXS/WAXS spectra of supercritically dried RF aerogels, synthesized at 85 °C. The signal from the wet CuAc gel, synthesized at the same temperature, is also shown for comparison.](image-url)
features provide a means of estimating the outer radius $R$ of the sphere. In Figure 8 the intensities of the two aerogel samples of Fig. 7 are plotted in the representation $Iq^4$ vs $q$. Both responses exhibit well defined first maxima and first minima that, moreover, give consistent values for the outer radius $R$. The aerogel containing only Na$_2$CO$_3$ yields $R = 71$ Å, while for the CuAc aerogel, $R = 28$ Å. At values of $q$ beyond the first minimum in Fig. 8, higher order oscillations are smeared out by the size dispersity of the clusters, and also by scattering from the roughness of their surfaces.

Further information on the inter-cluster distribution can be deduced from Fig. 7 in the region of lowest $q$. In the copper-free aerogel, the power law slope -1.4 indicates that the clusters are arranged in weakly branched quasi-linear arrays, as already observed in the corresponding wet gel. In the CuAc system, by contrast, the strong curvature and plateau in the scattering function at $10^{-2}$ Å$^{-1}$ reveal secondary clustering of the basic spheres on a length scale of about 100 Å. The flat response at the lowest values of $q$ is a sign of weak spatial correlation within these larger assemblies. The resolution of the SAXS measurements provides no information on the structure at length scales greater than 1000 Å.

Comparison of the wet gel response in Fig. 7 with that of the two aerogels reveals certain features of the parent gel that are conserved in each of the daughter aerogels. It should be recalled that owing to the water, the scattering contrast in the wet gel is lower than in the

![Figure 8. Plot of $Iq^4$ vs $q$ for RF aerogels synthesized without and with CuAc. Arrows indicate positions of the first maximum and minimum of the scattering function of a sphere multiplied by $q^4$.](image)
aerogels, which accounts for its lower overall intensity. In the aerogel containing only Na₂CO₃ the smaller clusters coalesce into larger units, while the quasi-linear inter-cluster arrays are preserved. In the CuAc aerogel, the small cluster units present in the parent gel appear to conserve their identity, but regroup into loose assemblies with a separation distance of about 2π/0.01 ≈ 600 Å. It seems probable that these gaps form part of the pore structure.

Table 1 summarizes the SAXS findings for the two aerogel systems. The values listed for the power law slopes indicate either a rough (n = -3.5) or a smooth (n = -4) surface of the spherical cluster. Also listed are the values of the apparent radius of gyration Rₐ, estimated from the data in the shoulder region of Fig 7. While the values of R and Rₐ in the aerogel containing only Na₂CO₃ are comparable, the substantial difference between these lengths in the CuAc aerogel lends support to the notion of secondary aggregation among the primary clusters in this system. It is important to note that the Cu-content of the CuAc aerogel is low (0.7±0.1 %w/w), i.e., this salt is almost completely removed during the drying process. The discrepancy between the structure of the two aerogels cannot therefore be attributed to copper in the network.

<table>
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<th></th>
<th>slope</th>
<th>R</th>
<th>Rₐ</th>
</tr>
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<tbody>
<tr>
<td>RF without CuAc</td>
<td>-3.5</td>
<td>71</td>
<td>67</td>
</tr>
<tr>
<td>RF with CuAc</td>
<td>-4</td>
<td>28</td>
<td>84</td>
</tr>
</tbody>
</table>

Table 1. Data derived from the SAXS curves of the polymer aerogels

![Figure 9. SEM images of RFgels without CuAc (a) and with CuAc (b) gelled at 85 °C, after supercritical drying (magnification: ×10000, scale bar = 1 µm.)](image)

Scanning electron microscopy probes the structure on a length scale much larger than that of the present SAXS measurements. The SEM images of the two fractured surfaces in
Figure 9 reveal significant differences in the large scale structure of the samples. RF without CuAc (Fig. 9a) possesses a three-dimensional filamentary architecture with a coarse pore structure of diameter approximately 0.5 µm, and a chaotic distribution on the scale of several µm. In the presence of copper (Fig. 9b), however, the filaments become more densely packed, with finer pores and a smoother long-range structure.

![N2 adsorption/desorption isotherms of RF gels synthesized without CuAc (○) and with CuAc (●). Inset: expanded view of the adsorption response in the low relative pressure region.](image)

The difference in morphology is also reflected in the nitrogen adsorption properties. The irreversible adsorption/desorption isotherms belong to Type IV in the IUPAC classification (Figure 10). The isotherms exhibit a wide hysteresis loop, especially in the case of copper-containing sample. The hysteresis loop of distorted Type A reveals the presence of mesopores formed by interstices between spherical particles of different size [29]. Table 2 lists the porosity data deduced from the adsorption isotherms. It is noteworthy to recall here that the Kelvin equation used to deduce porosity in the mesopore regime is not applicable for pores wider than 500 Å [30].
Table 2. Morphology data from N₂ adsorption measurements of the polymer aerogels*

<table>
<thead>
<tr>
<th>sample</th>
<th>( S_{\text{BET}} ) ( \text{m}^2/\text{g} )</th>
<th>( C )</th>
<th>( V_{\text{TOT}} ) ( \text{cm}^3/\text{g} )</th>
<th>( V_{0.94} ) ( \text{cm}^3/\text{g} )</th>
<th>( W_0 ) ( \text{cm}^3/\text{g} )</th>
<th>slope</th>
</tr>
</thead>
<tbody>
<tr>
<td>RF without CuAc</td>
<td>846</td>
<td>168</td>
<td>3.16</td>
<td>0.99</td>
<td>0.27</td>
<td>-3.9</td>
</tr>
<tr>
<td>RF with CuAc</td>
<td>2000</td>
<td>361</td>
<td>10.10</td>
<td>3.21</td>
<td>0.64</td>
<td>-4.7</td>
</tr>
</tbody>
</table>

*\( S_{\text{BET}} \): apparent surface area, \( C \): interaction parameter related to the net energy of adsorption; \( V_{\text{TOT}} \): total pore volume at \( p/p_0 \rightarrow 1 \), \( V_{0.94} \): pore volume derived from adsorbed volume at \( p/p_0 = 0.94 \), \( W_0 \): micropore volume from DR analysis, slope: slope of the DR plot

The presence of CuAc during the synthesis increases the specific surface area by a factor of more than two. As the surface area is known to be practically insensitive to the R/C ratio [6], this increase can be attributed unequivocally to the effect of CuAc. The parameter \( C \) and the slope of the DR plot indicate a stronger interaction with nitrogen gas in the CuAc treated sample (Table 2), due to the narrower micropores. Addition of CuAc to the system at the polymerisation stage greatly enhances the porosity for gas adsorption. Large pores contributing to the loose structure in micrograph 9a are undetectable by nitrogen adsorption. The larger value of \( V_{\text{TOT}} \) in the CuAc polymer reflects the narrowing of the wide pores, which are thus partially detectable by nitrogen adsorption.

Conclusions

The morphology of RF gels is influenced by the presence of CuAc. During the induction period of the sol-gel transition, dynamic light scattering detects the development of clusters in both systems, the size of which however is significantly greater in the presence of the copper. In the absence of copper, the clusters are open branched structures, whereas with copper, when polymerized at 40°C, they have a compact nucleus and a diffuse corona. The DLS correlation spectra are sensitive to multiple scattering, which is especially pronounced in the CuAc system. At the gel point itself, multiple scattering cannot be overlooked.

Within experimental error, the activation energy of the sol-gel reaction is the same with and without the CuAc catalyst. SAXS observations of the mature hydrogels detect differences between those synthesized at 40 °C and at 85 °C. These measurements also reveal the presence of water of hydration in the gels, the density of which is greater than in bulk water. The SAXS spectra of the gels synthesized at 85 °C with or without CuAc are practically indistinguishable. Surprisingly, however, although the copper salt is almost completely removed during the drying process, the structures of the two networks after supercritical drying are appreciably different. The presence of copper ions produces a much finer mesh size on both the submicron and nano scale and increases the BET surface area of
the aerogel by a factor of more than 2 with respect to those synthesized with Na$_2$CO$_3$ alone. The increase in the volume of wider pores detectable with gas adsorption is even more striking. Since it is known that the concentration of the catalyst hardly influences the porosity, the observed effects can be attributed solely to copper acetate.

Acknowledgements

We are grateful to the European Synchrotron radiation Facility for access to the French CRG beam line BM2 and to Cyrille Rochas and György Bosznai for their invaluable assistance. O.C. expresses gratitude for an Erasmus scholarship. This research was supported by the EU grant No. 218138 and the EU - Hungarian Government joint fund GVOP - 3.2.2 - 2004 - 07 - 0006/3.0.

References

Aerogélek szárítása

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ÖSSZEFOGLALÁS

A szerves és szervetlen alapú aerogélek különleges tulajdon-
ásaik miatt fontos, egyedi anyagokká váltak. Aerogéleket a ned-
ves gélből döntően csak szuperkritikus szárítással állíthatnak elő,
ment a mikroporócos gélszerkezet így őrizhető meg legjobban.
Munkánkban bemutatjuk a szilika aerogélek és a szénaképtek által
lános előállítási módjait és felhasználási lehetőségeit. Részletesen
ismertetjük a szuperkritikus szárítást irodalmi adatok és saját
munkának alapján.

Kulcsszavak: aerogél, szárítás, szuperkritikus

ABSTRACT

Aerogels, based on organic or inorganic polymerization, became
important specialty materials. From the vet gels the aerogels are
mainly produced by supercritical drying, because this method is
the best in preserving their microporous structure. In this study we
describe the general procedures of preparing silica aerogels and
carbon aerogels including their applications. Supercritical drying
is reported in details based on literature survey and our experimental
results.

Key-word: aerogel, supercritical drying

1. Bevezetés

A szerves illetve szervetlen alapú aerogélek előállítása
számottevő érdeklődést váltott ki az utódban előzőben.
Az aerogélek a legkisebb sűrűségű szilárd anyagok a világ-
on (pl. 0,003 g/cm³). Az aerogélek, bár szilárdak és megtart-
ják az alakjukat, rendkívül kevés szilárd anyagból állnak,
térfigatuk zöme levegő. Ennek köszönhetően rendkívül jó
hőszigetelők, de közös jellemzőjük a nagy fajlagos felület
 és pórúsírozatot is. A szuperkritikus öszzereknek különle-
ges, kitüntetett szerepe van az aerogéleken előállításában, már
a legelső aerogélektől kezdve. Munkánkban összefoglaljuk
a szilika aerogélek és a széngelek szárításának alapvető
kérdéseit, felhasználási lehetőségeit különös tekintettel
a nedves gél szárításának különböző megoldásaaira.

2. Szilika aerogélek

A legtöbben úgy gondolják, hogy az aerogélek a mo-
dern ipar termékei. Valójában ez az első aerogélt 1931-ben
Steven S. Kistler készítette el, a nevet is ő használta először.
Polimerizációs reakcióként Na-szilákit savas kondenzáci-
óját végezte el vízben, az igazi állástretest azonban a gél megszá-
rítása jelentette. A gél megszárítása alatt azt a folyamatot
értjük, amikor a polimerháló üregeiben levő folyadékok
lévegőre cseréljük le. Az oldószor egyszerű elpárolgatását
a gélszerkezet összeességét okozza, amely együtt jár a nagy-
néptékű szugorodással és a pórúsosság elvesztésével.

58. évfolyam (2009) különszám
Mivel a polimerizációs reakcióban víz felesleges, mellett végzik, a szuperkritikus száritás előtt a vizet célszerű többszörzi alkoholos mosásával eltávolítható a pórusokból is.

2.4. Szuperkritikus száritás
Az aeroszél nedves gélből történő létrehozásában a szuperkritikus száritásnak döntő szerepe van. A szuperkritikus alkohol előállításánál alapul száritási eljárások, a magas hőmérséklet (2. táblázat) és a tűzveszély miatt, rendkívül veszélyesek. Az 1980-as évek elején fejleszti-
ték ki a szuperkritikus szén-dioxidos száritási eljárást.

Magát a száritási módszert, annak befolyásoló paramétere-
it csak kevesen vizsgálták részletesen. Az alapelv azonban az volt, hogy folyadék halmozállapotú szén-dioxidtal mostának a gélt az autoklav térfogatának többszörzi kicserehő-
ig (kis áramlási sebességek mellett, mert az alkohol folyékony szén-dioxidra való lecserelegése a pórusokban diffúzió limitált), majd a hőmérsékletet és a nyomást párhuzamo-
man emelve a kritikus pont fölé hevertett a rendszert. Ezután következik a fokozatos nyomáscsökkenés. Egy alkoholos és egy szén-dioxidos eljárás összehasonlítása látható a 3. ábrán. Ugyancsak egy szén-dioxidos száritás paramé-
terei láthatóak a 4. ábrán. Novak és munkatársai 6 m térfogatú TMOS (tetrametil-oro-szilikát) monolit gél szá-
rítását vizsgálták. A használt autoklav 100 ml térfogató, tehát jelentősen meghaladja a gélcémet. A száritás kezdet-
en teljes mértékben tölthető van metanolnál, míg a gél körül ne keletkezzen fázis határfelület a nyomás alá helyezést megelőzően sem. A metanol és a folyékony szén-dioxid egymással korlátonul elegyedik. A nagy autoklav méret legfőbb okja a felhalmozások elkerülése, amely a monolit gélkék pedesztét okozhatja, illetve a nagy “oldószér” térfogat miatt megnövelt hajtóerő a diffúziós anyagtranszport miatt, mert így a diffúziós szakaszból a szén-dioxid főömegében közel nulla a metanol koncentrációja.

<table>
<thead>
<tr>
<th>Oldószér</th>
<th>$T_e$ (°C)</th>
<th>$P_e$ (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Szén-dioxid</td>
<td>31,1</td>
<td>73,8</td>
</tr>
<tr>
<td>Metanol</td>
<td>239,5</td>
<td>80,8</td>
</tr>
<tr>
<td>Etanol</td>
<td>241,0</td>
<td>61,4</td>
</tr>
</tbody>
</table>

58. évfolyam (2009) különszám

Széngéleket leggyakrabban rezorcin-formaldehyd (RF) hidrogelből állítanak elő [6]. Munkánk során a Lin és munkatársai [7] által módosított receptet követettük. 1,5990 g rezorcin, 0,0308 g Na₂CO₃ katalizátor 45 ml deszillált vízben, néhány percig mágneses kevertéssel feloldottunk. Az oldathoz 2,2 ml 37%-os formaldehyd oldatot adtunk. Kb. 5 perc kevételt után, a kevertetés fenntartásával, az oldat pH értékét hígított HNO₃ segítségével, 6,0-ra állítottuk be. Az eleget további 30 percig kevételtük.

Az oldatkészítés szabályomérsékleten történt. Az idő lefurdását után, a szintelen, vítszüksége a felkészítési szükséges értékén keresztül, 5 mműső átmérőjű és, kb. 10 cm hosszú üvegesobjektív volt fűrész és leforrastottuk. Az oldatot 1 hétig, 85 °C-on gázoltuk. A kapott gélpórusi vízzel telítették, amik az oldatalakoztatási folyamatot figyelmebe vevő kevőzélen. Az alkalmazott oldószerkezetet irodalmi tapasztalatok alapján hajtottuk végre: a hidrogénrakadat hatóerőszoros tőrésgátot acetonban áztattuk húrom napon keresztül, naponként friss oldószer beégett az alapanyagba.

3. Szerves aerogélek, széngélek

A szén gélek főbb felhasználási területeit mutatja az 5. ábra.

3. táblázat A különböző száritási módszerekkel kapott RF gélek tulajdonságai
A SEM felvételek elkészítéséhez JEOL 5500 típusú készülék használtunk, alacsony vákuum módban, másodlagos elektron detektorral. Az alkalmazott feszültség 20 kV volt, a pásztázási távolság pedig 20 mm. A tintákat a felületi töltődés elkerülése végett a felvételek készítése előtt aranyozni kellett.

Annak ellenére, hogy a gélek zsugorodása a fagyasztva szártítás esetén volt a legkisebb, úgy vélünk, hogy a szén-dioxidos szártítást tovább lehetne javítani hasonló eredmények eléréséig. Célunk egy olyan, jól reprodukálható eljárást kidolgozása volt, amely a gálszerkezet minél jobb megújulását eredményezve. Összehasonlítottuk a folyékony és a szuperkritikus CO₂-dal végzett szártításhatékonyságát is. Előbbi esetben az aceton-nedves gélrudakat tartalmazó szuperkritikus reaktort szabahőmérsékleten, 80 bar nyomáson folyékony CO₂-dal tölttük fel. Az aceton kimossása érdekében a reaktor háromszoros tőfogatnyi folyékony szén-dioxidgal öblítettük, ügyelve arra, hogy a gélrudak mindvégig oldószer alatt maradjanak. A művelet végén az extraktort felmelegítettük és a szén-dioxidot 45 °C-on távolítottuk el. Szuperkritikus szén-dioxidos extrakcióit alkalmazva különböző nyomásokon (vizsgált tartomány 100 – 300 bar) és hőmérsékleteken (33 – 53 °C) folyamatos, 1,2 cm/min sebességgel CO₂ áram mellett távolítottuk el az aceton a gélektől. A kontaktidőt 90 és 260 perc között változtattuk. A művelet végén a nyomáscsökkentést kb. 5 bar/min sebességgel hajtottuk végre.

<table>
<thead>
<tr>
<th>RF gél típusa</th>
<th>S BET</th>
<th>V TOT</th>
<th>V R</th>
<th>V TOT/V R</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cseppfolyós</td>
<td>RFA</td>
<td>270</td>
<td>0,36</td>
<td>0,01</td>
</tr>
<tr>
<td>Szuperkritikus</td>
<td>RFAA</td>
<td>582</td>
<td>0,67</td>
<td>0,21</td>
</tr>
</tbody>
</table>

A táblázat. Az optimalizált szuperkritikus szén-dioxidos, a cseppfolyós majd szuperkritikus szén-dioxidos eljárással és a fagyasztva szártított minták tulajdonságai.

Köszönnetnyilvánítás

A SEM felvételek a BME Szervetlen és Analitikai Kémiai Tanszékén készültek.

IRODALOMJEGYZÉK

Morphological Characterization of Oxidized and Metal Impregnated Spherical Carbons

Orsolya Czakkel
Imre Miklós Szilágyi
Erik Geissler
Nick Kanellopoulos
Krisztina László

Abstract The surface of microporous spherical carbon ($S_{\text{BET}} = 1457 \text{ m}^2/\text{g}$, pH = 7.9) was modified by nitric acid treatment and by Cu$^+$, Cu$^{2+}$ and Sn$^{2+}$ salt impregnation. The morphology and the surface properties of the samples were characterized by SEM/EDS, low temperature nitrogen adsorption and small angle X-ray scattering. The surface chemistry of the samples was investigated under wet conditions.

Oxidation by nitric acid changed the pH to 3.4 and slightly reduced the accessible porosity, but not the morphology or the Cu$^{2+}$ adsorption capacity. Surface chemistry, morphology and the species of the anion and of the metal were found to influence the result of the impregnation. The most remarkable change occurred in the pore size range $< 14 \text{ Å}$ due to pore blocking. This effect was a linear function of Cu$^{2+}$ loading below the saturation capacity. When SnCl$_2$ was used instead of Cu$^{2+}$ salts in aqueous phase, a redox reaction seemed to take place, resulting in greater surface roughness. Metal ions were not detected on the surface of the particles. Treatment with solid CuCl produced a practically complete CuCl film on the surface of the particles and metallic copper was formed as a by-product.

Keywords Cu$^+$-impregnation - Cu$^{2+}$-impregnation - Low temperature nitrogen adsorption - Sn$^{2+}$-impregnation - Surface oxidation

Introduction

CO$_2$ emission is a major problem with regard to global climate change. Modified combustion techniques cannot reduce CO$_2$ formation, but dependence on fossil fuels over the coming decades could be reconciled with our climate change commitments by developing CO$_2$ capture and sequestration technologies. Among the competing solutions, separation techniques for CO$_2$ are well placed. Carbon monoxide, however, is a valuable raw material for the synthesis of a large variety of chemicals. Separation of CO from gas mixtures by adsorption is therefore of great importance.

Solid adsorbents have been used for gas separation and purification since the early stages of gas adsorption applications. The most commonly used adsorbent is activated
carbon (AC) either in powdered (PAC) or in granular form (GAC). Activated carbon fibres (AFC) have also received increasing attention in recent years for separation of gas mixtures. The great advantage of activated carbons is their ability to separate gas mixtures at very low concentrations by virtue of their high adsorption capacity. Nevertheless, the CO$_2$/CO separation potential of carbon sorbents has not received the attention it deserves.

Further exploitation of solid/gas processes has revealed that the chemical properties of the adsorbent surface play an important role in addition to their porosity. Chemical oxidation, for example, may enhance the sorption of polar species. For air purification, e.g., to remove formaldehyde, oxidized carbons are found to perform well [1].

Impregnation by metals, especially transition metal salts, can also increase their receptive capacity, especially for gases of low molecular weight, low boiling point and appreciable polarizability. Impregnation with CuCl$_2$ and PdCl$_2$ has been found to increase CO adsorption by between 8 and 20-fold [2]. Those authors attempted to interpret qualitatively the CO uptake of the impregnated carbons using the perturbation energy, as the electronic states of both the adsorbate and adsorbent play an important role in the adsorption interaction.

Activated carbon-supported metals are believed to adsorb CO through complex formation between CO and the highly dispersed metal halides on the surface of the adsorbents [3]. Cu$^+$ can also selectively modify the CO adsorption on porous supports [4]. Since Cu$^+$ ions on the surface can form coordination bonds with CO and weaken the basicity of the surface, adsorbents displaying greater capacity and selectivity for CO than for CO$_2$ could be obtained. SnCl$_2$ impregnation was found to be also effective in increasing the adsorption ability of activated carbon. It acts in the form of SnO$_2$, since, on account of its relatively low melting point (313 K), SnCl$_2$·2H$_2$O can easily be oxidized to Sn$^{4+}$, making it a suitable agent for CO adsorption [5].

In this paper, a set of carbon-based samples, intended for use in CO/CO$_2$ separation, is characterized. The samples were prepared to study the influence of the surface oxidation, metal ion loading and the species of the metal and anion on the morphology of the resulting adsorbent.

**Experimental**

Sample Preparation

Microporous spherical carbon (SC) based on vinyl-pyridine – divinylbenzene co-polymer was used as starting material [6]. The particle size of the carbon varies between 500 and 1320 µm. The SCOX sample was prepared by treating SC with aqueous HNO$_3$ (cc HNO$_3$ : water = 1 : 1 by volume) in a Soxhlet apparatus.

Samples impregnated with Cu$^{2+}$ and Sn$^{2+}$ were prepared by soaking SC or SCOX in aqueous solutions of their salts. Impregnation was performed at room temperature, from 0.03 or 0.3 M metal salt solutions. The amount of aqueous solution was 16, 8, or 4 ml/g carbon. No pH setting was applied.

Cu$^+$ impregnated samples were prepared according to the method of Xie by mixing the carbon with freshly synthesized CuCl at a mass ratio of 2 : 1 in a rotating glass reactor at 623 K for 4 h under N$_2$ atmosphere [4].

A commercial mesoporous carbon, F400 (Calgon Carbon Corp. Pittsburg, PA, USA), was used as received, for comparison.

**SEM/EDS**

The morphology and surface composition of the samples were examined with a SEM/EDS JEOL 5500 electron microscope in combination with a secondary electron detector.

**Low Temperature Nitrogen Adsorption**

Nitrogen adsorption isotherms were measured at 77 K (Autosorb-1, Quantachrome). The apparent surface area was derived from the BET model. Micropore analysis was carried out according to the Dubinin–Radushkevich (DR) equation. The pore size distribution (PSD) was calculated with the Quantachrome software using both the nonlinear density function (NLDFT) and the Barrett, Joyner and Halenda (BJH) methods, respectively.

**SAXS**

SAXS measurements were made at the BM2 beam line at the European Synchrotron Radiation Facility in Grenoble, working at 18 keV in the transfer wave vector range 10$^{-2}$ Å$^{-1}$ ≤ q ≤ 1 Å$^{-1}$ [7].

2.5 pH

The carbons studied are characterized by the pH of their aqueous suspension, detected under standardized conditions [8]. As the carbon surfaces are decorated only with O-containing heteroatoms, the functional groups of different pK$_a$ range were determined by Boehm titration [9].

**Cu$^{2+}$ Adsorption**

Cu$^{2+}$ adsorption isotherms were measured at room temperature, by soaking SC or SCOX in an aqueous solution of Cu(CH$_3$COO)$_2$. The contact time was three days. The concentration of the aqueous solutions was measured by UVIKON 930 UV/Vis spectrophotometer at 766 nm.
Results and Discussion

The acidic treatment erodes the surface as shown in the SEM micrographs of Fig. 1.

The reversible low temperature nitrogen isotherms (Fig. 2) reveal the microporous character of the SC carbon, which was also retained during the oxidative treatment. Parameters deduced from the adsorption/desorption isotherms are listed in Table 1.

The PSD of all these samples are very similar in the micropore range. Figure 3a reveals a broad distribution with maxima at 7, 11, 15 and 18.5 Å. The oxidative treatment affects only the microporous region of the SC carbon. Porosity in the mesopore range was detected only in F400 (Fig. 3b). The slight upturn observed for SC and SCOX at the higher end of the mesopore range, owing to their smaller particle size, may be due to interparticle porosity.

In Fig. 4, the SAXS response of the SC and SCOX samples at low wave vector \( q \) exhibits power law behaviour, the slope of which is characteristic of scattering from a rough surface [10].

The pronounced shoulder for both SCs at \( q \approx 0.1 \text{ Å}^{-1} \) is the result of the microporous structure. By plotting the data in a Guinier representation (\( \log(I(q) \text{ vs. } q^2) \), not shown here) [11], the radius of gyration of the micropores were found to be 10.9 and 12.3 Å for SC and SCOX respectively. Comparison of the surface area, calculated by the method of Porod [11] (1560 and 1390 m²/g, respectively), with the nitrogen adsorption data reveals only limited inaccessible porosity [12].

The equivalent slope for F400 is smaller than 3, which indicates scattering from a volume that contains a densely branched structure. For this reason, in this sample the microporous behaviour appears much less pronounced, producing a scattering feature that is too weak to permit more detailed evaluation.

The SC and the F400 carbons have slightly basic character, as reflected in the values of pH in Table 2. Nevertheless, the distribution of the surface functionalities of different \( pK_a \) values must be very different. The high concentration of basic surface groups in the SC carbon originates from the nitrogen functionalities. In spite of the presence of nitrogen, the acidic treatment significantly reduces the pH of this carbon.

To study the interaction between the carbon surface of different chemistry and the metal cations, Cu\(^{2+} \) adsorption isotherms were measured for SC and SCOX from aqueous solutions of Cu(CH\(_3\)COO)\(_2\). The isotherms,
Table 1  Morphology data from low temperature N₂ adsorption measurements of the non-impregnated carbons

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{\text{BET}}$ (m²/g)</th>
<th>$V_{\text{TOT}}$ (cm³/g)</th>
<th>$d_{\text{ave}}$ (Å)</th>
<th>$W_0$ (cm³/g)</th>
<th>$w$ (Å)</th>
<th>$W_0/V_{\text{TOT}}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SC</td>
<td>1457</td>
<td>0.69</td>
<td>9.47</td>
<td>0.58</td>
<td>9.1</td>
<td>84</td>
</tr>
<tr>
<td>SCOX</td>
<td>1176</td>
<td>0.55</td>
<td>9.35</td>
<td>0.46</td>
<td>7.8</td>
<td>84</td>
</tr>
<tr>
<td>F400</td>
<td>1081</td>
<td>0.66</td>
<td>24.0</td>
<td>0.42</td>
<td>6.9</td>
<td>64</td>
</tr>
</tbody>
</table>

$S_{\text{BET}}$ is the apparent surface area, $V_{\text{TOT}}$ is the total pore volume from the isotherm at $p/p_0 = 0.94$, $d_{\text{ave}} = 2V_{\text{tot}}/S_{\text{BET}}$; $W_0$ and $w$ are the volume and the average width of the micropores, respectively.

which belong to type L in the Giles classification [13], were evaluated from the linear Langmuir plot (Table 3). The cation exchange capacity of SC and SCOX, measured by Boehm titration (Table 2), was found to be about an order of magnitude smaller than the corresponding copper uptake. This may be explained by the nitrogen-containing functional groups present, which may react as complexing agents and increase the copper adsorption.

SC and F400 were treated with aqueous Cu(CH₃COO)₂ solution under identical conditions to study the influence of the pore structure. The metal uptake for the microp-

![Graph](image1.png)

**Fig. 3** PSD of the carbon samples from the N₂ adsorption isotherms a by the NLDFT method b by the BJH method ( ■ SC, ○ SCOX, + F400)

![Graph](image2.png)

**Table 2** Surface chemical properties of SC, SCOX and F400 in aqueous phase

<table>
<thead>
<tr>
<th></th>
<th>SC</th>
<th>SCOX</th>
<th>F400</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.9</td>
<td>3.4</td>
<td>7.8</td>
</tr>
<tr>
<td>Acidic functional groups (µeq/g)</td>
<td>273</td>
<td>838</td>
<td>210</td>
</tr>
<tr>
<td>Basic functional groups (µeq/g)</td>
<td>538</td>
<td>223</td>
<td>*</td>
</tr>
</tbody>
</table>

* The amount of the basic functional groups in the surface could not be determined for this sample by the Boehm titration method

![Graph](image3.png)

**Fig. 4** SAXS response of the SC, SCOX and F400 carbons
Table 3 Parameters of the Langmuir equation* for SC and SCOX

<table>
<thead>
<tr>
<th></th>
<th>n&lt;sub&gt;m&lt;/sub&gt; (mmol/g)</th>
<th>K</th>
<th>R&lt;sup&gt;2&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>SC</td>
<td>2.2</td>
<td>14.5</td>
<td>0.9511</td>
</tr>
<tr>
<td>SCOX</td>
<td>2.1</td>
<td>18.8</td>
<td>0.9578</td>
</tr>
</tbody>
</table>

* n<sub>m</sub> is the monolayer capacity, K is the interaction parameter and R is the regression coefficient of the fit.

Porous SC was 1.9 mmol/g, and 1.1 mmol/g for F400. The PSDs and the structural parameters derived from the N<sub>2</sub> adsorption/desorption isotherms are displayed in Fig. 5 and Table 4, respectively.

These data show that metal impregnation causes partial blocking of the porosity and reduces the contact surface area and the volume of the accessible pores. The PSDs indicate that the ions are accommodated mainly within pores either smaller than 14 Å or larger than 50 Å. EDS results also confirmed that adsorption takes place within the pores [14], since no copper was detected on the outer surface of the impregnated particles. As has been reported in the literature [15], this increases the microporous character of the mesoporous carbon and leads to the increase of w and d<sub>ave</sub> in both carbons.

The sensitivity of the small pores to metal impregnation is also apparent upon comparing the porosity of SCOX carbons with different loadings (Fig. 6, Table 5).

For metal loading below the saturation capacity of SCOX (2.1 mmol/g, Table 3), the monotonic decrease in pores of size smaller than 14 Å visible in Fig. 6a is accompanied by a corresponding reduction of both the surface area and the pore volume that is proportional to the loading. The microporous character and the accessibility of the larger pores, however, are unaffected. When the loading exceeds 2.1 mmol/g a dramatic change in the structural parameters occurs.

When SCOX was loaded from the 0.03 M aqueous solutions of copper salts (16.0 ml/g carbon) with various anions at room temperature, different uptakes of copper ion were observed (Table 6). This finding indicates that the size and the charge of the anions and their different state of hydration may influence the sorption of the cations [16]. It should be noted that the effect of the anions on the pH was not investigated.

According to the EDS analysis, treatment with freshly prepared CuCl at elevated temperature in an inert atmosphere yielded spherical carbons with a CuCl-covered sur-

Table 4 Structural parameters from low temperature N<sub>2</sub> adsorption measurements for the microporous and mesoporous carbon

<table>
<thead>
<tr>
<th>Sample (Cu loading, mmol/g)</th>
<th>S&lt;sub&gt;BET&lt;/sub&gt; (m&lt;sup&gt;2&lt;/sup&gt;/g)</th>
<th>V&lt;sub&gt;TOT&lt;/sub&gt; (cm&lt;sup&gt;3&lt;/sup&gt;/g)</th>
<th>W&lt;sub&gt;0&lt;/sub&gt; (cm&lt;sup&gt;3&lt;/sup&gt;/g)</th>
<th>w (Å)</th>
<th>W&lt;sub&gt;0&lt;/sub&gt;/V&lt;sub&gt;TOT&lt;/sub&gt; (%)</th>
<th>d&lt;sub&gt;ave&lt;/sub&gt; (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SC</td>
<td>1457</td>
<td>0.69</td>
<td>0.58</td>
<td>9.10</td>
<td>84</td>
<td>9.47</td>
</tr>
<tr>
<td>SC/Cu (1.9)</td>
<td>722</td>
<td>0.36</td>
<td>0.28</td>
<td>10.4</td>
<td>78</td>
<td>19.9</td>
</tr>
<tr>
<td>F400</td>
<td>1081</td>
<td>0.66</td>
<td>0.42</td>
<td>6.90</td>
<td>64</td>
<td>24.0</td>
</tr>
<tr>
<td>F400/Cu (1.1)</td>
<td>484</td>
<td>0.34</td>
<td>0.24</td>
<td>11.0</td>
<td>71</td>
<td>28.1</td>
</tr>
</tbody>
</table>

Fig. 5 a NLDFT b BJH PSDs of SC (■), F400 (▲), SC/Cu (□) and F400/Cu (△)
Table 5 Structural parameters from low temperature N$_2$ adsorption measurements for the SCOX carbons with different loading

<table>
<thead>
<tr>
<th>Sample (Cu loading, mmol/g)</th>
<th>$S_{\text{BET}}$ (m$^2$/g)</th>
<th>$V_{\text{TOT}}$ (cm$^3$/g)</th>
<th>$W_0$ (cm$^3$/g)</th>
<th>$w$ (Å)</th>
<th>$W_0/V_{\text{TOT}}$ (%)</th>
<th>$d_{\text{ave}}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCOX</td>
<td>1176</td>
<td>0.55</td>
<td>0.46</td>
<td>7.8</td>
<td>84</td>
<td>9.35</td>
</tr>
<tr>
<td>SCOX/Cu (0.62)</td>
<td>956</td>
<td>0.47</td>
<td>0.39</td>
<td>9.5</td>
<td>83</td>
<td>20</td>
</tr>
<tr>
<td>SCOX/Cu (1.43)</td>
<td>734</td>
<td>0.38</td>
<td>0.30</td>
<td>10.5</td>
<td>79</td>
<td>21</td>
</tr>
<tr>
<td>SCOX/Cu (2.24)</td>
<td>128</td>
<td>0.12</td>
<td>0.06</td>
<td>15.9</td>
<td>50</td>
<td>38</td>
</tr>
</tbody>
</table>

Fig. 6  
(a) NLDFT, (b) BJH PSDs of metal-free SCOX (⊙) compared to SCOX after loading with 0.62 (▼), 1.43 (△) and 2.24 (+) mmol/g copper

face. However, part of the copper is reduced, forming copper wire, as shown in the electron micrographs of Fig. 8. This makes the mass determination of the sample uncertain.

The effect of Cu$^{2+}$ and Sn$^{2+}$ treatment is compared in Figs. 9–10 and in Table 7. These samples were prepared under identical conditions using copper acetate and tin chloride solutions. Uptake of tin is twice as high as that of copper, which is reflected in the reduced porosity and, as before, the loss is the most significant in the region of narrowest pores. The uptake is the result of a complex mechanism, which also involves (de)hydration and redox processes [17]. (The role of the anions was addressed previously.) The interaction between the carbon surface and the cations may be influenced by the geometrical constraints, i.e., size, electronegativity, effective charge and state of hydration of the ionic species (Table 8). Although ion exchange may be the dominant effect in the sorption mechanism, redox processes, even catalyzed by the solid surface, also may occur [18, 19]. A redox reaction seems to take place when SnCl$_2$ is used, which results in the appreciably rougher surface visible in the corresponding micrographs of Fig. 10b.

Table 6 Structural parameters from low temperature N$_2$ adsorption measurements for the SCOX carbons loaded with different copper salts

<table>
<thead>
<tr>
<th>Anion</th>
<th>Cu uptake (mmol/g)</th>
<th>$S_{\text{BET}}$ (m$^2$/g)</th>
<th>$V_{\text{TOT}}$ (cm$^3$/g)</th>
<th>$W_0$ (cm$^3$/g)</th>
<th>$w$ (Å)</th>
<th>$W_0/V_{\text{TOT}}$ (%)</th>
<th>$d_{\text{ave}}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>–</td>
<td>0</td>
<td>1176</td>
<td>0.55</td>
<td>0.46</td>
<td>7.8</td>
<td>84</td>
<td>9.4</td>
</tr>
<tr>
<td>CH$_3$COO$^-$</td>
<td>0.62</td>
<td>956</td>
<td>0.47</td>
<td>0.39</td>
<td>9.5</td>
<td>83</td>
<td>20</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>0.15</td>
<td>971</td>
<td>0.48</td>
<td>0.39</td>
<td>9.9</td>
<td>81</td>
<td>20</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>0.12</td>
<td>1280</td>
<td>0.61</td>
<td>0.52</td>
<td>9.0</td>
<td>85</td>
<td>19</td>
</tr>
</tbody>
</table>
Fig. 7  a NLDFT, b BJH PSDs of metal-free SCOX (○) compared to SCOX after loading with Cu(NO₃)₂ (×), CuSO₄ (♦) and Cu(CH₃COO)₂ (▼).

Table 7  Structural parameters from low temperature N₂ adsorption measurements for the SC carbons loaded with copper and tin

<table>
<thead>
<tr>
<th>Sample (cation loading, mmol/g)</th>
<th>( S_{\text{BET}} ) (m²/g)</th>
<th>( V_{\text{TOT}} ) (cm³/g)</th>
<th>( W_0 ) (cm³/g)</th>
<th>( w ) (Å)</th>
<th>( W_0/V_{\text{TOT}} ) (%)</th>
<th>( d_{\text{ave}} ) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SC</td>
<td>1457</td>
<td>0.69</td>
<td>0.58</td>
<td>9.1</td>
<td>84</td>
<td>9.47</td>
</tr>
<tr>
<td>SC/Cu (0.29)</td>
<td>712</td>
<td>0.37</td>
<td>0.30</td>
<td>11.3</td>
<td>81</td>
<td>20.74</td>
</tr>
<tr>
<td>SC/Sn (0.62)</td>
<td>533</td>
<td>0.30</td>
<td>0.21</td>
<td>11.5</td>
<td>70</td>
<td>22.58</td>
</tr>
</tbody>
</table>

Fig. 8  Scanning electron micrographs of SC/Cu⁺ at different magnifications. a 100 ×; scale bar: 100 µm  b 1000 ×; scale bar: 10 µm; copper wires on the surface of SC  c 10000 × times magnification of the carbon surface; scale bar: 1 µm.
Fig. 9  a NLDFT, b BJH PSDs of metal-free (■), copper (0.29 mmol/g) (▼) and tin (0.62 mmol/g) (×) loaded SC.

Fig. 10 Scanning electron micrographs of SC/Cu (a) and SC/Sn (b) at different magnifications (upper row: 5000 ×, scale bar: 5 µm; lower row: 10000 ×, scale bar: 1 µm).

Table 8 Properties of the cations

<table>
<thead>
<tr>
<th></th>
<th>Standard electrode potential $E^0$ (V)</th>
<th>Electronegativity (Pauling)</th>
<th>Ionization energies (kJ/mol)</th>
<th>Polarizability $(10^{-24} \text{ cm}^3)$</th>
<th>Ionic radius (Å)</th>
<th>Hydrated ionic radius (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu [20]</td>
<td>+0.3419</td>
<td>1.90</td>
<td>1958</td>
<td>6.10</td>
<td>Cu$^{2+}$: 0.72</td>
<td>2.07</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>6.00 [21]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4.19 [22]</td>
</tr>
<tr>
<td>Sn [23]</td>
<td>−0.1364</td>
<td>1.96</td>
<td>1412</td>
<td>7.7 [24]</td>
<td>Sn$^{2+}$: 0.93</td>
<td>6.00 [21]</td>
</tr>
</tbody>
</table>
Conclusions

Porous carbon samples of different surface chemistry were produced by oxidation and metal impregnation. Oxidation by nitric acid substantially decreased the pH and slightly reduced the accessible porosity, but no significant changes were observed either in the morphology or in the Cu$^{2+}$ adsorption capacity. Metal impregnation from aqueous phase was found to depend not only on the chemistry but also on the porosity of the carbon surface as well as the species of the anion and of the metal. The main structural changes were caused by blocking of pores of size smaller than 14 Å. Cu$^{2+}$ loadings below the saturation capacity produced a corresponding decrease of the apparent surface area, proportional to the loading. No metal was detected on the surface of the particles. When the samples were treated with solid CuCl, a practically complete CuCl film covered the surface of the particles, but metallic copper was formed as a by-product. When SnCl$_2$ was used instead of Cu$^{2+}$ salts in aqueous phase, a redox reaction appeared to take place, resulting in an appreciably rougher surface that is visible in SEM micrographs.

Acknowledgement. The spherical carbon (SC) was kindly provided by the INSIDE PORES Network of Excellence. Access to the CRG beam line BM2 at the European Synchrotron Radiation Facility, Grenoble, is gratefully acknowledged. We extend our thanks to G. Bosznai for sample preparation. This research was performed in the framework of the Hungarian – Greek Intergovernmental S&T Cooperation Programme (GR-43/03) and supported by the EU – Hungarian Government joint fund (GVOP-3.2.2-2004-07-0006/3.0).

References

Influence of drying on the morphology of resorcinol–formaldehyde-based carbon gels

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c Laboratoire de Spectrométrie Physique CNRS UMR 5588, Université J. Fourier de Grenoble, BP 87, F-38402 St Martin d’Hères Cedex, France

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Abstract

The method of drying resorcinol–formaldehyde (RF) gels influences the structure and gas adsorption capacity of the resulting networks as well as of their carbonized derivatives. Small angle X-ray scattering (SAXS) reveals the presence of submicroscopic clusters both in the RF gels and in the carbon gels, whose size, of the order of tens of nanometres, is consistent with SEM observations. Xerogels, obtained by heating the RF hydrogel in an inert atmosphere, have the most compact structure and display the lowest specific surface area (<900 m²/g). The highest surface area is found in the gel lyophilized after freeze-drying in t-butanol (>2500 m²/g), but the resulting carbon cryogel is not structurally stable, the measured surface area decreasing with time. Supercritical extraction with liquid carbon dioxide yields aerogels with an intermediate value for the surface area (ca. 1000 m²/g). Carbonization causes a reduction in the size of the elementary spheres (from 27 to 8 nm) in the case of the aerogels, while an increase (from 10 to 22 nm) is observed for the xerogels. The adsorption sites in the carbon gels are located principally in irregular spaces between monomer units. For the carbonized cryogels the specific surface area derived from SAXS is greater than that found by low temperature gas adsorption. This phenomenon is interpreted in terms of restricted pore size, which limits the access of gas molecules. By contrast, in the RF gels the SAXS-derived surface areas are substantially smaller than those measured by gas adsorption.

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Keywords: RF gel; Carbon gel; Drying; Nitrogen adsorption; SAXS

1. Introduction

Mesoporous carbons with high specific surface area have attracted a great deal of attention recently [1]. Because of their chemical and textural characteristics, they are expected to be materials of choice for thermal and phonic insulators, chromatography packing, adsorbents and catalyst supports [2]. For carbon gels a further important field of application is that of electrodes in electric double-layer capacitors [3–9].

Mesoporous carbon gels can be prepared from resorcinol and formaldehyde under controlled conditions [10,11]. The most common preparation methods follow the route developed by Pekala [10], who first prepared carbon gels derived from resorcinol–formaldehyde (RF). Between resorcinol and formaldehyde a polycondensation reaction takes place, yielding a three-dimensional polymer matrix, the RF hydrogel. From this gel, after solvent exchange and drying, followed by a prescribed heat treatment, a carbon gel (CG) can be

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formed that possesses a solid carbon skeleton. Other methods of preparing carbon gels exist, e.g., with other monomer combinations. Melamine/formaldehyde/cresol/phenolic resin [12], phenol/furfural [13], cresol/resorcinol/formaldehyde [14–16], polyurethane [17] or poly(vinyl-chloride) [18] can be used for the synthesis.

Three kinds of drying techniques are available to convert the hydrogel to a solid RF gel. The first is by drying in an inert atmosphere, which gives a RF xerogel [11]. A second method is freeze-drying, which yields a RF cryogel [19]. The third technique is by supercritical extraction with carbon dioxide, which results in a RF aerogel [10]. The pore structure and the surface area of the final carbon gel depend not only on the initial conditions of synthesis but also on the drying and carbonizing techniques [10,11,19]. With this technology, carbons with high surface area and controlled pore structure can be prepared.

Of the three drying methods outlined above, supercritical drying is the most useful for obtaining mesoporous RF gels, but the cost of the drying step is extremely high. With freeze-drying, which is also an effective way of preparing high surface area carbons with controlled pore structure, the drying step is much less expensive [20]. Moreover, the surface area, the pore volume and the mean pore diameter are largest for RF cryogels [19]. Shrinkage of these gels during the drying procedure is also the lowest. As to the third method, drying in an inert atmosphere is the simplest way to convert the RF hydrogel into a solid gel, but the surface area, pore volume and mean pore diameter of the xerogel are smaller than those of the aero- or the cryogel [11]. The drying method used in the gel preparation therefore exerts a strong influence on the adsorption properties of the final carbon gel.

The present paper reports the influence of drying on the morphology of RF-based carbon gels. The morphology was investigated by SEM, adsorption isotherms and SAXS.

### Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( S_{\text{BET}} )</td>
<td>apparent surface area</td>
</tr>
<tr>
<td>( V_{\text{tot}} )</td>
<td>total pore volume read at ( p/p_0 = 0.9 )</td>
</tr>
<tr>
<td>( V_{\text{tot,0}} )</td>
<td>total pore volume derived from extrapolation to ( p/p_0 = 1 )</td>
</tr>
<tr>
<td>( W_0 )</td>
<td>micropore volume</td>
</tr>
<tr>
<td>( \omega )</td>
<td>micropore width</td>
</tr>
<tr>
<td>( q )</td>
<td>scattering wave vector</td>
</tr>
<tr>
<td>( \lambda )</td>
<td>wavelength of incident X-radiation</td>
</tr>
<tr>
<td>( \theta )</td>
<td>scattering angle</td>
</tr>
<tr>
<td>( I(q) )</td>
<td>scattered intensity</td>
</tr>
<tr>
<td>( p/p_0 )</td>
<td>equilibrium relative pressure</td>
</tr>
<tr>
<td>( m )</td>
<td>exponent of power law for scattering</td>
</tr>
<tr>
<td>( q_{\text{max}} )</td>
<td>position of local maximum in ( I(q) )</td>
</tr>
<tr>
<td>( R )</td>
<td>outer radius of spherical clusters</td>
</tr>
<tr>
<td>( R_G )</td>
<td>radius of gyration of clusters</td>
</tr>
<tr>
<td>( \rho_{\text{He}} )</td>
<td>helium density of carbon gel</td>
</tr>
<tr>
<td>( d )</td>
<td>cluster diameter</td>
</tr>
<tr>
<td>( K )</td>
<td>“final” slope of ( I(q) )</td>
</tr>
<tr>
<td>( b )</td>
<td>scattering from atomic disorder</td>
</tr>
<tr>
<td>( Q )</td>
<td>second moment of scattering intensity</td>
</tr>
<tr>
<td>( S_X )</td>
<td>surface area derived from SAXS data</td>
</tr>
</tbody>
</table>

### 2. Experimental

#### 2.1. Materials

##### 2.1.1. Gel preparation

RF gels were prepared according to the method of Pekala [10]. 1.5990 g resorcinol (R), and 0.0308 g sodium carbonate (C) as catalyst (both from Merck), were dissolved in 48 ml distilled water. After homogenizing with 2.2 ml 37% aqueous formaldehyde (F), the pH of the solution was set to 6.0 by adding dilute HNO₃. The solution was stirred for 30 min and poured into glass vials (i.d. 4 mm, length ca. 10 cm), which were then sealed and cured at 85°C for 7 days. Over the one-week period the initially colourless solution became dark red as the RF hydrogel was formed.

##### 2.1.2. Drying methods

The diluent in the synthesized gels, water, is undesirable for the drying process, owing to its relatively low vapour pressure and large volume change on freezing [19]. A solvent exchange step is therefore necessary before drying.

The three drying methods employed to convert the hydrogel into a solid RF gel are: (1) drying in an inert atmosphere (to give a RF xerogel), (2) freeze-drying (RF cryogel) and (3) extraction with supercritical CO₂ (RF aerogel).

In methods (1) and (3), to reduce the drying time, the water in the pores is replaced by acetone. In method (2) the expansion of water during freezing must be eliminated to avoid destroying the gel structure. For this, however, acetone cannot be used because its freezing point is lower than the temperature of the freeze-drying process. In view of these constraints, water was exchanged with \( t \)-butanol for the freeze-drying method.

After the seven-day incubation the hydrogel gel rods were removed from the glass vials and immersed in three
times their own volume of the replacement solvent for 3 days, renewed with fresh solvent every day.

In method (1) the gel rods were filtered before drying, then placed in an oven in a flow of high purity nitrogen (99.996% from Linde, 50 ml/min) to ensure an inert atmosphere during the process. The temperature was raised to 45 °C (critical temperature) and maintained for 5 h. Then the temperature was increased to 110 °C, at 2 °C/min, and maintained for another 5 h.

Prior to freeze drying a pre-freezing period is necessary. The gel rods together with the excess t-butanol were precooled for 2 h at −20 °C. The frozen gel rods were then transferred into the freeze-drying apparatus, where the temperature was reduced to −45 °C. At this temperature the pressure was slowly reduced to 1 mbar and the frozen solvent was sublimated. The whole procedure took 1 day.

In the supercritical process, the acetone in the pores is replaced by liquid carbon dioxide. The gels were transferred to the reactor, which was then filled with room temperature liquid carbon-dioxide at 80 bar to enhance the solvent exchange. This procedure was repeated three times. Then the temperature was raised to 45 °C (critical point of CO₂; 31.1 °C; 73.8 bar), and the CO₂ gas was released in a controlled manner.

2.1.3. Carbonization

Heat treatment of the dried polymer gel in a high purity nitrogen atmosphere (99.996%, Linde) yielded the carbon gel (CG). Carbonization was performed in a rotary quartz reactor at 900 °C for 1 h in a 25 ml/min nitrogen flow.

2.2. Methods

2.2.1. Nitrogen adsorption

Nitrogen adsorption/desorption isotherms were measured at −196 °C with a Quantachrome Autosorb-1 computer controlled apparatus. Results reported here were obtained immediately after sample preparation unless mentioned otherwise. The apparent surface area was calculated using the Brunauer–Emmett–Teller (BET) model (\(S_{\text{BET}}\)). The total pore volume \((V_{\text{tot}})\) was derived from the amount of vapour adsorbed at relative pressure 0.90, assuming that the pores are then filled with liquid adsorbate. For the SAXS results, where the total pore volume inclusive of the macropores is required, \(V_{\text{tot2}}\) was estimated by extrapolating the final section of the isotherm to relative pressure 1. The micropore volume \((W_0)\) and the micropore width \((w)\) were derived from the Dubinin–Radushkevich (DR) plot. The pore size distribution in the micropore region was computed from density function theory (DFT).

Transformation of the primary adsorption data and the (micro)pore analysis were performed by the Quantachrome software.

2.2.2. SEM

Surface morphological investigations were made on a JEOL 5500 electron microscope in high vacuum mode with a secondary electron detector. The accelerating voltage was 20 kV and the working distance 20 mm. The samples were fastened to the copper sample holder by adhesive carbon tape. The RF gels were coated with Au/Pd in order to prevent charging. All the images were taken 18 months after sample preparation.

2.2.3. SAXS

SAXS measurements were made on the BM2 small angle camera at the European Synchrotron Radiation Facility (ESRF), Grenoble, France. At 16 keV and with sample to detector distances 156 and 22 cm, the q-range explored was \(0.008 < q < 1.5 \text{ Å}^{-1}\) \((q = (4\pi/n)\sin\theta/2)\), where \(\lambda\) is the wavelength of the incident radiation and \(\theta\) the scattering angle. An indirect illumination CCD detector (Princeton Instruments) with effective pixel size 50 μm, cooled by a Peltier effect device, was used. Intensity curves \(I(q)\), obtained by azimuthal averaging, were corrected for grid distortion, dark current, sample transmission and also for background scattering. The powdered samples were held in glass capillary tubes of diameter 1.5 mm. Intensities were normalised with respect to a standard sample (lupolen), assuming an effective sample thickness of 1 mm to account for the filling factor of the powder. The resulting error in the stated absolute values of the intensity is expected to be no greater than 25%.

3. Results

3.1. Comparison of drying methods

Drying the hydrogels yielded hard and brittle RF gels. All the gel rods shrunk during the drying process. The diameter of the RF xerogel rods was only about 50% of that of the original hydrogel, while the RF cryogel rods hardly changed in diameter.

The SEM images of the three different RF gels are shown in Fig. 1. The sample obtained by supercritical extraction exhibits a compact structure (Fig. 1(a)), but the individual microspheres are smaller than in the RF xerogel (Fig. 1(c)). Fig. 1(b) shows the freeze-dried RF gel. The structure, which is very loose, is the finest of all three samples. It consists of very small spheres of diameter approximately 30 nm, arranged in a filament-like structure to form a three-dimensional matrix. The network appears to be very fragile. Macroscopically, the rods are brittle.

The micrograph of the sample dried at high temperature in nitrogen (Fig. 1(c)) also reveals a somewhat compact structure, consisting of more or less uniform microspheres of diameter about 0.1 μm.
The pore structure of the gels was investigated by low temperature nitrogen adsorption measurements. The adsorption/desorption isotherms of all the three RF gels, shown in Fig. 2, belong to Type II in the IUPAC classification. This type of isotherm is identified with unrestricted monolayer–multilayer adsorption, and is characteristic of nonporous or macroporous adsorbents. The isotherms exhibit a narrow hysteresis loop, which is typical of thermodynamically irreversible adsorption processes. The hysteresis loops are of Type B.

Table 1 lists the porosity data deduced from the adsorption isotherms. These results show that the freeze-dried RF cryogel has the highest surface area and total pore volume. 25–30% microporosity was detected in these gels. The trend in the values of $V_{\text{tot}}$ as well as the shape of the isotherms above $p/p_0 \approx 0.1$ reflects the relative openness of the structures, which is also visible in the SEM micrographs. The most open RF gel also has the highest total pore volume.

The pore size distribution of all the three RF gels are very similar (Fig. 3, left). They show a maximum at 14 Å, while less intense shoulders on both sides of the maxima can also be identified. Further maxima are exhibited by the cryo- and the aerogels at 28 and 48 Å, respectively.

After drying, the RF gels were carbonized at 900 °C for 1 h under nitrogen atmosphere. The yield of the resulting carbon gels (CG) was 40–50% (Table 2). Fig. 4 shows the SEM images of the three different carbon gels obtained. The aerogel (Fig. 4(a)) conserves its compact structure during carbonization, but the basic microspheres are significantly larger (ca. 200 nm) than in the starting RF gel. Fig. 4(b) presents the carbon cryogel from the freeze-dried RF gel, for which the change in structure is the most pronounced. A very fine structure can be observed: the spheres no longer form individual chains, but rather two-dimensional ribbons, which constitute a loose 3D gel. The CG derived from the xerogel is shown in Fig. 4(c). Like in the carbon xerogel, the compact structure and uniform character of the constituent spheres are preserved during the pyrolysis.

The adsorption/desorption isotherms of the three carbon gels are also displayed in Fig. 2. The shape of their isotherms is similar to that of the corresponding starting RF gels, but in each case the initial part reflects the presence of microporosity. This property is most pronounced for the carbon cryogel. The hysteresis loops become wider in the carbon cryogel and aerogel. The abrupt upturn in the isotherms at high relative pressures is the signature of strong capillary condensation.

During carbonization, thermal degradation of the RF gels is combined with self-activation. The O-containing degradation products may work as an activating agent, since the oxygen content of the polymer gel is about 35%. Microporous structure develops during pyrolysis. The fraction of micropores is especially high in the carbon xerogel, where it approaches 80%. In the other two gels the microporous fraction is 50–57%. The increase of microporosity during carbonization is also reflected in the pore size distribution (Fig. 3, right).
mainly influences the $< 10 \text{Å}$ region. The peak maxima are shifted towards slightly smaller values, 12, 9.0 and 11 Å for aero-, cryo- and xerogel, respectively, and a new peak appears at 6.0 Å. Significant porosity below 6.0 Å develops in the cryogel. It should be borne in mind, however, that, owing to microporosity, the surface area derived from the BET model for the carbon gels gives only approximate information about the real surface area of the sample. The apparent surface area $S_{\text{BET}}$ and total pore volume ($V_{\text{tot}}$) of the RF and carbon gels were regularly remeasured over a period of 18 months. Within experimental error all the isotherms and the derived values remain constant except for the carbon cryogel. In this carbon sample

Table 1
Porosity data of RF and carbon gels from nitrogen adsorption measurements (−196 °C)$^a$

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{\text{BET}}$ (m$^2$/g)</th>
<th>$V_{\text{tot}}$ (cm$^3$/g)</th>
<th>$W_0$ (cm$^3$/g)</th>
<th>$w$ (Å)</th>
<th>$W_0/V_{\text{tot}}$</th>
</tr>
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<tbody>
<tr>
<td>RF aerogel</td>
<td>270</td>
<td>0.36</td>
<td>0.09</td>
<td>13.0</td>
<td>0.25</td>
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<tr>
<td>RF cryogel</td>
<td>570</td>
<td>0.76</td>
<td>0.22</td>
<td>13.3</td>
<td>0.29</td>
</tr>
<tr>
<td>RF xerogel</td>
<td>110</td>
<td>0.13</td>
<td>0.04</td>
<td>12.9</td>
<td>0.31</td>
</tr>
<tr>
<td>Carbon aerogel</td>
<td>1010</td>
<td>0.79</td>
<td>0.40</td>
<td>7.5</td>
<td>0.57</td>
</tr>
<tr>
<td>Carbon cryogel</td>
<td>2650</td>
<td>2.05</td>
<td>1.05</td>
<td>7.0</td>
<td>0.51</td>
</tr>
<tr>
<td>Carbon xerogel</td>
<td>891</td>
<td>0.44</td>
<td>0.34</td>
<td>5.4</td>
<td>0.77</td>
</tr>
</tbody>
</table>

$^a$ $S_{\text{BET}}$: specific surface area from BET-method; $V_{\text{tot}}$: total volume of pores read at $p/p_0 = 0.9$; $W_0$: micropore volume; $w$: micropore width.

Fig. 2. Low temperature nitrogen adsorption/desorption isotherms of the RF (open symbol) and carbon (solid symbol) gels. (a) Aerogels, (b) cryogels, (c) xerogels.
$S_{\text{BET}}$ was observed to decrease with time: in the freshly prepared specimen, $S_{\text{BET}} = 2650 \text{ m}^2/\text{g}$, but within 18 months its value fell gradually to 1160 m$^2$/g. As the samples were stored in closed containers, the change was probably caused by intrinsic structural modifications.

The q-range of the SAXS measurements reported here spans a higher spatial resolution scale than that covered by the SEM images. For this reason, structures larger than about 50 nm were not detected. The SAXS curves for the three sets of RF and carbon samples are shown in Fig. 5. The RF gels (open circles) display an extended range in which the intensity follows power law behaviour
\[ I(q) \propto q^{-m} \]
where the slope $m = 4$. This property is characteristic of scattering from smooth surfaces with a sharp boundary [21]. At the high-q end of the SAXS response, the RF samples exhibit a peak, at $q_{\text{max}} \approx 1.18 \text{ Å}^{-1}$, corresponding to an effective repeat distance $2\pi/q_{\text{max}} \approx 0.53 \text{ nm}$ between molecular units in the RF gel, i.e., close to the size of the resorcinol monomer. When the molecular units are reduced to carbon, the repeat distance scale shrinks and the peak migrates to higher q values beyond the

**Table 2**

Yield of the carbonization

<table>
<thead>
<tr>
<th>Type</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon aerogel</td>
<td>46.6</td>
</tr>
<tr>
<td>Carbon cryogel</td>
<td>40.7</td>
</tr>
<tr>
<td>Carbon xerogel</td>
<td>50.5</td>
</tr>
</tbody>
</table>

Fig. 3. Pore size distribution of the RF (left) and carbon (right) gels calculated from DFT. Aerogel: △ and ▲, cryogel: □ and ■, xerogel: ○ and ●.

Fig. 4. SEM images of carbon gels. (a) Carbon aerogel, scale bar = 0.5 µm, (b) carbon cryogel, scale bar = 0.5 µm, (c) carbon xerogel, scale bar = 1 µm.
observed SAXS range. By contrast, in the carbon gels a weak shoulder develops in the region \( q \approx 0.3 \, \text{Å}^{-1} \), from which a radius of gyration of approximately 0.5 nm can be deduced. In other carbon systems [22,23] this feature is generally attributed to basic structural units (BSU), i.e., the size of the characteristic folds in the turbostratic structure. In the present samples, however, the broad size distribution of the BSUs degrades the resolution of this feature: the estimated error of the radius of gyration is no better than 20%.

The deviation from power law behaviour visible at the low-\( q \) end of the spectra in Fig. 5 is the signature of large scale clustering. This feature is more clearly revealed in a representation that masks surface scattering, i.e., by plotting \( q^4 I(q) \) vs \( q \) [21]. Fig. 6 shows the oscillations in \( I(q) \) for the aerogel sample, both in the RF and the carbon gel. These oscillations can be interpreted in terms of spherical clusters, the radius \( R \) of which determines the position of the first maximum. In a monodisperse distribution of spheres, the first maximum in this representation occurs for \( qR = 2.74 \), yielding for the
RF and the carbon aerogel apparent values of $R$ equal to $27 \pm 4$ and $8 \pm 1$ nm, respectively. However, as the position of the first maximum is sensitive to size polydispersity, and as the attenuated oscillations in Fig. 6 indicate that the cluster size distribution is not monodisperse, a more reliable estimate of the radius of gyration $R_G$ is obtained using a Guinier representation $(\ln I$ vs $q^2$), not shown here).

Table 3 lists the values of $R_G$ obtained in this way for the different samples. To compare these sizes with those found from the SEM micrographs, it is reasonable to assume, first, that the spheres are uniform in density, which gives for their diameter $d = 2R_G\sqrt{5}/3$. Second, over a wide range of values of polydispersity the apparent value of $R_G$ remains approximately 80% of the median value. Comparisons with the SEM micrographs may thus plausibly be made by multiplying the values of $R_G$ listed in Table 3 by a factor of roughly 3.1. Table 4 summarizes the results. Given that estimates of $d$ from visual observations of SEM images are probably accurate to no more than one significant figure, the agreement between the two sets of observations is acceptable in all cases, with the notable exception of the carbon aerogel. This sample displays a two-level change during carbonisation: the SAXS results show that the radius of the clusters shrinks by more than a factor of 3, while the SEM results indicate that on the contrary they swell by about the same factor. As there is no reason to reject the evidence either of the SEM or the SAXS results, the two observations imply that a second level of clustering occurs during carbonization of the aerogel: shrunken carbon beads of diameter ca. 20 nm aggregate into units that are an order of magnitude larger. Such large clusters lie outside the detection window of the present SAXS observations. It is interesting to note that the cryogel and the xerogel display no such instability during carbonisation: their submicron-scale structures are preserved. By contrast, on scales larger than a micron the structure does evolve substantially, as seen in Figs. 2 and 4.

The specific surface area $S_X$ of the gels is derived from the X-ray measurements using the Porod approach [21]. As mentioned earlier, this method assumes that the adsorbing surfaces are flat on the length scale of the measurement, and have a sharp discontinuity in density at the interface between the uniform substrate and the outside medium. In practice, at the short length scales relevant to the systems investigated here, the substrate structure is far from regular. A region of the response is therefore sought where the intensity varies as

$$I(q) = Kq^{-4} + b$$

where $K$ is the final (Porod) slope and $b$ is the scattering from atomic disorder in the sample [25]. The surface area of the large clusters, which, as already seen, yields this type of scattering behaviour at low $q$, is too small to contribute significantly to the total internal surface area of the gels. The region of the spectrum that could give rise to significant adsorption is to be found above 0.3 Å$^{-1}$. Fig. 7(a) and (b), respectively, show the scattering from the this region in the RF and carbon aerogel, in the representation $Iq^4$ vs $q^4$, whereby

$$Iq^4 = K + bq^4$$

In this plot, the intercept with the ordinate axis is $K$ and the slope of the linear region is $b$. Inspection of Fig. 7(a) and (b) shows that the value of $K$ is more than an order of magnitude smaller in the RF gel than in the carbonized aerogel. The xero- and cryogels (not shown here) behave in a qualitatively similar way. With these values of $K$, the specific surface area can be determined from the expression [21]

$$S_X = \frac{V_{\text{tot}X}}{1 + V_{\text{tot}X}\rho_{\text{Te}}} \frac{\pi K}{Q}$$


<table>
<thead>
<tr>
<th>Sample</th>
<th>SEM (±10 nm)</th>
<th>SAXS</th>
<th>SEM (±10 nm)</th>
<th>SAXS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aerogel</td>
<td>50</td>
<td>70</td>
<td>200</td>
<td>20</td>
</tr>
<tr>
<td>Cryogel</td>
<td>30</td>
<td>30</td>
<td>&lt;30</td>
<td>20</td>
</tr>
<tr>
<td>Xerogel</td>
<td>100</td>
<td>70</td>
<td>100</td>
<td>60</td>
</tr>
</tbody>
</table>

$^a$ Total pore volume including interstrand spaces, from extrapolation of the final section of isotherms to $p/p_0 = 1$. The error incurred in this extrapolation is about 10%.

$^b$ Where $\rho_{\text{Te}} = 1.86$ g/cm$^3$ for the carbon and $\rho_{\text{Te}} = 1.3$ g/cm$^3$ for the polymer [24].

$^c$ Measurement performed 18 months after that listed in Table 1.
where \( \rho_{\text{He}} \) is the true density of the sample and \( Q \) is given by

\[
Q = \int_0^\infty [I(q) - b]q^2 \, dq
\]

The low-\( q \) behaviour of the integral was determined by extrapolating the intensity to \( q = 0 \) in a Guinier plot, i.e., \( \ln I(q) \) vs \( q^2 \). The helium density of the carbon gels was found to be \( \rho_{\text{He}} = 1.86 \, \text{g/cm}^3 \), while that for the RF gels, \( \rho_{\text{He}} = 1.3 \, \text{g/cm}^3 \), was taken from the literature [24]. In expression 4, the relevant pore volume \( V_{\text{totX}} \) defines the total unoccupied space in the sample, including the macropores. This is found from the adsorption isotherms by extrapolating the high relative pressure response, where liquid condenses in the intercluster space, to \( p/p_0 = 1 \).

Table 3 lists the values of \( K/Q \) found from each sample and the corresponding values of the X-ray surface area \( S_X \), calculated from Eqs. (4) and (5). For the carbon gels \( S_X \) is appreciably larger than \( S_{\text{BET}} \), except for the cryogel, where \( S_{\text{BET}} \) was found to decrease with time. It is not uncommon that \( S_X \) is greater than \( S_{\text{BET}} \), since X-rays detect all internal surfaces including those from which the gas molecules are excluded. The most striking result in Table 3, however, is that in the RF gels the measured value of \( S_X \) is substantially smaller than \( S_{\text{BET}} \). This finding contrasts with other SAXS measurements on RF gels [26-28] in which acceptable agreement is reported between the results of the two techniques. It has been argued that inclusion of long-range correlations can lead to an overestimate in the value of the integral \( Q \) [26], which, if true, would lead to \( S_X \) being underestimated. Exclusion of long range correlation, however, is normally associated with crystalline order, which is clearly absent from the present system. Among the samples investigated here, the one for which the existence of longer range order seems most plausible is the carbon aerogel, as it displays two levels of organisation. In this sample, however, \( S_X \) is substantially greater than \( S_{\text{BET}} \), which does not favour this argument. More specifically, the contribution to \( Q \) coming from the \( q \)-range below 0.01 \( \text{Å}^{-1} \) in the RF samples is much too small to account for the observed discrepancy. The nature of the present discrepancy is highlighted in Fig. 7(a) and (b). The linear range over which Eq. (3) applies in the RF gel is located at lower \( q \) than in the carbon gel. The difference is also illustrated in the ratio \( b/K \), which is significantly higher for the RF gels, indicating that the smooth surfaces that are normally associated with adsorption are outnumbered by irregular spaces between monomer units. These not only yield extra scattering but also create adsorption sites for gas molecules, probably by partially embedding the molecules in niches ("captation") [29]. No plausible surface scattering can be identified at higher \( q (>0.5 \, \text{Å}^{-1}) \), notably the region beyond the peak, where the slope is steeper than \(-4 \). It may be concluded that the principal gas adsorption sites in these samples are not smooth pores but irregular interstices.

4. Conclusions

This investigation compares the results of low temperature gas adsorption and SAXS on the structure and adsorption capacity of resorcinol–formaldehyde gels dried by three different procedures. The method of drying has a decisive influence both on the dried polymer networks and on their carbonized derivatives. SAXS reveals the presence of submicroscopic clusters both in the RF gels and in the carbon gels, the size of which, of the order of tens of nanometers, is consistent with SEM observations. Carbonization induces changes in the structure and hierarchy of the clusters that also depend on the drying technique. As expected, the xerogel, obtained by heating the RF hydrogel in an inert atmosphere, has the most compact structure, displaying the lowest specific surface area measured either by low temperature nitrogen adsorption or by SAXS. The highest surface area is found not with the aerogel dried under supercritical conditions but rather in the gel lyophilized after freeze-drying in \( t \)-butanol. The resulting carbon xerogel, however, is not stable, as the measured surface area decreases with time. The smaller degree of polymer clustering and hence larger surface area in the lyophilized system is probably a consequence of the superior solvent quality of \( t \)-butanol over liquid carbon dioxide.
A further contributing factor to the difference between the cryo- and the aerogel is that the former involves a single solvent substitution (water/t-butanol) while the latter requires two (water/acetone/carbon dioxide). In the carbonized aero- and cryogels the specific surface area derived from SAXS is greater than that found by low temperature gas adsorption. This phenomenon can be understood in terms of restricted pore size, which limits the access of gas molecules. By contrast, in the RF gels the SAXS-derived surface areas are substantially smaller than those measured by gas adsorption. It is believed that these gels do not display a significant fraction of smooth pores that can be identified by the standard SAXS technique but that the adsorption sites are located principally in irregular spaces between monomer units.

Acknowledgements

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References